ELSEVIER

Chemical Geology 186 (2002) 31–43

CHEMICAL GEOLOGY
INCLUDING
ISOTOPE GEOSCIENCE

www.elsevier.com/locate/chemgeo

# Precise isotope analysis of nanogram-level Pb for natural rock samples without use of double spikes

Takeshi Kuritani, Eizo Nakamura *

*The Pheasant Memorial Laboratory for Geochemistry and Cosmochemistry, Institute for Study of the Earth's Interior, Okayama University at Misasa, Tottori 682-0193, Japan*

Received 16 May 2001; accepted 21 December 2001

**Abstract**

A simple technique has been developed for the precise analysis of lead isotope in natural rock samples by thermal ionization mass spectrometry (TIMS). Two-stage column chromatography, using 100 and 10 μl columns, was used to minimize the amounts of impurities in separated lead samples. This dramatically improved the reproducibility of mass fractionation during mass spectrometry using an ion emitter made of a mixture of silicic acid and phosphoric acid. This improvement made it possible to precisely determine the Pb isotopic compositions of very small sample sizes, employing ''zero-time correction'' for mass discrimination, without requiring a double-spike technique. Using the present method, analytical reproducibility of $^{208}Pb/^{204}Pb$ of 0.02% and 0.06% ($2\sigma$) was attained for 100 and 1 ng of Pb, respectively, separated from natural rock samples. Furthermore, we obtained a reproducibility of 0.06% ($2\sigma$) for $^{208}Pb/^{204}Pb$ for 10 ng of Pb separated from GSJ JP-1 (peridotite), in which the Pb concentration was 0.09 ppm. The measured isotope compositions of USGS standard rocks AGV-1 and BCR-1 were comparable with the published values using the double-spike technique. These observations suggest that our simple technique is reliable in terms of both accuracy and precision for the determination of the Pb isotopic compositions of natural rock samples irrespective of rock chemistry and sample sizes from 1 to 100 ng of Pb. 

*Keywords:* Isotope analysis; Pb; Double spikes

## 1. Introduction

Lead isotope compositions of rock samples, as well as their strontium and neodymium data, can provide important constraints on dynamic processes that affect the Earth's evolution. For strontium and neodymium isotopes, highly precise analyses have been routinely made by thermal ionization mass spectrometry (TIMS). However, the analytical precision and accuracy of lead isotope analyses is often poor compared with those of strontium and neodymium. The principal cause of this difference is that an internal correction for the mass fractionation during measurements is possible for strontium and neodymium isotope analysis, using the accepted ratio of two nonradiogenic isotopes (e.g., $^{86}Sr/^{88}Sr = 0.1194$), but not for lead isotope analysis because $^{204}Pb$ is the only natural nonradiogenic.

The conventional method of lead isotope analysis involves determining a mass fractionation factor by analyzing a Pb standard material with a well-known

* Corresponding author. Tel.: +81-858-43-1215; fax: +81-858-43-2184.

*E-mail addresses:* kuritani@misasa.okayama-u.ac.jp (T. Kuritani), eizonak@misasa.okayama-u.ac.jp (E. Nakamura).

0009-2541/02/$ - see front matter 
PII: S0009-2541(02)00004-9

isotopic composition (e.g., NBS981), and then applying the same correction factor to unknown samples. However, this conventional method has been criticized on the ground that the reference materials can exhibit different isotopic fractionation behavior to rock samples due to impurities such as Cd, Zn, and organic materials (e.g., Woodhead et al., 1995). To overcome this problem, and to perform internal correction of mass fractionation, double (or triple)-spike techniques have been introduced in some laboratories (Hamelin et al., 1985; Woodhead et al., 1995; Todt et al., 1996; Powell et al., 1998; Galer, 1999; Thirlwall, 2000). This technique enables rigorous corrections of mass discrimination by spiking with an artificial solution enriched in two or three Pb isotopes (e.g., $^{207}Pb-^{204}Pb$). However, the problem of impurities in separated Pb samples remains even in the double-spike method for measuring small sample sizes ($<10$ ng of Pb), because the impurities drastically suppress the ionization efficiency of lead, which results in loss of precision and accuracy of data. Furthermore, routine determination of lead isotope compositions of samples with extremely low-level Pb ($<0.1$ ppm), such as ultramafic rocks, is not available even with double- or triple-spike method.

In this paper, we present an improved procedure of column chromatography to minimize the impurities, especially organic materials, in the separated lead samples. Using this procedure, the reproducibility of mass fractionation during mass spectrometry is much improved and the ionization efficiency of Pb for natural samples matches that of pure NBS981. We show that a modified method of the conventional normalization procedure using NBS981, instead of the double-spike method, enables to correct mass discrimination with sufficient precision to allow highly precise and accurate data to be obtained for even tiny amounts of Pb. The utility of our method is shown by measuring 0.2–100 ng of a pure NBS981 and 1–100 ng of Pb separated from natural rock samples. Lead isotopic compositions of the USGS standard rock samples AGV-1, BCR-1, and PCC-1 are also presented. The composition of GSJ JP-1 (peridotite), in which the Pb concentration is 0.09 ppm, has also been measured. Finally, the merits and demerits of the present method are evaluated in comparison with the conventional normalization method and the double-spike method.

## 2. Experimental

### 2.1. Apparatus and reagents

Isotopic measurements were performed using a modified Finnigan-MAT 261 (“Kiji”) solid-source thermal ionization mass spectrometer, equipped with six movable platforms for Faraday cup collectors, including the special double collector package for boron isotope analysis ($Cs_2BO_2^+$; $m/z=308$ and 309), a piggyback collector for Pb ($m/z=207$ and 208) and a fixed central one (Nakano and Nakamura, 1998), at the Pheasant Memorial Laboratory (PML). The accelerating voltage was adjusted to 10 kV. Faraday cup collectors were used with a $10^{11}$ Ω resistor that is capable of detecting ion currents from $10^{-14}$ to $10^{-10}$ A for isotopic determinations.

Two kinds of columns made of polyethylene were used for chemical separation of lead from natural rock samples. The volumes of the columns were 100 μl (8.8 mm long, 3.8 mm i.d.) and 10 μl (5.7 mm long, 1.5 mm i.d.). Bio-Rad AG-1X8 was used as the anion exchange resin. The preparation of reagents was essentially the same to that described in Yokoyama et al. (1999a). The water used in these analyses was prepared by deionization with a mixed-bed resin and filters using a Milli-Q® water system (Millipore), and then further purified by passing it through a Q-Pak cartridge equipped with 0.22 μm final filter (Millipore).

### 2.2. Procedure

#### 2.2.1. Chemical separation

The procedure of sample dissolution was similar to the method described by Manhes et al. (1978) and Koide and Nakamura (1990). The chemical procedure of Pb separation from natural rock samples consists of two steps. In the first step, the large column was used to remove most of the elements other than Pb. In the second step, the small column was used to remove trace contaminants of elements in the Pb fraction and organic materials derived from resin in the first column.

An anion exchange resin (0.1 ml) was charged into a polyethylene column. The resin bed was cleaned by flushing the column with 1.5 ml of 0.5 N $HNO_3$, followed by 1.5 ml of water, at a rate of $\sim$0.03 ml/

min. The column was then conditioned with 0.3 ml of 0.5 N HBr. The supernatant of the sample, dissolved in 1 ml of 0.5 N HBr, was loaded onto the column, with care taken not to introduce the fluoride deposits. Unlike the conventional method, 2.5 ml of 0.25 N HBr–0.5 N $HNO_3$ mixed acid was then introduced to remove the elements other than Pb. This is because the HBr–$HNO_3$ mixture is more efficient than using HBr alone with respect to the separation of Zn from Pb (Strelow, 1978; Lugmair and Galer, 1992). The lead sample was eluted with 1.0 ml of water. Prior to evaporation, one drop ($\sim$30 μl) of 0.05 N $H_3PO_4$ was added to the elute to avoid complete dryness.

In the second column chromatography, 0.01 ml of anion-exchange resin was charged into the column, and the resin bed was cleaned by flushing the column with 1.5 ml of 0.5 N $HNO_3$ and 1.5 ml of water, at a rate of about 0.01 ml/min. The column was conditioned with 0.1 ml of 0.5 N HBr. The dried sample collected from the first column chemistry was dissolved in 0.3 ml of 0.5 N HBr, and was loaded onto the column. For washing of contaminants in samples from the first column, 0.3 ml of 0.5 N HBr was introduced. Subsequently, 0.3 ml of water was added to the column as a Pb elution. The collected Pb elution was evaporated in a closed system of two-beaker Teflon® evaporator at 80 °C for several hours, after addition of 40 μl of 0.05 N $H_3PO_4$. In the case of relatively small sample sizes (<10 ng Pb), 30 μl of 0.015 N $H_3PO_4$ was added. After dryness, one drop of $HNO_3$ was added to the sample, which was then dried at 100 °C using the same evaporator as before, in order to decompose organic materials in separated Pb samples. For small sample sizes (<10 ng Pb), a second drop of $HClO_4$ was added before evaporating the sample to dryness.

### 2.2.2. Mass spectrometry

The dried Pb sample was dissolved in the emitter consisting of silicic acid and diluted phosphoric acid (Gerstenberger and Haase, 1997). The amounts of silicic acid and phosphoric acid were changed in proportion to the amounts of Pb loaded, based on the amounts recommended by Gerstenberger and Haase (1997) for 10 ng of Pb. The dissolved sample was loaded onto the top of trapezoid-shaped rhenium filament (Koide and Nakamura, 1990). The filament current was raised to 1 A, and held at this condition until the drop on the filament disappeared. The current was kept at 1 A for another 30 s, and the current was abruptly decreased to zero. The sample was then introduced into the mass spectrometer.

Determinations of Pb isotopic composition were carried out using five Faraday cup collectors appropriately configured to collect $^{204}Pb$, $^{205}Pb$, $^{206}Pb$, $^{207}Pb$, and $^{208}Pb$. The integration time for each isotopic ratio was 8 s. Idling and counting times for the baselines at 205.5 *m*/*z* were 8 and 16 s, respectively, and the baselines were measured after each block. One isotopic measurement run, consisting of 110 ratios in 10 blocks, took about 30 min. 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 prior to data acquisition by supplying a uniform current into the amplifiers.

The filament was heated slowly to 900 °C (5–10 min) and its temperature monitored using an autopyrometer. When the Pb loaded was relatively large (>20 ng), the temperature was held at 900 °C for 15–20 min, and then the current was raised slowly to a temperature of 1150–1250 °C (filament current of 1.8–2.0 A) in about 10 min. The ion current for $^{208}Pb$ would continue to increase slowly until it reached a value of about $3 \times 10^{-11}$ to $9 \times 10^{-11}$ A, the precise value depending on the amount of Pb in the sample. Data acquisition was then started.

For samples with <10 ng of Pb, the filament was heated to 900 °C slowly (5–10 min) and then the temperature was held at 900 °C for 5 min. The filament current was then raised slowly ($\sim$0.1 A/min) until the ion current for $^{208}Pb$ reached $2 \times 10^{-11}$ to $3 \times 10^{-11}$ A (temperature of 1100–1130 °C) for $\sim$10 ng of lead sample, $1 \times 10^{-11}$ to $2 \times 10^{-11}$ A (1070–1080 °C) for $\sim$5 ng, $4 \times 10^{-12}$ to $6 \times 10^{-12}$ A (1030–1050 °C) for $\sim$1 ng, and $3 \times 10^{-12}$ to $4 \times 10^{-12}$ A (1020–1040 °C) for $\sim$500 pg. In all the cases, the ion current for Pb would continue to increase just after reaching the specified temperature. Data acquisition was then started.

### 2.2.3. Data reduction

The raw scan data obtained from the mass spectrometry were corrected by the following two steps. First, mass discrimination during the analysis was corrected by the method of "zero-time correction"

(Tuttas and Habfast, 1982; Koide and Nakamura, 1990). The corrected data were then normalized by the conventional method using the normalization factor determined from the measured and recommended values for the Pb in the standard solution NBS981.

Isotopic ratio of samples evaporating into vacuum is different from that of the solid samples on filament, and this is called ''isotopic fractionation''. Because the amount and isotopic ratio of the remaining solid phase change progressively during spectrometer analysis, the isotopic ratio of the evaporating samples also changes with time. Although the fractionation pattern is a complicated function of the overall evaporation pattern of the sample, the mass fractionation is ideally a liner function of time if the following conditions are satisfied: (1) chemical form with which the sample is evaporating does not change during evaporation, (2) the ionization efficiency is constant, and (3) the ion current decays exponentially with time (Tuttas and Habfast, 1982).

In the zero-time correction method, the ''unfractionated ratio'', which may represent the isotopic ratio of sample evaporating from the initial solid state of the Pb sample, is calculated at the end of data acquisition. This ratio is then used to evaluate the mass fractionation during spectrometer analysis, as is the $^{86}Sr/^{88}Sr$ ratio for the Sr isotope measurements. The ''unfractionated ratio'' is calculated as follows (Koide and Nakamura, 1990). First, an integrated ion current (e.g., $^{208}Pb$) is calculated by integrating the current with time (Fig. 1a). The ion current from the beginning of heating to the start of acquisition is estimated by making the approximation that the ion current increases linearly with time till acquisition starts. Then, the relationship between isotope ratios and the integrated current can be regressed as a linear line (Fig. 1b). The ''unfractionated ratio'' is determined as the ratio of the integrated ion current extrapolated to zero. Although the mass fractionation is theoretically a linear function of time, integrated ion current is useful for the abscissa (Fig. 1b) to correct the mass fractionation from the beginning of sample heating to the start of acquisition (Tuttas and Habfast, 1982). If the ion current does not decay exponentially, the mass fractionation is a nonlinear function of time. However, the curvature of the fractionation pattern is so minor that linear regression can still be applied instead of nonlinear regression (Tuttas and Habfast, 1982).

For individual scan data (110 data), the mass fractionation for $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ ratios was evaluated using the calculated unfractionated $^{208}Pb/^{204}Pb$ ratio and the measured $^{208}Pb/^{204}Pb$ ratio. The $^{208}Pb/^{204}Pb$ ratio itself was corrected by the unfractionated $^{207}Pb/^{204}Pb$ ratio. We adopted the power law (e.g., Wasserburg et al., 1981) as a mass fractionation law. After this treatment, outliers were eliminated from the corrected scan data on the basis of a test of 95% confidence limit, and the averaged ratio (>100 scans) is presented as a corrected isotope composition. The ''unfractionated ratio'', therefore, does not always coincide with the corrected ratio. The uncertainty on a single run is evaluated from the standard deviation of the corrected scan data ($\sim$ 110 data). The corrected isotope compositions (average of the corrected scan data) were normalized using the average of the measured isotopic ratios of NBS981 accumulated in our laboratory and the recommended values of Todt et al. (1996).

## 3. Results and discussion

### 3.1. Mass spectrometry

#### 3.1.1. Tolerance of lead/emitter ratio

We used the amounts of emitter as recommended for 10 ng of Pb by Gerstenberger and Haase (1997), which was varied in proportion to the amount of Pb being loaded. In many cases, however, the concentrations of Pb in rock samples prior to the isotopic analyses are unknown. From this reason, the tolerance of the lead/emitter ratio was investigated. Although the double-spike method is free from this problem, this is important for the conventional normalization method to improve reproducibility of mass fractionation in spectrometer analysis.

The amount of emitter was adjusted to that required for 10 ng of lead, and the amounts of Pb were varied from 1 to 300 ng. The measured $^{208}Pb/^{204}Pb$ ratios of individual runs, for different amounts of Pb loaded, are shown in Fig. 2. As the amounts of lead either decrease or increase from 10 ng, the $^{208}Pb/^{204}Pb$ ratio tends to increase. The measured $^{208}Pb/^{204}Pb$ ratios for samples with 6–20 ng of Pb (indicated with arrow in Fig. 2) lie mainly within two standard deviations of the ratio for 10 ng. For a given amount of emitter, we can, therefore, reliably measure samples with amounts of Pb that are

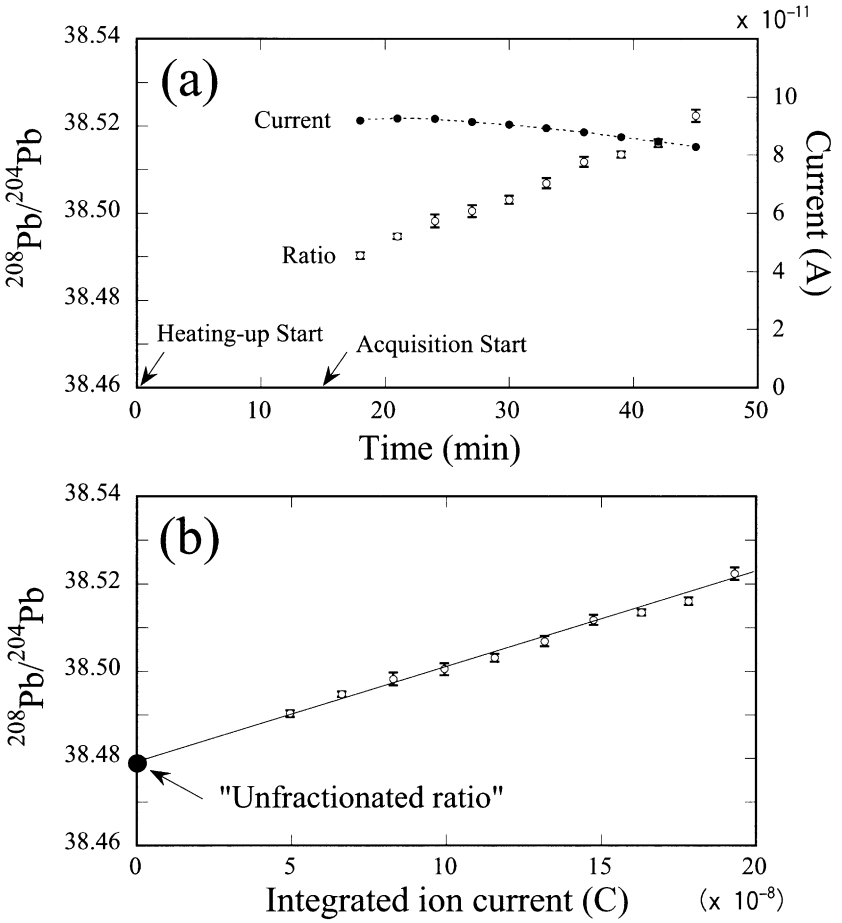


Fig. 1. (a) The raw block data (average of the 11 scan data) of the $^{208}Pb/^{204}Pb$ ratio and ion current of $^{208}Pb$ plotted against time, and (b) the raw block data plotted against the integrated ion current. The vertical bar shows one standard deviation ($1\sigma$) of the scanned data at each block. This example is for BCR-1 with 100 ng of Pb. In this measurement, the data acquisition was started 15 min from the beginning after heating from 900 °C. The solid line in (b) represents a regression line for the data against the integrated ion current. The intercept of the line with the ordinate is the "unfractionated" $^{208}Pb/^{204}Pb$ ratio. Note that the "unfractionated $^{208}Pb/^{204}Pb$ ratio" does not necessarily coincide with the corrected $^{208}Pb/^{204}Pb$ ratio. See text for the details.

0.5–2 times as much as that recommended for the concentration.

*3.1.2. NBS981 results*

Fig. 3 shows the $^{208}Pb/^{204}Pb$ ratios of NBS981 for various amounts of Pb from 0.2 to 100 ng. The internal precision of each run is normally less than the external precision. Both the zero-time correction and the data uncorrected (average of the scan data) are shown. The $^{208}Pb/^{204}Pb$ ratio of the uncorrected data increases with decreasing the sample sizes from 100 to 1 ng, suggesting more significant mass fractionation during smaller sample size measurements. In contrast to this variation, there is no systematic difference of the corrected data with sample sizes within the external precisions.

For given sample sizes, the analytical reproducibility (Table 1) for NBS981 is comparable to or better than the published values by the double-spike method (e.g., Woodhead et al., 1995) and also by MC–ICP–MS (Hirata, 1996; Belshaw et al., 1998; Rehkämper and Halliday, 1998), though that of a triple spike by

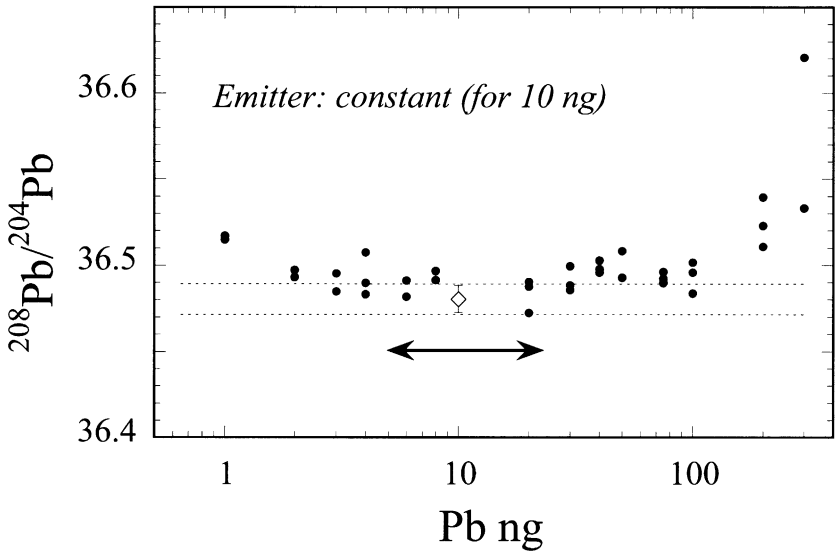


Fig. 2. The $^{208}Pb/^{204}Pb$ ratio of NBS981 (after the zero-time correction) with various amounts of lead from 1 to 300 ng, at the given amount of emitter recommended for 10 ng by Gerstenberger and Haase (1997). Arrow indicates the range of the amounts of Pb that we may measure reliably using the emitter for 10 ng.

Galer and Abouchami (1998) is better for ~10 ng sample sizes (see Thirlwall, 2000). These results suggest that the zero-time correction provides an accurate correction for mass discrimination. Our study shows that 100 ng of Pb is the maximum for precise isotope analysis of common lead, because the ion current of $^{208}Pb$ exceeds $10^{-10}$ A if the amount of Pb loaded is larger than 120 ng.

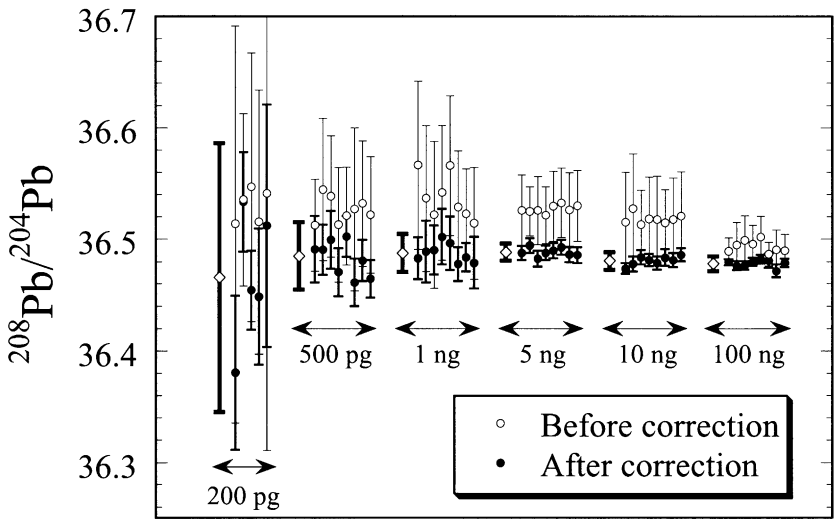


Fig. 3. Comparison of the $^{208}Pb/^{204}Pb$ ratios of NBS981 standard solution for various amounts of lead loaded on the filaments. The data before "zero-time correction" (open circles), which are the average of scan data, and those after the correction (filled circles) are shown. Error bars on these data plots indicate internal precision ($2\sigma$). The mean values of the corrected data for individual sample sizes are marked as open diamond with heavy error bars ($2\sigma$).

Table 1
Summary of the isotopic compositions of NBS981 standard after the zero-time correction, for various amounts of lead without procedures of column chemistry

| | $^{208}Pb/^{204}Pb$ | $^{207}Pb/^{204}Pb$ | $^{206}Pb/^{204}Pb$ | $^{208}Pb/^{206}Pb$ | $^{207}Pb/^{206}Pb$ |
|---|---|---|---|---|---|
| *Pb 100 ng* | | | | | |
| Mean ($n=8$) | 36.4779 | 15.4215 | 16.8846 | 2.16042 | 0.91334 |
| 2 × standard deviation | 0.0066 | 0.0020 | 0.0014 | 0.00025 | 0.00006 |
| Reproducibility (2$\sigma$), % | 0.018 | 0.013 | 0.008 | 0.011 | 0.007 |
| *Pb 10 ng* | | | | | |
| Mean ($n=8$) | 36.4805 | 15.4224 | 16.8867 | 2.16031 | 0.91329 |
| 2 × standard deviation | 0.0078 | 0.0022 | 0.0021 | 0.00024 | 0.00004 |
| Reproducibility (2$\sigma$), % | 0.021 | 0.014 | 0.013 | 0.011 | 0.004 |
| *Pb 5 ng* | | | | | |
| Mean ($n=8$) | 36.4881 | 15.4245 | 16.8874 | 2.16067 | 0.91338 |
| 2 × standard deviation | 0.0077 | 0.0023 | 0.0019 | 0.00026 | 0.00005 |
| Reproducibility (2$\sigma$), % | 0.021 | 0.015 | 0.012 | 0.012 | 0.005 |
| *Pb 1 ng* | | | | | |
| Mean ($n=8$) | 36.4874 | 15.4240 | 16.8874 | 2.16062 | 0.91334 |
| 2 × standard deviation | 0.0171 | 0.0046 | 0.0048 | 0.00064 | 0.00012 |
| Reproducibility (2$\sigma$), % | 0.047 | 0.030 | 0.028 | 0.030 | 0.013 |
| *Pb 500 pg* | | | | | |
| Mean ($n=8$) | 36.4849 | 15.4227 | 16.8867 | 2.16057 | 0.91331 |
| 2 × standard deviation | 0.0303 | 0.0092 | 0.0080 | 0.00091 | 0.00015 |
| Reproducibility (2$\sigma$), % | 0.083 | 0.059 | 0.047 | 0.042 | 0.017 |
| *Pb 200 pg* | | | | | |
| Mean ($n=5$) | 36.4657 | 15.4182 | 16.8867 | 2.15943 | 0.91304 |
| 2 × standard deviation | 0.1204 | 0.0330 | 0.0283 | 0.00412 | 0.00054 |
| Reproducibility (2$\sigma$), % | 0.330 | 0.214 | 0.167 | 0.191 | 0.059 |

Thirlwall (2000) reported that $^{207}Pb/^{206}Pb$ exhibits abnormal mass fractionation behavior during mass spectrometry at >1250 °C, which cannot be explained by isobaric interference. In this study, such an unusual mass fractionation has not been observed, probably because our measurements were always made at filament temperatures below 1250 °C.

### 3.2. Column chemistry

#### 3.2.1. Suppression of ionization of Pb by organic materials

Table 2 compares the ion beam intensity of $^{208}Pb$ at the beginning of data acquisition for samples of 1 ng NBS981, which have been both processed and unprocessed by column chromatography. If 1 ng of NBS981 is loaded directly onto the filament, without column chemistry, the ion beam intensity of $^{208}Pb$ commonly exceeds $5 \times 10^{-12}$ A shortly after the data acquisition, and precise data are obtained (Table 1 and Fig. 3). On the other hand, the ion beam intensity is too low to perform data acquisition if 1 ng of NBS981 is passed

Table 2
$^{208}Pb$ ion beam intensity just after the data acquisition, for 1 ng Pb of NBS981 with and without procedures of column chromatography

| Experiments | First column | Second column | $^{208}Pb$ ($\times 10^{-14}$ A) |
|---|---|---|---|
| #1 | × | × | 482 |
| #2 | × | × | 709 |
| #3 | × | × | 617 |
| #4 | ○ | × | 0 |
| #5 | ○ | × | 5 |
| #6 | ○ | × | 0 |
| #7 | ○ | ○ | 449 |
| #8 | ○ | ○ | 363 |
| #9 | ○ | ○ | 375 |

through only the first chromatographic column (Table 2). This results from the suppression of ionization of Pb by organic materials derived from the resin in the first chromatographic column.

In order to reduce the amount of contaminating resin in separated Pb samples, we have introduced a second round of column chromatography, using a 10 μl column. The amount of minute resin contaminating the Pb samples is thought to be proportional to the quantity of the Pb elution. Because the amount of the Pb elution decreases as the volume of column decreases, a small column volume enables the amount of resin to be reduced in the separated Pb samples. Although the ion beam intensity of $^{208}$Pb for samples through the two-stage column chromatography is slightly lower than that of the case without column chemistry (Table 2), we can obtain enough beam intensity to perform data acquisition.

Fig. 4 shows the result of five analyses of NBS981 through the two-stage column chromatography for various sample sizes from 1 to 100 ng Pb (Table 3). Although the analytical reproducibility is worse for pure NBS981 (except for the 10 ng Pb sample), the mean values are mostly identical for each sample size. This suggests that the interference of organic materials was suppressed sufficiently to obtain accurate data, although the impurities may affect the fractionation behavior in the mass spectrometer and cause a slight loss of analytical reproducibility.

Table 3
Summary of the isotopic compositions of NBS981 standard after the zero-time correction, for various amounts of lead through column chemistry

| | $^{208}$Pb/$^{204}$Pb | $^{207}$Pb/$^{204}$Pb | $^{206}$Pb/$^{204}$Pb |
|---|---|---|---|
| *Pb 100 ng* | | | |
| Mean ($n$=5) | 36.4761 | 15.4209 | 16.8854 |
| 2 × standard deviation | 0.0138 | 0.0043 | 0.0033 |
| Reproducibility (2$\sigma$), % | 0.038 | 0.028 | 0.019 |
| *Pb 10 ng* | | | |
| Mean ($n$=5) | 36.4836 | 15.4234 | 16.8878 |
| 2 × standard deviation | 0.0041 | 0.0008 | 0.0024 |
| Reproducibility (2$\sigma$), % | 0.011 | 0.005 | 0.014 |
| *Pb 5 ng* | | | |
| Mean ($n$=5) | 36.4859 | 15.4231 | 16.8875 |
| 2 × standard deviation | 0.0177 | 0.0047 | 0.0030 |
| Reproducibility (2$\sigma$), % | 0.049 | 0.031 | 0.018 |
| *Pb 1 ng* | | | |
| Mean ($n$=5) | 36.4914 | 15.4241 | 16.8910 |
| 2 × standard deviation | 0.0400 | 0.0102 | 0.0080 |
| Reproducibility (2$\sigma$), % | 0.110 | 0.066 | 0.048 |

### 3.2.2. GSJ JB-3 results

In order to assess our analytical performance for natural rock samples, we measured the isotopic compositions of a Geological Survey of Japan (GSJ) standard rock powder of JB-3 (basaltic rocks from Mt. Fuji; Ando et al., 1989), which contains 5.1 ppm of Pb

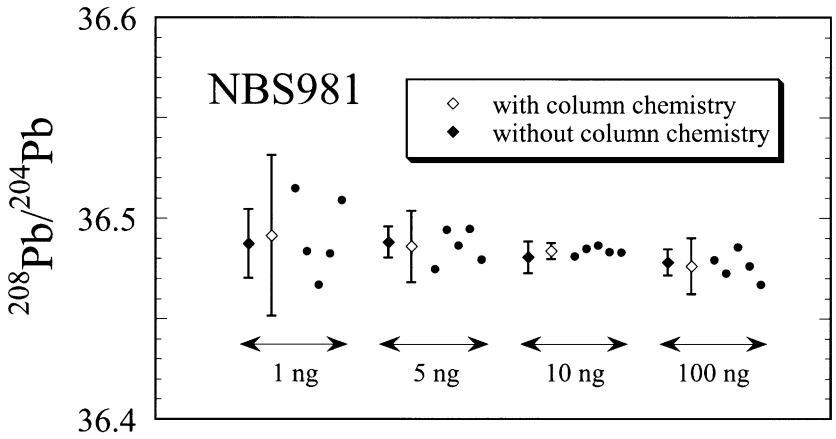


Fig. 4. Comparison of the $^{208}$Pb/$^{204}$Pb ratios of NBS981 with two-stage column chromatography for different sample sizes. The mean values of the data for individual sample sizes are marked as open diamond with error bars (2$\sigma$). Filled diamonds with error bars indicate the average data of pure NBS981 shown in Fig. 3.

Table 4
Summary of the isotopic compositions of GSJ JB-3 for various sample sizes

| | $^{208}Pb/^{204}Pb$ | $^{207}Pb/^{204}Pb$ | $^{206}Pb/^{204}Pb$ |
|---|---|---|---|
| *Pb 100 ng* | | | |
| Mean ($n=5$) | 38.2304 | 15.5294 | 18.2914 |
| 2 × standard deviation | 0.0065 | 0.0023 | 0.0018 |
| Reproducibility (2$\sigma$), % | 0.017 | 0.015 | 0.010 |
| *Pb 10 ng* | | | |
| Mean ($n=5$) | 38.2339 | 15.5306 | 18.2891 |
| 2 × standard deviation | 0.0137 | 0.0027 | 0.0022 |
| Reproducibility (2$\sigma$), % | 0.036 | 0.017 | 0.012 |
| *Pb 5 ng* | | | |
| Mean ($n=5$) | 38.2243 | 15.5267 | 18.2886 |
| 2 × standard deviation | 0.0112 | 0.0031 | 0.0031 |
| Reproducibility (2$\sigma$), % | 0.029 | 0.020 | 0.017 |
| *Pb 1 ng* | | | |
| Mean ($n=5$) | 38.2251 | 15.5273 | 18.2872 |
| 2 × standard deviation | 0.0234 | 0.0074 | 0.0069 |
| Reproducibility (2$\sigma$), % | 0.061 | 0.048 | 0.038 |

(Makishima and Nakamura, 1997). Table 4 summarizes measured isotopic compositions for various sample sizes containing from 1 to 100 ng of lead. Fig. 5 shows the comparison of the $^{208}Pb/^{204}Pb$ ratios (filled circles) among the different sample sizes. Because the rock powders for 1 ng of lead could not be weighed reliably, 1/10 of the aliquots of Pb elution, separated from a sample containing 10 ng Pb after the first column chromatography, was used and loaded into the second column. The resulting Pb elution then contained 1 ng of Pb. As is the case for NBS981 column chemistry, the $^{208}Pb/^{204}Pb$ ratios do not vary significantly with the amount of lead. The analytical reproducibility for the natural rock sample is also close to that for the analyses of NBS981 in all the sample sizes (cf. Table 3), suggesting that impurities, other than organic materials, do not significantly affect the behavior of mass discrimination.

In Fig. 5, the data of the sample JB-3, obtained after only the first column procedure, are compared with those that have passed through the two-stage column chromatography. The data for the 10 ng through only the first column plot with a significantly higher ratio than those that have been through the two-stage column chromatography procedure. For 100 ng of lead, on the other hand, the $^{208}Pb/^{204}Pb$ ratios of the samples with only the first column overlap those from the two stages of column separations, though the reproducibility is worse. The amount of interfering elements in the Pb elution of the first column is thought to decrease proportionally with decreasing sample size. On the other hand, the amount of organic materials derived from the first column chromatography is likely to be constant, irrespective of sample sizes. Therefore, the amounts of organic materials relative to that of Pb increase as the amount of lead in the sample decreases, and thus these impurities affect the behavior of the mass

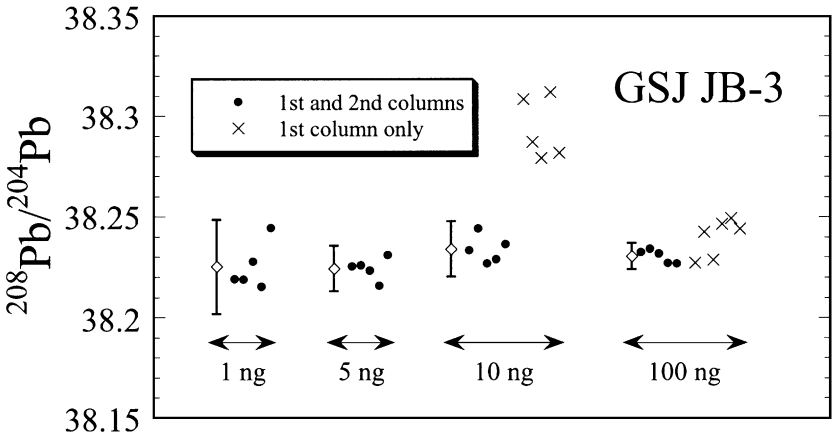


Fig. 5. Comparison of the $^{208}Pb/^{204}Pb$ ratios of GSJ JB-3 for various amount of lead loaded on the filaments (filled circles). The mean values of the data for individual amounts of lead are marked as open diamond with error bars (2$\sigma$). The data for samples passed through only the first column procedure are shown as crosses for comparison, for 10 and 100 ng of Pb.

fractionation more significantly as the sample size decreases.

Recovery yield of Pb from igneous rock samples are typically ~70% for peridotite, ~95% for basalt, and ~100% for andesite, dacite, and rhyolite. The loss of recovery results from the coprecipitation of Pb with fluorides during the rock digestion with HF (Yokoyama et al., 1999b). As described above, the fluoride deposits were removed from the sample solutions just before loading the sample into the first column. This is because most amounts of major elements, especially Mg, Ca, and Al, were separated as fluorides.

### 3.3. Lead blanks

Measured Pb blanks in reagents, along with the total procedural blank, are listed in Table 5. The blanks were determined using $^{206}$Pb-enriched spike (NBS983) by isotope dilution mass spectrometry. The total procedural blank, including the first and the second column chromatography, was 31 pg. The total procedural blank without the second column chemistry was 17 pg. A blank correction might therefore be necessary when this procedure is used for samples in which the Pb content is lower than 5 ng.

### 3.4. Application to rock standards

To assess the analytical reliability and accuracy of our procedure for natural rock samples, we analyzed the US Geological Survey standard samples AGV-1 (andesite), BCR-1 (basalt), PCC-1 (peridotite), and the GSJ standard sample JP-1 (peridotite) (Pb concentration of 37.0, 13.2, 7.9, and 0.09 ppm, respectively; Makishima and Nakamura, 1997). Before the analysis by TIMS, the presence of "impurity" elements was examined with ICP-MS for all the separated Pb samples. Apart from trace amounts of cadmium and indium, the Pb samples were free from elements other than Pb.

Table 5
Reagents and total procedural blank of Pb

| Reagents | pg/ml |
|---|---|
| $H_2O$ | 0.3 |
| HBr | 1.8 |
| HF | 1.1 |
| $HNO_3$ | 0.7 |
| Calculated total reagent blank (pg) | 2.7 |
| Total procedural blank (pg) | 31 |

Table 6 details the results for replicate analyses of the samples. Analytical reproducibility for the samples with 100 ng of Pb (AGV-1, BCR-1, PCC-1) are satisfactory, though those for AGV-1 and BCR-1 are slightly worse than that of the standard sample JB-3 presented above (Table 4). In spite of the low concentration of Pb in JP-1 samples (0.09 ppm), analytical reproducibility of 0.06% was attained for the $^{208}$Pb/$^{204}$Pb ratio. Relatively large variation of the $^{206}$Pb/$^{204}$Pb ratio may reflect the heterogeneity of the ratio in the rock sample, considering that the analytical reproducibility of the $^{208}$Pb/$^{204}$Pb ratio is commonly worse than that of the $^{206}$Pb/$^{204}$Pb ratio. Table 6 compares our results with those utilizing the double spike technique by Woodhead and Hergt (2000) for AGV-1 and BCR-1. Although their analytical reproducibility is significantly worse for natural rock samples than that reported in Woodhead et al. (1995), our values are identical within uncertainty to those of Woodhead and Hergt (2000). It is thus concluded that our simple technique, without use of a double spike, is reliable in terms of both accuracy and precision.

### 3.5. Evaluation of the present method

#### 3.5.1. Comparison with the conventional normalization method

Woodhead et al. (1995) and Thirlwall (2000) demonstrated that the conventional normalization method using NBS981 could result in a significant loss of accuracy, because pure Pb reference materials exhibit markedly different fractionation behavior to natural rock samples. The main sources of this difference are (1) the difference of the amount of Pb used for the determination of the reference isotopic composition of NBS981 from that separated from rock samples, which is usually not known exactly, and (2) the impurities in Pb samples separated from natural rocks (Woodhead et al., 1995).

If we adopt the conventional normalization method without the zero-time correction, the former problem (1) causes a significant loss in accuracy. This is actually

Table 6
Lead isotope compositions of standard rock samples

| | This study | | | Reference data | | |
|---|---|---|---|---|---|---|
| | $^{208}Pb/^{204}Pb$ | $^{207}Pb/^{204}Pb$ | $^{206}Pb/^{204}Pb$ | $^{208}Pb/^{204}Pb$ | $^{207}Pb/^{204}Pb$ | $^{206}Pb/^{204}Pb$ |
| AGV-1 (~100 ng) | 38.562 | 15.652 | 18.939 | | | |
| | 38.544 | 15.647 | 18.935 | | | |
| | 38.560 | 15.651 | 18.939 | | | |
| | 38.544 | 15.649 | 18.937 | | | |
| | 38.562 | 15.652 | 18.937 | | | ($n=5$) |
| Av. | 38.554 | 15.650 | 18.938 | 38.560 | 15.659 | 18.945 |
| $2\sigma$ | 0.019 | 0.004 | 0.003 | 0.037 | 0.014 | 0.014 |
| R.S.D.% | 0.050 | 0.028 | 0.016 | 0.096 | 0.092 | 0.074 |
| BCR-1 (~100 ng) | 38.714 | 15.630 | 18.817 | | | |
| | 38.725 | 15.633 | 18.814 | | | |
| | 38.714 | 15.628 | 18.815 | | | |
| | 38.721 | 15.632 | 18.820 | | | |
| | 38.730 | 15.632 | 18.818 | | | ($n=3$) |
| Av. | 38.720 | 15.631 | 18.817 | 38.703 | 15.630 | 18.814 |
| $2\sigma$ | 0.014 | 0.004 | 0.005 | 0.029 | 0.009 | 0.011 |
| R.S.D.% | 0.036 | 0.026 | 0.026 | 0.076 | 0.060 | 0.060 |
| PCC-1 (~100 ng) | 38.522 | 15.665 | 18.947 | | | |
| | 38.521 | 15.664 | 18.947 | | | |
| | 38.531 | 15.667 | 18.949 | | | |
| | 38.524 | 15.665 | 18.946 | | | |
| | 38.520 | 15.664 | 18.945 | | | |
| Av. | 38.523 | 15.665 | 18.947 | | | |
| $2\sigma$ | 0.009 | 0.002 | 0.003 | | | |
| R.S.D.% | 0.022 | 0.016 | 0.015 | | | |
| GSJ JP-1 (~10 ng) | 38.319 | 15.551 | 18.361 | | | |
| | 38.322 | 15.555 | 18.345 | | | |
| | 38.298 | 15.551 | 18.340 | | | |
| | 38.301 | 15.553 | 18.335 | | | |
| | 38.311 | 15.558 | 18.335 | | | |
| Av. | 38.310 | 15.554 | 18.343 | | | |
| $2\sigma$ | 0.021 | 0.006 | 0.021 | | | |
| R.S.D.% | 0.055 | 0.037 | 0.115 | | | |

R.S.D. is relative standard deviation ($2\sigma$). Reference data are from the double-spike method by Woodhead and Hergt (2000). The amount of lead loaded is shown in each rock sample. Note that the analytical reproducibility for the samples by Woodhead and Hergt (2000) is significantly worse than that reported for natural rock samples by Woodhead et al. (1995).

observed in Fig. 3, which shows that the averaged scan data of NBS981 (open circles) exhibit marked variation in the amounts of Pb. This problem is, however, solved by adopting the zero-time correction (Fig. 3), making it possible to determine accurately isotopic compositions over a wide range of 0.5–100 ng Pb.

The latter problem (2) might be more serious than the former problem. The interfering elements and organic materials derived from the resin during column chemistry could affect the performance of the emitter substance, and are believed to change the behavior of mass fractionation (Woodhead et al., 1995). By carrying out two stages of column chromatography, however, the reproducibility of mass fractionation during spectrometry analyses is drastically improved, which enabled us to obtain accurate data irrespective of rock chemistry on sample sizes from 1 to 100 ng of Pb (Fig. 5). Our improved procedure of chemical separation overcomes the problem of the impurities. This is also supported by the observation that the ion current and

beam stability of Pb during mass spectrometer were almost identical between pure reference materials (NBS981) and the separated Pb from geological samples, at a given amount of Pb.

*3.5.2. Comparison with the double-spike method*

The double-spike techniques can roughly be classified into those utilizing a $^{202}Pb-^{205}Pb$ mixed spike (Todt et al., 1996) and those with a $^{207}Pb-^{204}Pb$ spike (Woodhead et al., 1995; Powell et al., 1998; Thirlwall, 2000) or a $^{207}Pb-^{206}Pb-^{204}Pb$ triple spike (Galer, 1999). Although the former method needs only one spectrometric run for each sample, it is difficult for many analysts to handle the spike solution because of high cost. The latter method, on the other hand, requires two spectrometric runs for unknown samples, but the cost of the spike solutions is less. The present method, using the zero-time correction, is simple because it requires only one spectrometric run for each sample and the extra procedures and the cost for spike solutions are not necessary.

Our method avoids the problems described above but it does require two-stage column chromatography to obtain precise and accurate data. Its reliability depends on the assumption that the mass fractionation of unknown samples is similar to that of a pure Pb standard material. The separated Pb samples must therefore be mostly free of contaminants such as organic materials. On the other hand, the problem of impurities in separated Pb samples does not significantly affect the precise isotope analyses using the double-spike method, and one column pass is usually adequate for this method (e.g., Thirlwall, 2000). Note, however, that careful column chromatography, including a second round of column procedure, is required for samples with nanogram level of Pb ($< 10$ ng), even in the double-spike method, because the ionization of Pb is dramatically suppressed during mass spectrometry for samples without the second column chemistry, as demonstrated in this study.

Another drawback of the present method (and also the conventional method without double spiking) is that the data obtained always depend on the isotopic compositions of the reference Pb standard materials (i.e., external correction), and the recommended compositions have been frequently revised (e.g., Woodhead et al., 1995; Todt et al., 1996; Galer, 1999; Thirlwall, 2000). The reference values of the Pb standard material used for the normalization must therefore be always provided when the measured isotopic data are presented.

## Acknowledgements

We are grateful to Takuya Moriguti, Akio Makishima, Tetsuya Yokoyama, Ryoji Tanaka, and Tomohiro Usui for constructive discussions and technical assistance throughout this study. Constructive reviews and comments by M.F. Thirlwall and final reading by I.H. Campbell significantly improved the manuscript. We thank C. Sakaguchi, K. Kobayashi, H. Takei, and all the other members of Pheasant Memorial Laboratory for Geochemistry and Cosmochemistry at ISEI for their encouragements and for useful discussions. C.J. Allègre and C. Göpel are also thanked for editorial handlings. This work was supported by the Japanese Society for the Promotion of Science for Japan Junior Scientists (T.K.), and the Ministry of Education, Culture, Sports, Science and Technology (E.N.). **[CA]**

## References

Ando, A., Kamioka, H., Terashima, S., Itoh, S., 1989. 1988 values for GSJ rock reference samples, 'Igneous rock series'. Geochem. J. 23, 143–148.

Belshaw, N.S., Freedman, P.A., O'Nions, R.K., Frank, M., Guo, Y., 1998. A new variable dispersion double-focusing plasma mass spectrometer with performance illustrated for Pb isotopes. Int. J. Mass Spectrom. 181, 51–58.

Galer, S.J.G., 1999. Optimal double and triple spiking for high precision lead isotopic measurement. Chem. Geol. 157, 255–274.

Galer, S.J.G., Abouchami, W., 1998. Practical application of lead triple spiking for correction of instrumental mass discrimination. Mineral. Mag. 62, 491–492.

Gerstenberger, H., Haase, G., 1997. A highly effective emitter substance for mass spectrometric Pb isotope ratio determinations. Chem. Geol. 136, 309–312.

Hamelin, B., Manhes, G., Albarede, F., Allègre, C.J., 1985. Precise lead isotope measurements by the double spike technique: a reconsideration. Geochim. Cosmochim. Acta 49, 173–182.

Hirata, T., 1996. Lead isotope analyses of NIST standard reference materials using multiple collector inductively coupled plasma mass spectrometry couples with a modified external correction method for mass discrimination effect. Analyst 121, 1407–1411.

Koide, Y., Nakamura, E., 1990. Lead isotope analyses of standard rock samples. Mass Spectrosc. 38, 241–252.

Lugmair, G.W., Galer, S.J.G., 1992. Age and isotopic relationships among the angrites Lewis Cliff 86010 and Angra dos Reis. Geochim. Cosmochim. Acta 56, 1673–1694.

Makishima, A., Nakamura, E., 1997. Suppression of matrix effects in ICP-MS by high power operation of ICP: application to precise determination of Rb, Sr, Y, Cs, Ba, REE, Pb, Th and U at ng $g^{-1}$ levels in milligram silicate samples. Geostand. Newsl. 21, 307–319.

Manhes, G., Minster, J.F., Allègre, C.J., 1978. Comparative uranium–thorium–lead and rubidium–strontium study of the saint sèverin amphoterite: consequences for early solar system chronology. Earth Planet. Sci. Lett. 39, 14–24.

Nakano, T., Nakamura, E., 1998. Static multicollection of $Cs_2BO_2^+$ ions for precise boron isotope analysis with positive thermal ionization mass spectrometry. Int. J. Mass Spectrom. Ion Processes 176, 13–22.

Powell, R., Woodhead, J., Hergt, J., 1998. Uncertainties on lead isotope analyses: deconvolution in the double spike method. Chem. Geol. 148, 95–104.

Rehkämper, M., Halliday, A.N., 1998. Accuracy and long-term reproducibility of lead isotopic measurements by multiple-collector inductively coupled plasma mass spectrometry using an external method for correction of mass discrimination. Int. J. Mass Spectrom. 181, 123–133.

Strelow, F.W.E., 1978. Distribution coefficients and anion exchange behavior of some elements in hydrobromic–nitric acid mixtures. Anal. Chem. 50, 1359–1361.

Thirlwall, M.F., 2000. Inter-laboratory and other errors in Pb isotope analyses investigated using a $^{207}Pb-^{204}Pb$ double spike. Chem. Geol. 163, 299–322.

Todt, W., Cliff, R.A., Hanser, A., Hofmann, A.W., 1996. Evaluation of a $^{202}Pb-^{205}Pb$ double spike for high-precision lead isotope analysis. Geophys. Monogr. 95, 429–437.

Tuttas, D., Habfast, K., 1982. High precision lead isotope ratio measurements. Finnigan MAT Appl. Rep. 51, 3–19.

Wasserburg, G.J., Jacobsen, S.B., DePaolo, D.J., McCulloch, M.T., Wen, T., 1981. Precise determination of Sm/Nd ratios, Sm and Nd isotopic abundances in standard solutions. Geochim. Cosmochim. Acta 45, 2311–2323.

Woodhead, J.D., Hergt, J.M., 2000. Pb-isotope analyses of USGS reference materials. Geostand. Newsl. 24, 33–38.

Woodhead, J.D., Volker, F., McCulloch, M.T., 1995. Routine lead isotope determinations using a lead-207–lead-204 double spike: a long-term assessment of analytical precision and accuracy. Analyst 120, 35–39.

Yokoyama, T., Makishima, A., Nakamura, E., 1999a. Separation of thorium and uranium from silicate rock samples using two commercial extraction chromatographic resins. Anal. Chem. 71, 135–141.

Yokoyama, T., Makishima, A., Nakamura, E., 1999b. Evaluation of the coprecipitation of incompatible trace elements with fluoride during silicate rock dissolution by acid digestion. Chem. Geol. 157, 175–187.