Rb, Sr, Sm and Nd separation from rocks, minerals and natural water using ion-exchange resin

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Abstract

Rb, Sr and REE (Rare Earth Elements) from rock and mineral powder and natural water were separated by ion-exchange resin with hydrochloric acid (first column separation) as eluent. Sm and Nd were then separated using α-hydroxy isobutyric acid (HIBA) adjusted to pH = 4.5 (second column separation) from that REE fraction. Blanks of Rb, Sr, Sm and Nd in HCl were 0.006 ppb, 0.002 ppb, 0.001 ppb and 0.004 ppb, respectively but those for refined water (used) were 0.002 ppb, 0.0004 ppb, 0.001 ppb and 0.003 ppb. Blanks for Rb, Sr, Sm and Nd during whole procedure were 0.03-0.54 ng, 0.11-0.91 ng, 0.03-0.07 ng and 0.21-0.39 ng.

Key words: blank value, ion-exchange resin, Nd, Rb, separation, Sm, Sr.

Introduction

The two types of Thermal Ionization Mass Spectrometers (TIMS) were set up at the Faculty of Science and the Graduate School of Science and Technology, Niigata University. One is Finigan MAT 262 type equipped with nine dynamic Faraday Cups and one Secondary Electron Multiplier (SEM) and other is Finigan MAT 261 type (modified from MAT 260 type) equipped with five dynamic Faraday Cups and one SEM. The internal and external precessions of TIMS for both of $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ for GSJ (Geological Survey of Japan) standards were reported elsewhere (Miyazaki and Shuto, 1998). The Rb, Sr, Sm and Nd concentrations for GSJ and KIGAM (Korean Institute of Geology, Mining and Materials)

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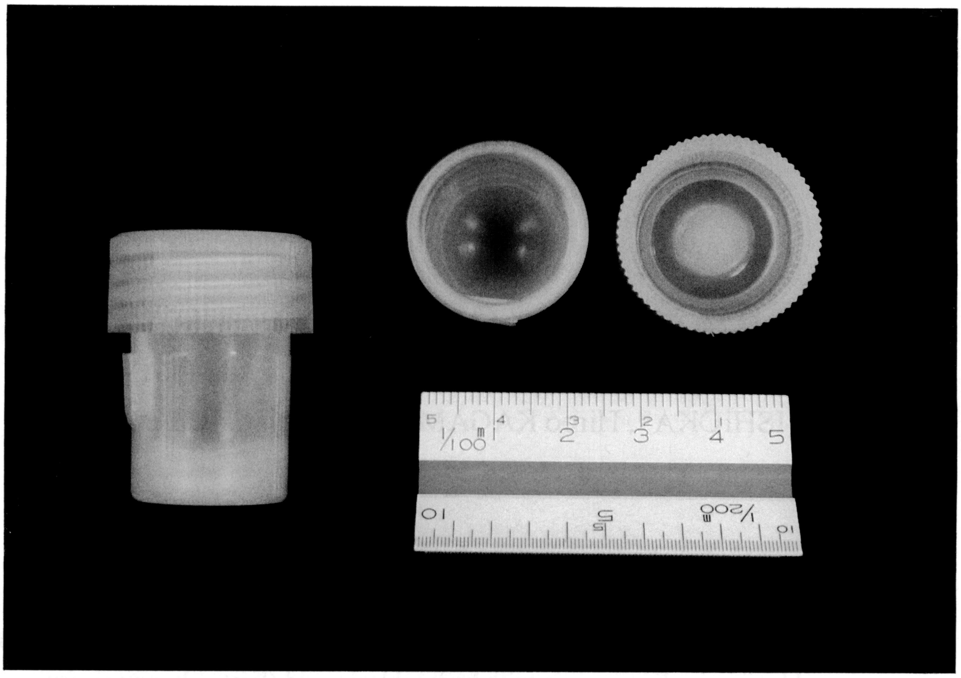

Fig. 1. Teflon vessel for decomposing rock powders.
Capacity of this vessel is 7ml (scale bar is 5 cm).

standard rock samples using isotope dilution method are also reported by Yuhara et al. (2000a). Recently, many isotopic and geochronological data have been published from as our laboratory as well (e.g., Shimura et al., 1998; Yuhara et al., 1998; Fujibayashi et al., 1999; Hamamoto et al., 1999; Ikawa et al., 1999; Ishioka and Iizumi, 1999; Kagami et al., 1999a, b; Kagashima, 1999; Rezanov et al., 1999; Shimakura et al., 1999; Yamashita et al., 1999; Yuhara et al., 1999; Fukase and Shuto, 2000; Kagami et al., 2000; Kondo et al., 2000; Miyazaki et al., 2000; Yuhara et al., 2000b). In this report, we describe Rb, Sr, Sm and Nd extraction (separation) method from rock and mineral powders and natural water using ion-exchange resin. Our method is modified as described by Kagami et al. (1982, 1987). Furthermore, we report blank value of both refined water, hydrochloric acid (used) and whole experiment procedures as well separately.

Decomposition methods

The rock powders for isotopic analyses were prepared using wolfram (tungsten) carbide or agate bowl mills. For Sr and Nd isotopic studies, 100 - 200 mg of sample powder was taken depending on concentration of Sr and Nd in rock samples. The silicate rock powders were completely decomposed using mixed acid (40% HF+ 65% HNO_3+ 70% $HClO_4$ +30% HCl) in a screwed teflon vessel (Fig. 1) at 110 °C for about one week. In case of refractory minerals

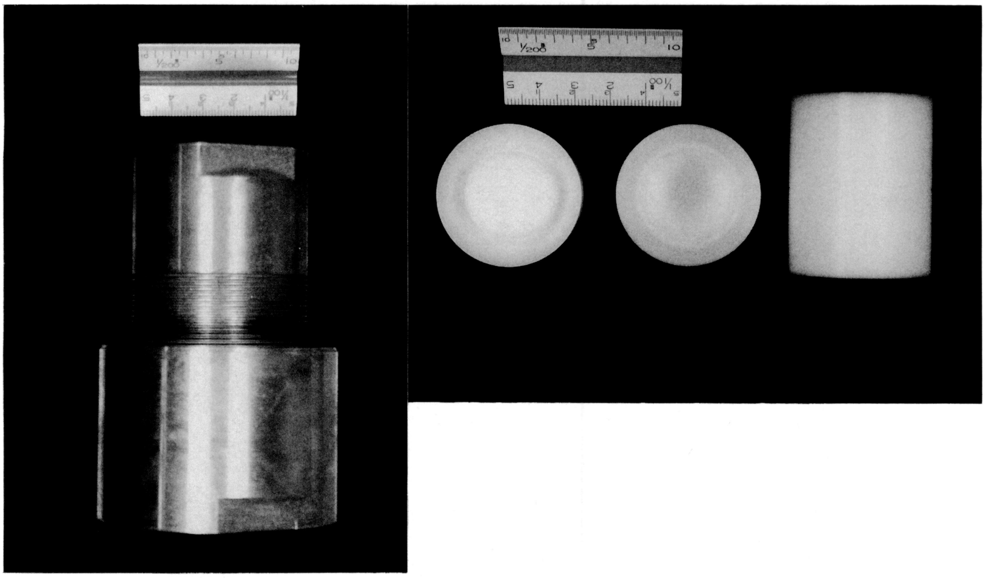

Fig. 2. Teflon vessel and sealed stainless steel jacket (scale bar is 5 cm).

(garnet, zircon, ilmenite, magnetite, spinel etc.) bearing samples, teflon vessel sealed with a stainless steel jacket (Krogh, 1973; Fig. 2) were used for decompositions at 210 °C for about one week. However, it rarely occurred that some of residual still left at the bottom of the teflon vessel. In such cases, we separated dissolved liquid and residual materials. The dissolved liquid was transferred in a separate teflon vessel and preserved. The residual materials (undissolved portion) were decomposed by another teflon vessel sealed with a stainless steel jacket at 210 °C for two or three days. In this procedure all the materials were dissolved completely. Mineral separates (separated by using magnetic separator, heavy liquid and hand picking successively) were also decomposed by following the same method as whole rock powder. Some time the small amount of inclusion minerals, which were also collected by acid reaching method, were analyzed as well. This method is very useful for geochronology of metamorphic rocks. The detail of it has been described in Hamamoto et al. (1999). The carbonate rock powders were decomposed with 0.2 mol acetic acid during about several minutes. After centrifuged it, the solution was taken analysis. The natural water (e.g., seawater, river water, rain water and hot spring water) needs to concentrate before doing separation as it contains very low amount of Sr and Nd. 50-100 ml (depending on the concentration of Sr and Nd in water sample) of this water was first passed through the ion-exchange resin where all the elements would adsorbed and retained within it. These elements were then collected by washing this resin with 6.0 mol HCl. After complete mixing and drying, it was finally taken in to 2.0 ml 2.5 mol HCl.

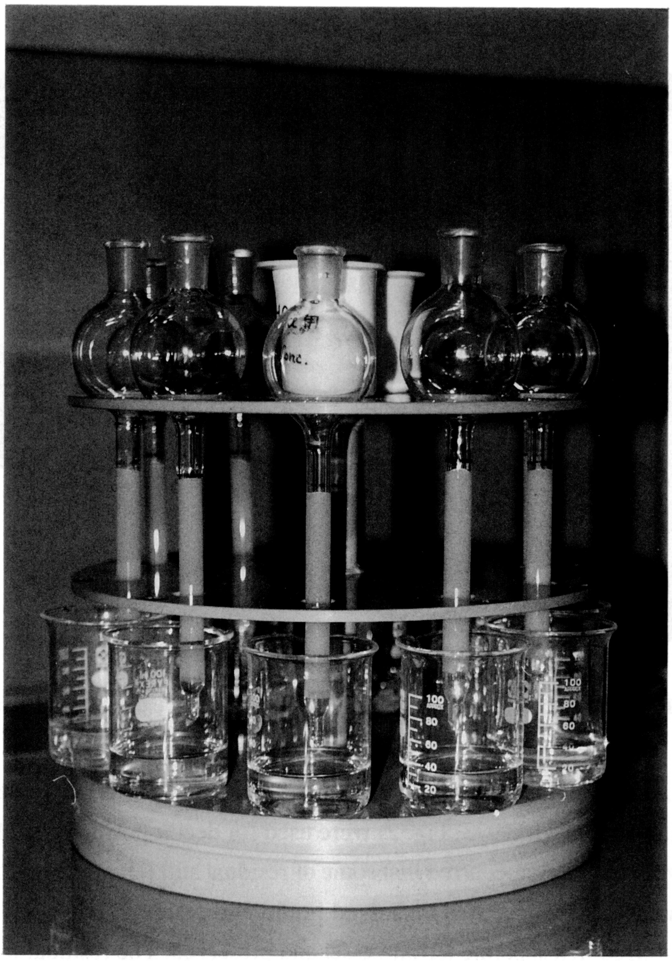

Fig. 3. First column with ion-exchange resin.

Separation of Rb, Sr, Sm and Nd

The separation of Rb, Sr, Sm and Nd were achieved using two different types of columns of ion-exchange resin (Bio-Rad, AG 50W-X8, 200-400 mesh hydrogen form) successively. One was big column (first column; Fig. 3), and other was small one. Rb, Sr and REE separation from sample solution was carried out using big (first) column where as Sm and Nd were separated from REE fraction using the small (second) column. It is very essential to separate Sr and Nd as much as possible from Rb and Sm respectively to avoid isobaric interference in 87 and 144 masses during mass spectrometric analyses.

Separation of Rb, Sr and REE

Rb, Sr and REE were separated in the first column with ion-exchange resin (Fig. 3) and

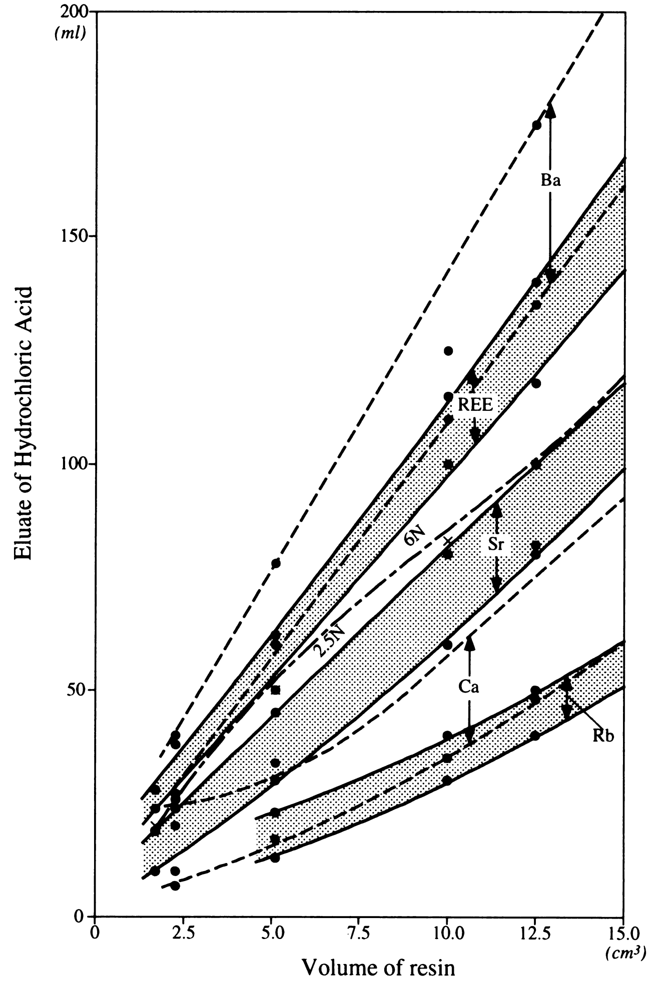

Fig. 4. Relationship of volume of ion-exchange resin and eluate hydrochloric acid.

HCl. The eluate volume (window) of elements is generally related with the volume of ion-exchange resin used and strength of the eluting medium (here HCl; Fig. 4). The calibration for Rb, Sr and REE windows using the ion-exchange resin of 5 cm^3 volume is given in Fig. 5. First decomposed sample was taken into 2.5 mol HCl. After centrifuging it at about 2000 r.p.m. for about ten minutes, only the supernatant was loaded into the first column (big one). After loading sample, the resin column was washed with 2.5 mol HCl. First 13 ml of 2.5 mol HCl was poured into the column and rejected. This eluate fraction (13 ml) was contained Fe, Ti and other elements. After is 10 ml of 2.5 mol HCl was added to the column and collected it in the clean teflon beaker as Rb sample. Then 7 ml of 2.5 mol HCl was poured into the resin and rejected it. This fraction (7 ml) was contained Ca. Next, 15ml of 2.5 mol HCl was added into the resin and collected it in the clean teflon beaker as Sr sample. Then 5 ml of 2.5 mol HCl was

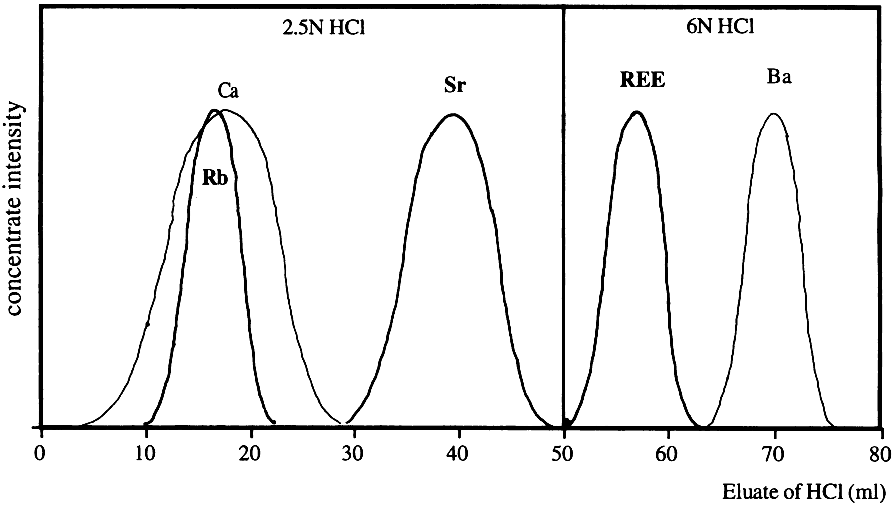

Fig. 5. Calibration of Rb, Sr, REE, Ca and Ba. Ion-exchange resin is controlled 2.5 mol HCl.

poured into the resin and rejected it. After this the strength of the eluting medium, i.e., HCl was changed from 2.5 mol to 6.0 mol. After eluting 5 ml of 2.5 mol HCl, 15 ml of 6.0 mol HCl was poured into the resin and collected the eluated solution in the clean teflon beaker as REE fraction. Sr and REE fractions were dried down on the hot plate and reserved them in small glass beaker where as Rb fraction in small teflon vessel. As Rb was eluated earlier in the resin column, lots of alkali earth elements like Ca were eluting along with it. This caused problem during loading it on to the filament during mass spectrometric analysis. Therefore, it needed further treatment (cleaning). 1.0 ml of 40% HF was added to these dried Rb fractions and centrifuged it at about 2000 r.p.m. for about 5 minutes. After the centrifuging, supernatant liquid were taken out and stored it into another teflon vessel. Then it was dried and become ready for mass spectrometric analysis.

Separation of Sm and Nd

Sm and Nd were separated using other column (small one) packed with some ion-exchange resin and 0.2 mol α-hydroxy isobutyric acid (HIBA) adjusted to pH = 4.5. The Sm and Nd windows were calibrated for 0.35 ml of same ion-exchange resin (Bio-Rad, AG 50W-X8, 200-400 mesh hydrogen form) using 0.2 mol HIBA adjusted to pH = 4.5 at constant temperature (20 °C) as eluting medium (Fig. 6). One important factor of this separation scheme was the strength of HIBA which is again depend on temperature (e.g., Kagami et al., 1987; Yamamoto and Maruyama, 1996). For that reason the room temperature was maintained as 20 °C through air conditioner.

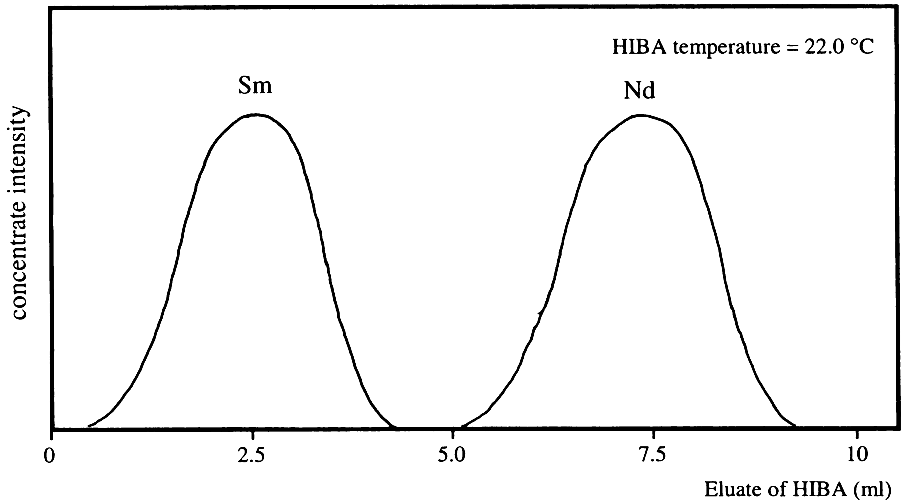

Fig. 6. Calibration of Sm and Nd. Ion-exchange resin is adjusted to pH=4.5.

Blanks of acids, refined water and whole procedure

The blank of refined water and hydrochloric acid used were measured by isotope dilution method using mixed spikes (^{84}Sr-^{87}Rb: Sr=0.016 ppm, Rb=0.11 ppm and ^{150}Nd-^{149}Sm: Nd=0.011 ppm, Sm=0.0019 ppm). Blanks for Rb, Sr, Sm and Nd in hydrochloric acid were as follows: Rb=0.006 ppb, Sr=0.002 ppb, Sm=0.001 ppb and Nd=0.004 ppb, but those in refined water were Rb=0.002 ppb, Sr=0.0004 ppb, Sm=0.001 ppb and Nd=0.003 ppb (Table 1). Blank during whole procedure was measured every month in our laboratory. The results are shown in Table 2. The whole procedure blank for Rb, Sr, Sm and Nd were 0.03-0.54 ng, 0.11-0.88 ng, 0.03-0.06 ng and 0.21-0.39 ng, respectively.

Conclusions

1) Both Rb, Sr, Sm and Nd extraction and separation were achieved using two types columns. Rb, Sr and REE were separated by ion-exchange resin and 2.5 mol and 6.0 mol hydrochloric acid as eluting medium (first column separation). Sm and Nd were them separated using ion-exchange resin and 0.2 mol α-hydroxy isobutyric acid with adjusted to pH = 4.5 from that REE fraction.

2) The blanks of refined water used hydrochloric acid used were Rb=0.006 ppb, Sr=0.002 ppb, Sm=0.001 ppb, Nd=0.004 ppb, and Rb=0.002 ppb, Sr=0.0004 ppb, Sm=0.001 ppb and Nd=0.003 ppb, respectively. The whole procedure blanks were Rb=0.03-0.54 ng, Sr=0.11-0.91 ng, Sm=0.03-0.07 ng and Nd=0.21-0.39 ng.

Table 1. Rb, Sr, Sm and Nd concentrations for refined water and hydrochloric acid.

	refined water	hydrochloric acid (EL grade)
sample weight (g)	101.2	63.24
Rb-Sr spike weight (g)	0.977	2.0734
Sm-Nd spike weight (g)	1.0245	2.0099
Rb concentration (ppb)	0.0023	0.0059
Sr concentration (ppb)	0.00037	0.0018
Sm concentration (ppb)	0.001	0.001
Nd concentration (ppb)	0.003	0.004

Table 2. Blank data for whole procedure.

	1997 July	1997 September	1998 June	1997 December
Rb (ng)	0.029	0.29	0.54	0.07
Sr (ng)	0.88	0.69	0.91	0.11
Sm (ng)	0.033	0.057	0.045	0.065
Nd (ng)	0.32	0.46	0.21	0.39

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