

Activation Analysis of Lanthanum and Europium in Sea Water and Lake Water

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Lanthanum and europium in sea water and lake water were determined by thermal neutron activation analysis. Convenient pre- and post-irradiation procedures were proposed and some samples were analysed. Rare earth elements were concentrated and separated by coprecipitating with ferric hydroxide or calcium oxalate. The precipitates were irradiated for one hour in the neutron flux of 5×10^{12} n/cm²·sec., and after a few hour cooling, the rare earth activities were separated by precipitating with lanthanum oxalate from the solution containing various hold back carriers and citric acid. Gamma-rays spectra were obtained and the decays of the 0.8~1.2 MeV photo-peak of ^{152m}Eu (plus ¹⁴⁰La) and the 1.6 MeV peak of ¹⁴⁰La were followed. The analytical results were as follows: $2.9 \sim 4.5 \times 10^{-2} \mu\text{g La/l}$ and $1.0 \sim 1.8 \times 10^{-3} \mu\text{g Eu/l}$ in sea water; $4.0 \sim 4.8 \times 10^{-2} \mu\text{g La/l}$ and $0.9 \sim 1.2 \times 10^{-3} \mu\text{g Eu/l}$ in lake water. The Eu/La ratios were estimated to be 0.043 ± 0.004 for sea water (13 determinations) and 0.022 ± 0.002 for lake water (4 determinations).

INTRODUCTION

For a long time, it has been recognized that the geochemical and the cosmochemical behaviors of the rare earth elements are a very interesting subject. The knowledge of the chemical behavior in the weathering-sedimentation cycle was particularly important, because the rare earth elements might be considered as an indicator of the geological processes. However, not only the problems are not yet answered, but also the fundamental data on the distribution of the rare earth abundance are poorly presented.

In 1961, Balshav and Khitrov¹⁾ determined the total rare earth elements occurring in the Indian Ocean water, and found $1.6 \sim 4.7 \times 10^{-7} \%$ (as the oxide) in deep and near-shore parts of the ocean and $0.3 \sim 1.4 \times 10^{-7} \%$ in the surface water; not more than 50% of which was associated with suspended matter. The much valuable study on the distribution of the individual rare earth abundance was carried by Goldberg and his co-workers²⁾, who determined all rare earth elements except promethium and terbium in sea water samples obtained off the coast near San Diego, California. The concentration dispersed in the range from $2.9 \times 10^{-3} \mu\text{g/l}$ of lanthanum to $1.1 \times 10^{-4} \mu\text{g/l}$ of europium.

The authors have been previously attracted by the geochemical behaviors of trace elements, and intended to determine the content of trace elements in sea water and other natural samples. In this paper, a comparatively simple chemical

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procedure were proposed for the neutron activation analysis of lanthanum and europium in sea water and lake water, and some analytical results were also presented.

EXPERIMENTAL

Materials — Ferric chloride solution, 10 mg Fe^{3+}/ml : Appropriate amounts of Mohr's salt was dissolved in diluted hydrochloric acid solution and was oxidized with hydrogen peroxide. After a part of ferric iron was precipitated as the hydroxide, the supernatant was made approximately a 8 *M* hydrochloric acid solution. Ferric iron was then purified by extraction with butyl acetate, followed by stripping into 0.1 *M* hydrochloric acid solution. After the extracting and stripping processes were three times repeated, the ferric chloride solution was diluted with water to make a 10 mg Fe^{3+}/ml solution.

Oxalic acid solution, 0.5 *M*: The reagent grade oxalic acid was twice recrystallized and was dissolved in water.

All the other reagents were the reagent grade, and employed without the further purification.

Sampling — Sea water or lake water samples were collected with a polyethylene vessel and after filtered if necessary, they were stocked in a 20 *l* polyethylene bottles. Immediately after the sampling (before the filtration), 150 *ml* of concentrated hydrochloric acid were added to each 20 *l* of water, in order to minimize the loss of trace amount of rare earth elements that was caused by the adsorption on the vessel wall.

Sampling locations: Sea water samples were collected from a depth of a few meter off the coast near Shirahama, Wakayama Prefecture. Lake water samples were obtained from the surface near Ōmimaiko, the Lake Biwa.

Pre-irradiation procedure* — For the separation and the concentration of rare earth elements, following two coprecipitation techniques were recommended.

Procedure A: Ferric hydroxide is used as a collector in this procedure, which can be applied for both of sea water and lake water samples. Ferric iron (50 mg) is added to a water sample and precipitated as ferric hydroxide, which is then dissolved in hydrochloric acid, reprecipitated from a smaller volume, filtered and dried.

Procedure B: The procedure is adopted to sea water samples. Calcium contained in the sample is allowed to precipitate as the oxalate, carrying rare earth elements. The first precipitation is followed in twice by the partial precipitations, because the amount of the first precipitate is too large to irradiate. To a sea water sample, oxalic acid enough to precipitate calcium is added, and calcium oxalate is precipitated at pH 2.2. The precipitate is dried, and ignited, followed by dissolving with hydrochloric acid. The second precipitation is carried by adding insufficient oxalic acid and the precipitate is similarly treated. The final precipitate is produced with 5 *ml* of the oxalic acid solution, filtered and dried.

Irradiation. — The ferric hydroxide or the calcium oxalate were packed in

* The detailed descriptions of the pre- and post-irradiation procedures were given in the Appendix.

a polyethylene capsule (ca. 10 mm long \times 13 mm in diameter). Six capsules, one standard containing 0.1 μ g of europium and 1 μ g of lanthanum, one blank and four samples, were stuffed in a polyethylene rabbit tube in the most cases, but sometimes the blank was omitted.

All the irradiations were performed for one hour in a pneumatic tube of the Kyoto University Reactor: The thermal neutron flux was 5×10^{12} n/cm².sec. at the reactor power of 1 MW.

Post-irradiation procedure. — Accompanying the pre-irradiation procedures described above, two post-irradiation procedures were designed as follows. The irradiated samples were treated after a few hour cooling.

Procedure A: The sample is digested with hot hydrochloric acid containing lanthanum carrier (10 mg), and the solution is filtered. The filter paper is ashed and treated with perchloric acid and hydrofluoric acid, and the residue is taken up with hydrochloric acid, which is combined to the above filtrate. Sodium and barium carriers are added and hydroxide is precipitated. After the hydroxide reprecipitated, is dissolved with hydrochloric acid, lanthanum oxalate is precipitated at pH 2.2, in the presence of some hold back carriers and citric acid, followed by centrifuging. The second and third precipitations are carried in the same manner, and the final precipitate is dried and employed for the radioactivity measurements.

Procedure B: After adding lanthanum carrier (1 mg), the irradiated sample is ignited to the carbonate. After this is dissolved with hydrochloric acid containing ferric iron and sodium carriers, ferric hydroxide is precipitated, which is treated with perchloric and hydrofluoric acid, followed by dissolving the residue with hydrochloric acid containing lanthanum carrier (9 mg). The precipitations of lanthanum oxalate are performed in the same way as in the procedure A, and the final precipitate is used for the radioactivity measurements.

Radioactivity measurement. — Gamma-rays spectra were obtained with a well-type NaI (Tl) scintillation detector (crystal, 76.2 mm in diameter \times 76.2 mm in thickness; hole, 19.0 mm in diameter \times 45.0 mm in depth) coupled to a TMC Gammascope, Model 101 (a 100 channel puls height analyser). The probe was surrounded with the 50 mm thick lead shielding. The energy calibration of the analyser was made with the 0.662 MeV gamma-rays of ¹³⁷Cs and with the 1.17 and 1.33 MeV gamma-rays of ⁶⁰Co.

RESULTS

Figures 1, 2 and 3 gave the typical gamma-rays spectra of the standard and some of the samples. In the spectra of the samples, four gamma-rays peaks were observed above 0.4 MeV: A large peak found in the 0.8~1.2 MeV region corresponded to the sum of the 0.841, 0.963 and 0.975 MeV gamma-rays following the decay of ^{152m}Eu and the 0.815 MeV gamma-rays following the decay of ¹⁴⁰La; an other distinct peak at 1.60 MeV corresponded to the 1.60 MeV gamma-rays accompanying the decay of ¹⁴⁰La; and other two peaks were attributed to the 0.49 MeV gamma-rays of ¹⁴⁰La and to the 1.33 and 1.38 MeV gamma-rays of ^{152m}Eu, respectively.

The decay was followed for one week or more. With the lapse of time, the spectrum in the 0.7~1.2 MeV region was gradually deformed. In the beginning

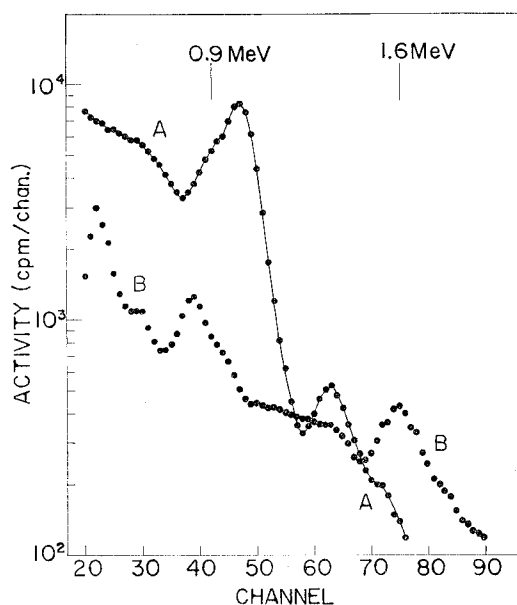


Fig. 1. Gamma-rays spectra of the standards.
A : $0.1 \mu\text{g}$ Eu, B : $1 \mu\text{g}$ La

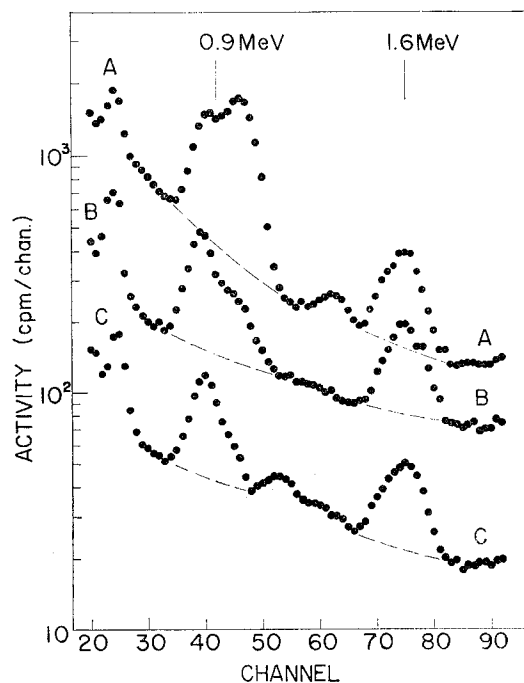


Fig. 2. Gamma-rays spectra of a sea water sample (10 l).
A : 20 h, B : 50 h, and C : 150 h after end of the irradiation.

of the measurements the spectrum resembled to that of $^{152\text{m}}\text{Eu}$, but it was quite alike the spectrum of ^{140}La after about 4 days' measurement.

The decay curves of the gamma-rays peaks in $0.75\sim 1.2$ MeV and near 1.6 MeV

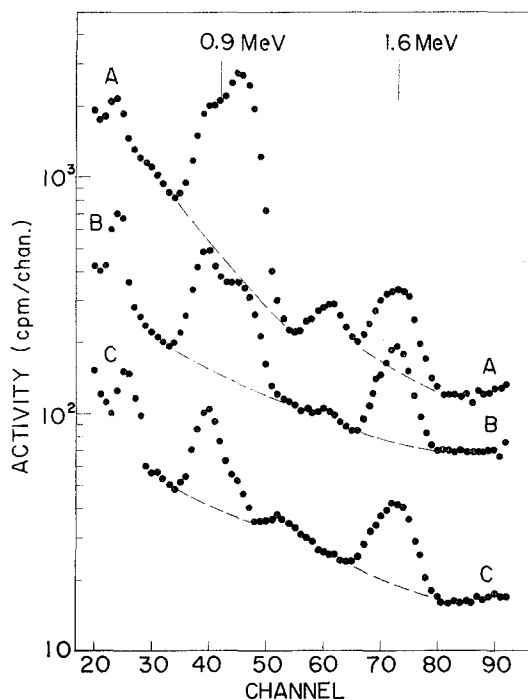


Fig. 3. Gamma-rays spectra of a lake water sample (10 l).
A : 20 h, B : 50 h, and C : 150 h after end of the irradiation.

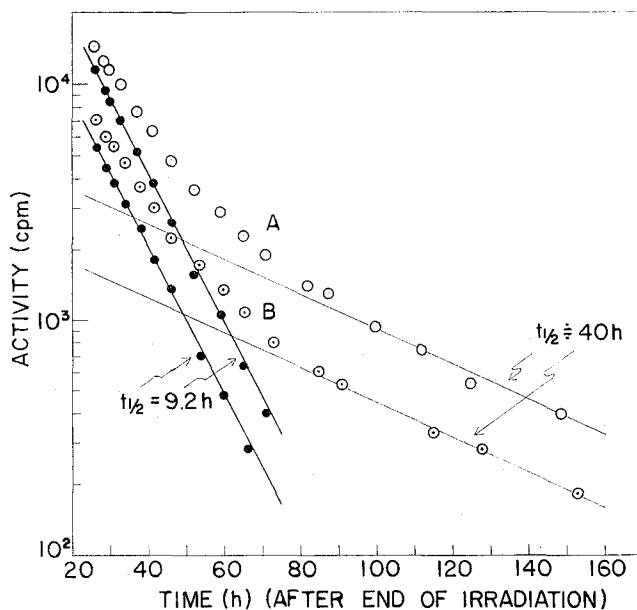


Fig. 4. Typical decay curves of the 0.75-1.2 MeV gamma-rays peak.
A : 10 l of a sample, B : 5 l of a sample.

were shown in Fig. 4 and Fig. 5, respectively. The activities of the area below the spectrum and above the dotted lined in Fig. 2 and Fig. 3 were counted. As

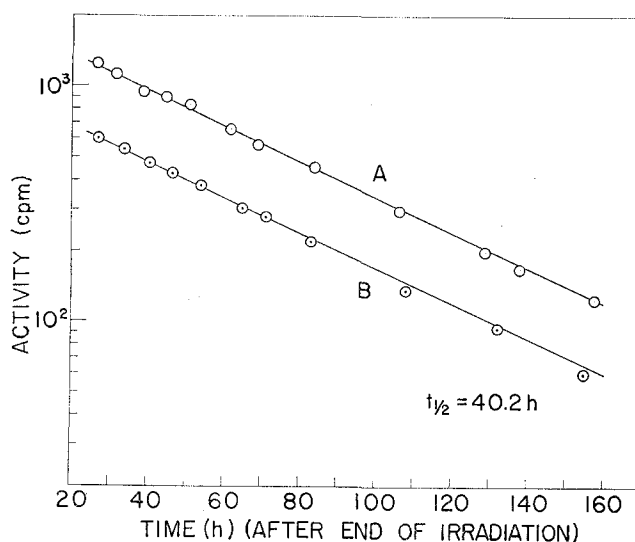


Fig. 5. Typical decay curves of the 1.6 MeV gamma-rays peak.
A: 10 l of a sample, B: 5 l of a sample.

seen in Fig. 4, the 0.75~1.2 MeV gamma-rays activities consisted of two components: The half life of the longer component was estimated to be approximately 40 h (^{140}La), and by subtracting this component the half life of the shorter component was obtained to be 9.2 h, which very well agreed with the value of $^{152\text{m}}\text{Eu}$. The 1.6 MeV gamma-rays activity was of almost single component, and the half life of 40.2 h was also in good agreement with the value of ^{140}La .

Europium and lanthanum were then determined by comparing the activity of the samples with that of the standard at a definite time. The results of the analysis were summarized in Table I.

Table I. Contents of Lanthanum and Europium in Sea Water and Lake Water.

	Sample	La ($\mu\text{g}/\text{l}$)	Eu ($\mu\text{g}/\text{l}$)	Eu/La	Procedure	
1	Sea water	$2.96 \pm 0.08 \times 10^{-2}$	$1.32 \pm 0.07 \times 10^{-3}$	0.046 ± 0.004	A	a)
2	Sea water	3.95 ± 0.36	1.78 ± 0.05	0.045 ± 0.004	B	a)
3	Sea water	3.75 ± 0.05	1.45 ± 0.05	$0.039 (\pm 0.002)$	B	b)
4	Lake water	4.36 ± 0.24	$0.96_4 \pm 0.03_6$	0.022 ± 0.002	A	a)
5	Lake water	—c)	1.10 ± 0.07	—	B	a)

a) Mean value of four determinations.

b) Mean value of two determinations.

c) La could not be determined, because Ca added as carrier was contaminated with La.

DISCUSSION

Because of the high sensitivity of the activation analysis, it is the fundamental problem that the reagents used in the pre-irradiation procedure are never contaminated with the element to be analysed. Rare earth elements are widely

distributed rather than to be rare, and there is the considerable probability of the contamination. Fortunately, ferric iron could be easily purified by the extraction of the chloro-complex: Gamma activities of the iron blank was negligible in comparison with those of the samples in the energy region above 0.7 MeV. In this region, oxalic acid did not show comparative activity, but calcium salts (carbonate, chloride and nitrate) were so much contaminated with lanthanum that the reagents could not be used even after the most parts of lanthanum were scavenged by the partial precipitation of calcium as the oxalate. Accordingly calcium could not be employed as a carrier of rare earth elements for the samples which did not contain calcium, such as lake water samples.

Most of the sea water samples were treated by the pre-procedure B. In this procedure, the first precipitation of calcium oxalate was followed by the partial precipitations, in order to decrease the amount of the precipitate and to effectively separate from many kinds of the minor components as well as the major components such as sodium, potassium, chlorine etc. Before the actual treatment of the samples, the coprecipitation behaviour of rare earth elements by the partial precipitation of calcium oxalate was investigated using $^{152,154}\text{Eu}$ as a radioactive tracer. Results are presented in Table II, which shows the loss of rare earth elements could be neglected through the pre-procedure B. Similarly, the coprecipitation recovery of the procedure A was obtained and it was confirmed that rare earth elements was approximately quantitatively recovered.

Table II. Coprecipitation Recovery of $^{152,154}\text{Eu}$ by the Fractional Precipitation of CaC_2O_4 .

Amt. of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ in solution (g/ca. 500 ml)	Add. amt. of 0.5 M Oxalic acid (ml.)	Amt. of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ pptd. as Oxalate (g)	Recovery of Eu (%)
14.7	15	1.08	99.2
14.7	15	1.08	98.9
7.35	15	1.08	99.6
7.35	5	0.37	99.8*
7.35	5	0.37	98.9
7.35	5	0.37	99.2
2.50	5	0.37	99.7
1.25	5	0.37	≈ 100
1.10	5	0.37	$\approx 100^*$

* ^{177}Lu was used

In the beginning of the research, only sea water samples were analysed and all the samples were treated by the pre-procedure B. In that time, a simple post-procedure was recommended; calcium oxalate was ignited and dissolved with hydrochloric acid, followed by the coprecipitation of rare earth elements with ferric hydroxide. However, the gamma-rays spectra of some samples were different from that of the standard: As seen from a typical example shown in Fig. 6, complicated four gamma-rays peaks were observed at about 0.5, 0.6, 0.8 and 0.9 MeV, and

sometimes considerably affected the 0.84~0.98 MeV gamma-rays following the decay of ^{152m}Eu . Although these peaks were distinct and sharp, it was impossible to estimate the nuclide from the energies of gamma-rays and the half lives, because of very slow decay of the activities.

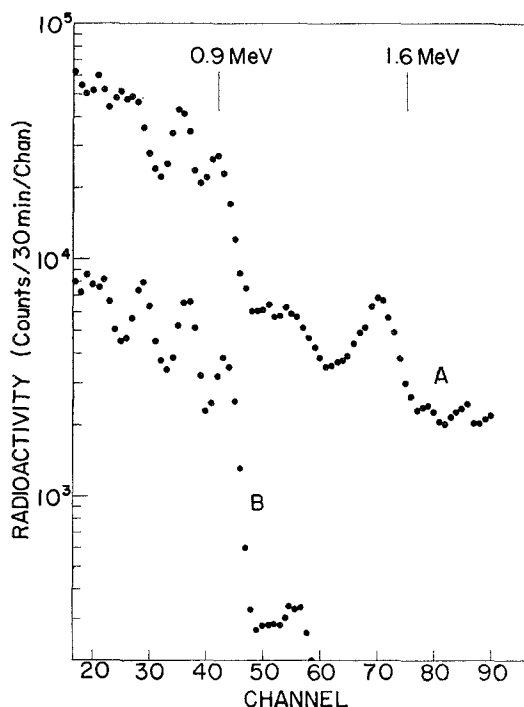


Fig. 6. Gamma-rays spectra of a sample containing interfering nuclides.
A : 20 h and B : 120 h after end of the irradiation.

The group separation in the quantitative chemical analysis was also attempted using silver, cadmium, tin, ferric iron, cobalt, manganese, zinc, strontium and sodium as carriers. The results revealed that the nuclide might belong to the 3rd group (precipitated as hydroxide from ammonium chloride-ammonia medium) or the 4th group (precipitated as sulphide from alkaline medium), but the nuclide still remained unknown. However, it was expected that the interfering nuclide could be removed from the rare earth elements, when the latter was precipitated as the oxalate in the presence of citric acid.

From this point of view, some of the counting samples (ferric hydroxide including 5 mg. of iron) was dissolved with hydrochloric acid, after ^{152m}Eu was decayed out. Lanthanum carrier (5 mg) and citric acid (ca. 0.1 M in the final concentration) were added to the solution, and lanthanum oxalate was precipitated at pH 2.2. The gamma-rays spectra of the precipitate and the supernatant were represented in Fig. 7. The latter spectra was quite the same with that of the sample before treatment, while the former did not show the gamma-rays peaks attributed to the unknown nuclide. The gross gamma activities were also measured, and the activity of the precipitate was only 1~2 % of the total activity. From these results, it was considered that the precipitation of the oxalate from citric acid

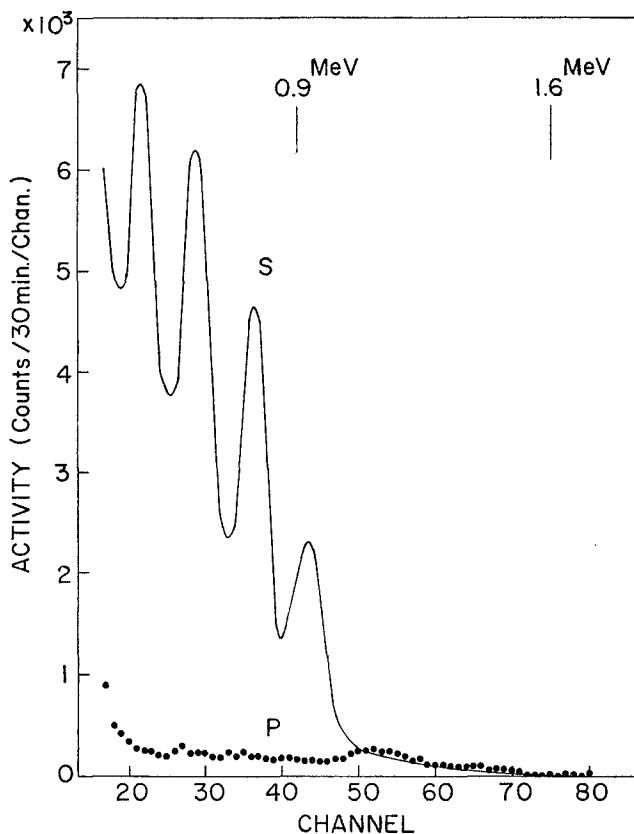


Fig. 7. Gamma-ray spectra of the supernatant (S) and lanthanum oxalate precipitate (P).

solution could be successfully applied to the separation of rare earth elements, and the post-procedures were improved as described above.

The concentration of lanthanum in sea water determined in this work is more than ten times the value reported by Goldberg²⁾ and two or three times as much as Riley's values³⁾, but it is much lower than the commonly referred content⁴⁾ ($0.3 \mu\text{g/l}$) and the expected one from the total concentration obtained by Balashov and Khitrov¹⁾. The difference may result from the nature of the sample waters, although the variety of the samples analysed in this work is too little to give the rigid data. The ratio of the europium content to the lanthanum content is estimated to be 0.043 ± 0.004 (13 determinations), which is considered to be in agreement with Goldberg's value²⁾ (0.039) and with Riley's value³⁾ (0.038).

The concentrations of both the rare earth elements in lake water are respectively of the same magnitude as those in sea water, but the europium vs. lanthanum ratio of 0.022 is comparatively low. In the present time, however, the result never lead to any conclusion, because of very a few determination.

Goldberg and his co-workers²⁾ discussed on the analytical results in comparison with the values of meteorites. According to their observation, sea water and marine environment showed a marked depletion in the heavier rare earth elements, relative to chondritic meteorites and the tendency of this depletion was more re-

markable in the sediments than in sea water. They stated that the reason for the depletion of heavier rare earth elements was due to the fractionation in the earth's crust, and the monotonic enrichment of heavy rare earth element in sea water might be attributed to the increasing stability of the heavier rare earth complexes with ligands dissolved in sea water or to the differential adsorption on solid phase. A similar concept for the fractionation in earth's surface was derived from the difference in the ratio of the rare earth content to the yttrium content in sediments and in meteorites⁵⁾. These works inform that the heavier rare earths play more important role rather than lighter ones. Accordingly, it is desirable to estimate the distribution of heavy rare earth elements. Although the best is to have the knowledge of the occurrence of all rare earth elements, the separation technique such as ion exchange method is time-consuming and troublesome to treat number of samples rapidly. Now it is practically required to design the simple technique for some heavy rare earth elements, *e. g.* dysprosium, ytterbium or lutetium. The authors will deal with the subject.

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REFERENCES

- (1) Yu. A. Balashov and L.M. Khitrov ; *Geochemistry, USSR, English Transl.*, **9**, 877 (1961).
- (2) E.D. Goldberg, M. Koide, R.A. Schmitt and R.H. Smith ; *J. Geophys. Res.*, **68**, 4209 (1963).
- (3) J.P. Riley and G. Skirrow ; *Chem. Oceanography I*, 164 (1965).
- (4) H.U. Svardrup, M.W. Johnson and R.H. Fleming ; *The Oceans* (1942) p. 220 Prentice-Hall. Inc.
- (5) L. Haskin and M.A. Gehl ; *J. Geophys. Res.*, **67**, 2537 (1962).

APPENDIX

Pre-irradiation procedure A :

- (1) To a sample (5 l or 10 l), add 3 ml FeCl₃ solution (30 mg Fe³⁺), and make the solution ammoniacal (pH 8~9).
- (2) Add 1 ml FeCl₃ solution (10 mg Fe³⁺) and NH₄OH, after a few hour standing.
- (3) Repeat the step (2).
- (4) After standing over night, decant the supernatant and centrifuge Fe(OH)₃ ppt.
- (5) Rinse the wall of the precipitation vessel with HCl (5 ml) and pour to the centrifuge tube containing the ppt.
- (6) Dissolve the hydroxide and transfer the solution to a 200 ml beaker.
- (7) Rinse the vessel and the tube with HCl (5 ml), and transfer to the beaker.
- (8) Repeat the step (7).
- (9) Wash the vessel and the tube with water, and transfer to the beaker.
- (10) Repeat the step (9).
- (11) Precipitate Fe(OH)₃ again with NH₄OH.
- (12) Filter the ppt. through a small filter paper (5A ; 55 mm in dia.), and dry at 100~110°C.

Pre-irradiation procedure B :

- (1) To a sea water sample (5 l or 10 l), add 0.5 M oxalic acid [H₂Ox] solution (40 ml or 80 ml), and adjust the pH to 2.2.
- (2) After standing over night, decant the supernatant and centrifuge CaOx ppt.

- (3) Ignite the oxalate to CaCO_3 in a platinum crucible.
- (4) Rinse out the precipitation vessel and the centrifuge tube with HCl (20 ml) and then with water.
- (5) Dissolve CaCO_3 with HCl solution used in the step (4), in a 500 ml beaker.
- (6) Dilute to about 300 ml, add 0.5 M H_2Ox solution (15 ml) and adjust the pH to 2.2.
- (7) Treat the same as in the step (2).
- (8) Treat the same as in the step (3).
- (9) Wash the centrifuge tube with HCl (10 ml) and then with water.
- (10) Dissolve CaCO_3 in the beaker.
- (11) Dilute to about 200 ml, and 0.5 M H_2Ox solution (5 ml) and adjust the pH to 2.2.
- (12) After standing over night, filter CaOx ppt. through a small filter paper (5C; 55 mm in dia.), and dry at $100\sim 110^\circ\text{C}$.

Post-irradiation procedure A:

- (1) Put an irradiated sample into a 100 ml beaker containing La^{3+} (10 mg) carrier and add HCl (1:1) (15~20 ml).
- (2) Heat and digest the solution including paper flocks, and filter through a small filter paper into a 50 ml centrifuge tube.
- (3) Ash the filter paper in a platinum crucible, add HClO_4 (0.5 ml) and HF (1~2 ml), and evaporate to almost dryness.
- (4) Dissolve the residue with HCl and combine it to the filtrate in the step (2).
- (5) Add Na^+ (10 mg) and Ba^{2+} (5 mg) hold back carriers, precipitate $\text{Fe}(\text{OH})_3$ and $\text{La}(\text{OH})_3$ with NH_4OH (pH 8~9), and centrifuge.
- (6) Dissolve the ppt. with HCl , and after add Na^+ carrier, precipitate and centrifuge again.
- (7) Dissolve the ppt. with HCl , and add Cd^{2+} (2 mg), Mn^{2+} (2 mg), Zn^{2+} (2 mg) and Na^+ (10 mg) hold back carriers.
- (8) Add 1 M citric acid solution (5 ml) and saturated H_2Ox solution (5 ml), dilute to 30~40 ml, and adjust the pH to 2.2.
- (9) Warm for a few minute, cool, check the pH, and centrifuge.
- (10) Treat the same as in the step (7), and add Fe^{3+} (5 mg) hold back carrier.
- (11)-(13) Treat the same as in the steps (8)-(10).
- (14) Add 1 M citric acid solution (1 ml) and saturated H_2Ox solution (1 ml), dilute to 7~8 ml, and adjust the pH to 2.2.
- (15) Warm, cool, check the pH, and centrifuge La_2Ox_3 in a 10 ml centrifuge tube.
- (16) Wash the ppt. with a citric acid oxalic acid mixture (0.1 M-0.1 M, pH 2.2), centrifuge, and dry at 110°C .
- (17) Close the tube with a gum stopper and put into a polyethylene sheath (to remove any chance of the contamination to NaI (TI) detector).

Post-irradiation procedure B:

- (1) Put an irradiated sample to a platinum crucible, and wet with La^{3+} (1 mg) carrier solution.
- (2) Dry and ignite to CaCO_3 .
- (3) Dissolve the ash with HCl in a 100 ml beaker, and add Fe^{3+} (5 mg) and Na^+ (10 mg) carriers.
- (4) Precipitate $\text{Fe}(\text{OH})_3$ and $\text{La}(\text{OH})_3$ with NH_4OH , and centrifuge.
- (5) Dissolve the ppt. with HCl , precipitate and centrifuge again.
- (6) Dissolve the ppt. with HClO_4 (1 ml), transfer to a platinum crucible, add HF (2~3 ml), add evaporate to almost dryness.
- (7) Treat the same as in the *procedure A*, and add La^{3+} (9 mg) carrier.
- (8)-(17) Treat quite the same as in the *procedure A*.