ANALYTICAL METHODS

LA-ICP-MS zircon U/Pb dating

Instrument set-up and Data acquisition

In situ laser–ablation inductively–coupled–plasma mass spectrometer (LA–ICPMS) determination of U–Pb age of the samples with number started by DX- was performed at the University of Science and Technology of China, Hefei, China, employing an Elan 6100 DRCII Q–ICPMS coupled to an ArF excimer laser ablation system (GeoLas Pro, 193nm wavelength). These analyses were carried out with a pulse rate of 10 Hz, energy density of 2.5 Jcm^{-2}, and static spot diameter of 44 µm. All analytical runs consisted of analyses of four unknown samples bracketed by two analyses of standard 91500.

For all analyses, zircon was ablated in a high-purity He (99.9995%) atmosphere (gas flow rate: 0.8 to 1.0 L/min). Ablation duration was 90s including a 40s gas and Hg blank measurement immediately preceding ablation. Prior to ablation for isotopic measurement, the zircon was pre-ablated for two laser pulses to remove surface contamination. Before entering the plasmas, the ablation-generated zircon aerosol of all analyses was mixed with high purity argon (99.9995%) makeup gas in the homogenizers, where adjacent peaks of laser pulses were homogenized. The Q–ICPMS measurements were carried out using time resolved analysis (TRA) operated in fast peak-hopping and DUAL detector mode using a short integration time.

Offline selection and integration of background and analytical signals, time-drift corrections, and quantitative calibrations for U–Pb isotope data were performed using the software ICPMSDataCal (Liu et al., 2008). For all masses, a mean blank value was calculated from the 40s blank measurement. All intensities acquired during ablation were then reduced by the corresponding mean blank value. $^{207}Pb/^{206}Pb$, $^{206}Pb/^{238}U$, $^{207}Pb/^{235}U$, and $^{208}Pb/^{232}Th$ ratios were corrected for both instrumental mass bias and depth (time) dependent elemental and isotopic fractionation using a linear interpolation (with time) for every ten or four analyses according to the variations of the external standards. For the analyses with $^{206}Pb/^{204}Mass > 200$, no correction was made for common Pb. Otherwise, a correction for the presence of common lead and lead loss was then applied using a Microsoft Excel spreadsheet template following the methods of Anderson (2002). Uncertainty of preferred values for the external standards was propagated to the ultimate results of the samples. Final statistics and age calculations were made using Isoplot/Ex_ver4.15 (Ludwig, 2003).

Zircon U-Pb age determination of the samples with number started by DXY- was conducted at the National Research Center for Geoanalysis, in Beijing, employing an ArF excimer laser ablation system (GeoLas Pro, 193nm wavelength). Laser ablation craters were approximately 40 μm in diameter. The repetition rate was 4 Hz. The laser influence on the sample surface was ~1.08 $J \cdot cm^{-2}$. He^2 (~0.7 L/min) was applied as a carrier gas. Ar^2 (~0.9 L/min) was used as the make-up gas and mixed with the carrier gas via a concentric connector. The cylindrical mixing chamber with ~140 cm^3 inner volume immediately before reaching the ICP torch was used to smooth signals produced at low laser repetition rates. The ion-signal intensities were acquired using a multiple collector-inductively coupled plasma-mass spectrometer (MC-ICP-MS, Neptune Plus, Thermo Fisher Scientific, Germany) in the static mode. The Jet sample cone and X skimmer cone were used along with the guard electrode (GE) turned on to achieve the best instrument sensitivity. The MC-ICP-MS instrument was fitted with 9 Faraday collectors and 7 ion-counting detectors. The ^{238}U and ^{232}Th signals were acquired by the Faraday cups with 1011 Ω resistor amplifiers. The ^{202}Hg, ^{204}Pb (^{204}Hg), ^{206}Pb, ^{207}Pb and ^{208}Pb were acquired by the ion-counting detectors. Each analysis incorporated a background acquisition of approximately 20-30 s (gas blank) followed by 50 s of data acquisition from the sample.

Off-line selection and integration of background and analytic signals, correction of element fractionation drift, and calculation of the element concentration and age were performed by Iolite Geochron4 package (Paton et al., 2010). Zircon 91500 and Plesovice were used as primary and secondary standards for U-Pb dating, respectively, and was analyzed twice every 8 sample analyses. Time- and depth- dependent drifts of U-Th-Pb isotopic ratios were corrected for every eight analyses according to the variations of 91500. Preferred U-Th-Pb isotopic ratios used for 91500 are from Wiedenbeck et al. (1995). Uncertainty of preferred values for the external standard 91500 was propagated to the ultimate results of the samples. Final statistics, age calculations, and concordia diagrams were made using Isoplot (version 4.15, Ludwig, 2003). The accuracy and precision of the analytical protocols employed during this study are demonstrated through the dating of well-studied, international zircon standards (91500 and Plesovice).

Zircon U-Pb age determination of two samples (YW181107-1 & 3) was conducted by an Agilent 7500x ICP-MS coupled to a GeoLas Pro 193 nm ArF excimer laser at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China. Helium was applied as a carrier gas which was mixed with Argon via a T-connector before entering the ICP-MS. Each analysis incorporated a background acquisition of approximately 30 s (gas blank) followed by 60 s of data acquisition from the sample. Off-line selection and integration of background and analytical signals, and time-drift correction and quantitative calibration for U-Pb dating were performed by ICPMSDataCal (Liu et al., 2008). Zircons 91500 and Plesovice were selected as primary and secondary standards for U-Pb dating, respectively, and were analyzed twice every 8 sample analyses. Uncertainty of preferred values for the external standard 91500 was propagated to the ultimate results of the samples. Concordia diagrams and weighted mean calculations were made using Isoplot (version 4.15, Ludwig, 2003).
The zircon U/Pb isotopic results are listed in Supplementary Tables 2 and 3.

Of note, in order to effectively correct the time-dependent elemental fractionation (matrix effect), we tried to select as same time period as possible for integration of background and analytical signals of the sample and the adjacent standards.

The accepted ages for distribution analysis were selected from a subset of both ≤10% discordance and ≤10% uncertainty (1σ), wherein the $^{206}Pb/^{238}U$ and $^{207}Pb/^{206}Pb$ ages were adopted for zircons younger and older than 1000 Ma, respectively. Age distributions are visualized as histograms with bin width =50 Ma.

Data Accuracy, Reproducibility, and Uncertainty

The accuracies and reproducibilities of U-Pb zircon analyses are monitored by interspersed measurements of natural zircons of good quality 91500 and Plesovice that are well characterized. Comparing to TIMS results (Weidenbeck et al 1995; Sláma et al. 2008), the weighted mean $^{206}Pb/^{238}U$ ages of 91500 and Plesovice resulted from analyses show very small offset (see below Table).

Table: Comparison of U–Pb data for standards 91500 and Plesovice used in this study with data obtained from previous studies

zircon	No. of analyses	$^{206}Pb/^{238}U$ age (Ma)	% age offset
91500			
Weidenbeck et al 1995 (ID-TIMS)		**1065.4±0.6**	
Yuan et al. 2008(LA-ICPMS)	21	1063.2±4.4	
Hefei (this study)	88	1059.7±6.8	-0.54
Beijing (this study)	69	1062.1±2.9	-0.31
Guiyang (this study)	32	1062.2±5.1	-0.31
Plesovice			
Sláma et al. 2008 (TIMS)		**337.13 ±0.37**	
Beijing (this study)	69	336.6±0.4	-0.15
Guiyang (this study)	32	338.9±2.5	+0.56

$^{40}Ar/^{39}Ar$ step heating analyses

Preparation of pure phlogopite or muscovite separates were accomplished via standard crushing, sieving, and heavy liquid and magnetic separation procedures, followed by hand picking. The mineral separates, Fish Canyon Tuff sanidine (Lanphere & Baadsgaard, 1997), and ZBH biotite (a sample standard in China; Fu et al., 1987) flux monitors were irradiated in an atomic reactor belonging to the Research Institute of Atomic Energy of China and set in an H8 hole for fast neutron irradiation. The irradiation duration and neutron dose for the analyzed minerals were 7.8 h and 1.83×10^{17} n/cm^2, respectively. The samples were analyzed after low temperature (250°C–300°C) degassing for 20–30 min. The J factor was estimated by replicate analyses of Fish Canyon Tuff sanidine, with an age of 27.55 ± 0.08 Ma, and the ZBH biotite standard, with an age of 133.3 ± 0.24 Ma, using a 1% relative standard deviation (1δ). J values for individual samples were determined by a second-order polynomial interpolation.

$^{40}Ar/^{39}Ar$ dating was conducted on populations of grains, and a precise analysis of the age spectrum was made. Interference of nuclear reactions by K and Ca was calculated by co-irradiation of pure salts of K_2SO_4 and CaF_2, using the values $^{40}Ar/^{39}Ar_K$ = 0.004782, $^{39}Ar/^{37}Ar_{Ca}$ = 0.00081, and $^{36}Ar/^{37}Ar_{Ca}$ = 0.0002398. Samples were loaded in aluminum packets into a Christmas-type double-vacuum furnace and step-heated in a classical fashion, usually from 550°C to 1500°C. The gas was purified using Ti and Al–Zr getters. Once cleaned, the gas was introduced into an MM-5400 mass spectrometer (Penguin Eng. Ltd), the Isotopic Laboratory, Institute of Geology, Chinese Academy of Geological Sciences, Beijing, and 4–5 min were allowed for equilibration before conducting a static analysis. Measured mass spectrometric ratios for the $^{40}Ar/^{39}Ar$ analysis were extrapolated to time zero, normalized to the $^{40}Ar/^{36}Ar$ atmospheric ratio, and corrected for neutron-induced ^{40}Ar from potassium, and ^{39}Ar and ^{36}Ar from calcium.

Dates and uncertainties were calculated using the computer program ISOPLOT v3.0 (Ludwig, 2003) from the Berkley Geochronological Center. The age spectra and isotope correlation plots were also generated using this program. The decay constant of ^{40}K was that suggested by Steiger & Jäger (1977). The uncertainty of the plateau age is given as 1s. Weighted mean plateau ages (WMPAs) are reported as the value where >50% of the ^{39}Ar released in contiguous steps is within a 1δ error. For relatively rapid cooling rates, the estimated closure temperatures for muscovite was selected as 400°C±50°C (Harrison et al., 1985; McDougall & Harrison, 1999). The analytical results are listed in Supplementary Table 4.

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