Rapid Purification of Alkali and Alkaline-earth Elements for Isotope Analysis ($\delta^7\text{Li}$, $\delta^{26}\text{Mg}$, $^{87}\text{Sr}/^{86}\text{Sr}$, and $\delta^{88}\text{Sr}$) of Rock Samples Using Borate Fusion Followed by Ion Chromatography with a Fraction Collector System

Daisuke ARAOKA,*† and Toshihiro YOSHIMURA**

* Geological Survey of Japan, National Institute of Advanced Industrial Science and Technology, Tsukuba Central 7, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8567, Japan
** Department of Biogeochemistry, Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima, Yokosuka, Kanagawa 237-0061, Japan

† To whom correspondence should be addressed.
E-mail: d-araoka@aist.go.jp
Abstract

For rapid, easy, and safe purification of alkali and alkaline-earth elements from rock samples for stable isotope analysis, we developed a semi-automated, high-throughput procedure using borate fusion and an ion chromatography system equipped with a fraction collector. This HF-free procedure for decomposition of silicate rock samples can be performed in a short time without isotope fractionation, and the purification procedure enables the collection of baseline-separated peaks of multiple target elements and the complete removal of interference matrices from reagents and samples. The accuracy of this procedure was verified by confirming the correspondence of stable isotopic values of Li, Mg, Sr (\(\delta^7\)Li, \(\delta^{26}\)Mg, \(\delta^{88}\)Sr) and radiogenic isotopic values of Sr (\(^{87}\)Sr/\(^{86}\)Sr) to previously reported values in various geochemical reference materials in which the concentration range of Li was 7.78–86.6 ng g\(^{-1}\), that of Mg was 0.02–26.9 % m/m, and that of Sr was 178–7240 ng g\(^{-1}\). These results demonstrate that this procedure, which allows concurrent multi-isotope analysis of alkali and alkaline-earth elements in the same sample, is applicable to a wide variety of sample types.

Keywords: Li isotope, Mg isotope, Sr isotope, borate fusion, ion chromatograph, fraction collector, geochemical reference material
Introduction

Isotopes of alkali and alkaline-earth elements such as Li and Mg in natural samples have been widely used for investigating various geochemical and biological processes because the large mass differences between the isotopes of Li (16%, $^6\text{Li}$ and $^7\text{Li}$) and of Mg (8%, $^{24}\text{Mg}$ and $^{26}\text{Mg}$) result in large isotopic variations in natural systems.\(^1\)\(^-\)\(^5\) Because both Li and Mg are fluid-mobile, their stable isotopic compositions ($\delta^7\text{Li}$ and $\delta^{26}\text{Mg}$) in silicate rocks and minerals are useful for deciphering fluid/melt–rock interactions from the Earth’s surface to the mantle.\(^6\)\(^-\)\(^9\) Sr isotopes (e.g. $^{87}\text{Sr}/^{86}\text{Sr}$) have also wide application such as geochronology and provenance studies.\(^10\)\(^,\)\(^11\) Recently, stable isotopic compositions and fractionation of Sr ($\delta^{88}\text{Sr}$) attract a great deal of attention for studies on planetary evolution and magmatic processes.\(^12\) The combined use of $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{88}\text{Sr}$ provides a tool to identify differences in Sr sources and the chemical reactions which have undergone in the Earth and planetary systems.

Recently, multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has become a widespread technique for rapid determination of stable and radiogenic isotope compositions of natural samples. The chemical purification of the target elements must be required for the isotopic analysis in order to avoid both isobaric and non-spectrometric interferences, both of which lead to inaccurate isotopic values for the samples.\(^13\)\(^-\)\(^16\) For geological samples, multiple-step column separation using various types of cation exchange resins is often employed both to recover analyte elements completely and to discard interference elements.\(^17\)\(^-\)\(^19\) However, during this purification procedure, steps must be taken to ensure complete recovery of analyte elements because isotopic fractionation easily occurs during column separation processes.\(^18\)\(^,\)\(^20\) Since the amounts of Li in most environmental and geological samples are tiny compared to the amount of Na, purified residue of Na must be avoided for accurate Li isotopic measurements.\(^15\) Furthermore, K and Ca, which are major
elements in environmental samples, interfere with Mg and Sr during column separation.\textsuperscript{13,21}

Moreover, to obtain precise and accurate measurements of stable isotopic compositions in silicate rock/mineral samples, all constituent minerals must be completely dissolved because isotopic composition varies among constituent mineral species.\textsuperscript{22,23} Usually, HF must be used in combination with HNO\textsubscript{3}, HCl, or HClO under high-temperature and high-pressure conditions to dissolve silicate rocks completely, a procedure which is both time-consuming and potentially very hazardous.\textsuperscript{13,14} Appropriate method based on constituent minerals in the samples should be chosen for complete dissolution and prevention of reprecipitation. Not only undissolved residues of refractory minerals such as spinel and phosphate in rock samples but also precipitation of the insoluble fluoride compounds results in inaccurate elemental and isotopic values.\textsuperscript{24,25}

Here, we developed a purification procedure that uses a borate fusion method and an ion chromatography (IC) system equipped with a fraction collector (FC) and allows rapid, easy, and accurate analysis of isotopic compositions of alkali and alkaline-earth elements in geological samples. Borate fusion is widely used in the earth and material sciences to prepare samples for X-ray fluorescence (XRF) analysis and many automated machines are available commercially. In this method, glass beads are made by melting powdered samples mixed with a borate flux as a fusing agent.\textsuperscript{26,27} A borate flux can dissolve silicates, carbonates, oxides, and sulfates in a short time. Thus, sample decomposition can be accomplished easily and rapidly as well as safely by a HF-free method by using an automated machine. High-purity borate flux is also readily available for potential use in isotopic studies of alkali and alkaline-earth elements. Moreover, glass beads are easily dissolved even in dilute acids. To achieve accurate isotopic measurements, however, separation of each element from solution matrices, particularly from Na in the case of sodium tetraborate fusion, is essential. IC is widely used to quantify cation and anion concentrations in sample solutions. Because of its high selectivity and short separation time, IC
has recently been used for sample purification prior to the determination of isotopic values of elements of interest.\textsuperscript{28–30} Notably, an IC-FC system can be used for automated simultaneous offline purification of multiple target elements from matrix elements derived from rock samples and fluxes together with quantitative determination of the concentration and purity of each analyte.\textsuperscript{31} The use of IC is advantageous due to better chromatographic resolution, shorter separation time, and high-throughput. Compared to the conventional open-column cation exchange and extraction chromatography, a separation of alkali and alkaline-earth elements can be achieved with simple isocratic elution using dilute 8 mM nitric acid. As for the optimum concentration range of major elements, about 100 samples per day can be purified for each isotopic measurement. Especially in the case of trace elements in environmental samples, such as Li in seawater, target elements can be concentrated for isotopic measurement by repeated collection of the purified Li fraction.\textsuperscript{31} In fact, Li and Mg isotopic values for IAPSO seawater standard by means of this IC-FC purification system were good agreement with the previously reported values.\textsuperscript{31} Therefore, versatile systems for rapid and easy purification for multiple target elements from samples of various rock types can be developed by using borate fusion in combination with an IC-FC system.

In this study, we tested this purification method by determining stable isotopic compositions of Li, Mg, and Sr as well as radiogenic isotopic compositions of Sr, as representative of isotope ratios of alkali and alkaline-earth elements, in some geochemical reference materials of igneous rocks and carbonates distributed by the Geological Survey of Japan (GSJ). In order to verify the accuracy, we then compared the determined isotopic compositions with previously reported values.

\textbf{Materials and Methods}
Samples

We measured Li isotopic compositions in JA1 (andesite), JB2 (basalt), JG2 (granite), and JR2 (rhyolite), Mg isotopic compositions in JA1, JA2 (andesite), JB2, JG1 (granodiorite), JGb1 (gabbro), JP1 (peridotite), JR2, JDo1 (dolomite), J Cp1(coral), and JCt1 (giant clam), and Sr isotopic compositions in JA2, JB2, JG1, JDo1, JCp1, and JCt1. These reference materials were selected because they have a wide range of Li, Mg, and Sr concentrations and because chemical compositions of igneous rocks vary from mafic to felsic (Table S1). In some of these reference materials, Li, Mg, and Sr isotopic compositions obtained by using the traditional preparation method (that is sample decomposition with acids and open-column chromatography) and MC-ICP-MS measurement have been previously reported.

Sample decomposition by borate fusion

A flowchart of sample decomposition by borate fusion and purification by the IC-FC system is illustrated in Fig. 1. To decompose silicate minerals as well as minor refractory minerals in igneous rock samples, a borate fusion method has been used for powdered samples to determine whole-rock compositions by XRF analyses. In general, lithium metaborate (LiBO₂), lithium tetraborate (Li₂B₄O₇), or both, are used as the flux, together with LiBr as the releasing agent. In this study we used high-purity (>99.0%) sodium tetraborate (Na₂B₄O₇; Spectromelt B10, Merck Millipore, Massachusetts, United States) and high-purity (>99.9%) KBr (Code No. 162-13721, Wako Pure Chemical Industries Ltd., Osaka, Japan) to make the glass beads for measurement of Li isotope ratios in the samples. According to the examination certificates of these reagents, all metallic elements are less than 10 μg g⁻¹ in sodium tetraborate and less than 0.5 μg g⁻¹, except for Na of 141 μg g⁻¹, in KBr. Depending on the contents of target elements in the samples, fused-glass beads were prepared from a mixture of 0.1 to 2.0 g of rock powder sample and 0.2 to 4.0 g of sodium tetraborate flux; as the releasing agent, about
33 wt % KBr was then added to one-fiftieth of the total weight. For complete fusion of all minerals, a sample weight of 0.1 g or heavier and a flux:sample ratio of 2:1 or higher were used because of high melt viscosity. The mixture was heated to 1000 °C for 10 min in a 95% Pt–5% Au crucible with an inner diameter of 30 mm using a semi-automatic high-frequency fusion device (HAG-M-HF, Herzog Automation Corp., Ohio, United States).

The glass beads were crushed and powdered in an agate mortar. Then, powdered glass was weighed as needed for isotope measurements and acidified with 10 mL of ultrapure 8 mM HNO₃ (TAMAPURE AA-100, Tama Chemical Corp., Kanagawa, Japan) in a perfluoroalkoxy alkane (PFA) vessel. The PFA vessel was placed in an ultrasonic bath heated to 50 °C for at least 2 h. The sample solutions of only the mafic rock samples (JB2, JGb1, and JP1) were colored because they contained higher concentrations of transition metal elements than those of the felsic rock samples. Although the glass beads were easily dissolved, excess silica formed a gelatinous precipitate with boric acid during the dissolution. By filtering the sample solutions through a 0.2 µm PTFE syringe filter, however, most of the silica was removed and the color of the solutions was changed to clear. No further precipitation of silica from the filtered solution occurred before IC separation. The carbonate reference materials were only dissolved in ultrapure 8 mM HNO₃.

The recovery of target elements was checked by measuring concentrations of alkali and alkaline-earth elements (Li, Na, Mg, K, Ca, and Sr) in the filtered solutions by ICP-MS (iCAP Qc, Thermo Fisher Scientific, Massachusetts, United States) at the Japan Agency for Marine-Earth Science and Technology. By comparing the elemental compositions of the filtered solutions calculated from the amounts of reagents and rock samples dissolved in the solution with those measured by ICP-MS, the yield of each element during the sample decomposition procedure can be calculated. Before the ICP-MS measurements, we added Be as an internal standard to HNO₃ for correction of instrumental drift. The reproducibilities of measurements of
each element were estimated to be better than 5% (2 RSD) by standard solution analyses. The detection limits in the ICP-MS analysis were 50 pg ml⁻¹ for Li and Na, 40 pg ml⁻¹ for Mg, 2 ng ml⁻¹ for K, 400 pg ml⁻¹ for Ca, and 2 pg ml⁻¹ for Sr, which is calculated by means of 3 SD of the 0.3 M HNO₃ blank solution analysis. In addition, to check for contamination of reagents and the procedural blanks of Li, Mg, and Sr during the sample decomposition, a procedural blank solution sample consisting of only the sodium tetraborate flux and releasing agent was also analyzed by the same procedure.

**Purification by the IC-FC system**

Li, Mg, and Sr in sample solutions were separated by IC on a 930 Compact IC Flex instrument (Metrohm AG, Herisau, Switzerland) coupled to an Agilent 1260 Infinity II Bio-Inert analytical-scale FC system (Agilent Technologies, California, United States). Before separation by the IC-FC system, all samples were diluted more than 10 times with Milli-Q water. This is because Li and Sr should be completely separated from Na and Ca, respectively, in the elution profiles. The diluted samples were eluted through a Metrohm Metrosep C6-250/4.0 column (packed with silica gel functionalized with carboxyl groups) with ultrapure 8 mM HNO₃ at a flow rate of 0.9 mL min⁻¹. A time-triggered mode was used for continuous collections of baseline-separated peaks of target elements. Then, this automated IC-FC system can purify more than 1000 ml of diluted samples at once. The other settings of the IC-FC system are described previously.³¹

The fractions of Li, Mg, and Sr were pooled in a 7 mL PFA vessel several times until the total collected amounts were more than 30 ng Li, 120 ng Mg, and 240 ng for Sr, the amounts required for a single isotopic measurement. The collected fractions were evaporated to dryness, and then the residue was redissolved in 0.3 M HNO₃. Finally, the purified Li (Mg) and Sr solutions were diluted to 100 ng g⁻¹ Li (Mg) and 200 ng g⁻¹ Sr for each isotopic measurement,
respectively. To check for contamination during the IC-FC purification procedure, elemental compositions in the purified solutions were determined by the ICP-MS analysis.

**Li, Mg, and Sr isotopic measurements**

Li, Mg, and Sr isotope compositions in the purified solutions were determined by MC-ICP-MS (Neptune Plus, Thermo Fisher Scientific, Massachusetts, United States) at GSJ. Isotopic measurements were performed in medium-mass-resolution mode with a high-sensitivity X-skimmer cone for Mg and in low-mass-resolution mode with a standard H-skimmer cone for Li and Sr. Instrumental mass discrimination was corrected by a standard-sample bracketing technique for all isotopic measurements. Standard (L-SVEC for Li, DSM3 for Mg, and and SRM 987 for Sr) solutions were also prepared by dilution with 0.3 M ultrapure HNO₃. The beam intensities for the 100 ng g⁻¹ Li and Mg solutions and the 200 ng g⁻¹ Sr solutions were approximately 2.0 V for ⁷Li, 5.0 V for ²⁴Mg, and 9.0 V for ⁸⁸Sr, respectively. Each analysis of samples and standards comprised 1 block of 40 cycles for Mg and Sr and 1 block of 30 cycles for Li with 4 s integration. Before each sample and standard measurement, background signal intensities were determined by analysis of 0.3 M ultrapure HNO₃ for 1 cycle with 30 s integration and subsequently subtracted from standard/sample signal intensities. The 2 SD values of each data for Mg isotopic compositions were calculated from triplicate measurements of each sample.

For Sr isotopic measurements, commercially available Zr AA-standard solution (Kanto Chemical Corp., Tokyo, Japan) was added to all samples and standards at a concentration of 200 ng g⁻¹ Zr for mass bias correction on ⁸⁸Sr/⁸⁶Sr determination. ¹³⁶⁶³Kr, ⁸⁴Sr, ⁸⁵Rb, ⁸⁶Sr, ⁸⁷Sr, ⁸⁸Sr, ⁹⁰Zr, and ⁹¹Zr ion-beams were collected simultaneously by Faraday cups in a static mode. ³⁷Kr and ⁸⁵Rb were used for the correction of isobaric interferences of ⁴¹Kr, ⁸⁶Kr, and ⁸⁷Rb. Radiogenic ⁸⁷Sr/⁸⁶Sr ratios and stable ⁸⁸Sr/⁸⁶Sr ratios were corrected for instrumental mass bias
by the $^{88}\text{Sr}/^{86}\text{Sr}$ ratio of 8.3752 and the $^{91}\text{Zr}/^{90}\text{Zr}$ ratio of 0.2181, respectively, followed by a standard-sample bracketing technique employed in order to improve the reproducibility of the measurements.\textsuperscript{16}

The measured stable isotopic ratios are reported as per mil (‰) deviations relative to standard reference materials (L-SVEC for Li, DSM3 for Mg, and SRM 987 for Sr):

\[ \delta^n\text{Li} = \left( \frac{^{7}\text{Li}^{6}\text{Li}}{^{7}\text{Li}^{6}\text{Li}} \right)_{\text{sample}} - 1 \times 1000 \] (1)

\[ \delta^{26}\text{Mg} = \left( \frac{^{26}\text{Mg}^{24}\text{Mg}}{^{26}\text{Mg}^{24}\text{Mg}} \right)_{\text{sample}} - 1 \times 1000 \] (2)

\[ \delta^{88}\text{Sr} = \left( \frac{^{88}\text{Sr}^{86}\text{Sr}}{^{88}\text{Sr}^{86}\text{Sr}} \right)_{\text{sample}} - 1 \times 1000 \] (3)

The analytical uncertainties were better than ±0.4‰ (2 SD) for $\delta^n\text{Li}$ and ±0.12‰ (2 SD) for $\delta^{26}\text{Mg}$ as estimated from the reproducibility of multiple measurements of monoelement standard solutions during each analytical session: 8.2 ± 0.4‰ (2 SD, $n$ = 53) for an in-house Li standard (Kanto Chemical Corp., Tokyo, Japan) and −2.61 ± 0.05‰ (2 SD, $n$ = 6) for the Cambridge 1 Mg standard. Within the analytical uncertainties, these values agree well with reported values for the same standards: 8.3 ± 0.4‰ (2 SD, $n$ = 47)\textsuperscript{64} and 8.5 ± 0.4‰ (2 SD, $n$ = 10)\textsuperscript{65} for $\delta^n\text{Li}$ and −2.58 ± 0.14‰ (2 SD, $n$ = 35)\textsuperscript{66} and −2.62 ± 0.04‰ (2 SD, $n$ = 6)\textsuperscript{17} for $\delta^{26}\text{Mg}$.

The analytical uncertainties for Sr isotopic compositions were better than ±0.00003 (2 SD) for $^{87}\text{Sr}/^{86}\text{Sr}$ and ±0.05‰ (2 SD) for $\delta^{88}\text{Sr}$ as estimated from the reproducibility of multiple measurements of purified Sr solution from IAPSO seawater standard by this IC-FC system during each analytical session: 0.70917 ± 0.00003 (2 SD, $n$ = 11) and 0.38 ± 0.05‰ (2 SD, $n$ = 11). These values also agree well with reported values for IAPSO seawater standard within the analytical uncertainties: 0.709169 ± 0.000029 (2 SD, $n$ = 5)\textsuperscript{62} and 0.709187 ± 0.000009 (2 SD, $n$ = 3)\textsuperscript{63} for $^{87}\text{Sr}/^{86}\text{Sr}$ and 0.370 ± 0.026‰ (2 SD, $n$ = 5)\textsuperscript{62} and 0.36 ± 0.03‰ (2 SD, $n$ = 3)\textsuperscript{63} for $\delta^{88}\text{Sr}$. 
Results and Discussion

Recovery during sample decomposition using borate fusion and purification by the IC-FC system

The yield of each element during the sample decomposition procedure was calculated and summarized in Table S2. More than 85% of Li, Mg, and Sr derived from reagents and rock samples, except for Mg in JG2, was dissolved and remained in the filtered solution, despite the wide compositional range of the samples (Table S1). In these igneous rock samples, the major elements K and Ca, as well as Na derived from the flux, were also dissolved and remained in solution after filtration (Table S2). These results suggest that alkali and alkaline-earth elements in the rock samples were fairly completely dissolved in 8 mM HNO3, and only excess Si and B with small amounts of alkali and alkaline-earth elements were removed by the filtering. Moreover, Li, Mg, or Sr concentrations in the procedural blank solution sample were below detection limits in the ICP-MS analysis. Thus, igneous rock samples can be safely dissolved by this HF-free method within half a day because the level of contamination from reagents was negligibly small.

The elution profile of each element in sample JB2 is shown in Fig. 2. Li, Mg, and Sr were completely separated from interference elements such as Na and Ca, indicating that interference matrices derived from reagents and rock samples could be removed by a IC separation with isocratic elution. In fact, concentrations of the interference matrices in the purified solutions were mostly below detection limits in the ICP-MS analysis. Although only Na in purified Li solutions were above detection limit, Na/Li ratios were much lower than 0.2, which had no effect on accurate Li isotopic measurements.15 Moreover, the introduction amounts of Li, Mg, and Sr calculated from the dilution rates of the introduced solutions agreed well with the purified amounts calculated from the beam intensities of these elements in the MC-ICP-MS.
analysis results (Table S3). These results suggest that just the target elements could be recovered completely with the negligibly small contamination of matrices through the IC-FC purification and quantified by online IC. When the sample solutions were introduced into the IC-FC system, they were diluted with a less than 8 mM solution of HNO₃, the same concentration as the IC eluent, which resulted in a stable background signal during sample introduction (Fig. 2). Therefore, the sample does not need to be dried after its decomposition, a significant time-saver compared with traditional sample decomposition and column separation procedures for elemental purification.

**Li, Mg, and Sr isotope ratios of reference materials**

Li, Mg, and Sr isotopic compositions of several geological reference materials in this study were summarized with previously reported data (Table S4). Although wide range of ⁸⁷Sr/⁸⁶Sr values in JG1 has been reported, all data in this study were in excellent agreement with previously reported data obtained by means of acid sample decomposition and multistep chromatographic separation with cation exchange resins (Fig. 3). Moreover, purification of replicate samples, Li in JR2, Mg in JB2, and Sr in JG1, yielded the same results within the analytical uncertainties (Table S4). Therefore, no isotopic fractionation occurred during sample decomposition by borate fusion, and isotopic compositions of the rock samples could be determined accurately despite a small loss of the target elements. Moreover, the results showed that blank for target elements derived from reagents and the purification system and residual sample matrices such as Na for Li and Ca for Sr did not affect the isotopic compositions obtained for the reference materials. Especially in carbonate standards (JDo1, JCp1, and JCT1), Sr and Mg isotopic compositions corresponded to previously reported values regardless of small Sr/Ca and Mg/Ca ratios. These results demonstrate that this procedure can be applied to samples in which rock constituent elements are present in both major and trace amounts (i.e., Li
concentrations from 7.78 to 86.6 ng g\(^{-1}\), Mg concentrations from 0.02 to 26.9 % m/m, and Sr concentrations from 178 to 7240 ng g\(^{-1}\)) for Li, Mg, and Sr isotopic analysis without any isotopic fractionation.

In addition to \(\delta^{26}\text{Mg}\), we also determined \(\delta^{25}\text{Mg}\) values (Table S4), which we used to calculate two isotope fractionation factors, \(\alpha_{25/24}\) and \(\alpha_{26/24}\), defined as follows:

\[
\begin{align*}
\alpha_{25/24} & = \frac{(\text{Mg}^{25/24})_{\text{sample}}}{(\text{Mg}^{25/24})_{\text{std}}} \\
\alpha_{26/24} & = \frac{(\text{Mg}^{26/24})_{\text{sample}}}{(\text{Mg}^{26/24})_{\text{std}}}
\end{align*}
\]

These two fractionation factors are related by following expression:

\[
\alpha_{25/24} = (\alpha_{26/24})^\beta
\]

In mass-dependent isotope fractionation, the value of the exponent \(\beta\) ranges from 0.511 to 0.521.\(^5\) Here, the average \(\beta\) value calculated from the sample data was 0.512 ± 0.013 (2 SD), which indicates no significant spectral interference affecting only one of the isotope pairs.\(^{31}\) This is also supported by correspondences of both \(^{87}\text{Sr}/^{86}\text{Sr}\) and \(^{88}\text{Sr}/^{86}\text{Sr}\) values in the samples with previously reported values (Table S4 and Fig. 3).

Thus, in this study, we developed a new purification system that can be applied to a wide variety of rock types with concentrations of sample matrices and target elements differing by orders of magnitude by using appropriate sample weights for borate fusion and dilution rates before introduction to the IC-FC system. Moreover, because each element in the samples was recovered during sample decomposition and was completely separated in the elution profile (Tables S2 and S3, and Fig. 2), the method could easily be modified, with a different releasing agent, for purification of all alkali and alkaline-earth metals including K in rock samples for stable isotope analysis.\(^{60}\)

**Conclusions**
Here, we developed a semi-automated, high-throughput purification procedure for stable and radiogenic isotope analysis of alkali and alkaline-earth elements in the rock samples by means of a borate fusion and an IC-FC system. This procedure can achieve rapid, easy, and safe (HF-free) decomposition of silicate rock samples without isotope fractionation during the decomposition and purification processes. Each analyte can be completely separated from other elements in the elution profile, and interference matrices derived from reagents and rock samples can also be removed during single-step IC-FC purification. To validate the accuracy of this procedure, we determined isotopic compositions of Li (δ⁷Li), Mg (δ²⁶Mg), and Sr (⁸⁷Sr/⁸⁶Sr and δ⁸⁸Sr) in GSJ igneous rock and carbonate reference materials with widely varying target element compositions (Li, 7.78–86.6 ng g⁻¹, Mg, 0.02–26.9 % m/m, and Sr, 178–7240 ng g⁻¹) and matrices. The obtained values were consistent with published values, indicating that this procedure can be applied to a wide variety of rock types for isotopic analysis of not only Li, Mg, and Sr but also other alkali and alkaline-earth elements by multiple-collector inductively coupled plasma and thermal ionization mass spectrometrics. We expect this offline collection of baseline-separated peaks to become a powerful tool for multi-isotope analyses to enable characterization of the sources and processes of alkali and alkaline-earth elements in natural systems.

Acknowledgements

We thank Izumi Matsunaga and Yoshiaki Kon of AIST and Yoshiko Yoshikawa of JAMSTEC for laboratory assistance, Yusuke Kono and Makoto Kunori of Metrohm Japan and Terunori Kinjo of Agilent Technology for installation of the IC-FC system, and Dr. Takeshi Ohno of Gakusyuin University for providing the Mg isotope standards. This study was supported by the Japan Society for the Promotion of Science (JSPS) KAKENHI grants-in-aid for Young
Scientists (B) to Daisuke Araoka (no. 16K21682) and (A) to Toshihiro Yoshimura (no. 16H05883).

Supporting Information

Tables S1-S4 are represented in supporting information. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.
References

1. D. Araoka, H. Kawahata, T. Takagi, Y. Watanabe, K. Nishimura, and Y. Nishio, *Miner. Deposita*, **2014**, *49*, 371.

2. T. Manaka, D. Araoka, T. Yoshimura, H. M. Z. Hossain, Y. Nishio, A. Suzuki, and H. Kawahata, *Geochem. Geophys. Geosyst.*, **2017**, *18*, 3003.

3. A. D. Schmitt, N. Vigier, D. Lemarchand, R. Millot, P. Stille, and F. Chabaux, *C. R. Geosci.*, **2012**, *344*, 704.

4. P. B. Tomascak, *Rev. Mineral. Geochem.*, **2004**, *55*, 153.

5. E. D. Young, and A. Galy, *Rev. Mineral. Geochem.*, **2004**, *55*, 197.

6. Y. J. Tang, H. F. Zhang, and J. F. Ying, *Int. Geol. Rev.*, **2007**, *49*, 374.

7. Y. J. Tang, H. F. Zhang, E. Deloule, B. X. Su, J. F. Ying, M. Santosh, and Y. Xiao, *Sci. Rep.*, **2014**, *4*, 4274.

8. F. Z. Teng, *Rev. Mineral. Geochem.*, **2017**, *82*, 219.

9. F. Z. Teng, Y. Hu, and C. Chauvel, *Proc. Natl. Acad. Sci. U. S. A.*, **2016**, *113*, 7082.

10. J. L. Banner, *Earth Sci. Rev.*, **2004**, *65*, 141.

11. J. M. McArthur, R. J. Howarth, and T. R. Bailey, *J. Geol.*, **2001**, *109*, 155.

12. B. L. A. Charlier, G. M. Nowell, I. J. Parkinson, S. P. Kelley, D. G. Pearson, and K. W. Burton, *Earth Planet. Sci. Lett.*, **2012**, 329–330, 31.

13. Y. An, F. Wu, Y. Xiang, X. Nan, X. Yu, J. Yang, H. Yu, L. Xie, and F. Huanga, *Chem. Geol.*, **2014**, *390*, 9.

14. Y. Nishio, and S. Nakai, *Anal. Chim. Acta*, **2002**, *456*, 271.

15. A. B. Jeffcoate, T. Elliott, A. Thomas, and C. Bouman, *Geostand. Geoanal. Res.*, **2004**, *28*, 161.

16. T. Ohno, and T. Hirata, *Anal. Sci.*, **2007**, *23*, 1275.

17. M. Bizzarro, C. Paton, K. Larsen, M. Schiller, A. Trinquier, and D. Ulfbeck, *J. Anal. At.*
18. T. Moriguti, and E. Nakamura, *Chem. Geol.*, **1998**, *145*, 91.

19. T. Yoshimura, M. Tanimizu, M. Inoue, A. Suzuki, N. Iwasaki, and H. Kawahata, *Anal. Bioanal. Chem.*, **2011**, *401*, 2755.

20. V. T. C. Chang, A. Makishima, N. S. Belshaw, and R. K. O’Nions, *J. Anal. At. Spectrom.*, **2003**, *18*, 296.

21. D. De Muynck, G. Huelga-Suarez, L. Van Heghe, P. Degryse, and Frank Vanhaecke, *J. Anal. At. Spectrom.*, **2009**, *24*, 1498.

22. A. Beinlich, V. Mavromatis, H. Austrheim, and E. H. Oelkers, *Earth Planet. Sci. Lett.*, **2014**, *392*, 166.

23. B. Wunder, A. Meixner, R. L. Romer, A. Feenstra, G. Schettler, and W. Heinrich, *Chem. Geol.*, **2007**, *238*, 277.

24. T. Hirata, H. Shimizu, T. Akagi, H. Sawatari, and A. Masuda, *Anal. Sci.*, **1988**, *4*, 637.

25. T. Yokoyama, A. Makishima, and E. Nakamura, *Chem. Geol.*, **1999**, *157*, 175.

26. K. Norrish, and J. T. Hutton, *Geochim. Cosmochim. Acta.*, **1969**, *33*, 431.

27. P. J. Potts, A. T. Ellis, P. Kregsamer, J. Marshall, C. Streli, M. Weste, and P. Wobrauschek, *J. Anal. At. Spectrom.*, **2001**, *16*, 1217.

28. S. García-Ruiz, M. Moldovan, and J. I. García Alonso, *J. Anal. At. Spectrom.*, **2008**, *23*, 84.

29. A. D. Schmitt, S. Gangloff, F. Cobert, D. Lemarchand, P. Stille, and F. Chabaux, *J. Anal. At. Spectrom.*, **2009**, *24*, 1089.

30. Y. Zakon, L. Halicz, and F. Gelman, *Anal. Chem.*, **2014**, *86*, 6495.

31. T. Yoshimura, D. Araoka, Y. Tamenori, J. Kuroda, H. Kawahata, and N. Ohkouchi, *J. Chromatogr. A.*, **2018**, *1531*, 157.

32. N. Imai, S. Terashima, S. Itoh, and A. Ando, *Geochem. J.*, **1995**, *29*, 91.

33. N. Imai, S. Terashima, S. Itoh, and A. Ando, *Geostandard. Newslett.*, **1996**, *20*, 165.
34. T. Okai, A. Suzuki, S. Terashima, M. Inoue, M. Nohara, H. Kawahata, and N. Imai,
    *Geochemistry*, **2004**, 38, 281.

35. M. Rosner, L. Ball, B. Peucker-Ehrenbrink, J. Blusztajn, W. Bach, and J. Erzinger,
    *Geostand. Geoanal. Res.*, **2007**, 31, 77.

36. K. Meredith, T. Moriguti, P. B. Tomascak, S. Hollins, and E. Nakamura, *Geochim. Cosmochim. Acta*, **2013**, 112, 20.

37. F. S. Genske, S. P. Turner, C. Beier, M. F. Chu, S. Tonarini, N. J. Pearson, and K. M. Haase,
    *Chem. Geol.*, **2014**, 373, 27.

38. T. Magna, J. M. D. Day, K. Mezger, M. A. Fehr, R. Dohmen, H. C. Aoudjehane, and C. B. Agee, *Geochim. Cosmochim. Acta*, **2015**, 162, 46.

39. L. Ackerman, J. Ulrych, Z. Řanda, V. Erban, E. Hegner, T. Magna, K. Balogh, J. Frána, M. Lang, and J. K. Novák, *Lithos*, **2015**, 224–225, 256.

40. T. Magna, V. Janousek, M. Kohut, F. Oberli, and U. Wiechert, *Chem. Geol.*, **2010**, 274, 94.

41. T. Magna, A. Deutsch, K. Mezger, R. Skala, H. M. Seitz, J. Mizera, Z. Randa, and L. Adolph, *Geochim. Cosmochim. Acta*, **2011a**, 75, 2137.

42. Y. Xiao, J. Hoefs, Z. Hou, K. Simon, and Z. Zhang, *Contrib. Mineral. Petrol.*, **2011**, 162, 797.

43. R. L. Romer, A. Mexiner, and K. Hahne, *Gondwana Res.*, **2014**, 26, 1093.

44. T. Magna, U. H. Wiechert, and A. N. Halliday, *Int. J. Mass Spectrom.*, **2004**, 239, 67.

45. T. Magna, M. Novak, J. Cempirek, V. Janousek, U. Wiechert, and V. Ullmann, *Geology*, **2016**, 44, 655.

46. P. A. E. Pogge von Strandmann, R. H. James, P. van Calsteren, S. R. Gislasen, and K. W. Burton, *Earth Planet. Sci. Lett.*, **2008**, 297, 462.

47. P. A. E. Pogge von Strandmann, T. Elliott, H. R. Marschall, C. Coath, Y. J. Lai, A. B. Jeffcoate, and D. A. Ionov, *Geochim. Cosmochim. Acta*, **2011**, 75, 5247.
48. F. Z. Teng, W. Y. Li, S. Ke, W. Yang, S. A. Liu, F. Sedaghatpour, S. J. Wang, K. J. Huang, Y. Hu, M. X. Ling, Y. Xiao, X. M. Liu, X. W. Li, H. O. Gu, C. K. Sio, D. A. Wallance, B. X. Su, L. Zhao, J. Chamberlin, M. Harrington, and A. Brewer, *Geostand. Geoanal. Res.*, 2015, 39, 329.

49. M. R. Handler, J. A. Baker, M. Schiller, V. C. Bennett, and G. M. Yaxley, *Earth Planet. Sci. Lett.*, 2009, 282, 306.

50. V. Mavromatis, Q. Gautier, O. Bosc, and J. Schott, *Geochim. Cosmochim. Acta*, 2013, 114, 188.

51. V. Mavromatis, P. Meister, and E. H. Oelkers, *Chem. Geol.*, 2014, 385, 84.

52. A. Immenhauser, D. Buhl, D. Richter, A. Niedermayr, D. Riechelmann, M. Dietzel, and U. Schulte, *Geochim. Cosmochim. Acta*, 2010, 74, 4346.

53. F. Planchon, C. Poulain, D. Langlet, Y. Paulet, and L. Andre, *Geochim. Cosmochim. Acta*, 2013, 121, 374.

54. B. F. Walter, A. Immenhauser, A. Geske, and G. Markl, *Chem. Geol.*, 2015, 400, 87.

55. H. C. Chao, C. F. You, H. C. Liu, and C. H. Chung, *Geochim. Cosmochim. Acta*, 2015, 165, 324.

56. I. Smet, D. De Muynck, F. Vanhaecke, and M. Elburg, *J. Anal. At. Spectrom.*, 2010, 25, 1025.

57. A. Ando, and K. Shibata, *Geochem. J.*, 1988, 22, 149.

58. J. Voigt, E. C. Hathorne, M. Frank, H. Vollstaedt, and A. Eisenhauer, *Geochim. Cosmochim. Acta*, 2015, 148, 360.

59. K. Nakayama, and T. Nakamura, *X-Ray Spectrom.*, 2008, 37, 204–209.

60. M. Watanabe, *Rigaku J.*, 2015, 31, 12.

61. I. Croudace, P. Warwick, R. Taylor, and S. Dee, *Anal. Chim. Acta*, 1998, 371, 217.

62. H. C. Liu, C. F. You, K. F. Huang, and C. H. Chung, *Talanta*, 2012, 88, 338.
63. S. J. Romaniello, M. P. Field, H. B. Smith, G. W. Gordon, M. H. Kim, and A. D. Anbar, J. Anal. At. Spectrom., 2015, 30, 1906.

64. Y. Nishio, K. Okamura, M. Tanimizu, T. Ishikawa, and Y. Sano, Earth Planet. Sci. Lett., 2010, 297, 567.

65. D. Araoka, Y. Nishio, T. Gamo, K. Yamaoka, and H. Kawahata, Geochem. Geophys. Geosyst., 2016, 17, 3835.

66. A. Galy, O. Yoffe, P. E. Janney, R. W. Williams, C. Cloquet, O. Alard, L. Halicz, M. Wadhwa, I.D. Hutcheon, E. Ramon, and J. Carignan, J. Anal. At. Spectrom., 2003, 18, 1352.

67. K. P. Jochum, U. Nohl, K. Herwig, E. Lammel, B. Stoll, and A. W. Hofmann, Geostand. Geoanal. Res., 2005, 29, 333.
Figure Captions

Fig. 1  Flowchart of sample preparation for isotopic analysis by borate fusion followed by purification in an IC-FC system.

Fig. 2  The elution profile in a diluted solution of sample JB2. The Li, Mg, and Sr fractions (black lines) could be collected without contamination by interference elements (dashed lines), and then pooled in a 7 mL PFA vessel until more than 30 ng of Li, 120 ng of Mg, and 200 ng of Sr, had been collected for the measurement of their isotopic ratios.

Fig. 3  Li, Mg, and Sr isotopic compositions of GSJ reference materials together with previously reported data. Sr isotopic compositions of the IAPSO seawater standard in this study are also shown. The detailed data and reference numbers are listed in Table S4. Published values, obtained by means of acid sample decomposition, multistep chromatographic separation with cation exchange resins, and MC-ICP-MS measurements, are from the GeoReM database. $\delta^7$Li values of JB2 and JG2 include only data published after 2013 and 2010, respectively. All errors are 2 standard deviations.
Fig. 1 Flowchart of sample preparation for isotopic analysis by borate fusion followed by purification in an IC-FC system.
Fig. 2 The elution profile in a diluted solution of sample JB2. The Li, Mg, and Sr fractions (black lines) could be collected without contamination by interference elements (dashed lines), and then pooled in a 7 mL PFA vessel until more than 30 ng of Li, 120 ng of Mg, and 200 ng of Sr, had been collected for the measurement of their isotopic ratios.
Fig. 3  Li, Mg, and Sr isotopic compositions of GSJ reference materials together with previously reported data. Sr isotopic compositions of the IAPSO seawater standard in this study are also shown. The detailed data and reference numbers are listed in Table S4. Published values, obtained by means of acid sample decomposition, multistep chromatographic separation with cation exchange resins, and MC-ICP-MS measurements, are from the GeoReM database. δ⁷Li values of JB2 and JG2 include only data published after 2013 and 2010, respectively. All errors are 2 standard deviations.
Graphical Index