# Nondestructive neutron activation analysis of rare earth elements in hot spring water samples in Kusatsu-shirane area, Japan

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# NONDESTRUCTIVE NEUTRON ACTIVATION ANALYSIS
# OF RARE EARTH ELEMENTS IN HOT SPRING WATER SAMPLES
# IN KUSATSU-SHIRANE AREA, JAPAN

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Hot spring water samples have been analyzed for their rare earth elements (REE's) determination by the nondestructive neutron activation method. Five REE's, La, Ce, Sm, Eu and Yb, have consequently been detected and determined with satisfactory precision. The method has been found to be simple and suited for the simultaneous analyses of several samples. To determine all the REE's, however, some pretreatment of the samples will be necessary.

## Introduction

The microanalysis of the rare earth elements (REE's) ($_{57}$La $-$ $_{71}$Lu) plays an important role in geochemistry, especially in cosmochemical study of meteorites. It is also a key subject of study in such fields as environmental chemistry and chemistry related to nuclear engineering.

So far, X-ray or ultraviolet spectroanalysis or isotope dilution analysis has usually been used for the determination of REE's in various samples. In these analyses, it is a common practice to enhance the concentrations of REE's by some method before the measurements. The isotope dilution analysis is a superb one, among various analytical methods, because of its high sensitivity and high precision. Using the method, for example, MASUDA et al.[1–3] determined La, Ce, Nd, Sm, Eu, Gd, Dy, Er, Yb and Lu in meteorites and other geochemical samples.

For a few years, we have been carrying out a study on the neutron activation analysis (NAA) of the REE's in various geochemical samples.[4,5] In this paper, we report

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on the nondestructive NAA of the REE's in hot spring water samples. To the best of our knowledge, few papers have so far been published that report the determination of the REE's in hot spring water samples.

## Experimental

### Hot spring water samples

Three hot springs, Kusatsu-yubatake, Bandaiko and Kagusa, in Kusatsu-shirane area, Japan were chosen for the present work. Kusatsu-shirane area is located at about the center of the Japanese Islands, about 150 km northwest of Tokyo and is a famous hot spring resort.

Some important information on the water samples of the hot springs and the contents of their major components are summarized in Table 1. As is seen in the table, they are all very acidic. This is one of the reasons why they were chosen for the study; judging from the chemical properties of the REE's, acidic water was expected to dissolve the REE's at higher concentrations than neutral or basic water.

Table 1
Some important information on hot spring water samples and contents
of major dissolved components in $\mu g/cm^3$

| Hot spring | Sampling date | Atmospheric temperature, °C | Water temperature, °C | pH |
|---|---|---|---|---|
| Kusatsu-yubatake | 1985. 9.30 | 14.0 | 60.0 | 2.24 |
| Bandaiko | 1985. 10.1 | 16.2 | 90.0 | 1.90 |
| Kagusa | 1986. 8.1 | 27.5 | 64.9 | 1.21 |

| $Na^+$ | $K^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $Fe^{2+}$ | $Fe^{3+}$ | $Al^{3+}$ | $Cl^-$ | $SO_4^{2-}$ | $H_2SiO_3$ |
|---|---|---|---|---|---|---|---|---|---|
| 38.4 | 11.8 | 73.4 | 31.8 | 14.9 | 0.01 | 57.8 | 311 | 843 | 252 |
| 110 | 32.0 | 85.9 | 43.9 | 2.33 | 0.03 | 53.6 | 649 | 1176 | 516 |
| 181 | 162 | 320 | 167 | 777 | 46 | 866 | 4640 | 7422 | 333 |

*Neutron source*

The neutron source used was the Musashi Institute of Technology Research Reactor (TRIGA Mark II, 100 kW). Table 2 lists the irradiation equipment available there. In this study, the irradiation pit alone was used, which is suited for irradiating relatively large samples.

Table 2
Irradiation equipment available at the Musashi Institute
of Technology Research Reactor (TRIGA Mark II, 100 kW)

| Irradiation equipment | Thermal neutron flux density, $n \cdot cm^{-2} \cdot s^{-1}$ | Fast neutron flux density, $n \cdot cm^{-2} \cdot s^{-1}$ | Cadmium ratio* |
|---|---|---|---|
| Central thimble | $3.8 \cdot 10^{12}$ | $9.8 \cdot 10^{11}$ | 5.5 |
| F-ring tube | $1.8 \cdot 10^{12}$ | $3.9 \cdot 10^{11}$ | 5.8 |
| Irradiation pit | $8.0 \cdot 10^{11}$ | $3.7 \cdot 10^{10}$ | 13 ~ 15 |
| Pneumatic tube | $1.5 \cdot 10^{12}$ | $4.3 \cdot 10^{11}$ | 5.0 |
| Cyclic pneumatic tube | $7.5 \cdot 10^{11}$ | $3.2 \cdot 10^{10}$ | 12 |

*The cadmium ratio is an index of the amount of thermal neutrons relative to that of the total neutrons. It is defined as the ratio of the saturated activity of a neutron-irradiated sample (Au) without cadmium wrappings to the saturated activity of the same sample with cadmium wrappings irradiated under the same conditions.

*Neutron irradiation and analysis*

Nondestructive neutron activation technique was employed. That is, the hot spring water samples were irradiated without any pretreatment. The standard sample that contained 10–50 $\mu$g of each REE per 50.0 cm$^3$ was prepared by diluting the standard solutions of the REE's for atomic absorption spectroscopy (purchased from Kanto Kagaku Co.) with distilled water. The volumes of the hot spring water samples and the standard samples used for the irradiation were all 50.0 cm$^3$, and they were contained in 100 cm$^3$ polyethylene bottles. For the blank test correction, two more 100 cm$^3$ polyethylene bottles, an empty one and the one containing 50.0 cm$^3$ pure water, were also prepared. All the bottles were irradiated simultaneously for 10 hours. Two flux monitors were facingly attached to the outside of each bottle in order to detect and correct the slight difference in neutron flux density among the various irradiatees.

The $\gamma$-ray measurement of each sample was carried out twice, first after one-week cooling and secondly after three-week cooling, by using a Ge(Li) semiconductor radiation detector (relative counting efficiency = 10.5% and the full width at half maximum at 1332 keV = 2.0 keV) and a 4096 channel pulse-height analyzer. Before the respec-
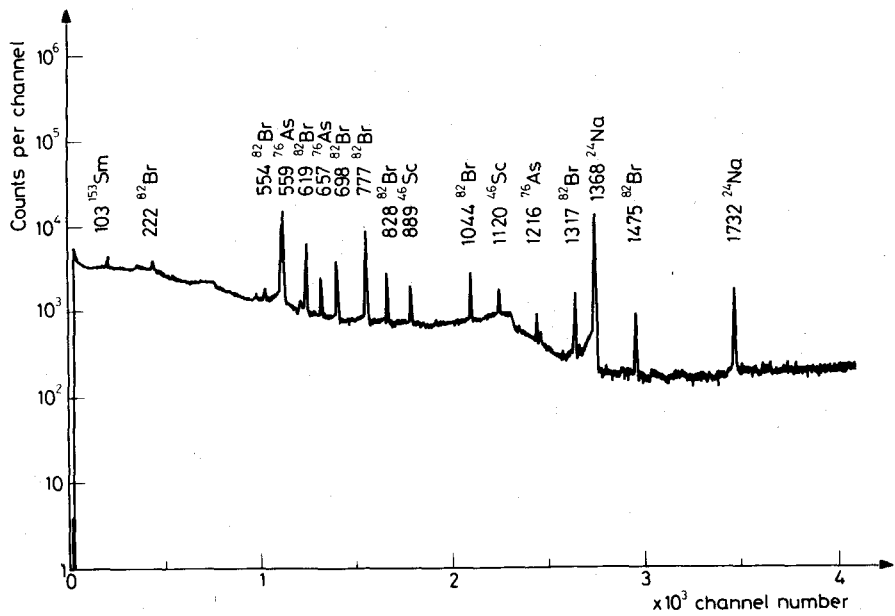
Fig. 1. Gamma-ray spectrum of the Bandaiko hot spring water sample. Cooling time was one week and the measuring time 2000 seconds
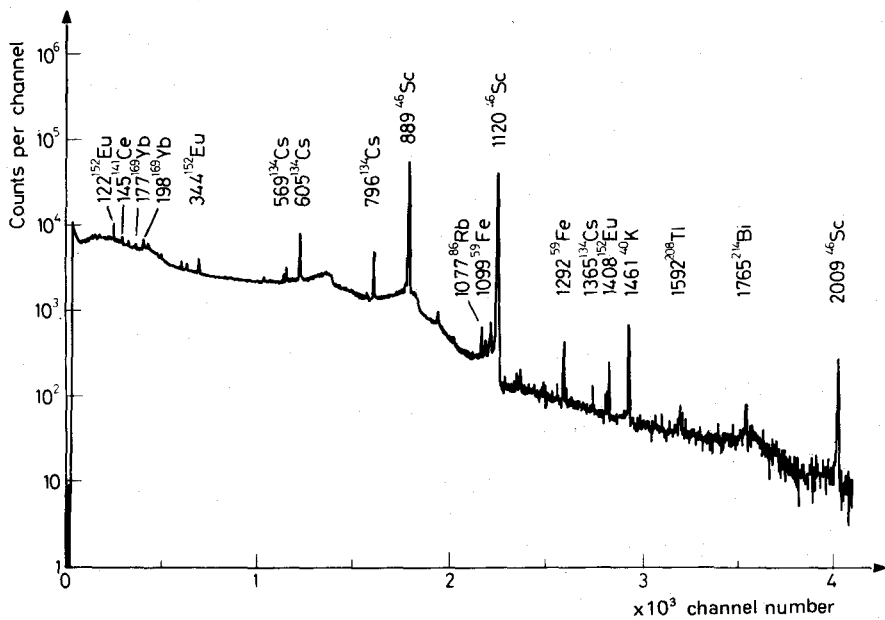


Fig. 2. Gamma-ray spectrum of the Bandaiko hot spring water sample. Cooling time was three week and the measuring time 80 000 seconds

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tive measurement, each sample was transfused into a new container. The measuring time was 2000 seconds and 80000 seconds for the first and the second measurements, respectively.

Examples of the $\gamma$-ray spectra obtained are shown in Figures 1 and 2. In Figure 1 is shown the $\gamma$-ray spectrum of the Bandaiko sample obtained after one-week cooling and in Figure 2 is shown the spectrum of the same sample at the three-week-cooling measurement. In the spectrum after one-week cooling (Fig. 1), peaks of relatively short-lived nuclides, $^{24}$Na (15 h) and $^{82}$Br (35.9 h) were observed, which interfered with the detection of peaks of some REE's. They disappeared in the spectrum after the three-week cooling, enabling to detect the peaks of such nuclides of REE's as $^{141}$Ce, $^{152}$Eu and $^{169}$Yb.

The nuclides used for the detection and determination of the REE's are listed in Table 3.

Table 3
Nuclides and $\gamma$-ray energies used for the determination
of the REE's in this work

| Target nuclide | Thermal neutron activation cross section (barn) | Nuclide used for detection | Half-life | $\gamma$-Ray energy, keV |
|---|---|---|---|---|
| $^{139}$La | 9.0 ± 0.3 | $^{140}$La | 40.3 h | 486.6, 1595.4 |
| $^{140}$Ce | 0.58± 0.06 | $^{141}$Ce | 32.5 d | 145.4 |
| $^{152}$Sm | 210 ± 10 | $^{153}$Sm | 47.1 h | 103.2 |
| $^{151}$Eu | 5 300 ±300 | $^{152}$Eu | 12.2 y | 121.8, 344.2 |
| $^{168}$Yb | 3 200 ±400 | $^{169}$Yb | 30.6 d | 177.0, 197.8 |

## Results

Five out of fifteen REE's were detected by the present nondestructive neutron activation technique: They are La, Ce, Sm, Eu and Yb. La and Sm were detected only in the $\gamma$-ray spectra taken after one-week cooling, since the nuclides used for the detection of these elements are short-lived. The other three REE's were detected, in most spectra after one-week cooling and necessarily in the spectra after three-week cooling, but they were always observed more clearly in the latter than in the former spectra. No REE was detected in the samples for the blank test. Thus, the blank test correction was unnecessary.

Table 4 lists the final analytical results of five REE's in the hot spring water samples. They were obtained from peak areas which were calculated by integrating the counts in the peaks. The results for elements other than REE's detected in this study are listed in Table 5.

## Discussion

The five REE's detected and determined by the present technique are either those whose abundances in nature are relatively rich among the REE's (La and Ce) or those whose neutron activation cross sections are relatively large (Sm, Eu and Yb; see Table 3).

Most peaks of the nuclides that were used for the determination of the corresponding REE's are located below 500 keV, especially between about 100 keV and about 200 keV, in the $\gamma$-ray spectra. There existed large interfering peaks above 500 keV and they enhanced the backgrounds of the peaks of the REE nuclides because of Compton effects, thus making it difficult to detect the REE's concerned. The major interfering nuclides in the present analysis were relatively short-lived $^{24}$Na (15 h; $E_\gamma$ = 1368 and 1732 keV) and $^{82}$Br (35.9 h; $E_\gamma$ = 554, 619, 777 keV, etc.) and relatively long-lived $^{46}$Sc (83.9 d; $E_\gamma$ = 889 and 1120 keV) and $^{59}$Fe (45.1 d; $E_\gamma$ = 1099 and 1292 keV).

The detection limits ($L_D$) were estimated by the equation $L_D = 3\sigma_B$ where $\sigma_B$ is the statistical error in the counts in the background area. The $L_D$ values for La, Ce, Sm, Eu and Yb in the three hot spring water samples are given in units of ppb in Table 6. Different samples give different $L_D$ values for an element mostly due to the difference in amounts of interfering nuclides. In Table 7 are shown the ratios of the

Table 4

The La, Ce, Sm, Eu and Yb contents (ppb) of the hot spring
water samples in Kusatsu-shirane area, Japan*

| Hot spring | La | Ce | Sm | Eu | Yb |
|---|---|---|---|---|---|
| Kusatsu-yubatate | 4.0±0.3 | 11±2 | 2.6±0.1 | 0.83±0.03 | 2.5±0.2 |
| Bandaiko | ND** | 11±1 | 2.9±0.1 | 0.95±0.03 | 2.8±0.2 |
| Kagusa | 120 ±3 | 251±1 | 27.4±0.7 | 6.01±0.09 | 18.0±0.8 |

*Errors are those in $\gamma$-ray counting.
**Not detected.

Table 5

Contents (ppm) of elements other than the REE's
in hot spring water samples determined in the present work

| Hot spring | Na · 10⁰ | Rb · 10⁻² | Cs · 10⁻³ | Sc · 10⁻³ | Fe · 10⁰ | Br · 10⁰ |
|---|---|---|---|---|---|---|
| Kusatsu-yubatake | 41 | 4.9 | 5.5 | 9.0 | 15 | 3.7 |
| Bandaiko | 110 | 11 | 20 | 21 | 2.5 | 12 |
| Kagusa | 140 | 65 | 71 | 190 | 850 | 37 |

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Table 6
Detection limits (ppb) of the elements determined
in the present work

| Element | Hot spring | | |
|---|---|---|---|
| | Kusatsu-yubatake | Bandaiko | Kagusa |
| Na* | 300 | 400 | 1000 |
| Sc | 0.03 | 0.04 | 0.2 |
| Fe | 200 | 300 | 1000 |
| Br* | 8 | 10 | 30 |
| Rb | 20 | 20 | 7 |
| Cs | 0.4 | 0.5 | 0.2 |
| La* | 2 | 4 | 5 |
| Ce | 2 | 2 | 6 |
| Sm* | 0.2 | 0.3 | 0.7 |
| Eu | 0.09 | 0.1 | 0.3 |
| Yb | 0.8 | 0.9 | 3 |

*The detection limits of these elements were obtained from the $\gamma$-ray spectra taken after one-week cooling. Those of the other elements listed were obtained from the spectra after three-week cooling.

Table 7
Ratios of determined values of elements
and the respective detection limits

| Element | Hot spring | | |
|---|---|---|---|
| | Kusatsu-yubatake | Bandaiko | Kagusa |
| Na* | 140 | 280 | 140 |
| Sc | 300 | 530 | 950 |
| Fe | 75 | 8.3 | 4300 |
| Br* | 460 | 1200 | 1200 |
| Rb | 2.5 | 5.5 | 93 |
| Cs | 14 | 40 | 360 |
| La* | 2.0 | — | 24 |
| Ce | 5.5 | 5.5 | 42 |
| Sm* | 13 | 9.7 | 39 |
| Eu | 9.2 | 9.5 | 20 |
| Yb | 3.1 | 3.1 | 6.0 |

*Elements were detected with relatively short-lived nuclides and the other elements were detected with relatively long-lived nuclides.

Table 8

The REE contents in the Bandaiko and Kagusa hot spring
water samples relative to those in the Kusatsu-yubatake sample

| Hot spring | REE | | | | |
|---|---|---|---|---|---|
| | La | Ce | Sm | Eu | Yb |
| Bandaiko | — | 1.0 | 1.1 | 1.1 | 1.1 |
| Kagusa | 30 | 23 | 11 | 7.2 | 7.2 |
| Kusatsu-yubatake | 1 | 1 | 1 | 1 | 1 |

Table 9

Abundances of the REE's in the Kusatsu-yubatake, Bandaiko and Kagusa
hot spring water samples normalized by their average abundances
in ordinary chondrites and by those in Leedey-84 chondrite (in parentheses)

| Hot spring | REE | | | | |
|---|---|---|---|---|---|
| | La | Ce | Sm | Eu | Yb |
| Kusatsu-yubatake | 0.012 | 0.013 | 0.013 | 0.011 | 0.012 |
| | (0.012) | (0.013) | (0.013) | (0.010) | (0.011) |
| Bandaiko | — | 0.013 | 0.014 | 0.012 | 0.013 |
| | ( — ) | (0.013) | (0.015) | (0.012) | (0.012) |
| Kagusa | 0.36 | 0.29 | 0.13 | 0.078 | 0.085 |
| | (0.37) | (0.30) | (0.14) | (0.073) | (0.077) |

determined values of the REE's to the corresponding $L_D$ values. The determination
of La in the Bandaiko sample was impossible. This is mostly due to the existence of
the large amounts of the interfering elements, Na and Br (cf: Tables 5 and 7). The
determined values of the other four REE's in the Bandaiko sample and those of the
five REE's in the Kusatsu-yubatake and Kagusa samples are much larger than the cor-
responding $L_D$ values. Thus, they are considered reliable enough.

The La, Ce, Sm, Eu and Yb contents in the Kagusa sample are larger than those
in the Kusatsu-yubatake and Bandaiko samples. The abundances of the REE's in the
Bandaiko and Kagusa samples normalized by those in the Kusatsu-yubatake sample
are listed in Table 8. The following can be deduced from the table: (1) The Kagusa
sample is rich in the REE's compared with the other two samples, (2) the lighter the
REE, the larger the degree of enrichment in the Kagusa sample, and (3) the Kusatsu-
yubatake and Bandaiko samples have similar REE compositions.

Another normalization is shown in Table 9; the La, Ce, Sm, Eu and Yb contents
were normalized by their average contents in ordinary chondrites[7] and by those in

Leedey-84 chondrite.[8] The REE contents normalized by ordinary chondrites lie within 0.012±0.001 and 0.013±0.001 for the Kusatsu-yubatake sample and for the Bandaiko sample, respectively. Not only the normalized REE contents are similar to each other in each sample but the two samples are similar in their REE compositions. On the other hand, the normalized value varies from 0.078 for Eu to 0.36 for La in the Kagusa sample. Especially the light REE's, La and Ce, show larger values. This means that Kagusa is different from the other two hot springs in the REE abundance pattern, although they are all in the same area.

## Conclusion

The findings of this work are summarized as follows.

(1) The nondestructive neutron activation technique was applied to detect and determine the REE's in hot spring water samples, and five REE's, viz. La, Ce, Sm, Eu and Yb, were consequently determined.

(2) The technique is simple to use and suited to analyze many samples at a time. However, it is not possible to determine all the REE's by this technique.

To determine the remaining REE's, it will be necessary to enhance their concentrations and to reduce the amounts of interfering nuclides by such a method as coprecipitation before the neutron activation analysis. We have already started our investigation along this direction.

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