New preconcentration technique of Zr, Nb, Mo, Hf, Ta and W employing coprecipitation with Ti compounds: Its application to Lu–Hf system and sequential Pb–Sr–Nd–Sm separation

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A new preconcentration technique of Zr, Nb, Mo, Hf, Ta and W has been invented employing coprecipiation with Ti compounds. Silicate samples were digested by HF with addition of Ti. Subsequent drying with $HClO_4$ resulting in complete elimination of fluorine produces Ti compounds (oxide/hydroxides). The sample was then dissolved with dilute nitric acid and centrifuged, and the residual Ti compounds were collected. The Ti compounds forming from 2 mg of Ti without matrix elements concentrate 84–98% of Zr, Nb, Mo, Hf, Ta and W. In 20 mg basaltic and 50 mg peridotitic matrices, the addition of 1 mg of Ti was appropriate and gave yields of 46–69 and 54–79%, respectively, for Zr, Nb, Mo, Hf, Ta and W. Exploiting this preconcentration, sequential separation protocols of Hf, Pb, Sr, Lu, Nd and Sm for isotope analysis are developed with total blanks of 16, 11, 60, 2.4, 3 and 0.4 pg, respectively. The method is suitable for Lu–Hf system studies with capability of simultaneous separation of Pb, Sr, Nd and Sm from the same sample digest as well as isotopic anomaly studies of Zr, Mo and W. As application examples, accurate Lu–Hf data and Pb isotope ratios were obtained for basalt (JB-3) and peridotite (JP-1) by MC-ICP-MS.

Keywords: coprecipitation, Ti compounds, Lu–Hf, Pb–Sr–Nd isotope analysis, preconcentration

INTRODUCTION

The Lu–Hf isotope system, where the β-decay of ^{176}Lu to ^{176}Hf is utilized, is widely applied to earth sciences as a geochronological and geochemical tracer. In the Lu–Hf system, the accurate determination of Lu and Hf concentrations as well as ^{176}Hf/^{177}Hf ratio is required. In order to obtain accurate Lu and Hf concentrations, isotope dilution (ID), in which enriched stable isotopes such as ^{176}Lu and ^{180}Hf are added to a sample, is generally employed (Patchett and Tatsumoto, 1980; Blichert-Toft et al., 1997; Blichert-Toft, 2001; Kleinhanns et al., 2002; Bizzarro et al., 2003; Lapen et al., 2004; Patchett et al., 2004). Furthermore, Lu and Hf must be separated from each other and from major elements or interfering elements. When the ^{176}Hf/^{177}Hf ratio is used as a geochemical tracer, it is greatly beneficial to purify Pb, Sr, Nd and Sm from the same sample digest, of which isotope ratios are also important tools in geo- and cosmochemistry and environmental sciences. However, such comprehensive chemical procedure has not been developed, and the Lu–Hf analysis is usually separately performed (e.g., Münker et al., 2001; Weyer et al., 2002).

In the sample digestion, alkaline fusion (Kleinhanns et al., 2002), lithium metaborate fusion (Bizzarro et al., 2003) and HF (Patchett and Tatsumoto, 1980; Blichert-Toft et al., 1997; Blichert-Toft, 2001; Lapen et al., 2004; Patchett et al., 2004) are used. The fusions have the disadvantage of higher blanks especially for Pb and Sr, although perfect isotopic equilibrium between sample and spike is expected, which is a prerequisite in ID. The HF digestion is clean, and rough separation of Hf from Lu can be performed simultaneously (Blichert-Toft et al., 1997), because Hf easily dissolves forming soluble HfF_6^{2-} (Makishima et al., 1999), while Lu coprecipitates in insoluble Ca–Mg–Al fluorides in HF (Yokoyama et al., 1999). However, there is a risk of imperfect isotopic homogenization between sample and spike, because Lu exists as insoluble LuF_3 or in fluorides and is never mixed as a soluble ion in HF solution. Repeated drying with HNO_3 is sometimes employed (Patchett et al., 2004; Lapen et al., 2004) however, the insoluble fluorides do not decompose and are only digested by drying with $HClO_4$ (Yokoyama et al., 1999). The drying with $HClO_4$ causes another problem in that the strong affinity of ClO_4^- ion on the anion exchange resin interferes with the anion exchange employed in Hf purification (Blichert-Toft et al., 1997; Lu et al., 2007a).

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To overcome these problems, we have invented a new Hf preconcentration technique employing $HClO_4$ drying which liberates Lu from the fluorides into solution to achieve the isotopic equilibrium of Lu. In the course of our experiments, we found that Ti compounds formed by elimination of fluorine concentrated Hf as well as Zr, Nb, Mo, Ta and W, leaving soluble major cations in silicate samples such as Na, Mg, Al, Ca or Fe in the solution. We examined the appropriate condition of forming Ti compounds in this study, and have developed a new preconcentration technique for Zr, Nb, Mo, Hf, Ta and W without using anion exchange chromatography. Yokoyama et al. (1999) first noticed the formation of the Ti compounds by this method, and found that Pb, Sr and rare earth elements (REEs) are not contained in the precipitates. This technique has relatively low blank, especially for Pb (11 pg) and Sr (60 pg) compared to fusion digestion. Therefore, the same sample digest for Lu–Hf analysis can be used for separation of Pb, Sr, Lu, Nd and Sm. Furthermore, the method is also applicable to preconcentration of Mo, which shows isotopic anomalies in some pre-solar materials (Yin et al., 2002) and W, which is used in the Hf–W cosmo/geo-chronometer (Halliday et al., 1996; Kleine et al., 2004). In this paper, details of the method are described, and sequential separation and analysis examples of silicate samples (basalt and peridotite) for the Lu–Hf system and Pb isotope ratios are shown.

EXPERIMENTAL

Reagents and silicate materials

Water, HF, HCl, HNO_3, NH_3(aq) and 2-hydroxy-2-methylpropanoic acid (HIBA) were purified as described elsewhere (Nakamura et al., 2003). Perchloric acid (TAMAPURE-AA-100, Tama Chemicals Co. Ltd., Japan) and ultrapure H_2O_2 (Kanto Chem. Co. Inc., Japan) were directly used. Amberchrom CG-71C (Rohm and Haas, Co., USA), AG 50W-X8 and AG 50W-X10 (mixture of X8 and X12) cation exchange resins (200–400 mesh, BioRad, USA), UTEVA and Sr resins (100–150 μm, Eichrom Technologies, Inc., USA) were used.

A 10000 μg ml^{-1} Ti plasma standard solution was purchased from Alfa Aesar (USA; Cat. No. 35759). After removal of trace F$^-$ following a method of Lu et al. (2007a), the solution was then passed through a 3-layered column with UTEVA (0.3 ml)-Sr resin (0.55 ml)-CG 71C (0.45 ml) to remove Hf, Pb and Sr in the Ti solution. The purified solution is ~5000 μg ml^{-1} Ti solution.

Spike solutions were prepared by dissolving enriched oxide isotopes, ^{176}Lu and ^{179}Hf, purchased from Oak Ridge National Laboratory (USA) with HNO_3 and HF, respectively. Concentrations of these individual spike solutions were calibrated using Lu and Hf standard solutions from Kanto Chem. Co. Inc. (Japan; Cat. No. 24253) and Alfa Aesar (USA; Cat. No. 14374), respectively. Details of the spike calibration for Hf are described in Lu et al. (2007a). The Lu standard solution was also used as the Lu isotope ratio standard with ^{176}Lu/^{175}Lu = 0.02652 (Patchett, 1983) for mass discrimination correction in MC-ICP-MS. The spike isotope ratio of Lu was determined to be 2.434 by MC-ICP-MS, which is consistent with 2.43 obtained by TIMS (Makishima et al., 1991). In recovery yield tests, a mixed plasma standard solution containing 100 μg ml^{-1} of Al, B, Cr, Si, V, Ti, Zr, Nb, Mo, Hf, Ta and W purchased from Alfa Aesar (USA; Cat. No. 44270) was used.

The silicate reference materials, JB-3 (basalt) and JP-1 (peridotite) issued by Geological Survey of Japan were further pulverized (Makishima and Nakamura, 1997) and used to evaluate accuracy and reproducibility of Lu and Hf concentrations and Hf and Pb isotope ratios analyses.

Sample digestion and Ti compounds formation

About 20 mg powder of JB-3 was weighed in a 7 ml Savillex beaker and known amounts of the Lu and Hf spike solutions were added. Then 0.2 ml of the Ti solution, which contains 1 mg of Ti, was added. The sample was decomposed with 1 ml of conc. HF and 0.5 ml of $HClO_4$ in an ultrasonic bath for one day. Then the sample was stepwise dried from 120 to 195°C following the standard drying procedure to remove F$^-$ in the sample (Yokoyama et al., 1999). The drying procedure was repeated twice with a further addition of 0.5 ml of $HClO_4$. Heating over 150°C is important to decompose stable FeF_3 into iron oxide/hydroxide, which retains F$^-$ in the sample.

About 50 mg of JP-1 was weighed into a Teflon bomb, and the Lu and Hf spikes and 0.2 ml of the Ti solution were added. Then 1 ml of HF was added and the bomb was sealed and heated at 245°C for 15 hrs. No undissolved spinels were observed after heating. After cooling, the sample was transferred into a 7 ml Savillex beaker with addition of 0.5 ml $HClO_4$, and dried in the similar manner to JB-3.

After digestion and drying, 0.3 ml of 6 mol l^{-1} HCl was added and dried at 120°C. Then the solution was finally dissolved with 2.2 ml of 0.5 mol l^{-1} HNO_3 in an ultrasonic bath. The solution was centrifuged, and the supernatant (2 ml) was transferred into another beaker with leaving white precipitates. Then another 2 ml of 0.5 mol l^{-1} HNO_3 was added and the supernatant (2 ml) was also removed into the beaker. As a result, the Ti compounds containing Zr, Nb, Mo, Hf, Ta and W and 4 ml of the sample solution containing Pb, Sr, Lu, Nd and Sm were obtained.

Purification of Hf

The Ti precipitates were dissolved with 1 drop of HF and 0.15 ml of $HClO_4$, and heated at 115°C for 5 hrs on a hot plate to remove F^-. Then 1 drop of H_2O_2 and 1 ml of 9 mol l^{-1} HNO_3 were added. If the sample color is not orange (the color of $[Ti(O_2)OH_{aq}]^+$) but pale yellow and/or white precipitates are observed, the dissolution procedure should be repeated. Hafnium was then separated from Ti, Zr, Nb, Mo, Ta and W using the UTEVA column chemistry with Hf yield of 88% (Lu *et al.*, 2007a), while almost all Ti is removed (Makishima *et al.*, 2002; Lu *et al.*, 2007a). The total procedural blank for Hf was 16 pg (*n* = 3). When recovery of Zr, Nb, Mo, Ta and W is required, the loading solution and Zr fraction (Lu *et al.*, 2007a) should be collected.

Sequential purification of Pb, Sr, Lu, Sm and Nd

The supernatant solution was passed through a two-layered column (23 mm length × 5 mm in diameter) packed with 0.15 ml of Sr resin on 0.30 ml of CG-71C, and the loading solution was recovered. After washing the column with 1.4 ml of 3 mol l^{-1} HNO_3, Sr was collected with 2 ml of 0.05 mol l^{-1} HNO_3, and Pb was recovered by the subsequent addition of 4 ml of 6 mol l^{-1} HCl. The yields of Sr and Pb in this column chemistry were 63 and 99%, respectively (Makishima *et al.*, 2007). Total procedural blanks were 11 and 60 pg (*n* = 3) for Pb and Sr. When there is no need to recover Pb and/or Sr from the sample solution, this column separation procedure is skipped.

Into the recovered loading solution, 2.1 ml of 6 mol l^{-1} HCl was added to make the sample solution into 6.1 ml of 2.1 mol l^{-1} HCl- 0.3 mol l^{-1} HNO_3. All the solution was then passed through a cation exchange column (23 mm length × 5 mm in diameter) packed with 0.45 ml of AG 50W-X10. After washing the major elements with 1.6 ml of 2.1 mol l^{-1} HCl- 0.3 mol l^{-1} HNO_3, REEs were collected with 4.8 ml of 6 mol l^{-1} HCl. The yields of Lu and Nd (and Sm) in this cation exchange column were 45% and 90%, respectively. The REE fraction was dried, and re-dissolved with 0.1 ml of 0.06 mol l^{-1} HCl, and loaded on a column (29 mm × 3.5 mm in diameter) packed with 0.3 ml of AG50W-X8 in NH_4^+ form. After washing with 4 ml of 0.05 mol l^{-1} HIBA (pH = 4.6), Lu was recovered with 3.2 ml of 0.05 mol l^{-1} HIBA. Then 0.8, 0.9, 1.3 and 3.3 ml of 0.2 mol l^{-1} HIBA were sequentially added for wash, Sm fraction, wash and Nd fraction, respectively (Nakamura *et al.*, 2003). Elution curves for Lu and Yb using 0.05 mol l^{-1} HIBA are shown in Fig. 1. In the Lu fraction, 90% of Lu is recovered with 4% of Yb. Yb separation from Lu is important because ^{176}Yb (abundance is 12.7%) is isobaric to ^{176}Lu (abundance is 2.6%). We tested effects of Yb on ^{176}Lu/^{175}Lu, and found that Yb do not interfere the Lu isotope ratio up to Yb/Lu = 15 after the
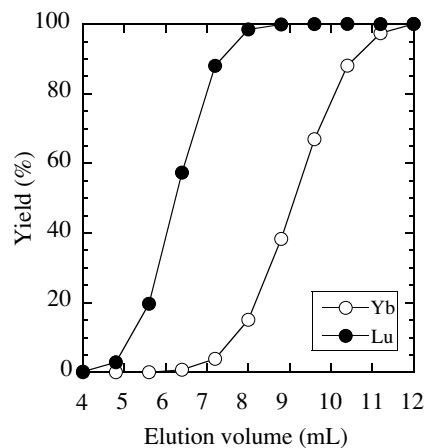

Fig. 1. Elution curves of Lu (solid circles) and Yb (open circles) in the HIBA column. The horizontal axis indicates the elution volume (ml) of 0.05 mol l^{-1} HIBA after sample loading. The vertical axis is the total yield (%) of each element from the elution of 4 ml. In the actual purification procedure of Lu, the fraction from 4 to 7.2 ml is collected.

interference correction described in Mass spectrometry for Lu determination section. Therefore, 4% of Yb in the Lu fraction can be negligible. Gruau *et al.* (1988) successfully separated Lu from Yb, using a 30 cm length column packed with 0.92 ml AG 50W-X12 resin and 0.1 mol l^{-1} HIBA (pH = 3.8) medium. However, they required total elution volume of ~19 ml to collect Lu, which is twice as much as of this study, requiring far longer separation time. The yields for Sm and Nd in the HIBA column were 86 and 88%. Thus, total recovery yields in the 3-step column chemistry of Lu and Nd (and Sm) were ~40% and ~80%. Total procedural blanks for Lu, Nd and Sm were 2.4, 3 and 0.4 pg (*n* = 3), respectively.

Mass spectrometry for simultaneous Hf isotope and concentration analysis

A MC-ICP-MS, Neptune, (Thermo Electron Corp., Germany) housed in PML, was used for simultaneous determination of Hf concentration and ^{176}Hf/^{177}Hf. The Hf fraction was dried and dissolved with 1 ml of 0.5 mol l^{-1} HF, which was also employed as washing and carrier solutions. The mass discrimination correction calculation for the spiked sample (Lu *et al.*, 2007a) was used with a normalizing value of ^{179}Hf/^{177}Hf = 0.7325. Isobaric interferences of ^{176}Yb and ^{176}Lu on ^{176}Hf were monitored by ^{171}Yb, ^{173}Yb and ^{175}Lu. In JB-3 and JP-1 analyses, ^{176}Yb/^{176}Hf and ^{176}Lu/^{176}Hf were <6 × 10^{-5}. When ^{176}Lu/^{176}Hf is >4 × 10^{-4}, data should be discarded, because the uncertainty of the Lu isotope ratio in the Hf fraction could be significant. After the mass discrimination correction, all data were normalized to ^{176}Hf/^{177}Hf = 0.282192 for

Table 1. Yields (%) of Ti, Zr, Nb, Mo, Hf, Ta and W by coprecipitation with Ti compounds

Ti amounts	No matrix	Basaltic matrix			Peridotitic matrix		
	2 mg	0.5 mg	1 mg	2 mg	0.5 mg	1 mg	2 mg
Ti	96	3	38	75	16	40	97
Zr	90	8	62	48	43	74	53
Nb	92	5	56	60	34	54	99
Mo	97	8	61	75	59	79	99
Hf	84	6	46	37	44	71	50
Ta	86	5	50	57	32	55	101
W	98	7	69	78	43	71	100

JMC 14374, which corresponds to $^{176}Hf/^{177}Hf = 0.282160$ for JMC 475. Details of the Hf mass spectrometry are described in Lu et al. (2007a).

Mass spectrometry for Lu determination

Lu concentration was calculated by ID using $^{176}Lu/^{175}Lu$. In the analysis of Lu, the same cup configuration, ICP and desolvator operating conditions for the Hf analyses (Lu et al., 2007a) were employed. The Lu fraction was dried and re-dissolved with 1 ml of 0.5 mol l^{-1} HNO$_3$, which was also used as washing and carrier solutions. The sample measurement was bracketed with 5 ng ml^{-1} standard solution measurements. Total washing and uptake times for one measurement were 960 and 90 s, and on-top background and sample data were integrated in 40 and 20 scans, respectively, with 4 s data acquisition per one scan. Isobaric interference of ^{176}Yb on ^{176}Hf was corrected in a similar manner to Hf, monitoring ^{171}Yb and ^{173}Yb and applying the exponential law. When ^{173}Yb intensity was $<5 \times 10^{-15}$ A, Yb ratios were directly used without mass discrimination correction. Isobaric interference of ^{176}Hf on ^{176}Lu was calculated by monitoring ^{177}Hf, ^{178}Hf and ^{179}Hf and following the same mass discrimination correction procedure for the Hf isotope ratio measurement (Lu et al., 2007a). The $^{176}Hf/^{177}Hf$ ratio of each sample obtained by the Hf isotope analysis was used for the Hf correction. When ^{177}Hf was $<5 \times 10^{-15}$ A, no iteration calculation (Lu et al., 2007a) for the mass discrimination correction was performed, because errors in measurement of small interference Hf peaks are large, and magnified in the mass discrimination calculation. Typical relative percent difference (RPD) of $^{176}Lu/^{175}Lu$ for the Lu 5 ng ml^{-1} standard solution was 0.006%. In the analysis of JB-3, blank contribution was negligible, however, blank correction of ~1% was performed in the JP-1 analysis.

Mass spectrometry for Pb

The Pb fraction for JB-3 and JP-1 was dissolved with 5 and 1 ml of 0.5 mol l^{-1} HNO$_3$, respectively. An aliquot of 0.25 ml for JB-3 and JP-1 was taken and an appropriate amount of the $^{204}Pb–^{207}Pb$ spike was added. Pb isotope ratios of the solutions with and without spike were measured by MC-ICP-MS without Tl addition, and the Pb isotope ratios were calculated. Details of this simple double spike technique are described in Makishima et al. (2007), however, the $^{204}Pb–^{207}Pb$ spike was newly prepared with isotope ratios of $^{207}Pb/^{206}Pb = 34.95321$, $^{204}Pb/^{206}Pb = 38.60695$ and $^{208}Pb/^{206}Pb = 1.788433$ (K. Yamashita, unpublished data).

RESULTS AND DISCUSSION

Yields of Zr, Nb, Mo, Hf, Ta and W in the Ti coprecipitation procedure

Recovery yields of Ti, Zr, Nb, Mo, Hf, Ta and W in the Ti coprecipitation procedure were examined for three matrix compositions: (i) no matrix; (ii) basaltic composition; and (iii) peridotitic composition. In the case of no matrix material, the Ti solution containing 2 mg of Ti and the mixed standard solution containing 10 μg of each element were mixed and processed through the sample digestion protocols. Then the Ti compounds were separated and dissolved in HF, and recovery yields for Ti, Zr, Nb, Mo, Hf, Ta and W were measured by a sector field ICP-MS, ELEMENT (Finnigan, Germany) housed in PML using middle-range resolution, following the analytical condition (Lu et al., 2007b). Analytical errors are estimated to be <8%. The yields for Ti, Zr, Nb, Mo, Hf, Ta and W are shown in Table 1, and were 84–98%. This result means that the coprecipiation is a very effective means of separating these elements as precipitates.

The yield test for the basaltic composition was performed using 20 mg of JB-3 with the addition of 0.5, 1 and 2 mg of Ti to estimate the appropriate amount of Ti. In the 0.5 mg run, the yields for Zr, Nb, Mo, Hf, Ta and W were 5–8%. It is clear that Ti of 0.5 mg is not sufficient to form large enough sizes or amounts of Ti-compound particles to be separated by centrifuging. In this case, white precipitates were not observed by eye.

Table 2. Lu–Hf analytical results for JB-3 and JP-1

	Sample weight (g)	$^{176}Hf/^{177}Hf$	$2\sigma_m$	Hf concentration ($\mu g\ g^{-1}$)	Lu concentration ($\mu g\ g^{-1}$)	Lu/Hf
JB-3						
#1	0.02543	0.283231	0.000004	2.663	0.3724	0.1398
#2	0.01931	0.283214	0.000009	2.683	0.3743	0.1395
#3	0.01791	0.283222	0.000007	2.668	0.3718	0.1394
#4	0.01886	0.283224	0.000006	2.680	0.3730	0.1392
Average		0.283223		2.674	0.3729	0.1395
Reproducibility (2σ)		0.000014		0.019	0.0021	0.0005
JP-1						
#1	0.05534	0.282303	0.000022	0.116	0.00386	0.0333
#2	0.05686	0.282324	0.000011	0.117	0.00401	0.0341
#3	0.05491	0.282300	0.000015	0.115	0.00393	0.0343
Average		0.282309		0.116	0.00393	0.0339
Reproducibility (2σ)		0.000026		0.003	0.00015	0.0011

However, in the 1 and 2 mg runs, the yields increased to 46–69% (mean = 57) and 37–78% (mean = 59), respectively. Except for Ti, there seems to be no significant difference between 1 and 2 mg runs, therefore, 1 mg was chosen in order to minimize the blank effect from the Ti solution added. The yield of Hf was 37–46% (mean = 42) in both cases. As Hf concentration in the basalt is generally high compared to the peridotite, the deterioration of the yield does not cause significant problems in the Hf isotope analysis.

The yield measurement in the peridotitic matrix was performed by 50 mg of JP-1 with addition of 0.5, 1 and 2 mg of Ti. The yields for Zr, Nb, Mo, Hf, Ta and W were 34–59% (mean = 42), 54–79% (mean = 67) and 50–101% (mean = 84), respectively. As the Ti amount increases, the yields of Ti, Nb, Mo, Ta and W increase, but the yields of Hf and Zr are almost constant in 50–71% (mean = 61) and 53–74% (mean = 63), respectively. Therefore, as in the basaltic matrix, the 1 mg addition of Ti was also chosen for the peridotitic matrix. The total Hf yield in the peridotitic composition is ~60%, slightly higher than that in basalt. Compared to the basaltic matrix, the Ti compounds seem to form more easily, and larger amounts of Zr, Nb, Mo, Hf, Ta and W can be collected in the peridotitic matrix. This is advantageous because Hf concentration in peridotite is generally low (<0.2 $\mu g\ g^{-1}$).

The yields for Hf and Zr are slightly lower than other elements in all three cases. This may be caused by the higher stability of fluoro- and chloro-complexes of Hf and Zr than Ti, Nb and Ta. Mo and W show higher yields, possibly by their tendency of forming oxo-complexes resulting in easier coprecipitation with Ti oxide/hydroxide.

Analytical results for the Lu–Hf system

Ratios of $^{176}Hf/^{177}Hf$, Hf and Lu concentrations and Lu/Hf ratios for JB-3 and JP-1, together with the sample amount, are shown in Table 2. Average $^{176}Hf/^{177}Hf$ values for JB-3 and JP-1 were 0.283223 ± 0.000014 (error is 2σ reproducibility; $n = 4$) and 0.282309 ± 0.000026 ($n = 3$), respectively. Average Hf concentrations for JB-3 and JP-1 were 2.674 and 0.116 $\mu g\ g^{-1}$ with 2σ reproducibility of 0.71 and 2.4%, respectively. Lu *et al.* (2007a) obtained $^{176}Hf/^{177}Hf$ ratios 0.283220 ± 0.000006 and 0.282297 ± 0.000024, and Hf concentrations of 2.68 ± 0.02 $\mu g\ g^{-1}$ (2σ, $n = 10$) and 0.124 ± 0.10 $\mu g\ g^{-1}$ (2σ, $n = 5$) for JB-3 and JP-1, respectively, employing a Hf spike but without a Lu spike, using the same MC-ICP-MS technique. Our analytical results are consistent with those of the previous study, thus it is concluded that there are no effects of the Lu spike on the Hf measurement and the Hf isotope ratio obtained is accurate. Although the Hf concentration is 0.124 $\mu g\ g^{-1}$ and only ~50 mg of the powder is used for JP-1 analysis (total Hf is ~6 ng), no blank correction is required, because the Hf blank is 16 pg. Lu *et al.* (2007a) obtained a total Hf blank of 4 pg after 2-step column chemistry using anion exchange and UTEVA columns. The higher blank of this study may come from the Ti solution.

The average Lu concentrations of JB-3 and JP-1 were 0.3729 and 0.00393 $\mu g\ g^{-1}$ with 2σ reproducibilities of 0.56% ($n = 4$) and 3.7% ($n = 3$). The $^{176}Yb/^{176}Lu$ ratio in the analysis of JB-3 and JP-1 was 0.17–0.55 and 0.13–0.20, and $^{176}Hf/^{176}Lu$ was 0.02–0.16 and 0.03–0.04, respectively. Although these contributions of Yb and Hf on Lu are not negligible in the Lu measurement and are variable from sample to sample, the Lu concentration is independent of the correction, indicating the validity of the correction and the accuracy of the results.

Makishima and Nakamura (1997, 2006) obtained Lu concentrations of 0.382 and 0.377 $\mu g\ g^{-1}$ for JB-3 with

Table 3. Pb isotope ratios for JB-3 and JP-1.

	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb
JB-3 (Pb: 4.85 μg g^{-1}; Makishima and Nakamura, 2006)			
#1	18.298	15.540	38.257
#2	18.296	15.538	38.250
#3	18.298	15.539	38.256
#4	18.297	15.540	38.256
Average	18.297	15.539	38.255
Reproducibility (2σ)	0.001	0.002	0.007
Makishima *et al.* (2007)	18.296	15.538	38.249
JP-1 (Pb: 0.0765 μg g^{-1}; Makishima and Nakamura, 2006)			
#1	18.34	15.54	38.29
#2	18.37	15.57	38.37
#3	18.36	15.56	38.34
Average	18.36	15.56	38.33
Reproducibility (2σ)	0.03	0.03	0.08
NBS 981			
Average (*n* = 9)	16.943	15.501	36.728
Reproducibility (2σ)	0.001	0.002	0.005
Makishima *et al.* (2007)	16.942	15.499	36.720

2σ reproducibility of 5.8% and 2.9%, and 0.0047 and 0.0042 μg g^{-1} for JP-1 with 2σ reproducibilities of 23% and 19%, using flow injection (FI)-ICP-MS with a calibration curve method and pseudo-FI-ID (isotope dilution)-IS (internal standardization) ICP-MS, respectively. The ID results for Lu of this study are consistent with those of previous studies, but the reproducibility of this study using ID-MC-ICP-MS is 5 times better. As the total Lu blank was 2.4 pg, the blank correction for JP-1 was ~1%, however, the correction is far smaller than the reproducibility of 3.8%.

The averages of Lu/Hf were 0.1395 and 0.0339 with 2σ reproducibility of 0.37 and 3.1%, respectively. The reproducibility of the former is small enough to be used in Lu–Hf age dating or age correction. The reproducibility of the latter is larger than that of the former, probably due to sample heterogeneity and low concentrations of Lu and Hf.

Analytical results for Pb isotope ratios

Pb isotope ratios for JB-3, JP-1 and NBS 981 of this study as well as those of Makishima *et al.* (2007) (no data for JP-1) are shown in Table 3. Pb concentrations (Makishima and Nakamura, 2006) in JB-3 and JP-1 are also shown in the table. Averages of ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb for NBS 981 were 16.943, 15.501 and 36.728 with 2σ reproducibility of 0.009, 0.010 and 0.012% (*n* = 9), which are identical to those of Makishima *et al.* (2007), indicating that there is no difference in ac-

curacy using the new batch of the double spike. Averages of ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb for JB-3 were 18.297, 15.539 and 38.255 with 2σ reproducibility of 0.006, 0.012 and 0.018% (*n* = 4), respectively. The averages are also identical to those by Makishima *et al.* (2007), indicating that there are no effects on accuracy from the Ti coprecipitation procedure.

Averages of ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb for JP-1 were 18.36, 15.56 and 38.33 with 2σ reproducibility of 0.19, 0.17 and 0.12% (*n* = 4), respectively. Under ideal conditions, a 4 ng ml^{-1} Pb solution, as used in the JP-1 analysis, should give 2σ reproducibility of 0.06–0.09% (see table 1 of Makishima *et al.*, 2007). These lower reproducibilities may be caused by sample heterogeneity. The blank effects for JB-3 and JP-1 on the isotope ratios should be <0.001 and <0.03%, considering Pb amounts used in analysis of ~90 and ~4 ng, total blank of 11 pg and assuming isotope ratio differences of <10% between sample and blank.

Application to other isotope studies

The preconcentration technique developed in this study with subsequent separation of Sr, Nd and Sm has total blanks of 60, 3 and 0.4 pg with total yields of ~60, ~80 and ~80%, respectively. Therefore, this method is also applicable to conventional Sr isotope and Sm–Nd system measurements using TIMS (Nakamura *et al.*, 2003). Furthermore, the preconcentration technique can be applied to isotope anomaly studies of Zr and Mo or

Hf–W cosmo/geo-chronology (Halliday *et al.*, 1996; Sahoo and Masuda, 1997; Yin *et al.*, 2002; Kleine *et al.*, 2004; Quitte *et al.*, 2005). The method is also applicable to simultaneous separation of Rb and U by collection of the loading and washing solutions in the cation exchange column for REE separation, and of Th by further addition of 6 mol l⁻¹ HCl after REE collection.

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