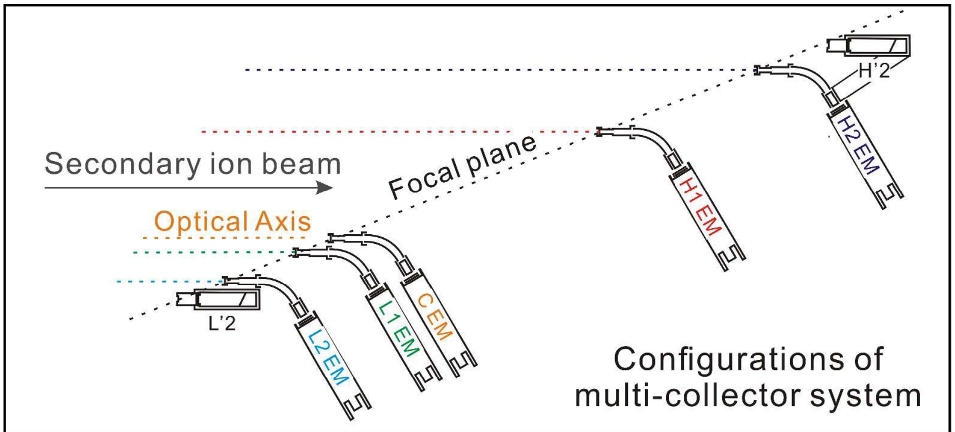
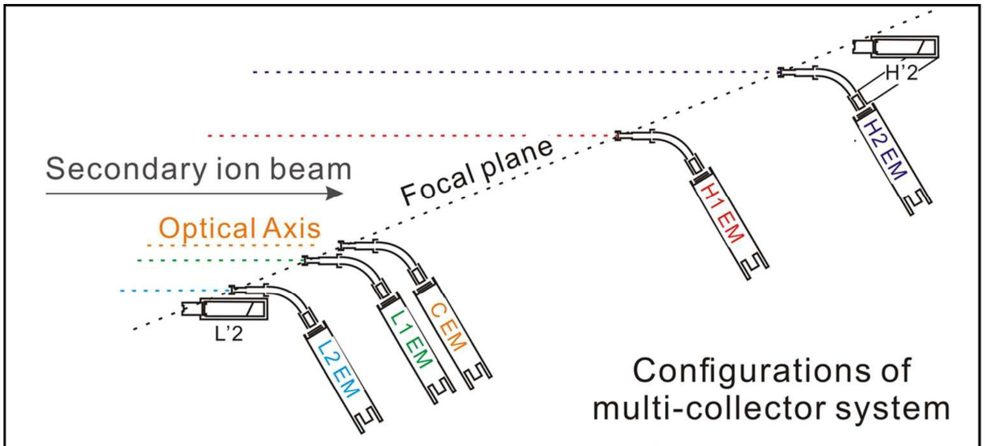
A hybrid "dynamic multi-collector U-Pb dating technique" takes advantages of both the static multi-collector mode and peak-hopping mono-collector mode.

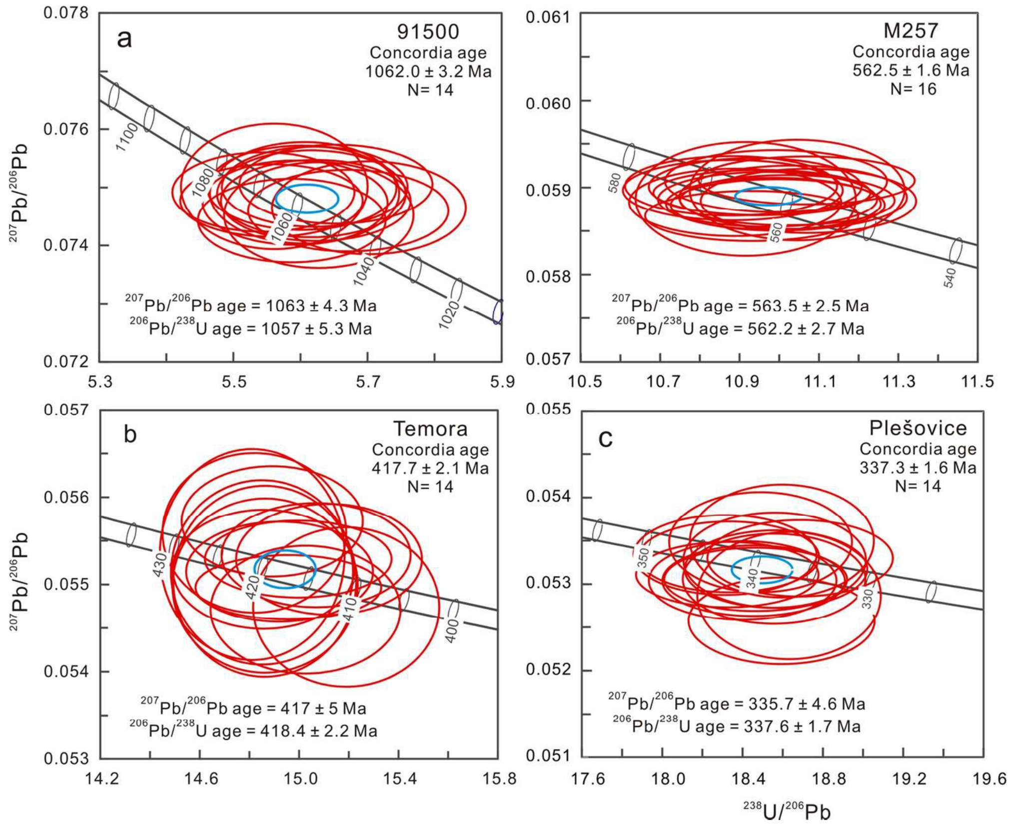


Step	Species in Detectors					Counting time (s)
	L2	L1	C	H1	H2	
1			$^{90}Zr_2{}^{16}O$			4
2		$^{90}Zr_2{}^{16}O$				4
3	^{204}Pb	^{206}Pb	^{207}Pb			60
4		^{238}U		$^{232}Th^{16}O$	$^{238}U^{16}O$	2
5		$^{238}U^{16}O_2$				2

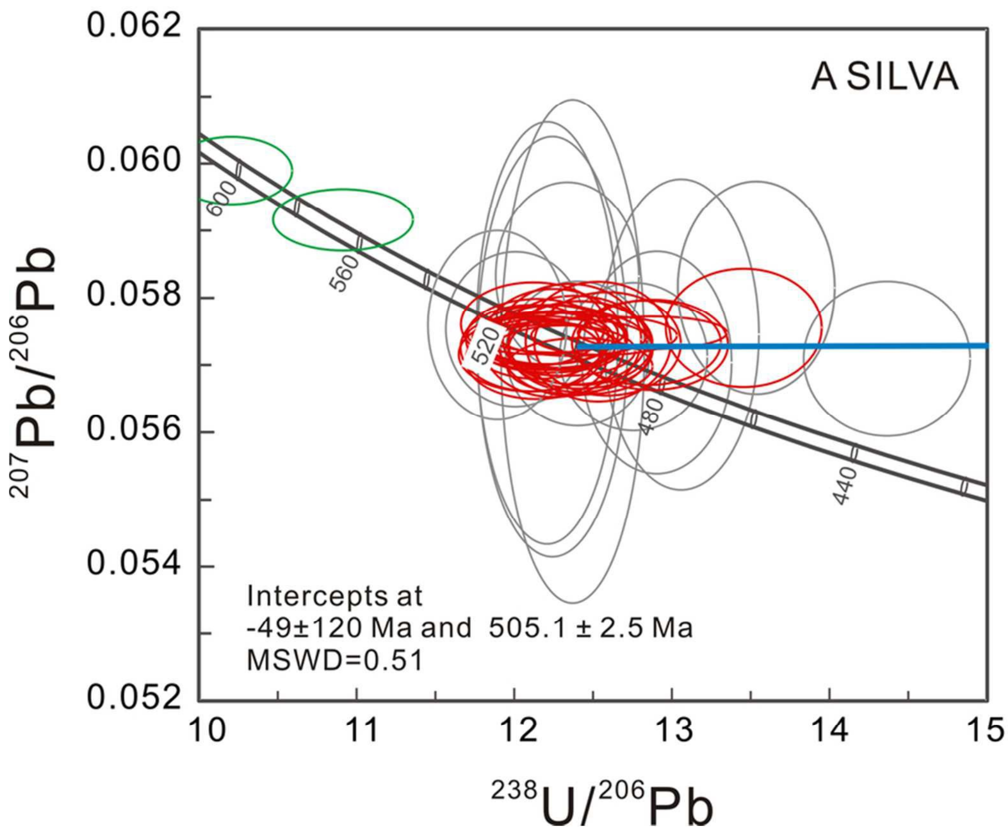


Step	Species in Detectors					Counting time (s)
	L2	L1	C	H1	H2	
1			$^{90}Zr_2{}^{16}O$			4
2		$^{90}Zr_2{}^{16}O$				4
3	^{204}Pb	^{206}Pb	^{207}Pb			60
4		^{238}U		$^{232}Th^{16}O$	$^{238}U^{16}O$	2
5		$^{238}U^{16}O_2$				2

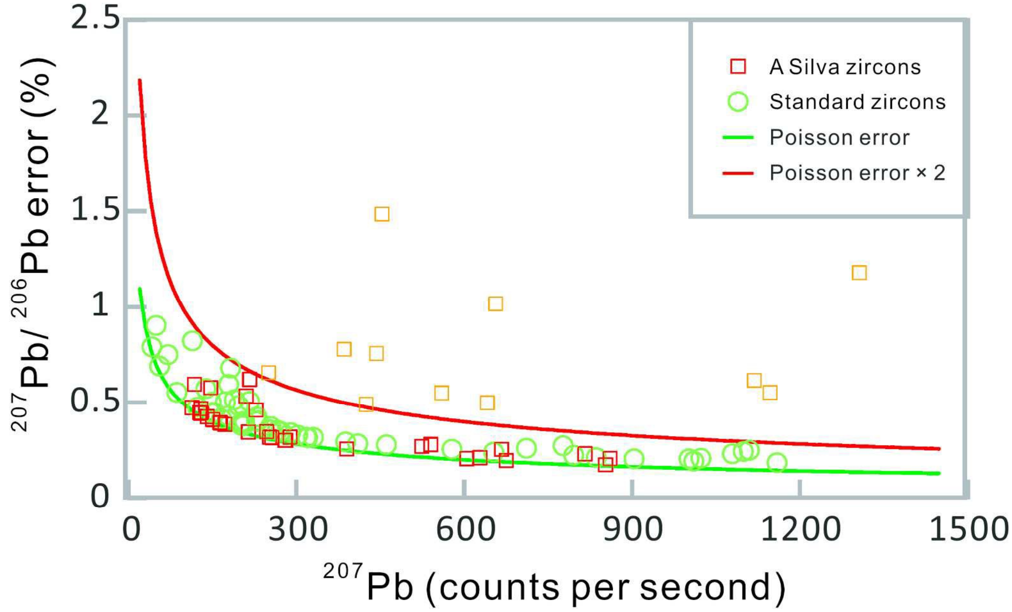
104x80mm (300 x 300 DPI)



138x112mm (300 x 300 DPI)



74x61mm (300 x 300 DPI)



197x121mm (300 x 300 DPI)

Towards higher precision SIMS U-Pb zircon geochronology via dynamic multi-collector analysis

Yu Liu[1], Qiu-Li Li[1]*, Guo-Qiang Tang[1], Xian-Hua Li[1] and Qing-Zhu Yin[2]

[1] State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China

[2] Department of Earth and Planetary Sciences, University of California at Davis, One Shields Avenue, Davis, CA 95616, USA

submission to ***JAAS***

* *Corresponding author*

E-mail: liqiuli@mail.iggcas.ac.cn

Phone: 86-10-82998535

Fax: 86-10-62010846

Abstract

The U-Pb dating system has been widely used in geochronology because the system contains two independent parent/daughter pairs yielding three ages (i.e., $^{238}U/^{206}Pb$, $^{235}U/^{207}Pb$ and $^{207}Pb/^{206}Pb$ ages) to internally check self-consistency. Among numerous U-bearing minerals, zircon has been recognized as the premier mineral for U-Pb geochronology owing to its moderate U content, negligible initial unradiogenic Pb (or common Pb) and occurrence in a wide range of rock types. With development of Secondary Ion Mass Spectrometry (SIMS) and in-situ dating method, the $^{238}U/^{206}Pb$ zircon age uncertainty could be achieved to ~1 % level. However, the $^{207}Pb/^{206}Pb$ age uncertainty of Phanerozoic zircon is always much poor, when single-collector SIMS is used. The low level precision often hampers effective examination of concordance of young zircon between U-Pb and Pb/Pb ages, which is crucial to the data quality evaluation and chronological interpretations. In this study, we developed a hybrid “dynamic multi-collector U-Pb dating technique”. It takes advantages of both the static multi-collector mode and peak-hopping mono-collector mode. The technique is able to simultaneously measure high-precision $^{207}Pb/^{206}Pb$ ratio as in the static multi-collector mode without trade off in analytical precision of $^{238}U/^{206}Pb$ ratio of the conventional peak-hopping mono-collector mode. Four zircon reference meterials (91500， M257, Temora and Plešovice) were measured to demonstrate that this new analytical protocol is able to achieve a higher precision for $^{207}Pb/^{206}Pb$ age by a factor of two than the conventional mono-collector mode within same consuming working time. It is possible to simultaneously obtain $^{207}Pb/^{206}Pb$ age and $^{238}U/^{206}Pb$ age with comparable quality to effectively evaluate the concordance of U-Pb system for Phanerozoic samples.

Keywords: Zircon U-Pb dating, SIMS, dynamic multi-collector mode , high precision

1. Introduction

U-Pb isotopic system has been widely used in geochronology since the discovery of radioactivity (Mattinson, 2013) partly because the system contains two independent parent/daughter pairs with favorable half-lifes. In fact three ages can be obtained on the same U-bearing mineral to check for its internal self-consistency, i.e., $^{238}U/^{206}Pb$ and $^{235}U/^{207}Pb$ ages based on decay of ^{238}U to ^{206}Pb and ^{235}U to ^{207}Pb, respectively, and $^{207}Pb/^{206}Pb$ age independent of Pb/U measurement by incorporation of the two decay systems. Among numerous U-bearing minerals, zircon has been recognized as the premier mineral for U-Pb geochronology owing to its moderately U content, negligible initial unradiogenic Pb (or common Pb) and occurrence in a wide range of rock types (Ireland and Williams, 2003; Parrish et al., 2003).

Since the introduction of Secondary Ion Mass Spectrometry (SIMS) to *in situ* U-Pb isotopic analysis on zircon, especially after the invention of large-geometry, double-focusing instruments, including the SHRIMP (Sensitive High Resolution Ion Microprobe) and Cameca IMS-1270/1280HR, geochronology entered a new era. SIMS U-Pb zircon dating primarily uses two analytical modes: (1) conventional U-Pb age determination using peak-hopping mode on mono-collector system (Ireland and Williams, 2003; Parrish et al., 2003; Whitehouse et al. 1997) and (2) high-precision $^{207}Pb/^{206}Pb$ age determination using static mode on multi-collector system (Li et al., 2009, 2010). Conventional mono-collector mode is widely used in routine analysis. It determines $^{206}Pb/^{238}U$ and $^{207}Pb/^{206}Pb$ ages, and deduces $^{207}Pb/^{235}U$ age from the former two measurements. Precision of the mono-collector SIMS U-Pb zircon age determination has achieved ~1-2 % level with propagation of uncertainty of Pb/U fractionation calibration by external standardization. However, the Pb-Pb age uncertainty is much poorer, particularly for Phanerozoic samples (Ireland and Williams, 2003). The low level precision often hampers effective examination of the concordance of U-Pb system for Phanerozoic zircons, which is crucial to the data quality evaluation and chronological interpretations. As an example reported in Castiñeiras et al. (2010), two zircon samples from granodiorites showed a "concordant" age between U-Pb and Pb-Pb ranging between 540 and 460 Ma by conventional mono-collector mode SIMS analysis. According to the geological settings and cathodeluminescence (CL) images of zircons, those granodiorites should have a relatively simple age distribution. Thus, the widely variable ages are most likely due to poor $^{207}Pb/^{206}Pb$ age uncertainties that cannot effectively ensure the concordance of U-Pb system.

Precise $^{207}Pb/^{206}Pb$ age determination by mono-collector mode for Phanerozoic zircons is difficult, because: (1) there is a very limited range of radiogenic $^{207}Pb/^{206}Pb$ ratio for Phanerozoic samples, varying from 0.058 to 0.046 between 540 Ma and present-day; (2) the abundance of ^{235}U is less than 1% in total U ($^{238}U/^{235}U$ = 137.82), leading to little radiogenic ^{207}Pb; (3) $^{207}Pb/^{206}Pb$ ratio is sensitive to common Pb correction. All of these would collectively results in significant error magnification for ages determined in Phanerozoic samples. To overcome this shortcomings, the $^{207}Pb/^{206}Pb$ age of zircon can be alternatively determined by using static mode on a multi-collector SIMS, with advantages of (1) direct $^{207}Pb/^{206}Pb$ age determination with no need for Pb/U calibration by external standardization and (2) significant improvement of $^{207}Pb/^{206}Pb$ age precision (Li, 2009, 2010). However, this multi-collector mode gives only $^{207}Pb/^{206}Pb$ age without corresponding U-Pb ages simultaneously, making examination of U-Pb concordance impossible. Thus, this mode is only suitable for dating samples simple history, i.e., with closed U-Pb isotopic system. Yet, without measurement, it is impossible to know samples concordancy *a priori*.

In order to effectively evaluate the concordance of U-Pb system, it is necessary to take advantages of both mono-collector mode (simultaneous determination of $^{238}U/^{206}Pb$ and $^{235}U/^{207}Pb$ ages) and multi-collector mode (high-precision determination of $^{207}Pb/^{206}Pb$ age). In this study we developed a hybrid dynamic multi-collector (HDMC) U-Pb dating technique on SIMS. We demonstrate that this new analytical protocol is able to achieve a higher precision of U-Pb zircon geochronology by a factor of two compared with the routine SIMS dating technique.

2 Analytical method

2.1 Sample preparation

Zircon Reference Materials (RM) and unknown samples are planted in two epoxy resin mounts in this study: Mount A643 containing four well-characterized zircon RMs, and Mount A1527 containing two RMs and two unknown samples (A Silva-1 and A Silva-2) collected from the A Silva granodiorite in NW Spain. Detailed geological background can be found in Castiñeiras et al. (2010). Zircon grains were polished to section the crystals in half for analysis. Transmitted and reflected light micrographs as well as cathodeluminescence (CL) images were obtained to reveal the internal structure of zircons. After cleaning with ethanol and deionized water, the mounts were vacuum-coated with ~30 nm high purity gold to ensure a resistance of less than 20 ohm across the sample surface.

2.2 Instrument settings

U-Pb age determination was performed using CAMECA ims-1280HR SIMS at the institute of Geology and Geophysics, Chinese Academy of Sciences in Beijing. The instrument is a large-geometry, double-focusing mass spectrometer, with radius of 585 mm for both ESA and sector magnet. It is equipped with a high density Duo-plasmatron ion source to produce O^- or O_2^- primary ions. The secondary ion optics can be optimized to almost full transmission up to 5000 mass resolving power (MRP). Electron-multiplier (EM) of mono-collector is usually used in the conventional U-Pb dating procedure. Selected isotope masses were measured in peak jumping mode one by one by changing the magnet settings. Multi-collector system is also equipped in this instrument (Figure 1). Five movable collector units are motorized, with EM or Faraday cup attached. All collectors in multi-collector system share the same MRP setting, which is fixed at 2400, 4800 or 8000 (50 % peak height definition here and after). The maximum mass dispersion is about 17 % and the minimum mass gap is about 0.4% a.m.u. Based on this configuration, all Pb isotopes can be measured simultaneously, but not uranium or uranium oxides.

The O_2^- primary ion beam was accelerated at -13 kV potential, with intensity varying between 5 and 12 nA. A 200 μm aperture was used after the primary beam mass filter (PBMF) to produce a uniformly illuminated spots on the sample surface, with 30 × 20 μm in size.

After an appropriate vacuum was obtained (< 10^{-8} Torr) in sample chamber, high purity (99.999 %) oxygen gas was introduced onto the sample surface (oxygen flooding). Under the pressure of ~5 × 10^{-6} Torr in sample chamber, the Pb^+ sensitivity can be enhanced to a value of ~26 cps/nA/ppm for zircon (at 8000 MRP), doubling the intensity compared to analysis without using oxygen flooding.(Whitehouse et al., 1997; Li et al., 2009) The secondary ions were extracted at initial energy of 10 keV. Entrance slit and field aperture (FA) was opened to 60 μm and 7000 μm, respectively, to match the 8000 MRP settings. Energy slit was closed to a bandwidth of 60 eV to reduce the energy dispersion. In order to fit the secondary ion beam into the smaller multi-collectors, compromised setting of voltages for rectangular lenses was applied in this study compare to the settings for conventional mono-collector U-Pb dating method.

During the HDMC mode measurements, yield calibration of each detector is a key procedure to ensure the accuracy of zircon age determination. A constant $^{90}Zr_2{}^{16}O^+$ signal (~1.0 x10^5 cps) was used to calibrate the secondary ion yields of each EMs on the movable trolleys relative to the C and L1 detectors, which were used for

^{207}Pb and ^{206}Pb determination. Before age calculation, the yield of each measurement was applied to its Pb isotopic ratio. Using a primary beam of ~10 nA, uncertainty of the relative yields was around 0.1 − 0.2 % in most cases, which was also propagated to the final Pb isotopic ratios.

The detector configuration is shown in Fig 1. All detectors (L2, L1, C, H1 and H2) are equipped with electron multipliers. Acquisition was divided into 5 sequences. $^{90}Zr_2{}^{16}O^+$ beam was measured by C and L1 during first two sequences. $^{204}Pb^+$, $^{206}Pb^+$ and $^{207}Pb^+$ were determined on L2, L1 and C simultaneously during the third sequence, similar to the configurations of the static multi-collector mode (Li et al., 2009). In the fourth sequence, $^{238}U^+$, ^{232}Th $^{16}O^+$ and $^{238}U^{16}O^+$ were measured on L1, H1 and H2 simultaneously. Finally, ^{238}U $^{16}O^{2+}$ was detected on L1. Counting time for each step was 4, 4, 60, 2 and 2 s respectively; the waiting time was 4, 1.04, 1.52, 2 and 1.52s.

Before data acquisition, each spot was pre-sputtered on a square area around 50 µm length of a side (25 µm raster + ~25 µm spot size) for 120 s to remove the surface contaminations and to enhance the yield of secondary ions. Secondary beam was centered in FA and entrance slit to ensure similar condition for each analysis. Energy calibration was also performed by scanning the sample high voltage. Mass calibration was performed before each analysis by centering the peak of $^{90}Zr_2{}^{16}O^+$ in detector C. Each measurement consists of 7 cycles, and the total analytical time is ~14 min.

2.3 Calibration and correction

Because the $^{206}Pb^+$, $^{238}U^+$ and $^{238}U^{16}O_2{}^+$ signals were determined using the same detector (L1) in this study, calibration of the Pb/U fractionation was as same as the conventional mono-collector U-Pb dating mode described by Li et al. (2009), which was based on a linear relationship between ln($^{206}Pb^{+}/^{238}U^{+}$) and ln($^{238}U^{16}O_2^{+}/^{238}U^{+}$). Pb/U fractionation was calibrated against zircon RM M257 (561.3 Ma, Nasdala et al., 2008) during the first session and zircon RM Temora (417 Ma, Black et al., 2003) in the second session. Uranium concentrations were calibrated against zircon M257 with U concentrations ~840 ppm (Nasdala et al., 2008). The worst reproducibility of these four RMs analyzed during first session is around 1% (1σ) and was propagated to the all RMs in the first session. A long-term external reproducibility, an error of 1.5% (1 RSD%) for $^{206}Pb/^{238}U$ measurements of the zircon RMs (Qinghu zircon, Li et al., 2010, 2013; Yang et al., 2014) was propagated to the unknowns in the second session. Thus, the reported analytical error of U/Pb ratio includes internal error from data acquisition and propagation of external error of U/Pb fractionation calibration.

Accurate common Pb correction is the premise to obtain accurate $^{207}Pb/^{206}Pb$ age for Phanerozoic zircons (Li et al., 2009). Non-radiogenic ^{204}Pb is ordinarily used to reflect the common Pb content. Because ^{204}Pb signal is very low in zircon, we use NIST 610 glass to precisely determine the position of ^{204}Pb peak. Common Pb isotopic compositions could influence the age correction to varying degrees. When the measured $^{206}Pb/^{204}Pb$ is higher than 10,000, common Pb composition variation has negligible influence to the final Pb-Pb age error (Li et al., 2009). Thus, it is not vital to know the initial common Pb isotopic compositions of the dated zircons when the measured $^{206}Pb/^{204}Pb$ >10,000. An average Pb of present-day crustal composition

($^{206}Pb/^{204}Pb$ = 18.703, $^{207}Pb/^{204}Pb$ = 15.629, Stacey and Kramers, 1975) is used for the common Pb correction assuming that it is largely due to surface contamination introduced during sample preparation in the laboratory. Error propagation from common Pb correction to $^{207}Pb/^{206}Pb$ age measurement follows those described by Li. et al.(2009).

3. Analytical results

SIMS U-Pb isotopic analyses were performed in two sessions. Four well-characterized zircon RMs in Mount A643 were determined firstly to demonstrate analytical precision and accuracy of our new HDMC dating method. One unknown zircon sample on Mount A1527 were analyzed in the second session to examine their concordance of U-Pb system. The results are listed in Table 1 and 2, and shown in Fig. 2 and 3. Uncertainties for individual analysis in the data tables are at 1σ level. Data reduction was carried out using the Isoplot/Ex v.4.0 program (Ludwig, 2003).

3.1 Dating results of zircon RMs

M257 zircon

The M257 zircon was a 5.15 g gemstone specimen from Sri Lanka. Detailed information could be found in Nasdala et al. (2008). This RM has TIMS-determined $^{206}Pb/^{238}U$ age of 561.3 ± 0.3 Ma, with mean isotopic ratios (2 SD) of 0.09100 ±0.00003 for $^{206}Pb/^{238}U$ and 0.7392 ± 0.0003 for $^{207}Pb/^{235}U$. The U-Pb system is concordant within uncertainty of decay constants. This RM exhibits remarkably low heterogeneity, with a virtual absence of any internal textures even in cathodoluminescence images, which makes it an ideal RM for element concentrations, U-Pb age, oxygen isotope and Li isotope measurement (Nasdala et al., 2008; Li et al., 2011). In this study, M257 was used as primary RM to calibrate the Pb/U fractionation. Sixteen analyses were performed on M257 zircon and yielded a weighted mean of $^{207}Pb/^{206}Pb$ at 0.058840 ± 0.000053 with Mean Square of Weighted Deviates (MSWD) = 1.05, corresponding to a $^{207}Pb/^{206}Pb$ age of 561.6 ± 2.2 Ma, which is consistent with the recommended TIMS-determined $^{206}Pb/^{238}U$ age of 561.3 ± 0.3 Ma (Nasdala et al., 2008). The corresponding IMF for $^{207}Pb/^{206}Pb$ is 0.03 ±1.0 ‰. The U-Pb ages are self-calibrated, so not described here.

91500 zircon

The 91500 zircon was a 238 g gem-class mineral collected by Harvard Mineralogical Museum in Cambridge, Massachusetts, USA, with a recommended $^{207}Pb/^{206}Pb$ age of 1065.4 ± 0.3 Ma and $^{238}U/^{206}Pb$ age of 1062.4 ± 0.4 Ma determined by isotope dilution-thermal ionization mass spectrometry (ID-TIMS) method (WIEDENBECK, 1995). Fourteen SIMS HDMC mode U-Pb measurements were conducted on 91500 zircon. The weighted mean of $^{207}Pb/^{206}Pb$ and $^{238}U/^{206}Pb$ ratio is 0.07476 ± 0.00015 (MSWD = 0.64) and 5.610 ± 0.031 (MSWD = 0.73), respectively, corresponding to a $^{207}Pb/^{206}Pb$ age of 1062.1 ± 3.9 Ma and a $^{206}Pb/^{238}U$ age of 1057.4 ± 5.3 Ma. The calculated IMF for $^{207}Pb/^{206}Pb$ is -1.6 ± 1.8 ‰. All the ages are in good agreement within error with the recommended values.

Temora zircon

Temora zircon was separated from the Middledale Gabbroic Diorite in the Lachlan Orogen of eastern Australia. The ID-TIMS analysis gives $^{238}U/^{206}Pb$ and $^{207}Pb/^{206}Pb$ age 416.8 ± 1.3 Ma and 418.2 ± 1.3 Ma, respectively (Black,2003). Fourteen SIMS analyses were carried out on Temora zircon. All the analyses are concordant, giving the weighted mean of $^{207}Pb/^{206}Pb$ and $^{238}U/^{206}Pb$ ratios of 0.05498 ± 0.00018 (MSWD=1.5) and 14.907 ± 0.081 (MSWD = 0.83), respectively, corresponding to a $^{207}Pb/^{206}Pb$ age of 412 ± 5 Ma and a $^{238}U/^{206}Pb$ age of 418.4 ± 2.2 Ma. The calculated IMF for $^{207}Pb/^{206}Pb$ is -2.2 ± 3.3 ‰.

Plešovice zircon

Plešovice zircon came from a potassic granulite facies rock at the Plešovice quarry located at the southern Bohemian Massif, Czech Republic. It was dated by ID-TIMS technique, with a recommended $^{238}U/^{206}Pb$ age of 337.1 ± 0.4 Ma (Sláma, 2008). Fourteen SIMS analyses were conducted on Plešovice zircon grains. All the analyses are concordant, giving the weighted mean of $^{207}Pb/^{206}Pb$ and $^{238}U/^{206}Pb$ ratio of 0.05319 ± 0.0001 (MSWD =0.94) and 18.60 ± 0.10 (MSWD = 0.41), respectively, corresponding to a $^{207}Pb/^{206}Pb$ age of 337.1 ± 3.8 Ma and a $^{238}U/^{206}Pb$ age of 337.6 ± 1.7 Ma.. The calculated IMF for $^{207}Pb/^{206}Pb$ is -0.2 ± 2 ‰.

3.2 Dating results of unknown zircons

There were 25 analyses on Temora zircon as U/Pb calibration RM in session 2, and yielded an Pb-Pb age of 413 ± 3 Ma (MSWD=1.03) . The corresponding IMF on $^{207}Pb/^{206}Pb$ was calculated as -1.5 ‰ and applied to unknowns. The Qinghu zircon, an in-house RM for U-Pb age and Hf-O isotopic microanalyses (Li, 2013), was alternately analyzed as an unknown sample together with the unknown zircons. The purpose of Qinghu zircon measurement in our Lab is to monitor the long-term accuracy of SIMS U–Pb age determination calibrated against the external RM. Nine analyses of the Qinghu zircon yield a Pb-Pb age of 158 ± 6 Ma and a $^{238}U/^{206}Pb$ age of 160.6 ± 1,5 Ma, in good agreement within errors with the ID-TIMS result of 159.5 ± 0.2 Ma (Li, et al., 2009).

The unknown zircons A Silva-2 was collected from the center of part of the A Silva granodiorite, a small pluton that intruded into the metasediments at the upper unit of the Órdenes Complex in NW Spain (Castiñeiras et al., 2010). A total of 46 analyses were conducted on 41 zircons. Two analyses are obviously older than the main population. They are most likely xenocrysts, thus they are ruled out in the discussion of the crystallization age. All the remained data are pooled together and plotted on the Tera–Wasserburg inverse concordia diagram (Figure 3), which clearly show a Pb-loss trend. A discordia line was constructed to yield a lower intercept at -49 ± 120 Ma and an upper intercept of 505.1 ± 2.5 Ma. Eighteen analyses shown in gray color are high in common Pb, with the measured $^{206}Pb/^{204}Pb$ ratio much less than 10000. At the same time, we also noted that some of observed $^{207}Pb/^{206}Pb$ ratio errors are more than two times larger than the expected Possion error (Figure 4). Excluding those data with unexpected errors, the remaining 26 analyses are characteristically low in common Pb, with the $^{206}Pb/^{204}Pb$>10,000. These 26 analyses yielded a weighted mean of $^{207}Pb/^{206}Pb$ of 0.05736 ± 0.00006, corresponding to a $^{207}Pb/^{206}Pb$ age of 505.4 ± 2.5 Ma (2SE).

4. Discussion and concluding remarks

4.1 Improvement of this technique

Using the newly developed HDMC technique, Pb isotopes are measured using the multi-collector mode. The counting time of all Pb isotopes are 420 s (7 cycles of 60 seconds acquisition in sequence 3 as shown in Fig. 1), in stark contrast to an order magnitude less counting time for ^{204}Pb, ^{206}Pb and ^{207}Pb in the conventional mono-collector mode. HDMC mode in this study is broadly similar to those reported by using the static multi-collector mode (Li et al., 2009, 2010), and improved the Pb-Pb age precision by a factor of ~2 - 3 compared with those by using the mono-collector mode. For example, two Phanerozoic zircon EMs, TEMORA and Plešovice, yielded around or less than 1% percent error for Pb-Pb ages, comparable to the uncertainty of $^{206}Pb/^{238}U$ age by SIMS (Black et al., 2004; Li et al., 2010; Yang et al., 2014).

Above mentioned situation is pooling multiple analyses on high quality zircon. For single-spot analysis, to achieve a similar precision for Pb-Pb and $^{206}Pb/^{238}U$ age could be estimated in advance. For examples, based on the counting statistics and our working condition (~10 nA, 420 s counting time, ~ 25 cps/ppm/nA Pb^+ sensitivity), to achieve a Pb-Pb age uncertainty comparable with 1.5% U-Pb age uncertainty (a long term uncertainty for single-spot zircon SIMS U-Pb age measurement, Li et al., 2010; Yang et al., 2014) on 500 Ma sample requires the ^{207}Pb counts higher than 300 cps, corresponding to zircon U concentration > 300 ppm. This calculation considers negligible uncertainty contribution from common lead correction. This calculation implies that to achieve a high precision Pb-Pb age for single spot analyses on Phanerozoic zircons is quite difficult, and need multiple conditions, including of not only high U content and negligible common Pb with sample, but also improved analytical techniques.

4.2 limitations on the accuracy of $^{207}Pb/^{206}Pb$ age

With mono-collector to collect all signals, one may not worry about the EM yield. With multi-collector mode, the researchers always worry the stability of the relative yields for different EMs, which is important to calculate the accurate ratios. As a normal method, an external reference material with known Pb isotopes is used to measure and monitor the relative yield, for example, NIST610 Pb isotopes (Li et al., 2009). In fact, this method could be considered as an integrated way including the relative yield and IMF of Pb isotope, however, with assumption that there is no matrix effect on Pb isotope analyses. Li et al. (2010) found there is about 8‰/amu mass fractionation difference when measuring Pb isotopes on NIST610 with and without oxygen flooding by a Cameca 1280 SIMS. It indicates that the IMF for Pb isotopes of NIST610 is not stable on different instrumental conditions. Whether there is matrix effect or how much it affects is still unknown. In this study, we use the signal of zircon matrix peak by peak-jumping on tow EMs to measure and monitor the stability of the relative yields. This method may avoid the possible matrix effect on IMF for Pb isotopes. However, the IMF for Pb isotopes in zircon need evaluation.

The mass fractionation of Pb isotopes in zircon is difficult to make an accurate measurement because of low Pb concentrations in zircon and the difficulty of resolving any PbH isobars (Ireland and Williams, 2003). Numbers of good agreements between SIMS and conventional ID-TIMS Pb isotopes analyses of zircon samples has been used to suggest that the IMF is minimal. Stern et al.(2009) did a comprehensive research on IMF for $^{207}Pb/^{206}Pb$ in zircon by SHRIMP, and found that the calculated IMF ranges from +3.6‰ to -2.4‰/amu. According to our measurements on four zircon RMs, the M257 and Plešovice zircons show almost no detectable IMF, while 91500 and TEMORA zircons have about -2‰/amu for Pb isotopes. Whether these IMF difference is related to matrix effects, such as U-Pb concentrations, radioactive damage, remains to be researched. However, it is recommended that the overall uncertainty of $^{207}Pb/^{206}Pb$ isotopes need incorporate a measurement of IMF with appropriate error propagation (Stern et al., 2009). Thus, the limitation on accuracy of $^{207}Pb/^{206}Pb$ age is defined by the variation of IMF, i.e. around 2‰, which limits to around 4 Ma.

4.3 Crystallization age of A Silva granodiorite

Many studies have been carried out for the emplacement age of A Silva, with the aim of elucidating the regional geological evolution (Peucat et al., 1990; Ribeiro et al., 2007; Castiñeiras, 2010). According to the geological settings and cathodeluminescence (CL) images of zircons, this granodiorite seems have a relatively simple age distribution. However, the previous SIMS U-Pb determination showed a "concordant" age range between 540 and 460 Ma, which is out of the expectation (Castiñeiras, 2010). Although the authors realized the age distribution have suffered lead loss by later event, it is difficult to judge the concordance of young zircon from ordinary mono-collector SIMS U-Pb data. Thus, this A Silva zircon was chosen to show the ability of the method on discriminating the concordance of Phanerozoic samples.

According to the data in Table 2 and Fig. 3, there are several defects on this zircon, which make the U-Pb dating analyses rather complicated. Firstly, nearly one third of zircon grains contains much high common lead, with ^{204}Pb counts higher than 1 cps, 10 times higher than those in RMs. These high common lead is unlikely from zircon crystal lattice, but most likely from micro-inclusions. Inclusions bring not only high common lead, but also produce a heterogeneous analytical area. This could explain why the grains with high common lead are apt to yield unexpected analytical uncertainties (Table 2, Fig. 4). This kind of zircon grains is difficult to produce high precision Pb-Pb age by single spot analysis. Thus, it is not easy to evaluate the U-Pb system concordance. Secondly, there are inherited components. Among 46 analyses, two inherited zircon grains with age of 600 Ma and 560 Ma, were detected. Thirdly, this zircon sample suffered lead loss. It is noticed that several analyses give consistent Pb-Pb age but much younger $^{206}Pb/^{238}U$ age than the main population, indicating radiogenic Pb loss. Except the inherited data, all analyses construct a regression line on Tera-Wasserburg Plot and give a lower intercept of -49±120 Ma and a upper intercept of 505.1 ± 2.5 Ma, indicating a present Pb-loss event. Thus, this upper intercept of 505.1 ± 2.5 Ma is suggested as the best estimate of the zircon crystallization age. In another calculation way, these data construct a very good Pb-Pb isochron (MSWD = 0.6) with $^{204}Pb/^{206}Pb$ vs. $^{207}Pb/^{206}Pb$ (Fig. 5). This good regression line indicates high precision $^{204}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ has been achieved by our newly developed HDMC-SIMS technique.

Compared with the data by mono-collector mode (Castiñeiras et al. 2010), the uncertainty of $^{206}Pb/^{238}U$ ages of both studies are similar, while precision of their $^{207}Pb/^{206}Pb$ ages in this study show a significant improvement. Our newly-developed HDMC SIMS U-Pb dating technique takes advantages of both the static multi-collector mode and peak-hopping mono-collector mode. It is able to simultaneously measure high-precision $^{207}Pb/^{206}Pb$ ratio as in the static multi-collector mode (Li et al., 2009) without trade off in analytical precision of $^{238}U/^{206}Pb$ ratio of the conventional peak-hopping mono-collector mode. We conclude that this new technique has potential to produce high precision U-Pb and Pb-Pb ages to provide valuable evaluation on the concordance of U-Pb zircon system as young as 500 Ma.

Acknowledgement

We thank Dr. F. Díaz García for providing zircons from A Silva granodiorite, and H.X. Ma for preparing zircon mounts. The paper has benefited from review comments of two anonymous reviewers. This work was supported by Chinese National 973 Project (Grant 2013CB835005), the National Natural Science Foundation of China (41222023, 41221002 and 41203016).

References

Black, L.P. et al., 2003. TEMORA 1: a new zircon standard for Phanerozoic U-Pb geochronology. Chemical Geology, 200(1-2): 155-170.

Black, L.P., 2005. The use of Multiple Reference samples for the monitring of Ion Microprobe Performance during zircon $^{207}Pb/^{206}Pb$ Age determinations. Geostandards and Geoanalytical Research, 29, 169-182.

Castiñeiras, P., Garcia, F.D., Barreiro, J.G., 2010. REE-assisted U-Pb zircon age (SHRIMP) of an anatectic granodiorite: Constraints on the evolution of the A Silva granodiorite, Iberian allochthonous complexes. Lithos, 116(1-2): 153-166.

Finch, R.J., Hanchar, J.M., 2003. Structure and chemistry of zircon and zircon-group minerals. Zircon, 53: 1-25.

Harley, S.L., Kelly, N.M., 2007. Zircon Tiny but Timely. Elements, 3(1): 13-18.

Ireland, T.R., Williams, I.S., 2003. Considerations in Zircon Geochronology by SIMS. Reviews in Mineralogy and Geochemistry, 53(1): 215-241.

Li, Q.L., Li, X.H., Liu, Y., Tang, G.Q., Yang, J.H., Zhu, W.G., 2010. Precise U–Pb and Pb–Pb dating of Phanerozoic baddeleyite by SIMS with oxygen flooding technique. Journal of Analytical Atomic Spectrometry, 25: 1107–1113

Li, X.H., Li, Q.L., Liu, Y., Tang, G.Q., 2011, Further characterization of M257 zircon standard: A working reference for SIMS analysis of Li Isotopes. Journal of Analytical Atomic Spectrometry. 26, 352-358.

Li, X.H., Liu, Y., Li, Q.L., Guo, C.H., Chamberlain, K.R., 2009. Precise determination of Phanerozoic zircon Pb/Pb age by multicollector SIMS without external standardization. Geochemistry. Geophysics. Geosystems., 10(4): Q04010.

Ludwig, K.R., 2003. ISOPLOT 3.0: a geochronological toolkit for Microsoft Excel. Berkeley Geochronology Center, pp. Spec. Pub 4.

Mattinson, J.M., 2013. Revolution and Evolution: 100 Years of U-Pb Geochronology. Elements, 9(1): 53-57.

Nasdala, L. et al., 2008. Zircon M257 - a Homogeneous Natural Reference Material for the Ion Microprobe U-Pb Analysis of Zircon. Geostandards and Geoanalytical Research, 32(3): 247-265.

Parrish, R.R., Parrish, R.R., Noble, S.R., 2003. Zircon U-Th-Pb Geochronology by Isotope Dilution — Thermal Ionization Mass Spectrometry (ID-TIMS). Reviews in Mineralogy and Geochemistry, 53(1): 183-213.

Peucat, J.J. et al., 1990. Geochemical and geochronological cross section of the deep Variscan crust: The Cabo Ortegal high-pressure nappe (northwestern Spain). Tectonophysics, 177(1–3): 263-292.

Ribeiro, A. et al., 2007. Geodynamic evolution of the SW Europe Variscides. Tectonics, 26(6): TC6009.

Sláma, J. et al., 2008. Plesovice zircon -- A new natural reference material for U-Pb and Hf isotopic microanalysis. Chemical Geology, 249(1-2): 1-35.

Stern, R.A., Bodorkos, S., Kamo, S.L., Hickman, A.H., Corfu, F. 2009. Measurement of SIMS Instrumental Mass Fractionation of Pb isotopes During Zircon Dating. Geostandards and Geoanalytical Research, 33, 145-168.

Whitehouse, M.J., Claesson, S., Sunde, T., Vestin, J., 1997. Ion microprobe U□Pb zircon geochronology and correlation of Archaean gneisses from the Lewisian Complex of Gruinard Bay, northwestern Scotland. Geochimica et Cosmochimica Acta, 61(20): 4429-4438.

Whitehouse, M.J., Kamber, B.S., Assigning dates to thin geneissic veins in high-grade metamorphic terrances: A cautionary Tale From Akilia, Southwest Greenland. Journal of Petrology, 2005, 46(2), 258-318.

WIEDENBECK, M. et al., 1995. THREE NATURAL ZIRCON STANDARDS FOR U-TH-PB, LU-HF, TRACE ELEMENT AND REE ANALYSES. Geostandards and Geoanalytical Research, 19(1): 1-23.

Williams, I.S., 1992. Some observations on the use of zircon U-Pb geochronology in the study of granitic rocks. Earth and Environmental Science Transactions of the Royal Society of Edinburgh, 83(1-2): 447-458.

Yang, Y.N., Li, Q.L., Liu, Y., Tang, G.Q., Ling, X.X., Li, X.H. Zricon U-Pb dating by

454 Secondary Ion Mass Spectrometry. Earth Science Frontiers (China University of
455 Geosciences (Beijing); Peking University), 2014, 21, 81-92.

456

Figure Captions:

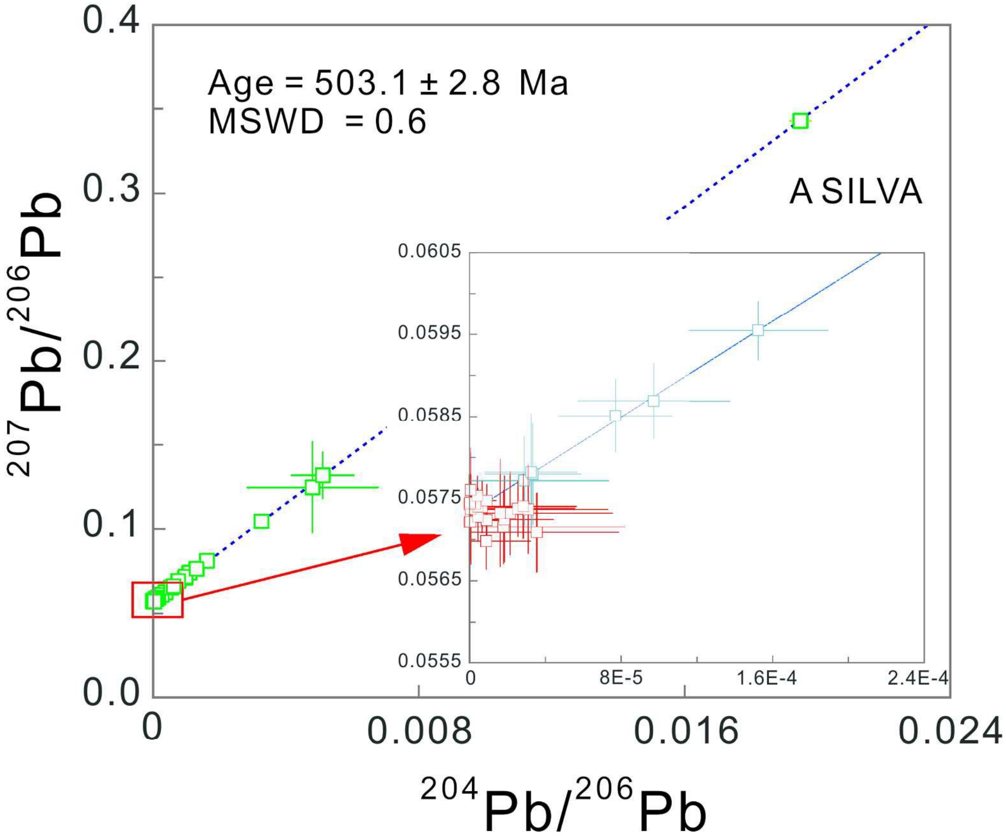
Fig. 1 Schematic diagram of the Cameca IMS-1280HR multi-collection system. All the detectors are equipped with EMs for this study. The detector C was set near the secondary optical axis of the instrument.

Fig. 2 The Tera–Wasserburg inverse U-Pb diagram of four zircons RMs, 91500 (a), M257 (b), Temora (c), and Plešovice (d). Data-point error ellipses are 2σ. The solid blue oval in each plot indicates the average of the measurements.

Fig. 3 The Tera–Wasserburg inverse U-Pb diagram for zircons from A Silva granodiorite. Two green ovals represent analyses on xenocrystal zircons. The ellipses in gray color indicate the data with high common lead and unexpected large uncertainties of $^{207}Pb/^{206}Pb$ two times higher than Possion error. The ovals in red are the ones with low common lead and uncertainties of $^{207}Pb/^{206}Pb$ within two times Possion error.

Fig.4 Correlation between precisions of $^{207}Pb/^{206}Pb$ ratio and ^{207}Pb intensity. The green line represents the expected uncertainties from the counting statistics of ^{207}Pb signal, calculated as 1/sqrt (total ^{207}Pb counts). Uncertainties come from ^{206}Pb was neglected because of around 20 times higher counting rate compared to ^{207}Pb. The green circle are the measured data of four zircon RMs on Mount A643. The squires in red are the data of A Silva.

Fig.5 Pb-Pb isochron constructed from $^{204}Pb/^{206}Pb$ ratio vs. $^{207}Pb/^{206}Pb$ ratio on the A Silva 2 zircon sample.



181x153mm (300 x 300 DPI)