Small-volume Lu-Hf and U-Pb isotope determination of complex zircons by solution and laser ablation MC-ICP-MS

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Abstract

There is an increasing need for solution and laser ablation analysis methods suited to the determination of the Lu-Hf and U-Pb isotope signatures of small volumes of zircon corresponding to sub-nanogram amounts of Hf. This study presents a reduced-volume laser ablation protocol with consecutive U-Pb and Lu-Hf isotopic analyses resulting in a total pit depth of 18 µm using a 25 µm laser ablation spot. This results in excavation of ~40 ng of zircon, equating to ~0.4 ng of Hf and uncertainties ~1 ε_{Hf} (2s). The laser technique presented here is ideally suited to complex, finely zoned zircons for which drilling to depth would intersect different zones. The possibility of reducing the total laser ablation pit depth to ~10 µm is demonstrated by decreasing the integration time for Hf isotope analysis without serious compromise of the uncertainty. Furthermore, the capability to determine the Hf isotope composition of the same amount of Hf using solution MC-ICP-MS is also demonstrated, as is the suitability of analyzing solutions not subject to Hf-HREE separation. For both solution and laser ablation methods, this study investigates possible methods of Yb interference correction, the potential for matrix effects, and the accurate determination of $^{176}Lu/^{177}Hf$. Using the approaches described here, acceptable uncertainty levels are achieved to resolve complexity at the level of

25x18 μm (diameter x depth), and therefore this method has the potential to yield geologically meaningful results for rocks containing complexly-zoned zircons.

1. Introduction

Zircon Lu-Hf and U-Pb isotopic datasets are ubiquitous in modern geologic studies and are produced using either high-precision dissolution-based techniques or lower-precision microbeam methods. Zircon Lu-Hf solution analyses are often determined for whole grain dissolutions, which can result in the homogenization of distinct isotopic zones, thereby representing mixtures without geologic significance. A proper evaluation of complex zircons via solution methods necessitates micro-sampling (e.g. Hawkins and Bowring, 1997), yet the targeted domains are often of insufficient size to obtain meaningful levels of precision with standard solution-based measurement procedures. Conventional techniques for laser ablation analyses typically sample ~2-3 ng Hf and conventional solution analyses >5 ng Hf, often on the order of ~25 ng. A cylindrical pit of zircon 30 μm in diameter and depth yields approximately 1-2 ng of Hf, depending on Hf concentration; for <1 ng Hf, conventional analytical methods result in uncertainties great enough to effectively prohibit discrimination of variation. The amount of material required for Hf isotope analysis by laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) typically results in Lu-Hf laser ablation spots of ~35-50 μm in diameter and depths of 30-40 μm; these parameters are sufficiently large as to potentially sample multiple distinct zones with depth in highly-zoned zircon. A benefit of this approach is that the time series of the analyses enable inspection of variations of ^{176}Lu/^{177}Hf and ^{176}Hf/^{177}Hf with depth. One consequence of conventional 'high-volume' Lu-Hf ablation, however, is that the U-Pb age information, usually obtained via SIMS or LA-ICP-MS on an adjacent spot, may become decoupled from the Lu-Hf isotope information. The mismatch of these two isotope datasets can result in an initial ε_{Hf} signature calculated with the wrong age (see discussion in Amelin et al., 2000). To combat this, two techniques are commonly used—coupled Pb-Hf isotope analysis, where the ^{207}Pb/^{206}Pb is periodically measured during a Hf isotope analysis (e.g. Kemp et al., 2010) or laser ablation split stream (LASS) (Yuan et al., 2008; Fisher et al., 2014), where two mass spectrometers simultaneously analyze the divided ablation particle stream. Pit volumes remain high for both methods, with total pit depths of ~40 μm or more (Fisher et al. 2014; Ibanez et al., 2015; Kemp et al., 2010), so unless these zones can be clearly discriminated, the potential remains for sampling and integrating multiple zones with depth.

To determine compositions of complexly zoned zircons, small-volume solution and laser ablation analysis methods are required. Previous studies have focused on the minimization of sample volumes for Lu-Hf solution analysis of zircon (Bast et al., 2015; d'Abzac et al., 2016). With the ultimate goal of low-volume analysis of meteorite samples, Bast et al (2015) successfully analyzed chemically-isolated Hf solutions with sub-nanogram amounts using a Neptune Plus MC-ICP-MS equipped with a Jet sample cone and 10^{12} Ω resistors to maximize Hf measurement precision. They obtained 1.5-4.0 ε_{Hf} precision (2 sigma, after propagation for systematic uncertainties) for analyses of 0.5 ng of Hf. However, chemical separation of Hf potentially increases blank, is more time-consuming and requires separate analysis of $^{176}Lu/^{177}Hf$ for age correction, thereby limiting the achievable Hf isotope precision by removing material. To maximize efficiency (maintain the maximum amount of sample and lowest blank) therefore requires the analysis of zircon solutions without chemical separation (hereafter referred to as 'neat'). D'Abzac et al. (2016) investigated the effect of eliminating the chemical separation process for small-volume zircon and baddeleyite solutions on the resultant Lu-Hf isotopic data. Using a Neptune Plus MC-ICP-MS and a Jet sample cone, they analyzed <0.2 ng of Hf, achieving ~2 ε_{Hf} (2SE) precision (excluding propagation for systematic uncertainties).

In this study, we aimed to optimize low-volume analysis techniques for samples containing sub-nanogram amounts of Hf for both solution and laser ablation analysis of zircons bearing complexity on the ~20 μm scale. To maintain precision levels around 1 ε_{Hf} (2s), a level considered appropriate for most geologic interpretations, analysis of this small amount of material requires a reconsideration of the sample introduction and data processing methods. To build upon previous small-volume Hf method-development studies, we focused on solution measurements with small (100 μL) total uptake to optimize the signal to noise ratio (SNR) and permit precise simultaneous measurement of $^{176}Lu/^{177}Hf$. Furthermore, we contribute methods to match this level of precision with laser ablation analysis. To maximize use of the available sample, we forgo traditional Hf-HREE separation chemistry (so that ^{176}Lu/^{177}Hf can be determined simultaneously with Hf isotopes). To achieve this, a number of questions need to be addressed, including: Are the Hf isotope data of zircon samples accurate when analyzed as neat solutions? Under these conditions, is the Yb isobaric interference correction robust, especially at relatively high HREE/Hf? Is the blank contribution significant when analyzing such small amounts of material? Are special analysis conditions required to obtain robust data while promoting Hf efficiency? How does running neat solutions affect the accuracy and quantification of Lu/Hf? To address these and other questions, a series of tests were performed using zircon reference materials and natural sample sets for solution and laser ablation analysis.

2. Analytical methods

To investigate the need for chemical separation of Hf with sub-nanogram sized samples, we determined the Hf isotope composition of a 91500 zircon solution with and without Hf separation chemistry. This solution, as well as laser ablation data for 91500, also provided a dataset for the assessment of the stability and accuracy of the ^{176}Lu/^{177}Hf determination. A solution of the Mud Tank zircon was used to test the effect of matrix load on the robustness of the Yb correction. The JMC475 Hf isotope reference solution was used throughout the study and two natural sample sets demonstrate the precision obtained by these methods. The sample materials are described below. The blank contribution of the different sample processing and introduction methods was assessed.

2.1 Reference materials and samples

Reference zircon 91500 is from Kuehl Lake, Ontario, and the ^{206}Pb/^{238}U age has been determined to be 1065.4 ± 0.3 Ma (Wiedenbeck et al., 1995). The ^{176}Hf/^{177}Hf is 0.282306 ± 8 and the ^{176}Lu/^{177}Hf is 0.000311 (Woodhead and Hergt, 2005; Blichert-Toft, 2008). Because the ^{176}Lu/^{177}Hf was not presented in these studies with an associated uncertainty, we normalized our data to 0.00030 ± 3 (2s), which, based on previous laser ablation experiments, is considered as an accurate representation of the natural Lu/Hf variation (i.e. 10%) in zircon 91500. The 91500 standard solution used in this study was prepared by a bulk dissolution in HF that was subsequently evaporated and redissolved in 2% HNO_3. For neat solutions, no further modifications were made to the sample. For the comparison of neat and separated solutions, an aliquot of this solution was processed through Hf-HREE-Zr separation chemistry modified after Münker et al., (2001) (Supplementary Table 1). Zircon 91500 was used as the primary reference material for the solution and laser Lu-Hf isotopic analyses of natural samples in this study, as well as for experiments to determine the effect of amount of matrix on the measured $^{176}Lu/^{177}Hf$ and its uncertainty. In the experiment conducted to evaluate the viability of running neat versus purified zircon Hf solutions, 91500 served as a secondary reference material.

In this study, the **JMC475 Hf solution** was used as a reference material for Hf isotopes (assuming $^{176}Hf/^{177}Hf = 0.282160$; Nowell et al., 1998) with variable additions ('dopants') of Lu and/or Yb to evaluate oxide formation in the plasma and to evaluate isobaric interference corrections on mass 176. Dopant levels targeted a total Yb/Hf of ~0.25 and Lu/Hf of ~0.005 to 0.25 to evaluate the accuracy of our interference corrections. JMC475 was used as a primary reference material in experimental evaluations of neat versus purified Hf solutions of zircon 91500.

Mud Tank zircon (731.65 ± 0.49 Ma, $^{206}Pb/^{238}U$ age, 95% confidence, MSWD=1.9, n=6, Horstwood et al., 2016) is a widely-used U-Pb reference material sourced from a carbonatite in the Northern Territory, Australia (Black and Gulson, 1978). This sample has fairly homogeneous $^{176}Hf/^{177}Hf$, 0.282507 ± 6, but a high degree of heterogeneity of $^{176}Lu/^{177}Hf$, with a typical value ~0.000042, though there is a small zircon sub-population of this sample for which $^{176}Lu/^{177}Hf$ is much higher, ~0.00014 (Woodhead and Hergt, 2005). The Mud Tank solutions used in this study are washes from the U-Pb separation chemistry of two large Mud Tank zircon grains. One of these grains has a typical $^{176}Lu/^{177}Hf$ of ~0.00001 (z2) and the other has a higher $^{176}Lu/^{177}Hf$ of ~0.0001 (z1). Aside from wash collection from U-Pb columns in 3N HCl, evaporation, and dilution, no further chemical separations were made. Therefore, these solutions are effectively 'neat' solutions excluding U, Pb, and Si. Aliquots of these Mud Tank solutions were doped with a known amount of Lu to evaluate matrix effects on the Lu-Hf ratio and with Yb to evaluate the effect of varying Yb/Hf on two different methods of Yb isobaric interference correction. In this study, Mud Tank zircon serves as a secondary reference material.

***Zimb-95-24* -** This sample is a zircon separate from a modern river sand collected in the Sebakwe river in the Midlands of Zimbabwe and is used to demonstrate the applicability of the successive low-volume U-Pb and Lu-Hf laser ablation methods.

Granitic zircon samples - Zircon grains from a granite suite were analyzed for Lu-Hf isotopes by solution methods. The zircons were subsampled before chemical abrasion and were processed as part of a regional geological CA-ID-TIMS U-Pb study, which will form the focus of another paper but the analytical merits of the data will be discussed here.

2.2 Isotopic analysis

Zircon Lu-Hf isotopic analyses were performed on a Thermo Scientific Neptune Plus MC-ICP-MS at the Natural Environment Research Council Isotope Geosciences Laboratory (NIGL) of the British Geological Survey (BGS) in Nottingham, United Kingdom. Cup configuration and analytical conditions for Lu-Hf isotopic analyses (solution and laser) are listed in Table 1. A Jet sample cone was used to maximize Hf transmission efficiency, however, instrument tuning conditions were optimized for low oxide production in the plasma (see Section 4.4 for discussion).

Dissolved zircon solutions (various pre-treatments outlined in Section 2.1) and the JMC475 Hf solution were redissolved in 100 µL of 2% HNO_3 solution with 0.1M HCl (to stabilize Lu) and 0.1 M HF (to stabilize Hf). Samples and reference materials were introduced using a Cetac Technologies Aridus II nebulizer with a PFA-50 nebulizer tip operating at a flow rate of ~43 µL /min. Nitrogen was added at 5 ml/min to optimize Hf ionization efficiency, decrease oxide formation, and restrict non-linear mass dependent Hf fractionation (Hu et al., 2012).

To maximize precision and the efficient use of sample, we used a sample aliquot with higher concentration and minimized volume to maximize the SNR of the analysis. This required changing the sample introduction method to minimize or avoid the introduction of air between aspiration of wash and aspiration of the sample, which destabilizes the plasma, induces inter-element (Lu/Hf) fractionation, impacts isobaric interference corrections, and causes spiking of the background from the desolvation system. The requirements for introduction were developed manually and later automated to allow efficient analysis. For both manual and automated runs, washout between samples was ~15 minutes in length and the instrument electronic baseline was determined during these intervals. For manual analysis, the uptake probe of the nebulizer was placed into a 1.5 ml micro-centrifuge tube containing 300 µL of blank acid. One hundred seconds of stable washout were collected as background until <50 µL of blank acid remained, at which point the sample was injected and mixed with the remaining wash acid. In this way, a stable ion signal was quickly reached, resulting in a greater fraction of the sample signal to be utilized in data processing.

For automated analysis, a Teledyne Cetac Technologies MVX-7100 low-volume autosampler was used to inject 100 µL of sample into the desolvating nebulizer in alternation with 100 µL acid blanks. This system uses syringe pumps to load a sample onto a loop of tubing while the rest of the system is being flushed by a wash acid, before switching a valve to push the sample into the introduction system. The sample is isolated from surrounding blank acid by small air-locks (10-25 µL) on either side.

Reference materials JMC475, 91500, and Mud Tank were run at varying concentrations (3 - 40 ppb) to determine reproducibility of Hf isotopic measurements at varying total nanograms (0.3 - 4 ng) Hf analyzed. Natural zircon sample solutions were run at 1-40 ppb Hf (0.1 - 4 ng). The stability of inter-element isotopic ratios was monitored and analyses or portions of analyses with significant variation, indicating destabilization of the flow injection rate and/or background spiking from the desolvator, were excluded from the final interpretation. Total procedural blanks for Hf-HREE-Zr separation chemistry were run using a dynamic collection protocol with a secondary electron multiplier to determine Hf concentration and Hf isotopic compositions (presented in Table 1 and conditions reported in Table 2). All solution analyses were acquired in time resolved analysis (TRA) mode using a 0.262 sec integration period, acquiring many thousands of cycles, and the data were imported into the Iolite (Paton et al., 2011) data processing package for reduction and interrogation.

For **laser ablation analyses**, zircons were mounted in epoxy, polished to equatorial sections, and imaged via cathodoluminescence (CL) (Fig. 1) on the BGS FEI Quanta 600 scanning electron microscope (SEM). Ablation spot selection was guided by CL images and transmitted light to distinguish between distinct zones and to avoid inclusions and cracks. The mounts were washed in 2% HNO_3, ethanol, and water before analysis. Laser ablation pit depths were determined using the SEM in secondary electron mode. Observations were made on a tilted stage at 40.2 degrees (see Supplementary Figure 1) while in variable pressure mode (P ~ 0.45 torr). The accuracy of the pit depth measurements is estimated to be better than 5%.

Zircons were ablated using an ESI (New Wave Research Division) UP193FX excimer laser system fitted with a custom-built, low-volume cell (Horstwood et al., 2003). Typical Hf signals were ~6-10 V of ^{180}Hf. Instrument operation parameters are in Table 2. The mass spectrometer was tuned using Yb and Lu-doped JMC475 Hf solutions introduced using the Aridus II desolvating nebulizer, with the goal of maximizing Hf detection efficiency while minimizing oxide production. Unknowns were run in blocks of 10-12 bracketed by measurements of reference zircons 91500, Mud Tank, and Plešovice.

Zircon Lu-Hf isotopic data were reduced in Iolite (Paton et al., 2011) using 91500 as the primary reference material (weighted mean ^{176}Hf/^{177}Hf = 0.282298 ± 2, MSWD = 1.5, n= 75, and ^{176}Lu/^{177}Hf = 0.000319 ± 18, 2SD). The principles of the uncertainty propagation protocol shown in Horstwood et al., (2016) are here applied to Hf isotope data. Reported uncertainties for ^{176}Hf/^{177}Hf and ^{176}Lu/^{177}Hf are analytical uncertainties combined in quadrature with excess variance of the primary reference (zircon 91500) on a per session basis. Hf stable isotope ratios (^{178}Hf/^{177}Hf and ^{180}Hf/^{177}Hf) were monitored for data quality.

Two separate collector configurations for laser ablation U-Pb analysis were used in this study (A and B, Table 3)—the standard collector configuration used for U-Pb isotopic analysis at NIGL as well as an amended configuration to permit Faraday collection of the ^{206}Pb beam for high-Pb samples. U-Pb isotopic data were collected in two sessions (session 1: configuration A, session 2: configuration B) using a Nu Instruments Nu-Plasma HR MC-ICP-MS. Analytical set-up and instrument operation parameters are in Table 3. Zircon material was ablated using the same laser ablation system as for the Lu-Hf measurements. Laser conditions and spot sizes varied depending on the expected U (and thus *Pb) concentration of the zircons and are listed in Supplementary Table 6. The large age range encompassed by the detrital sample (~270-3300 Ma) required the use of both collector configurations to optimize the precision of our measurements while sampling the smallest possible volume. The samples that were youngest and/or low-U were analyzed using configuration A with a 25 µm spot and a fluence of 2.7 J/cm^2 (Fig. 2a). The same spot parameters resulted in a signal too large to accurately measure using ion counters for samples that were older or high-U, so smaller spot sizes of 15 µm (Fig. 2b and 2c) were applied using configuration B. A ^{235}U- ^{203}Tl-^{205}Tl solution was co-aspirated into the plasma in the same way as that detailed in Horstwood et al. (2003) via a Nu Instruments DSN-100 desolvating nebulizer. Data were collected in time-resolved analysis mode using the Nu Plasma HR instrument software, with normalization and uncertainty propagation utilizing an in-house Excel spreadsheet. A common Pb correction was not required. GJ-1 was used as a primary reference material with the reference values defined in Horstwood et al. (2016). For the detrital zircon sample analyzed in this study (Zimb-95-24), reported data point uncertainties include propagation for systematic components following Horstwood et al. (2016). Calculated ages and plots were generated with Isoplot (Ludwig, 2003) and using decay constants from Jaffey et al. (1971) and ^{238}U/^{235}U of 137.818 (Hiess et al., 2012). Discordance was calculated using ^{207}Pb/^{206}Pb and ^{206}Pb/^{238}U dates for zircons >1 Gyr and ^{206}Pb/^{238}U and ^{207}Pb/^{235}U dates for zircons < 1 Gyr.

2.3 Yb correction for solution and laser work

For all analyses, the correction of ^{176}Yb interference on ^{176}Hf was assessed in two separate ways. The ^{176}Yb isobar was evaluated using Yb mass bias determined using: 1) direct measurement of ^{172}Yb/^{173}Yb, and 2) by pre-calibration of the Yb mass bias to Hf mass bias (see Nowell & Parrish, 2001). The first method is the traditional approach used in most Lu-Hf studies, but the second method is ideal for low-Yb samples. In this method, the Yb mass bias is determined using calibrated ^{176}Yb/^{173}Yb, which is determined at the start of each session by analyzing Yb-doped JMC475 solutions. This value was found to be extremely stable at 0.79435-0.79455 across all analytical sessions using the low oxide tuning conditions employed. The assessment and validity of both correction methods are discussed in Section 4.2. Equations 1 and 2 outline how the ^{176}Yb isobar is determined in method 1 (utilizing ^{172}Yb/^{173}Yb = 1.35274 and ^{176}Yb/^{173}Yb = 0.7962; Chu et al., 2002).

Equations 3 and 4 outline how ^{176}Yb/^{173}Yb is pre-calibrated in method 2 and how this is applied to determine the magnitude of the ^{176}Yb isobar.

$$\beta_{Yb,method\ 1} = \frac{\ln\left(\frac{^{173}Yb/^{172}Yb_{reference}}{^{173}Yb/^{172}Yb_{measured}}\right)}{\ln\left(\frac{M173}{M172}\right)} \quad \textbf{(equation 1)}$$

$$^{176}Yb_{calculated,method\ 1} = {}^{173}Yb_{measured} \times \left(\frac{^{176}Yb}{^{173}Yb}\right)_{reference} \times \left(\frac{M173}{M176}\right)^{\beta_{Yb}} \quad \textbf{(equation 2)}$$

$$\frac{^{176}Yb}{^{173}Yb}_{method\ 2} = \frac{\left(\frac{^{176}Yb}{^{173}Yb}\right)_{calibrated}}{\left(\frac{M^{176}Yb}{M^{173}Yb}\right)^{\beta_{Hf}}} \quad \textbf{(equation 3)}$$

$$^{176}Yb_{calculated,method\ 2} = {}^{173}Yb_{measured} \times \left(\frac{^{176}Yb}{^{173}Yb}\right)_{method\ 2} \quad \textbf{(equation 4)}$$

2.4 Lu/Hf normalization for solution and laser work

For solution analyses of zircons, corrections were applied to the ^{176}Lu/^{177}Hf to account for inter-element fractionation in the plasma and induced bias due to amount of matrix. The uncertainty of the ^{176}Lu/^{177}Hf for these analyses is fully propagated to include excess variance from: 1) the in-session primary reference material, 2) matrix bias correlated with concentration, and 3) the long-term excess variance of ^{176}Lu/^{177}Hf measurements for zircon 91500 in sessions where it was not self-normalized. The matrix bias corrections of the ^{176}Lu/^{177}Hf and its uncertainty are outlined in Section 4.3.

Zircon ^{176}Lu/^{177}Hf laser ablation data were normalized and corrected for drift using zircon 91500 as the primary reference material. The laser ^{176}Lu/^{177}Hf uncertainties are dominated by the excess variance, ±3.1% (2s) derived from zircon 91500. Population statistics suggest that this is an over-propagation and likely relates to the 5-10% heterogeneity of Lu/Hf exhibited by 91500 which, in our experience, is the most homogeneous zircon reference material for Lu/Hf. For future studies, until a more homogeneous material is documented, NIST610 could be used to quantify session excess variance for Lu/Hf and the data could still be normalized to 91500 as a matrixmatched reference material. Recent experiments by the authors indicate that more appropriate Lu/Hf population statistics (MSWD ~ 1) are achieved when propagated in this way, suggesting that this is a suitable way of quantifying this uncertainty.

2.5 Procedural blank size and isotopic composition

For the Hf separation chemistry, the amount of Hf blank introduced during the separation procedure was quantified to determine its impact on the Lu-Hf isotopic composition of small samples. The data collection routine required peak jumping across the ion counter and the ^{176}Hf/^{177}Hf was determined in two ways; one with ^{176}Hf on an ion counter and ^{177}Hf on a Faraday detector, and a second collection method with both masses (^{176}Hf and ^{177}Hf) collected by ion counters. The resultant Hf blanks were ~ 1-2 pg Hf (Table 1), even with the extensive Zr-Hf wash steps of our separation procedure (Supplementary Table 1). Furthermore, the ^{176}Hf/^{177}Hf composition of our procedural blank was 0.2820 ± 0.0009 (MSWD=0.22, n=3, IC-IC, Table 2), which is similar to the bulk Earth today and a value for which the blank correction of >0.3 ng Hf samples is minor or negligible.

For automated solution analyses, the blank averaged 4 pg total Hf. For manual solution analyses, the typical background measurement was ~20 fg Hf, i.e. 200 times less than the blank using the MVX-7100. These amounts are insignificant in comparison to the amount of Hf (0.1-4.1 ng) in the natural zircon solutions that were processed. Continued development work using the MVX-7100ul workstation is expected to decrease this blank contribution significantly.

3. Experimental results

3.1 Low-volume solution Lu-Hf analyses

The long-term reproducibility of the reference materials used in this study are included in Supplementary Table 2 (and are not self-normalized). The full solution dataset is presented in Supplementary Table 3. The granitic zircon solution Lu-Hf results are presented in Table 4. The samples have been anonymized. Subsampled zircon domains that survived chemical abrasion yielded 0.1 to 4.1 ng Hf. An analytical cut-off of 0.3 ng Hf was selected when considering the data (see Fig. 3a-c and Section 4.1), however, data for samples having <0.3 ng Hf are included in Table 4 for reference. A matrix bias was noted (see Section 4.3) and a correction applied to the normalized ^{176}Lu/^{177}Hf. The sample ^{176}Lu/^{177}Hf ranged from 0.000499 to 0.004859 and the fully-propagated 2σ uncertainty was <3% for samples containing >0.3 ng Hf. The largest Yb/Hf of the samples was ~0.2, which is at the highest end of the range of terrestrial zircons. Figure 3a shows the relationship between the ^{176}Hf/^{177}Hf measurement uncertainty and total ng of Hf processed for these samples.

The long-term weighted mean of neat 91500 solutions before normalization was 0.282302 ± 3 (MSWD 2.6, n=32) and the ^{176}Lu/^{177}Hf was 0.000293 ± 32 (2SD, n=32, defining an excess variance of 10.0%, which was used in uncertainty propagation for zircon samples). After normalization to 91500 and full uncertainty propagation, Mud Tank (z1) validation results were ^{176}Hf/^{177}Hf = 0.282492 ± 9 (MSWD 1.4, n=13) and ^{176}Lu/^{177}Hf = 0.000105 ± 3 (MSWD 0.66, n=13).

3.2 Low-volume laser ablation analyses

3.2.1 U-Pb

A 5% discordance filter was applied to the laser ablation U-Pb analyses and the data for 77 analyses of sample Zimb-95-24 are presented in Table 5. The data point uncertainties range from 1.2 to 4.0 (% 2σ) for the ^{206}Pb/^{238}U ages of the zircons and 0.2 to 22 (% 2σ) for the ^{207}Pb/^{206}Pb ages of the zircons. The higher ^{207}Pb/^{206}Pb uncertainties mostly arise when determining low-Pb samples on the ion-counter-Faraday ^{207}Pb-^{206}Pb configuration. Figure 4a demonstrates the ^{238}U-^{206}Pb and ^{207}Pb/^{206}Pb age precision obtained for these 10 second analyses as a function of U concentration, indicating little compromise in the achievable uncertainty compared to more conventional ablation approaches. Validation data for secondary reference materials (91500 and Plešovice zircon) were normalized to GJ-1, the primary reference material, and are presented in Supplementary Table 4 and Supplementary Figure 2a-b.

3.2.2 Lu-Hf

A summary of the laser ablation zircon Lu-Hf isotopic data for U-Pb discordance-filtered analyses (<5%) of detrital sample Zimb-95-24 is presented in Table 5 with all data provided in Supplementary Table 5. Figure 4b highlights the ^{176}Hf/^{177}Hf measurement precision (2SE%) in relation to Yb/Hf, demonstrating that the uncertainty does not correlate strongly with the size of the correction and that a <1 epsilon uncertainty is mostly still attained despite sampling only ~0.3 ng Hf. The ^{176}Lu/^{177}Hf of the samples ranges between 0.000007 and 0.001398. Uncertainties of the ^{176}Hf/^{177}Hf range from 0.7 to 1.1 ε_{Hf}. Before normalization, the ^{176}Hf/^{177}Hf of the primary reference material, zircon 91500, was 0.282298 ± 4 (0.0014%, MSWD = 1.5, n=75) and ^{176}Lu/^{177}Hf was 0.000319 ± 18 (2SD, n=75, defining an excess variance of 5.7%, which was used in uncertainty propagation for Zimb-95-24 zircons). After normalization to 91500 including uncertainty propagation for excess variance (especially in Lu/Hf), Mud Tank validation results were 0.282514 ± 4 (^{176}Hf/^{177}Hf, 0.0014% 2s, MSWD=2.3, n=55) and 0.000084±1 (^{176}Lu/^{177}Hf, 1.2% 2s, MSWD=0.3, n=55). Plešovice validation results were 0.282483 ± 4 (^{176}Hf/^{177}Hf, 0.0014% 2s, MSWD=0.8, n=54) and 0.000099±1 (^{176}Lu/^{177}Hf, 1.0% 2s, MSWD=15, n=54).

4. Discussion

4.1 The necessity of chemical separation of Hf from zircon solutions

The majority of zircon Lu-Hf analysis methods have been influenced by whole rock ICP-MS procedures, which require chemical separation of Hf from potential interferants Lu and Yb as well as from Zr, which is thought to influence Hf ionization in the plasma (Barovich et al., 1995; Blichert-Toft et al., 1997; Corfu et al., 1992; Münker et al., 2001; Peters et al., 2015). Some studies present zircon Lu-Hf isotopic data in which the samples were subject to separation of HREEs and/or Zr from Hf in preparation for ICP-MS analysis (e.g. Amelin et al., 1999; Iizuka et al., 2015) while others have run zircon solutions ‘neat’ (e.g. Davis et al., 2005; Schoene et al., 2012; d’Abzac et al., 2016). Because chemical separation takes time, introduces additional blank, and necessitates the removal of an aliquot before chemical separation to measure the ^{176}Lu/^{177}Hf of the sample, thereby restricting the efficiency of the Hf isotope determination for small samples, we compared the results of running zircon 91500 neat to those subjected to HREE and Zr separation chemistry to determine the acceptability of analyzing neat solutions.

In order to verify that neat solutions would be viable to analyze in this way, potential discrepancies in $^{176}Hf/^{177}Hf$, $^{178}Hf/^{177}Hf$, and $^{180}Hf/^{177}Hf$ between separated and neat 91500 solutions were investigated (Fig. 5, Supplementary Fig. 3). Figure 5 shows the $^{176}Hf/^{177}Hf$ results for 91500 analyzed at varying concentrations during this study, using purified Hf or neat solutions. The $^{176}Hf/^{177}Hf$ weighted means of the two analysis types (subdivided by Hf concentration) are indistinguishable. The weighted mean $^{176}Hf/^{177}Hf$, $^{178}Hf/^{177}Hf$, and $^{180}Hf/^{177}Hf$ of these subpopulations are compiled in Supplementary Figure 3. The nonradiogenic $^{178}Hf/^{177}Hf$ and $^{180}Hf/^{177}Hf$ isotope ratios are monitors of data quality. Additionally, Figure 3b-c demonstrate that these methods return acceptable values and uncertainties for the natural samples, with the exception of $^{180}Hf/^{177}Hf$ extending to higher values for the smallest samples (<0.2 ng Hf; Fig. 3b). Since the $^{178}Hf/^{177}Hf$ remains stable, this may imply a relationship with a ^{90}Zr dimer at low total Hf, and therefore we have selected a lower limit analytical cut-off at 0.3 ng Hf. The introduction of Zr into the plasma during solution analysis (with an assumed Zr/Hf ~50, the natural samples in this study contained between 5 and 200 ng of Zr) has not made an observable impact on the $^{176}Hf/^{177}Hf$ measurement. This was also the observation and conclusion of d'Abzac et al. (2016).

The equivalence of Hf isotopic ratios of the two analysis types (neat and separated) demonstrates that, at the chosen run amounts (0.1-4.1 ng Hf) under low oxide (and thus more robust) plasma conditions, there is no significant benefit to chemical separation of Hf. Furthermore, the level of precision achieved in either case is equivalent to precision obtained with conventional methods on sample amounts 10 times greater, so the equivalence of these ratios is not attributable to loss of analytical resolution (i.e. large uncertainties). The analysis of neat solutions maximizes the total Hf yield, which would be compromised during a separated solution procedure by Hf separation efficiency as well as by the removal of an aliquot for Lu/Hf measurement. Additionally, we found it difficult to achieve a clean Zr-Hf separation, as our method requires >150 column volumes of eluting acid to bring the Zr/Hf of the Hf elution step down from 50 to <5 (Supplementary Table 1 for method). Furthermore, incomplete separation of Hf from Lu and Yb results in a problematic correction for these interferants because it is difficult to accurately measure small ion beams, yet the Yb and Lu beams will still represent significant interferences on the 176 mass. The analysis of neat solutions has not resulted in an apparent bias in our Hf isotopic results and this approach enables the simultaneous determination of Hf isotopic and ^{176}Lu/^{177}Hf composition. For these reasons, the analysis of neat dissolved zircon solutions is the most efficient method for Lu-Hf isotope analysis, particularly for studies concerned with minimizing sampling volume.

4.2 Yb correction methods for solution and laser ablation Hf isotope analysis

The data described in this study largely show mutual agreement between ^{176}Hf/^{177}Hf calculated using an Yb correction derived by measuring the Yb mass bias compared to the Yb correction derived through precalibration of the ^{176}Yb/^{173}Yb using the Hf mass bias. This agreement is demonstrated for the laser ablation analyses of the Zimbabwe sample (Fig. 6a) as well as the analyses of granitic and variably Yb-doped Mud Tank zircon solutions (Fig. 6b, Fig. 7a). However, a detailed examination of the solution data (Fig. 6b, Fig. 7a) highlights a small discrepancy. The samples generally correspond to a 1:1 line, indicating agreement between the two Yb-correction methods (Fig. 6b), however, there is a minor bias that is more pronounced for samples with high Yb/Hf (see color key in Fig. 6b). In almost all cases, this bias is within uncertainty of the 1:1 line, and therefore is not interpreted to be significant. With respect to the Yb-doped Mud Tank results, the Yb solution used did not have an unnatural Yb isotopic composition, nor did it contain Hf. The ^{180}Hf/^{177}Hf and ^{178}Hf/^{177}Hf of these analyses do not exhibit any trends with level of Yb dopant or with ^{176}Hf/^{177}Hf (Supplementary Figure 4). These solutions were doped to higher Yb/Hf than most terrestrial zircons, and the Yb/Hf of the natural samples of this study were at the highest end of the range for natural zircons. Therefore, the behavior exhibited is for relatively extreme examples. The Yb correction derived from the direct measurement of Yb mass bias under-corrects the ^{176}Yb isobar (using the accepted value of ^{176}Hf/^{177}Hf for Mud Tank zircon, 0.282507 ± 3; Woodhead and Hergt, 2005), and this scales to a higher degree of undercorrection for aliquots with larger Yb/Hf. The ^{176}Hf/^{177}Hf results determined by pre-calibrating the mass bias relationships between Yb and Hf are accurate to ±0.7 ε_{Hf} units, suggesting that the precalibration method of Yb correction is more reliable for our work. At this time, the cause of this bias for the Yb-corrected data using the measured Yb ratio is unknown. Despite the high REE levels indicated by the Yb/Hf of the solution samples (Fig. 6b), it is not anticipated that this bias is related to MREE oxides as indicated by Payne et al. (2013), due to the maintenance of low-oxide conditions in our analytical set-up. More importantly, the Mud Tank experiments used an Yb dopant only—MREE therefore did not vary between the analyses, which were all run at the same matrix concentration, and the similarity in scale of bias for the solution samples and the Mud Tank experiments suggests there must be another cause. Figure 7b and 7c demonstrate the degree of bias between the two Yb correction methods relative to the amount of Yb present. Generally, solutions with higher [Yb] exhibited a larger degree of bias between the two methods of Yb correction. Additionally, Figure 8 demonstrates that the pre-calibrated Yb correction using Hf mass bias is more precise at REE concentrations too low for Yb to be accurately measured on a Faraday collector (<0.01 V ^{173}Yb). For all of these reasons, the data presented was corrected by the pre-calibration method.

The nature of the offset may be the result of non-mass dependent fractionation of Yb in the plasma, much like has been recorded for the Nd isotopic system (Newman et al., 2009). If that were the case, the expected offset would be the largest for analyses with the highest [Yb] that were corrected with directly-measured Yb isotopic ratios, which is consistent with our results (Fig. 7c).

One laser ablation datum deviates significantly from the 1:1 line in Figure 6a; this is for a zircon (which is 13% discordant and would therefore normally be excluded on the basis of discordance filtering, see note in Table 5) for which the ^{176}Yb/^{177}Hf (~0.27) is unusually high and outside the range encompassed by most natural zircons (see Figure 1 of Fisher et al., 2011). While MREE oxides could produce this effect (Payne et al., 2013), our maintenance of low oxide tuning conditions should mitigate the influence of MREEs and our Yb-doped Mud Tank and granitic zircon solution results suggest another cause is more likely. The highest level of admixed Yb dopant of our Mud Tank analyses was targeted to be comparable to the Yb level in this aberrant laser ablation analysis and yet the degree of bias is 3 times greater (9 vs 3 epsilon Hf units, see Figures 6a and 7a). Since an adjacent ablation on the same zircon crystal yielded a much lower degree of Yb enrichment and agreement between the two Yb correction methods, a reasonable explanation may be that inadvertent ablation of an inclusion or an altered domain affected the analysis.

Since both methods of Yb correction generally return equivalent values, we suggest that both results be considered for quality control of zircon laser ablation Lu-Hf isotopic data. Final data can be reported using the Yb correction pre-calibrated for the Yb-Hf mass bias relationship, but lack of agreement with data corrected using the measured Yb ratio will highlight potentially problematic data which can be further scrutinized and excluded from final interpretation as appropriate.

4.3 Lu-Hf uncertainty & age correction

The initial Hf isotopic signature is of interest for most zircon Lu-Hf studies, and the ^{176}Lu/^{177}Hf is a necessary component of its calculation. Because the ^{176}Lu/^{177}Hf of zircon is <<1 and the decay rate of ^{176}Lu is slow relative to the timescale of terrestrial processes, the amount of radiogenic ingrowth for most terrestrial zircon grains is of minor enough magnitude that the ^{176}Lu/^{177}Hf uncertainty is a negligible component of initial Hf uncertainty (see Fig. 9, with a ±10% variation in ^{176}Lu/^{177}Hf uncertainty expressed as a 20% variation). However, sub-nanogram Hf isotopic analyses will contain femto to sub-picogram amounts of Lu, making precise measurement difficult and therefore the ^{176}Lu/^{177}Hf uncertainty must be properly accounted for. Our goals for Lu/Hf determinations thus included an evaluation of reproducibility of solution ^{176}Lu/^{177}Hf, something that has not been addressed in other small-volume Lu-Hf studies, in part to confirm that the uncertainty of the age-corrected Hf isotopic signature would not be appreciably affected by the level of precision maintained for analyses of just ~30-40 ng of zircon.

Neat Mud Tank and 91500 zircon solutions were doped with Lu to evaluate variation in ^{176}Lu/^{177}Hf resulting from the concentration of zircon matrix, as well as at varying levels of Lu/Hf for the same matrix concentration. We were able to resolve a matrix-related bias, approximated by relating the concentration of Hf in the sample and the resultant ^{176}Lu/^{177}Hf for solutions run with 0.5, 1.0, and 2.0 ng Hf. The total matrix-related bias for neat Mud Tank and 91500 zircon solutions doped to Lu/Hf~0.0007 show an approximate -0.2% shift in ^{176}Lu/^{177}Hf per ppb Hf in the sample solution

(Supplementary Fig. 5). Following normalization to the reference material, a correction was applied to the ^{176}Lu/^{177}Hf sample results to account for this matrix bias.

The determination of ^{176}Lu/^{177}Hf uncertainty was a multi-stage process. The excess variance of the session reference material, 91500, was added to our standard-corrected ^{176}Lu/^{177}Hf uncertainties. This was done according to sample concentrations; samples run with subnanogram Hf amounts were corrected with 91500 run at 0.3 ng per analysis (3 ppb solution, 0.0042% 1s) and samples containing nanograms of Hf were corrected with 91500 run at 2.0 ng per analysis (20 ppb solution, 0.03- 0.11% 1s). A low-concentration reference material was used to determine session excess variance because it is most representative of the sample sizes evaluated. Next, an excess uncertainty related to the Lu concentration was determined. To do this, the long-term excess variance of 0.5, 1.0, and 2.0 ng neat analyses of 91500 were calculated to derive a simple relation between the Lu concentration and excess variance of 91500. This was applied as a propagation to the sample ^{176}Lu/^{177}Hf uncertainty, in quadrature. Finally, the long-term excess uncertainty for the entire analytical program was determined (0.013% 1s for 20 ppb Hf solution and 1.25% for 3 ppb Hf) and applied. The resulting ^{176}Lu/^{177}Hf uncertainties of the zircon samples were commonly ~2.5-3% for ≥0.3 ng Hf analyses, with a few outliers with uncertainties as high as ~6-13% for 0.1 ng Hf analyses. This level of ^{176}Lu/^{177}Hf uncertainty will comprise a negligible component of initial ε_{Hf} uncertainty for the vast majority of terrestrial applications but is significant for determining accurate age-corrected Hf signatures of Archaean and Hadean zircons (Fig. 9).

4.4 Importance of tuning the instrument for low oxides

In MC-ICP-MS isotope studies, the analytical set-up is usually optimized for maximum ion transmission. On a ThermoScientific Neptune Plus, this includes the addition of a Jet sample cone and an X skimmer cone. However, the resultant signal maximization also promotes increased oxide formation in the plasma and generally results in increased sensitivity to matrix composition and plasma loading, production of polyatomic interferences, and space-charge repulsion in the plasma. Payne et al. (2013) demonstrated the need for quantification of REE oxide production in plasmas in such cases. The production of oxides is problematic for several reasons. First of all, different elements form oxides at different rates, resulting in inter-element fractionation. Accurate Lu/Hf is necessary for the determination of Hf isotopic data corrected for age and therefore maintenance of low oxide conditions is critical. There are multiple REE oxides that directly interfere with masses of interest for Lu-Hf isotopic measurements, including those masses utilized for isobaric interference corrections. In particular, Gd and Dy oxides interfere with Yb and Hf mass bias corrections, resulting in spurious Hf isotope ratios at modest oxide levels (Payne et al., 2013) and/or for solutions with high concentrations of REEs (d'Abzac et al., 2016).

The possible impact of Gd and Dy oxide formation on the results presented here may be inferred using the relative values of oxide production of these elements to HfO^+. Payne et al (2013) demonstrated that the GdO^+ formation rate is ~3 times greater than the formation rate of HfO^+, when using desolvated solution methods. Of the various analytical sessions in our study, the rate of HfO^+ formation was <0.05% and was as low as 0.007%. This would suggest GdO^+ production rates of ~0.02-0.15% which, for the range of Yb/Hf compositions determined in this study, could result in a bias to higher epsilon Hf values by 0 – 0.8 epsilon units, but will be partly reduced by the complex interplay of the interference mass spectrum on the Yb correction. For the most part, this level of bias is well within the determined uncertainty range of our data and the agreement between the two cited methods of Yb correction would suggest that it is insignificant. The formation of MREE oxides therefore does not appear to have had a significant effect on the results under the run conditions described here. However, the role of MREE oxides with respect to the accuracy of interference corrections in zircon Hf isotope determinations should be considered when dealing with high-REE/Hf zircons.

4.5 Minimization of sampling volume during solution analysis and laser ablation

The lower limit of Hf required for solution analyses run with our methods is about 0.3 ng. Below this limit, the $^{180}Hf/^{177}Hf$ values diverge from the expected value (Fig. 3b) and the precision of the $^{176}Hf/^{177}Hf$ measurement exceeds 1 epsilon unit (Fig. 3a), a limit considered appropriate for most applications. 0.3 ng Hf equates to approximately 30 ng of zircon. For sessions with the highest detection efficiency, ~1 epsilon unit precision was achieved using only 0.2 ng Hf (~20 ng zircon). Running solution samples preconcentrated in 100 μl of liquid using a modified sample introduction protocol has therefore successfully increased the signal-to-noise ratio of the analysis and enabled shorter analysis durations, while maintaining precision.

Multiple analytical protocols were tested for laser ablation analyses to minimize the volume of zircon analyzed for the U-Pb and Lu-Hf systems. This resulted in a range of pit morphologies. To quantify the amount of material excavated with each type of analysis, a SEM was used to image and calculate the depth of the pits. Although the geometry of the pits is variable, we assume that they are perfectly cylindrical and calculate the volume of the pits using the maximum depth measured, and calculate the total mass of zircon ablated. Pit depths and estimates of maximum volume of ablated material are presented (Supplementary Table 6) for a variety of U-Pb spots as well as for Lu-Hf spots overlapping U-Pb spots (Fig. 2 for pit images). The 10-second Hf analyses ablated <16 μm deep, consuming around 40 ng of zircon. Ideally, a total ablation pit depth of 10 μm or less for both U-Pb and Hf analyses would increase the likelihood that a different age zone had not been penetrated during the Hf analysis. The time-resolved data reduction allowed for verification that only a single zone of Hf isotopic composition had been sampled (within the resolution of the data). Considering only the first half of each analysis therefore allows an assessment of the uncertainty achievable on a five second, <8 μm deep analysis consuming just 20 ng zircon. The highest uncertainty of the five-second analyses is ~2 epsilon Hf (Fig. 10). The ^{176}Lu/^{177}Hf uncertainties did not change appreciably. Therefore, the utility of analyses sampling just 8 μm deep in a five-second analysis depends on the degree of uncertainty acceptable for the considered geologic application and the nature of the sample (e.g. length scale and degree of zonation, detrital or non detrital). It is therefore feasible to subsample small volumes of zircon material, permitting combined Lu-Hf and U-Pb analysis of individual growth zones at a fine scale (~10 μm). These small-volume Hf laser ablation analyses could be coupled with U-Pb single pulse methods (e.g. Cottle et al., 2009) to result in ablation amounts of just ~18 ng of zircon (25 μm spot, 8 μm deep) for combined Lu-Hf and U-Pb isotopic information. Although there is then disparity between the volumes upon which the U-Pb and Lu-Hf information have been determined, it is reasonable to assume homogeneity at the 10-20 μm level and heterogeneity can still be detected using time-resolved analysis data processing, discarding the data point if necessary. It is notable that for analyses of 30-40 ng zircon, solution and laser ablation analyses resulted in the same uncertainties (Fig. 11) and that it is possible to handle and determine such small amounts of zircon by solution methods.

4.6 Moving forward with low-volume Lu-Hf analyses

The focus of this study is low-volume coupled Lu-Hf and U-Pb isotope analysis of zircon. The Lu-Hf solution method employed, namely the introduction of small amounts of material either manually or via the Cetac MVX-7100, is translatable to other minerals and isotope systems. Instead of focusing on the subdivision of complexly-zoned, high-[Hf] minerals such as zircon (or small baddeleyites, as in d'Abzac et al., 2016), our solution method can be applied to lower-[Hf] samples, such as bulk meteorite splits (e.g. Bast et al., 2015). In combination with a host of other analytical improvements, e.g. Jet sample cones and 10^{12} ohm resistors, the increase in SNR brought about by running 100 µL volumes and by quantifying blank size and its isotopic composition will facilitate measurement of smaller amounts of material at higher precision than previously managed. This will enable sampling of complex samples at a higher spatial resolution, including meteorites, whole rocks, garnet, and other minerals.

The most critical work for advancing low-volume zircon Lu-Hf studies via laser or solution methods will be technique development that increases Hf efficiency while maintaining low levels of oxide production. Beyond the consideration of the elements that are typically of interest (Hf, Lu, and Yb) in these studies when monitoring oxide formation, it is also advisable to monitor the levels of production of Gd and Dy oxides because these will impact the Yb and Hf mass biases, respectively. The formation of these oxides can be documented at the beginning and end of an analytical session using Gd, Dy- doped JMC475 Hf solutions. Additionally, synthetic zircons variably doped with REEs (MUNzirc; Fisher et al., 2011) can be used to monitor oxide production throughout an LA-ICP-MS session. The synthetic MUNzirc zircons are widely used in laboratories performing Lu-Hf laser ablation analyses.

The low-oxide production, high analyte efficiency approach in this study is also transferable to isotope systems other than Lu-Hf, particularly in cases for which oxide production levels must remain low, most notably for the Sm-Nd isotope system.

Additionally, the laser ablation methods of this study result in improved high-resolution sampling of zoned zircons, with combined U-Pb and Lu-Hf ablation amounts as low as 30 ng of zircon. The coupling of five-second Lu-Hf ablations with single pulse U-Pb work (Cottle et al., 2009), resulting in 25 μm spots 8 μm deep, will result in finer-scale coupled zircon analyses, something which is not achievable with conventional methods.

5. Conclusions

In this study, methods are established for coupled Lu-Hf and U-Pb isotope analyses of zircon, focusing on low-volume solution and laser ablation methods corresponding to 20-40 nanograms of zircon. These techniques enable the analysis of complex zircons in cases where age zonation could easily result in the decoupling of U-Pb and Lu-Hf isotope information, potentially producing spurious initial Hf isotopic results. Our reduced-volume laser ablation protocol provides an alternative to split-stream analysis and consumes less zircon. Consecutive U-Pb and Lu-Hf isotopic analyses are utilized and result in a total spot size and pit depth of 25 and 18 μm, respectively, thereby excavating just ~40 ng of zircon. We demonstrate that by integrating only part of the Hf isotope data, appropriate levels of uncertainty can be obtained on just ~20 ng total of ablated zircon. For our solution measurements, sample introduction protocols were optimized to consume just 100 μL of solution, resulting in a 10-fold decrease in required sample size over conventional approaches. This was achieved with comparable levels of uncertainty and total sample volume as measured by laser ablation, using just 0.3-0.4 ng of Hf while achieving uncertainties ~1 ε_{Hf}. These solution measurements can be conducted either manually or automatically, allowing for this method to become routine. By optimizing for low levels of oxide production instead of maximizing Hf detection efficiency, we conclude that Yb correction methods of neat zircon washes determined using either direct measurement of Yb mass bias or by pre-calibration of Yb mass bias to Hf mass bias are both suitable, with the latter approach providing more accurate data for high Yb/Hf samples. ^{176}Lu/^{177}Hf can also be accurately determined during the same sample analysis, increasing efficiency compared to conventional solution analysis approaches. Solution and laser ablation methods are demonstrated to utilize equivalent amounts of material, achieving the same uncertainty level (~1 ε_{Hf}) necessary for resolving complexity on the scale of 10-20 microns and therefore can yield meaningful results for complex zircons.

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Figure Captions

Figure 1. Representative CL images of Zimb-95-24 zircons with ablation spots (orange circles) or box rasters (orange squares) indicated. All scale bars are 100 µm.

Figure 2. SEM images of different laser ablation spot types of this study; scale bars are 20 µm and all analyses consisted of about 10 seconds of ablation. a) U-Pb analysis pit with a 25 µm spot and a 2.7 J/cm^2 fluence; b) U-Pb analysis pit with a 15 µm spot and a 2.7 J/cm^2 fluence; c) U-Pb analysis box raster with a 10 µm spot and a fluence of 3.2 J/cm^2; d) Lu-Hf analysis pit with a 25 µm spot and 6.5 J/cm^2 fluence.

Figure 3. For zircon solution analyses in this study, the relationship between the approximate nanograms of Hf analyzed and: a) measurement uncertainty (in epsilon Hf units, excluding propagation for systematic and excess uncertainty); b) ^{180}Hf/^{177}Hf; and c) ^{178}Hf/^{177}Hf. The shift in ^{180}Hf/^{177}Hf at lower Hf concentration motivates our lower limit cut-off of 0.3 ng Hf, which is indicated by the dashed gray line (see Sections 4.1 and 4.5). Analyses are color-coded by analytical session to demonstrate the shift in analytical uncertainty under different tuning conditions.

Figure 4. Precision of laser ablation analyses of natural sample Zimb-95-24, for: a) U-Pb dates as a function of U concentration, indicating little compromise in the measured uncertainty compared to more conventional ablation approaches; and b) ^{176}Hf/^{177}Hf as a function of Yb/Hf, demonstrating that the uncertainty is not a function of the magnitude of correction of the Yb interference. In part b, epsilon Hf units are indicated with horizontal lines and black symbols represent the 2SE% of the analyses while the gray symbols represent full systematic uncertainty propagation (2S%).

Figure 5. Interference- and mass bias-corrected ^{176}Hf/^{177}Hf results for zircon reference material 91500 during this study, demonstrating that the results are indistinguishable for zircon solutions with and without separation of isobaric interferences. Neat solutions are indicated by gray symbols and solutions that underwent Hf-HREE separation chemistry are indicated by white symbols. Symbol shape denotes Hf concentration of analysis. The weighted average, 2SE, and MSWD of each population are listed. The Yb interference correction was empirically-derived with ^{176}Yb/^{173}Yb = 0.79435-0.79455, depending on the session.

Figure 6. Comparison of ^{176}Hf/^{177}Hf results using two different Yb correction methods (x-axis: calibrated to standards and Hf mass bias, and y-axis: by directly measuring the ^{173}Yb/^{172}Yb of the solution). A 1:1 line is plotted for reference and the color of analysis symbols is scaled for ^{176}Yb/^{177}Hf (color bar, at right). The majority of the samples conform to a 1:1 relationship; which validates both Yb correction methods. In a), the exception is a zircon spot analysis with unusually high ^{176}Yb/^{177}Hf, which is discussed in the text.

Figure 7. a) Comparison of two methods of Yb correction for analyses of 20 ppb Hf Mud Tank zircon with variable amounts of admixed Yb above natural Yb levels (^{176}Yb/^{177}Hf ~0.0004) in Mud Tank. A stock solution of one zircon dissolution was used for these analyses. The isotopic variability following each Yb correction method is of greater magnitude for higher Yb beams. A 1:1 line is plotted for reference. The accepted value is 0.282507± 3 and is indicated by a gray box (Woodhead and Hergt, 2005). b) The deviation

from the accepted value for Mud Tank zircon of Yb-corrected $^{176}Hf/^{177}Hf$ resulting from Yb correction with measured Yb (square symbols) and from Yb correction using precalibration of the Hf mass bias (circle symbols), plotted against Yb signal of Yb-doped Mud Tank solutions. c) The difference between $^{176}Hf/^{177}Hf$ results using the two Yb correction methods plotted against measured Yb signal (V), indicating an increase in the difference between the two methods with increasing Yb concentration.

Figure 8. Uncertainty in $^{176}Hf/^{177}Hf$ resulting from Yb correction using measured Yb (square symbols) versus precalibration using Hf mass bias (circle symbols), plotted against measured Yb beam (V) (for analyses with <0.04 V ^{173}Yb) of Yb-doped JMC solutions as well as neat and variably Yb-doped zircon 91500 and Mud Tank solutions of this study.

Figure 9. Effect of 20% variation of measured $^{176}Lu/^{177}Hf$ of zircons of varying age (0.5, 1.0, 2.5, and 4.0 Ga). If the $^{176}Lu/^{177}Hf$ is mismeasured by 20%, the absolute shift in epsilon Hf will be about 0.6 epsilon units for most 4 Ga zircons but will be within analytical uncertainty for most zircons younger than about 2.5 Ga. This illustrates that the age correction for Hf ingrowth matters most for Archean and Hadean zircons that have relatively high HREE/Hf.

Figure 10. Comparison of laser ablation results for a) $^{176}Hf/^{177}Hf$ uncertainties and b) $^{176}Lu/^{177}Hf$ uncertainties of 10 and 5 second integrations of the same analysis.

Figure 11. The relationship between measurement uncertainty (in epsilon Hf units) and the approximate total nanograms of Hf analyzed in laser ablation analyses (black circles) of Zimb-95-24 zircons and zircon reference materials (assuming 35 ng of zircon ablated and Hf concentrations normalized relative to ~0.64 Hf wt% of zircon 91500; Belousova et al., 2002). The gray field in the background is from solution analysis of granitic zircons in this study (Fig. 3a). The degree of uncertainty is comparable for solution and laser ablation methods.

Supplementary Figure 1. Schematic showing how pit depths were calculated. The sample stage was tilted to 40 degrees and therefore the true depth is equal to the apparent depth divided by sine of 40 degrees (m=apparent depth, d=true depth).

Supplementary Figure 2a. Validation results of secondary reference material zircon 91500 for laser ablation analyses. The analysis spot type is denoted in each plot. The accepted $^{207}Pb/^{206}Pb$ age for this sample is 1065.4 ± 0.3 Ma (Wiedenbeck et al., 1995).

Supplementary Figure 2b. Validation results of secondary reference material zircon Plešovice for laser ablation analyses. The analysis spot type is denoted in each plot. Configurations A and B refer to collection schemes in Table 3. The accepted $^{206}Pb/^{238}U$ age of this sample is 337.13 ± 0.37 Ma (Sláma et al., 2008).

Supplementary Figure 2c. Lu-Hf laser ablation validation results of secondary zircon reference materials Mud Tank and Plešovice. The weighted means are within uncertainty of the accepted compositions (Woodhead and Hergt, 2005; Sláma et al., 2008), $^{176}Hf/^{177}Hf$ = 0.282514 ± 5 (Mud Tank zircon; MSWD 2.3, n=55) and $^{176}Hf/^{177}Hf$ = 0.282484 ± 4 (Plešovice; MSWD 1.7, n=54).

Supplementary Figure 3. Weighted mean mass bias-corrected $^{176}Hf/^{177}Hf$, $^{178}Hf/^{177}Hf$ and $^{180}Hf/^{177}Hf$ results of zircon reference material 91500 run at 40, 20, and 3 ppb Hf. Symbol shape denotes Hf concentration of analysis. Neat solutions are indicated by gray symbols and solutions that underwent Hf-HREE separation chemistry are indicated by white symbols. There are no significant differences in the measured $^{176}Hf/^{177}Hf$, $^{178}Hf/^{177}Hf$ and $^{180}Hf/^{177}Hf$ of purified zircon Hf and neat solutions.

Supplementary Figure 4. $^{180}Hf/^{177}Hf$ versus $^{178}Hf/^{177}Hf$ of Mud Tank solution analyses. Symbol color corresponds to concentration of Yb as in Figure 7.

Supplementary Figure 5. Regression of $^{176}Lu/^{177}Hf$ versus ppb Hf for a) Lu-doped 91500 solution; b) Lu-doped Mud Tank solution; and c) undoped 91500 solution analyses; all of which document a shift of ~0.2% per ppb Hf in the analysis solution. In c, the 91500 solutions analyzed at varying concentration are self-normalized to the 20 ppb concentration analyses.

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