Precise isotope determination of trace amounts of Sr in Magnesium-rich samples

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Complete separation of Sr for the isotopic analysis of Mg-rich samples, such as ultramafic rocks and their constituent minerals, was established by adopting a combination of cation-exchange chromatography in H+ form and pyridinium form with a DCTA complex using extremely small volumes of cation-exchange resin (1 ml and 0.5 ml respectively). This method made it possible to efficiently separate nanogram sizes of Sr from coexisting large amounts of Mg and Ca with a reduced total elution volume of only 24 ml. The method also resulted in the reduction of procedural blanks for Sr and Rb to 32 and 25 pg, respectively.

Applying static multicollection mass spectrometry with Ta-oxide as an ionization activator on a V-shaped W single filament, the isotopic composition of 10 to 20 ng Sr samples separated from 40 to 55 mg of ultramafic rock standard (PCC-1) was determined with analytical precision of <0.005% and reproducibility of <0.006%. These precise analyses were performed with a high 88Sr+ ion beam intensity (>1.5 x 10^-11 A). Our efficient chemical separation procedure also ensured the absence of Ca and Mg interference to Sr ionization. The Ta-oxide readily eliminated Rb prior to the Sr isotopic analysis in the mass spectrometer. This improved the analytical reliability of isotope dilution mass spectrometry (IDMS) for the simultaneous determination of Sr isotopic composition and concentration. The measured isotopic compositions of spiked PCC-1 agreed within error with those obtained from unspiked measurements. Rb/Sr ratio analyses for PCC-1 using IDMS provided analytical reproducibilities of better than 2%. These achievements indicate that our IDMS technique is capable of yielding trace Rb and Sr concentrations simultaneously with Sr isotopic composition in Mg-rich samples with an analytical reliability similar to that obtained from larger samples (~1 mug) of common silicate rock samples.

Keywords: Ultramafic rock, Sr isotope analysis, Ta-oxide activator, DCTA, Pyridine, Cation exchange chromatography, Isotope dilution mass spectrometry, Precision, Reproducibility, Accuracy

I. Introduction

It has been difficult to precisely determine the isotopic composition of Sr in ultramafic rocks and their constituent mafic minerals, a problem which hampers our understanding of the chemical evolution of the mantle. The difficulty is caused by very low Sr concentrations and the very high Mg contents in mantle-derived materials. Both affect the chemical separation of Sr and the subsequent mass spectrometry. To overcome these problems, efficient chemical separation of Sr from such materials and high sensitivity measurements of the isotopic composition are required.

Generally, Sr is separated from silicate samples using H+ form cation-exchange chromatography (e.g. Walker et al., 1989; Reisburg et al., 1989) after dissolution with a mixed acid consisting of HF, HClO4 and HNO3. In this...
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case, however, large amounts of ion-exchange resin in a long column (e.g. 20 cm: Walker et al., 1989), necessitating large elution volume and long separation time are required. This method consequently involves a large procedural Sr blank. The large elution volumes are required because the difference in distribution coefficients for the H⁺ form cation-exchange resin is small between alkaline earth elements such as Sr, Ca and Mg (Waki, 1965). In order to enhance the difference in distribution coefficients among the alkaline earth elements, complexing agents such as lactate (Lerner and Rieman, 1954), acetate (Honda, 1954), EDTA (Honda, 1954; Davis, 1959; Wade and Seim, 1961), formate (Tsubota and Kitano, 1960), DCTA (Strelow and Weinert, 1970) and citrate (Birck and Allègre, 1978) have been used. Using these agents, the elution sequences are severely dependent on the pH of the ion-exchange medium in the column. However, it is difficult to buffer the medium to get the critical pH for optimal separation. Although these techniques improve the separation efficiency in comparison to the H⁺ form cation-exchange chromatography with HCl as an eluant, they still require large volumes of ion-exchange resin and eluant (100–950 ml: Lerner and Rieman, 1954; Wade and Seim, 1961).

Birck (1986) developed pyridinium form ion-exchange chromatography with DCTA (1, 2-diaminocyclo hexanetetraacetic acid) as a complexing agent for the separation of K, Rb and Sr from silicates. DCTA results in the largest difference in complexing strengths between Sr and the other alkaline earth elements (Strelow and Weinert, 1970), leading to more effective separation of Sr from Ca- and Mg-rich samples compared to other complexing agents. In addition, the buffering problem in this method was largely reduced by substituting ammonia as a medium for pyridine which is a weak volatile base (Birck, 1986). These characteristics of DCTA with pyridine consequently reduced the ion-exchange resin volume to 1 ml and the eluant volume to <40 ml thereby reducing the procedural blanks for Sr and Rb to 80 and 12 pg, respectively (Birck, 1986). Therefore, this method is thought to be the most suitable for the separation of trace amounts of Sr in comparison to the previous methods. However, the capability of the method has not been evaluated in detail for the measurement of Sr isotopes in Mg-rich ultramafic rocks and their constituent minerals.

In this study, we have established the most reliable analytical technique for the isotopic measurement of trace amounts of Sr in Mg-rich samples. Here, we report detailed chemical separation and mass spectrometric procedure for precise Rb-Sr isotope systematics.

II. Experimental section

1. Mass Spectrometer

All isotopic measurements were performed on a thermal ionization mass spectrometer, Finnigan MAT 261, equipped with 4 movable Faraday cup collectors and a fixed center cup. The measurement of Rb concentration was, however, carried out using a secondary electron multiplier (SEM). In order to eliminate the difference in the characteristics between amplifiers attached to the individual collectors, amplifier gain factors were measured for static multicollection mass spectrometry (SMCMS) prior to data acquisition by supplying a uniform current into the amplifiers. Accelerating voltage was adjusted to 10 kV. Faraday cup collectors and SEM were used with 10¹¹ and 10¹⁰ Ω resistors capable of measuring 10⁻¹₀ to 10⁻¹⁴ and 10⁻¹₂ to 10⁻¹⁵ A ion currents, respectively.

2. Reagents

Ion-exchange resin. Cation-exchange resin, Bio-Rad AG 50W-X12 (200–400 mesh), was soaked with 3 N HF for 1 hour. The resin was then successively cleaned in a poly-
propylene column with 2 N NaCl, distilled water and 3 N HCl, prior to final washing by alternate addition of 6 N HCl and distilled water. The resin was subsequently preserved in distilled water.

**Water.** Water deionized with a mixed-bed resin was subboiled first in a pure-quartz subboiling still (Kuehner et al., 1972), and then in a two-bottle-Teflon still (Mattinson, 1972).

**Hydrochloric Acid.** Analytical grade 35% HCl was diluted to 6 N with once distilled water and then subboiled using a pure-quartz still. The distillate was again subboiled using a two-bottle Teflon still.

**Perchloric Acid.** Ultra-pure distilled 70% HClO₄ (TAMAPURE-AA-100) obtained from the Tama Chemical Co. LTD. was directly used.

**Hydrofluoric Acid and Nitric Acid.** Analytical grade 48% HF and 61% HNO₃ were distilled twice using a two-bottle Teflon still.

**Phosphoric Acid.** Analytical grade 85% phosphoric acid was diluted to 40% with once distilled water and then passed through 1 ml of a AG 50 W-X12 resin bed column. The resulting solution was heated in order to concentrate phosphoric acid by evaporating water.

**Aqueous ammonia.** Analytical grade 25% ammonia water and twice distilled water were placed separately in a two-bottle Teflon still. The ammonia was allowed to diffuse into the water at room temperature to obtain an appropriate concentration of ammonia water.

**Tantalum oxide.** Analytical grade tantalum chloride was added to distilled water in a Teflon bottle to produce tantalum oxide. The Ta-oxide precipitate was collected by centrifuging and was then washed with distilled water. The Ta-oxide was dissolved in concentrated HF and subsequently 6 N HCl was added to the Ta solution. The solution was neutralized with ammonia to precipitate Ta-oxide and then washed with 0.1 N HCl. This treatment was repeated to remove impurities in the Ta-oxide. A 20 μg Ta/μl solution was prepared by dissolving the purified oxide in a solution consisting of (all percentages are by volume) 1.2% concentrated HF, 1.1% H₃PO₄, 5% HNO₃ and 92.7% water. This solution was used as an ionization activator for Sr and Rb in the mass spectrometer.

**Pyridine.** Analytical grade pyridine was subboiled once in a two-bottle Teflon still.

**DCTA.** Analytical grade DCTA was repeatedly washed with 0.5 N HCl and rinsed with distilled water until its pH exceeded 4. Finally, the DCTA was dried on a hot plate at 50°C.

**0.06 M DCTA in 0.5 N pyridine (D.P.E.).** Purified DCTA was dissolved in distilled pyridine and then diluted with distilled water, resulting in 0.06 M DCTA and 0.5 N pyridine solutions. This solution was subsequently passed through a cation resin bed column.

**Strontium standard solution.** National Institute of Standards and Technology standard reference material (NIST SRM) 987 was used as a standard for Sr isotope measurements. NIST SRM 987 (SrCO₃) was dissolved in 2.5 N HCl to produce a 1,000 ppm mother standard solution, and then diluted with 2.5 N HCl to appropriate concentrations.

**Strontium spike.** NIST SRM 988 solution containing 100 ppm Sr 99.89% enriched in ⁸⁷Sr, was used as a spike for isotope dilution mass spectrometry (IDMS). The Sr spike solution was diluted to 0.6350 ppm with distilled water.

**Rubidium spike.** ⁸⁷Rb-enriched (98.00%) rubidium carbonate, provided by Oak Ridge National Laboratory was dissolved in 2.5 N HCl to produce a 0.1987 ppm spike solution.

3. **Procedure**

1. **Mass spectrometry.** Prior to sample loading, V-shaped W filaments (2 mm top×0.025 mm thick×0.75 mm wide) were outgassed for 30 minutes at a filament current of 4.5 A and
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A 10^-6 Torr pressure. Prior to sample loading, 0.5 μl of Ta solution was placed on the filament and then evaporated to dryness at a filament current of 1.0 A. Afterwards, the filament current was slowly raised to 2.5 A and flashed at 3.5 A. The separated Sr sample was dissolved in 1 μl of concentrated HNO₃ and then loaded onto the Ta-oxide film. The sample was subsequently dried at 2.0 A. The loaded sample was covered by 10 μg of the Ta-oxide film using the same procedure as for forming the Ta-oxide film bed. Rb samples were loaded with 1 μl of Ta solution and then dried similarly to the Sr samples. The loaded samples were then introduced into the mass spectrometer.

When the vacuum in the ion source reached <1×10^-7 Torr, the filament current was immediately raised to 1.8 A for measurement of both Rb and Sr. The filament current for Rb analysis was then increased at a rate of 0.05 A/min until the 87Rb⁺ ion beam reached approximately 3×10^-13 A with the SEM at which point data acquisition was started. The 87Rb/85Rb ratio in the Sr sample was measured under the above conditions in order to examine the contamination of spiked Rb. The filament current for Sr analysis was then rapidly raised and kept at 2.8 A for 5 minutes. The filament current was subsequently increased at a rate of 0.03 A/min until the 85Sr⁺ ion beam current was >1.5×10^-11 A with the Faraday cup collector. Data acquisition was then started.

Determination of Sr isotopic composition was carried out by SMCMS using 5 Faraday cup collectors appropriately configured to collect 84Sr, 86Rb, 88Sr, 86Sr and 88Sr. The isobaric interference of 87Rb to 87Sr was corrected by monitoring 85Rb. The integration time for one ratio was 8 seconds. Idling and counting times for the baselines at 84.5, 85.5, 86.5, 87.5 and 88.5 m/e were 8 and 16 seconds, respectively, and the baselines were measured after each block. One isotopic measurement run consisted of 110 ratios in 10 blocks and took about 40 minutes including the gain calibration. The collected Sr isotopic data are normalized to 86Sr/88Sr = 0.1194.

Rb measurement was made by a peak jumping method (PJMS) between 85Rb and 85Rb and 85.5 m/e base line with the SEM. The integration times for baseline and each mass peak were 16 and 8 seconds, respectively. The idling times for the baseline and each scan were 8 and 4 seconds, respectively. The isotope measurement contained 21 ratios in 3 blocks.

(2) Decomposition of sample. The powdered rock sample was weighed in a 7 ml PFA Teflon beaker. For IDMS, precisely known weights of the spike solutions were added to the sample prior to dissolution. A 4:1 mixture of concentrated HF and HClO₄, was then added to the sample. The volume of mixed acid used for the sample decomposition was proportional to the sample weight, i.e. 0.5 ml for a 80 mg sample. The sample, spike and acid mixture was heated overnight at 110°C in a tightly sealed beaker. The completely decomposed sample was then evaporated to dryness using a closed-system Teflon evaporator. The dried residue was dissolved in 1 ml of 6 N HCl and the tightly sealed beaker placed on a hot plate at a temperature of 110°C for 3 hours. The solution was then evaporated to dryness in order to convert the sample to chloride form. When fluoride deposits still appeared in the 6 N HCl solution, the above process was repeated until a clear solution was obtained.

(3) Chemical separation of Rb and Sr. Our chemical procedure consists of: (1) rough removal of major elements using cation-exchange chromatography in H⁺ form and (2) purification of Sr and Rb in pyridinium form. The outline for the procedure employed in this study is summarized in Fig. 1.
propylene column (5 mm in diameter × 50 mm in length) and the resin bed was successively cleaned with 10 ml each of 1.5 N HF, 6 N HCl and water at a rate of 0.1 ml/min. The column was then conditioned with 1 ml of 4 N HCl. The chloride-form sample obtained in (2) above was dissolved in 1 ml of 4 N HCl and loaded onto the column. 2 ml of 2.8 N HCl was then introduced into the column. Sr was collected together with Rb by the subsequent addition of 7 ml of 2.8 N HCl. Collection of light rare earth elements can be made by adding 5 ml of 6 N HCl after the Sr collection as reported by Shibata et al. (1989). The Sr and Rb containing fraction was evaporated to dryness in the closed-system evaporator.

(b) Sr and Rb purification. 0.5 ml cation-exchange resin was charged into a polypropylene column (4.5 mm in diameter × 30 mm in length). The resin bed was successively cleaned with 5 ml each of 1.5 N HF, 6 N HCl and water at a rate of 0.07 ml/min. The resin was then conditioned by 0.5 ml of 25% pyridine. The dried sample obtained after the separation of major elements was converted to pyridinium chloride by adding 2 drops of 25% pyridine and then dried at 50°C. The dried sample was dissolved in 3 ml of D.P.E. This solution was loaded onto the column. 3 ml D.P.E., 3.5 ml water and 0.5 ml 1.5 N HCl were then successively added to the column to remove Mg, Ca and pyridine. Rb was collected by 2 ml of 2.8 N HCl, and Sr was finally eluted by 2 ml of 6 N HCl. These Sr and Rb fractions were evaporated to dryness in the closed-system evaporator and then loaded on W filaments for mass spectrometry.

III. Results and discussions

1. Mass spectrometry

In SMCMS, all isotopes of elements of interest are measured simultaneously. For the analysis of small sample sizes, this method is superior to PJMS because: (1) data acquisition time is short and (2) time drift correction for ion beam decay is not necessary. However, some problems with multicollector mass spectrometers have been noted (e.g. Makishima and Nakamura, 1991), especially concerning differences in Faraday cup efficiencies which cause systematic errors in the determination of isotopic ratios. Makishima and Nakamura (1991) examined the relative Faraday cup efficiencies (RFCE's) in our 5 collector mass spectrometer. They concluded that the RFCE's are nearly unity and identical within analytical error so that the RFCE correction does not make a noticeable difference in the measured isotope ratio. For this reason, we did not correct the Sr isotope ratios for RFCE
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We essentially followed the Ta-oxide method of Birck and Allegre (1978) for the ionization of Sr and Rb and used the V-shaped single W filament. This method has the following advantages: (1) the V-shaped filament enables us to load a sample with a constant width (2 mm) on the surface; (2) the measuring temperatures for Rb (800-1,000°C) and Sr (1,300-1,500°C) are sufficiently different so that Rb can be eliminated prior to the measurement of Sr resulting in the reduction of $^{87}$Rb interference on $^{87}$Sr; (3) the method yields stable and high intensity Sr ion beams compared to other methods such as the Re triple, Ta-Re double and Ta single filament methods. These advantages make the Ta-oxide method more suitable for small sample size analysis.

The relationship between ion current and analytical precision ($2\sigma_m$) in the individual runs for 10 and 100 ng Sr samples is shown in Fig. 2. The precision decreases exponentially with increasing ion beam intensity. In the 10 ng analyses, a stable ion beam lasts for $>1$ hour at an $^{88}$Sr$^+$ ion current of approximately $1.5 \times 10^{-11}$ A resulting in an analytical precision of $0.000023$. When the ion current was $>2 \times 10^{-11}$ A, the ion beam intensity decayed rapidly so that the analytical error increased. This observation indicates that there is a limit to the analytical precision of approximately $+0.000020$ for a 10 ng Sr sample with the present method although this can be statistically decreased by increasing the number of collected ratios during a run.

In order to examine analytical precision, reproducibility and accuracy for the isotopic measurement of trace amounts of Sr, we have repeatedly analyzed 10 to 100 ng aliquots of Sr from NIST SRM 987 standard with an $^{88}$Sr$^+$ ion current of $>7 \times 10^{-12}$ A. The analytical precision for each run was $<\pm0.000040$ (Fig. 3). The mean values and $2\sigma_m$ reproducibilities for 10, 50 and 100 ng samples are $0.710232\pm22$ ($n=8$), $0.710233\pm14$ ($n=5$) and $0.710239\pm11$ ($n=5$), respectively, and agree within analytical error. These values are also comparable to those obtained from routine isotopic measurements of large ($\approx1 \mu g$) Sr samples using other methods (Table 1). We therefore conclude that the results of our mass spectrometry are reliable even for trace amounts of Sr as small as 10 ng.

2. Dissolution of sample

Because of the extremely low abundance of Sr in ultramafic rocks and mafic minerals, it is crucial to increase the Sr recovery yield during
all stages of the chemical separation procedure. However, when these samples are decomposed with the HF-HClO₄ mixed acid, large amounts of Mg- and Ca-fluorides are formed. These fluorides retain much of the Sr in the samples and could not be easily dissolved with the addition of a small volume of HCl. For instance, when 100 mg of ultramafic rock sample was dried after decomposition and then forced to dissolve in 1 ml 4 N HCl, large amounts of Mg- and Ca-fluorides still remained and only 10% of the Sr was dissolved. In order to increase the yield at the stage of sample dissolution, all the fluorides must be changed into chloride. To achieve the complete elimination of fluoride from the sample, the decomposed sample was repeatedly dried and then heated with 1 ml 6 N HCl in a tightly sealed Teflon beaker at 110°C until a clear solution was obtained. After this treatment, the dried sample was able to completely dissolve in 1 ml 4 N HCl for the subsequent column chemistry and almost 100% of the Sr in the sample was recovered into the solution.

3. Chemical separation of Sr and Rb from Mg-rich sample

(1) H⁺ form ion-exchange chromatography. The matrix effect of rock composition on the chromatography was examined using about 50 mg each of basalt (GSJ JB-1a: Ando et al., 1987) and ultramafic rock (GSJ JP-1: Ando et al., 1987). The elution curves of Mg, Ca, Rb and Sr are shown in Fig. 4. When the sample is very enriched in Mg (i.e., ultramafic rock containing >40% MgO), Sr elution largely overlaps Mg elution in contrast to the case for basalts where the two elements are well separated. Furthermore, all of the Ca appears during Sr elution for both the basalt and ultramafic rock. These effects are due to the similarity in the distribution coefficients of these alkaline earth elements to the ion-exchange resin in H⁺ form which makes it difficult to efficiently separate Sr from Mg and Ca in ultramafic rocks using a small column. Since the D.P.E. solution used for the final separation of Sr and Rb is a very weak base, it is difficult to dissolve large amounts of dried sample after the decomposition. However, if the decomposed sample is directly loaded with D.P.E. onto the resin bed, the insoluble deposits readily sticks to the column walls. To avoid these problems, rough separation of the major elements must precede the final separation of Sr.

(2) Purification of Sr and Rb. In this process, Sr and Rb were purified from the fraction of Mg-Ca-Sr-Rb mixture obtained after the above procedure. Ion-exchange chromatography in pyridinium form using a DCTA complex results in large differences in distribution coefficients between Sr and the other alkaline earth and transition elements. Furthermore,

Table 1. Interlaboratory comparison of Sr isotopic analyses of NIST 987 standard

<table>
<thead>
<tr>
<th>Laboratory*</th>
<th>⁸⁷Sr/⁸⁶Sr</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANU</td>
<td>0.71022</td>
<td>(1)</td>
</tr>
<tr>
<td>DTM</td>
<td>0.710279</td>
<td>(2)</td>
</tr>
<tr>
<td>Caltech</td>
<td>0.710255</td>
<td>(3)</td>
</tr>
<tr>
<td>PML (ISEI)</td>
<td>0.710232</td>
<td>(4)</td>
</tr>
<tr>
<td>10ng loads</td>
<td>0.710233</td>
<td>(4)</td>
</tr>
<tr>
<td>50ng loads</td>
<td>0.710239</td>
<td>(4)</td>
</tr>
</tbody>
</table>

References: (1) Nakamura et al. (1990), (2) Carlson (1984), (3) Saleeby et al. (1989) (4) this study

* ANU: Australian National Univ., Canberra, DTM: Department of Terrestrial Magnetism, Carnegie Institution of Washington, Caltech: California Institute of Technology, PML (ISEI): This laboratory
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Fig. 4. Elution sequence for basalt (A) and ultramafic rocks (B) using a 1 ml cation exchange resin in the H\(^+\) form with HCl. 20 µg each of Sr and Rb were added to the rock powders which were then decomposed by the procedure described in the previous section. The resulting sample, dissolved in 1 ml 4 N HCl, was then loaded onto the 1 ml cation-exchange column. These elements were semi quantitatively determined by atomic absorption spectroscopy and are presented as relative abundances in the 1 ml fraction.

The distribution coefficients of alkaline earth and transition elements are less than 1 (Birck, 1986), while that of Sr exceeds 50. It is, therefore, expected that these elements except for Sr can be easily eluted out during sample loading and the subsequent washing with D.P.E..

The elution sequence of the pyridinium form resin with D.P.E. is presented in Fig. 5 for basalt (A) and ultramafic rock (B) samples after the coarse removal of major cations. It is clear that Ca was completely removed before the collection of Sr and Rb in both cases. Although Mg in the basaltic sample was also perfectly separated from Sr and Rb, a very small amount of Mg appeared in a portion of the Rb for the ultramafic sample. In comparison with the basalt, a relatively large amount of Mg was collected with Sr and Rb during the first stage rough separation of the ultramafic rock. Moreover, this Mg may not be completely washed out by such the small volume of D.P.E. (6 ml) eluant used. However, the Mg does not overlap with the subsequent Sr elution. The minor amount of Mg appearing in the Rb fraction could be completely removed from the resin by further washing with D.P.E.. This is, however, not necessary because the small amount of Mg does not affect the mass spectrometry for Rb.

The Sr recovery yield for the whole separation procedure, from sample decomposition to the final Sr isolation, was >90% for the basalt and >75% for the ultramafic rock.

4. Blank

For the isotopic analysis of nanogram sized Sr samples, the blank effect is a serious problem. We have, therefore, minimized the Sr blank in the course of this study in the follow-
Fig. 5. Elution sequence for basalt (A) and ultramafic rocks (B) using a 0.5 ml resin in pyridinium form with D.P.E., water and HCl. The sample (after coarse removal of major elements) containing 20 µg each of Sr and Rb was loaded onto the 0.5 ml cation-exchange column. These elements were semi-quantitatively determined by atomic absorption spectroscopy and are presented as relative abundances in the 1 ml fraction.

...ing ways: (1) purification of reagents by repeated subboiling distillation and ion-exchange chromatography; (2) evaporation of sample solution to dryness in the closed-system; and (3) use of a small volume of ion-exchange resin to reduce eluant volume.

Sr blanks determined by IDMS are shown in Table 2. The total procedural blank for Sr was 32 pg, which is 2.5 times better than that of Birck (1986), and the blank $^{87}$Sr/$^{86}$Sr ratio was 0.716. These results indicate that the blank effect is negligible and within analytical uncertainties if the sample size of Sr is >10 ng. Nevertheless, all concentration analyses in this study are blank-corrected even though the corrections are generally <0.5%.

Rb blanks for reagents and the total procedural blank are also shown in Table 2. For the IDMS determination of Rb, the blank correction was generally <2% for the ultramafic sample.

### Table 2. Reagents and procedural blanks for Sr and Rb

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Sr</th>
<th>Rb</th>
<th>pg/ml</th>
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<tbody>
<tr>
<td>2D H2O</td>
<td>0.1</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>2D HCl (6M)</td>
<td>1.0</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>2D HNO3 (6.8M)</td>
<td>1.2</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>2D HF (41M)</td>
<td>3.0</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>HClO4 (12M)</td>
<td>4.0</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>1D Pyridine</td>
<td>2.1</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>D.P.E.</td>
<td>1.6</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>DCTA</td>
<td>36</td>
<td>124</td>
<td></td>
</tr>
</tbody>
</table>

Total blank is 32 pg. Reagent blank for HClO4, pyridine, and D.P.E. were measured for 10 ml of liquid. Other reagent blanks were measured for 30 ml of liquids. The DCTA blank was obtained by subtracting the blanks in 1D pyridine and 2D H2O from those in D.P.E. 1D and 2D H2O from those in D.P.E. 1D and 2D indicate once and twice distilled, respectively. Total blank was obtained by IDMS of the whole procedure of analysis without sample.
Table 3. Isotopic compositions and concentration of Sr and Rb spikes

<table>
<thead>
<tr>
<th></th>
<th>Sr spike</th>
<th>Rb spike</th>
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<tbody>
<tr>
<td>Concentration</td>
<td>0.6350 ppm</td>
<td>0.1987 ppm</td>
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<td>Isotopic composition</td>
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<tr>
<td>$^{87}\text{Sr}/^{86}\text{Sr}$</td>
<td>1713.64</td>
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<tr>
<td>$^{87}\text{Sr}/^{84}\text{Sr}$</td>
<td>0.154292</td>
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<tr>
<td>$^{88}\text{Sr}/^{86}\text{Sr}$</td>
<td>0.679183</td>
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<tr>
<td>$^{87}\text{Rb}/^{85}\text{Rb}$</td>
<td>48.87</td>
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</tbody>
</table>

5. Analytical reproducibility in rock standards

To assess the analytical reliability of our procedure for natural samples, we analyzed the U.S. Geological Survey (USGS) standard samples BCR-1 (Columbia River basalt) and PCC-1 (peridotite in Cazadero ultramafic mass). In addition, we also used IDMS for the simultaneous determination of Sr isotopic composition and concentration following the calculation method described in Yoshikawa (1990). Isotopic compositions and concentrations of Sr and Rb spikes used in this study are given in Table 3.

In the IDMS, the Rb isotopic composition in the Sr sample was measured prior to the Sr isotopic measurement in order to determine the effect of the Rb spike contamination on the natural isotopic composition of Rb in the Sr fraction. When separation of spiked Rb from Sr was incomplete, the measured $^{87}\text{Rb}/^{85}\text{Rb}$ ratio in the Sr fraction was 0.66, a large deviation from the natural ratio of 0.38571 (Catanzaro et al., 1969). The $^{87}\text{Rb}/^{85}\text{Rb}$ in the Rb fraction for the concentration analysis ranged from 1.0 to 2.0. Although Rb is nearly totally evaporated before the ionization of Sr in the mass spectrometer with the Ta-oxide method, such a high $^{87}\text{Rb}/^{85}\text{Rb}$ ratio affects the measured Sr isotopic ratio. Consequently the measured Sr isotopic composition was significantly different from that obtained from analysis of an unspiked sample. When the Rb isotopic ratio in the Sr sample deviates largely from the natural ratio, therefore, more careful handling of the Sr isotopic analysis is necessary. For this purpose, the filament current was kept at 2.8 A after the Rb analysis until no more Rb could be detected by the SEM. Generally this was achieved after about 10 minutes. No Sr could be detected during this treatment indicating that no Sr loss occurred prior to data acquisition.

The isotopic compositions of $\sim 1 \mu g$ Sr aliquots individually separated from both spiked (using $^{87}\text{Rb}$ and $^{84}\text{Sr}$) and unspiked BCR-1 were determined using methods described in the previous sections (Fig. 6). The mean $^{87}\text{Sr}/^{86}\text{Sr}$ values (with $2\sigma$ analytical reproducibilities) from 5 and 10 runs of unspiked and spiked BCR-1 are 0.704998±15 and 0.704991±12, respectively. These values, obtained by two different methods, are indistinguishable within analytical error and are close to those obtained by other laboratories (Table 4). In the IDMS, the $^{87}\text{Rb}/^{85}\text{Rb}$ ratio in the Sr fraction, measured just before Sr data acquisition, ranged from 0.390 to 0.410. The near concordance of these values with the natural Rb ratio implies that Sr separation from Rb in BCR-1 was nearly perfect. The mean concentration of Rb obtained using IDMS was 47.1±1.0 (1 s) ppm. On the other hand, the mean Sr content obtained simultaneously with the Sr isotopic ratio was 330±2 ppm. These values are in good agreement
Table 4. Sr isotopic analyses of BCR-1 in comparison to those from other laboratories

<table>
<thead>
<tr>
<th>Laboratory*</th>
<th>(^{87}\text{Sr}/^{86}\text{Sr} )</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANU</td>
<td>0.70494 ±1</td>
<td>(1)</td>
</tr>
<tr>
<td>DTM</td>
<td>0.70488 ±4</td>
<td>(n=2)</td>
</tr>
<tr>
<td>Cabrere</td>
<td>0.70499 ±3</td>
<td>(n=8)</td>
</tr>
<tr>
<td>Max-Planck</td>
<td>0.704992 ±12</td>
<td>(n=6)</td>
</tr>
<tr>
<td>PML (USED)</td>
<td>0.704998 ±15</td>
<td>(n=5)</td>
</tr>
<tr>
<td></td>
<td>0.704991 ±12</td>
<td>(n=8)</td>
</tr>
</tbody>
</table>

References: (1) Nakamura et al. (1990), (2) Drash et al. (1986), (3) Carlson (1984), (4) White and Pachett (1984), (5) unspiked runs in this study, (6) spiked runs in this study

* Acronyms same as in Table 1.

with the recommended values (Rb=47 ppm, Sr=330 ppm) of Gouindaraju (1984).

Unspiked and spiked isotopic analyses of 10 to 20 ng Sr aliquots individually separated from 40 to 55 mg of PCC-1 were also carried out and the results are given in Table 5 and Fig. 7. The average \(^{87}\text{Sr}/^{86}\text{Sr} \) ratios of unspiked runs (with \(2\sigma_m \) analytical reproducibility) was 0.710585 ± 0.000040 and agreed within error with the ratio obtained from the spiked runs (0.710566 ± 0.000041). The integrated mean value for the two sets of data is 0.710577 ± 0.000029. The precision and reproducibility of the PCC-1 analyses are slightly larger than those for BCR-1 because of lower ion intensity during mass spectrometry caused by the much smaller sample size of Sr. In Sr mass spectrometry for small sample sizes, coexisting Ca and Mg suppress the ionization of Sr and cause ion beam instability. However, Ca and Mg in the Sr separated from PCC-1 and BCR-1 were negligible in the mass spectrometer, indicating that these alkaline earth elements were completely removed from the Sr sample by our chemical separation procedure. Consequently, we measured the Sr isotopic ratios at a \(^{88}\text{Sr}^+ \) ion beam current > 7 × 10⁻¹² A, comparable to beam currents obtained from 10 ng of NIST 987 derived Sr.

In the spiked runs, the measured \(^{87}\text{Rb}/^{85}\text{Rb} \) ratio in the Sr fraction ranges from 0.440 to 0.657 (Table 5) indicating that, unlike in the basalt, the separation of Rb from Sr in the

Table 5. Rb isotopic compositions in Sr, and Sr fractions, concentrations of Rb, and Sr isotopic compositions of PCC-1 determined by unspiked and spiked analyses

<table>
<thead>
<tr>
<th>Sr (ng)</th>
<th>(^{87}\text{Rb}/^{85}\text{Rb} )</th>
<th>(^{87}\text{Sr}/^{86}\text{Sr} )</th>
<th>2(\sigma_m )</th>
<th>Sr (ppm)</th>
<th>Rb (ppm)</th>
<th>Rb/Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>unspiked samples</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>0.3891</td>
<td>0.710623</td>
<td>±39</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>0.3891</td>
<td>0.710626</td>
<td>±27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>0.3834</td>
<td>0.710563</td>
<td>±20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>0.3861</td>
<td>0.710517</td>
<td>±20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>0.3912</td>
<td>0.710638</td>
<td>±20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>0.3853</td>
<td>0.710541</td>
<td>±19</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mean</td>
<td>0.710585</td>
<td></td>
<td>±40</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| spiked samples |
| 14      | 0.4399          | 0.710604        | ±17         | 0.3720    | 0.0588   | 0.1582 |
| 17      | 0.6569          | 0.710591        | ±14         | 0.3893    | 0.0600   | 0.1542 |
| 19      | 0.4533          | 0.710551        | ±19         | 0.3770    | 0.0604   | 0.1603 |
| 15      | 0.6189          | 0.710517        | ±18         | 0.3885    | 0.0600   | 0.1546 |
| mean    | 0.710566        | mean 0.3817     | ±41         | 1σ ±85    | ±7       | ±29   |
| 2\(\sigma_m \) |

Note: Sr amounts analyzed are estimated assuming the recovery yield of 75% in the chemical separation.
ultramafic rock was not complete. Therefore, to avoid the isobaric interference of $^{87}$Rb on $^{87}$Sr during IDMS, we had to rely more on the mass spectrometric evaporation of Rb prior to Sr analysis as earlier described. Although there is no detailed evaluation of Sr isotopic analyses of Mg-rich silicate samples so far, Pankhurst and O'Nions (1973) reported a single IDMS $^{87}$Sr/$^{86}$Sr determination of 0.7109±0.0008 for PCC-1. This is considerably higher than our value and their analytical precision is two times an order of magnitude worse than ours (Fig. 7). The discrepancy between our $^{87}$Sr/$^{86}$Sr ratio and that of Pankhurst and O'Nions (1973) may be caused by their failure to fully correct for the isobaric interference of contaminating, spike-derived $^{87}$Rb on $^{87}$Sr. It may also be caused by their poor mass spectrometric technique employing peak jumping, single Ta filament method without the Ta-oxide activator and unstable, low intensity ion beams.

The mean concentrations of Rb and Sr in PCC-1 determined by IDMS are 0.0598±0.0007 ppm and 0.3817±0.0085 ppm, respectively. These values are essentially consistent with values (Rb=0.054−0.088 ppm, Sr=0.36−0.417 ppm) previously reported by Pankhurst and O’Nions (1973) and Stueber and Ikuramuddin (1974). Furthermore, the reproducibility of the Rb/Sr ratio is better than 2% (1σ) even for the nanogram amounts of Rb and Sr obtainable in the ultramafic rock.

From these observations, we conclude that our IDMS technique for elemental and isotopic analyses of Sr in ultramafic rocks is reliable and yields results which are comparable, in terms of analytical precision and reproducibility, to those obtainable from more Sr-rich and relatively Mg-poor basaltic rocks. As shown in Yoshikawa and Nakamura (1992), this newly established method has made possible the precise determination of the Sr isotopic composition, simultaneously with the Rb and Sr contents, of single-grain clinopyroxenes (~1 mg) in mantle-derived materials and meteorite chondrules (~2 mg). This suggests that the method will be very advantageous in detailed investigations of the isotopic evolution of the smallest domains of the Earth's mantle and of meteorites.

IV. Conclusions

(1) Complete separation of Sr from Mg and Ca has been achieved for mantle-derived materials by a combination of cation-exchange chromatography in H+ form and pyridinium form with the DCTA complex. This method largely reduced total elution volume to 24 ml for the separation of Rb and Sr resulting in overall reduction of procedural blanks to 25 pg for Rb and 32 pg for Sr.

(2) The complete separation of Sr coupled with SMCMS using the Ta-oxide method have made it possible to determine the isotopic composition of at least 10 ng of Sr for ultramafic rocks with analytical precision and reproducibilities comparable to those routinely obtained for larger sample size analyses (~1
µg) of basaltic rocks.

(3) IDMS for the determinations of Rb and Sr concentrations simultaneous with Sr isotopic composition was evaluated for small quantities of ultramafic sample. The IDMS was significantly affected by the contamination of Rb spike into the Sr fraction. Using Ta-oxide as an ionization activator with a single V-shaped W filament, this problem was solved by eliminating the Rb to less than the detection limit of the SEM while avoiding Sr loss on the filament prior to Sr data acquisition. This treatment improved the analytical reliability of IDMS for Sr isotopic composition to a quality comparable with that obtained from unspiked analyses. Accordingly, the reproducibilities of Sr isotopic and Rb/Sr ratio analyses for nanogram-sized samples of PCC-1 have been improved to better than 0.006% and 2% respectively.

(4) The techniques established in this study will extend the application of Rb-Sr isotope systematics to detailed investigations of the fine isotopic structure of the mantle and meteorites using smaller samples.

Acknowledgements: We are very grateful to J.L. Birck for valuable discussion on the chemical separation of Sr and the mass spectrometry. We thank A. Makishima, T. Ishikawa, T. Shibata and H. Yokose for technical help on the operation of mass spectrometry and continuous discussion in the course of this study. We are deeply indebted to S. Nohda and Y. Matsui for providing a precious NIST 988 spike and USGS rock standards, respectively. We are also indebted to M. Maboko, C.T. Herzig and P.M. Black for improving this paper. This research is supported in part by the Monbusho (Ministry of Education, Science and Culture, Japan) International Scientific Research Program to S. Akimoto, by a Grant-in-Aid for Scientific Research to E. Nakamura.

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Precise isotope determination of trace amounts of Sr


**Mgに富む試料中の微量Srの高精度同位体測定法**

芳川 雅子・中村 染三

H⁺型とビリジン型陽イオン交換クロマトグラフィーによる化学分離法を用いことで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩石を含む試料を用いることで、超純鉱質岩やその類似岩