# Precise determination of Phanerozoic zircon $\mathrm{Pb} / \mathrm{Pb}$ age by multicollector SIMS without external standardization 

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[1] Zircon has long been recognized as the best geochronometer and the most important timekeeper in geosciences. Modern microbeam techniques such as SIMS and LA-ICPMS have been successfully applied to in situ U-Pb zircon age determinations, at spatial resolutions of $20-30 \mu \mathrm{~m}$ or less. Matrix-matched calibration by external standardization of well-characterized natural zircon references is a principal requirement for precise microbeam $\mathrm{U}-\mathrm{Pb}$ zircon age determination due to fractionation effects between Pb and U , which usually result in an external age error exceeding $1 \%$. Alternatively, zircons with a closed $\mathrm{U}-\mathrm{Pb}$ system can be directly dated by measurement of ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ isotopic ratio without external standardization, which has been a common practice for zircons older than 1.0 Ga , but not for relatively young ( $<1.0 \mathrm{Ga}$ and particularly Phanerozoic) ones because of limitations of analytical precision. We describe in this paper a method of ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ measurement on Phanerozoic zircons using a new generation of large radius magnetic sector multicollector Cameca IMS-1280 SIMS. In combination with multicollector mode, a Nuclear Magnetic Resonance (NMR) magnet controller and oxygen flooding techniques, we achieve precisions of ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ ratio of $<0.1 \%$ and $0.1 \sim 0.2 \%$, propagating to $\mathrm{Pb} / \mathrm{Pb}$ age errors $<0.4 \%$ and $1-$ $3 \%$ (excluding U decay constant uncertainties), for zircons of latest Neoproterozoic and late Paleozoic to Mesozoic age, respectively. Therefore, the multicollector SIMS is capable of direct determination of zircon $\mathrm{Pb} / \mathrm{Pb}$ ages as young as Mesozoic age with uncertainties of geological significance. This technique is useful for direct dating of zircons in thin sections. Moreover, it has significance for dating of some other U-rich minerals (i.e., baddeleyite and zirconolite) that are not suitable for SIMS U-Pb dating by external standardization.

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## 1. Introduction

[2] Zircon, $\mathrm{ZrSiO}_{4}$, is a common U-rich accessory mineral occurring in a wide range of rocks, and has long been recognized as the best geochronometer based on the radioactive decay of U to Pb and the most important timekeeper in geosciences. U-Pb zircon dating techniques achieve great advancements during the past half century [e.g., Davis et al., 2003]. Among them, recent developments in microbeam analysis using SIMS (secondary ion mass spectrometer) and laser ablation (LA)-ICPMS have been widely, successfully applied in U-Pb zircon geochronology [e.g., Ireland and Williams, 2003; Košler and Sylvester, 2003; Yuan et al., 2008].
[3] It is well known that significant fractionation effect between Pb and U is a major problem with U-Pb zircon age determination using microbeam techniques. The principle strategy to overcome this effect is matrix-matched calibration by analysis of well-characterized natural zircon standards. Thus, precision and accuracy of $\mathrm{U}-\mathrm{Pb}$ zircon age data are highly controlled by the characterization (particularly homogeneity and concordance) of radiogenic $\mathrm{Pb} / \mathrm{U}$ ratios of the zircon standards. Despite great efforts of development of natural zircon standards for many years in geoscience community, the ideal zircon $\mathrm{U}-\mathrm{Pb}$ age standards are still rare. For instance, the SL13 zircon, a gem quality mineral from Sri Lanka with an assigned age of 572 Ma , has long been used a standard for SHRIMP U-Pb zircon age determination. However, it has been recognized that SL13 has a bimodal distribution of ${ }^{206} \mathrm{~Pb} /{ }^{238} \mathrm{U}$ ages: an original crystallization at 580 Ma and Pb loss at 565 Ma [Compston, 1999]. In general, with present $\mathrm{Pb} / \mathrm{U}$ calibration techniques, the precision of SIMS determinations of ${ }^{206} \mathrm{~Pb} /{ }^{238} \mathrm{U}$ appears limited to about $1 \%$ [Ireland and Williams, 2003].
$[4]{ }^{238} \mathrm{U}$ and ${ }^{235} \mathrm{U}$ decay respectively to produce ${ }^{06} \mathrm{~Pb}$ and ${ }^{207} \mathrm{~Pb}$ at different rates (half-life of ${ }^{238} \mathrm{U}$ and ${ }^{235} \mathrm{U}$ are 4468 Ma and 704 Ma , respectively), thus the ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ isotope ratio provides a direct measure of age that is independent of $\mathrm{Pb} / \mathrm{U}$ measurement. In other words, there is a clear advantage for microbeam $\mathrm{Pb} / \mathrm{Pb}$ age measurement over $\mathrm{U} / \mathrm{Pb}$ in a closed $\mathrm{U}-\mathrm{Pb}$ system, because $\mathrm{Pb} / \mathrm{U}$ calibrations of standard, which usually has $1 \%$ or larger uncertainties, is not necessary. In fact, direct measurement of $\mathrm{Pb} / \mathrm{Pb}$ age by SIMS is a common practice for zircons and other U-rich minerals older than 1.0 Ga , but not for the relatively young ( $<1.0 \mathrm{Ga}$ and
particularly Phanerozoic) samples because of limitations of analytical precision.
[5] We developed in this study a new method of ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ measurements on young (Phanerozoic) zircons using a large radius magnetic sector multicollector Cameca IMS-1280 SIMS, with aims of achieving ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ analytical precision of $\sim 0.2 \%$ or better for Phanerozoic (late Paleozoic and Mesozoic) zircons. Our results indicate that the multicollector SIMS is able to determine zircon Pb / Pb ages as young as the Mesozoic age with uncertainties of within a few million years that are of geological significance.

## 2. Error Propagations of Radiogenic ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ Age Measurements

[6] Despite the aforementioned advantage of SIMS $\mathrm{Pb} / \mathrm{Pb}$ zircon age measurement, there is also a disadvantage in SIMS ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ age measurement for young ( $<1.0 \mathrm{Ga}$ and particularly Phanerozoic) samples due to the following reasons. (1) ${ }^{235} \mathrm{U}$ comprises $<1 \%$ in natural U and so little radiogenic ${ }^{207} \mathrm{~Pb}$ is produced in the Phanerozoic that it is difficult to be measured in situ with high precision; (2) the change in radiogenic ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ for Phanerozoic samples is small, varying from 0.058 to 0.046 between 540 Ma and present day; (3) radiogenic ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ measurement is very sensitive to the common Pb correction; and (4) there are significant error magnifications for Phanerozoic $\mathrm{Pb} / \mathrm{Pb}$ age measurements.
[7] Figure 1 illustrates the error propagations of ${ }^{207} \mathrm{~Pb}{ }^{/ 206} \mathrm{~Pb}$ age measurements. It is clearly shown that uncertainties of radiogenic ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ measurements propagate small errors in early Precambrian samples, but significantly magnified errors in Phanerozoic ones. For example, a $1 \%$ error of radiogenic ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ measurement in 3200 Ma , $1600 \mathrm{Ma}, 800 \mathrm{Ma}, 400 \mathrm{Ma}, 200 \mathrm{Ma}$ and 100 Ma old samples results in $0.5 \%, 1.2 \%, 2.7 \% 5.7 \%$, $11.7 \%$ and $23 \%$ errors in the calculated ages, respectively. Therefore, radiogenic ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ measurements with precisions of $\sim 0.2 \%$ are minimum requirements for dating Paleozoic and Mesozoic crystals with age uncertainties of geological significance. This precision requirement is still not as good as that of routine measurement by IDTIMS that usually gives precision better than $0.1 \%$ for ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ measurement, but it has never been achieved in previous in situ SIMS measurements.


Figure 1. Error propagation between radiogenic ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ ratio and ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ age.
[8] It is noteworthy that uncertainties in the uranium decay constants $\left(0.14 \%\right.$ for ${ }^{235} \mathrm{U}$ and $0.11 \%$ for ${ }^{238} \mathrm{U}$ [Jaffey et al., 1971]) are an important source of external error in $\mathrm{U}-\mathrm{Pb}$ and $\mathrm{Pb} / \mathrm{Pb}$ zircon geochronology [e.g., Schoene et al., 2006] regardless of the dating techniques. To present data at each level of error propagation, the calculated $\mathrm{U}-\mathrm{Pb}$ and $\mathrm{Pb} / \mathrm{Pb}$ age errors in this study are reported in the manner of $\pm \mathrm{X} / \mathrm{Y}$ at $95 \%$ confidence interval, unless otherwise noted, where X is the internal error including standard calibration (for U-Pb age) and common lead correction but ignoring the decay constant error(s), and Y includes the decay constant error(s) of Jaffey et al. [1971]. The algorithms of Ludwig [1980] and the statistical reduction and plotting program Isoplot/Ex [Ludwig, 2001] were used to calculate ages, uncertainties, weighted means, and the generation of $\mathrm{U}-\mathrm{Pb}$ concordia plots.

## 3. Strategy of Improving Precision of Radiogenic ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ Measurement

[9] Increase of the counting time on ${ }^{207} \mathrm{~Pb}$ can improve the precision of ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ measurements to some extent, but there are practical limits as it increases risk of partial signal loss due to instrumental drift in monocollector SIMS [e.g., Ireland and Williams, 2003]. In addition, signal variation also hampers the improvement of analytical precision by using monocollector SIMS. In fact, it is very rare to achieve precision of better than $0.5 \%$ for ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ measurements of Phanerozoic zircons by using monocollector SIMS, as evidenced by large numbers of zircon age data determined by SHRIMP and Cameca SIMS in the literature.
[10] The precision of ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ measurements could be significantly improved by using a new generation multicollector SIMS such as the Cameca IMS-1280 SIMS. Simultaneous detection of ${ }^{206} \mathrm{~Pb}$ and ${ }^{207} \mathrm{~Pb}$ signals using multicollector mode can eliminate the effect of signal variation. In addition, this new generation SIMS is equipped with an NMR magnet controller that consists of a set of NMR probe and associated electronics. The NMR control, which is used in multicollector mode when no mass peak switching is required, provides a much better stability of magnetic field than the Hall probe system.
[11] Oxygen flooding is another very useful technique in the Cameca SIMS to improve the precision of ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ measurements. Previous investigations demonstrated that introduction of oxygen into the sample chamber (oxygen flooding) of the Cameca SIMS increase the secondary ion yield by $\sim 200 \%$ for zircon analysis [e.g., Schuhmacher et al., 1994; Quidelleur et al., 1997; Whitehouse et al., 1999]. Whereas, the $\mathrm{Pb}^{+}$ion yield increases only by $\sim 20 \%$ under the same oxygen flooding conditions for SHRIMP [Ireland and Williams, 2003].
[12] It is anticipated that ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ measurements with precisions of $\sim 0.2 \%$ or better might be achieved for Phanerozoic zircons by using the new generation large geometry Cameca IMS1280 SIMS in combination with multicollector mode, an NMR magnet controller and oxygen flooding techniques.

## 4. Analytical Procedures

[13] $\mathrm{Pb} / \mathrm{Pb}$ and $\mathrm{U} / \mathrm{Pb}$ dating of zircon was conducted using the Chinese Academy of Sciences Cameca IMS-1280 ion microprobe (CASIMS) at the Institute of Geology and Geophysics in Beijing. We use the monocollector mode to determine zircon $\mathrm{Pb} / \mathrm{Pb}$ and $\mathrm{U} / \mathrm{Pb}$ ages, and use the multicollector mode to determine zircon $\mathrm{Pb} / \mathrm{Pb}$ ages only.
[14] U-Pb ID-TIMS dating of the Qinghu zircon was performed at the University of Wyoming, USA, using a modified chemical abrasion method after Mattinson [2005] and a Micromass Sector 54 thermal ionization mass spectrometer.

### 4.1. Monocollector Mode

[15] The $\mathrm{O}_{2}^{-}$primary ion beam was accelerated at -13 kV , with an intensity of $\sim 10 \mathrm{nA}$. The aperture illumination mode (Kohler illumination) was used

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with a $200 \mu \mathrm{~m}$ primary beam mass filter (PBMF) aperture to produce even sputtering over the entire analyzed area. The ellipsoidal spot is about $20 \times$ $30 \mu \mathrm{~m}$ in size. Positive secondary ions were extracted with a 10 kV potential.
[16] Oxygen flooding was used to increase the $\mathrm{O}_{2}$ pressure to $\sim 5 \times 10^{-6}$ Torr in the sample chamber, enhancing $\mathrm{Pb}^{+}$sensitivity to a value of $25-28 \mathrm{cps} /$ $n A / p p m$ for zircon. This great enhancement of $\mathrm{Pb}^{+}$ sensitivity is crucial to improve precision of ${ }^{207} \mathrm{~Pb} /{ }^{26} \mathrm{~Pb}$ zircon measurement.
[17] In the secondary ion beam optics, a 60 eV energy window was used, together with a mass resolution of $\sim 5400$ (defined at $10 \%$ peak height) to separate $\mathrm{Pb}^{+}$peaks from isobaric interferences. Precise mass calibration was kept by using an automatic routine in the Cameca Customisable Ion Probe Software (CIPS) to scan over large peaks such as ${ }^{94} \mathrm{Zr}_{2}{ }^{16} \mathrm{O}$ and ${ }^{177} \mathrm{Hf}^{16} \mathrm{O}_{2}$ and extrapolate the mass to B field curve for peaks between these reference points. The field aperture was set to $7000 \mu \mathrm{~m}$, and the transfer optic magnification was adjusted to 200. Rectangular lenses were activated in the secondary ion optics to increase the transmission at high mass resolution. A single electron multiplier was used on ion-counting mode to measure secondary ion beam intensities by peak jumping sequence: $196\left({ }^{90} \mathrm{Zr}_{2}^{16} \mathrm{O}\right.$, matrix reference for centering the secondary ion beam as well as energy and mass adjustment), $200\left({ }^{92} \mathrm{Zr}_{2}^{16} \mathrm{O}\right.$, reference of mass 200.5), 200.5 (background), $203.81\left({ }^{94} \mathrm{Zr}_{2}^{16} \mathrm{O}\right.$, for mass calibration), 203.97 $(\mathrm{Pb}), 206(\mathrm{~Pb}), 207(\mathrm{~Pb}), 208(\mathrm{~Pb}), 209$ $\left({ }^{177} \mathrm{Hf}^{16} \mathrm{O}_{2}\right.$, for mass calibration), 238 (U), 248 $\left({ }^{232} \mathrm{Th}^{16} \mathrm{O}\right), 270\left({ }^{238} \mathrm{U}^{16} \mathrm{O}_{2}\right.$ ), and 270.1 (reference mass), 1.04, $0.56,4.16,0.56,6.24,4.16,6.24$, $2.08,1.04,2.08,2.08,2.08$, and 0.24 s (the integration time is based on the unit time of 0.08 s ), respectively. Each measurement consists of 10 cycles, and the total analytical time is $\sim 16 \mathrm{~min}$.
[18] zzzzzzCalibration of $\mathrm{Pb} / \mathrm{U}$ ratios is based on an observed linear relationship between $\ln \left({ }^{206} \mathrm{~Pb} /{ }^{238} \mathrm{U}\right)$ and $\ln \left({ }^{238} \mathrm{U}^{16} \mathrm{O}_{2} /{ }^{238} \mathrm{U}\right)$, as same as those reported by Whitehouse et al. [1997]. The relationship between ${ }^{206} \mathrm{~Pb} /^{238} \mathrm{U}$ and ${ }^{238} \mathrm{U}^{16} \mathrm{O}_{2} / 238 \mathrm{U}$ can be approximated over a wide range of ${ }^{238} \mathrm{U}^{16} \mathrm{O}_{2}{ }^{238} \mathrm{U}$ by a power law relationship. Since the range of measured ${ }^{238} \mathrm{U}^{16} \mathrm{O}_{2}{ }^{238} \mathrm{U}$ ratios is small in both standard and unknowns during a particular analytical session, a linear function is chosen to approximate this relationship, with a slope of the $\ln \left({ }^{206} \mathrm{~Pb} /{ }^{238} \mathrm{U}\right)-$ $\ln \left({ }^{238} \mathrm{U}^{16} \mathrm{O}_{2} /^{238} \mathrm{U}\right)$ calibration line being 1.3. $\mathrm{Pb} / \mathrm{U}$ calibration was performed relative to the 1065 Ma
standard zircon 91500 with Th and U concentrations of $\sim 29$ and 80 ppm respectively [Wiedenbeck et al., 1995]. U and Th concentration determination of unknowns is based on observed correlation between ${ }^{238} \mathrm{U}^{16} \mathrm{O}_{2},{ }^{232} \mathrm{Th}^{16} \mathrm{O}$ and ${ }^{90} \mathrm{Zr}_{2}^{16} \mathrm{O}$ for the standard. It is noteworthy that this determination of U and Th is considered approximate because of $\sim 15 \%$ heterogeneity in U and Th contents for 91500 [Wiedenbeck et al., 2004].

### 4.2. Multicollector Mode

[19] The multicollector assembly fitted to this large geometry Cameca IMS-1280 SIMS instrument consists of five movable trolleys, each of which may be equipped with either electron multiplier (EM) or Faraday cup (FC). Figure 2 shows the multicollector configuration for $\mathrm{Pb} / \mathrm{Pb}$ dating of zircon.
[20] In the secondary ion beam optics, a 60 eV energy window was used throughout, together with a mass resolution of $\sim 4800$ (defined at $50 \%$ peak height), as the mass resolution is fixed at 2500 , 4800 and 8000 in multicollector mode in the Cameca IMS-1280 SIMS. This mass resolution, equivalent to mass resolution of $\sim 4000$ defined at $10 \%$ peak height, is capable of effective separation of the main interferences of molecules of $\mathrm{Zr}, \mathrm{Hf}, \mathrm{Si}$ and O , such as $\mathrm{Zr}_{2} \mathrm{O}$ (requiring a mass resolution of $\sim 1200$ ) and HfSi (requiring $\sim 3700$ ). While it is generally thought that to resolve HREE dioxides such as $\mathrm{YbO}_{2}$ requires a resolution of $\sim 5100$ [e.g., Ireland and Williams, 2003], Bosch et al. [2002] demonstrated $\mathrm{YbO}_{2}$ can be readily separated at $\sim 3500$. Our SIMS analyses in this study indicated that the measured ${ }^{206} \mathrm{~Pb} /{ }^{204} \mathrm{~Pb}$ ratios of two standard zircons (BR266 and Plešovice) by multicollector mode at a resolution of $\sim 4000$ are comparable with those by single-collector mode at a resolution of $\sim 5400$, suggesting that $\mathrm{YbO}_{2}$ has negligible interference with the Pb isotope measurements at resolution of $\sim 4000$. The multicollection mode was used to measure secondary ion beam intensities of ${ }^{204} \mathrm{~Pb},{ }^{206} \mathrm{~Pb}$ and ${ }^{207} \mathrm{~Pb}$, with integration times of 6 s . After a $180-\mathrm{s}$ presputtering with $20 \mu \mathrm{~m}$ raster, the energy calibrations were checked by scanning sample HV (from -20 to $>80 \mathrm{eV}, 4 \mathrm{eV}$ step, 5 eV gap) on mass ${ }^{206} \mathrm{~Pb}$, beam centering control using ${ }^{206} \mathrm{~Pb}$ by scanning deflector for field aperture (DTFA) X/Y (500 dig.) and deflector for contrast aperture (DTCA) X (900 dig.). The NMR controller was used in multicollector measurement to stabilize the magnetic field, with an instrumental drift ( $\Delta \mathrm{M} /$ M) less than 2.5 ppm over 16 h (Figure 3). Each


Figure 2. Multicollector configuration for zircon ${ }^{204} \mathrm{~Pb},{ }^{206} \mathrm{~Pb}$, and ${ }^{207} \mathrm{~Pb}$ measurement.
measurement consists of 40 cycles, and the total analytical time is $\sim 10 \mathrm{~min}$.

### 4.3. Correction of Common Pb

[21] Correction of common Pb was made by measuring ${ }^{204} \mathrm{~Pb}$ amount. ${ }^{204} \mathrm{~Pb}$ provides the direct measure of common Pb , though its low abundance makes the correction relatively imprecise. Accurate peak positioning for ${ }^{204} \mathrm{~Pb}$ is crucial for proper estimation of common Pb . In monocollector mode, ${ }^{204} \mathrm{~Pb}$ isotope was calibrated by centering the ${ }^{94} \mathrm{Zr}_{2}^{16} \mathrm{O}$ peak at nominal mass 204, and then a +0.167 amu mass offset was applied to ${ }^{204} \mathrm{~Pb}$ (Figure 4a). In multicollector mode, a high-uranium zircon containing high ${ }^{204} \mathrm{~Pb}$ was used to calibrate the Pb peaks (Figure 4 b ). An average of the isotopic compositions of Pb blank ( ${ }^{206} \mathrm{~Pb} /{ }^{204} \mathrm{~Pb}=$ $17.8,{ }^{207} \mathrm{~Pb} /{ }^{204} \mathrm{~Pb}=15.5,{ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}=0.87$ ) in Beijing TIMS laboratories is used for the common Pb assuming that the low levels of common Pb are thought to be largely laboratory-derived. Because our measured zircon ${ }^{206} \mathrm{~Pb} /{ }^{204} \mathrm{~Pb}$ ratios in this study are mostly higher than 10,000 , the common Pb corrections and the calculated $\mathrm{U}-\mathrm{Pb}$ ages were insensitive to the choice of common Pb isotopic compositions. The high ${ }^{206} \mathrm{~Pb} /{ }^{204} \mathrm{~Pb}$ ratios measured by SIMS in this study are consistent with low-blank TIMS measurements on the same standards [e.g., Stern and Amelin, 2003; Sláma et al.,

2008] (see also Table 4), which demonstrate that these gem-quality standard zircons are relatively free of initial Pb .
[22] In the multicollector mode analysis, the unradiogenic ${ }^{206} \mathrm{~Pb}$ and ${ }^{207} \mathrm{~Pb}$, which were calculated on the basis of the average of measured ${ }^{204} \mathrm{~Pb}$ of 40 analytical cycles, were subtracted from the measured ${ }^{206} \mathrm{~Pb}$ and ${ }^{207} \mathrm{~Pb}$. Because the average of measured ${ }^{204} \mathrm{~Pb}$ counts of 40 analytical cycles gives more precise ( $\sim 10-30 \%$ ) and reasonable estimate of the common Pb than that of each cycle, correction of common Pb will contribute a very small error source to the final radiogenic ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ results when the measured ${ }^{206} \mathrm{~Pb} /{ }^{204} \mathrm{~Pb}$ values are higher than 10,000 (see detailed discussion below).

### 4.4. Impact of Common Pb Correction on the Age Uncertainty

[23] It is noteworthy that radiogenic ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ measurement is sensitive to the common Pb correction. We evaluate below quantitatively the impact of common Pb correction on the ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ age uncertainty.
[24] The radiogenic $\left.\left({ }^{207} \mathrm{~Pb}\right)^{206} \mathrm{~Pb}\right)$ * ratio can be calculated using the following equation:

$$
\begin{align*}
\left(\frac{{ }^{207} P b}{206 P b}\right)^{*} & =\frac{\left(\frac{{ }^{207} P b}{206}\right)_{m b}-\left(\frac{{ }^{207} P b}{206 P b}\right)_{c} \times f_{206}}{1-f_{206}} \\
& \left.=\frac{\left(\frac{{ }^{207} P b}{206}\right)_{m}-\left(\frac{{ }^{207} P b}{206}\right)_{c} \times\left(\frac{206 P b}{{ }^{204} P b}\right)_{c} \times\left(\frac{{ }^{204} P b}{206}\right)_{m}}{1-\left(\frac{206}{204} \mathrm{~Pb}\right.}\right)_{c} \times\left(\frac{204}{206 P b}\right)_{m} \tag{1}
\end{align*}
$$



Figure 3. Variations of magnetic field controlled by the NMR controller, which provides a long-term magnetic field drift ( $\Delta \mathrm{M} / \mathrm{M}$ ) within 2.5 ppm in 16 h . The time interval between field measurements is 1 s , and the integration time for each measurement is 1 s .



Figure 4. (a) Mass scan of zircon in the region close to mass 204 showing ${ }^{94} \mathrm{Zr}_{2}{ }^{16} \mathrm{O},{ }^{176} \mathrm{Hf}^{28} \mathrm{Si}$, and ${ }^{204} \mathrm{~Pb}$ peaks at a mass resolution of $\sim 5400 .{ }^{204} \mathrm{~Pb}$ isotope was calibrated by centering the ${ }^{94} \mathrm{Zr}_{2}{ }^{16} \mathrm{O}$ peak, then adding a +0.167 amu mass offset. (b) Pb mass scan of a high-uranium zircon in Cameca IMS-1280 multicollector array at a mass resolution of $\sim 4000$ (defined at $10 \%$ peak height), with more than one third of the peak width being flat at the $99 \%$ level.
where $\mathrm{c}=$ the common Pb composition; $\mathrm{m}=$ the measured value, and $f_{206}$ is the percentage of common ${ }^{206} \mathrm{~Pb}$ in total ${ }^{206} \mathrm{~Pb}$, calculated as:

$$
\begin{equation*}
f_{206}=\left(\frac{{ }^{206} P b}{204 P b}\right)_{c} \times\left({ }^{204} P b{ }^{206 P b}\right)_{m} \tag{2}
\end{equation*}
$$

[25] Uncertainty of $\left({ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}\right)^{*}\left(\sigma_{\mathrm{z}}\right)$ can be propagated using the following equation:

$$
\sigma_{z}=\sqrt{\left(\frac{\partial Z}{\partial A}\right)^{2} * \sigma_{A}^{2}+\left(\frac{\partial Z}{\partial B}\right)^{2} * \sigma_{B}^{2}+\left(\frac{\partial Z}{\partial C}\right)^{2} * \sigma_{C}^{2}+\left(\frac{\partial Z}{\partial D}\right)^{2} * \sigma_{D}^{2}}
$$

where $Z$ refers to $\left({ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}\right)^{*}$, and $\mathrm{A}, \mathrm{B}, \mathrm{C}$ and D to $\left({ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}\right)_{\mathrm{m}},\left({ }^{204} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}\right)_{\mathrm{m}},\left({ }^{206} \mathrm{~Pb} /{ }^{204} \mathrm{~Pb}\right)_{\mathrm{c}}$ and $\left({ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}\right)_{\mathrm{c}}$, respectively. In equation (3), each differential term ( $\partial$ ) reflects the partial differential of function Z with respect to one variable, holding all others constant. The partial differentials are then multiplied by the absolute (not relative) uncertainties for each variable. The uncertainty on Z is equal to the square root of the sum of the squares of all these terms.
[26] Variations of common Pb compositions are estimated as ${ }^{206} \mathrm{~Pb} /{ }^{204} \mathrm{~Pb}=17.6 \pm 1$, and


Figure 5. Correlation between uncertainties of the radiogenic ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ ages of $2060 \mathrm{Ma}, 560 \mathrm{Ma}$, and 160 Ma and the measured ${ }^{206} \mathrm{~Pb} /{ }^{204} \mathrm{~Pb}$ values, along with assigned uncertainties of measured ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ and ${ }^{206} \mathrm{~Pb} /{ }^{204} \mathrm{~Pb}$. Dashed lines include uncertainties of common Pb compositions ( ${ }^{206} \mathrm{~Pb} /{ }^{204} \mathrm{~Pb}=17.6 \pm 1,{ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}=0.87 \pm 0.05$ ); solid lines exclude uncertainties of common Pb compositions. SIMS measurements in this study have errors of ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ and ${ }^{206} \mathrm{~Pb}{ }^{204} \mathrm{~Pb}$ mostly ranging from $0.1 \%$ to $0.8 \%$ and $10 \%$ to $30 \%$, respectively, By comparison, TIMS measurements usually have errors of ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ and ${ }^{206} \mathrm{~Pb} /{ }^{204} \mathrm{~Pb}<0.1 \%$ and $<2 \%$, respectively. For SIMS measurements, common Pb correction has only little effect on the final $\mathrm{Pb} / \mathrm{Pb}$ age uncertainty when the measured ${ }^{206} \mathrm{~Pb} /{ }^{204} \mathrm{~Pb}>10,000$.

Table 1. SIMS Baddeleyite $\mathrm{Pb} / \mathrm{Pb}$ Data

|  |  |  |  |  |  |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |

[^0]${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}=0.87 \pm 0.05$, which overlap with the range of Phanerozoic terrestrial Pb [Stacey and Kramers, 1975]. For SIMS measurements in this study, uncertainties of $\left({ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}\right)_{\mathrm{m}}$ vary from 0.1 to $0.8 \%$, and $\left({ }^{204} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}\right)_{\mathrm{m}}$ from 10 to $40 \%$.
[27] Figure 5 illustrates the relationship between uncertainties of the radiogenic ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ ages of $2060 \mathrm{Ma}, 560 \mathrm{Ma}$ and 160 Ma and the measured ${ }^{206} \mathrm{~Pb} /{ }^{204} \mathrm{~Pb}$ values, along with assigned uncertainties of measured ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ and ${ }^{206} \mathrm{~Pb} /{ }^{204} \mathrm{~Pb}$. It is clearly shown that uncertainty of ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ age by SIMS measurements are derived predominantly from the uncertainty of ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ and the measured ${ }^{206} \mathrm{~Pb} /{ }^{204} \mathrm{~Pb}$ values. For SIMS measurements with ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ error $\geq 0.2 \%$ and ${ }^{206} \mathrm{~Pb} /{ }^{204} \mathrm{~Pb}$ error $\geq 10 \%$, uncertainties of common Pb compositions have little or negligible contribution to the final ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ age uncertainty when the measured ${ }^{206} \mathrm{~Pb} /{ }^{204} \mathrm{~Pb}$ values exceed 10,000 . In contrast, when ${ }^{206} \mathrm{~Pb} /{ }^{204} \mathrm{~Pb}$ error $\leq 2 \%$ (typical of TIMS measurements), uncertainties of common Pb compositions can affect the ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ age uncertainty significantly when the measured ${ }^{206} \mathrm{~Pb} /{ }^{204} \mathrm{~Pb}$ value $<10,000$.

### 4.5. Correction of Instrumental Mass Fractionation of $\mathbf{P b}$ Isotopes

[28] During the multicollector mode measurements, a constant ${ }^{90} \mathrm{Zr}_{2}^{16} \mathrm{O}^{+}$signal $\left(\sim 1.0 \times 10^{5}\right.$ cps ) was used to calibrate the secondary ion yields of each of the EMs on the movable trolleys relative to the axial EM. The yields of all EMs were further fine-tuned against the repeated ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ measurements of Phalaborwa baddeleyite.
[29] Previous SIMS measurements of Pb isotope compositions of zircons and baddeleyite have demonstrated that instrumental mass fractionation of Pb isotopes is negligible [e.g., Compston et al., 1984; Whitehouse et al., 1997; Wingate and Giddings, 2000; Li et al., 2005]. In fact, it is very difficult to make an accurate measurement of instrumental mass fractionation within relatively poor precisions of Pb isotope ratios by using monocollector mode SIMS, because of low Pb concentrations in zircon and baddeleyite and the difficulty of resolving any PbH isobars $(\mathrm{M} / \Delta \mathrm{M}=$ $33,000)$. A number of studies have shown that measurements of ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ ratio from wellcharacterized reference zircons and baddeleyites are generally in agreement with the recommended values within analytical errors, and there appears to be a mutual cancellation of the hydrides and fractionation that raise and lower the ${ }^{207} \mathrm{~Pb} /^{206} \mathrm{~Pb}$


Figure 6. Comparison of weighted average ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ ages for Phalaborwa baddeleyite determined by Cameca IMS-1280 SIMS using monocollector and multicollector modes. Uncertainties are $95 \%$ confidence level. Data point error bars are $2 \sigma$.
respectively [e.g., Whitehouse et al., 1997; Ireland and Williams, 2003]. In practice, instrumental mass fractionation corrections were generally not made in SIMS zircon and baddeleyite $\mathrm{Pb} / \mathrm{Pb}$ age determination. Our measurements of the well-characterized Phalaborwa baddeleyite by using monocollector mode yield a weighted mean ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ ratio of $0.12708 \pm 0.00020(95 \%$ confidence interval, hereafter), corresponding to an age of $2058.0 \pm 2.8 /$ 6.6 Ma (Table 1 and Figure 5). This age is in agreement within errors with the age of $2059.60 \pm$ 0.35 Ma (excluding decay constant errors) determined by TIMS [Heaman and LeCheminant, 1993; Heaman, 2009]. Measurements of the Phalaborwa baddeleyite by using multicollector mode give more precise ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ ratio of $0.12727 \pm 0.00007$ corresponding to an age of $2060.6 \pm 1.0 / 6.1 \mathrm{Ma}$ (Figure 6), indicating negligible instrumental mass fractionation associated with the sputtering process. No correction of instrumental mass fractionation was made on ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ measurement of zircons. A factor of 1.000456 , the ratio of our measured ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}(0.12727) /$ the recommended ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}(0.127212)$, was applied to fine-tune the yield of EM at H 1 (detecting ${ }^{207} \mathrm{~Pb}$ ) relative to the axial EM (detecting ${ }^{206} \mathrm{~Pb}$ ).

### 4.6. ID-TIMS Methods for Qinghu Zircon

[30] Six single zircons that were free of inclusions and internal fractures were selected for analysis. Five grains were annealed at $850^{\circ} \mathrm{C}$ for 48 h and dissolved in two steps following the chemical abrasion method of Mattinson [2005]. The first dissolution step used HF and $\mathrm{HNO}_{3}$ in a $180^{\circ} \mathrm{C}$ oven for 12 h . The liquid was discarded, and the
Table 2. Zircon U-Pb Data Determined by Monocollector SIMS Mode

Table 2. (continued)

Table 2. (continued)

| Sample Spot | $\underset{(\mathrm{ppm})}{\mathrm{U}}$ | $\begin{gathered} \mathrm{Th} \\ (\mathrm{ppm}) \end{gathered}$ | Th/U | ${ }^{206} \mathrm{~Pb} /{ }^{204} \mathrm{~Pb}_{\mathrm{m}}{ }^{\text {a }}$ | $\begin{aligned} & f_{206}{ }^{\mathrm{b}} \\ & (\%) \end{aligned}$ | ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ | $\begin{gathered} \pm 1 \sigma \\ (\%) \end{gathered}$ | ${ }^{207} \mathrm{~Pb} /{ }^{235} \mathrm{U}$ | $\begin{aligned} & \pm 1 \sigma \\ & (\%) \end{aligned}$ | ${ }^{206} \mathrm{~Pb} /{ }^{238} \mathrm{U}$ | $\begin{gathered} \pm 1 \sigma \\ (\%) \end{gathered}$ | $\begin{gathered} \mathrm{t}_{207 / 206}(\mathrm{Ma}) \\ \end{gathered}$ | $\pm 1 \sigma$ | $\begin{gathered} \mathrm{t}_{207 / 235} \\ (\mathrm{Ma}) \end{gathered}$ | $\pm 1 \sigma$ | $\begin{gathered} \mathrm{t}_{206 / 238} \\ \text { (Ma) } \end{gathered}$ | $\pm 1 \sigma$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| QH@20 | 547 | 250 | 0.458 | $3.54 \mathrm{E}+4$ | 0.05 | 0.0489 | 1.13 | 0.166 | 1.66 | 0.0246 | 1.21 | 144.4 | 26.4 | 156.0 | 2.4 | 156.7 | 1.9 |
| QH@21 | 791 | 335 | 0.423 | $5.30 \mathrm{E}+4$ | 0.04 | 0.0489 | 0.91 | 0.169 | 1.51 | 0.0251 | 1.21 | 143.3 | 21.3 | 158.9 | 2.2 | 160.0 | 1.9 |
| QH@22 | 628 | 338 | 0.538 | $2.31 \mathrm{E}+4$ | 0.08 | 0.0494 | 1.16 | 0.167 | 1.67 | 0.0246 | 1.20 | 165.4 | 26.9 | 156.9 | 2.4 | 156.4 | 1.9 |
| QH@23 | 969 | 460 | 0.475 | $5.26 \mathrm{E}+4$ | 0.04 | 0.0495 | 0.83 | 0.170 | 1.47 | 0.0248 | 1.21 | 173.3 | 19.3 | 159.2 | 2.2 | 158.2 | 1.9 |
| QH@24 | 803 | 399 | 0.497 | $6.57 \mathrm{E}+4$ | 0.03 | 0.0496 | 0.92 | 0.170 | 1.53 | 0.0248 | 1.20 | 174.9 | 21.3 | 159.1 | 2.2 | 158.0 | 1.9 |
| QH@25 | 840 | 366 | 0.436 | $3.96 \mathrm{E}+4$ | 0.05 | 0.0489 | 0.90 | 0.169 | 1.50 | 0.0251 | 1.20 | 140.7 | 20.9 | 158.4 | 2.2 | 159.5 | 1.9 |
| QH@26 | 1156 | 506 | 0.437 | $6.60 \mathrm{E}+4$ | 0.03 | 0.0485 | 0.76 | 0.166 | 1.42 | 0.0249 | 1.20 | 121.9 | 17.7 | 156.0 | 2.1 | 158.3 | 1.9 |
| QH@27 | 791 | 379 | 0.479 | $3.08 \mathrm{E}+4$ | 0.06 | 0.0490 | 0.97 | 0.168 | 1.55 | 0.0248 | 1.20 | 147.5 | 22.6 | 157.3 | 2.3 | 158.0 | 1.9 |
| QH@28 | 526 | 237 | 0.452 | $3.65 \mathrm{E}+4$ | 0.05 | 0.0492 | 1.18 | 0.170 | 1.69 | 0.0251 | 1.21 | 155.6 | 27.4 | 159.5 | 2.5 | 159.8 | 1.9 |
| QH@29 | 727 | 310 | 0.427 | $3.03 \mathrm{E}+4$ | 0.06 | 0.0485 | 1.03 | 0.168 | 1.58 | 0.0251 | 1.20 | 122.3 | 24.0 | 157.4 | 2.3 | 159.8 | 1.9 |
| QH@30 | 1009 | 525 | 0.520 | $4.02 \mathrm{E}+4$ | 0.05 | 0.0488 | 1.70 | 0.168 | 2.09 | 0.0249 | 1.21 | 140.6 | 39.5 | 157.5 | 3.1 | 158.7 | 1.9 |

[^1]remaining grains were rinsed and cleaned in HCl and $\mathrm{HNO}_{3}$. A mixed ${ }^{205} \mathrm{~Pb}-{ }^{233} \mathrm{U}-{ }^{235} \mathrm{U}$ tracer solution (ET535) was added to the microbombs for isotope dilution determination of Pb and U abundances. Final dissolution used HF and $\mathrm{HNO}_{3}$ at $240^{\circ} \mathrm{C}$ and included a sixth, untreated grain that was analyzed to monitor absolute Pb and U concentrations. Additional details are given in the notes to Table 4.

## 5. Analytical Results

[31] Three zircon samples from different rock types with ages ranging from the latest Neoproterozoic to middle Jurassic were chosen for analysis in this study. Zircon grains, together with a zircon U-Pb standard 91500 and Phalaborwa baddeleyite, were cast in transparent epoxy mount, which was then polished to section the crystals in half for analysis. Zircons were documented with transmitted and reflected light micrographs as well as cathodoluminescence (CL) images to reveal their internal structures, and the mount was vacuum-coated with high-purity gold prior to SIMS analysis. SIMS UPb and $\mathrm{Pb} / \mathrm{Pb}$ data by using monocollector and $\mathrm{Pb} /$ Pb data by using multicollector modes are presented in Tables 2 and 3, respectively.

### 5.1. BR266 Zircon

[32] This is a gem-quality zircon from Sri Lanka and used as an ion microprobe reference material for $\mathrm{U}-\mathrm{Pb}$ zircon dating by the Geological Survey of Canada. It has a slightly discordant ${ }^{206} \mathrm{~Pb} /{ }^{238} \mathrm{U}$ and ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ ages dated by TIMS at $559.0 \pm 0.3 \mathrm{Ma}$ and $562.2 \pm 0.5 \mathrm{Ma}$ (excluding decay constant errors), respectively [Stern, 2001; Stern and Amelin, 2003]. These dates overlap within error of chemically abraded TIMS dates ( $559.27 \pm 0.11 \mathrm{Ma}$ and $562.00 \pm 0.50 \mathrm{Ma}$, respectively) produced by Schoene et al. [2006].
[33] Thirty measurements of $\mathrm{U}-\mathrm{Pb}$ isotopes were conducted on BR266 zircon by using monocollector mode, and the data are plotted in Figure 7a. The measured $\mathrm{U}-\mathrm{Pb}$ isotopes are marginally concordant when the decay constant error is included. The weighted mean of ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb},{ }^{207} \mathrm{~Pb} /{ }^{235} \mathrm{U}$ and ${ }^{206} \mathrm{~Pb} /{ }^{238} \mathrm{U}$ ratios is $0.058966 \pm 0.000096$, $0.7313 \pm 0.0036$ and $0.08997 \pm 0.00041$, respectively, corresponding to age of $565.7 \pm 3.5 / 5.8 \mathrm{Ma}$, $557.4 \pm 2.1 / 2.2 \mathrm{Ma}$ and $555.3 \pm 2.4 / 2.5 \mathrm{Ma}$, respectively. A U-Pb concordia age is calculated at $558.6 \pm 2.1$ (excluding decay constant errors), or $557.2 \pm 2.3 \mathrm{Ma}$ (including decay constant errors),

Table 3. Zircon $\mathrm{Pb} / \mathrm{Pb}$ Data Determined by Multicollector SIMS Mode

| Sample Spot | ${ }^{206} \mathrm{~Pb} /{ }^{204} \mathrm{~Pb}_{\mathrm{m}}{ }^{\text {a }}$ | $\begin{gathered} \pm 1 \sigma \\ (\%) \end{gathered}$ | ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}_{\mathrm{m}}{ }^{\text {a }}$ | $\begin{aligned} & \pm 1 \sigma \\ & (\%) \end{aligned}$ | ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}_{\mathrm{c}}{ }^{\text {b }}$ | $\begin{gathered} \pm 1 \sigma \\ (\%) \end{gathered}$ | $\begin{gathered} \mathrm{t}_{207 / 206} \\ (\mathrm{Ma}) \end{gathered}$ | $\pm 1 \sigma$ | $\begin{gathered} { }^{207} \mathrm{~Pb} \\ (\mathrm{cps}) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| BR266 |  |  |  |  |  |  |  |  |  |
| BR266@1r | $2.96 \mathrm{E}+05$ | 23.0 | 0.05892 | 0.195 | 0.05887 | 0.196 | 562.1 | 4.3 | 1158 |
| BR266@2r | $3.95 \mathrm{E}+05$ | 26.5 | 0.05905 | 0.202 | 0.05901 | 0.203 | 567.4 | 4.4 | 1129 |
| BR266@3r | $3.53 \mathrm{E}+05$ | 22.8 | 0.05879 | 0.196 | 0.05875 | 0.197 | 558.0 | 4.3 | 1145 |
| BR266@4r | $9.57 \mathrm{E}+05$ | 42.2 | 0.05893 | 0.195 | 0.05891 | 0.196 | 563.8 | 4.3 | 1160 |
| BR266@5r | $2.10 \mathrm{E}+05$ | 19.5 | 0.05910 | 0.196 | 0.05903 | 0.198 | 568.2 | 4.3 | 1150 |
| BR266@6r | $3.60 \mathrm{E}+05$ | 23.7 | 0.05883 | 0.197 | 0.05879 | 0.197 | 559.3 | 4.3 | 1142 |
| BR266@7r | $1.85 \mathrm{E}+05$ | 18.5 | 0.05890 | 0.196 | 0.05882 | 0.198 | 560.3 | 4.3 | 1147 |
| BR266@8r | $3.92 \mathrm{E}+05$ | 24.2 | 0.05900 | 0.196 | 0.05896 | 0.197 | 565.7 | 4.3 | 1147 |
| BR266@9r | $5.77 \mathrm{E}+05$ | 31.7 | 0.05903 | 0.195 | 0.05900 | 0.196 | 567.2 | 4.3 | 1161 |
| BR266@10r | $4.27 \mathrm{E}+05$ | 27.5 | 0.05919 | 0.198 | 0.05916 | 0.199 | 572.9 | 4.3 | 1126 |
| BR266@11r | $3.37 \mathrm{E}+05$ | 23.4 | 0.05892 | 0.196 | 0.05888 | 0.197 | 562.5 | 4.3 | 1151 |
| BR266@12r | $3.35 \mathrm{E}+05$ | 23.4 | 0.05904 | 0.197 | 0.05899 | 0.197 | 566.8 | 4.3 | 1144 |
| BR266@13r | $2.20 \mathrm{E}+05$ | 20.3 | 0.05886 | 0.196 | 0.05879 | 0.198 | 559.4 | 4.3 | 1148 |
| BR266@14r | $2.99 \mathrm{E}+05$ | 22.8 | 0.05896 | 0.209 | 0.05891 | 0.210 | 563.8 | 4.6 | 1098 |
| BR266@15r | $3.88 \mathrm{E}+05$ | 25.8 | 0.05899 | 0.228 | 0.05895 | 0.228 | 565.3 | 5.0 | 1046 |
| BR266@16r | $4.67 \mathrm{E}+05$ | 29.4 | 0.05903 | 0.205 | 0.05899 | 0.206 | 566.9 | 4.5 | 1051 |
| BR266@17r | $3.52 \mathrm{E}+05$ | 24.1 | 0.05869 | 0.205 | 0.05865 | 0.205 | 554.0 | 4.5 | 1055 |
| BR266@18r | $3.00 \mathrm{E}+05$ | 22.2 | 0.05907 | 0.205 | 0.05903 | 0.206 | 568.0 | 4.5 | 1053 |
| BR266@19r | $1.97 \mathrm{E}+05$ | 20.7 | 0.05890 | 0.205 | 0.05883 | 0.207 | 560.6 | 4.5 | 1053 |
| BR266@20r | $5.66 \mathrm{E}+05$ | 34.3 | 0.05898 | 0.205 | 0.05895 | 0.206 | 565.3 | 4.5 | 1051 |
| BR266@21r | $2.37 \mathrm{E}+05$ | 21.2 | 0.05897 | 0.203 | 0.05891 | 0.205 | 563.9 | 4.5 | 1071 |
| BR266@22r | $2.00 \mathrm{E}+05$ | 21.1 | 0.05892 | 0.216 | 0.05885 | 0.217 | 561.4 | 4.7 | 1052 |
| BR266@23r | $2.66 \mathrm{E}+05$ | 22.9 | 0.05884 | 0.203 | 0.05878 | 0.205 | 559.0 | 4.5 | 1067 |
| BR266@24r | $3.16 \mathrm{E}+05$ | 26.1 | 0.05885 | 0.205 | 0.05881 | 0.206 | 559.9 | 4.5 | 1052 |
| BR266@25r | $1.79 \mathrm{E}+05$ | 18.4 | 0.05887 | 0.204 | 0.05879 | 0.206 | 559.3 | 4.5 | 1063 |
| Plešovice |  |  |  |  |  |  |  |  |  |
| Ples@1r | $7.58 \mathrm{E}+04$ | 20.3 | 0.05354 | 0.335 | 0.05334 | 0.344 | 343.4 | 7.8 | 391 |
| Ples@2r | $1.57 \mathrm{E}+04$ | 11.6 | 0.05416 | 0.388 | 0.05322 | 0.445 | 338.2 | 10.0 | 325 |
| Ples@3r | $1.42 \mathrm{E}+05$ | 15.7 | 0.05339 | 0.200 | 0.05329 | 0.203 | 341.2 | 4.6 | 1100 |
| Ples@4r | $1.06 \mathrm{E}+05$ | 19.5 | 0.05361 | 0.284 | 0.05347 | 0.289 | 349.0 | 6.5 | 545 |
| Ples@5r | $1.76 \mathrm{E}+05$ | 23.7 | 0.05324 | 0.280 | 0.05316 | 0.283 | 335.5 | 6.4 | 558 |
| Ples@6r | $1.48 \mathrm{E}+05$ | 20.7 | 0.05343 | 0.248 | 0.05333 | 0.251 | 342.9 | 5.7 | 715 |
| Ples@7r | $1.38 \mathrm{E}+05$ | 23.5 | 0.05326 | 0.313 | 0.05315 | 0.318 | 335.2 | 7.2 | 447 |
| Ples@8r | $1.04 \mathrm{E}+05$ | 21.2 | 0.05347 | 0.352 | 0.05333 | 0.357 | 342.9 | 8.1 | 355 |
| Ples@9r | $6.15 \mathrm{E}+04$ | 18.4 | 0.05339 | 0.358 | 0.05315 | 0.369 | 335.2 | 8.4 | 343 |
| Ples@10r | $1.54 \mathrm{E}+05$ | 25.9 | 0.05347 | 0.304 | 0.05337 | 0.308 | 344.7 | 7.0 | 476 |
| PleS@11r | $1.31 \mathrm{E}+05$ | 22.8 | 0.05308 | 0.338 | 0.05296 | 0.342 | 327.3 | 7.8 | 386 |
| Ples@12r | $1.66 \mathrm{E}+05$ | 25.5 | 0.05355 | 0.322 | 0.05346 | 0.325 | 348.5 | 7.3 | 424 |
| Ples@13r | $3.56 \mathrm{E}+04$ | 11.5 | 0.05372 | 0.317 | 0.05331 | 0.332 | 341.9 | 7.5 | 555 |
| Ples@14r | $6.93 \mathrm{E}+04$ | 12.6 | 0.05322 | 0.249 | 0.05301 | 0.256 | 329.2 | 5.8 | 777 |
| Ples@15r | $4.35 \mathrm{E}+04$ | 10.8 | 0.05338 | 0.249 | 0.05304 | 0.260 | 330.5 | 5.9 | 709 |
| Ples@16r | $3.15 \mathrm{E}+04$ | 13.4 | 0.05336 | 0.348 | 0.05290 | 0.370 | 324.3 | 8.4 | 363 |
| Ples@17r | $1.00 \mathrm{E}+05$ | 22.4 | 0.05342 | 0.314 | 0.05327 | 0.321 | 340.4 | 7.3 | 445 |
| Ples@18r | $4.19 \mathrm{E}+04$ | 11.1 | 0.05388 | 0.263 | 0.05353 | 0.275 | 351.5 | 6.2 | 633 |
| Ples@19r | $1.73 \mathrm{E}+05$ | 24.1 | 0.05329 | 0.306 | 0.05320 | 0.309 | 337.4 | 7.0 | 467 |
| Ples@20r | $1.67 \mathrm{E}+05$ | 20.2 | 0.05330 | 0.233 | 0.05321 | 0.236 | 337.7 | 5.3 | 806 |
| Ples@21r | $1.23 \mathrm{E}+05$ | 23.4 | 0.05339 | 0.288 | 0.05327 | 0.294 | 340.4 | 6.7 | 528 |
| Ples@22r | $1.02 \mathrm{E}+05$ | 23.5 | 0.05343 | 0.344 | 0.05329 | 0.351 | 341.0 | 7.9 | 371 |
| Ples@23r | $3.18 \mathrm{E}+05$ | 17.6 | 0.05337 | 0.149 | 0.05332 | 0.150 | 342.5 | 3.4 | 1980 |
| Ples@24r | $2.63 \mathrm{E}+05$ | 25.3 | 0.05337 | 0.252 | 0.05331 | 0.253 | 342.2 | 5.7 | 695 |
| Ples@25r | $1.04 \mathrm{E}+05$ | 20.3 | 0.05320 | 0.299 | 0.05306 | 0.305 | 331.3 | 6.9 | 491 |
| Qinghu_S1 |  |  |  |  |  |  |  |  |  |
| Q $\overline{1} 1 @ 1 \mathrm{l}$ | $4.92 \mathrm{E}+04$ | 20.4 | 0.04941 | 0.449 | 0.04911 | 0.469 | 153 | 11 | 216 |
| QH1@2r | $6.32 \mathrm{E}+04$ | 21.7 | 0.04935 | 0.468 | 0.04912 | 0.481 | 154 | 11 | 207 |
| QH1@3r | $5.47 \mathrm{E}+04$ | 24.1 | 0.04942 | 0.536 | 0.04915 | 0.555 | 155 | 13 | 153 |
| QH1@4r | $8.09 \mathrm{E}+04$ | 21.1 | 0.04957 | 0.358 | 0.04939 | 0.368 | 166 | 9 | 342 |
| QH1@5r | $8.24 \mathrm{E}+04$ | 25.3 | 0.04937 | 0.446 | 0.04919 | 0.457 | 157 | 11 | 219 |
| QH1@6r | $9.43 \mathrm{E}+04$ | 24.1 | 0.04973 | 0.429 | 0.04958 | 0.437 | 175 | 10 | 239 |

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Table 3. (continued)

| Sample Spot | ${ }^{206} \mathrm{~Pb} /{ }^{204} \mathrm{~Pb}_{\mathrm{m}}{ }^{\text {a }}$ | $\begin{aligned} & \pm 1 \sigma \\ & (\%) \end{aligned}$ | ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}_{\mathrm{m}}{ }^{\text {a }}$ | $\begin{gathered} \pm 1 \sigma \\ (\%) \end{gathered}$ | ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}_{\mathrm{c}}{ }^{\text {b }}$ | $\begin{gathered} \pm 1 \sigma \\ (\%) \end{gathered}$ | $\mathrm{t}_{207 / 206}$ <br> (Ma) | $\pm 1 \sigma$ | $\begin{gathered} { }^{207} \mathrm{~Pb} \\ (\mathrm{cps}) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| QH1@7r | $7.56 \mathrm{E}+04$ | 23.4 | 0.04917 | 0.442 | 0.04897 | 0.453 | 146 | 11 | 224 |
| QH1@8r | $2.25 \mathrm{E}+04$ | 15.0 | 0.05015 | 0.451 | 0.04950 | 0.499 | 172 | 12 | 216 |
| QH1@9r | $9.60 \mathrm{E}+04$ | 29.1 | 0.04975 | 0.476 | 0.04960 | 0.486 | 176 | 11 | 193 |
| QH1@10r | $3.23 \mathrm{E}+04$ | 24.8 | 0.04936 | 0.642 | 0.04890 | 0.688 | 143 | 16 | 106 |
| QH1@11r | $8.64 \mathrm{E}+04$ | 18.4 | 0.04930 | 0.301 | 0.04913 | 0.309 | 154 | 7 | 484 |
| QH1@12r | $3.72 \mathrm{E}+04$ | 23.4 | 0.04964 | 0.581 | 0.04925 | 0.616 | 160 | 14 | 131 |
| QH1@13r | $4.08 \mathrm{E}+04$ | 19.1 | 0.04943 | 0.488 | 0.04907 | 0.511 | 151 | 12 | 184 |
| QH1@14r | $7.06 \mathrm{E}+04$ | 22.3 | 0.04976 | 0.398 | 0.04956 | 0.411 | 174 | 10 | 277 |
| QH1@15r | $1.45 \mathrm{E}+05$ | 37.8 | 0.04948 | 0.550 | 0.04938 | 0.557 | 166 | 13 | 188 |
| QH1@16r | $3.55 \mathrm{E}+04$ | 19.0 | 0.04957 | 0.474 | 0.04915 | 0.505 | 155 | 12 | 195 |
| QH1@17r | $5.82 \mathrm{E}+04$ | 23.9 | 0.04957 | 0.587 | 0.04932 | 0.603 | 163 | 14 | 151 |
| QH1@18r | $8.35 \mathrm{E}+04$ | 26.5 | 0.04918 | 0.470 | 0.04900 | 0.481 | 148 | 11 | 198 |
| QH1@19r | $8.79 \mathrm{E}+04$ | 25.6 | 0.04931 | 0.456 | 0.04914 | 0.466 | 155 | 11 | 210 |
| QH1@20r | $3.94 \mathrm{E}+04$ | 26.5 | 0.04973 | 0.681 | 0.04935 | 0.716 | 165 | 17 | 94 |
| QH1@21r | $7.96 \mathrm{E}+04$ | 27.5 | 0.04922 | 0.549 | 0.04903 | 0.561 | 149 | 13 | 173 |
| QH1@22r | $5.36 \mathrm{E}+04$ | 21.2 | 0.04973 | 0.508 | 0.04946 | 0.524 | 170 | 12 | 170 |
| QH1@23r | $1.22 \mathrm{E}+05$ | 31.8 | 0.04955 | 0.468 | 0.04943 | 0.475 | 168 | 11 | 200 |
| QH1@24r | $6.15 \mathrm{E}+04$ | 23.9 | 0.04986 | 0.524 | 0.04962 | 0.539 | 177 | 13 | 160 |
| QH1@25r | $8.43 \mathrm{E}+04$ | 22.5 | 0.04909 | 0.431 | 0.04892 | 0.440 | 144 | 10 | 235 |
| QH1@26r | $9.80 \mathrm{E}+04$ | 25.6 | 0.04946 | 0.440 | 0.04931 | 0.448 | 163 | 10 | 226 |
| QH1@27r | $2.59 \mathrm{E}+04$ | 19.9 | 0.04959 | 0.685 | 0.04902 | 0.731 | 149 | 17 | 103 |
| QH1@28r | $3.93 \mathrm{E}+04$ | 20.7 | 0.04964 | 0.497 | 0.04927 | 0.525 | 161 | 12 | 177 |
| Qinghu_S2 |  |  |  |  |  |  |  |  |  |
| Q $\bar{H} 2 @ 1 \mathrm{r}$ | $6.28 \mathrm{E}+04$ | 25.6 | 0.04921 | 0.549 | 0.04898 | 0.566 | 147 | 13 | 145 |
| QH2@2r | $9.10 \mathrm{E}+04$ | 29.3 | 0.04930 | 0.497 | 0.04914 | 0.508 | 155 | 12 | 177 |
| QH2@3r | $9.58 \mathrm{E}+04$ | 31.5 | 0.04939 | 0.507 | 0.04924 | 0.518 | 159 | 12 | 170 |
| QH2@4r | $4.40 \mathrm{E}+04$ | 24.2 | 0.04983 | 0.634 | 0.04950 | 0.659 | 172 | 15 | 109 |
| QH2@5r | $4.02 \mathrm{E}+04$ | 22.8 | 0.04982 | 0.595 | 0.04945 | 0.623 | 169 | 15 | 124 |
| QH2@6r | $2.59 \mathrm{E}+04$ | 19.9 | 0.04949 | 0.618 | 0.04892 | 0.667 | 144 | 16 | 120 |
| QH2@7r | $5.05 \mathrm{E}+04$ | 25.6 | 0.04938 | 0.610 | 0.04909 | 0.632 | 152 | 15 | 117 |
| QH2@8r | $2.83 \mathrm{E}+05$ | 34.6 | 0.04967 | 0.328 | 0.04961 | 0.331 | 177 | 8 | 407 |
| QH2@9r | $5.69 \mathrm{E}+04$ | 20.3 | 0.04953 | 0.493 | 0.04927 | 0.507 | 161 | 12 | 180 |
| QH2@10r | $4.71 \mathrm{E}+04$ | 24.9 | 0.04960 | 0.509 | 0.04929 | 0.536 | 162 | 13 | 169 |
| QH2@11r | $9.70 \mathrm{E}+04$ | 25.5 | 0.04941 | 0.439 | 0.04926 | 0.447 | 160 | 10 | 227 |
| QH2@12r | $4.46 \mathrm{E}+04$ | 21.4 | 0.04951 | 0.474 | 0.04918 | 0.498 | 156 | 12 | 194 |
| QH2@13r | $3.81 \mathrm{E}+04$ | 22.5 | 0.04937 | 0.551 | 0.04898 | 0.583 | 147 | 14 | 144 |
| QH2@14r | $5.05 \mathrm{E}+04$ | 19.9 | 0.04931 | 0.449 | 0.04902 | 0.467 | 149 | 11 | 217 |
| QH2@15r | $4.80 \mathrm{E}+04$ | 25.6 | 0.04968 | 0.593 | 0.04937 | 0.617 | 165 | 15 | 125 |
| QH2@16r | $1.08 \mathrm{E}+05$ | 27.7 | 0.04930 | 0.430 | 0.04916 | 0.438 | 155 | 10 | 348 |
| QH2@17r | $4.39 \mathrm{E}+04$ | 26.5 | 0.04993 | 0.642 | 0.04960 | 0.671 | 176 | 16 | 106 |
| QH2@18r | $4.07 \mathrm{E}+04$ | 18.8 | 0.04944 | 0.480 | 0.04907 | 0.504 | 151 | 12 | 203 |
| QH2@19r | $4.87 \mathrm{E}+04$ | 18.7 | 0.04937 | 0.451 | 0.04907 | 0.468 | 151 | 11 | 215 |
| QH2@20r | $7.03 \mathrm{E}+04$ | 21.2 | 0.04981 | 0.452 | 0.04960 | 0.462 | 176 | 11 | 215 |
| QH2@21r | $3.96 \mathrm{E}+04$ | 17.6 | 0.04956 | 0.456 | 0.04919 | 0.478 | 157 | 11 | 211 |
| QH2@22r | $4.33 \mathrm{E}+04$ | 20.7 | 0.04968 | 0.554 | 0.04934 | 0.576 | 164 | 13 | 151 |
| QH2@23r | $3.93 \mathrm{E}+04$ | 20.3 | 0.04951 | 0.527 | 0.04914 | 0.553 | 155 | 13 | 161 |
| QH2@24r | $3.40 \mathrm{E}+04$ | 19.7 | 0.04951 | 0.533 | 0.04908 | 0.566 | 152 | 13 | 154 |
| QH2@25r | $6.47 \mathrm{E}+04$ | 23.5 | 0.04932 | 0.519 | 0.04909 | 0.533 | 152 | 12 | 219 |
| QH2@26r | $4.63 \mathrm{E}+04$ | 21.3 | 0.04947 | 0.486 | 0.04915 | 0.508 | 155 | 12 | 186 |
| QH2@27r | $3.80 \mathrm{E}+04$ | 22.4 | 0.04937 | 0.532 | 0.04898 | 0.565 | 147 | 13 | 155 |
| QH2@28r | $2.33 \mathrm{E}+04$ | 21.2 | 0.04965 | 0.747 | 0.04902 | 0.805 | 149 | 19 | 79 |
| QH2@29r | $6.95 \mathrm{E}+04$ | 30.0 | 0.04958 | 0.498 | 0.04937 | 0.516 | 165 | 12 | 176 |

[^2]

Figure 7. (a) U-Pb concordia diagram showing SIMS analytical data for BR266 zircon. (b) Comparison of weighted average ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ ages for BR266 zircon determined by Cameca IMS-1280 SIMS using monocollector and multicollector modes. Uncertainties are $95 \%$ confidence level. MSWD is the mean square of weighted deviates, MSWD1 is the MSWD of concordance, and MSWD2 is the MSWD of concordance plus equivalence. Data point error ellipses/bars are $2 \sigma$.
which is lower than the TIMS ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ age of $562.2 \pm 0.5 \mathrm{Ma}$. Our data concur with the slight discordance of U-Pb system of BR266 determined by TIMS [Stern, 2001; Stern and Amelin, 2003].
[34] Twenty-five measurements of ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ ratios were obtained by multicollector mode, with a weighted mean ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ of $0.05890 \pm 0.00005$ ( $0.085 \%$ ) corresponding to ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ age of $563.4 \pm 1.8 / 4.9 \mathrm{Ma}$ (Figure 7b). This age is in good agreement within errors with the ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ age of $562.2 \pm 0.5$ Ma determined by TIMS [Stern, 2001; Stern and Amelin, 2003]. The ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ age uncertainty determined by using multicollector mode is $0.32 \%$ (excluding decay constant errors), improved by a factor of $\sim 2$ compared to the age uncertainty of $0.62 \%$ for thirty measurements obtained by using monocollector mode.

### 5.2. Plešovice Zircon

[35] This zircon comes from a potassic granulite facies rock at the Plešovice quarry in the southern Bohemian Massif, Czech Republic. It has a concordant $\mathrm{U} / \mathrm{Pb}$ age with a weighted mean ${ }^{206} \mathrm{~Pb} / /^{238} \mathrm{U}$ date of $337.13 \pm 0.37 \mathrm{Ma}$ (excluding decay constant error) and a well-defined Hf isotopic composition, and is being considered as a potential zircon reference for $\mathrm{U}-\mathrm{Pb}$ and Hf isotopic microanalysis [Sláma et al., 2008].
[36] Thirty measurements of $\mathrm{U}-\mathrm{Pb}$ isotopes were obtained for Plešovice zircon by using monocollector mode. All the analyses are concordant within analytical errors. The weighted mean of ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb},{ }^{207} \mathrm{~Pb} /{ }^{235} \mathrm{U}$ and ${ }^{206} \mathrm{~Pb} /{ }^{238} \mathrm{U}$ ratios is $0.05319 \pm 0.00017,0.3947 \pm 0.0022$ and 0.05372 $\pm 0.00024$, respectively, corresponding to ages of


Figure 8. (a) U-Pb concordia diagram showing SIMS analytical data for Plešovice zircon. (b) Comparison of weighted average ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ ages for Plešovice zircon determined by Cameca IMS-1280 SIMS using monocollector and multicollector modes. MSWD is the mean square of weighted deviates, MSWD1 is the MSWD of concordance, and MSWD2 is the MSWD of concordance plus equivalence. Data point error ellipses/bars are $2 \sigma$.


Figure 9. (a) Photomicrographs of five single grains of Qinghu zircon analyzed by CA-TIMS. Grains are arranged left to right, with grains A and B on the top and grains $\mathrm{C}-\mathrm{E}$ on the bottom. Grain A is 250 microns in length for scale. (b) Cathodoluminescence images for representative Qinghu zircon grains.
$340.3 \pm 8.4 / 8.5 \mathrm{Ma}, 337.8 \pm 1.6 / 1.7 \mathrm{Ma}$ and $337.3 \pm$ $1.5 / 1.5 \mathrm{Ma}$, respectively. A concordia U-Pb age is calculated at $337.4 \pm 1.5 / 1.5 \mathrm{Ma}$ (Figure 8a). Our $\mathrm{U}-\mathrm{Pb}$ age is in good agreement with the reported ${ }^{206} \mathrm{~Pb} /{ }^{238} \mathrm{U}$ age of $337.13 \pm 0.37 \mathrm{Ma}$ by TIMS [Sláma et al., 2008].
[37] Twenty-five measurements by using multicollector mode yielded indistinguishable ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ ratios within analytical errors, with a weighted mean of $0.053252 \pm 0.000058$ ( $0.11 \%$ ) corresponding to a ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ age of $339.6 \pm 2.5 /$ 5.1 Ma (Figure 8b). The ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ age uncertainty of $0.74 \%$ (excluding decay constant error)
determined by using multicollector mode is improved by a factor of $\sim 3$ relative to that of $2.5 \%$ obtained by using monocollector mode.

### 5.3. Qinghu Zircon

[38] The Qinghu zircon was separated from a felsic syenite rock at a large quarry in the Qinghu alkaline complex near the border between Guangdong and Guangxi Provinces, South China [Li et al., 2004]. This complex was previously dated at $156 \pm 6 \mathrm{Ma}$ by LA-ICPMS [Li et al., 2001]. Zircons from this sample are all euhedral, range mostly from 200 to $500 \mu \mathrm{~m}$ in length, and have length to width ratios of $\sim 3: 1$. They are transparent and light brown in color (Figure 9a), showing clear euhedral concentric zoning under CL (Figure 9b).
[39] TIMS data from the five chemically abraded zircons cluster on Concordia (Table 4 and Figure 10) with a weighted mean ${ }^{206} \mathrm{~Pb} /{ }^{238} \mathrm{U}$ date of $159.38 \pm$ 0.12 $\mathrm{Ma}(\mathrm{MSWD}=1.6)$ and $\mathrm{a}{ }^{207} \mathrm{~Pb} /{ }^{235} \mathrm{U}$ date of $159.68 \pm 0.22(\mathrm{MSWD}=0.4)$. The U-Pb dates agree within the decay constant uncertainties, and the degree of discordance is similar to those from other CA-TIMS dated standards [e.g., Schoene et al., 2006]. The concordia age is $159.45 \pm 0.16 \mathrm{Ma}$ ( $2 \sigma$, including decay errors [Ludwig, 1998]). Data from the untreated grain display a younger ${ }^{206} \mathrm{~Pb} /{ }^{238} \mathrm{U}$ date $(157.9 \mathrm{Ma})$ and are interpreted to reflect minor Pb loss.
[40] Thirty analyses by monocollector SIMS mode give concordant $\mathrm{U}-\mathrm{Pb}$ and $\mathrm{Pb}-\mathrm{Pb}$ results within analytical errors. The weighted mean of ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb},{ }^{207} \mathrm{~Pb} /{ }^{235} \mathrm{U}$ and ${ }^{206} \mathrm{~Pb} /{ }^{238} \mathrm{U}$ ratios is $0.04923 \pm 0.00016,0.1700 \pm 0.0011$ and $0.02506 \pm$ 0.00011 , respectively, corresponding to ages of $158.9 \pm 7.6 / 8.7 \mathrm{Ma}, 159.45 \pm 0.97 / 0.98 \mathrm{Ma}$, and $159.56 \pm 0.69 / 0.71 \mathrm{Ma}$, respectively. The calculated Concordia U-Pb age of $159.5 \pm 0.6 / 0.7 \mathrm{Ma}$ (Figure 11a) is in good agreement with the TIMS data.
[41] ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ ratios were analyzed by using multicollector SIMS mode in two separated sessions, with sessions 1 and 2 consisting of twentyeight and twenty-nine measurements, respectively. Both sessions yield indistinguishable weighted mean ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ ratios within errors: $0.049252 \pm$ $0.000089(0.18 \%)$ and $0.049232 \pm 0.000094$ ( $0.19 \%$ ), corresponding to ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ ages of $159.8 \pm 4.2 / 6.0$ and $158.9 \pm 4.5 / 6.2$, respectively (Figure 11b). The ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ age error determined by multicollector mode is $2.6-2.8 \%$ (excluding decay constant error), which is improved by a
Table 4. U-Pb TIMS Zircon Data ${ }^{\text {a }}$

| Sample | Weight (mcg) | $\begin{gathered} \mathrm{U} \\ (\mathrm{ppm}) \end{gathered}$ | Sample Pb |  | Initial Pb |  | $\begin{gathered} \mathrm{Pb}^{*} / \\ \mathrm{Pb}_{\mathrm{c}} \end{gathered}$ | $\begin{gathered} \mathrm{Th} / \\ \mathrm{U} \end{gathered}$ | Meas. ${ }^{206} \mathrm{~Pb} /$${ }^{204} \mathrm{~Pb}$ | ${ }^{206} \mathrm{~Pb} /$ | $\begin{aligned} & { }^{208} \mathrm{~Pb} / \\ & { }^{206} \mathrm{~Pb} \end{aligned}$ | Corrected Atomic Ratios |  |  |  |  |  | $\begin{gathered} 206 / 238 \\ \text { Age (Ma) } \end{gathered}$ | err | $\begin{gathered} 207 / 235 \\ \text { Age (Ma) } \end{gathered}$ | err | $\begin{gathered} 207 / 206 \\ \text { Age (Ma) } \end{gathered}$ | Rho |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  | $\begin{gathered} { }^{206} \mathrm{~Pb} / \\ { }^{238} \mathrm{U} \end{gathered}$ | $\begin{gathered} { }^{207} \mathrm{~Pb} / \\ { }^{235} \mathrm{U} \end{gathered}$ |  |  |  |  |  | $\begin{aligned} & { }^{207} \mathrm{~Pb} / \\ & { }^{206} \mathrm{~Pb} \end{aligned}$ |  |  |  |  |  |  |  |
|  |  |  | ppm |  |  |  | ppm |  |  |  |  |  | rad. | \%err | rad. | \%err | rad. |  |  |  |  |  |  | \%err |
| Qinghu Zircon ${ }^{\text {b }}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| sA CA st | 13.5 | 807.0 | 20.7 |  | 0.280 | 3.8 |  | 39.5 | 0.40 | 2497 | 4585 | 0.13 | 0.025019 | (0.21) | 0.17020 | (0.33) | 0.0493 | (0.23) | 159.30 | $\pm 0.34$ | 159.59 | $\pm 0.52$ | 164 | 0.70 |
| sB CA st | 24.3 | 694.6 | 18.0 |  | 0.004 | 0.1 |  | 132 | 0.47 | 8173 | 281829 | 0.15 | 0.025026 | (0.06) | 0.17025 | (0.17) | 0.0493 | (0.14) | 159.34 | $\pm 0.10$ | 159.64 | $\pm 0.27$ | 164 | 0.51 |
| sC CA $s d$ |  | 1342.3 | 33.9 | 118 | 0.347 | 1.2 | 26.6 | 0.35 | 1711 | 6155 | 0.11 | 0.025024 | (0.09) | 0.17054 | (0.53) | 0.0494 | (0.48) | 159.33 | $\pm 0.14$ | 159.89 | $\pm 0.84$ | 168 | 0.54 |
| sD CA $s d$ | 3.5 | 989.5 | 25.8 |  | 0.138 | 0.5 | 24.3 | 0.47 | 1517 | 11388 | 0.15 | 0.025058 | (0.09) | 0.17081 | (0.68) | 0.0494 | (0.63) | 159.55 | $\pm 0.14$ | 160.12 | $\pm 1.09$ | 169 | 0.64 |
| sE CA sd | 2.3 | 1212.8 | 31.9 | 72 | 0.345 | 0.8 | 17.9 | 0.50 | 1110 | 5594 | 0.16 | 0.025024 | (0.10) | 0.17085 | (0.86) | 0.0495 | (0.80) | 159.33 | $\pm 0.16$ | 160.15 | $\pm 1.38$ | 172 | 0.70 |
| sG st | 4.7 | 1105.4 | 28.6 | 134 | 1.103 | 5.2 | 15.4 | 0.37 | 994 | 1595 | 0.12 | 0.024802 | (0.07) | 0.16868 | (0.48) | 0.0493 | (0.45) | 157.93 | $\pm 0.12$ | 158.28 | $\pm 0.77$ | 163 | 0.54 |
| Paired Single Daly Run Data |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| sA CA $s d$ | 13.5 | 807.0 | 20.7 | 280 | 0.256 | 3.4 | 39.8 | 0.40 | 2512 | 4635 | 0.13 | 0.025045 | (0.21) | 0.17021 | (0.33) | 0.0493 | (0.24) | 159.46 | $\pm 0.34$ | 159.60 | $\pm 0.52$ | 162 | 0.69 |
| sG $s$ d | 4.7 | 1105.4 | 28.6 | 134 | 1.052 | 4.9 | 15.3 | 0.37 | 988 | 1578 | 0.12 | 0.024807 | (0.08) | 0.16871 | (0.51) | 0.0493 | (0.47) | 157.97 | $\pm 0.13$ | 158.29 | $\pm 0.80$ | 163 | 0.54 |

${ }^{\text {a }}$ Samples are as follows: $\mathrm{s}_{-}$, single zircon grain; CA , chemically abraded; $s t$, static Pb run; $s d$, single Daly multiplier Pb run. Paired single Daly data are from Daly Pb runs on the same beads after static analysis. Weight is zircon grain weight prior to first step of either CATIMS or total dissolution. U and Pb concentrations for CA method analyses are based on this weight and may be underestimations, depending on how much material was dissolved and leached in the first step. Picograms (pg) sample and initial Pb from the second dissolution step are measured directly. The weights and concentrations from
the bulk dissolved grain are all accurate. Sample Pb is sample Pb (radiogenic + initial) corrected for laboratory blank of 3.2 pg . initial Pb is common Pb corrected for laboratory blank of 32 pg Pb . Isotopic composition of blank is $18.719 \pm 0.97\left({ }^{206} \mathrm{~Pb} /{ }^{204} \mathrm{~Pb}\right), 15.662 \pm 0.57\left({ }^{207} \mathrm{~Pb} /{ }^{204} \mathrm{~Pb}\right)$, and $38.226 \pm 1.42\left({ }^{208} \mathrm{~Pb}{ }^{204} \mathrm{~Pb}\right) . \mathrm{Pb} / \mathrm{Pb}_{\mathrm{c}}$ is radiogenic Pb to total common Pb (blank + initial) $\mathrm{Th} / \mathrm{U}$ calculated from radiogenic ${ }^{208} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ and ${ }^{206} \mathrm{~Pb} /{ }^{238} \mathrm{U}$ date; meas. is measured ${ }^{206} \mathrm{~Pb} /{ }^{204} \mathrm{~Pb}$ corrected for mass discrimination and tracer. Corrected atomic ratios: ${ }^{206} \mathrm{~Pb}$ / ${ }^{204} \mathrm{~Pb}$ corrected for blank, mass discrimination and tracer, all others corrected for blank, mass discrimination, tracer and initial Pb , values in parentheses are 2 sigma errors in percent. Isotopic compositions of initial Pb are $18.455 \pm 0.12,15.617 \pm 0.082$, and $38.337 \pm$
0.226 , based on Stacey and Kramers $[1975] \mathrm{Pb}$ evolution model. Rho is ${ }^{206} \mathrm{~Pb} /{ }^{238} \mathrm{U}$ versus ${ }^{207} \mathrm{~Pb}{ }^{235} \mathrm{U}$ error correlation coefficient. Mineral dissolution and chemistry were adapted from methods developed by Krogh [1973], Parrish et al. [1987], and Mattinson [2005]. Five of the six grains were dissolved in steps using the CATIMS method [Mattinson, 2005]. Final dissolutions were spiked with a mixed ${ }^{205} \mathrm{~Pb} /{ }^{233} \mathrm{U} /{ }^{235} \mathrm{U}$ tracer (ET535). Pb and U samples were loaded onto single rhenium filaments with silica gel and graphite, respectively; isotopic compositions were measured on a Micromass Sector 54 mass for Pb of $0.060 \pm 0.06 \% / \mathrm{amu}$ for static Faraday runs and $0.185 \pm 0.06 \% / \mathrm{amu}$ for single Daly runs were determined by replicate analyses of NIST SRM 981 . U fractionation was determined internally during each run. Procedural blanks averaged 3.2 pg Pb for zircon during the course of the study. Isotopic composition of the Pb blank was estimated as $18.719 \pm 0.97,15.662 \pm 0.57$, and $38.226 \pm 1.42$ for 206/204, $207 / 204$, and $208 / 204$, respectively. U blanks were consistently less than 0.2 pg . Concordia coordinates, intercepts, and uncertainties were calculated using MacPBDAT and ISOPLOT programs (based on Ludwig [1988, 1991];; initial Pb isotopic compositions were estimated by the Stacey and Kramers [1975] evolution model for $160 \mathrm{Ma}(6 / 4,7 / 4,8 / 4: 18.455 \pm 0.12,15.617 \pm 0.082$, and $38.337 \pm 0.226)$. The


Figure 10. Conventional U-Pb Concordia diagram of ID-TIMS data from Qinghu zircon. Concordia swath depicts uncertainties due to errors in U decay constants. Yellow ellipses reflect data from five chemically abraded zircons following the method of Mattinson [2005]. The Concordia age is based on these data, giving the best estimate of the crystallization age. The blue ellipse represents data from an untreated, bulk dissolved grain and displays Pb loss. Data point error ellipses are $2 \sigma$.
factor of $\sim 3$ relative to the age error of $7.6 \%$ obtained by using monocollector mode.

## 6. Discussion and Concluding Remarks

[42] Our results presented above indicate that Paleozoic and Mesozoic zircon ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ ages can be precisely and accurately dated by using multicollector SIMS without external standardization. The precision of zircon $\mathrm{Pb} / \mathrm{Pb}$ age determinations depend mostly on the radiogenic Pb contents (or U contents and the age of the dated zircons). Figure 12 shows that analytical errors of the measured ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ ratio (common Pb uncorrected) decrease quickly with increasing ${ }^{207} \mathrm{~Pb}$ intensity between 100 and $1,000 \mathrm{cps}$, and reaches at $\sim 0.2 \%$ with ${ }^{207} \mathrm{~Pb}>1,000 \mathrm{cps}$.
[43] It is noted that the uncertainties in ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ ratios measured by multicollector are very close to the expected errors from the counting statistics (Figure 12). Similarly, the uncertainties in the ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ ratios measured by monocollector are also consistent with, or slightly poorer than, the expected errors from counting statistics (figure not shown). The total counting time for ${ }^{207} \mathrm{~Pb}$ is 62.4 s and 240 s by monocollector and multicollector, respectively. Therefore, the counting statistics uncertainties in ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ ratios by monocollec-
tor are expected to be 2 times higher than those by multicollector for the same zircon and/or baddeleyite samples (assuming constant $U$ contents). It can be seen that the measured ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ uncertainty of BR266 zircon (with fairly uniform U content) by monocollector mode is averaged at $\sim 0.48 \%$ (Table 2), which is 2.4 times higher than the averaged uncertainty of $\sim 0.20 \%$ by multicollector mode (Table 3). Therefore, the differences in the precision of the two techniques are mainly due to the fact that the Pb peaks are measured for 4 times longer in multicollector mode as well as elimination of the signal variation effect by simultaneous detection of Pb peaks using multicollector mode. For zircons in age of the latest Neoproterozoic to the early Paleozoic with $U$ contents of $\sim 1000 \mathrm{ppm}$, such as BR266 zircon, multicollector SIMS measurement is capable of achieving precisions of ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ ratio of $<0.1 \%$ by pooling 25 measurements, propagating an age error of $<0.5 \%$ (excluding decay constant errors). For the late Paleozoic and Mesozoic (Jurassic) zircons with a few hundreds to one thousand ppm $\mathrm{U},{ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ ratio can be measured with fairly good precision between $0.1 \%$ and $0.2 \%$ by pooling $25-30$ measurements, propagating an age error between $\sim 0.8 \%$ and $\sim 3 \%$ (excluding decay constant errors). Such $\mathrm{Pb} / \mathrm{Pb}$ age precision is nearly comparable with, or slightly poorer than, the ${ }^{206} \mathrm{~Pb} /{ }^{238} \mathrm{U}$ age precisions obtained by conventional monocollector SIMS with external standard calibration.
[44] Our results demonstrate that the multicollector SIMS technique is suitable for determination of $\mathrm{Pb} /$ Pb ages of Mesozoic zircons with precisions of geological significance. This technique is therefore applicable to direct dating of zircons in thin sections without requisition of mineral separation, mounting and external standard calibration, making the microbeam $\mathrm{U}-\mathrm{Pb}$ dating very efficient and petrographically significant. More importantly, it has significant implications for precise determinations of some other U-rich minerals that are not suitable for SIMS U-Pb dating by external standard calibration. For instance, baddeleyite $\left(\mathrm{ZrO}_{2}\right)$ is a very favorable mineral for dating mafic and ultramafic igneous rocks, but it is only suitable for SIMS ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$, rather than ${ }^{206} \mathrm{~Pb} /{ }^{238} \mathrm{U}$, measurement owing to the "crystal orientation effect" that bias ${ }^{206} \mathrm{~Pb} /{ }^{338} \mathrm{U}$ ratio [Wingate and Compston, 2000]. Zirconolite $\left(\mathrm{CaZrTi}_{2} \mathrm{O}_{7}\right)$ also has remarkable properties for $\mathrm{U}-\mathrm{Pb}$ geochronology, and could become a dominant tool for dating mafic igneous rocks [Heaman and LeCheminant, 1993; Rasmussen and Fletcher, 2004]. However, it can only be



Figure 11. (a) Conventional U-Pb Concordia plot showing SIMS analytical data for Qinghu zircon. (b) Comparison of weighted average ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ ages for Qinghu zircon determined by Cameca IMS-1280 SIMS using monocollector and multicollector modes. MSWD is the mean square of weighted deviates, MSWD1 is the MSWD of concordance, and MSWD2 is the MSWD of concordance plus equivalence. Data point error ellipses/bars are $2 \sigma$.


Figure 12. Correlation between the analytical error of measured ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ ratio and ${ }^{207} \mathrm{~Pb}$ intensity for zircon and baddeleyite. The expected uncertainties from the counting statistics, estimated as $1 /\left({ }^{207} \mathrm{~Pb} \text { intensity } \times 240 \mathrm{~s}\right)^{1 / 2}$ because ${ }^{206} \mathrm{~Pb}$ intensity is about $10-20$ times higher than ${ }^{207} \mathrm{~Pb}$, of each measurements are shown for comparison. It is noted that the oxygen flooding can enhance $\mathrm{Pb}^{+}$sensitivity by a factor exceeding 5 for baddeleyite.
precisely dated by SIMS ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ measurement, because this mineral has a highly variable composition (due to extensive substitutions) that makes a matrix-matched zirconolite $\mathrm{U}-\mathrm{Pb}$ age reference unavailable.
[45] The Plešovice zircon is a newly developed reference for $\mathrm{U}-\mathrm{Pb}$ and Hf isotopic microbeam analysis [Sláma et al., 2008]. Both LA-ICPMS and TIMS analyses give a consistent U-Pb age of 337 Ma , but the reported SIMS measurements result in a wider range of $\mathrm{U}-\mathrm{Pb}$ age between $328.1 \pm 4.2 \mathrm{Ma}(1 \sigma)$ and $353 \pm 2.8 \mathrm{Ma}(1 \sigma)$, with a weighted mean of $341.4 \pm 1.3 \mathrm{Ma}(2 \sigma)$ (excluding decay constant errors). Because of the wide age variation, the authors consider that the Plešovice zircon is not an ideal age reference material for high spatial resolution (SIMS) measurements [Sláma et al., 2008]. Our SIMS measurements, however, yield very consistent U-Pb ages with the LA-ICPMS and TIMS data. It seems that the Plešovice zircon is fairly homogeneous in $\mathrm{U}-\mathrm{Pb}$ age at a spatial resolution of $\sim 20-30 \mu \mathrm{~m}$, and can be used as a good U-Pb zircon age reference for SIMS measurement. We noted that Sláma et al. [2008] used a smaller primary ion beam of $\sim 15 \mu \mathrm{~m}$ than our measurements, and further examinations of homogeneity in $\mathrm{U}-\mathrm{Pb}$ age at a spatial resolution $<20 \mu \mathrm{~m}$ are likely needed.

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[^0]:    ${ }^{\mathrm{a}}$ The values of ${ }^{206} \mathrm{~Pb} /{ }^{204} \mathrm{~Pb}_{\mathrm{m}}$ and ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}$ are the measured values.
    ${ }^{\mathrm{b}}$ The value of ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}_{\mathrm{c}}$ is the calculated value after ${ }^{204} \mathrm{~Pb}$ correction.

[^1]:    ${ }^{\mathrm{a}}$ The value of ${ }^{206} \mathrm{~Pb} /{ }^{204} \mathrm{~Pb} \mathrm{~m}$ is the measured value.
    ${ }^{\mathrm{b}} \mathrm{f}_{206}$ is the percentage of common ${ }^{206} \mathrm{~Pb}$ in total ${ }^{206} \mathrm{~Pb}$.

[^2]:    ${ }^{\mathrm{a}}$ The values of ${ }^{204} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}_{\mathrm{m}}$ and ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}_{\mathrm{m}}$ are the measured values.
    ${ }^{\mathrm{b}}$ The value of ${ }^{207} \mathrm{~Pb} /{ }^{206} \mathrm{~Pb}_{\mathrm{c}}$ is the calculated value after ${ }^{204} \mathrm{~Pb}$ correction.

