

Precise lead isotope analysis using Multiple Collector-Inductively Coupled Plasma-Mass Spectrometry (MC-ICP-MS): Analytical technique and evaluation of mass fractionation during Pb separation

Jun-Ichi Kimura* and Natsuko Nakano*

Abstract

A precise Pb isotope analytical method using a double-focusing MC-ICP-MS routinely yields Pb isotope ratio sample data with an external reproducibility of <170 ppm. This is achieved by making (a) an isobaric overlap correction of ^{204}Hg on ^{204}Pb , (b) an external mass fractionation correction using $^{203}\text{Tl}/^{205}\text{Tl}$, and (c) a mass-dependent mass fractionation correction between Tl and Pb using a sample-standard bracket method. We also report that Pb isotope ratios are fractionated during the single column-single bead anion exchange procedure described in a previous report in this series, particularly if single bead Pb purification is used. If a sufficiently large volume of elutant (in this case >1 ml 6 NM HCl) is collected in the first column separation, there is no measurable fractionation of Pb isotopes. Single step Pb separation is sufficient for MC-ICP-MS, and consequently relatively rapid sample throughput is achievable, in combination with the rapid measurement possible with MC-ICP-MS (15 samples a day).

Key words: Pb isotope, MC-ICP-MS, chemical separation grossular, prehnite, chlorite, vesuvianite, amphibole

Introduction

Lead isotope measurements are widely utilized in the geological sciences for age dating and isotopic fingerprinting of rocks (Dickin, 1995). Although Pb isotope analysis is a powerful tool, the presence of only one isotope which is not the product of radioactive decay (^{204}Pb), has limited application and realization of the full potential of this isotopic system (Abouchami *et al.*, 2000; Baker *et al.*, 2004). Unlike the Nd or Sr isotopic systems, mass fractionation cannot be corrected for Pb by using a pair of invariant isotopes. Several laboratories have developed double-spike (DS) or triple-spike (TS) measurement techniques (Dodson, 1963; Gale, 1970; Hofman, 1971) for mass fractionation correction by both thermal ionization mass spectrometry (TIMS) and multiple collector inductively coupled plasma mass spectrometry (MC-ICPMS) (Todt *et al.*, 1996; Woodhead and Hergt, 1997; Galer and Abouchami, 1998; Galer, 1999; Thirlwall, 2000; Woodhead and Hergt, 2000; Thirlwall, 2002; Baker *et al.*, 2004). These studies have demonstrated that Pb isotopic ratios (e.g., $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$) are reproducible within ± 100 ppm.

MC-ICPMS can potentially correct for mass bias of lead isotopes by simultaneously analyzing doped thallium ($^{205}\text{Tl}/^{203}\text{Tl} = 2.3889$ (Thirlwall, 2002)). This is possible because the mass bias of elements of similar mass is relatively constant, and essentially does not change during analysis (Hirata, 1996). However, Thirlwall (2002) made the

important observation that the relative mass bias between Tl and Pb differed between standards and samples during individual analysis sessions, resulting in errors of up to 400 ppm/amu in Tl-corrected Pb isotope analysis compared with the DS technique. A solution to this problem was presented by Woodhead (2002), who deliberately induced change in matrix by analyzing different Pb cuts from samples, and thus calibrated the relative fractionation between Tl and Pb. Subsequently, Baker *et al.* (2004) further examined the DS-MC-ICP-MS and Tl-collected MC-ICP-MS techniques by rigorous analysis of the long-term reproducibility of both methods. Although they used the method proposed by Woodhead (2002), results from the Tl-corrected method were not reproducible during the study, even for the SRM 981 standard.

Although several sources of analytical error and causes of deteriorating reproducibility have been examined in the literature (e.g., mass dependent mass bias (Hirata, 1996), matrix dependent Tl-Pb mass bias fractionation (Woodhead, 2002), tailing of Pb peaks affecting mid-mass baselines (Thirlwall, 2001)). However, the effect of isobaric overlap of ^{204}Hg on ^{204}Pb (Hirata, 1996) has previously been ignored. This interference has been neglected by most analysts in the past, because signal intensities are almost undetectable. We found that the ^{204}Hg interference changes either day-by-day or sample-by-sample, due to differences in the levels of Hg impurities present in individual bottles of Ar gas, and to differences in concomitant Hg between sample separates, respectively. Although almost invisible, the Hg interference affects analytical results for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$ by > 400 ppm, due to the relatively minor amount of ^{204}Pb present. The on peak background method (Baker *et al.*,

*Dept of Geoscience, Faculty of Science and Engineering, Shimane University, Matsue 690-8504

2004) can correct for Hg overlap to some extent, but signal instability induced by the nebulizer or the MC-ICP-MS instrument itself can have a large effect, resulting in poor reproducibility. This is particularly true if the Hg interference is large. Hg interference can thus be the cause of day-by-day (by gas impurities) or sample-by-sample (by concomitant Hg) fractionation. In this study, we apply an Hg overlap correction to eliminate the ^{204}Pb interference. Even though the Hg interference is accounted for, mass dependent fractionation between Tl and Pb still deviates due to interface cone conditions. We here propose an analytical technique using (a) an isobaric overlap correction of ^{204}Hg on ^{204}Pb , (b) an external mass fractionation correction using $^{203}\text{Tl}/^{205}\text{Tl}$, and (c) a mass-dependent mass fractionation correction between Tl and Pb by the sample-standard bracket method. The external analytical reproducibility of igneous rock samples is smaller than 170 ppm compared with DS-MC-ICP-MS (Baker *et al.*, 2004) and DS-TIMS (Ishizuka *et al.*, 2003; Kuritani and Nakamura, 2003). We also examine isotopic fractionation during chemical separation of lead from samples, and report measurable fractionation during single bead separation (Kimura *et al.*, 2003).

Analytical Method

The Pb separation method used was the same as that reported by Kimura *et al.* (2003). We used two-step Pb purification, firstly utilizing a mini-column to separate Pb, and secondly a single-bead technique for purification. We briefly describe the procedure below.

1. Chemicals

The chemicals used were TAMA PURE AA 10 grade HF and HNO_3 , AA 100 grade HBr (Tama Chemicals Co.), and HCl distilled from Electra grade acid (Kanto Chemicals Co.). De-ionized water (DIW) was prepared by distillation and ion exchange with a MilliPore Milli-Q filter. The anion resin used for Pb separation was Dowex 1 X 8, using 200-400 mesh for column separation, and 16-20 mesh for the single bead purification.

2. Pb Separation

For each analysis, 100 mg of powdered rock sample were weighed and transferred to 15 ml Teflon beakers. Five mls of mixed acid (1 to 4 mixture of 15.4 NM HNO_3 and 20.4 NM HF) was added to each beaker and held overnight at 100°C . The samples were then evaporated to complete dryness at 115°C . Two mls of 8.8 NM HBr acid were then added, followed by heating at 90°C to complete dryness. One ml of 0.6 NM HBr was then added to digest the dried sample, and the solution transferred to a vial and centrifuged for 20 minutes at 6000 rpm.

The first step separation was carried out using anion columns (5 mm diameter, 50 mm length) containing 0.3 ml

Dowex 1 X 8 resin (200-400 mesh). Three 1 ml aliquots of 6 NM HCl were sequentially added to the columns, followed by 1 ml of deionized water (DIW) for washout. The columns were then conditioned by addition of 0.5 ml 0.6 NM HBr. The entire supernatant of the centrifuged sample was then loaded in the column. The concomitant elements were first removed by sequential addition of three 0.2 ml aliquots of 0.6 NM HBr, followed by three of 0.4 ml, and finally three of 0.8 ml. Lead was then eluted by addition of 1 ml 6 NM HCl. This solution was subsequently evaporated to dryness at 90°C .

The second stage single bead purification was carried out using the procedure of Manton (1988). Single 0.3 ml aliquots of 0.6 NM HCl were added to each of the dried Pb separates for digestion. Single beads (16-20 mesh) of Dowex 1 X 8 were then dropped into each solution. The beakers were capped and rotated for > 4 hours at 6 rpm. The single beads were then dropped in 2 ml Teflon beakers filled with 0.2 ml DIW and rotated for > 4 hours for reverse extraction of the Pb. The resin beads were then removed, and the solutions evaporated to dryness at 90°C .

3. MC-ICP-MS Analysis

3.1 Standard and sample solutions

Stock solution of ca. 2000 ppm was prepared by digesting Pb wire of the NIST SRM 981 standard. The thallium stock solution used was 1000 ppm AAS standard solution from Wako Chemicals Co. These were each diluted to 200 ppb in a 0.1% HNO_3 DIW solution for SRM 981 standard analysis. The analyzed rock samples were standards from the igneous rock series of the Geological Survey of Japan, namely JB-1 b, JB-2, and JB-3 (basalts), and JA-1 and JA-2 (andesites). The dried Pb separates from either (a) single column separation or (b) two-step column-bead separation were all diluted by a 0.1% HNO_3 solution containing 200 ppb Tl to approximately 200 ppb Pb prior to MC-ICP-MS analyses.

3.2 Instrument setups

Isotopic analyses were performed using a VG ELEMENTAL Plasma 54 (P 54), which is a double-focusing MC-ICP-MS. A high sensitivity cone called X-cone (or Super Cone) was fitted at the sampling interface. We also used a CETAC Aridus desolvation nebulizer for signal enhancement and minimization of oxide molecular interferences. Operating conditions are summarized in Table 1. Corrector amplifier gains were measured daily, prior to analysis. The specification of gain calibration reproducibility for the P 54 is 150 ppm, which is about three times greater than in the latest models. Assignments of masses to nine Faraday collectors are shown in Table 2. All data were acquired by static multi-collection mode. Background analyses were made for 10 seconds in each measurement block at lower and higher mid-mass of each isotopes, rather than by the on-peak zero (Baker *et al.*, 2004) method. Peak tailing (Thirlwall, 2001) has never been a particular

Table 1. Instrumental operating conditions for the MC-ICP-MS and Aridus desolvating nebulizer.

Instrument	VG ELEMENTAL VG Plasma 54
RF power	1300W
Accelerating voltage	5910 V
Analyzer pressure	$<1 \times 10^{-8}$ mbar
Cones	Nickel with X-cone
Argon gas flows	
Plasma	13 l/min
Auxiliary	1.2 l/min
Nebulizer	0.7 l/min
Sample introduction	CETAC Aridus desolvator
Sweep gas	3.4 l/min
N ₂ gas	0.14 l/min
Sample uptake rate	50 ul/min
Sensitivity	30-50 V/ppm

problem for double-focusing MC-ICP-MS instruments of this type (Baker *et al.*, 2004), perhaps due to high vacuum at the analyzer region that prevents scatter of ions from the beam axis. An analytical block consists of ten 10-second acquisitions, and 3 to 5 analytical blocks were usually measured for each sample (total acquisition time is 10-15 minutes for each sample, including washout).

3.3 Mass bias and interference corrections

Several models to correct for mass fractionation have been proposed (e.g., linear law or exponential law (Walder *et al.*, 1993)). Although exponential correction is recommended, no correction model can completely eliminate the mass fractionation in a MC-ICP-MS. Hirata (1996) proposed that the mass-dependent mass fractionation factor between particular elements ($\Delta F = F_1/F_2$, where F_1 and F_2 are exponential mass bias factors for certain elements) is always the same for a double-focusing MC-ICP-MS. He showed differences in mass bias factors between elements were in linear relation to average mass numbers, and therefore predictable for Hg, Tl, and Pb. We measured $^{203}\text{Tl}/^{205}\text{Tl}$ (1000 ppm AAS standard from Wako Chemicals) and $^{206}\text{Pb}/^{208}\text{Pb}$ (NIST SRM 981) and obtained mass-dependent mass bias factors of $\Delta F = 0.999631$ for $F_{\text{Pb}}/F_{\text{Tl}}$ and $\Delta F = 0.9998155$ for $F_{\text{Tl}}/F_{\text{Hg}}$, between Pb and Hg. The mass ratios used for mass bias determinations were initially $^{203}\text{Tl}/^{205}\text{Tl} = 2.3889$ (Thirlwall, 2002) and $^{206}\text{Pb}/^{208}\text{Pb} = 2.16707$ (Todt *et al.*, 1996). We then applied the ΔF factors to mass bias corrections for Hg, Tl and Pb based on the exponential law. The ΔF factors were built into exponential correction calculations because the measured Tl mass bias factor varied time-to-time and day-to-day, largely depending on instrumental set up. Beam intensities corrected for ΔF -corrected mass bias were then used for calculation of subtraction of ^{204}Hg signals from ^{204}Pb and eventually of Pb isotope ratios. Analytical results for GSJ standard rocks of the SRM 981 standard during analytical sessions over a month are listed in Table 3. The reproducibility of SRM 981 is $< \sim 170$ ppm for $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$, and $< \sim 200$

Table 2. Faraday collectors used to measure Hg-Tl-Pb isotope ratios and potential interferences.

Collector	L4	L3	L2	L1	AX	H1	H2	H3	H4
Mass	201	202	203	204	205	206	207	208	209
Isotope	^{201}Hg	^{202}Hg	^{203}Tl	^{204}Pb	^{205}Tl	^{206}Pb	^{207}Pb	^{208}Pb	
Interference	ReO^+	WO^+	ReO^+	^{204}Hg					

ppm for $^{208}\text{Pb}/^{204}\text{Pb}$ (Table 3). This suggests correction in our method is appropriate.

Discussion

1. Hg interference on ^{204}Pb

Hg mass 204 (^{204}Hg) interferes seriously in lead analysis (Hirata, 1996). ^{204}Hg interferes with the minor isotope ^{204}Pb , and therefore affects key Pb isotope ratios such as $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$. This interference has been underestimated or even neglected in the past, perhaps due to the low signal intensity from the minor amount of Hg usually present. Hg impurities originate from Ar gas and/or residual Hg in sample solutions after column separation. Figure 1 illustrates the errors induced by ^{204}Hg isobaric signals (in ppm) on ^{204}Pb . These data were measured in a single day, and the errors induced by Hg vary from almost zero up to ~ 200 ppm of the ^{204}Pb intensities. The total Pb beam intensities during the analyses ranged from 2 to 9 V. The results clearly show that although ^{204}Hg contribution is only at the 0.0000005 to 0.000008 V level, resulting Pb isotope ratios suffer from serious interferences of as much as 200 ppm. Moreover, the Hg-induced errors deviate in a single day or even between samples, suggesting variation in concomitant Hg between individual Ar gas bottles and Hg impurities in the sample separates. Consequently, we strongly suggest applying Hg interference correction for Pb isotope analysis by MC-ICP-MS. Baker *et al.* (2004) observed errors of in Pb isotope ratios of > 400 ppm when using the Tl corrected method. At least part of such

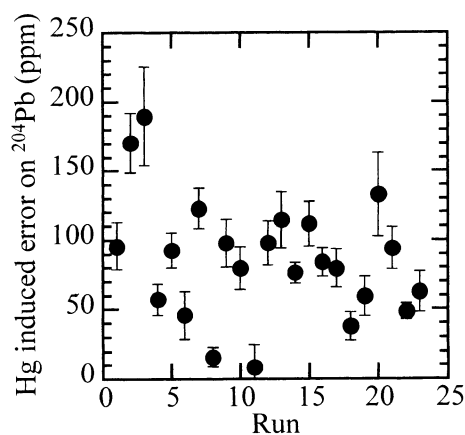


Fig. 1. ^{204}Hg -induced errors on ^{204}Pb (ppm) analyzed in 23 analysis sessions over 8 hours. Error bars indicate propagated errors from ^{204}Hg intensities (2-s). Differences of as much as 200 ppm are observed between samples.

Table 3. Initial MC-ICP-MS results for NIST SRM 981 and basalts and andesites issued by the Geological Survey of Japan. Results from previous publications are also listed for comparison.

Standard	$^{206}\text{Pb}/^{204}\text{Pb}$	2SE	$^{207}\text{Pb}/^{204}\text{Pb}$	2SE	$^{208}\text{Pb}/^{204}\text{Pb}$	2SE	Method	Reference
Jb-1b	18.3639	0.0021	15.5401	0.0024	38.6136	0.0079	Conventional TIMS	Kimura et al. (2003)
Jb-1b	18.3974	0.0045	15.5828	0.0052	38.7577	0.0168	Conventional TIMS	Kimura et al. (2003)
Jb-1b	18.3843	0.0032	15.5653	0.0038	38.6989	0.0121	Conventional TIMS	Kimura et al. (2003)
Jb-1b	18.3793	0.0046	15.5623	0.0046	38.6939	0.0141	Conventional TIMS	Kimura et al. (2003)
Jb-1b	18.3763	0.0035	15.5573	0.0039	38.6788	0.0125	Conventional TIMS	Kimura et al. (2003)
JB-1b	18.3802	0.0244	15.5615	0.0308	38.6886	0.1031	Conventional TIMS	average
JB-1b	18.3790	0.0033	15.5600	0.0033	38.6810	0.0035	MC-ICPMS(1column)	This study
JB-1b	18.3740	0.0094	15.5570	0.0094	38.6730	0.0096	MC-ICPMS(column-bead)	This study
JB-2	18.3320		15.5550		38.2230		Conventional TIMS	Shimoda & Nohda (1995)
JB-2	18.3310		15.5470		38.2370		Conventional TIMS	Koide & Nakamura (1989)
JB-2	18.3327		15.5603		38.2662		Conventional TIMS	Nohda (1999)
JB-2	18.3357		15.5463		38.2590		Conventional TIMS	Kimura et al. (2003)
JB-2	18.3328	0.0040	15.5522	0.0134	38.2463	0.0398	Conventional TIMS	average
JB-2	18.3390	0.0070	15.5610	0.0020	38.2730	0.0030	DS-TIMS	Ishizuka et al. (2003)
JB-2	18.3435	0.0017	15.5619	0.0016	38.2784	0.0050	DS-MCICPMS	Baker et al. (2004)
JB-2	18.3360	0.0032	15.5560	0.0032	38.2480	0.0033	MC-ICPMS(1column)	This study
JB-2	18.3360	0.0063	15.5548	0.0062	38.2463	0.0052	MC-ICPMS(column-bead)	This study
JB-3	18.2870		15.5270		38.2080		Conventional TIMS	Koide & Nakamura (1989)
JB-3	18.2947		15.5300		38.2412		Conventional TIMS	Nohda (1999)
JB-3	18.2933		15.5280		38.2517		Conventional TIMS	Kimura et al. (2003)
JB-3	18.2930	0.0086	15.5308	0.0100	38.2400	0.0451	Conventional TIMS	average
JB-3	18.2970	0.0020	15.5380	0.0020	38.2590	0.0020	DS-TIMS	Kuritani & Nakamura (2003)
JB-3	18.2890	0.0034	15.5320	0.0035	38.2240	0.0036	MC-ICPMS(1column)	This study
JA-1	18.2890		15.5220		38.2280		Conventional TIMS	Shimoda & Nohda (1995)
JA-1	18.3030		15.5380		38.2420		Conventional TIMS	Koide & Nakamura (1989)
JA-1	18.3120		15.5495		38.3025		Conventional TIMS	Nohda (1999)
JA-1	18.3035		15.5350		38.2660		Conventional TIMS	Kimura et al. (2003)
JA-1	18.3019	0.0191	15.5361	0.0226	38.2596	0.0652	Conventional TIMS	average
JA-1	18.3070	0.0035	15.5400	0.0036	38.2510	0.0036	MC-ICPMS(1column)	This study
JA-1	18.3002	0.0088	15.5399	0.0088	38.2464	0.0089	MC-ICPMS(column-bead)	This study
JA-2	18.4180		15.6400		38.7670		Conventional TIMS	Koide & Nakamura (1989)
JA-2	18.4030		15.5990		38.6550		Conventional TIMS	Shimoda & Nohda (1995)
JA-2	18.4105	0.0212	15.6195	0.0580	38.7110	0.1584	Conventional TIMS	average
JA-2	18.3960	0.0036	15.6030	0.0037	38.6480	0.0039	MC-ICPMS(1column)	This study
JA-2	18.3915	0.0088	15.6004	0.0114	38.6370	0.0087	MC-ICPMS(column-bead)	This study
SRM981	16.9370	0.0046	15.4940	0.0044	36.7010	0.0043	MC-ICPMS	This study
SRM981	16.9340	0.0050	15.4910	0.0051	36.6938	0.0051	MC-ICPMS	This study
SRM981	16.9349	0.0050	15.4916	0.0051	36.6951	0.0051	MC-ICPMS	This study
SRM981	16.9340	0.0030	15.4910	0.0030	36.6930	0.0030	MC-ICPMS	This study
SRM981	16.9335	0.0033	15.4906	0.0034	36.6905	0.0038	MC-ICPMS	This study
SRM981	16.9332	0.0040	15.4901	0.0040	36.6897	0.0041	MC-ICPMS	This study
SRM981	16.9357	0.0040	15.4917	0.0040	36.6946	0.0040	MC-ICPMS	This study
SRM981avg	16.9346	0.0027	15.4914	0.0025	36.6940	0.0074	MC-ICPMS	This study
SRM981	16.9356	0.0023	15.4891	0.0030	36.7006	0.0011	DS-TIMS	Todt et al. (1996)
SRM981	16.9407		15.4971		36.7245		TS-TIMS	Galer & Abouchami (1998)
SRM981	16.9416	0.0013	15.5000	0.0013	36.7262	0.0031	DS-MCICP	Baker et al. (2004)

analytical error could originate from uncorrected Hg during analysis over a long period by changes in Hg impurities in samples and Ar gas bottles.

2. Problems in the Pb isotope ratios of SRM 981 standard

New results for the isotope ratios of SRM 981 were published (Galer and Abouchami, 1998; Baker *et al.*, 2004) during the course of our analysis. These results show that all heavier isotopes have greater abundances relative to ^{204}Pb , ~ -350 ppm for $^{206}\text{Pb}/^{204}\text{Pb}$, ~ -700 for $^{207}\text{Pb}/^{204}\text{Pb}$, and ~ -700 ppm for $^{208}\text{Pb}/^{204}\text{Pb}$ (Table 3). The new ratios were determined by DS-TIMS (Galer and Abouchami, 1998) or DF-ICP-MS (Baker *et al.*, 2004) and the two sets of proposed values are almost identical (see Table 3). The reason why the ratios differ from those of Todt *et al.* (1996) is largely due to differences in the mass discrimination factor determined by measurement of SRM 982 “equal atom” Pb standard. As the mass discrimination factor of lead cannot be internally determined by any mass spectrometry, normalization using a common standard is

crucial. In fact, Todt *et al.* (1995) determined the isotope ratios of their nucleosynthetic $^{205}\text{Pb}/^{203}\text{Pb}$ spike, and Baker *et al.* (2004) determined the isotope ratios of their $^{207}\text{Pb}/^{204}\text{Pb}$ spike based on isotope ratios of SRM 982 $^{208}\text{Pb}/^{206}\text{Pb} = 1.00016$. If problems persist while analyzing SRM 982, systematic errors can propagate through mass discrimination factors and affect all isotopic ratios.

Binary plots of the Pb isotope ratios to identify correlations between them are a simple test for systematic error. All isotope ratios of SRM 981 plot on a regression line derived from our MC-ICP-MS results (Fig. 2). This linear correlation is believed to originate from mass discrimination effect (Woodhead, 2002), which is not sufficiently corrected for. Isotope ratios from Todt *et al.* (1995) plot within the errors of our results. This is matter of course, because our data is corrected against their ratios. The data from both Baker *et al.* (2004) and Galer and Abouchami (1998) also plot on the regression line, suggesting that the discrepancies observed are simply due to mass discrimination effect.

Table 4. (A). MC-ICP-MS results corrected for newly published SRM 981 isotope ratios by means of the standard bracket method. Comparisons with DS-TIMS, DS-MC-ICP-MS (for JB-2 and JB-3), and conventional TIMS results (for JB-1 b, JA-1, and JA-2) are also shown. (B) Comparisons of Pb isotope ratios obtained by single column separation and single column-single bead separation methods.

A. Comparison between DS-MC-ICP-MS, DS-TIMS, and this study							
Standard	$^{206}\text{Pb}/^{204}\text{Pb}$	2SE	$^{207}\text{Pb}/^{204}\text{Pb}$	2SE	$^{208}\text{Pb}/^{204}\text{Pb}$	2SE	Method Reference
SRM981	16.9346	0.0027	15.4914	0.0025	36.6940	0.0074	MC-ICPMS This study
SRM981	16.9416	0.0013	15.5000	0.0013	36.7262	0.0031	DS-MCICP Baker et al. (2004)
Correction factor	1.000413		1.000553		1.000879		
JB-1b							
	18.3878	0.0244	15.5701	0.0308	38.7226	0.1031	Conventional TIMS average
JB-1b	18.3866	0.0033	15.5686	0.0033	38.7150	0.0035	MC-ICPMS(1column) This study
Difference (ppm)	-68		-99		-196		
JB-2							
	18.3404	0.0040	15.5608	0.0134	38.2799	0.0398	Conventional TIMS average
JB-2	18.3390	0.0070	15.5610	0.0020	38.2730	0.0030	DS-TIMS Ishizuka et al. (2003)
JB-2	18.3435	0.0017	15.5619	0.0016	38.2784	0.0050	DS-MCICPMS Baker et al. (2004)
JB-2	18.3436	0.0032	15.5646	0.0032	38.2816	0.0033	MC-ICPMS(1column) This study
Difference (ppm)	3		174		84		
JB-3							
	18.3006	0.0086	15.5393	0.0100	38.2736	0.0451	Conventional TIMS average
JB-3	18.2970	0.0020	15.5380	0.0020	38.2590	0.0020	DS-TIMS Kuritani & Nakamura (2003)
JB-3	18.2965	0.0034	15.5406	0.0035	38.2576	0.0036	MC-ICPMS(1column) This study
Difference (ppm)	-25		167		-37		
JA-1							
	18.3094	0.0191	15.5447	0.0226	38.2932	0.0652	Conventional TIMS average
JA-1	18.3146	0.0035	15.5486	0.0036	38.2846	0.0036	MC-ICPMS(1column) This study
Difference (ppm)	280		249		-225		
JA-2							
	18.4106		15.6076		38.6890	0.1584	Conventional TIMS Shimoda & Nohda (1995)
JA-2	18.4036	0.0036	15.6116	0.0037	38.6820	0.0039	MC-ICPMS(1column) This study
Difference (ppm)	-380		256		-181		
B. Comparison between single column and column-bead separation methods							
Standard	$^{206}\text{Pb}/^{204}\text{Pb}$	2SE	$^{207}\text{Pb}/^{204}\text{Pb}$	2SE	$^{208}\text{Pb}/^{204}\text{Pb}$	2SE	Method Reference
JB-1b	18.3866	0.0033	15.5686	0.0033	38.7150	0.0035	MC-ICPMS(1column) This study
JB-1b	18.3816	0.0094	15.5656	0.0094	38.7070	0.0096	MC-ICPMS(column-bead) This study
Difference (ppm)	-272		-193		-207		
JB-2	18.3436	0.0032	15.5646	0.0032	38.2816	0.0033	MC-ICPMS(1column) This study
JB-2	18.3436	0.0063	15.5634	0.0062	38.2799	0.0052	MC-ICPMS(column-bead) This study
Difference (ppm)	0		-77		-45		
JA-1	18.3146	0.0035	15.5486	0.0036	38.2846	0.0036	MC-ICPMS(1column) This study
JA-1	18.3077	0.0088	15.5485	0.0088	38.2800	0.0089	MC-ICPMS(column-bead) This study
Difference (ppm)	-371		-6		-120		
JA-2	18.4036	0.0036	15.6116	0.0037	38.6820	0.0039	MC-ICPMS(1column) This study
JA-2	18.3991	0.0088	15.6090	0.0114	38.6710	0.0087	MC-ICPMS(column-bead) This study
Difference (ppm)	-245		-167		-285		

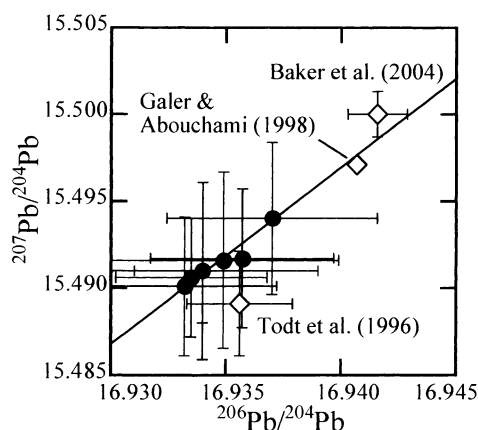


Fig. 2. Mass fractionation observed in $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ results for SRM 981. The linear regression line is generated from our results over the analytical sessions. The regression line intersects the reference isotope ratios proposed by Baker *et al.* (2004). All results lie on the mass fractionation line, suggesting that the difference in results originates from that effect.

3. Comparison of Pb isotope ratios in GSJ igneous rock standards

There may be several reasons for the origin of the discrepancies in the ratios of the SRM 981 standard (Baker *et al.*, 2004), however, recent two publications reported identical ratios for Pb isotope ratios. We therefore decided to normalize our results to Baker *et al.* (2004)'s SRM 981 isotope ratios. The correction factors and recalculated results are shown in Table 4. For the GSJ igneous standards, DS-TIMS and DS-MC-ICP-MS data are available for JB-2 (Ishizuka *et al.*, 2003; Baker *et al.*, 2004) and JB-3 (Kuritani and Nakamura, 2003). Our SRM 981-normalized results agree with other DS-mass spectrometry results at the $< \sim 170$ ppm level. As noted above, our vintage facility can attain calibration reproducibility of better than 150 ppm. Our results presented here are, therefore, achievable best precisions and accuracies.

Our SRM 981 results plot on a tightly constrained linear trend (Fig. 2), indicating that mass discrimination is not fully corrected by the TI correction method. This is perhaps

due to change in the sampling cone condition, which can alter the mass dependent mass fractionation factor. The $2\text{-}\sigma$ errors exceed 200 ppm, and this can be corrected for. Normalization of measured SRM 981 ratios against standard values considerably improves the residual mass fractionation. To do this, sample-standard bracket measurement is recommended. There is no doubt that measurements with the high precision and accuracy ($< \sim 170$ ppm) reported here are sufficient for almost all applications of lead isotope systems in the geosciences. The excellent agreement between DS-mass spectrometry and our MC-ICP-MS results clearly show that our analytical technique is another useful approach for precise Pb isotope analysis.

Additionally, comparison between averages of conventional TIMS results and our MC-ICP-MS data also agree within 300 ppm in most cases (Table 3) (Shimoda and Nohda, 1995; Nohda, 1999). The average TIMS values listed in Table 3 were re-calculated using the same correction factors used for our MC-ICP-MS data, because the TIMS values were collected against “old” SRM 981 mass discrimination factors. Considering the relatively poor precision of conventional TIMS, the agreement is better than that we expected. Overall, the results for five GSJ basalts and andesites determined in this study contribute to examination of analytical precision and accuracy for natural rock samples.

4. Mass fractionation during column separation

Mass fractionation during column separation of lead isotopes has also been reported (Thirlwall, 2001; Baker *et al.*, 2004). Insufficient recovery can occur during column separation and single bead separation procedures, as reported previously (Kimura *et al.*, 2003). The effect of imperfect recovery has been investigated here. Results are shown in the lower part of Table 4. We have analyzed Pb isotopes either by single column separation or by column-single bead two-step separation methods. Measurable differences are apparent between the two methods (Table 4), with the isotopic ratios always lower in the two-step purification method. Single bead Pb purification can yield recoveries of about 60%, due to the large Pb memory of larger single resin beads (Kimura *et al.*, 2003). Although this technique is particularly useful for separation of lead from complex matrices such as organic materials (Manton, 1988), heavier mass isotopes tend to remain in the resin bead during the reverse-extraction in DIW. The lower $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ isotopic ratios observed are the expected result of mass fractionation (Baker *et al.*, 2004).

In contrast, no measurable isotopic fractionations were observed for single column separation method, as discussed above. Purification of lead is critical for TIMS analysis, but the relative robustness of MC-ICP-MS with respect to concomitant elements allow the use of the simplest single column separation procedure. Although a relatively large

volume of eluent (Baker *et al.*, 2004) (in our case 1 ml 6 NM HCl) is necessary for complete separation from the column, the applicability of single column separation contributes greatly to higher throughput of Pb isotopes by MC-ISP-MS.

Conclusions

We analyzed precise Pb isotope ratios for NIST SRM 981 and basalt and andesite igneous rock standards from the Geological Survey of Japan, using MC-ISP-MS. Refined analytical techniques using single column lead separation and mass spectrometry using Tl mass bias correction, Hg interference correction, and standard bracket methods have considerably improved analytical precision and reproducibility. The Pb isotope ratios determined for basalt standards JB-2 and JB-3 fit very well with DS-TIMS and DS-ICP-MS methods in the range of $< \sim 170$ ppm. This demonstrates that our method is versatile and has comparable reproducibility with the double spike method. We also confirmed fractionation of Pb isotope ratios during separation of Pb from samples. Single bead separation can cause measurable fractionation, but is still only at a level of ~ 200 ppm. Conventional single column separation is acceptable if Pb is collected at sufficient amount. The overall throughput of our method is 10 to 15 samples within four days, including all digestion, separation, and analysis, considerably faster than conventional TIMS methodology.

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References

- Abouchami, W., Galer, S. J. G. and Hofmann, A. W., 2000, High precision lead isotope systematics of lavas from the Hawaiian Scientific Drilling Project. *Chemical Geology*, **169**, 187-209.
- Baker, J., Peate, D., Waight, T. and Meyzen, C., 2004, Pb isotope analysis of standards and samples using ^{207}Pb - ^{204}Pb double spike and thallium to correct for mass bias with a double-focusing MC-ICP-MS. *Chemical Geology* **211**, 275-303.
- Dickin, A. P., 1995, *Radiogenic Isotope Geology*. Cambridge University Press, New York, pp. 452.

- Dodson, M. H., 1963, A theoretical study of the use of internal standards for precise isotopic analysis by the surface ionization technique: Part I- General first-order algebraic solutions. *Journal of Scientific Instrumentation*, **40**, 1.
- Gale, N. H., 1970, A solution in closed form for lead isotopic analysis using double spike. *Chemical Geology*, **6**, 305-310.
- Galer, S. J. G., 1999, Optimal double and triple spiking for high precision Pb isotopic measurement. *Chemical Geology*, **157**, 255-274.
- Galer, S. J. G. and Abouchami, W., 1998, Practical application of lead triple spiking for correction of instrumental mass discrimination. *Mineralogical Magazine*, **62 A**, 491-492.
- Hirata, T., 1996, Lead isotope analysis of NIST standard reference materials using multiple-collector-inductively coupled plasma mass spectrometry coupled with modified external correction method for mass discrimination effect. *Analyst*, **121**, 1407-1411.
- Hofman, A. W., 1971, Fractionation corrections for mixed isotope spikes of Sr, K and Pb. *Earth and Planetary Science Letters*, **10**, 397-402.
- Ishizuka, O., Taylor, R. N., Milton, J. A. and Nesbitt, R. W., 2003, Fluid-mantle interaction in an intra-oceanic arc: constraints from high-precision Pb isotopes. *Earth and Planetary Science Letters*, **211**, 221-236.
- Kimura, J.-I., Kawahara, M. and Iizumi, S., 2003, Lead isotope analysis using TIMS following single column-single bead Pb separation. *Geoscience Report of Shimane University*, **22**, 49-53.
- Kuritani, T. and Nakamura, E., 2003, Highly precise and accurate isotopic analysis of small amounts of Pb using ^{205}Pb ^{204}Pb and ^{207}Pb - ^{204}Pb , two double spikes. *Journal of Analytical Atomic Spectrometry*, **18**, 1464-1470.
- Manton, W. I., 1988, Separation of Pb from young zircons by single-bead ion exchange. *Chemical Geology*, **73**, 147-152.
- Nohda, S., 1999, Precise isotopic measurements of lead by fused silica-gel. *Geochemical Journal*, **33**, 133-139.
- Shimoda, G. and Nohda, S., 1995, Lead isotope analyses: An application to GSJ standard rock samples. *Human and Environmental Studies*, **4**, 29-36.
- Thirlwall, M. F., 2000, Inter-laboratory and other errors in Pb isotope analyses investigated using a ^{207}Pb - ^{204}Pb double spike. *Chemical Geology*, **163**, 299-322.
- Thirlwall, M. F., 2001, Inappropriate tail corrections can cause large inaccuracy in isotope ratio analysis by MC-ICPMS. *Journal of Analytical Atomic Spectrometry*, **16**, 1121-1125.
- Thirlwall, M. F., 2002, Multicollector ICP-MS analysis of Pb isotopes using ^{207}Pb - ^{204}Pb double spike demonstrates up to 400 ppm/amu systematic errors in Tl-normalization. *Chemical Geology*, **184**, 255-279.
- Todt, W., Cliff, R. A., Hanser, A. and Hofmann, A. W., 1996, Evaluation of a ^{202}Pb - ^{205}Pb double spike for high-precision lead isotope analysis. *Geophysical Monograph*, **95**, 429-437.
- Walder, A. J., Abell, I. D., Platzner, I. and Freedman, P. A., 1993, Lead isotope ratio measurement of NIST 610 glass by laser ablation inductively coupled plasma mass spectrometry. *Spectrochimica Acta*, **48 B**, 397-402.
- Woodhead, J. D., 2002, A simple method for obtaining highly accurate Pb isotope data by MC-ICP-MS. *Journal of Analytical Atomic Spectrometry*, **17**, 1381-1385.
- Woodhead, J. D. and Hergt, J. M. (1997). Application of the "double spike" technique to Pb-isotope geochronology. *Chemical Geology*, **138**, 311-321.
- Woodhead, J. D. and Hergt, J. M., 2000, Pb-isotope analyses of USGS reference materials. *Geostandards Newsletter*, **24**, 33-38.

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(要 旨)

木村純一・中野菜都子, 2004, マルチコレクター誘導結合プラズマ質量分析 (MC-ICP-MS) を用いた精密鉛同位体比測定: 分析手法および鉛分離時に起こる質量分別, 島根大学地球資源環境学研報告, **23**, 9-15

NIST 981 ならびに地質調査所標準岩石の玄武岩および安山岩の MC-ICP-MS 高精度鉛同位体分析を行った。シングルコラムによる鉛抽出, タリウムによる質量分別補正, 水銀の重なり補正, および SRM 981 を用いたスタンダードブラケット法を用いることにより, JB-2 および JB-3 の鉛同位体比はこれまで測定されたダブルスパイク-TIMS 法やダブルスパイク-MC-ICP-MS 法の結果と 170 ppm の誤差範囲内で極めてよく一致した。ダブルスパイクを用いない我々の方法は, それらと比較しうる精度と再現性をもち, 分解から分析まで 4 日間で 10-15 試料の高精度迅速分析が可能になった。