

Hf and Lu isotopic reference values for the zircon standard 91500 by MC-ICP-MS

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Abstract

The Hf and Lu isotopic ratios of the zircon standard 91500 have been redefined by multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS). The chemical protocol consists of a high-pressure and high-temperature acid dissolution of zircon followed by optimized two-step ion-exchange chromatography with an overall recovery better than 94%. Instrumental calibration involved an extensive characterization of standard solutions for Hf [JMC-475 250 ppb: $^{176}\text{Hf}/^{177}\text{Hf}=0.282161\pm 16$ (2 S.D.)] and Lu [JMC standard 50 ppb: $^{175}\text{Lu}/^{176}\text{Lu}=37.72\pm 2$ (2 S.D.)]. A total of 59 Hf isotopic measurements on the zircon standard 91500, including four independent dissolutions and purifications, were carried out on two Nu Plasma MC-ICP-MS instruments. The average $^{176}\text{Hf}/^{177}\text{Hf}$ is 0.282302 ± 8 (2 S.D.) and the two MC-ICP-MS instruments give overlapping results within error. These high precision data [external error: 27 ppm (2 S.D.) for 59 measurements and 10 ppm for a single day; internal error: 10 ppm (2 S.D.)] are reproducible between duplicates and underscore the stability of the analytical protocol. The Lu isotopic composition of the zircon standard 91500 has also been redefined: $^{175}\text{Lu}/^{176}\text{Lu}=37.74\pm 8$ (2 S.D.). With the growing use of in situ measurement techniques using MC-ICP-MS technology, such precise reference values will be important for the calibration of laser ablation analyses in the future.

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1. Introduction

Since the early 1980s (e.g. Patchett and Tatsumoto, 1980; Patchett et al., 1981; Vervoort et al., 1996), Hf isotopes in geologic materials have been used as a powerful petrogenetic tracer. The advent of multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS) in the early 1990s resulted in a significantly increased number of studies using Hf

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isotopes (e.g. Blichert-Toft et al., 1997; Salters and White, 1997; Vervoort and Blichert-Toft, 1999; Chauvel and Blichert-Toft, 2001). By the late 1990s, the range of accessible sample types was expanded due to significant improvements in chemical procedures (Lee et al., 1999; Amelin et al., 2000; Scherer et al., 2001; Münker et al., 2001). Zircon (ZrSiO_4) is the major reservoir of Hf in most crustal rocks and is characterized by low Lu/Hf. Recent studies (e.g. Amelin et al., 1999, 2000; Bodet and Schärer, 2000; Griffin et al., 2000; Wilde et al., 2001), in addition to using zircon in U–Pb geochronology, demonstrate that the Hf isotopic composition of zircon can be used to better understand various crustal processes and to constrain continental crust growth. In situ analysis of Hf isotopes in zircon by laser ablation MC-ICP-MS (LA-MC-ICP-MS) is increasingly used in the geological community due to the precise spatial control required for zircons with complex internal morphology (Griffin et al., 2000, 2002; Machado and Simonetti, 2001). This in situ analysis technique, however, is associated with important isobaric interferences by ^{176}Lu and ^{176}Yb on ^{176}Hf , significant elemental fractionation, higher matrix effects, and larger memory effects relative to analysis after dissolution and chemical Hf separation and results in lower precision. High-precision analysis of standard zircons by a complete dissolution technique can be used to define specific MC-ICP-MS reference values. In this paper, we recommend new values of $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{175}\text{Lu}/^{176}\text{Lu}$ for the zircon standard 91500, as measured on two different MC-ICP-MS instruments, after complete dissolution and chemical separation of four different fractions of the zircon standard 91500.

2. Sample preparation and chemistry

2.1. Sample dissolution

The zircon standard 91500, distributed by the CRPG (Nancy, France) is a split from an original homogenous crystal of 238 g (as reported in Wiedenbeck et al., 1995). Although considered isotopically homogeneous with respect to the systems U–Th–Pb and Lu–Hf, slight chemical heterogeneity has been observed in different analyzed fractions of zircon 91500: U=71–86 ppm, Pb=13–16 ppm, Th=28.1–29.2 ppm, Lu=11–13 ppm, and Hf=5610–6360 ppm

(Wiedenbeck et al., 1995; Belousova et al., 2002), and U=73.11–82.51 ppm and Pb=13.87–14.99 ppm (Neymark et al., 2000). The original splits were reduced to sub-millimetric sizes into an agate mortar. The crushed splits were soaked in a dilute nitric acid bath to digest any organic residue. Dissolution of the zircon standard 91500 consisted of two-step high pressure and high temperature (180 °C) dissolution in sealed Teflon® bombs. Acid digestion was carried out sequentially with both HF+HNO₃ (respectively 20 and 5 µl) and HCl (25 µl) following the procedure of Krogh (1973). All of the acids used during the chemical treatment were purified by sub-boiling of analytical grade reagents. During the four independent chemical treatments, we respectively treated 0.20, 0.28, 0.27 and 0.30 mg of zircon. Alternative dissolution techniques using sintering reagents such as Na₂O₂ (Kleinhanns et al., 2002) or Li₂B₄O₇ (Münker et al., 2001) have been designed for whole rocks and avoid the use of strong HF, which limits the risk of REE-fluoride precipitation. We did not consider these techniques, as during our study, REE-fluoride precipitation did not occur during sample preparation.

2.2. Chromatography

Several recent studies have recommended the use of specific resins (i.e. Eichrom®) for chromatographic purification of Hf, Nd and Lu from zircon (e.g. Yang and Pin, 2000; Münker et al., 2001). In this study, we used both Biorad® and HDEHP-coated Teflon resins. Both the lower cost and the higher recovery motivated this choice. All concentration analyses required for column calibrations were carried out by ICP-MS at the Royal Museum for Central Africa, Belgium.

2.2.1. HFSE–REE separation

BIORAD® polypropylene columns (0.8-cm diameter, 11-cm height) with cationic exchange AG50W-X8 (200–400 mesh) resin were used to separate the high field strength elements (HFSE) and the rare earth elements (REE). Ti behaves similarly to Zr and Hf during ion-exchange processes and was shown to be responsible for significant Hf isotopic variation during analyses on a P54 and an Isoprobe (Blichert-Toft et al., 1997; Münker et al., 2001). Owing to the Ti-poor matrix of zircon, Ti extraction either on an additional cationic resin, which is typically used for basalts

(Blichert-Toft et al., 1997), or by using H₂SO₄ (Barovich et al., 1995; Scherer et al., 2001) was not necessary in our study on a Nu Plasma MC-ICP-MS. We also performed tests on Hf–Ti mixed solutions and found that Ti/Hf ratios up to 30 do not significantly affect the ¹⁷⁶Hf/¹⁷⁷Hf of the JMC-475 at 250 ppb. In addition, in order to demonstrate that it is not necessary to separate Hf from Zr for analysis by MC-ICP-MS, we carried out a set of experiments on the Nu015 in Brussels. These indicate that Zr/Hf ratios up to 1:800 have no effect on Hf isotopic composition and only a moderate effect on the precision, in contrast to thermal ionization mass spectrometry (TIMS).

The elutions were processed with both 0.1 N HF/1 N HCl and 4N HCl (Table 1), following normal-phase chromatography (Patchett and Tatsumoto, 1980). The elution scheme allowed for complete separation between the heavy REE and the HFSE, as confirmed by monitoring both the ¹⁷²Yb and ¹⁷⁵Lu beams during Hf MC-ICP-MS analysis. To estimate the nature of both ¹⁷⁵Lu and ¹⁷²Yb signals, we compared the signal amplitude provided by a 100-ppt Yb solution with the observed signal during analysis of zircon solutions. The 100-ppt Yb solution provided a significantly higher signal than the ones monitored on our sample solutions, indicating that the latter were much

less concentrated than 100 ppt and that the ¹⁷⁶Yb interference was therefore likely to represent background noise. Random scattering of the ¹⁷²Yb and the ¹⁷⁵Lu signals was also confirmed by analyses after gain calibrations of all the collectors with a “sample-free” plasma, which allowed us to subtract the instrument contribution to the collectors. Similarly, the potential mass interference of ¹⁶⁰Gd¹⁶O on ¹⁷⁶Hf was considered unlikely. Despite the high REE content of zircon, our elution procedure removed all the REE from the HFSE elution fraction during the first purification step.

2.2.2. Lu/Yb-light REE separation

This separation was carried out using HDEHP-coated Teflon® resin (Teflon® powder supporting BIS-(2 ethylhexyl) orthophosphoric acid) following reverse-phase chromatography (Winchester, 1962; Patchett and Tatsumoto, 1980). The resin was stored in quartz columns (0.5-cm diameter and 17-cm height). In addition to the low cost and the higher Lu recovery, the extraction of Lu and Nd can be processed with HCl only (Table 1). Both alkalic basalt (LVLK-132 from the Kerguelen Archipelago; Weis et al., 1993) and zircon solutions were used for column calibration. Because we were able to correct the measurements for ¹⁷⁶Yb and ¹⁷⁶Lu isobaric interferences, an extensive Lu–Yb separation was not necessary and Yb could also be used for external mass bias correction for the Lu measurement. As suggested by Blichert-Toft et al. (1997), the potential production of GdO in the plasma source could be responsible for a theoretical isobaric interference on mass 176 (Lu and Yb). However, our reproducible elution curves indicate no Gd present in the Lu–Yb fraction; thus, we did not need to use a complex peak-stripping procedure (Albarède, 1995). A simple mass balance approach was used to estimate the recovery and yields an overall recovery of 94%.

2.3. Blanks levels

Because the Hf concentration in the zircon standard 91500 is relatively high (0.59±0.01 wt.%, Wiedenbeck et al., 1995; 0.64±0.09 wt.%, Belousova et al., 2002), blank level estimations by isotopic dilution were not necessarily required. Therefore, both MC-ICP-MS and high-resolution ICP-MS analyses were used for this purpose. The MC-ICP-MS at the Uni-

Table 1
Chromatographic purification procedures

Steps	Acid	Volume	Function
<i>(A) Hf purification procedure on AG50W-X8 200–400 mesh resin</i>			
1	0.1 N HF/1 N HCl	300 µl	Sample loading
2	0.1 N HF/1 N HCl	3×100 µl	Rinsing
3	0.1 N HF/1 N HCl	2 ml	Zr–Hf collect
4	0.1 N HF/1 N HCl	1 ml	Discard Zr matrix
5	4 N HCl	2.5 ml	Discard whole matrix
6	4 N HCl	12.5 ml	REE collect
7	6 N HCl–24 N HF–H ₂ O	12–12–12 ml	Cleaning
<i>(B) REE purification procedure on HDEHP-coated Teflon resin</i>			
1	0.16 N HCl	1 ml	Sample loading
2	0.16 N HCl	3×0.5 ml	Rinsing
3	2.5 N HCl	7 ml	LREE elution
4	2.5 N HCl	5 ml	LREE elution
5	2.5 N HCl	4.5 ml	HREE elution
6	2.5 N HCl	0.5 ml	Lu–Yb collect
7	6 N HCl	6.5 ml	Lu–Yb collect
8	6 N HCl	30 ml	Cleaning

versité Libre de Bruxelles was calibrated with solutions containing 50–100 ppt Hf and Lu. The signals provided by these solutions were then considered as references for ultra-low concentrations. Analyses from simple digestion solutions as well as total blank solutions yielded undetectable Hf and Lu signals indicating that Hf and Lu concentrations were significantly lower than 50 ppt for both the dissolution blank and the total blank. The negligible Hf and Lu dissolution blanks were confirmed by HR-ICP-MS analyses using a Faraday detection system. Hf and Lu blanks were respectively measured at 20 and 15 pg.

3. Results of analysis by MC-ICP-MS

Analyses were carried out on two Nu Plasma MC-ICP-MS (Nu Instruments): the Nu015 at the Université Libre de Bruxelles in Belgium and the Nu021 at the Pacific Centre for Isotopic and Geochemical Research at the University of British Columbia in Canada (the machine numbers refer to their serial numbers). Acquisition time for the isotopic analyses was 14 min, consisting of three blocks of 20 measurements with a 10-s integration time. An instrumental blank was measured before each analysis by deflecting the beam at 0.5 mass from the analysis configuration. Other specifications concerning the Lu and Hf isotopic analyses are listed in Table 2.

The Nu015 and Nu021 provide average $^{176}\text{Hf}/^{177}\text{Hf}$ ratios of the Hf standard JMC-475 that are in agreement with each other and those reported in the literature (see below). Three different types of solution introduction devices were used: a Meinhart spray chamber using a low free-uptake ($\sim 80 \mu\text{l}/\text{min}$) for Hf on the Nu015, a cyclonic spray chamber ($\sim 100 \mu\text{l}/\text{min}$) for Hf on the Nu021, and a Cetac Aridus desolvating device equipped with an Elemental Scien-

tific PFA spray chamber for Lu on the Nu015. Two different skimmer cone models (normal vs. wide angle) were tested to improve sensitivity.

3.1. Hf isotopic analyses

A 250-ppb JMC-475 isotopic standard solution was used to calibrate the instruments. The standard was made up in 0.05 N $\text{HNO}_3/0.05 \text{ N HF}$ to minimize memory effects. More than 100 JMC-475 measurements on the Nu015 from August to December 2001 give an average $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of 0.282161 ± 16 (2 S.D.) and 20 analyses on the Nu021 in January 2002 provide a value of 0.282161 ± 8 (2 S.D.). All of these results are in agreement with published MC-ICP-MS values (Blichert-Toft et al., 1997; Chauvel and Blichert-Toft, 2001). For all Hf isotopic measurements, ^{176}Hf was assigned to the axial collector. The Hf measurements are internally corrected for mass bias using the stable ratio of $^{179}\text{Hf}/^{177}\text{Hf}$. As suggested by Rehkämper et al. (2001), this correction is based on the exponential law (Russell et al., 1978). The analysis routine systematically includes Lu and Yb monitoring and our $^{176}\text{Hf}/^{177}\text{Hf}$ ratios are thus Lu- and Yb-corrected (always entirely negligible).

3.2. Lu isotopic analyses

Because only small sample sizes were concerned in this study (a single analysis requires at least 56 pg Lu), high sensitivity for Lu was required. Therefore, all of the Lu analyses were done using a Cetac Aridus desolvating nebulization system equipped with an Elemental Scientific PFA spray chamber. The Aridus was operated at a spray chamber temperature of 105 and 160 °C for the desolvating membrane. The solution used to calibrate the instrument was a mixed 50 ppb Lu–Yb standard solution (AAS, Alfa Aesar).

Table 2

Compared characteristics of the two MC-ICP-MS instruments (Nu015 and Nu021) based on analysis of the JMC-475 standard solution

	External precision based on 100 measurements	External precision on 1 day	Internal precision based on 100 measurements	Internal precision on 1 day	Sensitivity WA6 cone ^a (V/ppm)	Sensitivity normal cone (V/ppm)
Nu015	57 ppm (2 S.D.)	30 ppm (2 S.D.)	9 ppm (2 S.D.)	10 ppm (2 S.D.)	39	25
Nu021		28 ppm (2 S.D.)		9 ppm (2 S.D.)	36	

Nu015–Nu Plasma at the Université Libre de Bruxelles; Nu021–Nu Plasma at the University of British Columbia.

^a Wide angle cone.

Because Lu has only two naturally occurring isotopes, this admixed Yb solution is essential for constraining the instrumental mass fractionation using the $^{174}\text{Yb}/^{171}\text{Yb}$ ratio of 2.229 ± 0.016 (Rosman and Taylor, 1998). All of the published measurements to date fall within the range 37.47–37.71 (Patchett and Tatumoto, 1980; Patchett, 1983; De Bièvre et al., 1984; Blichert-Toft et al., 1997). Our instrumental value for the Lu–Yb standard solution was $^{175}\text{Lu}/^{176}\text{Lu} = 37.72 \pm 2$ (2 S.D.).

As Yb is naturally abundant in zircons and its chemical behavior is very similar to that of Lu, we chose to exploit this natural presence by using it for instrumental mass bias correction, and thus avoided the

laborious Lu–Yb separation. The ^{176}Yb contribution to the ^{176}Lu peak was deduced using the stable $^{176}\text{Yb}/^{173}\text{Yb}$ ratio.

4. The Hf isotopic composition of zircon standard 91500

The Hf and Lu isotopic compositions of the zircon standard 91500 were measured precisely by MC-ICP-MS. A total of 59 measurements were carried out, including 47 analyses on the Nu015 representing three different total dissolutions, and 12 analyses on the Nu021 representing a single dissolution (Table 3;

Table 3
Hf isotopic compositions of the zircon standard 91500 by MC-ICP-MS

Run #	Dissolution #	MC-ICP-MS	$^{176}\text{Hf}/^{177}\text{Hf}$	$^{180}\text{Hf}/^{177}\text{Hf}$	Run #	Dissolution #	MC-ICP-MS	$^{176}\text{Hf}/^{177}\text{Hf}$	$^{180}\text{Hf}/^{177}\text{Hf}$
1	1	ULB	0.282295±6	1.88651±3	31	3	ULB	0.282309±4	1.88653±2
2	1	ULB	0.282299±6	1.88652±3	32	3	ULB	0.282306±5	1.88652±3
3	2	ULB	0.282295±5	1.88654±3	33	3	ULB	0.282306±5	1.88651±3
4	2	ULB	0.282299±5	1.88654±3	34	3	ULB	0.282301±6	1.88656±3
5	2	ULB	0.282294±4	1.88655±2	35	3	ULB	0.282308±6	1.88656±3
6	2	ULB	0.282298±5	1.88654±3	36	3	ULB	0.282309±7	1.88652±3
7	2	ULB	0.282302±5	1.88653±3	37	3	ULB	0.282305±6	1.88654±3
8	2	ULB	0.282295±5	1.88655±3	38	3	ULB	0.282305±8	1.88654±2
9	2	ULB	0.282300±5	1.88652±3	39	3	ULB	0.282301±7	1.88654±2
10	2	ULB	0.282300±4	1.88654±2	40	3	ULB	0.282306±6	1.88654±3
11	2	ULB	0.282301±3	1.88651±3	41	3	ULB	0.282305±6	1.88653±2
12	2	ULB	0.282300±4	1.88650±3	42	3	ULB	0.282306±4	1.88655±3
13	2	ULB	0.282302±4	1.88653±3	43	3	ULB	0.282298±5	1.88652±3
14	2	ULB	0.282300±3	1.88655±2	44	3	ULB	0.282309±7	1.88656±3
15	2	ULB	0.282299±5	1.88652±3	45	3	ULB	0.282298±8	1.88654±2
16	2	ULB	0.282306±4	1.88651±3	46	3	ULB	0.282303±6	1.88654±2
17	2	ULB	0.282299±5	1.88651±2	47	3	ULB	0.282299±6	1.88653±2
18	2	ULB	0.282299±5	1.88652±3	48	4	UBC	0.282302±3	1.88655±2
19	2	ULB	0.282297±3	1.88653±3	49	4	UBC	0.282300±4	1.88654±2
20	2	ULB	0.282306±4	1.88654±2	50	4	UBC	0.282300±4	1.88651±2
21	2	ULB	0.282299±4	1.88654±2	51	4	UBC	0.282300±4	1.88653±2
22	3	ULB	0.282302±5	1.88653±3	52	4	UBC	0.282303±4	1.88656±2
23	3	ULB	0.282303±6	1.88650±3	53	4	UBC	0.282306±4	1.88654±2
24	3	ULB	0.282299±7	1.88649±3	54	4	UBC	0.282305±5	1.88655±2
25	3	ULB	0.282301±7	1.88655±3	55	4	UBC	0.282308±4	1.88653±2
26	3	ULB	0.282300±5	1.88654±3	56	4	UBC	0.282305±5	1.88655±2
27	3	ULB	0.282300±5	1.88654±3	57	4	UBC	0.282303±3	1.88654±2
28	3	ULB	0.282301±5	1.88651±3	58	4	UBC	0.282307±4	1.88655±2
29	3	ULB	0.282308±6	1.88653±3	59	4	UBC	0.282308±5	1.88654±2
30	3	ULB	0.282304±5	1.88655±3	Average value			0.282302±8 (2 S.D.)	1.88653±3 (2 S.D.)

All the reported errors are 2 S.E., except where noted.

ULB JMC-475 average value: $^{176}\text{Hf}/^{177}\text{Hf} = 0.282161 \pm 16$ (2 S.D.).

UBC JMC-475 average value: $^{176}\text{Hf}/^{177}\text{Hf} = 0.282161 \pm 8$ (2 S.D.).

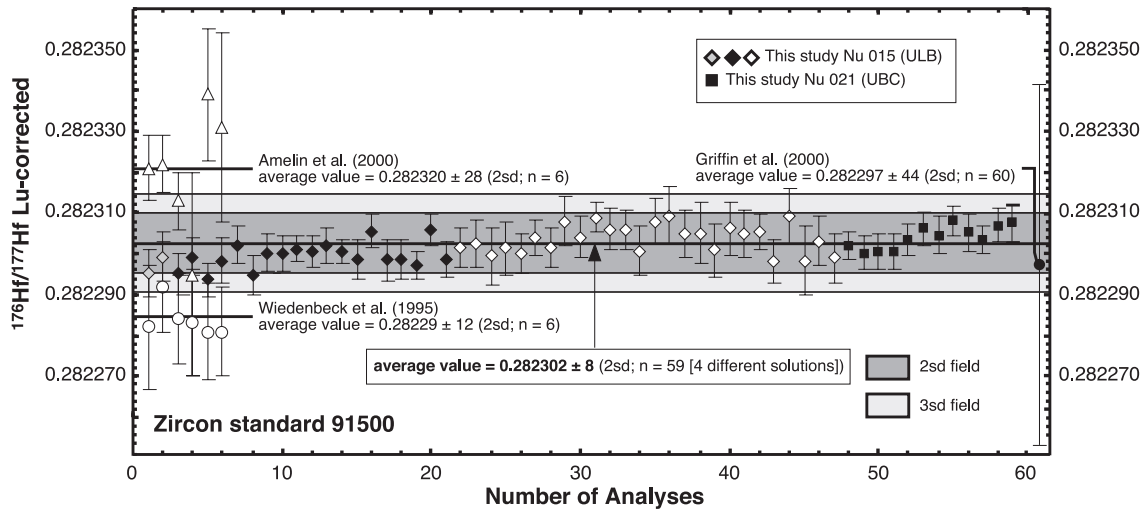


Fig. 1. $^{176}\text{Hf}/^{177}\text{Hf}$ vs. number of analyses for the zircon standard 91500 from this study and previous studies. This comparison is based on absolute values and their associated error domains. The complete dissolution method for Hf isotopes in zircon analyzed by MC-ICP-MS is characterized by both smaller external and internal errors relative to the other studies. The use of two different instruments (Nu015 and Nu021) indicates that neither the chemistry nor the analysis by MC-ICP-MS introduces a statistical bias.

Fig. 1). The average $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of all measurements is 0.282302 ± 8 (2 S.D.). The external precision is 27 ppm (2 S.D.) over the 59 measurements and 10 ppm on a single day of measurements. The average internal error on all measurements is 10 ppm (2 S.D.).

Several previous studies present Hf isotopic data on the zircon standard 91500 (Wiedenbeck et al., 1995; Amelin et al., 2000; Griffin et al., 2000;

Machado and Simonetti, 2001) and these results are summarized in Table 4 and Fig. 1. Comparison with these data underscores the higher precision and stability provided by the procedure presented in this study. The original reference publication by Wiedenbeck et al. (1995) presents TIMS U–Th–Pb and Lu–Hf data as well as trace element and REE concentrations on three zircon standards. Their average

Table 4

Comparison of reported Hf isotopic compositions of the zircon standard 91500

	Method	$^{176}\text{Hf}/^{177}\text{Hf}$ Lu-corrected zircon 91500	Average $^{176}\text{Hf}/^{177}\text{Hf}$ JMC-475
Wiedenbeck et al. (1995)	TIMS	0.282284 ± 6 (2 S.E.) ^{a,b}	–
	TIMS	0.28229 ± 12 ^c	0.282072 ± 19 ^d
	TIMS	–	0.282150 ± 16 ^d
	TIMS	–	0.282138 ± 11 ^d
Amelin et al. (2000) ^b	MC-ICP-MS	0.282320 ± 28 ^b	0.282162 ± 14
Griffin et al. (2000)	LA-MC-ICP-MS	0.282297 ± 44	0.282161 ± 34
Machado and Simonetti (2001)	LA-MC-ICP-MS	0.282270 ± 123	0.282159 ± 33
This study	MC-ICP-MS	0.282302 ± 8	0.282161 ± 16
JMC-475 reference value ^e	MC-ICP-MS	–	0.28216 ± 1

All the reported errors are 2 S.D., except where noted.

^a This value represents a weighted mean including various collector configurations.

^b Corrected for the difference between the measured JMC-475 and the accepted value.

^c 2 S.D. has been estimated from the reported 2 S.E. on the basis of the number of independent measurements.

^d JMC-475 values from the three different collector configurations as reported in Wiedenbeck et al. (1995).

^e Chauvel and Blichert-Toft (2001).

$^{176}\text{Hf}/^{177}\text{Hf}$ value on the zircon standard 91500 was based on six analyses by TIMS (Fig. 1) and they suggest that technical problems explain some of the extreme $^{176}\text{Hf}/^{177}\text{Hf}$ ratios for the JMC-475 standard (e.g. 0.282072 ± 19 (1 S.D.): AxH1H2 configuration). These extreme ratios were rejected by Nowell et al. (1998) in their compilation to reduce the range in published ratios for JMC-475. However, it is important to note that the difference between the Wiedenbeck et al. (1995) JMC-475 normalization reference value (0.282142) and the value used in this study (0.282161) is equivalent to the observed difference between their $^{176}\text{Hf}/^{177}\text{Hf}$ on the zircon standard 91500 and our value.

The three other studies using MC-ICP-MS instruments (Amelin et al., 2000; Griffin et al., 2000; Machado and Simonetti, 2001) present higher average $^{176}\text{Hf}/^{177}\text{Hf}$ ratios than the Wiedenbeck et al. (1995) value (Table 4; Fig. 1). However, because of larger associated errors, these authors did not consider their values to be systematically different. The five independent analyses from Amelin et al. (2000) seem to indicate a difference with respect to the Wiedenbeck et al. (1995) value, especially if one considers that the lowest of their $^{176}\text{Hf}/^{177}\text{Hf}$ ratios is outside the 2 S.D. error limits (28) and could not be included in the average calculation. The mean $^{176}\text{Hf}/^{177}\text{Hf}$ value of Amelin et al. (2000) (0.282320 ± 28) therefore represents a minimum value. Three of the zircon fractions analyzed by Amelin et al. (2000) were extremely small (0.006–0.007 mg) leading to significantly increased errors and more scatter in the results (Fig. 1).

The two LA-MC-ICP-MS studies (Griffin et al., 2000; Machado and Simonetti, 2001) illustrate the differences between complete dissolution procedures and in situ laser-ablation. The Machado and Simonetti (2001) value (0.282270 ± 123) is not reported in Fig. 1 because it falls within the range of the other LA-MC-ICP-MS value. Also, this value has such an important error that the resulting scale of the diagram would be inappropriate for discussion and comparison with the other data. The average $^{176}\text{Hf}/^{177}\text{Hf}$ value (0.282297 ± 44) obtained by Griffin et al. (2000) by LA-MC-ICP-MS is close to our proposed value (0.282302 ± 8) (Table 4; Fig. 1), although the error encompasses all of the published TIMS and MC-ICP-MS data. They also indicate that the range of observed $^{176}\text{Hf}/^{177}\text{Hf}$ ratios lies just outside 3 S.D.

of the mean. Machado and Simonetti (2001) suggest that this could be the consequence of a slight isotopic heterogeneity in the zircon standard as sampled by the laser. Given the slight chemical heterogeneity documented in zircon 91500, this may indeed be possible and needs to be confirmed by additional studies. However, the lower associated precision of the laser-ablation method compared with the complete dissolution method can also be explained by the relatively poor constraints on instrumental artefacts such as important isobaric interferences and/or instrumental mass bias. Despite the slight differences between all of the proposed values, the grouping of all the MC-ICP-MS data (including this study) to higher $^{176}\text{Hf}/^{177}\text{Hf}$ values relative to the original Wiedenbeck et al. (1995) value confirms the coherence of MC-ICP-MS data and allows for the definition of a specific MC-ICP-MS $^{176}\text{Hf}/^{177}\text{Hf}$ reference value as proposed in this study.

5. The Lu isotopic composition of zircon standard 91500

We also present Lu isotopic data for the zircon standard 91500. Despite the low concentrations involved (10 and 20 ppb), the Lu isotopic compositions are reproducible for both standard solutions (described in Section 3.2) and for duplicate samples. The two different sample sizes treated for these analyses explain the important difference in internal errors. The average $^{175}\text{Lu}/^{176}\text{Lu}$ of the zircon standard 91500 is 37.74 ± 8 (2 S.D.) (Table 5). These results show that coherent values can be obtained on small zircon fractions following two independent chemical

Table 5
Lu isotopic compositions of the zircon standard 91500 and the AAS standard solution

Zircon 91500			AAS standard solution		
Run #	$^{175}\text{Lu}/^{176}\text{Lu}$	2 S.E.	Analysis type	$^{175}\text{Lu}/^{176}\text{Lu}$	2 S.D.
1	37.801	0.112	instrument calibration	37.72	0.02
2	37.684	0.042	analytical session	37.72	0.01
Average	37.74	0.08			
		(2 S.D.)			

All reported errors are 2 S.E., except where indicated.

procedures. Although the total recovery of Lu from the zircon dissolution was not quantitatively determined, the intensities during the analytical session were in agreement with the expected intensities based on the 94% recovery determined for the alkali basalt as discussed in Section 2.2.2. Thus, the weak HF solutions used in this study did not lead to significant REE-fluoride precipitation as found in some other studies (Münker et al., 2001; Kleinhans et al., 2002).

6. Conclusions

This study presents a complete chemical procedure for the extraction and analysis by MC-ICP-MS of Hf and Lu isotopes in zircon. The method provides high-purity solutions with yields greater than 94% for the elements of interest. Critical interferences on mass 176 were accurately corrected for both Hf and Lu isotopic measurements yielding exact as well as reproducible results. Redefined reference values for the Hf and Lu isotopic compositions of the standard zircon 91500 are: $^{176}\text{Hf}/^{177}\text{Hf}=0.282302\pm 8$ (2 S.D.) and $^{175}\text{Lu}/^{176}\text{Lu}=37.74\pm 8$ (2 S.D.). Comparison of the results from this study with previously published values indicates a significant improvement in terms of both internal and external precision. We consider this issue to be of the utmost importance considering the growing use of in situ measurement techniques. The significant improvement in both internal and external precision will be useful for calibrating laser-ablation MC-ICP-MS techniques, which are designed to investigate isotopic variations on the single-crystal scale. The complete dissolution method presented in this study allows a better control on matrix effects, memory effects, isotopic fractionation and elemental fractionation and can be used on simple morphology zircon with limited compositional zoning.

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