— Original Paper —

Precise Pb isotope analysis of igneous rocks using fully-automated double spike thermal ionization mass spectrometry (FA -DS- TIMS)

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A fully-automated (FA) technique applying ^{207}Pb-^{204}Pb double spike (DS) to thermal ionization mass spectrometry (TIMS) has been developed (FA- DS- TIMS). A long-term baseline is measured prior to the sample measurement runs and is applied to all of the acquired sample data, avoiding sample wasting caused by frequent baseline measurements during sample runs. FA- DS-TIMS offers reliable fully automated sequential analyses of 10 samples in one batch, including 10 natural runs and 10 runs doped with a spike enriched ^{207}Pb and ^{204}Pb. This cuts operating labor costs, although the measurement time is longer than a conventional TIMS or an identical run using multi collector-inductively coupled plasma-mass spectrometry (MC-ICP-MS).

The isotopic ratios of the ^{207}Pb-^{204}Pb double spike used in this study are ^{206}Pb/^{204}Pb = 0.10203, ^{207}Pb/^{204}Pb = 3.8717 and ^{208}Pb/^{204}Pb = 0.18865 when normalized to NIST SRM 982 ^{208}Pb/^{206}Pb = 1.00016. Average values for NIST SRM 981 containing 7.5 and 15 ng Pb are ^{206}Pb/^{204}Pb = 16.9390 ± 0.0017, ^{207}Pb/^{204}Pb = 15.4972 ± 0.0017, ^{208}Pb/^{204}Pb = 36.7213 ± 0.0045 (errors are 2SD, n = 12). These are within error of recently reported values obtained by DS-TIMS and DS-MC-ICP-MS. The reproducibility of ^{208}Pb/^{204}Pb in this study is 0.003% using 15 ng Pb, and 0.009% using 7.5 ng Pb. These are similar to, or better than, those reported by various other methods. The average values for JB-2 containing 20ng Pb are ^{206}Pb/^{204}Pb = 18.3419 ± 0.0027, ^{207}Pb/^{204}Pb = 15.5622 ± 0.0026, ^{208}Pb/^{204}Pb = 38.2814 ± 0.0078 (errors are 2SD, n = 5) and are comparable to those reported in recent studies. These results show that the new technique is reliable in terms of both accuracy and precision.

Keywords : Pb isotope, ^{207}Pb-^{204}Pb double spike, fully-automated TIMS, NIST SRM 981, JB-2

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1. Introduction

Pb isotopes are a fundamental and powerful tool in understanding geodynamic processes such as material recycling in the Earth's interior, or in surface environments, throughout the Earth's history. Pb isotopes are analyzed by thermal ionization mass spectrometry (TIMS) and multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS). Mass fractionation occurring within mass spectrometers has been a major obstacle preventing the measurement of precise Pb isotope ratios, as naturally occurring Pb has only one stable isotope, ^{204}Pb. Several approaches have been developed to correct for this mass fractionation. In the case of TIMS, 1) a conventional fractionation correction using a mass fractionation factor determined by analyzing a standard, which is then applied to all unknowns, 2) a zero-time correction (Kuritani and Nakamura, 2002), and 3) double, triple or two-double spike methods (e.g. Dodson, 1963; Hofmann, 1971; Hamelin et al., 1985; Woodhead et al., 1995; Galer and Abouchami, 1998; Thirlwall, 2000; Kuritani and Nakamura, 2003) have been applied. While for MC-ICP-MS, 1) an external fractionation correction using Tl (e.g. Thirlwall, 2000; Tanimizu and Ishikawa, 2006), 2) a combination between double spike (DS) with Tl external correction (Baker et al., 2004), and 3) DS without Tl correction (Makishima et al., 2007) have been applied.

These procedures have resulted in a dramatic improvement in the precision and accuracy of Pb isotopes measured by MC-ICP-MS and these now match those of DS-TIMS (Tanimizu and Ishikawa, 2006; Makishima et al., 2007). As a result, many laboratories use MC-ICP-MS, particularly for samples containing relatively large amounts of Pb (>10 ng), because the analytical time required for MC-ICP-MS is shorter than that of TIMS. However, recent instrumental developments in TIMS have enabled reliable automated analyses of up to 10 samples set on one filament magazine to be performed. This cuts labor costs, although the analytical time remains longer than MC-ICP-MS.

At IFREE we have been improving the conventional TIMS technique, reaching a reproducibility of 0.017% (2RSD% ^{208}Pb/^{204}Pb for 100 ng of Pb) (Miyazaki et al., 2007). However, the method is not applicable to analyze small amounts of sample (< 25 ng) (Miyazaki et al., 2003a). In order to achieve precise Pb isotope analysis on such small samples, we have developed a fully-automated ^{207}Pb-^{204}Pb double spike (DS) method for TIMS. We briefly describe the analytical procedure of this method and report its results for Pb isotope analyses on NIST SRM 981 and JB-2 standards.

2. ^{207}Pb-^{204}Pb DS-TIMS

The DS method requires an individual sample to be separated into two aliquots, one of which is doped with a spike enriched in two isotopes (in this case ^{207}Pb and ^{204}Pb) (Dodson, 1963). Both aliquots are consecutively analyzed in the mass spectrometer; the 'natural run' refers to the undoped aliquot, the 'spiked run' the doped aliquot. Three Pb isotope ratios are measured with a common denominator (i.e., either ^{206,207,208}Pb/^{204}Pb, ^{204,207,208}Pb/^{206}Pb, ^{204,206,208}Pb/^{207}Pb or ^{204,206,207}Pb/^{208}Pb) for each run, and together with the known isotope ratios of the spike, derive the mass discrimination factor of the natural run, and consequently the true isotope ratios of the natural and the spiked runs. Several methods have been discussed in the literature to derive these values, of which there are two types; iterative calculations (Dodson, 1963; Woodhead et al., 1995), and direct calculations (Hofmann, 1971; Hamelin et al., 1985; Galer, 1999; Thirlwall, 2000; Kuritani and Nakamura, 2003). The latter was applied in this study.

A schematic illustration of the double spike method (^{207}Pb-^{204}Pb double spike), as proposed by Hofmann (1971), is illustrated in Fig. 1. The 'true' isotopic compositions of the unknown and doped mixtures are plotted at points *U* and *M*, respectively, while points *u* and *m* correspond to the measured isotopic compositions of the unknown and the doped mixture. Point *S* corresponds to the isotope composition of the Pb double spike. Assuming the linear

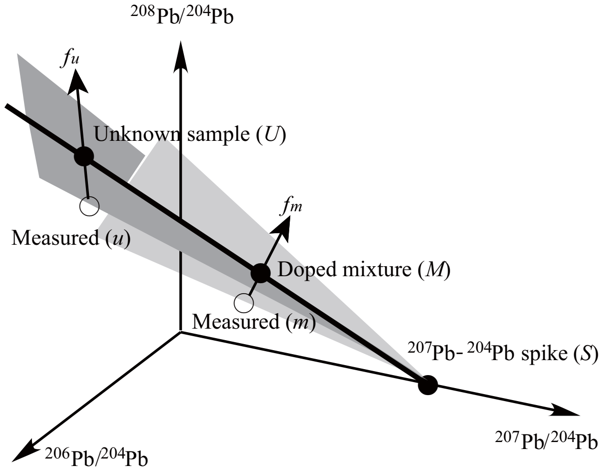

Fig.1. Three dimensional graphical representation of the double spike, after Galer (1999). For definitions of symbols see text.

fractionation law, the true isotope ratios of the unknown (U_i) and mixture (M_i) can be expressed as:

$$U_i = u_i\,(1 + \varepsilon_U \cdot \Delta_i) \tag{1}$$

$$M_i = m_i\,(1 + \varepsilon_M \cdot \Delta_i) \tag{2}$$

where u_i and m_i are the measured isotope ratios of the unknown and doped mixture, ε_U and ε_M are the fractionation factors per AMU of U and M, and Δ_i is the mass difference between the numerator and denominator isotopes (subscript i is for the three lead isotope ratios). The mixing equation between the U_i and S_i (isotope ratios of Pb double spike) gives the isotope ratios of the doped mixture (M_i):

$$M_i\,(1 + q) = U_i + S_i \cdot q \tag{3}$$

where q is the ratio between the reference isotope in the spike and the unknown ($^{204}\mathrm{Pb}_{\mathrm{spike}}/^{204}\mathrm{Pb}_{\mathrm{unknown}}$) in the doped mixture. Combining equations (1), (2) and (3) gives the following equation:

$$(m_i - S_i) \cdot q + m_i \cdot \Delta_i \cdot (1 + q) \cdot \varepsilon_M - u_i \cdot \varepsilon_U \cdot \Delta_i = u_i - m_i \tag{4}$$

which can be expressed in terms of the matrix equation:

$$A \cdot \begin{pmatrix} q \\ r \\ \varepsilon_U \end{pmatrix} = B \tag{5}$$

where $r = (1 + q)$ and the matrix A and vector B are given by:

$$A = \begin{pmatrix} m_1 - S_1 & m_1 \cdot \Delta_1 & -u_1 \cdot \Delta_1 \\ m_2 - S_2 & m_2 \cdot \Delta_2 & -u_2 \cdot \Delta_2 \\ m_3 - S_3 & m_3 \cdot \Delta_3 & -u_3 \cdot \Delta_3 \end{pmatrix} \tag{6}$$

and:

$$B = \begin{pmatrix} u_1 - m_1 \\ u_2 - m_2 \\ u_3 - m_3 \end{pmatrix} \tag{7}$$

The solution to Eq. (5), and therefore ε_U, follows by multiplying both sides of Eq. (5) by the inverse of A. The propagated error for the corrected isotope ratios of the unknown is calculated using a model from Hamelin et al. (1985).

3. Experimental

3.1. Reagents and isotope standard materials

TAMAPURE®-AA grade 38 % HF, 68 % HNO_3, 20 % HBr and 98 % H_3PO_4 (Tama Chemicals Co., Ltd) were used without any additional purification. Water was de-ionized to a resistivity of > 18.3 MΩcm^{-1} by a Milli-Q® system (Millipore®) and finally distilled at 80 °C using a two-bottle Teflon® still. An ionization activator was prepared from silicic acid colloidal solution (Nissan Chemical Industries, Ltd.), as described in Miyazaki et al. (2005). A high-purity Pb metal, NIST SRM 981 and 982, which were digested in and diluted with 0.5 M HNO_3 to give a concentration of 10 ppm, were used as a Pb isotope standard.

3.2. DS calibration

^{204}Pb- and ^{207}Pb- enriched spikes were obtained from the Oak Ridge National Laboratory, USA. ^{207}Pb-^{204}Pb double spike composition and the spike/sample mixing ratio have been optimally determined by an error simulation after Galer (1999). The ^{207}Pb-^{204}Pb double spike solution was diluted with 0.5 M HNO_3 to 7 ppm, and calibrated using NIST SRM 982. ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios of NIST SRM 982, used for this calibration and determined following the conventional method (Miyazaki et al. 2003a), were 36.7570, 17.1674 and 36.7629 when normalized to ^{208}Pb/^{206}Pb = 1.00016 (Catanzaro et al., 1968). The isotopic composition of the ^{207}Pb-^{204}Pb double spike, including the effect of the loading blank (0.6 pg of Pb), were ^{206}Pb/^{204}Pb = 0.10203, ^{207}Pb/^{204}Pb = 3.8717 and ^{208}Pb/^{204}Pb = 0.18865.

3.3. Sample preparation

All the chemical procedures were performed in a class 100 clean room. The powdered silicate rock standard (JB-2) was decomposed in a closed 7 ml Teflon® perfluoroalkoxy (PFA) screw cap vials (Savillex®) with a 1 : 4 mixture of 15 M HNO_3 and 20 M HF on a hot plate at 100 °C over night. After reaching complete dryness at 115 °C, the sample was dissolved with 2 ml of 8 M HBr. Then the sample was completely dried again, this time at 90 °C, after which a further 1 ml of 8 M HBr was added. Once more the sample was heated at 90 °C until complete dryness was achieved before 1 ml of 0.5 M HBr was added to digest the dried sample and it was centrifuged for 20 minutes at 4000 rpm. The supernatant was transferred to another PFA vial.

The remaining precipitate was rinsed with 0.5 ml 0.5 M HBr and centrifuged, and the supernatant was then added to the same PFA vial. The supernatant was loaded into an anion column containing 0.1 ml Bio-Rad AG 1X8 resin (200 – 400 mesh), which was previously washed and conditioned with 1 ml of 1 M HNO_3, 1 ml of H_2O and 0.6 ml of 0.5 M HBr. The Pb fraction was collected with 2.5 ml of H_2O after the elution of concomitant elements using 2.5 ml of a mixed acid composed of 0.25 M HBr and 0.5 M HNO_3. One drop of 0.075 M H_3PO_4 was added and the Pb fraction was evaporated at 90 °C. The dried Pb fraction was dissolved with 0.3 ml of 0.5 M HBr and loaded onto a refilled 0.1 ml anion exchange resin, which was previously washed and conditioned with 1 ml of 1 M HNO_3, 1 ml of H_2O and 0.6 ml of 0.5 M HBr. The Pb fraction was collected with 2.5 ml of H_2O after the elution of concomitant elements using 4 ml of 0.5 M HBr. The amount of Pb dissolved in the fraction was accurately determined by isotope dilution mass spectrometry (ID-TIMS).

The chemically separated Pb fraction was split between the natural and the spiked runs (2/3 : 1/3). In the case of NIST SRM 981, a 10 ppm solution was split 10 ng : 5 ng for the 15 ng run, and 5 ng : 2.5 ng for the 7.5 ng run between the natural and spiked runs, respectively. A ^{207}Pb-^{204}Pb DS solution (7 ppm) was added to the spiked run aliquot (0.33 µl for 20 ng run, 0.25 µl for 15 ng run and 0.125 µl for 7.5 ng run). 20 µl of 0.05 M H_3PO_4 was added to the 20 ng and 15 ng runs, and 30 µl of 0.0015 M H_3PO_4 to the 7.5 ng run, before the natural and spiked run aliquots were put on a hot plate at 90 °C for several hours to reduce the liquid volume. Upon reaching dryness, one drop of 15 M HNO_3 was added to the sample, which was then dried at 100 °C, in order to decompose organic materials. The total procedural blank for Pb was less than 6 pg, which was negligible in our routine analysis.

3.4. Mass spectrometry

The dried Pb sample was dissolved in ionization activator silica gel. The amount of ionization activator required depended on the quantity of Pb loaded (e.g., 1 µl for 15 ng). The loads were concentrated on the top of trapezoid-shaped Re-filament (0.7 mm wide, 0.034 mm thick). The Re-filament used in this study was supplied by Thermo Fisher Scientific (Miyazaki et al., 2003b). The filament current was gradually increased to 1 A, and held at this condition until the drop on the filament disappeared. The current was then rapidly decreased to zero.

Pb isotope measurements were carried out on a Thermo Finnigan TRITON TI® thermal ionization mass spectrometer (TIMS), equipped with nine Faraday cup collectors at the Institute for Research on Earth Evolution (IFREE), Japan Agency for Marine Earth Science Technology (JAMSTEC). An accelerating voltage of 10 kV was used for Pb isotope analysis. The Faraday collectors were set to detect the following isotopes simultaneously: ^{204}Pb (Low2), ^{206}Pb (Center), ^{207}Pb (High1) and ^{208}Pb (High2). An amplifier with a 10^{12} Ω feedback resistor (hereafter termed the 10^{12} Ω amplifier) was assigned to the Low2 Faraday collector for the smallest ^{204}Pb ion beam. Other collectors were connected to each 10^{11} Ω amplifier, after evaluating the stability using the amplifier check programs in the TRITON software (Noise test and EL test).

The advantage of using the 10^{12} Ω amplifier is that it reduces the statistical error caused by a low ion beam intensity on a minor isotope, such as ^{204}Pb. The larger resistor value increases the gain of the amplifiers 10 times, while the Johnson noise of the resistors only increases by a factor of the square root of 10. Thus, this promises an improvement in the signal to noise ratio by a factor of 3 (Schwieters et al., 2006). Fig. 2 compares the raw isotope ratios of ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb measured using a 10^{12} Ω amplifier with those measured using a 10^{11} Ω amplifier for ^{204}Pb (average intensity about 0.05V). For a given ^{204}Pb intensity, the raw isotope ratios measured using the 10^{12} Ω amplifier provide clearer

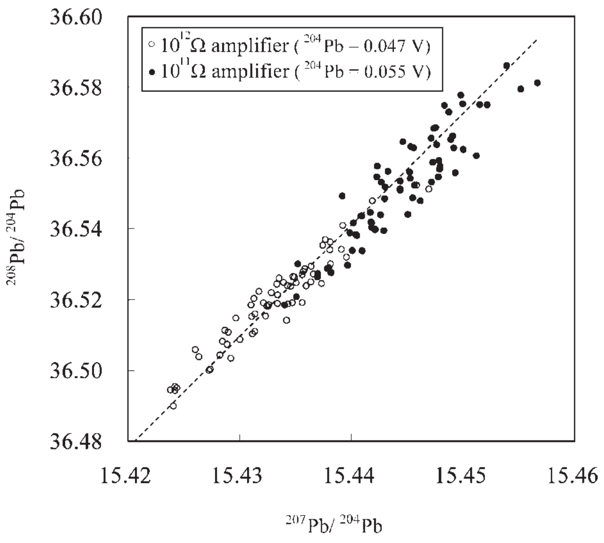

Fig.2. Comparison between raw isotope ratios of ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb measured using a 10^{12} Ω amplifier and a 10^{11} Ω amplifier. Averaged ^{204}Pb intensities measured by 10^{12} Ω and 10^{11} Ω amplifiers were 0.047 V and 0.055 V, respectively.

correlations than the those using the 10^{11} Ω amplifiers.

Gain factors for each amplifier were calibrated automatically by passing a constant electric current through them. The gain factor between the 10^{11} Ω amplifiers and the 10^{12} Ω amplifier was recalibrated using a calibration factor, determined through repetitive measurements of NIST SRM 981 following conventional methods (Miyazaki et al. 2003a).

3.5. Program for FA- DS- TIMS

On the TRITON TI®, operation conditions, such as gain calibration, baseline measurement, filament heating, focusing of the ion beam, and sample measurement, are programmed on a "method file". By combining several "method files" into a "sequence file", we can automatically measure several samples in one sequential run.

Usually, baseline measurements are frequently performed during sample measurement runs. However, when there are only small amounts of sample, wasting sample during baseline measurements needs to be avoided. As a result, we adopted a single long-term baseline measurement performed prior to the sample measurement runs. Table 1 shows the combination of four method files including the long baseline measurement. The baseline was measured for 15 minutes. The baseline data is stored and used for each successive sample measurement run. However, 60 minutes can elapse between the baseline measurement and the following sample measurement. During this time baseline drift may occur. To monitor this possibility, one phantom blank sample measurement was performed at the very end of the analytical sequence by measuring isotope ratios without an ion source filament. This raw intensity data without the ion beam is used to perform the baseline correction for each sample by interpolating the baseline drift, if necessary. This is processed during offline calculations.

Twenty-one filaments can be installed on one magazine set in the mass spectrometer. This allows ten samples, in addition to the standard, to be automatically measured in one sequential run. Fifty-five raw isotope

Table 1. Combination of method files for fully-automated DS measurement (for one sample on filament).

Method File	Operation	Acquired data	Time
1	Gain calibration	Gain data (stored in operating computer)	≈15 min
2	Baseline measurement	Baseline data (stored in operating computer)	≈15 min
3-1	Filament heating (1190-1260°C) and Focusing of the ion beam	-	< 60 min
3-2	Sample measurement	Raw intensity data of sample (used for off-line calculation)	≈15 min
4	Blank measurement for baseline drift collection	Raw intensity data without ion beam (used for off-line calculation)	≈15 min

Table 2. Pb isotope ratios measured in NIST SRM 981.

		^{206}Pb / ^{204}Pb	2SE	^{207}Pb / ^{204}Pb	2SE	^{208}Pb / ^{204}Pb	2SE
15 ng	#1	16.9377	0.0019	15.4961	0.0018	36.7196	0.0042
	#2	16.9390	0.0013	15.4969	0.0013	36.7202	0.0030
	#3	16.9393	0.0015	15.4978	0.0015	36.7225	0.0034
	#4	16.9388	0.0015	15.4973	0.0015	36.7216	0.0034
	#5	16.9383	0.0014	15.4966	0.0013	36.7215	0.0031
	#6	16.9387	0.0017	15.4972	0.0016	36.7215	0.0037
	#7	16.9396	0.0016	15.4977	0.0015	36.7229	0.0035
	average ± 2SD	16.9388	0.0013	15.4971	0.0012	36.7214	0.0024
	RSD (%)		0.004		0.004		0.003
7.5 ng	#1	16.9407	0.0018	15.4990	0.0018	36.7247	0.0041
	#2	16.9401	0.0031	15.4977	0.0029	36.7215	0.0068
	#3	16.9388	0.0024	15.4966	0.0023	36.7183	0.0055
	#4	16.9394	0.0020	15.4979	0.0019	36.7241	0.0045
	#5	16.9380	0.0020	15.4960	0.0020	36.7168	0.0046
	average ± 2SD	16.9394	0.0021	15.4974	0.0023	36.7211	0.0069
	RSD (%)		0.006		0.007		0.009
15 ng and 7.5 ng	average ± 2SD	16.9390	0.0017	15.4972	0.0017	36.7213	0.0045
	RSD (%)		0.005		0.006		0.006
Previous studies (using DS or TS)							
			2SD		2SD		2SD
Woodhead et al. (1995)	TIMS ^{207}Pb - ^{204}Pb DS ～100 ng Pb (n = 109)	16.937	0.004	15.492	0.005	36.708	0.013
Todt et al. (1996)	TIMS ^{202}Pb - ^{205}Pb DS 80 ng Pb (n = 11)	16.9356	0.0023	15.4891	0.0030	36.7006	0.0113
Galer & Abouchami (1998)	TIMS ^{207}Pb - ^{206}Pb - ^{204}Pb TS ～10 ng Pb (n = 60)	16.9405	0.0015	15.4963	0.0016	36.7219	0.0044
Thirlwall (2000)	TIMS ^{207}Pb - ^{204}Pb DS ～20 ng Pb (n = 41)	16.9409	0.0022	15.4956	0.0026	36.7228	0.0080
Thirlwall (2002)	MC-ICP-MS ^{207}Pb - ^{204}Pb DS 7 and 44 ng Pb (n = 36)	16.9417	0.0029	15.4996	0.0031	36.724	0.009
Kuritani & Nakamura (2003)	TIMS ^{207}Pb - ^{204}Pb DS 15 ng (n = 16)	16.9424	0.0018	15.5003	0.0017	36.7266	0.0042
Baker et al. (2004)	MC-ICP-MS ^{207}Pb - ^{204}Pb DS 20 - 40 ng Pb (n = 95)	16.9416	0.0011	15.4999	0.0011	36.7258	0.0031
Kuritani et al. (2006)	TIMS ^{207}Pb - ^{204}Pb, (^{205}Pb - ^{204}Pb) Pb-ID-DS ～40 ng Pb (n = 5)	16.9419	0.0016	15.4998	0.0016	36.7253	0.0045
Makishima et al. (2007)	MC-ICP-MS ^{207}Pb - ^{204}Pb DS 4 ng Pb	16.9417	*0.0024*	15.4988	*0.0025*	36.7196	*0.0066*

2SD = 2 × standard deviation, RSD = relative standard deviation (1SD), 2SE = 2 × standard error propagated through the double-spike mass bias correction
Uncertainties shown in italics are the values re-calculated here from the RSD (%) in the previous studies.

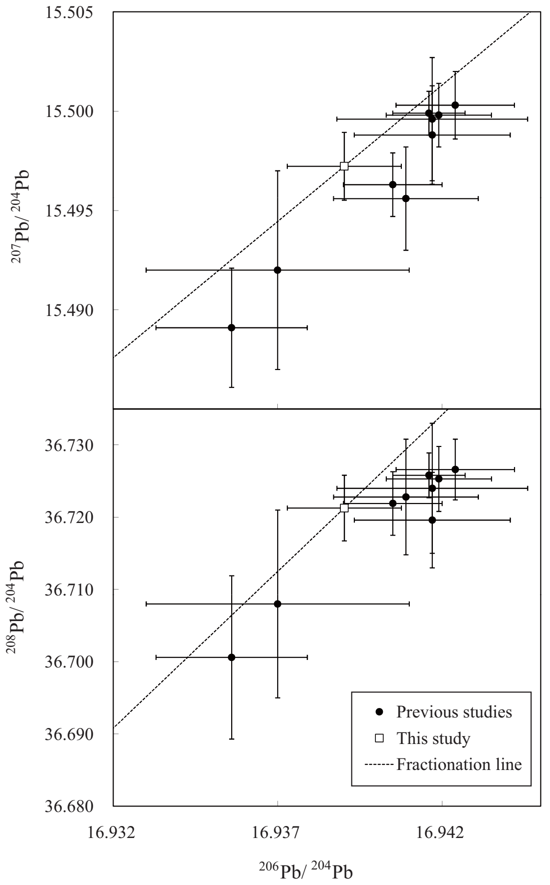

Fig.3. Comparison between average values for NIST SRM 981 obtained in this study and previous studies. Error bars define 2SD. Data and sources of previous studies are listed in Table 2.

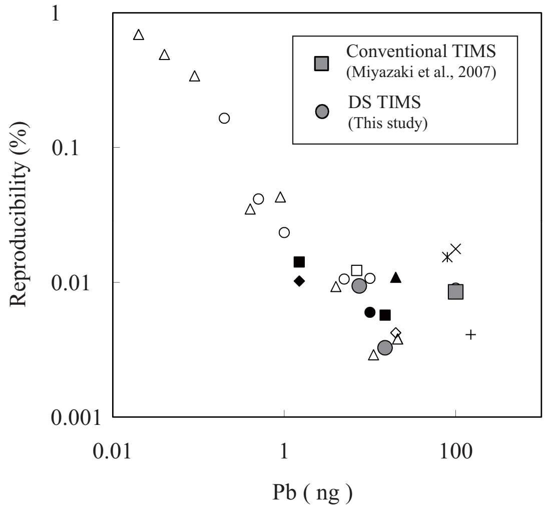

Fig.4. Comparison of reproducibility (RSD%) of $^{208}Pb/^{204}Pb$ against the amount of Pb in each measurement. ◆ two-DS TIMS, ■ DS TIMS (Kuritani and Nakamura, 2003); ▲ DS TIMS (Thirlwall, 2000); × DS TIMS (Woodhead et al., 1995); ✻ DS TIMS (Todt et al., 1996); ● TS TIMS (Galer and Abouchami, 1998); + MC-ICP-MS with Tl add. (Tanimizu and Ishikawa, 2006); □ DS MC-ICP-MS (Thirlwall, 2002); ◇ DS MC-ICP-MS (Baker et al., 2004); △ DS MC-ICP-MS (Makishima et al., 2007); ○ Zero-time corr. TIMS (Kuritani and Nakamura, 2002).

ratios ($^{204}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$) of natural and spiked runs were used for offline calculations on an Excel® spreadsheet, a copy of which is available from the corresponding author.

4. Results and discussion

4.1. Measurements of NIST SRM 981 standard

The Pb isotope ratios of NIST SRM 981 (7.5 – 15 ng) measured following this procedure at the IFREE laboratory are shown in Table 2. After mass discrimination correction using the ^{207}Pb-^{204}Pb DS, the averages for 7.5 – 15 ng of NIST SRM 981 are $^{206}Pb/^{204}Pb = 16.9390 \pm 0.0017$, $^{207}Pb/^{204}Pb = 15.4972 \pm 0.0017$, $^{208}Pb/^{204}Pb = 36.7213 \pm 0.0045$ (errors are 2SD, n = 12). The differences between the average values for the 7.5 ng and 15 ng runs are within 1 standard deviation. Our results are compared with those of previous studies that used DS or TS-TIMS and DS-MC-ICP-MS in Table 2, Fig. 3. This shows that the $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios measured in this study (7.5 – 15 ng, n = 12) overlap, within the error limits, with the previous studies (except for Todt et al., 1996).

Fig. 4 compares the reproducibility (1RSD%) of $^{208}Pb/^{204}Pb$ obtained in this study with those from previous studies against the amounts of Pb measured in each analysis. The 1RSD for $^{208}Pb/^{204}Pb$ of 0.003 % using 15 ng from this study is similar to those for DS-MC-ICP-MS and better than those for DS-TIMS in previous studies. Using 7.5 ng Pb the 1RSD for $^{208}Pb/^{204}Pb$ is 0.009 %, which is similar to those of previous studies using DS-MC-ICP-MS and zero-time correction TIMS.

4.2. Measurements of JB-2

The Pb isotope ratios of JB-2 determined in this study are summarized in Table 3. The averages for 20 ng Pb in JB-2 after the mass discrimination correction using the ^{207}Pb-^{204}Pb DS are $^{206}Pb/^{204}Pb = 18.3419 \pm 0.0027$, $^{207}Pb/^{204}Pb = 15.5622 \pm 0.0026$, $^{208}Pb/^{204}Pb = 38.2814 \pm 0.0078$ (errors in 2SD, n = 5). Although the observed relative uncertainties of $^{206}Pb/^{204}Pb$ (0.007 %), $^{207}Pb/^{204}Pb$ (0.008 %), and $^{208}Pb/^{204}Pb$ (0.010 %) are larger than those for 15 ng Pb in NIST SRM 981 (0.004 %, 0.004 %, and 0.003 %, respectively), they are comparable to those in DS-TIMS data measured by Thirlwall (2000). The Pb isotope ratios of JB-2 reported in studies since 2000 are compared with our data in Table 3 and Fig. 5. The $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios obtained in this study are consistent with those of the other studies,

Table 3. Pb isotope ratios measured in JB-2.

		q	^{206}Pb / ^{204}Pb	2SE	^{207}Pb / ^{204}Pb	2SE	^{208}Pb / ^{204}Pb	2SE
20 ng	#1	4.540	18.3418	0.0026	15.5616	0.0023	38.2794	0.0055
	#2	4.509	18.3427	0.0012	15.5632	0.0011	38.2831	0.0030
	#3	4.373	18.3438	0.0016	15.5641	0.0014	38.2875	0.0036
	#4	4.846	18.3403	0.0014	15.5614	0.0013	38.2792	0.0035
	#5	4.737	18.3411	0.0021	15.5610	0.0019	38.2780	0.0049
	average ± 2SD		18.3419	0.0027	15.5622	0.0026	38.2814	0.0078
	RSD (%)			0.007		0.008		0.010
Previous studies								
	Ishizuka et al. (2003) (n = 5)		18.3390		15.5610		38.2730	
	Baker et al. (2004) (n = 14)		18.3435		15.5619		38.2784	
	Tanimizu and Ishikawa (2006)* (n = 7)		18.3436		15.5624		38.2786	

* Corrected against NIST SRM 981 of Baker et al. (2004), 2SD = 2 × standard deviation, RSD = relative standard deviation (1SD).
2SE = 2 × standard error propagated through the double-spike mass bias correction.
q is the ratio between the reference isotope in the spike and the unknown ($^{204}Pb_{spike}/^{204}Pb_{unknown}$) in the doped mixture.

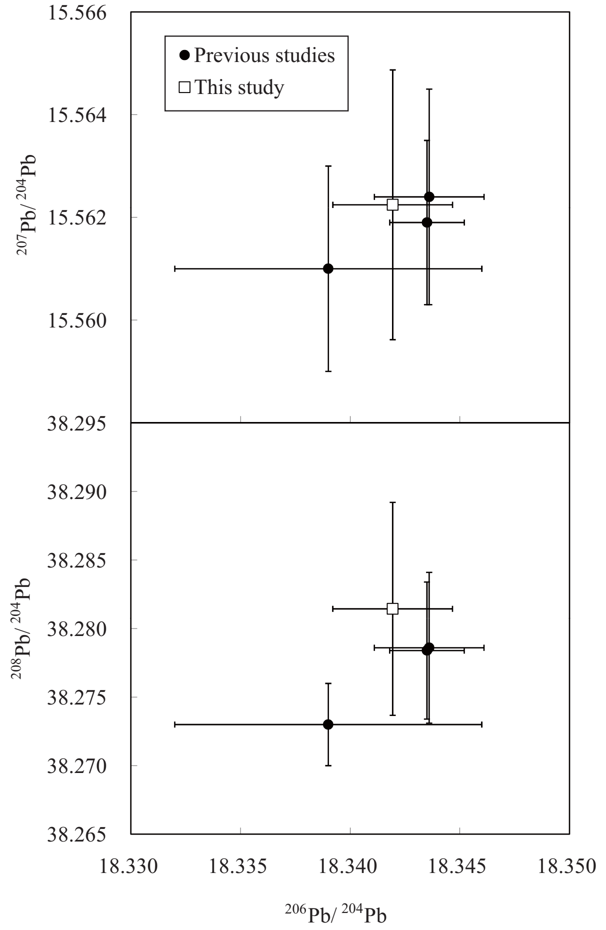

Fig.5. Average Pb isotope ratios obtained for JB-2 compared with previous studies. Error bars define 2SD. Data and sources of previous studies are listed in Table 3.

within error. The analytical accuracy and reproducibility using this technique is shown to be sufficient to allow precise measurements of Pb isotopes in igneous rocks.

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