Hf isotopic compositions of the standard zircons and baddeleyites used in U–Pb geochronology

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Abstract

Zircon and baddeleyite U–Pb geochronological dating is widely used in solid Earth sciences and the advent of rapid in-situ methods of analysis, such SIMS and ICP-MS, has re-emphasized the importance of having uniform standards. Recently, it has been shown that Hf isotopic data can provide important information on these minerals since they contain high concentrations of Hf, but have low Lu/Hf ratios, which results in negligible age correction. However, the complex internal structures that result from multiple thermal events, such as inherited cores and metamorphic overgrowths, require that the Hf isotopic data be measured with high spatial resolution. However, the isobaric interferences of ^{176}Yb and ^{176}Lu on ^{176}Hf hamper the precise determination of the ^{176}Hf/^{177}Hf ratio during in-situ laser ablation MC-ICPMS analysis. It is shown here that mass biases of Yb (β_{Yb}) and Hf (β_{Hf}) change with time during analyses and behave differently for solutions and solid material. Therefore, it is suggested that the mean β_{Yb} value of the individual spot be used to obtain the precise isotopic composition for in-situ zircon and baddeleyite Hf isotopic analyses. For low Yb/Hf (^{176}Yb/^{177}Hf < 0.001) zircon and baddeleyite, the different methods used to obtain the β_{Yb} value have little effect on the accuracy of the Hf isotopic composition. However, the appropriate Yb isotopic abundance is necessary for high Yb/Hf (^{176}Yb/^{177}Hf > 0.001) zircons and baddeleyites, since the interference of ^{176}Yb on ^{176}Hf is significant. Using the mean β_{Yb} value of the individual spot and newly published Yb isotopic abundance data, six standard zircons and two standard baddeleyites, have been investigated using a Neptune MC-ICPMS, with 193 nm laser. For zircons, the obtained ^{176}Hf/^{177}Hf ratios are 0.282307±31 (2SD) for 91500, 0.282680±31 (2SD) for TEMORA, 0.281729±21 (2SD) for CZ3, 282177±17 (2SD) for CN92-1, 0.282983±17 (2SD) for FM0411, and 281234±11 (2SD) for Phalaborwa. The baddeleyites from Phalaborwa and SK10-2 have ^{176}Hf/^{177}Hf ratios of 0.281238±12 and 0.282738±13 (2SD). These results agree well with the values obtained by the solution method and indicate that these standards have different Hf isotopic compositions, in which the extremely low ^{176}Lu/^{177}Hf and ^{176}Yb/^{177}Hf values of CZ3 zircon and Phalaborwa baddeleyite make them excellent standards for machine calibration during in-situ zircon Hf isotopic measurement, with the other standards being more suitable for the development of the correction method.
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1. Introduction

It has been recognized that the zircon ($ZrSiO_4$) Lu–Hf isotopic system is a powerful tool to decipher crust and mantle evolution of the Earth (Kinny and Maas, 2003; Harrison et al., 2005; Hawkesworth and Kemp, 2006).

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Zircon normally contains 0.5–2 wt.% Hf, which can be analyzed relatively easily and results in an extremely low Lu/Hf ratio (normally $^{176}Lu/^{177}Hf$ ratio<0.002) and, subsequently, negligible radiogenic growth of ^{176}Hf by beta decay of ^{176}Lu. Therefore, the $^{176}Hf/^{177}Hf$ ratio of zircon can be regarded as the initial value when it crystallized. Zircon also has a high resistance to later thermal events, for example, the oldest rock so far identified is about 3.8 Ga, but the most ancient zircon preserved is 4.4 Ga (Wilde et al., 2001). Experimental calibration has shown that the zircon Hf closure temperature is ∼200 °C higher than that of Pb (Cherniak et al., 1997a,b; Cherniak and Watson, 2000), indicating that Hf has remained isotopically closed during most of the later thermal events, even during high-grade metamorphism. Furthermore, zircon is a common accessory mineral in a wide range of rocks, and commonly preserves a very complex growth history. Its inherited cores and metamorphic overgrowths can be used to identify and distinguish various protoliths and geological processes from which the zircon was formed or later modified. Lastly, zircon is also an important mineral for U–Pb geochronology, O isotope and trace elemental analyses; all of these data combined together can provide invaluable information on crust and mantle evolution.

As with zircon, baddeleyite (ZrO_2) also has high Hf concentrations and is an important mineral for U–Pb and Hf isotopic analyses (Heaman and LeCheminant, 1993; Scharer et al., 1997; Bodet and Scharer, 2000; Scherer et al., 2001; Soderlund et al., 2004, 2005). However, being different from zircon, baddeleyite occurs mostly in mafic–ultramafic rocks (such as kimberlite and dolerite), mantle xenoliths and rarely in metamorphic rocks (Heaman and LeCheminant, 1993). Considering its crystallization under SiO_2 undersaturated conditions, baddeleyite cannot be formed by contamination of felsic crust, and hence can provide the initial Hf isotopic ratio of the mafic–ultramafic magma or mantle protolith. In addition, baddeleyite is unstable and would transform into zircon during later thermal/metamorphic events (Davidson and van Breemen, 1988). In this case, the baddeleyite–zircon association could provide information on both magmatism and metamorphism. Rarely, metamorphic baddeleyite can provide information about the metamorphic process (Rubatto and Scambelluri, 2003).

However, the difficulty of separating Zr from Hf by chemistry and the high ionization potential in mass spectrometers hampers the analysis of Hf. Generally, Hf isotope measurements can be carried out by TIMS (Thermal Ionization Mass Spectrometry) and hot-SIMS (Secondary Ion Mass Spectrometry) through dissolving the bulk grain and separating the pure Hf element from other interfering and matrix elements (Salters, 1994; Blichert-Toft et al., 1997). But this purification process is laborious and time-consuming, and requires special skills, although much progress has occurred recently (Bizzarro et al., 2003). Moreover, any spatial information of Hf isotope variation in zircon cannot be achieved because the whole grain is destroyed during this process.

Kinny et al. (1991) firstly attempted zircon in-situ Hf analysis using the SHRIMP (Sensitive High Resolution Ion Micro Probe) technique. With a ∼25 μm spot size, the small amount of analytical material, low ionization efficiency and single-collector ion counting meant the precision of the obtained Hf isotopic ratio was one order of magnitude less than that obtained by the TIMS technique of bulk analyses (Kinny et al., 1991). Consequently, this method is not widely adopted (Kinny and Maas, 2003). In addition, the expensive equipment, maintenance, and limited availability of machine time are also big obstacles for its general use. The advent of LA-MC-ICPMS (Laser Ablation Multi-Collector Inductively Coupled Plasma Mass Spectrometry) technique in recent years is proving to be an ideal tool for in-situ Hf isotopic ratio measurement on single grains of zircon (Thirlwall and Walder, 1995; Griffin et al., 2000, 2002; Machado and Simonetti, 2001; Woodhead et al., 2004; Iizuka and Hirata, 2005). The aerosol of samples ablated by the high energy laser is carried by Ar or He carrier gas into the ICP torch where almost all elements in the plasma are ionized at temperature higher than 8000 °C. The precision and accuracy of Hf isotope ratios determined by LA-MC-ICPMS can not only compare with those of TIMS, but the sample preparation is much easier and efficiency of analyses is much higher than those of TIMS as well. By the use of Back Scattered Electron (BSE) or Cathodoluminecence (CL) images of zircon, the Hf isotope ratios of zoned zircon can also be obtained.

However, standard materials are generally needed to monitor machine drift and are used for external calibration during in-situ analyses by LA-MC-ICPMS and SIMS. Undoubtedly, standard zircons and baddeleyites used in U–Pb geochronology, such as SHRIMP, TIMS and LA-ICPMS techniques, are an ideal choice to meet this requirement. However, their suitability for standard Hf material has been little investigated. To date, although there are numerous papers on the Hf compositions of standard zircon 91500 (Wiedenbeck et al., 1995; Amelin et al., 2000; Xu et al., 2004; Woodhead et al., 2004; Iizuka and Hirata, 2005; Nebel-Jacobsen et al., 2005; Harrison et al., 2005; Qi et al., 2005; Hawkesworth and Kemp, 2006) and TEMORA (Xu et al., 2004; Woodhead et al., 2004; Harrison et al., 2005; Qi et al., 2005; Hawkesworth and

Kemp, 2006), others are poorly known, although CZ3 and CN92-1 have been reported by Xu et al. (2004) and Kemp et al. (2006), and an additional 5 standards (266, FC-1, Mud Tank, Monastery and QGNG) have been reported by Woodhead and Hergt (2005) in order to test their suitability as standards. As suggested by Woodhead and Hergt (2005), more data and inter-laboratory comparisons are necessary to evaluate the suitability of the above zircons as standard Hf material. In this paper, we present new Hf isotopic analyses for zircon 91500, TEMORA, CZ3 and CN92-1 based on one-year data accumulation in our laboratory, combined with some new analyses of Phalaborwa zircons and baddeleyite. In addition, the suitabilities of a zircon megacryst (FM0411) from basalt and baddeleyites from gabbro are also evaluated for use as in-house Hf standards. To achieve this, various protocols were evaluated for the isobaric interference correction of ^{176}Yb and ^{176}Lu on ^{176}Hf and an updated correction method has been developed for data acquisition.

2. Instrumentation

All our measurements were carried out using a Neptune MC-ICPMS hosted at the Institute of Geology and Geophysics, Chinese Academy of Sciences in Beijing. This machine is a double focusing multi-collector ICP-MS and has the capability of high mass resolution measurements in multiple collector modes. Detailed descriptions for this instrument can be found in Weyer and Schwieters (2003). Due to the zoom design of ion optical magnification, a large mass dispersion of 810 mm and an increased focal depth is achieved. The maximum distance between the outermost cup positions corresponds to a relative mass range of 17%. The present instrument is equipped with eight motorized Faraday cups and one fixed central channel, where the ion beam can be switched between a Faraday detector and an SEM detector. In-situ monitoring of the detector position directly at the optical bench of the multi-collector ensures precise and reproducible cup positioning. The external precision of measurements is further improved by utilizing a rotating amplifier concept, in which all Faraday cups are sequentially connected to all amplifiers, canceling out any gain calibration errors.

An ArF excimer laser ablation system was used for laser ablation analysis. This Geolas CQ laser ablation system includes: a) Lamda Physik Excimer laser COMPex 102 operated at 193 nm with a pulse width of ca. 15 ns; b) Digitally-based software package from Digilaz™; c) Microstepping translation stage with a 0.25-micron step size. The 193-nm UV laser has much higher photon energy than any other laser and results in a denser and more effective thermomechanical shock, with negligible thermal heating, which can lead to melting of the sample instead of the mechanical shock required for ablation. The combined affects of superior energy transfer, absorption, and conversion allow a low power UV laser beam (only a few mJ) to produce more transportable particulate materials from a smaller crater than an IR laser of much higher power (>200 mJ) can produce from a lager crater. The very short wavelength of 193 nm leads to less fractionation during ablation than the traditional 266 and 213 UV wavelength. The Geolas CQ system has the laser homogenized by two 18×18 small lens homogenizers and can drill a perfectly cylindrical and flat-bottomed pit on the surface of the sample. Seven different spot sizes of 3, 6, 16, 32, 63, 94 and 127 μm can be accessed via rotating a built-

Table 1
Laser ablation and LA-MC-ICPMS instrumentation parameters

Neptune MC-ICPMS	
Instrument	Neptune
RF forward power	1303 W
RF reflected power	<3 W
Cooling gas	15.2 l/min
Auxiliary gas	0.6 l/min
Sample gas	~ 1.2 l/min (optimized daily)
X-position	~ −0.4 mm (optimized daily)
Y-position	~ −0.5 mm (optimized daily)
Z-position	~ 0.5 mm (optimized daily)
Extraction	−1997 V
Focus	−656 V
Detection system	Nine Faraday collectors
Acceleration voltage	10 kV
Interface cones	Nickel
Spray chamber	Glass cyclonic
Nebulizer type	Micromist PFA nebulizer
Sample uptake rate	50 μl/min
Uptake mode	Free aspiration
Instrument Resolution	~ 400 (low)
Mass analyzer pressure	$4–8 \times 10^{-9}$ mbar
Typical sensitivity on ^{180}Hf	~ 16 V/ppm (10^{-11} Ω resistors)
Sampling mode	One run=9 blocks of 10 cycles for solution
	One run=1 block of 200 cycles for laser
Integration time	4.194 s for solution
	0.131 s for laser
Baseline/background determination	ca. 1 min on peak in 2% HNO_3
Laser ablation system	
Instrumentation	Lambda Physik COMpex
Bean	UV 193 (ArF excimer)
Laser energy	~ 100 mJ/cm^2
Spot size	31.5–94.5 μm
Pulse rate	5–15 Hz
He gas to cell	0.8 to 0.9 l/min (optimized daily)

in aperture wheel. However, in this study, only 32-, 63- and 94-μm spot sizes were applied, due to the limitation of zircon grain sizes and the need to obtain sufficient material for precise analysis. The laser repetition rate was operated at 6–15 Hz for higher signal intensity. Helium gas was flushed into the sample cell to minimize aerosol deposition around the ablation pit and to improve transport efficiency (Kuper and Brannon, 1992; Eggins et al., 1998; Günther and Heinrich, 1999; Jackson et al., 2004). The operational settings used in this study are summarized in Table 1.

3. Analytical method

3.1. Measurement of standard solutions

The JMC 475 standard solution with 200 ppb Hf was used for evaluating the reproducibility and accuracy of the instrument during Hf isotope measurement. Signals of Hf isotopes were measured in static mode. One run of Hf isotope ratio for JMC 475 standard solution consists of a baseline measurement at half mass positions and 90 cycles of sample signal collection. The 90 cycles of signals are divided into 9 blocks so as to complete the 9 rotations of the amplifiers connected to the Faraday cups, in order to eliminate amplifier gain errors between different amplifiers. The integration time of signal for one cycle was set at a value of 4 s and the total time of one measurement lasted about 10 min and consumed about 100 ng of sample for each measurement.

The results of ^{176}Hf/^{177}Hf for JMC475 Hf standard solution over one year are shown in Fig. 1. Its average ^{176}Hf/^{177}Hf ratio, determined using measurement conditions described above, is 0.282158 ± 16 ($n=140$, 2SD) normalized to ^{179}Hf/^{177}Hf$=0.7325$ using an exponential law for mass bias correction. This value is identical to that recommended by Blichert-Toft et al. (1997) and Nowell et al. (1998).

We also present the ^{176}Hf/^{177}Hf ratio of our in-house standard solution JMC14374 which was purchased from Alfa Aesar of Johnson Matthey Company (stock no. 14374, plasma standard solution). This standard solution was delivered in August, 2003 and has not been certified for Hf isotope abundances. The average ^{176}Hf/^{177}Hf value of this standard solution from 167 measurements over two years is 0.282189 ± 19 ($n=167$, 2SD, Fig. 2a). To find a suitable signal collection method for laser ablation analysis on a single zircon whose endurance is much shorter than that of the solution, we have tried a wide range of integration times and number of collection cycles. Since the integration times of our Neptune machine are designed at 0.131, 1, 4 and 8 s, a signal collection model for one block with 200 cycles, in which one cycle has 0.131 s integration time and total time for one measurement lasts about 30 s, was the most optimal model for laser ablation analyses, since more data were obtained and less time is required. Using this model, 159 analyses of JMC14374 over two years yield a weighted average ^{176}Hf/^{177}Hf value of 0.282180 ± 39 (2SD, Fig. 2b). This value is the same as that in the normal model, except for a factor of
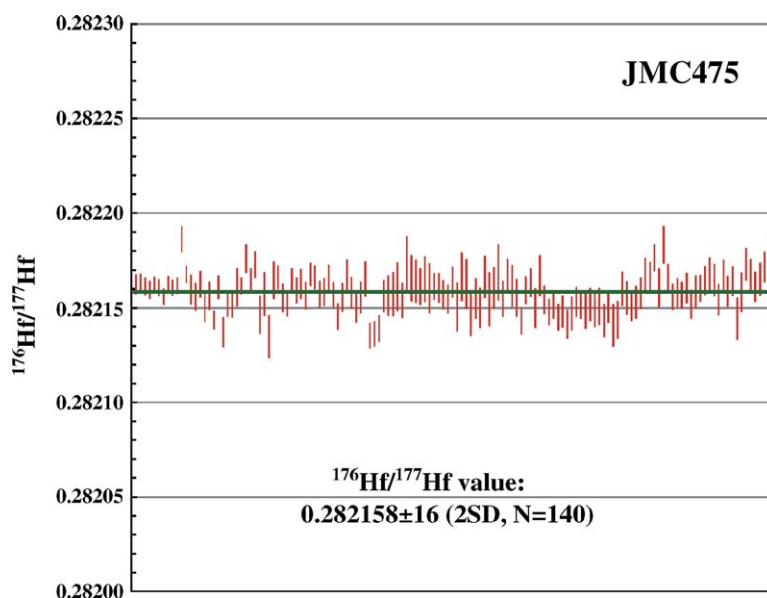

Fig. 1. Hf isotopic analyses of JMC475 standard solution over the past two years. The 140 analyses yield a ^{176}Hf/^{177}Hf value of 0.282158 ± 18 (2SD), identical to the result recommended by Blichert-Toft et al. (1997) and Nowell et al. (1998), within uncertainties.
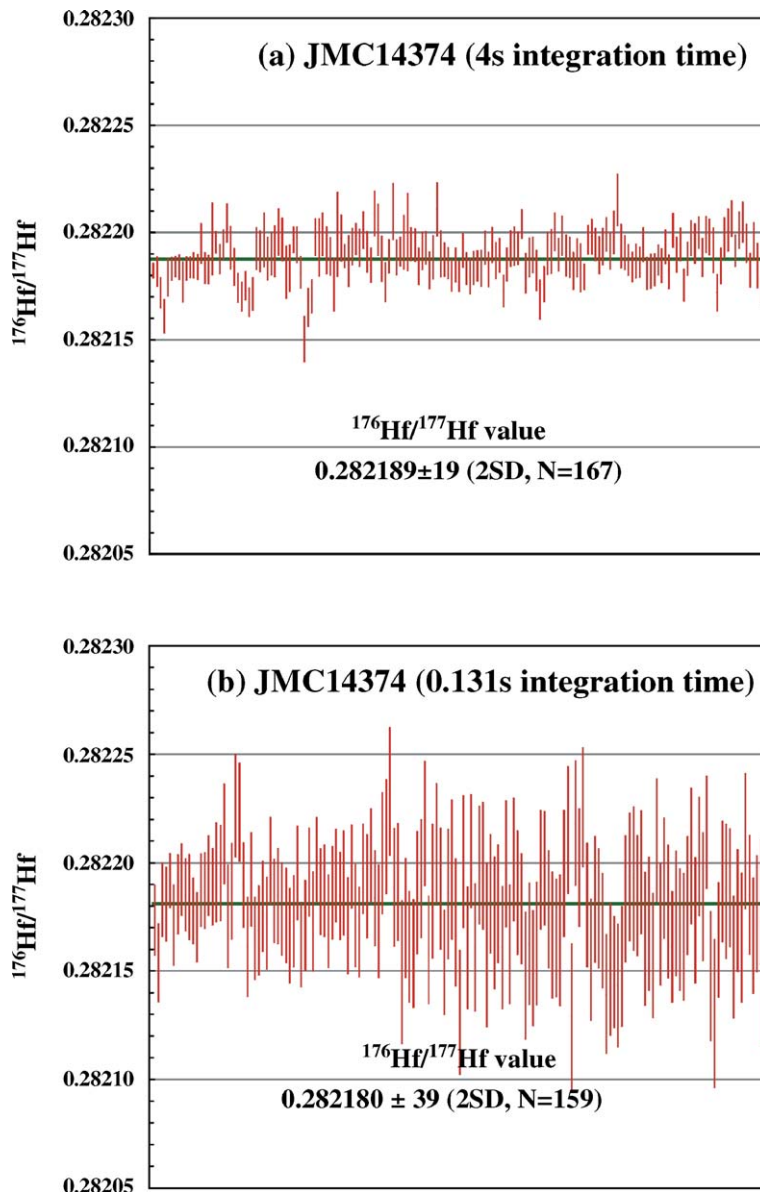
Fig. 2. Hf isotopic analyses of JMC14374 standard solution with integrated times of 2 and 0.131 s, respectively. For the former case, 167 sets of analyses give a [176]Hf/[177]Hf value of 0.282188±14 (2SD). For the latter case, which is more suitable for laser ablation analyses, 58 sets of analyses give a [176]Hf/[177]Hf value of 0.282180±28 (2SD), identical within uncertainties.

two lower precision, which indicates that this signal collection model could be used for laser ablation analysis for zircon Hf isotope measurements and will not change the true value of $^{176}Hf/^{177}Hf$ of zircons analyzed.

3.2. Isobaric interference corrections of Lu and Yb

During in-situ zircon and baddeleyite Hf analyses, isobaric interference corrections of ^{176}Lu and ^{176}Yb on ^{176}Hf have to be precisely processed. Due to the extremely low $^{176}Lu/^{177}Hf$ in zircon (normally <0.002),

the isobaric interference of ^{176}Lu on ^{176}Hf is negligible (Iizuka and Hirata, 2005). However, the interference of ^{176}Yb on ^{176}Hf must be carefully corrected since the contribution of ^{176}Yb to ^{176}Hf could profoundly affect the accuracy of the measured $^{176}Hf/^{177}Hf$ ratio.

According to the literature, five kinds of correction protocols have been applied in laser ablation analyses. One method (Model 1) is by adding Yb solution into JMC475 standard, and then using a modified $^{176}Yb/^{173}Yb$ or $^{176}Yb/^{172}Yb$ value that gives a correct $^{176}Hf/^{177}Hf$ ratio (Thirlwall and Walder, 1995; Griffin et

al., 2000, 2002). After measuring the $^{176}Yb/^{173}Yb$ value of a highly pure Yb standard solution, Machado and Simonetti (2001) obtained the β_{Yb} value via comparison with the recommended $^{176}Yb/^{173}Yb$ ratio of 0.78761 by Blichert-Toft et al. (1997) (Model 2). Considering that the mass bias of Yb (β_{Yb}) changes throughout analysis time and varies with the nature of the sample matrix, Chu et al. (2002) advocated determining the relationship between the true β_{Yb} and β_{Hf} values from solution (Model 3). However, Woodhead et al. (2004) proposed that the β_{Yb} value can be directly obtained from the $^{173}Yb/^{171}Yb$ ratio on the zircon sample itself (Model 4). Subsequently, Iizuka and Hirata (2005) proposed to use the mean $^{173}Yb/^{171}Yb$ ratio in the same spot to calculate the β_{Yb} value (Model 5), and then the signal intensity of ^{176}Yb was calculated based on the signal intensity of ^{173}Yb and the calculated β_{Yb}.

In our previous study (Xu et al., 2004), the mixtures of Yb and Hf standard solution (JMC14374) were measured and an empirical relationship of $\beta_{Yb} = 0.8725 \times \beta_{Hf}$ is obtained. However, when all our solution data are combined together, the obtained relationship is $\beta_{Yb} = 0.8947 \times \beta_{Hf}$, or $\beta_{Yb} = 0.9632 \times \beta_{Hf} + 0.1333$ if a more general unconstrained empirical regression is constructed (Fig. 3). It is clear that β_{Yb} vs. β_{Hf} has a non-zero Y-intercept and the relationship changed with analysis time, indicating that the β values cannot be assumed to be constant through time. It is also shown that the β_{Yb} and β_{Hf} values of zircon standard TEMORA by laser
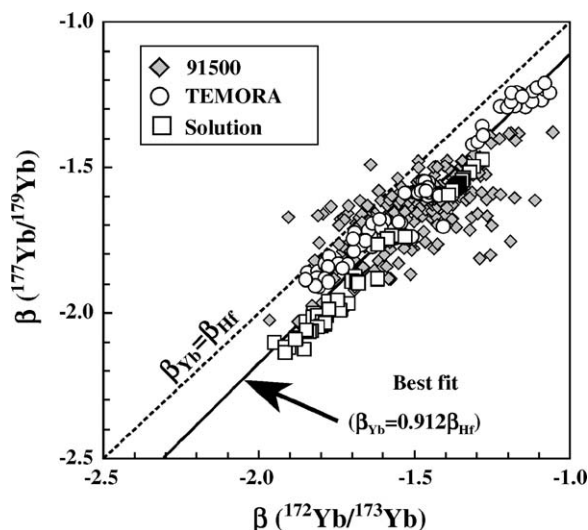
ablation deviate from the $\beta_{Yb} = \beta_{Hf}$ line, indicating that β_{Yb} must be determined separately from that of β_{Hf}. Moreover, the relationships of β_{Yb} and β_{Hf} values between the solution and TEMORA zircon samples are significantly different; no single mathematical formulation can adequately describe the variation observed both within and between individual analytical sessions as suggested by Woodhead et al. (2004). Therefore, β_{Yb} value based on the solution data is not applicable to the zircon in-situ ablation analyses.

To evaluate the difference between the individual β_{Yb} value of Woodhead et al. (2004) (Model 4) and mean β_{Yb} value of Iizuka and Hirata (2005) (Model 5) for Yb correction during in-situ laser analyses, a single day of analyses of three zircon standards, TEMORA, 91500 and CZ3 is used for comparison. As shown in Fig. 4, the obtained $^{176}Hf/^{177}Hf$ precision of individual analyses using Model 4 is half that of Model 5. However, the weighted average values of $^{176}Hf/^{177}Hf$ under different models are similar within uncertainty. Even for CZ3, the extremely low Yb concentration results in a large error of β_{Yb} value, but the interference of ^{176}Yb to ^{176}Hf is also limited. Therefore, in our following analyses, we apply the mean β_{Yb} value in the same spot for the interference correction of ^{176}Yb on ^{176}Hf in order to get precise data for the individual analysis.

It is noted that the under- or over-estimation of the β_{Yb} value undoubtedly affect the accurate correction of ^{176}Yb and thus the obtained $^{176}Hf/^{176}Hf$ ratios (Woodhead et al., 2004). As shown in Fig. 5a, the uncertainties of the obtained $^{176}Hf/^{176}Hf$ ratios for TEMORA are positively related to the uncertainties of the calculated β_{Yb} and β_{Yb} values, indicating that the analytical uncertainties of the Hf isotopic compositions come mainly from the uncertainties of calculated β_{Yb} and β_{Yb} values. It is also shown that the uncertainties caused by β_{Yb} are much higher than those caused by β_{Hf} (Fig. 5b). However, it should be pointed out that these derivations, within the analytical precisions of different spot sizes, should be considered as the maximum errors caused by β uncertainty. Therefore, it is concluded that the mean β_{Yb} value obtained from zircon itself could provide accurate correction of the ^{176}Yb interference to ^{176}Hf.

However, the above method using mean β_{Yb} value to correct the interference of ^{176}Yb to ^{176}Hf might be problematic for complex zircons. When drilling through zoned zircons which have heterogeneous REE distributions, the Yb bias may change during a single run. In this case a bulk Yb bias will provide a potentially inaccurate correction. Our suggestion for this situation is using the plot of individual Yb bias versus time within a given run to sort the different parts, and then correct the

Fig. 3. Mass bias correlation between β_{Hf} ($^{177}Hf/^{179}Hf$) and β_{Yb} ($^{172}Yb/^{173}Yb$) for solution (JMC14374 standard solution 1 ppm +0.2 ppm Yb) and TEMORA. It is indicated that β_{Yb} and β_{Hf} changed during analytical time and show significant matrix effects.
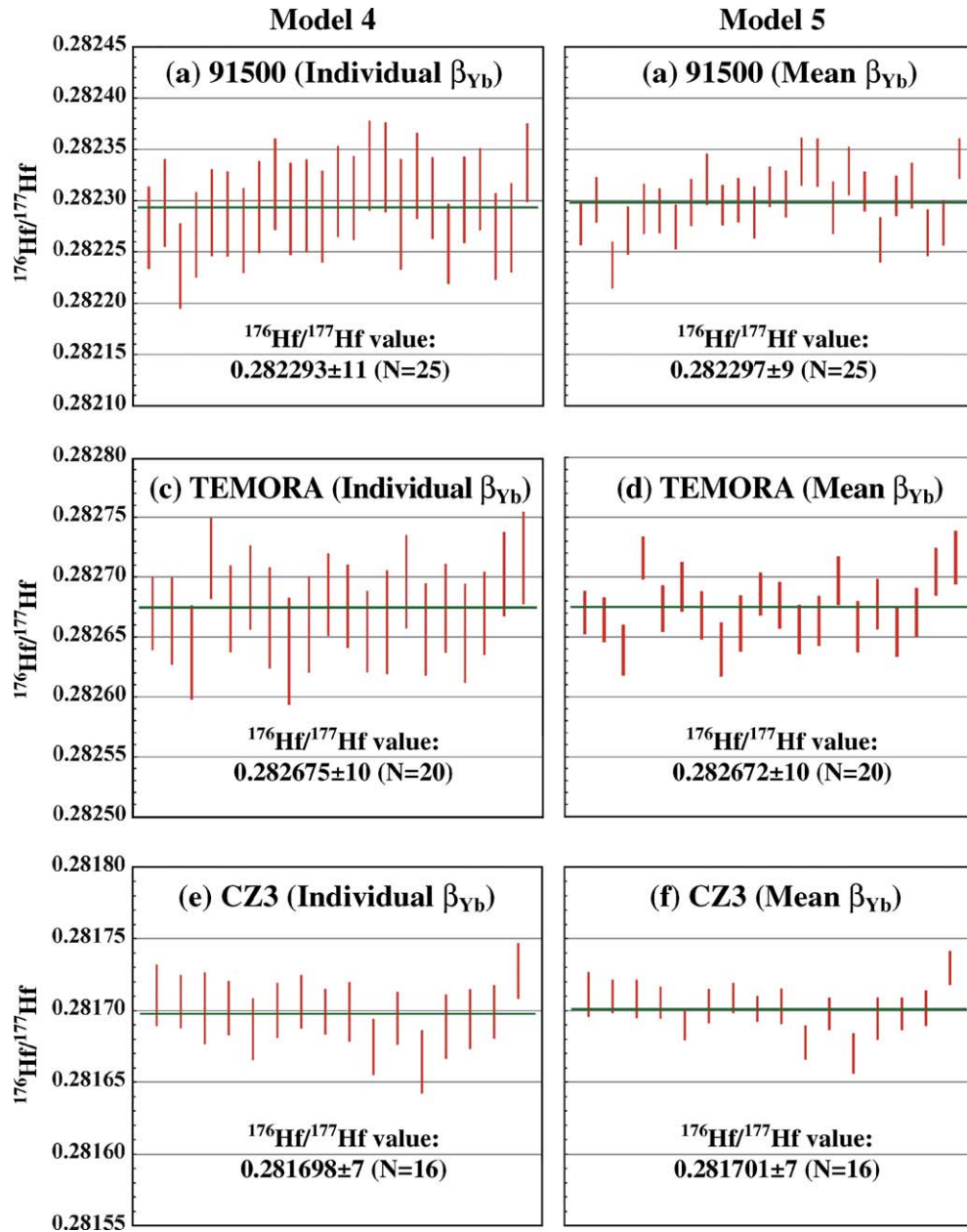
Fig. 4. ^{176}Hf/^{177}Hf corrections using individual β_{Yb} and mean β_{Yb} values for different zircons during in-situ laser ablation. It is shown that the β_{Yb} value obtained by different methods has little effect on the precision and accuracy of the ^{176}Hf/^{177}Hf ratio.

interference according to their average β_{Yb} values. Fortunately, this situation did not exist for the standard materials studied in this paper since they show homogeneous REE compositions.

3.3. Yb isotopic composition

Before we could get accurate Hf isotopic data, an accurate and precise Yb isotopic composition is needed.

Unfortunately, uniformly accepted Yb isotopic abundance values are not available, although much work has been done on this aspect (Fig. 6, McCulloch et al., 1977; Holliger and Devillers, 1981; DeBievre and Taylor, 1993 ; Chu et al., 2002; Lapen et al., 2003; Segal et al., 2003; Thirlwall and Anczkiewicz, 2004; Vervoort et al., 2004; Amelin and Davis, 2005), which has led different laboratories to apply different values for the interference correction during laser ablation analyses (Thirlwall and
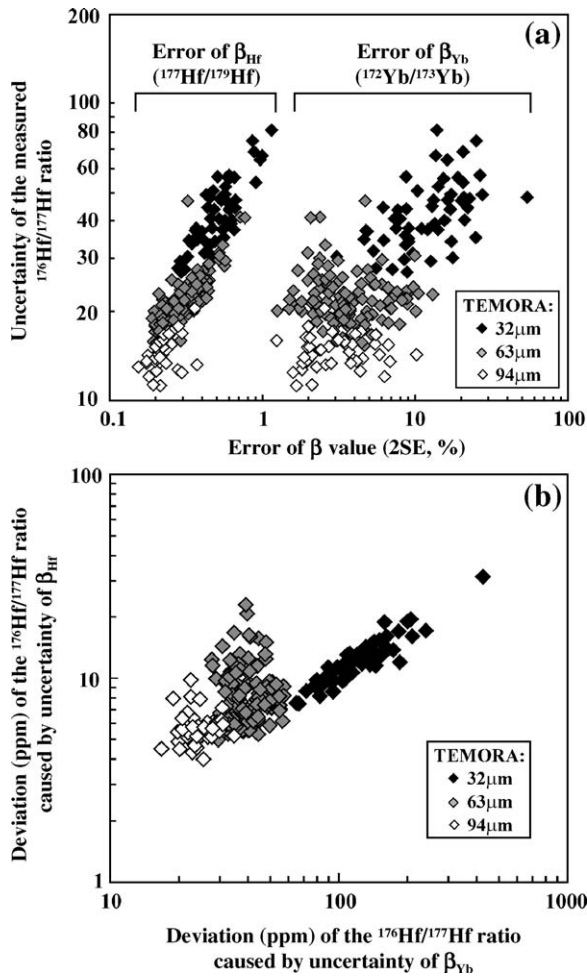
Fig. 5. (a) Relationship between the uncertainties of the measured $^{176}Hf/^{177}Hf$ ratios and errors of calculated β_{Yb} and β_{Hf} values for TEMORA. (b) Variations of the potential loss of accuracy caused by deviations of calculated β_{Yb} and β_{Hf} values.

Walder, 1995; Griffin et al., 2000, 2002; Woodhead et al., 2004; Iizuka and Hirata, 2005; Harrison et al., 2005; Kemp et al., 2006). In order to solve this uncertainty, we have calculated the $^{176}Hf/^{177}Hf$ ratios of 91500 and TEMORA for those analysis spots in Fig. 4 using different $^{176}Yb/^{172}$ ratios (Fig. 7). It can be seen that the obtained $^{176}Hf/^{177}Hf$ ratios of 91500 changed from 0.282408 ± 9 ($^{176}Yb/^{172}Yb=0.5804$), 0.282324 ± 9 ($^{176}Yb/^{172}Yb=0.5865$) to 0.282297 ± 9 ($^{176}Yb/^{172}Yb=0.5887$). For TEMORA, the $^{176}Hf/^{177}Hf$ ratios changed from 0.283032 ± 46 ($^{176}Yb/^{172}Yb=0.5804$), 0.282767 ± 14 ($^{176}Yb/^{172}Yb=0.5865$) to 0.282672 ± 10 ($^{176}Yb/^{172}Yb=0.5887$) with significant improvement of precision. The higher Yb concentration of TEMORA results in much larger differences than in 91500 for different $^{176}Yb/^{172}Yb$ values. Clearly, the $^{176}Hf/^{177}Hf$ values obtained for

91500 and TEMORA with $^{176}Yb/^{172}Yb=0.5887$ or 0.5865 are compatible to the previously published data, and the values using $^{176}Yb/^{172}Yb=0.5887$ are closer to the accepted values obtained by the solution method (see below). Therefore, in our subsequent analyses, $^{176}Yb/^{172}Yb=0.5887$ was used and the β_{Yb} value obtained from the sample itself is applied for the Yb correction.

In summary, a reasonable and precise correction of Yb interference on Hf is vital in obtaining precise and accurate $^{176}Hf/^{177}Hf$ values for in-situ zircon analyses. When the appropriate $^{176}Yb/^{172}Yb$ value is applied, precise and accurate $^{176}Hf/^{177}Hf$ ratios can be obtained. For low Yb samples, the method used for obtaining the β_{Yb} value is not important due to the small correction. However, for high Yb zircons, the β_{Yb} value has to be obtained from the analyzed spot itself.

Taking as an example of our analyses of granitic rocks from NE China, both samples GW0217-1 and GW0217-2 come from the same pluton, but GW0217-1 has much higher $^{176}Yb/^{177}Hf$ ratios (0.12–0.44) than GW0217-2 (0.02–0.16). Using the previous correction method of Xu et al. (2004), the $^{176}Hf/^{177}Hf$ values are 0.283116 ± 52 (GW0217-1) and 0.283004 ± 19 (GW0217-2) (Fig. 8), respectively. It is noted, however, that there is a positive linear relationship between $^{176}Yb/^{177}Hf$ and $^{176}Hf/^{177}Hf$ for these two samples. However, if the value of $^{176}Yb/^{172}Yb=0.5887$ is used and the mean β_{Yb} value from individual spot is applied, the obtained values of $^{176}Hf/^{177}Hf$ are 0.282976 ± 21 (GW0217-1) and 0.282976 ± 9; identical within analytical uncertainty, although the high Yb/Hf sample GW0217-1 has slightly lower precision. Importantly, no positive linear relationship between
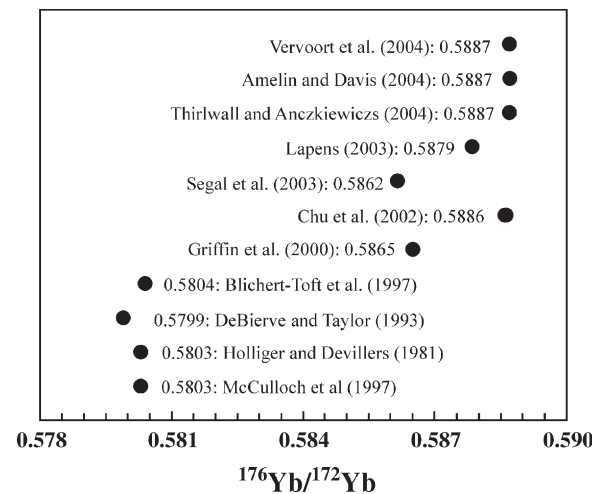

Fig. 6. Comparison of $^{176}Yb/^{172}Yb$ determinations by different researchers.
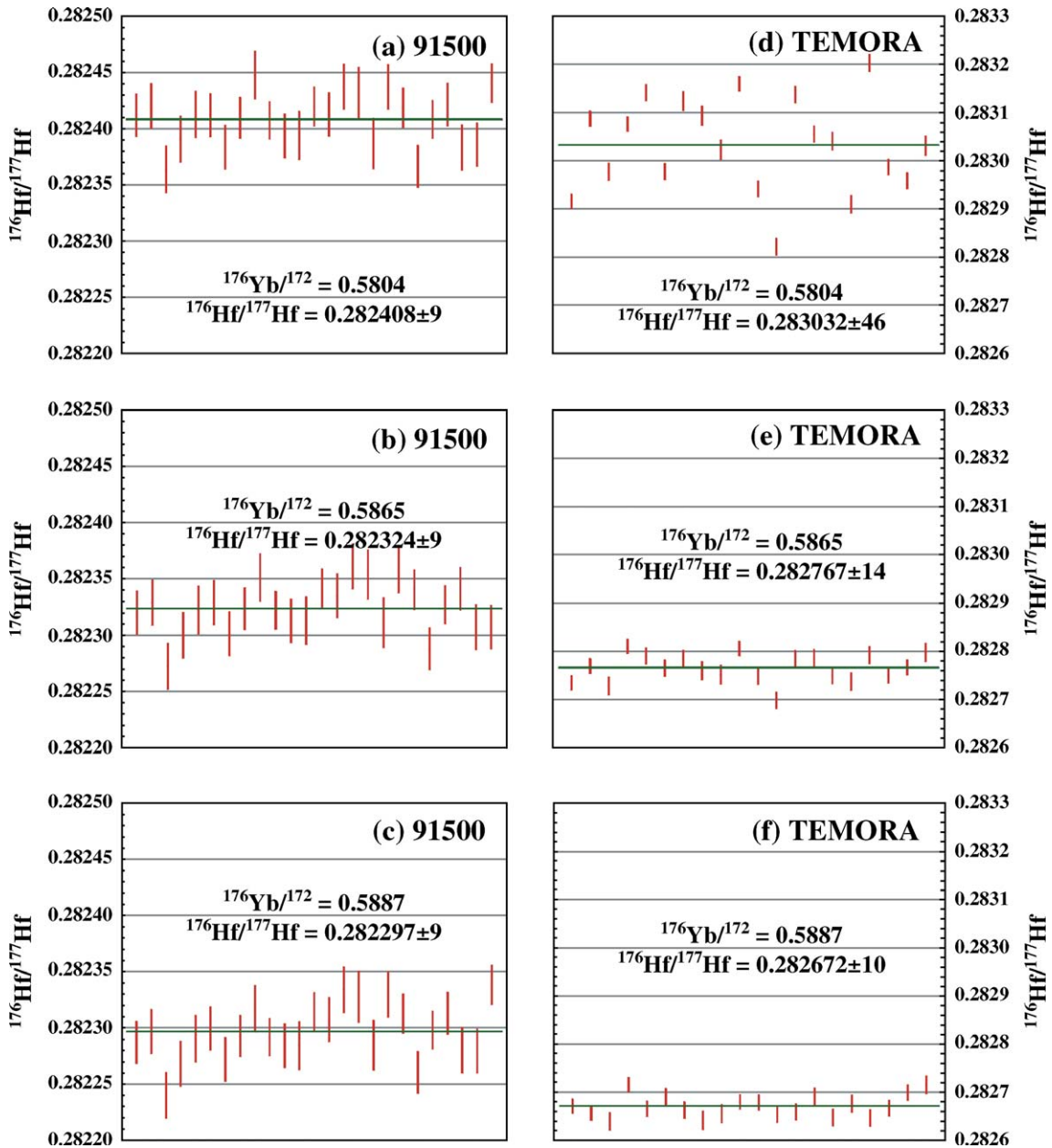
Fig. 7. ^{176}Hf/^{177}Hf ratio calculations for 91500 and TEMORA using various ^{176}Yb/^{172}Yb values proposed by different researchers. It is indicated that the most reasonable ^{176}Hf/^{177}Hf value can be obtained when ^{176}Yb/^{172}Yb=0.5887 is applied.

^{176}Yb/^{177}Hf and ^{176}Hf/^{177}Hf ratios is observed using the new correction method.

4. Standard zircon measurements

Our previous experiments demonstrated that the obtained ^{176}Hf/^{177}Hf ratios are identical, within analytical uncertainty, under in-situ or line scan conditions (Xu et al., 2004). Therefore, in our following studies, in-

situ analyses with spot sizes of 32, 63 and 94 μm were obtained. Normally, a signal intensity of ∼ 10 V at ^{180}Hf mass can be obtained using the laser repetition rate of 10 Hz and a 63-μm laser beam with energy density of 15 J/cm^2. The data are listed in Table 2. It is noted that we define the data obtained in a single day as one "set". However, for some standards (Phalaborwa zircon and Phalaborwa and SK10-2 baddeleyites), the "set" means analyses obtained during part of a single day.

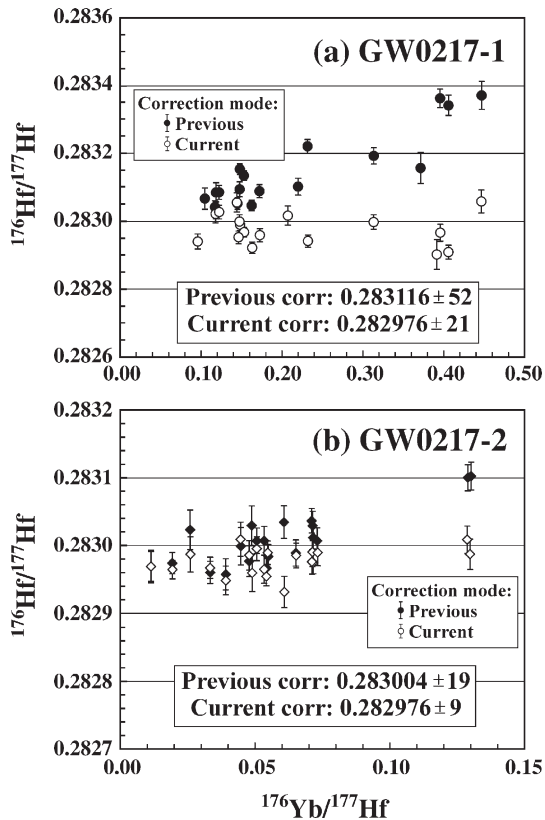Fig. 8. Comparison of analyzed results for zircons from a Mesozoic granite in NE China under different correction models for Yb. It is shown that high precise $^{176}Hf/^{177}Hf$ values can still be obtained for zircons with $^{176}Yb/^{177}Hf$ values as high as 0.4 using current correction protocols. See text for detail explanation.

4.1. 91500

This standard, preserved in the Harvard Mineralogical Museum, is a single crystal with a weight of 238 g. It was collected from the Renfrew district of Ontario, Canada. As one of the most widely distributed standards, it has been extensively used for U–Pb age, trace element and Hf isotopic analyses (Wiedenbeck et al., 1995, 2004 Horn et al., 2000; Amelin and Zaitsev, 2002; Chen et al., 2002; Kosler et al., 2002; Cox et al., 2003; Tiepolo et al., 2003; Yuan et al., 2004). The crystal analyzed in this study is a fragment about $5 \times 3 \times 2$ mm. Our analyses during the past two years indicate that this standard is relatively homogeneous in Hf isotopic composition although its Hf concentration is not as high as other standards investigated. The $^{176}Hf/^{177}Hf$ ratios varied from 0.282274 ± 6 to 0.282332 ± 12 with an average value of 0.282307 ± 31 (2SD) (Table 2, and Fig. 9a), and its average $^{176}Yb/^{177}Hf$ and $^{176}Lu/^{177}Hf$ ratios are 0.0077 ± 25 (0.0066–0.0126) and

0.00029 ± 3 (0.00027–0.00032), respectively. In order to evaluate the reliability of our laser ablation analyses, three pieces of 91500 were prepared for solution analyses on our Neptune machine. Ten measurements yield a $^{176}Hf/^{177}Hf$ value of 0.282300 ± 20 (2SD, Table 3), which is identical to the value obtained by laser ablation analyses.

Hf isotope compositions of 91500 have been analyzed by solution and laser ablation techniques in several laboratories (Table 4), but the results are not entirely consistent with each other. The first reported $^{176}Hf/^{177}Hf$ value of $0.282284 \pm 3(1\sigma)$ was measured by Wiedenbeck et al. (1995) using the ID (isotopic dilution)-TIMS method. The value was averaged from 6 of 7 repeat analyses, with one higher value of 0.282329 rejected because it deviates significantly from the other analyses. It is also noted that this value was reported relative to their assumed $^{176}Hf/^{177}Hf$ value of 0.282142 for JMC475, about 20 ppm lower than the presently accepted value. In order to compare this result with other data, a $^{176}Hf/^{177}Hf$ value of 0.282302 ± 8 (2SD) is reported here, as opposed to the presently accepted value of 0.282160 for JMC475. The subsequent ID-MC-ICPMS analyses by Amelin et al. (2000) gave a $^{176}Hf/^{177}Hf$ value of 0.282320 ± 28 and $^{176}Lu/^{177}Hf = 0.000302 \pm 29$ from 6 analyses. Recently, several precise $^{176}Hf/^{177}Hf$ ratios have been reported for solution analyses on MC-ICPMS, such as the 0.282302 ± 8 (2SD, $N=59$) by Goolaerts et al. (2004), 0.282306 ± 8 (2SD, $N=30$) by Woodhead et al. (2004), 0.282305 ± 12 (2SD, $N=13$) by Nebel-Jacobsen et al. (2005), 0.282310 ± 34 (2SD, $N=8$) by Qi et al. (2005), 0.282298 ± 20 (2SD, $N=27$) by Richards et al. (2005) and 0.282289 ± 20 (2SD, $N=9$) by Davis et al. (2005). In terms of laser ablation analyses, Griffin et al. (2000, 2002) used the Nu plasma MC-ICPMS and obtained a value of 0.282297 ± 44 for $^{176}Hf/^{177}Hf$ and 0.00030 for $^{176}Lu/^{177}Hf$ from 60 measurements. Machado and Simonetti (2001) obtained a value of 0.282270 ± 123 for $^{176}Hf/^{177}Hf$ and 0.000308 ± 34 for $^{176}Lu/^{177}Hf$. Li et al. (2003) obtained a value of 0.282285 ± 37 (2SD) for $^{176}Hf/^{177}Hf$ and a value of 0.00033 ± 6 for $^{176}Lu/^{177}Hf$ from 13 measurements on Isoprobe MC-ICPMS. Our previous analyses yield a $^{176}Hf/^{177}Hf$ value of 0.282321 ± 24 (2SD, $N=65$) (Xu et al., 2004). The subsequent analytical results are 0.282293 ± 28 (2SD, Woodhead et al., 2004), 0.282321 ± 46 (2SD, $N=35$, Iizuka and Hirata, 2005), 0.282315 ± 28 (2SD, $N=25$, Harrison et al., 2005) and 0.282302 ± 18 (2SD, Hawkesworth and Kemp, 2006). Combining all the reported values in the literature with this study by the solution method, an average $^{176}Hf/^{177}Hf$ value of 0.282303 ± 8 (2SD, $n=9$) is obtained. However, if all the individual analyses are included, the obtained $^{176}Hf/^{177}Hf$ value is 0.282303 ± 21 (2SD, $n=111$). Therefore, we propose that ~0.282305 could be recommended as the

Table 2
Hf isotopic analytical results of present study

Sample	Measuring date	$^{176}Yb/^{177}Hf$	$^{176}Lu/^{177}Hf$	$^{176}Hf/^{177}Hf$	Spot no.
Standard zircons					
91500	2004-03-04	0.00986±17	0.000313±08	0.282329±21	20
91500	2004-03-05	0.00973±35	0.000305±07	0.282330±31	12
91500	2004-04-06	0.00804±18	0.000278±03	0.282283±07	16
91500	2004-04-09	0.01046±31	0.000302±06	0.282290±44	9
91500	2004-04-10	0.00820±32	0.000281±03	0.282330±08	32
91500	2004-04-11	0.01259±17	0.000318±03	0.282325±23	26
91500	2004-04-14	0.00874±41	0.000285±06	0.282319±24	12
91500	2004-04-16	0.00927±38	0.000275±02	0.282307±28	14
91500	2004-07-12	0.00855±18	0.000307±14	0.282311±16	8
91500	2004-07-13	0.00796±09	0.000299±01	0.282313±10	15
91500	2004-07-16	0.00832±10	0.000304±04	0.282314±16	8
91500	2004-07-18	0.00690±08	0.000284±02	0.282314±13	20
91500	2004-07-19	0.00711±20	0.000289±08	0.282298±09	6
91500	2004-07-20	0.00776±13	0.000296±03	0.282293±05	18
91500	2004-08-12	0.00925±14	0.000307±03	0.282312±11	14
91500	2004-08-13	0.00876±27	0.000301±05	0.282301±09	7
91500	2004-09-14	0.00784±23	0.000302±04	0.282325±08	23
91500	2004-09-15	0.00784±13	0.000300±03	0.282303±09	26
91500	2005-04-12	0.00844±24	0.000270±03	0.282298±17	9
91500	2005-04-19	0.00701±08	0.000274±01	0.282297±13	27
91500	2005-04-20	0.00674±13	0.000273±02	0.282330±22	16
91500	2005-04-22	0.00681±13	0.000276±02	0.282329±20	15
91500	2005-04-23	0.00695±09	0.000280±02	0.282317±20	18
91500	2005-05-26	0.00715±39	0.000273±05	0.282326±21	11
91500	2005-05-27	0.00695±23	0.000276±04	0.282298±31	11
91500	2005-05-30	0.00698±15	0.000278±03	0.282332±12	22
91500	2005-05-31	0.00685±12	0.000276±02	0.282323±18	22
91500	2005-06-01	0.00703±12	0.000277±03	0.282325±13	29
91500	2005-06-04	0.00730±16	0.000272±01	0.282323±15	32
91500	2005-06-16	0.00752±13	0.000279±02	0.282301±09	25
91500	2005-07-08	0.00790±15	0.000283±04	0.282296±13	13
91500	2005-07-18	0.00708±11	0.000293±04	0.282301±07	14
91500	2005-07-20	0.00704±06	0.000279±01	0.282299±06	55
91500	2005-08-19	0.00690±18	0.000287±06	0.282300±20	8
91500	2005-08-20	0.00674±07	0.000285±02	0.282294±16	13
91500	2005-08-23	0.00683±09	0.000281±02	0.282305±11	25
91500	2005-08-24	0.00683±04	0.000283±01	0.282280±11	12
91500	2005-08-25	0.00698±07	0.000280±02	0.282292±07	15
91500	2005-08-26	0.00679±05	0.000281±01	0.282309±09	35
91500	2005-09-01	0.00695±05	0.000287±01	0.282278±05	17
91500	2005-09-05	0.00697±06	0.000286±02	0.282310±08	20
91500	2005-09-08	0.00696±05	0.000287±02	0.282300±05	20
91500	2005-10-12	0.00689±04	0.000283±02	0.282274±06	30
91500	2005-10-13	0.00660±04	0.000277±01	0.282283±06	27
Average (2SD)		**0.0077±25**	**0.00029±3**	**0.282307±31**	**44**
TEMORA	2004-03-05	0.035±03	0.0012±01	0.282687±11	26
TEMORA	2004-03-08	0.038±07	0.0011±01	0.282684±24	11
TEMORA	2004-03-10	0.033±07	0.0011±02	0.282664±24	14
TEMORA	2004-07-16	0.035±02	0.0012±03	0.282683±07	3
TEMORA	2004-08-12	0.037±07	0.0013±03	0.282681±19	4
TEMORA	2004-10-21	0.048±23	0.0013±11	0.282689±33	5
TEMORA	2004-10-22	0.037±03	0.0011±02	0.282688±10	12
TEMORA	2004-10-23	0.034±02	0.0010±01	0.282701±11	22
TEMORA	2005-04-14	0.031±04	0.0012±02	0.282682±17	9
TEMORA	2005-05-27	0.018±05	0.0010±03	0.282647±40	5
TEMORA	2005-06-08	0.028±12	0.0008±04	0.282698±44	5

Table 2 (*continued*)

Sample	Measuring date	$^{176}Yb/^{177}Hf$	$^{176}Lu/^{177}Hf$	$^{176}Hf/^{177}Hf$	Spot no.
Standard zircons					
TEMORA	2005-06-16	0.022±04	0.0009±02	0.282671±10	5
TEMORA	2005-06-24	0.033±05	0.0012±02	0.282657±33	6
TEMORA	2005-08-19	0.025±06	0.0012±02	0.282671±23	8
TEMORA	2005-08-23	0.025±07	0.0011±03	0.282683±26	7
Average (2SD)		**0.032 ± 15**	**0.0011 ± 3**	**0.282680 ± 31**	**15**
CZ3	2004-04-16	0.00125±12	0.000032±3	0.281709±16	12
CZ3	2004-07-18	0.00095±11	0.000034±2	0.281730±13	15
CZ3	2005-08-23	0.00094±10	0.000035±3	0.281728±11	25
CZ3	2005-09-01	0.00091±02	0.000034±1	0.281737±06	14
CZ3	2005-09-05	0.00093±02	0.000035±1	0.281738±08	16
CZ3	2005-09-08	0.00096±05	0.000035±1	0.281731±11	09
Average (2SD)		**0.00099 ± 26**	**0.000034 ± 2**	**0.281729 ± 21**	**6**
CN92-1	2004-07-05	0.0106±48	0.00074±20	0.282167±08	7
CN92-1	2004-07-06	0.0230±14	0.00081±02	0.282162±16	5
CN92-1	2004-07-11	0.0239±24	0.00083±07	0.282173±10	8
CN92-1	2004-07-12	0.0228±11	0.00087±04	0.282186±14	11
CN92-1	2004-07-13	0.0223±70	0.00082±02	0.282188±23	4
CN92-1	2004-07-14	0.0320±31	0.00094±15	0.282178±17	7
CN92-1	2004-07-19	0.0184±07	0.00072±02	0.282177±13	6
CN92-1	2005-06-16	0.0188±05	0.00077±01	0.282172±06	20
CN92-1	2005-08-19	0.0162±21	0.00078±05	0.282184±13	10
CN92-1	2005-08-20	0.0189±02	0.00076±02	0.282174±18	4
CN92-1	2005-08-24	0.0195±09	0.00077±02	0.282180±08	5
CN92-1	2005-08-26	0.0187±03	0.00077±01	0.282166±09	28
Average (2SD)		**0.020 ± 10**	**0.00080 ± 12**	**0.282177 ± 17**	**12**
FM0411	2005-06-16	0.00449±24	0.000145±09	0.282977±10	20
FM0411	2005-07-18	0.00679±07	0.000178±02	0.282991±15	22
FM0411	2005-08-23	0.00570±05	0.000177±02	0.282968±12	25
FM0411	2005-08-25	0.00580±09	0.000170±02	0.282977±12	10
FM0411	2005-08-26	0.00549±04	0.000176±02	0.282986±14	24
FM0411	2005-09-01	0.00555±17	0.000177±04	0.282988±05	18
FM0411	2005-09-05	0.00585±23	0.000185±08	0.282977±04	11
FM0411	2005-09-08	0.00574±21	0.000181±03	0.282991±12	6
FM0411	2005-10-12	0.00482±38	0.000162±10	0.282991±07	21
Average (2SD)		**0.0058 ± 13**	**0.00017 ± 2**	**0.282983 ± 17**	**9**
Phalaborwa	2005-08-19	0.0210±05	0.00062±2	0.281231±32	8
Phalaborwa	2005-08-23	0.0177±02	0.00054±1	0.281241±12	21
Phalaborwa	2005-08-26	0.0182±01	0.00054±1	0.281224±10	22
Phalaborwa	2005-09-01	0.0186±02	0.00054±1	0.281239±13	7
Phalaborwa	2005-09-01	0.0103±14	0.00023±3	0.281237±13	9
Phalaborwa	2005-09-01	0.0142±12	0.00041±3	0.281232±5	14
Phalaborwa	2005-09-01	0.0070±07	0.00021±2	0.281238±13	15
Phalaborwa	2005-09-01	0.0085±07	0.00025±3	0.281232±9	10
Average (2SD)		**0.014 ± 11**	**0.0004 ± 3**	**0.281234 ± 11**	**8**
Standard baddeleyites					
Phalaborwa1	2005-10-12	0.000091±07	0.0000033±1	0.281239±4	12
Phalaborwa1	2005-10-12	0.000063±03	0.0000024±1	0.281241±7	16
Phalaborwa1	2005-10-12	0.000062±02	0.0000024±1	0.281243±7	19
Phalaborwa1	2005-10-12	0.000064±04	0.0000024±1	0.281225±7	18
Phalaborwa1	2005-10-13	0.000075±02	0.0000023±1	0.281239±4	15
Phalaborwa1	2005-10-13	0.000091±13	0.0000028±4	0.281239±6	15
Phalaborwa1	2005-10-13	0.000102±17	0.0000031±5	0.281239±7	18
Average (2SD)		**0.000078 ± 33**	**0.0000027 ± 8**	**0.281238 ± 12**	**7**
Phalaborwa2	2005-10-12	0.000098±02	0.0000036±6	0.281208±6	18
Phalaborwa2	2005-10-13	0.000109±15	0.0000033±5	0.281191±5	16
Phalaborwa2	2005-10-13	0.000099±20	0.0000030±5	0.281193±6	16
Average (2SD)		**0.000102 ± 12**	**0.0000033 ± 6**	**0.281197 ± 19**	**3**

Table 2 (*continued*)

Sample	Measuring date	$^{176}Yb/^{177}Hf$	$^{176}Lu/^{177}Hf$	$^{176}Hf/^{177}Hf$	Spot no.
Standard baddeleyites					
SK10-2	2005-08-20	0.0052 ± 10	0.00020 ± 3	0.282729 ± 08	14
SK10-2	2005-08-23	0.0060 ± 08	0.00021 ± 3	0.282733 ± 15	14
SK10-2	2005-08-26	0.0062 ± 08	0.00022 ± 3	0.282742 ± 13	18
SK10-2	2005-09-01	0.0070 ± 02	0.00026 ± 2	0.282744 ± 07	20
SK10-2	2005-10-13	0.0064 ± 09	0.00023 ± 3	0.282733 ± 07	14
SK10-2	2005-10-13	0.0069 ± 09	0.00023 ± 3	0.282745 ± 09	18
Average (2SD)		**0.0063 ± 13**	**0.00023 ± 4**	**0.282738 ± 13**	**6**

$^{176}Hf/^{177}Hf$ value for 91500 zircon, and we use this value for external corrections for our following analyses.

4.2. TEMORA

This standard is from the town of Temora, geologically within the Lachlan Fold Belt in SE Australia. The zircons occur in a gabbroic diorite. The U–Pb age and chemical composition of the host rock can be found in the literature (Black et al., 2003a,b; Yuan et al., 2004). During our previous experiment (Xu et al., 2004), 24 analyses using the 94-μm beam size gave a weighted average $^{176}Hf/^{177}Hf$ value of 0.282684 ± 14 (2σ) or 0.282684 ± 66 (2SD, $N=24$). The analyses also indicated that this zircon standard has some variations in its Hf isotope compositions (Xu et al., 2004). Comprehensive analyses by Woodhead et al. (2004) give $^{176}Hf/^{177}Hf$ value of 0.282686 ± 7 (2SD) using the solution technique and 0.282680 ± 24 (2SD) for laser MC-ICPMS analyses. Recently, Qi et al. (2005) obtained a $^{176}Hf/^{177}Hf$ value of 0.282706 ± 20 (2SD, $N=7$) from solution analyses. Harrison et al. (2005) and Hawkesworth and Kemp (2006) obtained the $^{176}Hf/^{177}Hf$ values of 0.282684 ± 36 (2SD) and 0.282687 ± 24 (2SD), respectively, by the laser ablation technique. Our analyses over 15 separate days yielded a $^{176}Hf/^{177}Hf$ value of 0.282680 ± 31 (2SD)(Table 2 and Fig. 9b). It is noted that our analyses show a wide range of $^{176}Yb/^{177}Hf$ (0.018–0.038, with a weighted average of 0.032 ± 15 and one exception of 0.048 ± 23) and $^{176}Lu/^{177}Hf$ (0.0008–0.0013, with an average of 0.0011 ± 3).

In this study, four pieces of TEMORA were also prepared for solution analyses (Table 3). Sixteen measurements yield a $^{176}Hf/^{177}Hf$ value of 0.282685 ± 11 (2SD), which agrees well with the value obtained by laser ablation, and is identical to the values of 0.282686 ± 7 (2SD) by Woodhead et al. (2004) and 0.282706 ± 20 (2SD) by Qi et al. (2005) obtained by the same solution method (Table 4). If all these individual analyses are averaged, the obtained $^{176}Hf/^{177}Hf$ value is 0.282691 ± 22 (2SD, $n=26$), which we therefore recommended as the $^{176}Hf/^{177}Hf$ value of this standard.

4.3. CZ3

CZ3 is a single grain of zircon of gem quality from Sri Lanka. It was selected as a U–Pb geochronology standard for SHRIMP analyses because of its homogeneity in terms of U and Pb (Pidgeon et al., 1994; De Laeter and Kennedy, 1998). Conventional thermal ionization mass spectrometry U/Pb isotopic data on CZ3 gives a uranium concentration of 551 ppm and a concordant age of 564 Ma. Our previous laser ablation analyses yielded a weighted average $^{176}Hf/^{177}Hf$ value of 0.281704 ± 17 (2SD, $N=16$) (Xu et al., 2004), identical to the 0.281697 ± 12 (2SD, $N=15$) reported by Kemp et al. (2006). This value is also similar to the results of another Sri Lanka zircon (SL7) by SHRIMP (0.28186 ± 19) and TIMS (0.28160 ± 6), within uncertainties (Kinny et al., 1991). In this study, an additional 6 days of analyses were conducted and yielded a mean $^{176}Hf/^{177}Hf$ value of 0.281729 ± 21 (2SD) (Fig. 9c, Table 2). Our data also indicate that this zircon has a very low $^{176}Yb/^{177}Hf$ ratio (mostly ranging from 0.00091–0.00125 with an average of 0.00099 ± 26) and $^{176}Lu/^{177}Hf$ ratio (0.000032–0.000035, with an average of 0.000034 ± 2). Due to the limited supply, we prepare only two pieces of this standard for solution analyses. Four measurements yield a $^{176}Hf/^{177}Hf$ value of 0.281732 ± 7 (2SD, Table 3), which is identical to the value obtained by laser ablation analyses.

4.4. CN92-1

This standard was used by Montreal University of Canada and is currently used in Hong Kong University for U–Pb geochronology (Feng et al., 1993; Xia et al., 2004). Although this zircon shows some discordance in a U–Pb concordia diagram, the $^{207}Pb/^{206}Pb$ ratios remain uniform and give a weighted $^{207}Pb/^{206}Pb$ age of 1143 ± 0.8 Ma by TIMS (Machado and Gauthier, 1996) and an upper intercept age of 1144 ± 10 Ma by laser ablation ICP-MS analyses (Xia et al., 2004). Xu et al. (2004) reported a $^{176}Hf/^{177}Hf$ value of 0.282200 ± 6
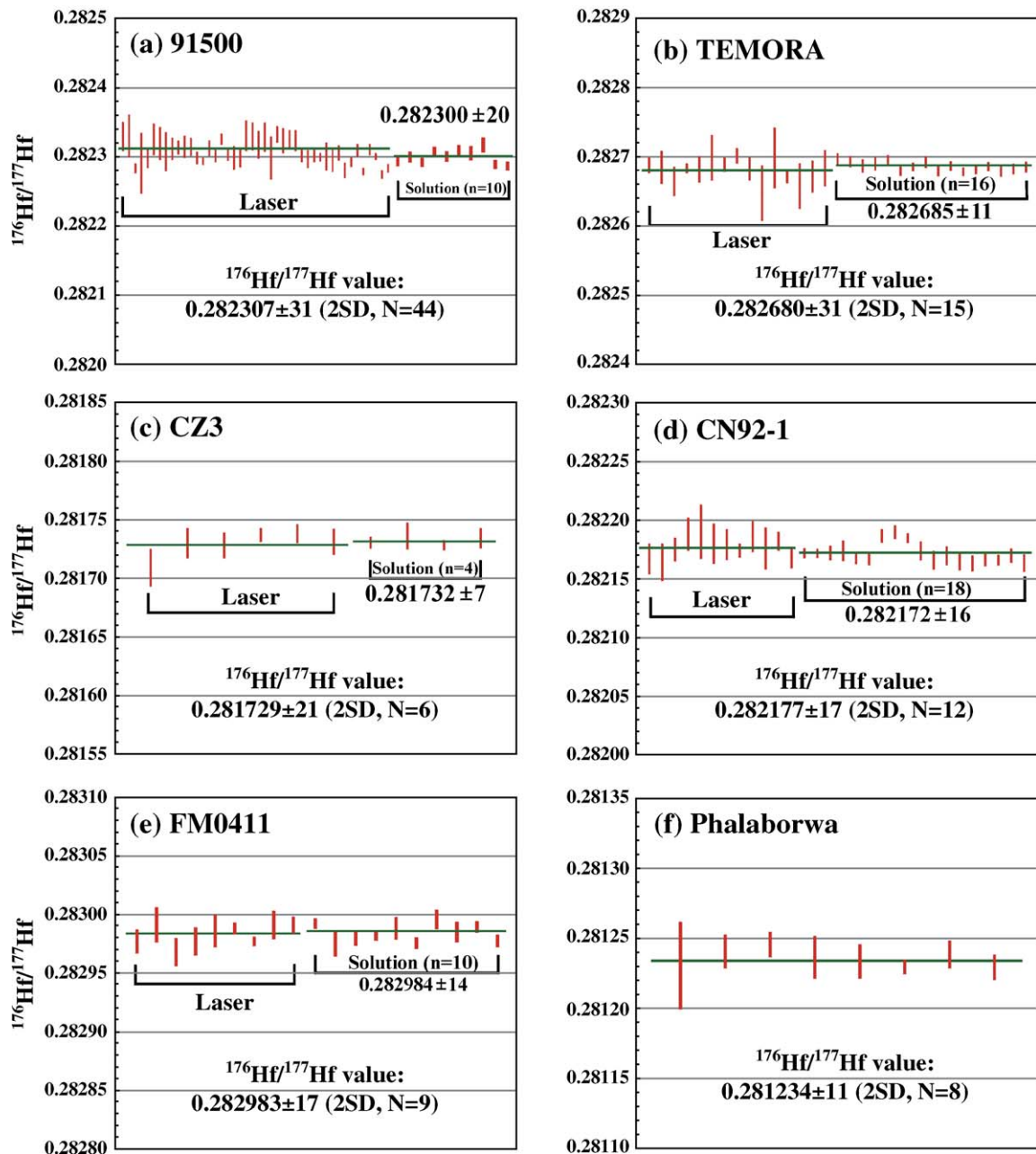
Fig. 9. $^{176}Hf/^{177}Hf$ values of standard zircons of (a) 91500, (b) TEMORA, (c) CZ3, (d) CN92-1, (e) FM0411 and (f) Phalaborwa obtained in this study. 91500 is normalized to JMC475 as 0.282160, and the others are normalized to 91500 as 0.282305.

(2σ) or ±19 (2SD, N=20). In this study, analyses on twelve separate days yield a $^{176}Hf/^{177}Hf$ ratio of 0.282177±17 (2SD) with $^{176}Yb/^{177}Hf$ and $^{176}Lu/^{177}Hf$ values of 0.0106–0.0320 (average of 0.020±10) and 0.00072–0.00094 (average of 0.00080±12), respectively (Fig. 9d, Table 2).

Eighteen measurements of 4 pieces of this standard using the solution method yield a $^{176}Hf/^{177}Hf$ value of

0.282172±16 (2SD) (Table 3), confirming the reliability of our laser ablation analyses.

4.5. FM0411

This grain is a euhedral zircon megacryst measuring 6 mm wide by 8 mm long. It was collected from Cenozoic basalt at Mingxi in southeastern China and

Table 3
Hf isotopic data of standard zircon and baddeleyite by solution method

Sample no.	Standard	^{176}Hf/^{177}Hf (2σ)	Re-analysis (2σ)	Mean ^{176}Hf/^{177}Hf (2SD)
91500-1	Zircon	0.282294±8	0.282299±8	**0.282300 ± 20** (*n*=10)
		0.282291±6	0.282308±9	
91500-2	Zircon	0.282308±6	0.282305±10	
		0.282300±7	0.282317±11	
91500-3	Zircon	0.282289±6	0.282286±6	
TEMORA-1	Zircon	0.282695±9	0.282692±8	**0.282685 ± 11** (*n*=16)
			0.282686±10	
TEMORA-2	Zircon	0.282689±10	0.282694±8	
TEMORA-3		0.282679±7	0.282691±8	
		0.282685±6	0.282679±8	
			0.282686±7	
TEMORA-4	Zircon	0.282678±6	0.282679±8	
		0.282681±7	0.282682±7	
		0.282685±7	0.282685±8	
CZ3	Zircon	0.281730±5	0.281736±11	**0.281732 ± 7** (*n*=4)
CZ3	Zircon	0.281728±4	0.281734±9	
CN92-1-1	Zircon	0.282172±4	0.282172±4	**0.282172 ± 16** (*n*=18)
		0.282172±6	0.282174±9	
		0.282167±5	0.282167±5	
CN92-1-2	Zircon	0.282186±6	0.282190±6	
			0.282185±4	
CN92-1-3	Zircon	0.282174±8	0.282170±8	
		0.282166±8	0.282165±8	
		0.282163±7	0.282167±6	
CN92-1-4	Zircon	0.282166±5	0.282170±6	
			0.282164±8	
FM0411-1	Zircon	0.282992±05	0.282975±11	**0.282984 ± 14** (*n*=10)
FM0411-2	Zircon	0.282979±06	0.282982±04	
FM0411-3	Zircon	0.282988±10	0.282976±05	
FM0411-4	Zircon	0.282996±08	0.282985±09	
FM0411-5	Zircon	0.282989±05	0.282977±05	
Phalaborwa1-1	Baddeleyite	0.281228±3	0.281229±2	**0.281229 ± 11** (*n*=17)
		0.281233±4	0.281227±3	
		0.281223±4	0.281232±4	
			0.281224±4	
Phalaborwa1-2	Baddeleyite	0.281224±4	0.281232±4	
			0.281221±4	
Phalaborwa1-3	Baddeleyite	0.281221±4	0.281230±4	
			0.281219±4	
Phalaborwa1-4	Baddeleyite	0.281237±4	0.281235±4	
		0.281238±4	0.281233±4	
Phalaborwa2-1	Baddeleyite	0.281209±4	0.281210±4	**0.281206 ± 19** (*n*=20)
		0.281206±4	0.281211±4	
			0.281200±4	
Phalaborwa2-2	Baddeleyite	0.281198±4	0.281197±5	
		0.281194±5	0.281193±5	
			0.281194±5	
Phalaborwa2-3	Baddeleyite	0.281203±4	0.281205±4	
		0.281203±4	0.281204±4	
			0.281202±4	
Phalaborwa2-4	Baddeleyite	0.281224±4	0.281217±4	
		0.281218±4	0.281221±5	
			0.281218±4	
SK10-2-1	Baddeleyite	0.282745±08	0.282743±06	**0.282739 ± 13** (*n*=10)
SK10-2-2	Baddeleyite	0.282735±13	0.282734±09	
SK10-2-3	Baddeleyite	0.282751±09	0.282740±04	
SK10-2-4	Baddeleyite	0.282714±22	0.282729±09	
SK10-2-5	Baddeleyite	0.282737±16	0.282737±05	

Table 4
Compilations of Hf isotopic data of the standard zircons and baddeleyites

Standard	$^{176}Yb/^{177}Hf$	$^{176}Lu/^{177}Hf$	$^{176}Hf/^{177}Hf$	Method	JMC475	References
91500		0.00029 ± 1	0.282284 ± 6	TIMS	0.282142	Wiedenbeck et al. (1995)
91500		0.00031 ± 3	0.282320 ± 28	MC-ICPMS	0.282163	Amelin et al. (2000)
91500			0.282302 ± 8	MC-ICPMS	0.282161	Goolaerts et al. (2004)
91500		0.00031	0.282306 ± 8	MC-ICPMS	0.282160	Woodhead et al. (2004)
91500		0.00033	0.282305 ± 12	MC-ICPMS	0.282160	Nebel-Jacobsen et al. (2005)
91500			0.282310 ± 34	MC-ICPMS	0.282160	Qi et al. (2005)
91500			0.282298 ± 20	MC-ICPMS	0.282160	Richards et al. (2005)
91500		0.00022 ± 5	0.282289 ± 20	MC-ICPMS	0.282160	Davis et al. (2005)
91500			0.282300 ± 20	MC-ICPMS	0.282160	This study
91500		0.00030 ± 5	0.282297 ± 44	LA-MC-ICPMS	0.282161	Griffin et al. (2000)
91500		0.00031 ± 3	0.282270 ± 123	LA-MC-ICPMS	0.282159	Machado and Simonetti (2001)
91500	0.011 ± 4	0.00033 ± 6	0.282285 ± 37	LA-MC-ICPMS	0.282167	Li et al. (2003)
91500			0.282321 ± 24	LA-MC-ICPMS	0.282160	Xu et al. (2004)
91500			0.282296 ± 28	LA-MC-ICPMS	0.282160	Woodhead et al. (2004)
91500	0.0073 ± 34	0.00030 ± 12	0.282321 ± 46	LA-MC-ICPMS	0.282154	Iizuka and Hirata (2005)
91500		0.00029 ± 6	0.282315 ± 28	LA-MC-ICPMS	0.282160	Harrison et al. (2005)
91500			0.282302 ± 18	LA-MC-ICPMS	0.282160	Hawkesworth and Kemp (2006)
91500	0.0077 ± 25	0.00029 ± 3	0.282307 ± 31	LA-MC-ICPMS	0.282160	This study
TEMORA		0.00109	0.282686 ± 7	MC-ICPMS	0.282160	Woodhead et al. (2004)
TEMORA			0.282706 ± 20	MC-ICPMS	0.282160	Qi et al. (2005)
TEMORA			0.282685 ± 11	MC-ICPMS	0.282160	This study
TEMORA			0.282684 ± 66	LA-MC-ICPMS	0.282160	Xu et al. (2004)
TEMORA			0.282680 ± 24	LA-MC-ICPMS	0.282160	Woodhead et al. (2004)
TEMORA		0.0011 ± 5	0.282684 ± 36	LA-MC-ICPMS	0.282160	Harrison et al. (2005)
TEMORA			0.282687 ± 24	LA-MC-ICPMS	0.282160	Hawkesworth and Kemp (2006)
TEMORA	0.032 ± 15	0.0011 ± 3	0.282680 ± 31	LA-MC-ICPMS	0.282160	This study
CZ3			0.281732 ± 7	MC-ICPMS	0.282160	This study
CZ3			0.281704 ± 17	LA-MC-ICPMS	0.282160	Xu et al. (2004)
CZ3			0.281697 ± 12	LA-MC-ICPMS	0.282160	Kemp et al. (2006)
CZ3	0.00099 ± 26	0.000034 ± 2	0.281729 ± 21	LA-MC-ICPMS	0.282160	This study
CN92-1			0.282172 ± 16	MC-ICPMS	0.282160	This study
CN92-1			0.282200 ± 19	LA-MC-ICPMS	0.282160	Xu et al. (2004)
CN92-1	0.020 ± 10	0.00080 ± 12	0.282177 ± 17	LA-MC-ICPMS	0.282160	This study
FM0411			0.282984 ± 14	MC-ICPMS	0.282160	This study
FM0411			0.282977 ± 21	LA-MC-ICPMS	0.282160	Qiu et al., 2005
FM0411			0.282969 ± 28	LA-MC-ICPMS	0.282160	Qiu et al., 2005
FM0411	0.0058 ± 13	0.00017 ± 2	0.282983 ± 17	LA-MC-ICPMS	0.282160	This study
Phalaborwa zir.	0.014 ± 11	0.0004 ± 3	0.281234 ± 11	LA-MC-ICPMS	0.282160	This study
Phalaborwa badl.			0.281105 ± 54	LA-MC-ICPMS		Horn et al. (1999)
Phalaborwa badl.1			0.281229 ± 11	MC-ICPMS	0.282160	This study
Phalaborwa badl.1	0.000078 ± 33	0.0000027 ± 8	0.281238 ± 11	LA-MC-ICPMS	0.282160	This study
Phalaborwa badl.2			0.281206 ± 19	MC-ICPMS	0.282160	This study
Phalaborwa badl.2		0.00000467 ± 1	0.281184 ± 17	MC-ICPMS	0.282163	Scherer et al. (2001)
Phalaborwa badl.2	0.000102 ± 12	0.0000033 ± 6	0.281197 ± 19	LA-MC-ICPMS	0.282160	This study
SK10-2 badl.			0.282739 ± 13	MC-ICPMS	0.282160	This study
SK10-2 badl.	0.0063 ± 13	0.00023 ± 4	0.282738 ± 13	LA-MC-ICPMS	0.282160	This study

serves as the in-house Hf standard in our laboratory. CL image reveals that the grain is homogeneous with oscillatory zoned structure. TIMS U–Pb analyses indicate that there is little radiogenic Pb, consistent with the young eruption age of the host basalt.

Nine sets of laser ablation analyses were conducted on this grain during the last four months of 2005 (Table 2). It shows uniform Hf isotopic compositions. The obtained $^{176}Hf/^{177}Hf$ ratio is 0.282983 ± 17 (2SD), with $^{176}Yb/^{177}Hf$ and $^{176}Lu/^{177}Hf$ values of 0.0058 ± 13 (0.0045–0.0068)

and 0.00017 ± 2 (0.00015–0.00019), respectively (Fig. 9e). In order to evaluate the reliability of the above analyses, five aliquots were digested for chemical separation and then ten solution measurements made. The obtained $^{176}Hf/^{177}Hf$ ratio is 0.282984 ± 14 (2SD, Table 3), identical, within uncertainties, to the result obtained by laser analyses.

4.6. Phalaborwa zircon

The Phalaborwa igneous complex in South Africa contains pyroxenites in its outer part, and apatite–magnetite rock and carbonatites in the central parts. The Phalaborwa zircon had previously been used as an internal standard in U–Pb geochronology (Kroner and Willner, 1998; Chen et al., 2002), but its Hf isotopes are poorly studied.

Our Phalaborwa zircon was donated by A Kroner. The grain-size ranges from 80 to 500 μm. Due to grain limitations, only eight sets from 7 grains were analyzed. The analyses show uniform Hf isotopes and yield a $^{176}Hf/^{177}Hf$ value of 0.281234 ± 11 (2SD) (Fig. 9f). The obtained $^{176}Yb/^{177}Hf$ and $^{176}Lu/^{177}Hf$ ratios are 0.014 ± 11 (0.0070–0.0210) and 0.0004 ± 3 (0.00023–0.00062), respectively. Due to limited supply, this standard was not prepared for solution analysis.

4.7. Phalaborwa baddeleyite

As with zircon, baddeleyite is also a suitable mineral for in-situ Hf analyses due to its extremely high Hf concentration (Scharer et al., 1997; Bodet and Scharer, 2000; Scherer et al., 2001; Soderlund et al., 2004). Baddeleyite from the Phalaborwa carbonatitie of South Africa has been commonly used as a standard in order to overcome the potential matrix effects (Nemchim and Pidgeon, 1998; Wingate, 2000, 2001; Wingate et al., 2000; Rubatto and Scambelluri, 2003), and its U–Pb age and chemical composition can be found in the following papers (Eriksson, 1984; Heaman and LeCheminant, 1993; Reischmann, 1995; Reischmann et al., 1995; Horn et al., 2000; Wingate and Compston, 2000; Hirata, 2001; Scherer et al., 2001; French et al., 2002). However, only few Hf isotopic analytical results have been published. Using the laser coupled ISOPROBE MC-ICPMS, Horn et al. (1999) reported a $^{176}Hf/^{177}Hf$ ratio of 0.281105 ± 54 (2SD) from 5 spots. Later, Scherer et al. (2001) obtained $^{176}Hf/^{177}Hf$ values of 0.281193 ± 14 (2SE, spiked) and 0.281181 ± 14 (2SE, unspiked) using the TIMS method, with a $^{176}Lu/^{177}Hf$ ratio of 0.00000467 ± 1. If the two sets of $^{176}Hf/^{177}Hf$ data are combined together, the average value is 0.281187 ± 17 (2SD), which is significantly higher than that obtained by Horn et al. (1999).

Our Phalaborwa baddeleyite was provided by the Mineralogical Research Company. The rock specimen is $30 \times 21 \times 5$ mm in size, containing more than 10 baddeleyite crystals and crystal fragments. The largest perfect and broken crystals are 2 and 13 mm long, respectively. Our analyzed crystal is $7 \times 5 \times 2.5$ mm in size and has one broken edge. Seven sets of laser analyses indicate that its Hf isotopic composition is homogeneous with an average value of $^{176}Hf/^{177}Hf$ ratio of 0.281238 ± 12 (2SD, Table 2). Its average $^{176}Yb/^{177}Hf$ and $^{176}Lu/^{177}Hf$ ratios are 0.00008 ± 3 (0.000062–0.000102) and 0.0000027 ± 8 (0.0000023–0.0000033), respectively (Fig. 10a). Seventeen measurements of 4 pieces of this standard using the solution method yield a $^{176}Hf/^{177}Hf$ value of 0.281229 ± 11 (2SD, Table 3), identical to the value obtained by laser ablation within uncertainty.

In addition, three sets of laser ablation analyses were also made on grains of this mineral donated by E. Scherer. The obtained $^{176}Hf/^{177}Hf$, $^{176}Yb/^{177}Hf$ and $^{176}Lu/^{177}Hf$ ratios are 0.281197 ± 19 (2SD), 0.00010 ± 1 and 0.0000033 ± 6, respectively (Fig. 10b, Table 2). Twenty measurements of 4 pieces of this standard using the solution method yield a $^{176}Hf/^{177}Hf$ value of 0.281206 ± 19 (2SD, Table 3), identical to the value obtained by laser ablation within uncertainty. The above obtained $^{176}Hf/^{177}Hf$ values from this mineral fraction are also compatible within uncertainties with the values determined by Scherer et al. (2001) using the solution method. However, the $^{176}Lu/^{177}Hf$ ratio (0.00000467 ± 1) obtained by Scherer et al. (2001) is a little higher than we determined (~ 0.000003) by laser ablation analyses. During our analyses, it was confirmed that baddeleyite has abundant cleavages on which the laser analyses show much higher $^{176}Lu/^{177}Hf$ values; whereas the spots avoiding cleavages and fractures show uniform $^{176}Lu/^{177}Hf$ value of ~ 0.000003. This variation may correspond to the differences in U–Pb ages recorded for different crystal orientations using the SHRIMP ion microprobe (Wingate and Compston, 2000).

4.8. SK10-2 baddeleyite

SK10-2 baddeleyite is an in-house standard in our laboratory. It was collected from the Yinmawanshan gabbro in the Liaodong Peninsula, China. This pluton contains abundant baddeleyite with a grain-size of 50–260 μm (with most of them > 100 μm). U–Pb LA-ICPMS analyses on co-existing zircons yield an age of 32.1 ± 0.5 Ma (Yuan et al., 2004), and the SIMS U–Pb analyses give the same age result (Wu, F.Y., unpublished data).

Six sets of laser analyses were obtained on this standard, and they indicate that its Hf isotopic
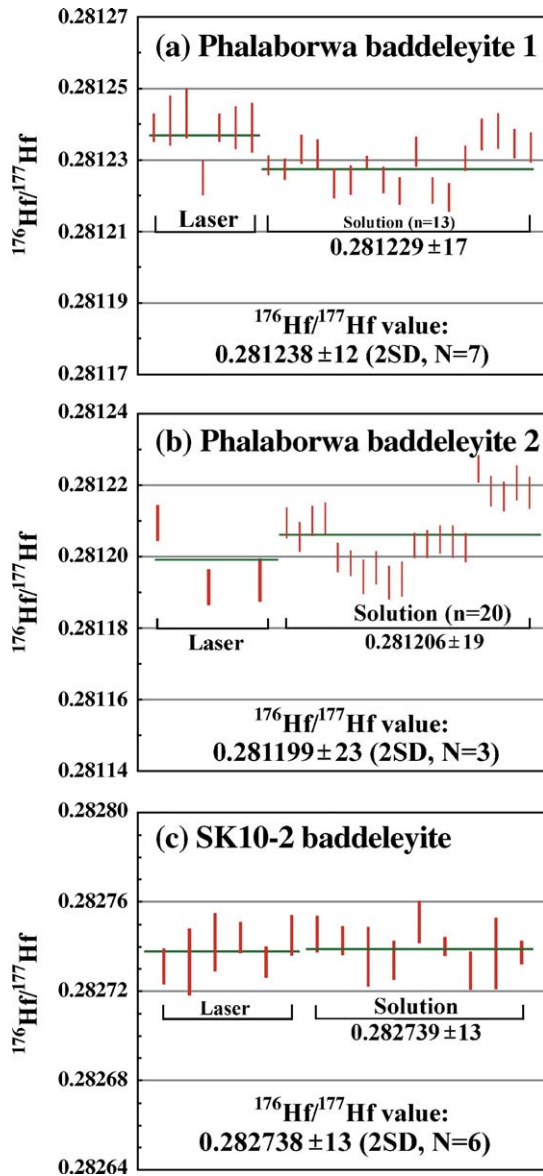
Fig. 10. $^{176}Hf/^{177}Hf$ values of Phalaborwa 1 (a), Phalaborwa 2 (b) and SK10-2 (c) baddeleyites. The laser values are normalized to 91500 of 0.282305, and the solution values are normalized to JMC475 as 0.282160.

composition is homogeneous. The obtained $^{176}Hf/^{177}Hf$ ratio is 0.282738±13 (2SD) with average $^{176}Yb/^{177}Hf$ and $^{176}Lu/^{177}Hf$ ratios of 0.0063±13 (0.0052–0.0070) and 0.00023±4 (0.00020–0.00026), respectively (Fig. 10c). In order to evaluate the reliability of the above analyses, five aliquots were digested for chemical separation and then ten solution measurements conducted. The obtained $^{176}Hf/^{177}Hf$ ratio is 0.282737±20 (2SD) (Fig. 10c). If the analysis with low precision is excluded, the remaining measurements yield a value of 0.282739±13 (2SD) for the

$^{176}Hf/^{177}Hf$ ratio, identical to the result obtained by laser ablation analyses, within uncertainties.

5. Discussion

During in-situ zircon Hf analyses by LA-MC-ICPMS, standard material is needed to calibrate the machine and monitor for mass drift. It is generally acceptable to use a standard solution to check the machine, but this method is not applicable during practical analyses, since the change between the solution and solid samples would take too much time, and would also change the machine conditions. Presently, standard 91500 is widely used as a standard for in-situ zircon Hf analyses since it is considered to be homogeneous. However, this reliability is not well established. Recently, Nebel-Jacobsen et al. (2005) found that there was some heterogeneity of Hf isotopic composition in 91500. Among their 14
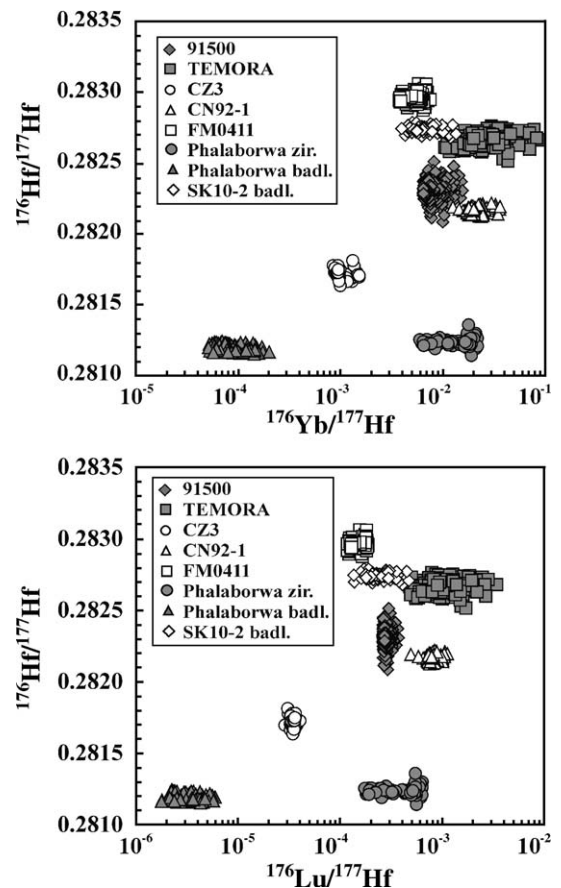

Fig. 11. Comparison of Hf isotopic compositions for different standard zircons and baddeleyites in terms of $^{176}Lu/^{177}Hf$ vs. $^{176}Yb/^{177}Hf$. See text for details.

solution analyses from 3 fragments, 13 analyses had $^{176}Hf/^{177}Hf$ ratios ranging from 0.282295 to 0.282315, but one exceptional outlier had a $^{176}Hf/^{177}Hf$ ratio of 0.282251. Among their data, two analyses showed much higher Hf concentrations (~29700 ppm) than the others (5991–6807 ppm).

Besides homogeneity, another pre-condition for a zircon standard in laser ablation analysis is that the obtained $^{176}Hf/^{177}Hf$ ratio is independent of the correction method. This means that either there is almost no correction or a precise and reasonable correction can be applied.

The Hf isotopic compositions of the above six zircon and two baddeleyite standards are summarized in Fig. 11. All these standards show a consistent and narrow range of $^{176}Hf/^{177}Hf$, $^{176}Lu/^{177}Hf$ and $^{176}Yb/^{177}Hf$ ratios, indicating their suitability as a Hf standard. Comparatively, CZ3 has extremely low $^{176}Lu/^{177}Hf$ and $^{176}Yb/^{177}Hf$ values, and CN92-1 and TEMORA have higher $^{176}Lu/^{177}Hf$ and $^{176}Yb/^{177}Hf$ values with TEMORA showing larger variations than the others. In terms of $^{176}Hf/^{177}Hf$ ratios, zircon 91500 shows a slightly greater variation than the others, indicating some inhomogeneity within the sample. It is shown in Fig. 12, for CZ3, that there was only about 10 and 20 ppm maximum deviation caused by the Yb interference correction for $^{176}Hf/^{177}Hf$ ratios using 63- and 32-μm spot sizes, respectively, which suggests that CZ3 could serve as an excellent standard for external correction. However, other standards are more suitable than CZ3 for calibration of the isobaric interference cor-

rection, since they have high $^{176}Lu/^{177}Hf$ and $^{176}Yb/^{177}Hf$ values. In particular, as shown in Fig. 12, TEMORA has the highest Yb/Hf ratio, hence more precise β_{Yb} value and $^{176}Hf/^{177}Hf$ ratio than 91500 and FM0411. Therefore, TEMORA is the best standard for isobaric interference correction.

For baddeleyite, the SK10-2 standard contains high and constant concentrations of Yb and Lu, which make the determination of its β_{Yb} value precise. Therefore, SK10-2 is also a good candidate for a standard in the development of the correction protocol. However, the available data indicate that the Phalaborwa baddeleyite is a better Hf standard than the others for the machine calibration. Both the TIMS analyses by Scherer et al. (2001) and our laser analyses indicate that Phalaborwa baddeleyite has extremely low $^{176}Yb/^{177}Hf$ (~0.00008) and $^{176}Lu/^{177}Hf$ (~0.000003) ratios; hence its ^{176}Lu and ^{176}Yb corrections should be negligible. Moreover, this mineral has high Hf concentrations of about 15,000 ppm (Scherer et al., 2001), about 2–3 times more than 91500. Therefore, Phalaborwa baddeleyite is the best Hf standard for machine calibration according to presently available data.

6. Conclusions

(1) During MC–ICPMS analyses, mass biases of Yb (β_{Yb}) and Hf (β_{Hf}) change with time and behave differently for material in solution or in the solid state. Precise Hf isotopic compositions can be obtained when the mean β_{Yb} value of the individual analytical spot is applied for in-situ analysis correction.

(2) During zircon in-situ analyses, isobaric interference of ^{176}Yb on ^{176}Hf is significant, although the different methods of obtaining the β_{Yb} value have little effect on the accuracy of the Hf isotopic composition for low Yb/Hf zircons.

(3) Using mean β_{Yb} values and the newly published Yb isotopic abundances, six standard zircons have been analyzed using a Neptune MC-ICPMS, attached with a 193-nm laser. The obtained $^{176}Hf/^{177}Hf$ ratios are 0.282307±31 (2SD) for 91500; 0.282680±31 (2SD) for TEMORA, 0.281729± 21 (2SD) for CZ3, 282177±17 (2SD) for CN92-1, 0.282983±17 (2SD) for FM0411 and 0.281234± 11 (2SD) for Phalaborwa. The Phalaborwa and SK10-2 baddeleyites have $^{176}Hf/^{177}Hf$ ratios of 0.281238±12 (2SD) and 0.282738±13 (2SD), respectively. These values are identical to those obtained by the solution method, indicating the reliability of our laser ablation analyses.
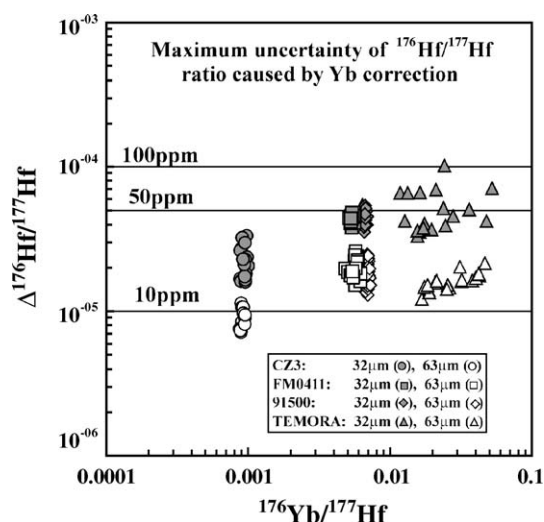

Fig. 12. Maximum potential loss in accuracy of $^{176}Hf/^{177}Hf$ resulting from miscalculation of β_{Yb} (2SE) for standard zircons CZ3, FM0411, 91500 and TEMORA (Data of August 26, 2005, 15 Hz for the 32 μm and 8 Hz for the 63 μm spot sizes).

(4) It is shown that CZ3 zircon and Phalaborwa baddeleyite have very low $^{176}Lu/^{177}Hf$ and $^{176}Yb/^{177}Hf$ values and could be considered as excellent standards for machine calibration and external correction during in-situ zircon Hf isotopic analyses. The other standards are more suitable for experiments of isobaric interference correction, since they have high $^{176}Lu/^{177}Hf$ and $^{176}Yb/^{177}Hf$ ratios, with consistent $^{176}Hf/^{177}Hf$ ratios.

Acknowledgments

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