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Cite this: *J. Anal. At. Spectrom.*, 2011, **26**, 1868

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TECHNICAL NOTE

Quasi-simultaneous determination of U-Pb and Hf isotope compositions of zircon by excimer laser-ablation multiple-collector ICPMS†

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Received 2nd April 2011, Accepted 28th April 2011
DOI: 10.1039/c1ja10116a

A method for quasi-simultaneous determination of U-Pb ages and Hf isotope compositions on a single zircon spot is developed, by use of a multiple-collector ICPMS coupled with an excimer laser-ablation system. The ICPMS used in this study is equipped with variable zoom lens to change the dispersion of the analyzer and bring ion beams into the collector coincidentally. This feature allows rapid switching between U-Pb and Hf collector configuration, which is used to quasi-simultaneously determine the zircon U-Pb and Hf isotope compositions. The analytical results on three reference zircon standards, 91500, CZ3 and Plesovice and one nature zircon sample, agree with literature/known values, thereby demonstrating feasibility of the method.

1. Introduction

Zircon ($ZrSiO_4$) incorporates high concentration of uranium and negligible lead when it forms and thus is readily amenable to U-Pb age determination. Furthermore, zircon contains a very high concentration of Hf with an extremely low Lu/Hf ratio, thus it is also ideal for Hf isotope study.[1] However, complex growth history may result in ambiguous data when it is measured as a whole grain by traditional thermal-ionization mass spectrometry (TIMS) method and *in situ* measurement by micro-beam analytical techniques is necessary. Application of SHRIMP (sensitive high resolution ion micro probe) to zircon U-Pb age determination has achieved great success while the development of Hf isotope measurement by ion probe technique is hampered due to interferences from rare earth element hydroxides, other polyatomic species and relatively low ionization efficiency.[2] Recent U-Pb analyses of zircons using laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS, both quadrupole and multiple collector-ICPMS) have made significant strides in generating precise and accurate ages.[3,4] A great advancement of zircon Hf isotope analyses has also been made by use of LA-MC-ICPMS technique,[5–9] due to the high ionization efficiency of the plasma source and little polyatomic interference. LA-(MC)-ICPMS technique also has other advantages of easy sample preparation, high productivity and low cost, it has become the first choice of zircon U-Pb and Hf isotope analyses today.

In order to get correlative U-Pb age and Hf isotope composition at the same growth zone of complicated zircons, previous measurements by LA(-MC)-ICPMS have been carried out either on different spots of the same growth domain of single zircons (one spot for U-Pb analysis and second for Hf isotope),[10] or on concentric spots with different sizes (a small crater for U-Pb dating at first and sequentially a larger crater on the same locations for Lu-Hf isotope analysis).[11] Woodhead *et al.* (2004)[7] simultaneously determined $^{207}Pb/^{206}Pb$ ages and Hf isotope data for zircon from a single ablation using an excimer laser-ablation MC-ICPMS (Nu Plasma) configuration. Unfortunately, determination of U-Pb age was not successful. Simultaneous measurement of U-Pb and Hf isotope compositions from a single laser-ablation was firstly described by Yuan *et al.* (2008),[12] who suggested to split the laser-generated aerosol into two mass spectrometers for U-Pb age and Hf isotope composition measurement, respectively. Here, we report results of quasi-simultaneous determination of zircon U-Pb age and Hf isotope composition by a single mass spectrometer coupled with an excimer laser-ablation system.

2. Instrumentation

A Nu Plasma HR MC-ICPMS (Nu Instruments, UK) coupled with a 193 nm excimer laser ablation system (Resolution M-50, Resonetics LLC, USA), installed at the Department of Earth Sciences, the University of Hong Kong, was employed in this study. The MC-ICPMS is fitted with a modified collector block (U-Pb block), which contains 12 Faraday collectors and 4 ion counting detectors dispersed on the low mass side of the array, allowing simultaneous acquisition of ion signals ranging from mass ^{204}Pb to ^{238}U, an important factor in obtaining highly precise and accurate U-Pb age determinations. The collector system incorporates a unique fixed collector array, rather than the traditional adjustable collectors, and a series of variable zoom lenses which can change the dispersion of the analyte and

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c1ja10116a

bring ion beams into the collectors coincidentally. Changes in dispersion are controlled by tuning the voltages on the zoom lens array. These changes are almost instantaneous, allowing rapid switching between different mass ranges. This feature was exploited for simultaneous determination of zircon U-Pb and Hf isotope compositions in this contribution.

The laser-ablation system employed in this study is an ArF excimer 193 nm RESOlution M-50 (Resonetics RRL, USA), which has been described in detail by Müller *et al.* (2009).[13] This system allows quick response to changes in the sample or ablation conditions (99% signal washout in less that 1.5 s) due to its innovative sample cell design. We choose 40 μm for spot size and 5 Hz for laser repetition rate in this study. Energy intensity on target was adjusted to ~5 J cm^{-2}. Helium gas, which carries the laser ablated sample aerosol from sample cell, is mixed with argon carrier gas and nitrogen as additional di-atomic gas to enhance sensitivity,[9] and finally flows into the MC-ICPMS torch for analysis.

3. Analytical protocol

The instrument settings and operating conditions for both the laser ablation system and MC-ICPMS used in this study are listed in Table 1. Prior to analysis, gas flow rates of argon make up gas, helium and nitrogen carrier gas were optimized to achieve maximum sensitivity with low oxide production ($^{254}UO/^{238}U < 2\%$). The collector assignment for this method is shown in Table 2, which constitutes two cycles, one to measure U-Pb and the other to measure Hf isotope. Each cycle was conducted with static mode for 2 s and peak-jumping was involved between cycles with a magnet settle time of 1 s. When tuning the machine, the voltages of zoom lens were optimized to ensure coincidence and flat-topped peak shapes for U-Pb and Hf isotopes respectively, by ablating international standard of NIST SRM 612 glass. The optimized zoom lens settings were stored and invoked accordingly between cycles to maintain the coincidence and flat-topped peak shapes for both cycles. The zircon was pre-ablated for three laser pulses to remove surface contamination before analysis. Each analysis incorporated a background acquisition of approximately 40 s (gas blank, closing the laser shutter) followed by 60 s data acquisition for the sample. A plot of signal evolving for a typical analytical run is shown in Fig. 1.

For U-Pb cycle, ^{207}Pb, ^{206}Pb, and ^{204}Pb (+^{204}Hg) signals were measured on the ion counting channels, whereas ^{238}U was acquired on a Faraday collector. Corrections for instrumental drift, mass bias and elemental fractionation were all conducted by a 'standard-sample-standard' bracketing external standardization technique. One piece of standard zircon GJ-1 with size of ~2 × 2 × 2 mm is used for calibration. It was analyzed twice every five analyses. Since our collector configuration does not allow simultaneous measurement of ^{202}Hg and ^{204}(Pb + Hg) intensity is typically <10^{-5} voltage, which is at same level of gas black (Fig. 1), the common lead correction was not applied in this study. This configuration can not measure an internal element (usually ^{29}Si), so no U and Pb concentration are given. Off-line data reduction (including selection and integration of background and analyte signals) was performed by software *ICPMSDataCal*.[14] Time-dependent drifts were corrected using a linear interpolation (with time) for every five analyses according to the variations of the standard zircon GJ-1. Uncertainty of preferred values for the external standard GJ-1 was propagated to the ultimate results of the samples. Concordia diagrams and weighted mean calculations were made using Isoplot/Ex_ver3.[15]

Masses acquired for Hf isotope cycles are 179–172. Measured isotope ratio of $^{176}Hf/^{177}Hf$ were normalized to $^{179}Hf/^{177}Hf = 0.7325$,[16] using exponential correction for mass bias. Isobaric interference of ^{176}Yb and ^{176}Lu on ^{176}Hf was corrected by monitoring ^{172}Yb and ^{175}Lu respectively. *In situ* measured $^{173}Yb/^{172}Yb$ ratio is used for mass bias correction for both Yb and Lu because of their similar physicochemical properties. Ratios used for the corrections are 0.5887 for $^{176}Yb/^{172}Yb$ and 0.02655 for $^{176}Lu/^{175}Lu$.[17]

Table 1 Operating conditions and instrument parameters

Laboratory and sample preparation	
Laboratory name	Dept of Earth Sciences, University of Hong Kong
Sample type/mineral	Zircons
Sample preparation	Conventional mineral separation, 1 inch resin mount
Laser ablation system	
Make, model and type	Resonetics LLC USA, RESOlution M-50, ArF excimer
Ablation cell and volume	Two-volume laser-ablation cell (Laurin Technic, Australia), effective volume ~1–2 cm^3
Laser wavelength	193nm
Pulse width (ns)	~20ns
Fluence (J cm^{-2})	5 J cm^{-2}
Repetition rate (Hz)	5 Hz
Spot size (μm)	40 um
Sampling mode/ pattern	spot
Carrier gas	500 ml min^{-1} He + 2 ml min^{-1} N_2, Ar make-up gas.
Ablation duration	60 s
ICPMS Instrument	
Make, model and type	Nu Instruments, Nu Plasma HR, MC-ICPMS
Sample introduction	Ablation aerosol
RF power (W)	1300 W
Make-up gas flow	400 ml min^{-1} Ar
Detection system	mixed Faraday-multiple ion counting array
Masses measured	172–179, 204, 206, 207, 238
Data Processing	
Gas blank	30 s on-peak zero subtracted
Calibration strategy	GJ-1 used as primary reference material
Reference material information	GJ-1 $^{206}Pb/^{238}U$ 602.3 ± 1 Ma, $^{207}Pb/^{206}Pb$ 609.2 ± 0.7 Ma (in-house TIMS, unpublished)
Data processing package used	ICPMSDataCal (Liu *et al.*, 2010)[14]
Uncertainty level and propagation	Ages are quoted at 2 sigma absolute, propagation is by quadratic addition. Reproducibility and age uncertainty of reference material are propagated.
Other information	Sample line of 3.5 m from ablation cell to torch and a 30 s washout time after the laser stopped firing.

4. Results and discussion

Test zircons used in this study are three zircon standards (91500, CZ3 and Plesovice) and one unknown nature zircon sample MG136-1. The U-Pb and Hf isotope analytical results obtained in this study are listed in the electronic supplementary material, Tables 3 and 4.†

Table 2 Configuration of the collector array used for this study. Note there are gaps in the collector array between ExH, H3, H2, H1 and L1; between L8 and IC0; between IC2 and IC3

	ExH	H3	H2	H1	L1	L2	L3	L4	L5	L6	L7	L8	IC0	IC1	IC2	IC3
Cycle 1	238													207	206	204
Cycle 2					179	178	177	176	175	174	173	172				

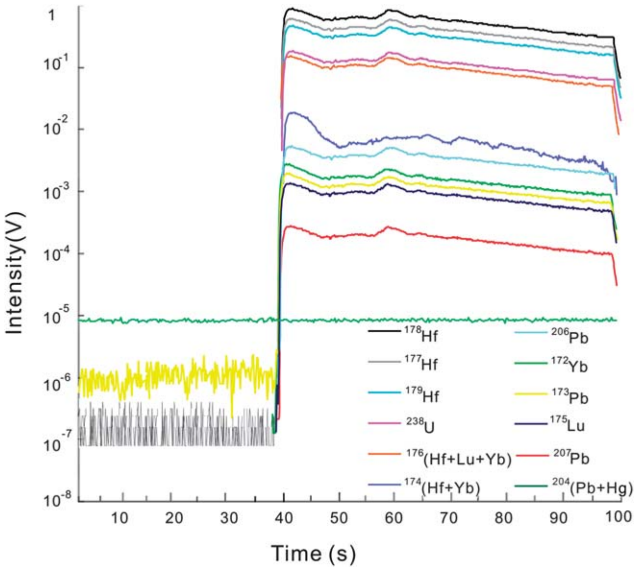

Fig. 1 A plot of signal evolving for a typical analytical run.

4.1. Zircon standard 91500

This zircon has been extensively used in LA-ICPMS and SIMS labs for U-Pb and Hf isotope analyses.[8,12,18–20] ID-TIMS analyses for this zircon gave a weighted mean $^{207}Pb/^{235}U$ age of 1063.5 ± 0.6 Ma (2σ) and $^{206}Pb/^{238}U$ age of 1062.4 ± 0.8 Ma (2σ).[18] One ~4 × 2 × 2 mm fragment was analyzed and 35 U-Pb and Hf isotope data sets were obtained in this study. The U-Pb data are shown in the concordia diagram Fig. 2A, yielding a weighted mean $^{207}Pb/^{235}U$ age of 1067.5 ± 3.9 Ma (95% confidence, MSWD = 1.4) and a weighted mean $^{206}Pb/^{238}U$ age of 1066.2 ± 4.2 Ma (95% confidence, MSWD = 1.09). Both ages are well within the error of the reported ID-TIMS age. Hf isotope results for this zircon range from 0.282257 ± 0.000023 (2σ) to 0.282349 ± 0.000029 (2σ), with a weighted mean of 0.282307 ± 0.000010 (95% confidence, MSWD = 1.4, Fig. 2B), consistent with the literature values (ranging from 0.282270 to 0.282321)[7,8,18,19] and the recommended value of 0.282305 by Wu *et al.* (2006).[8]

4.2. Zircon standard CZ3

CZ3 is also a single grain zircon with *gem* quality from Sri Lanka. It is homogenous in terms of U and Pb and has been widely used as a SHRIMP U-Pb zircon standard. TIMS U-Pb isotope analyses on this zircon yields a concordant age of 564 Ma.[21] Several small fragments (~300 × 300 × 200 μm) in one mount were analyzed and thirty three sets of U-Pb-Hf data were obtained in this study. The U-Pb data cluster together on the concordia diagram (Fig. 2C) and yield a weighted mean $^{207}Pb/^{235}U$ age of 565.8 ± 2.8 Ma (95% confidence, MSWD = 1.7) and a weighted mean $^{206}Pb/^{238}U$ age of 564.4 ± 2.4 Ma (95% confidence, MSWD = 0.74), which are identical to the TIMS age. A weighted mean of 0.281725 ± 0.000018 (95% confidence, Fig. 2D) was obtained for the Hf isotope composition. The value agrees well with 0.281729 ± 0.000021 (2σ) reported by Wu *et al.* (2006).[8]

4.3. Zircon standard Plesovice

The studied zircon comes from a potassic granulite in Czech Republic. It has been used as a calibration and reference material for U-Pb and Hf isotope measurements by laser ablation ICPMS

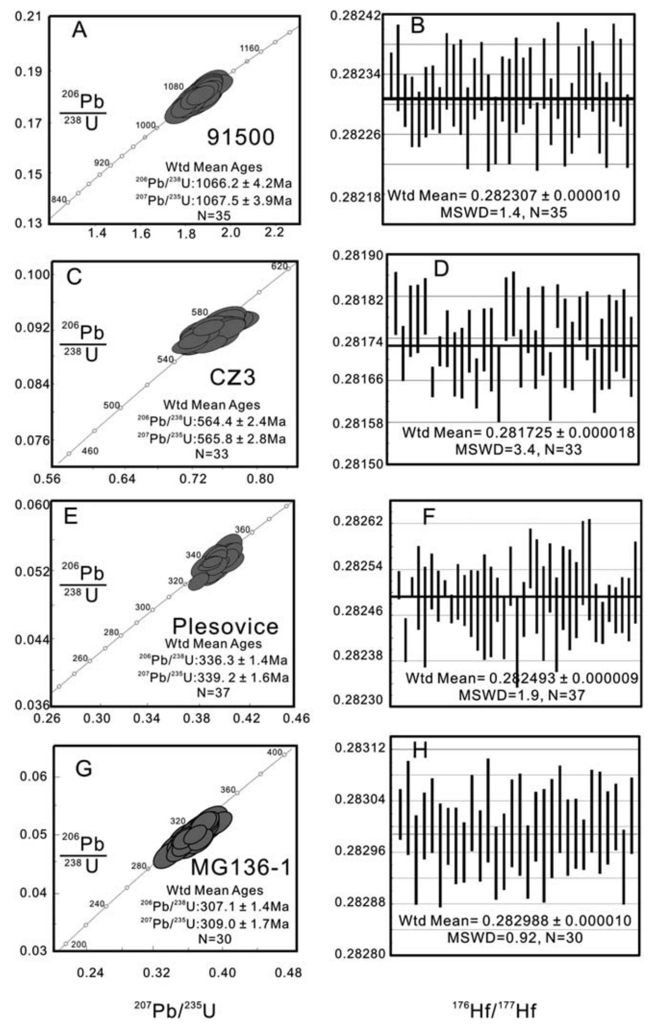

Fig. 2 U-Pb age and Hf isotope analytical results for three standard zircons 91500, CZ3 and Plesovice and an unknown zircon sample MG136-1. (A), (C), (E) and (G) are concordia diagrams.; (B), (D), (F) and (H) are the weighted average of Hf isotope ratios. Uncertainties represent 2σ. MSWD is the mean square of weighted deviates.

since 2008.[22] Although the zircon is heterogeneous in trace element composition due to primary growth zoning, it is homogeneous in terms of U-Pb and Hf isotope compositions within and between the grains. This zircon standard gives a concordant U-Pb age with a weighted mean $^{206}Pb/^{238}U$ age of 337.13 ± 0.37 Ma (ID-TIMS, 95% confidence)[22] and a $^{176}Hf/^{177}Hf$ value of 0.282482 ± 0.000013 (2σ).[22] One euhedral zircon megacryst grain with a size of about 2 × 1 × 1 mm was repeatedly analyzed 37 times in this study. The obtained U-Pb data are displayed on the concordia diagram of Fig. 2E, which gives a weighted mean $^{207}Pb/^{235}U$ age of 339.2 ± 1.6 Ma (95% confidence, MSWD = 1.4) and a weighted mean $^{206}Pb/^{238}U$ age of 336.3 ± 1.4 Ma (95% confidence, MSWD = 1.04). Both ages are identical to the reported ID-TIMS age.[22] Hf isotope compositions obtained in this study gives a weighted mean of 0.282493 ± 0.000009 (95% confidence, MSWD = 1.9 n = 37, Fig. 2F), which is also identical to the literature value.[22]

4.4. Zircon sample MG136-1

The sample MG136-1 is a massive, coarse to medium grained alkali-feldspar granite collected from the West Junggar, Xinjiang Autonomous Region of China. Zircon grains from this sample are light-yellow, transparent to semi-transparent and occur as euhedral, stubby prismatic crystals 100–150 μm long with length to width ratios of 1.5–2.0. Our precious SHRIMP results for this sample yielded a weighted mean $^{206}Pb/^{238}U$ age of 308.3 ± 6.1 Ma (95% confidence, n = 9) and a weighted mean $^{207}Pb/^{235}U$ age of 323 ± 24 Ma (95% confidence, n = 9).[23] A weighted mean $^{176}Hf/^{177}Hf$ value of 0.282999 ± 0.000030 (95% confidence, n = 17) was also obtained previously by LA-MC-ICPMS at the Institute of Geology and Geophysics, Chinese Academy of Sciences in Beijing.[23] Thirty zircon grains from the same mount were analyzed in this study. The obtained U-Pb data are displayed on the concordia diagram of Fig. 2G. These data give a weighted mean $^{206}Pb/^{238}U$ age of 307.1 ± 1.4 (95% confidence, MSWD = 1.05) and $^{207}Pb/^{235}U$ age of 309.0 ± 1.7 (95% confidence, MSWD = 1.4), within 1σ error of our previous results. Hf isotope compositions obtained in this study give a weighted mean of 0.282988 ± 0.000010 (95% confidence, Fig. 2H), which is also within 1σ error of our previous results.

5. Conclusions

This paper reports a successful application of a MC-ICPMS coupled with an excimer 193 nm laser ablation system to quasi-simultaneous measurement of zircon U-Pb and Hf isotope compositions on the same single spot (40 μm in diameter). Our results for three reference zircon standards (91500, CZ3 and Plesovice) and one natural zircon sample agree well with literature values and our previous results, thereby demonstrating that this relatively simple instrumentation can be used to quasi-simultaneously determine zircon U-Pb age and Hf isotope composition on one single spot.

Acknowledgements

This study was supported by research grants from the Chinese National 973 Program (2007CB411308) and Hong Kong Research Grant Council (HKU7043079), 100 Talents Program of the Chinese Academy of Sciences to Dr X.-P. XIA, Hong Kong-Germany Joint Research Scheme and Croucher funding for a joint laboratory between GIG and HKU. Three anonymous referees are thanked for their constructive comments. This is contribution No. IS-1331 from GIGCAS.

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