Europium Isolation from Silicate Rock Samples Exposed to Hiroshima Atomic Bomb Neutrons

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A method was devised for isolating europium from silicate rock samples, and was applied to the measurement of gamma-rays from $^{152}$Eu in silicate rocks exposed to the Hiroshima atomic bomb. Rock samples were powdered and fused with sodium hydroxide. A cation exchange separation technique was used to separate europium from the foreign ions. The amount of europium isolated was determined by electrothermal atomic absorption spectrophotometry.

Keywords: Europium-152, silicate rock, ion exchange separation, electrothermal atomic absorption spectrophotometry, gamma-ray spectrometry, Hiroshima atomic bomb

Recently, the residual radioactivity of $^{152}$Eu has been measured in materials which were exposed to the Hiroshima and Nagasaki atomic bombs (A-bombs). These measurements aimed at evaluating the neutron doses from these nuclear weapons. The long-lived radioactive nuclide, $^{152}$Eu (12.5 y) was produced in a variety of materials, including rock and concrete, because of the large cross section of the $^{151}$Eu(n,$\gamma$)$^{152}$Eu reaction (5900 b for thermal neutrons). Gamma-rays emitted by $^{152}$Eu can be measured with a Ge detector surrounded by a lead shield. Only a few residual radionuclides can be measured with such a detector.

Large stones in the vicinity of the Hiroshima hypocenter are potentially useful for evaluating neutron fluence because their europium content is sufficient for determination of neutron absorption. $^{152}$Eu activity in samples is less than $2\times10^{-2}$ Bq per 1 g of rock even in case of rocks which were near the Hiroshima hypocenter. Therefore, for accurate gamma-ray measurements, europium must be efficiently separated chemically, and a small $^{152}$Eu gamma-ray source must be available.

Determination of the quantity of europium in the $^{152}$Eu gamma-ray source is necessary for estimating the neutron fluence from a nuclear weapon. Moreover, for efficient isolation of europium, the europium content must be determined rapidly and precisely during the procedure. In the present study, europium was isolated from silicate rock samples by alkaline fusion and cation exchange separation. Electrothermal atomic absorption spectrophotometry (ET-AAS) was used to measure the europium concentration. Preliminary measurements of $^{152}$Eu gamma-ray spectra have been completed. In the present study, this procedure allowed the preparation of europium samples for measurement of $^{152}$Eu activity in rock samples exposed to the Hiroshima A-bomb.

Experimental

Reagents and samples

Aqueous europium standards were prepared by diluting the 1000 ppm standard solution for AAS (Kanto Chemical Co. Ltd.). The hydrochloric acid was of special grade, made for poisonous metal analysis (Kanto Chemical Co. Ltd.). The other reagents used were also of special grade.

Specimens of a tombstone exposed 100 m from the Hiroshima A-bomb hypocenter were analyzed. This monument was composed of two kinds of granodiorite rock, termed Agi-stone and Iyo-stone.

Reference rock samples JA-1, JR-1 and JB-2 by the Geological Survey of Japan (GSJ), were used to establish the europium isolation procedure.
Apparatus

A Perkin-Elmer atomic absorption spectrophotometer (Model 5000), a graphite furnace (Model HGA-500) equipped with an auto-sampler (Model AS40) and a Hitachi stripchart recorder (Model 056) were used for determining europium by ET-AAS. The light source in the spectrophotometer consisted of a hollow cathode lamp made by Hamamatsu Photonics Co., Ltd. Perkin-Elmer pyrolytically-coated graphite tubes (PG-tube) were used (part no. 091544, lot no. VI-215-628 and 6-08050-069). The standard conditions are shown in Table 1.

Gamma-ray spectra from $^{152}$Eu were measured with a Princeton Gamma-Tech Model IGCIISD pure Ge detector (54.5 cm³), a NAIG multi-channel analyzer system equipped with an ADC (Model E-552), and a NEC personal computer (Model PC-9800).

Sample preparation for gamma-ray measurements

Twenty gram samples of tombstone rock exposed to the Hiroshima A-bomb were powdered in an alumina-mortar, and fused with 120 g of sodium hydroxide in four 200 ml capacity nickel crucibles. The fusion cakes were dissolved in 2000 ml of water. After centrifugation at 3500 min⁻¹ for 15 min, the supernatant was discarded. The precipitate was dissolved in 100 ml of hydrochloric acid and 2000 ml of water.

The cations in the solution were absorbed by cation exchange resins. Then most matrix ions such as alkali, alkaline earth metal ions, Al³⁺ and Fe³⁺ were eluted by 1700 ml of 1.75 M hydrochloric acid, and the europium was eluted by 750 ml of 4 M hydrochloric acid. A cation exchange column, 30 mm in diameter and 200 mm in length (Dowex 50W-X8, 50-100 mesh), was used to accomplish this separation. The elution was performed at a flow rate of 2.5 ml/min. Ten ml of the 750 ml of europium fraction were used to determine the europium by ET-AAS.

After 10 ml of 200 ppm Fe³⁺ ion solution were added to the rest solution, a sodium hydroxide solution was added in order to adjust the pH of the solution to 10. While the solution stood overnight at room temperature, the europium hydroxide was coprecipitated together with iron hydroxide. The precipitate was collected by filtration through a 25 mm diameter Nucleopore filter (0.4 µm pore size). The precipitate in the filter was dried in a desiccator and used for the gamma-ray measurements. After such $^{152}$Eu gamma-ray measurements, the europium in this precipitate was again dissolved in 20 ml of hydrochloric acid and diluted with water to 200 ml. The ET-AAS mentioned above was used to determine the europium. To confirm the isolation procedure, europium in GSJ-reference rock samples was likewise isolated and determined. For this, 1 g of sample was used. Columns and nickel crucibles of smaller size were therefore substituted.

Results and Discussion

Condition of AAS measurements

Many ET-AAS measurements of europium have been performed by atomizing at relatively high temperatures (2500 - 2800°C) to avoid memory in the graphite tube.9-13 In this study, the memory of europium was lessened from 70% to 25% as the temperature was increased from 1900° C to 2400° C. When the atomization temperature was above 2500° C, the peak height was nearly constant and no memory was observed.

One percent absorbance was achieved at 14 pg europium under the standard conditions of ET-AAS with the PG-tube, but the sensitivity obtained with a graphite tube not pyrolytically coated (NPG-tube) was about 1/10 that of a PG-tube. The present sensitivity was comparable to the value previously reported9-13.

Table 1 Instrumental parameters for determinations of europium by electrothermal atomic absorption spectrophotometry

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>Wavelength</td>
<td>459.4 nm</td>
</tr>
<tr>
<td>Spectral band width</td>
<td>0.14 nm</td>
</tr>
<tr>
<td>Sample volume</td>
<td>20 µl</td>
</tr>
<tr>
<td>Argon gas flow rate</td>
<td>0.01 l/min</td>
</tr>
<tr>
<td>at atomization step</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Operation</th>
<th>Temp. /°C</th>
<th>Ramp time/s</th>
<th>Hold time/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drying</td>
<td>150</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>Ashing</td>
<td>500</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>Atomization</td>
<td>2600</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>Cleaning</td>
<td>2700</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

![Fig. 1 Diminution of a pyrolytically-coated graphite tube life in the ET-AAS of europium. The circle and error bar show the mean value and standard deviation of absorbance assessed after every ten measurements of 20 ppb europium solution.](image-url)
and was sufficient for the present purpose, because the isolated europium in 20 µl was in the 1000–3000 pg range. If a PG-tube is used many times, sensitivity and precision tend to decline as the pyrolytically-coated surface changes with each firing. Measurements were repeated for a 20 ppb europium solution in order to estimate tube life. The mean value and standard deviation of the peak height for every ten measurements were calculated and are shown in Fig. 1. The sensitivity and precision are nearly constant through about 70 measurements. Therefore a PG-tube can safely be used for about 70 firings under the present conditions.

Interferences by coexisting elements
Most of the alkali and the alkaline earth metals in the sample and the reagents could be transferred to the supernatant solution when the fusion cake was dissolved. These metals were discarded at this stage. The residual alkali and alkaline earth metals were also discarded by eluting them with 1500 ml of 1.75 M hydrochloric acid used for the cation-exchange separation. Al³⁺ and Fe³⁺ were also discarded in this stage. Most of the other elements in the rock sample and the flux were eliminated during these procedures, and these interferences in the ET–AAS measurement were not serious. Thus, in this study, the examination of interference was restricted only to major elements in the silicate rock, and to lanthanum, cerium, samarium and gadolinium. These rare earth metals can comprise about 10 times the europium in these rock samples, and portions of them may be co-eluted with the europium. However, determining europium by AAS was not hampered by interference which arose from the Fe³⁺ ions used to precipitate europium in preparing the sample. In the preliminary study, we noted a different trend in the interference by iron, namely, a large negative error of about 42% which occurred at 10⁴ the iron-to-europium ratio in PG-tubes of an old lot. Mazzucotelli and Frache12 reported that sodium and iron gave a positive error in the measurement of europium with NPG-tubes. A positive error was also experienced in this study even when a PG-tube was used, if it had been used more than 70 times. These discrepancies depend mainly on the quality of graphite tubes, that is, carbon atoms of surface layers of tubes may interact with europium under the presence of Fe³⁺ ions, which will cause an enhancement or depression of absorption signals. The reason of such interferences can not be clarified in this study, but the interferences can be prevented by pyrolytical coating. The large negative error mentioned above seems to have been caused by the insufficient pyrolytical coatings for the PG-tubes of the old lot.

Coexisting lanthanum, cerium, samarium and gadolinium did not cause any interference when those metals were less than 1000 times the concentration of europium. The present ET–AAS method was therefore completely free of interference by foreign ions coexisting in the gamma-ray source or in the eluent from the cation exchange column.

Neutron activation analysis (NAA) is superior to ET–AAS for the detection limit, provided that high neutron flux is available. However, it is expensive and needs a lot of time. For the determination of isolated europium, a sufficient detection limit with a better precision was obtained by the ET–AAS. In this case, 20 µl of sample solution is enough for a measurement. Therefore, the rest of the sample can be used for repeated determinations of the ^{152}Eu/Eu ratio, if necessary. Moreover, the ET–AAS enabled us to examine europium concentrations in sample solutions at each step of the isolation procedure. Therefore we used the ET–AAS as a readily available and precise method in this study.

Europium in silicate rock samples
The europium content of the GSJ-reference rock samples was measured by the above method; results obtained are shown in Table 3. Two measured values for each sample agreed with each other within 10%,
and with values reported in the literature, as well. Several $^{152}$Eu gamma-ray sources were prepared for measuring the rock samples, Agi-stone and Iyo-stone. After the gamma-ray measurements were completed, the sources were dissolved in hydrochloric acid, and the content of europium in the sources was determined by ET-AAS. The values shown in Table 4 are in good agreement, within a 4% error. These results show that the present method is quite adequate to isolate and collect europium.

Comparison of Tables 3 and 4 shows that the reproducibility in the irradiated rock samples is better than that in the GSJ-reference rock samples. The europium contents of the former samples were measured after the additional procedure of coprecipitation with iron hydroxide and re-dissolution of the precipitate. These were done for more concentrated solutions (75–100 ppb). The AAS measurements for the latter samples were performed directly for the dilute solution (3–10 ppb) eluted from the cation exchange column. Therefore, the high concentrations of europium in the solutions used for ET-AAS measurements resulted in an increase of precision in the case of the gamma-ray source.

### Measurement of $^{152}$Eu gamma-rays

Figure 2 shows a typical gamma-ray spectrum for a 20 g powdered rock sample from the tombstone. Figure 3 shows a similar spectrum for the isolated europium samples. Those spectra indicate that the isolation of europium excluded natural radioisotopes from the rock sample. Peaks of gamma-rays from natural radioisotopes remained in the spectrum for the isolated europium sample, as shown in Fig. 3. These were caused by the natural radioisotopes in the lead shield and the detector. They could be eliminated from the spectrum by subtracting the background spectrum which was measured without the sample.

The detection efficiency of the 344.3 keV gamma-ray for the isolated sample was about twice that for the powdered rock sample. In addition, the isolation of europium permits us to avoid self-absorption of gamma-rays in the sample and correcting for sample size. A calibration source of $^{152}$Eu which was made for the gamma-ray intensity determination has nearly the same chemical composition as the sample of $^{152}$Eu isolated from the rock powder. The isolated europium source was 17.5 mm in diameter and 4 mg/cm² thick, and the self-absorption for 344.3 keV $^{152}$Eu gamma-ray was less than 0.02%. This europium-isolation procedure is therefore necessary, and it proved quite satisfactory for the present study. The ratio of $^{152}$Eu/Eu in the tombstone and the estimation of

<table>
<thead>
<tr>
<th>Sample</th>
<th>Eu/μg</th>
<th>Average/μg</th>
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<tbody>
<tr>
<td>Agi-stone</td>
<td>19.2, 18.0</td>
<td>19.2(1.2)</td>
</tr>
<tr>
<td></td>
<td>18.4, 21.2</td>
<td></td>
</tr>
<tr>
<td>Iyo-stone</td>
<td>15.8, 15.4, 15.5</td>
<td>15.6(0.2)</td>
</tr>
</tbody>
</table>

a. The standard deviation is shown in parentheses.
neutron fluence from the Hiroshima A-bomb will be reported in the near future.

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