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RESEARCH ARTICLE

Analytical effect of stabilizer volume and shape on zircon U–Pb dating by nanosecond LA-ICP-QMS

Dongyang Xiong[1,2], Longfei Guo[1,2], Chenxi Liu[1,2], Long Wang[1,2], Yanrong Liu[1,2] and Xijuan Tan[1,2*]

Abstract

In this paper, we evaluated the effect of seven stabilizers with different shapes (including cylinder, cubic and ball shape) on zircon U–Pb dating analysis by laser ablation inductively coupled plasma quadrupole mass spectrometry (LA-ICP-QMS) in detail. In the case of stabilizer volume examined, the analytical efficiency of cylinder stabilizers (21.2, 25.1, 35.3 and 125 mL) were investigated in terms of signal stabilization, signal rising/washout time and U–Pb dating accuracy. By using zircon 91500 as reference material for external calibration, the $^{206}Pb/^{238}U$ age of zircon Plešovice was determined by a nanosecond LA-ICP-QMS, where the stabilizer was placed directly after the ablation cell and sample aerosols carried by helium passed through the stabilizer and subsequently mixed with make-up gas (argon) before ICP. It was found that transient signal oscillations were invisible and signal intensities were comparable using all the stabilizers, while signal rising time was 2.0-fold and washout time was 27.6-fold for stabilizer with volume of 125 mL to that of 21.2 mL. The obtained average $^{206}Pb/^{238}U$ age of zircon Plešovice was 335.53 ± 1.02, 361.73 ± 5.04, 340.10 ± 1.98 and 341.21 ± 5.17 Ma (2σ, $n \geq 5$), respectively, giving average relative deviations of a single point of age (1σ) less than 2.0%. Among the corresponding $^{206}Pb/^{238}U$ ratios, it was also found that the value (0.05343 ± 0.87‰, 1σ, $n = 5$) obtained using 21.2 mL of cylinder stabilizer highly agreed with that of 0.05384 ± 0.74‰ (1σ, $n = 5$) using the commercially available "squid" stabilizer. The analytical efficiency of the 21.2 mL of cylinder stabilizer was then compared to that of cubic shape stabilizer (18.5 mL) and ball shape stabilizer (14.1 mL). Results showed that there were no significant differences of the obtained $^{206}Pb/^{238}U$ ages using stabilizers with volume in the range of 14.1–21.2 mL. But both cubic and ball shape stabilizers exhibited washout time over 270 s. We also studied the particle filter effect of the stabilizers by packing the 21.2 mL of cylinder stabilizer with 1.0 g of stainless wire. Despite the average $^{206}Pb/^{238}U$ age deviation was only − 0.81%, spiky signals occasionally occurred which might be ascribed to the use of a nanosecond laser and relatively low density of stainless wire in the stabilizer. This study confirmed that an empty stabilizer with volume of 21.2 mL and cylinder shape was preferred to produce smoothing signals. The improved analytical accuracy of zircon U–Pb dating using such a stabilizer ensured the future application to trace element analysis by LA-ICP-QMS.

Keywords: Signal stabilizer, Signal oscillation, Nanosecond LA-ICP-QMS, Zircon U–Pb dating

Introduction

Zircon ($ZrSiO_4$), which is characterized by low contents of common Pb and enrichment of U and Th, is a ubiquitous accessary mineral existing in many types of terrestrial and extraterrestrial rocks (Wu and Zheng 2004). Because of its high closure temperature of U–Pb diffusion and the large resistance against thermal and mechanical alteration, zircon is a good recorder for magmatic,

*Correspondence: tanxijuan@hotmail.com; tanxijuan@chd.edu.cn
[1] Laboratory of Mineralization and Dynamics, Chang'an University, 126 Yanta Road, Xi'an 710054, China
Full list of author information is available at the end of the article

metamorphic and hydrothermal crystallization processes (Lee et al. 1997). Furthermore, the non-radiogenic Pb tends to be excluded from crystallizing zircon, causing Pb is of time-dependent and in situ radiogenic decay in the crystal (Cherniak and Watson 2000). These unique properties make zircon mineral eminently suited for age, origin and thermal history study based on U–Th–Pb geochronology (Mundil et al. 2004). Nowadays, zircon U–Pb dating has become a standard U–Th–Pb system which provides accurate and robust geochronological information for both magmatic and metamorphic events (Nardi et al. 2013; Wang et al. 2020; Jara et al. 2021).

The U–Th–Pb dating methods are based on the radioactive decay of multiple parent isotopes (^{238}U, ^{235}U, and ^{232}Th) to different stable isotopes of Pb (^{206}Pb, ^{207}Pb and ^{208}Pb) (Jeong et al. 2018). Thermal ionization mass spectrometry (TIMS) is one of the well-known U–Th–Pb dating techniques. But such a bulk analytical method requires chemical dissolution and purification in an ultra-clean laboratory environment, concentration quantification of U, Th, Pb using isotope dilution technique, and determination of the isotopic composition of Pb. Additionally, if the studied zircons come from complex evolution regions, they usually have multi-stage internal structures and contain multi-stage evolution history. By using TIMS as the U–Pb dating technique, different ages present in such kind of zircons are often lost due to the "integration" effect of sample dissolution, thus providing quasi-continuous processes or instantaneous "events" (Schaltegger et al. 2015). The introduction of in situ spot analytical techniques has enabled precise U–Pb dating for zircons which were crystalized from both single- and multi-stage evolution. Secondary ion mass spectrometry (SIMS) and sensitive high resolution ion micro-probe (SHRIMP) are two powerful in situ tools for zircon U–Pb dating analysis (Yang et al. 2014; Hu et al. 2017; Amaral et al. 2021). Despite no requirement of time-consuming sample digestion and purification procedures, these methods suffer from shortcomings involving expensive instrumentation, high daily cost, and relatively low sample throughput (Kröner et al. 2014). Since Fryer et al. (1993) first reported the successful application of laser ablation inductively coupled plasma quadrupole mass spectrometry (LA-ICP-QMS) to zircon U–Pb dating analysis, this technique has become an alternative in situ zircon dating method which is characterized by easy access to instrumentation, simple sample preparation, and short assay time (approximately two minutes per analysis) (Solari et al. 2015; Chew et al. 2017; Neymark et al. 2021).

Currently, LA-ICP-QMS gains wide acceptance as a zircon U–Pb dating approach providing results with reasonable accuracy and precision (Li et al. 2015). However, uncertainty control for zircon U–Pb dating analysis by LA-ICP-QMS remains challengeable due to matrix effect (Luo et al. 2018; Thompson et al. 2018), mass fractionation during ablation process (Košler et al. 2014) and/or within ICP (Košler et al. 2015), etc. Among multiple sources affecting quantification uncertainties of LA-ICP-QMS analysis, aliasing (or spectral skew) leading to oscillations in the transient signals (Günther et al. 2000; Schilling et al. 2007) can cause significant bias for obtained results (Hattendorf et al. 2019; Norris et al. 2021; Tan et al. 2021). This aliasing effect is particularly pronounced when low dispersion aerosol transport systems are used. To minimize transient signal oscillations, stabilizers (or signal smooth devices) are highly suggested to be installed downstream the LA cell. According to literature work, there were several designs of smooth devices applied in LA-ICP-QMS analysis. For instance, baffled-type and cyclone-type devices developed by Tunheng and Hirata (2004) were able to reduce LA signal oscillations at 2 Hz of repetition rate by almost an order of magnitude. A commercially available "squid" signal smooth device was specifically designed for a low-dispersion, two-volume LA cell by Müller et al. (2009). "Wire-type" and "wave-type" signal smooth devices reported by Hu et al. (2012, 2015) were applied to high resolution U–Pb dating analysis at repetition rates of 1–2 Hz. Recently, Kon et al. (2020) concluded that signal stability and washout time were a trade-off correlation based on the comparison study for a series of cylinder signal stabilizers (including baffled-type, "squid" type and wire type, etc.). They also pointed out that signal variations and washout time correlated with the volume of signal smooth device despite their different inner structures. To the best of our knowledge, there has been no analytical influence study of both stabilizer volume and shape on zircon U–Pb dating by LA-ICP-QMS to date.

Here, by using zircon 91500 as a reference material for external calibration, the analytical efficiencies of seven signal stabilizers with different shapes (including cylinder, cubic and ball shape) on ^{206}Pb/^{238}U age study of zircon Plešovice by a nanosecond LA-ICP-QMS were evaluated. Through a detailed discussion of signal stabilization effect, signal rising/washout time and zircon U–Pb dating accuracy, and the analytical efficiency comparison of the studied stabilizers to commercially available "squid" signal smooth device, a reasonable volume range of the utilized stabilizers and suitable stabilizer shape were proposed for routine zircon U–Pb dating analysis by LA-ICP-QMS.

Materials and methods

Instrumental apparatus and operating conditions of LA-ICP-QMS

This study was carried out using an Agilent 7700x ICP-QMS (Agilent, USA) connected to a 193 nm ArF excimer nanosecond LA system in the Laboratory of Mineralization and Dynamics, Chang'an University. This Analyte Excite LA system (Photon Machines, USA) provides a maximum energy fluence of 15 J/cm^2 and contains a HelEx Active two-volume LA cell (Müller et al. 2009). By applying 0.7 L/min of He to the main volume, such an LA cell enables the signal duration for a single laser pulse to fall below 200 ms (full width at 1% signal maximum). The utilized ICP-QMS was equipped with a Pt shielding plate and a silicon shielding cap to enhance signal sensitivity. Generally, the signal of ^{238}U can reach 2500 cps/s for 1 μg/g of U when using 5 Hz of laser repetition rate and 40 μm of spot size.

Here, ablation was accomplished in a helium atmosphere (He, 99.999% purity). Argon gas (Ar, 99.996% purity) was used as the make-up gas and mixed with the sample aerosols from the ablation cell or the signal stabilizer by a T-connector before entering the ICP. In this work, the background signals of ^{204}Pb and ^{202}Hg were less than 100 cps/s.

The LA-ICP-QMS was optimized daily to achieve highest possible sensitivity for low- to high-mass isotopes prior to U–Pb zircon dating analysis. After the system had been stabilizing for at least one hour, the carrier gas flow rate was optimized while ablating NIST SRM 610 silicate glass using a fixed spot size of 40 μm and a repetition rate of 5 Hz. Apart from analyte sensitivity, the daily optimization targets were a ThO^+/Th^+ ratio not higher than 0.5% and an achieved $^{238}U^+/^{232}Th^+$ signal intensity ratio near 1.05. Other parameters (including sampling depth, lens voltage) and ICP-QMS instrument's PA factor calibrations were updated on a daily basis. Typical operating parameters for the ICP-QMS and LA system are summarized in Table 1.

Sample preparation

Standard zircon 91500 and zircon Plešovice as the studied sample were placed on a glass plate and covered by a polyvinylchloride (PVC) cup with a diameter of 2.54 cm. Then suitable amount of mixture of epoxy and curing agent was introduced into the cup. After the standards were mounted, the surfaces were sequentially treated by using 5000 mesh of abrasive paper, 7000 mesh of abrasive paper and 1 μm of polishing fluid. Thereafter, the samples were sequentially cleaned by sonication using ethanol (99.7%) and ultrapure water (Milli-Q, Millipore, Bedford, MA, USA). Prior to LA-ICP-QMS analysis, the surfaces of all the standard material and zircon sample were carefully cleaned using ethanol and dried before being placed into the LA cell.

Signal stabilizers

Three categories of signal stabilizers (i.e. cylinder, cubic and ball shape, see Fig. 1) made of glass material were applied to the analytical effect study. Here, four volumes of about 21.2 mL (3 cm i.d., 3 cm in length), 25.2 mL (4 cm i.d., 2 cm in length), 35.3 mL (3 cm i.d., 5 cm in length) and 125 mL (4 cm i.d., 10 cm in length) were customized for cylinder stabilizers, while the volume for cubic shape stabilizer was 14.1 mL (3 cm i.d.) and ball shape stabilizer was 18.0 mL (3 × 4 × 1.5 cm in width, length and height, respectively). All the signal stabilizers were sonicated sequentially in 5% HNO_3 solution (v/v) for 10 min and then 5 min in ultrapure water. After being dried, one cylinder signal stabilizer of 21.2 mL was filled with 1.0 g of stainless wire (width: 0.56 mm, thickness: 0.05 mm) and then flushed using 1.0 L/min of Ar about 30 min prior to LA-ICP-QMS analysis. In this work, all the studied signal stabilizers were directly installed after

Table 1 Operating parameters for LA-ICP-QMS in this work

ICP-MS	Agilent 7700x	Laser ablation	Analyte excite
RF power, W	1450	Laser type	ArF excimer
Plasma gas, L/min Ar	15.0	Wavelength, nm	193
Auxiliary gas, L/min Ar	1.0	Pulse duration, ns	5
Make-up gas, L/min Ar	0.8	Repetition rate, Hz	5
Detector mode	Dual	Fluence, J/cm^2	5.9
Scan mode	Peak jumping	Spot size, μm	35
Settling time, ms	1	Sampling strategy	Single spot
Sweeps/reading	1	Pulses/spot	200
Data collecting mode	TRA	Carrier gas, L/min He	0.2 Inner cup 0.6 Main volume
Sampling depth, mm	5		

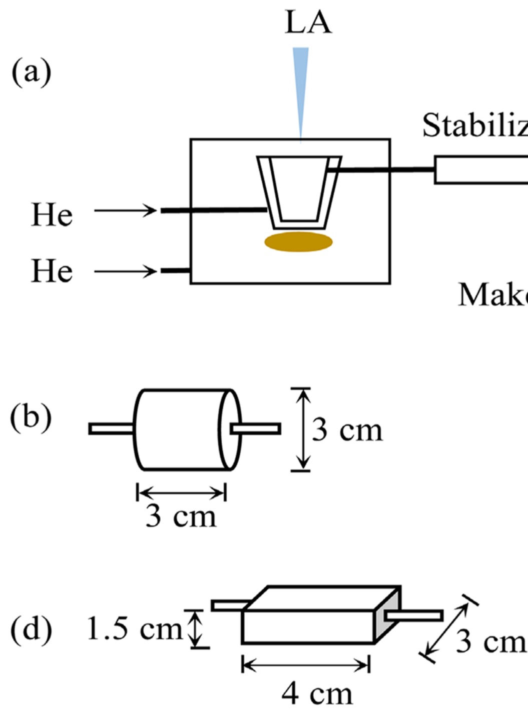

Fig. 1 Schematic diagram of the utilized LA-ICP-QMS system and the studied stabilizers. **a** Depicted the connection of signal stabilizer with the LA-ICP-QMS system. **b**–**d** showed the cylinder, ball and cubic shape stabilizers. Here 21.2 mL of cylinder stabilizer was shown as a representative of cylinder stabilizers

the LA cell and only carrier gas He together with ablated sample aerosols passed through the stabilizers. Following the signal stabilizer, the sample aerosols carried by He mixed with the make-up gas (Ar) and then reached the ICP. The brief schematic view of this current LA-ICP-QMS system was shown in Fig. 1.

Method description

Zircon samples were ablated using hole drilling mode and ICP-QMS data were recorded under peak jumping mode. The dwell times were set as 10 ms for ^{29}Si, ^{49}Ti, ^{91}Zr, ^{93}Nb and ^{181}Ta, 50 ms for ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb, 20 ms for ^{232}Th and ^{238}U, respectively. Each LA-ICP-QMS analysis consisted of 10 s background signal acquisition and 40 s data collection while ablating standards and samples. One complete assay cycle consisted of a sequence of 1 spot analysis of NIST SRM 610, 2 spot analyses of zircon 91500, 4–6 spot analyses of zircon samples, 1 spot analysis of NIST SRM 610, and 2 spot analyses of zircon 91500. All data were collected in time-resolved analysis (TRA) mode, and data reduction was carried out using "ICPMSDataCal" with zircon 91500 as the external calibrator and ^{91}Zr as the internal standard element in age calculation (Liu et al. 2008). Here, the preferred values of zircon 91500 were taken from the GeoReM database (Jochum et al. 2005). The calculated ^{206}Pb/^{238}U ages were expressed in form of million year (Ma).

Results and discussion

Analytical effect for volume of signal stabilizers

In previous study, Tunheng and Hirata (2004) showed that the size distribution of sample aerosols in signal stabilizers was highly dependent on various parameters including stabilizer volume, geometry, flow path and sample location in the stabilizer. In this present work, by comparing to the properties of commercially available "squid" signal stabilizer which has a total volume of about 16.3 mL (Müller et al. 2009), we first assessed the analytical effect of stabilizer volume on zircon U–Pb dating to confirm the optimum volume range of stabilizers for this current utilized LA-ICP-QMS configuration.

Signal variation and signal rising/washout time from stabilizer volume

Here, four stabilizers in cylinder shape with different volume patterns (i.e. 21.2, 25.1, 35.3 and 125 mL) were investigated in terms of signal stabilization, signal rising/washout time when analyzing standard zircon 91500. Figure 2 shows the recorded transient signal of ^{91}Zr isotope using cylinder stabilizers with different volume and the "squid" signal stabilizer. As it can be seen from

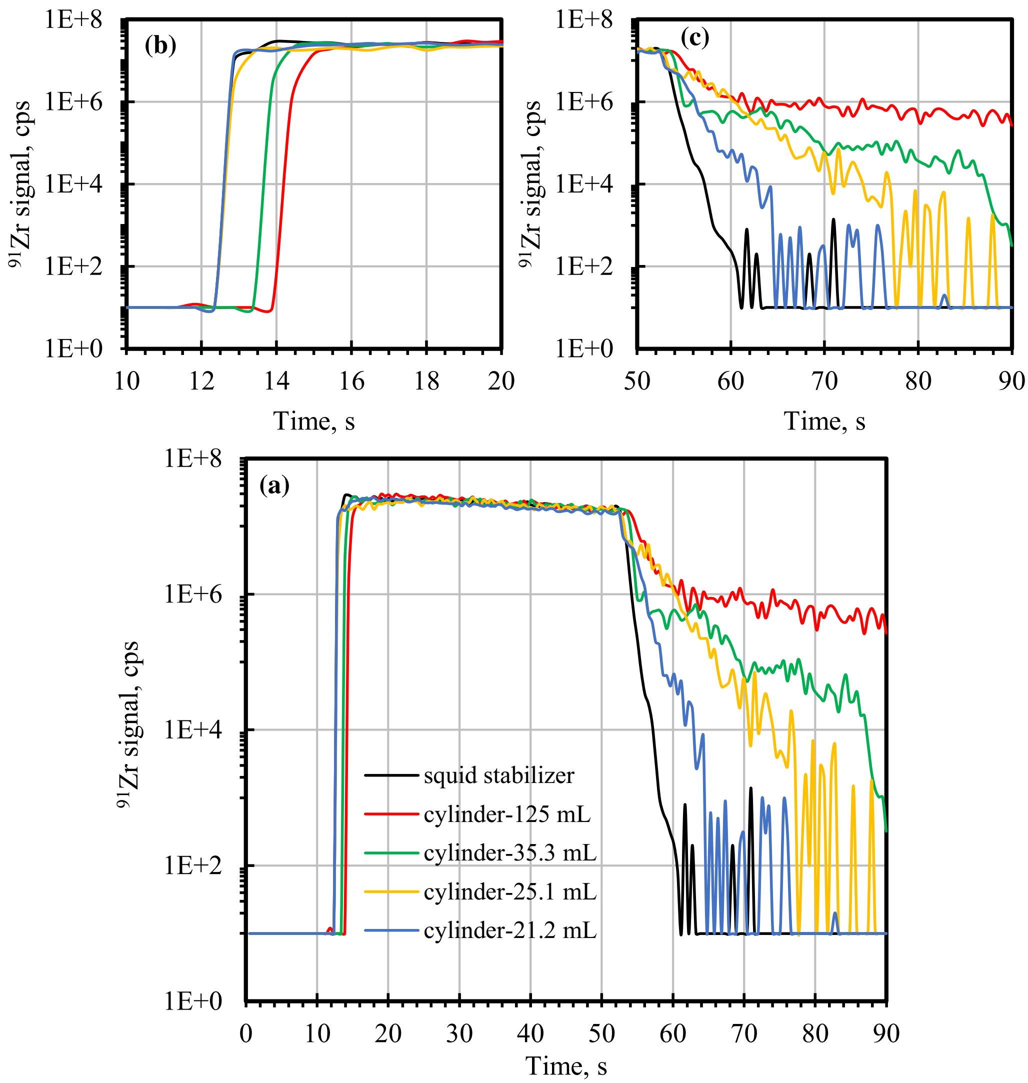

Fig. 2 Transient signal profiles of ^{91}Zr intensity of zircon standard 91500 with 35 µm of spot size and 5 Hz of laser repetition rate using "squid" signal stabilizer and cylinder stabilizers with different volumes. **a** Presented the signal profiles of ^{91}Zr versus assay time, while **b**, **c** Showed the signal rising and washout curves when using "squid" signal stabilizer and 21.2, 25.1, 35.3 and 125 mL of cylinder stabilizers, respectively

Fig. 2a, there were no visible oscillations and obvious signal intensity loss for the application of the studied cylinder stabilizers. It is also clear from Fig. 2b that the signal rising time was approximately 2.5 s for stabilizers with volume less than 25.1 mL, which was identical to the value using "squid" signal stabilizer. However, with stabilizer volume larger than 25.1 mL the signal rising time became longer, showing values of about 4.5 s and 5.0 s for 35.3 mL and 125 mL of stabilizers, respectively. As for signal washout time, Fig. 2c reveals that it highly correlated with cylinder stabilizer volume. For example, the washout time for ^{91}Zr signal intensity to background levels was over 53 s using 25.1 mL of stabilizer, which undoubtedly resulted in low sample analytical throughput. It was also worth noting that when using 35.3 mL of stabilizer the signal washout curve apparently differed from those using other cylinder stabilizers, showing signal intensity dropped sharply within the first 3 s and then gradually went down.

Analytical influence of stabilizer volume on zircon U–Pb dating

To further evaluate the analytical property of the four designed stabilizers, the U–Pb dating results of zircon Plešovice by LA-ICP-QMS were compared in deviations of obtained $^{206}Pb/^{238}U$ age and the average relative

Table 2 U–Pb dating results for zircon Plešovice by LA-ICP-QMS ($n \geq 5$)

Stabilizer		$^{206}Pb/^{238}U$ Age (Ma, 1σ)	RE (%)	Average age deviation (%)*	Signal washout time (s)
Type	Volume (mL)				
Squid	16.3	338.08 ± 1.40	1.34	+ 0.28	~ 9.3
Cylinder	21.2	335.53 ± 1.02	1.59	− 0.48	< 20
	25.1	361.73 ± 5.04	1.64	+ 7.3	> 53
	35.3	340.10 ± 1.98	1.46	+ 0.88	> 140
	125	341.21 ± 5.17	1.35	+ 1.2	> 240
	21.2 (with 1.0 g stainless wire)	334.40 ± 1.71	1.28	− 0.81	~ 5.7
Cubic	18.0	342.76 ± 2.45	1.49	+ 1.7	> 270
Ball	14.1	340.34 ± 2.36	1.68	+ 0.95	> 270
Without stabilizer	–	348.07 ± 1.94	1.88	+ 3.3	~ 3.1
		332.11 ± 2.63	1.66	− 1.5	

*The referred $^{206}Pb/^{238}U$ age of zircon Plešovice is 337.13 ± 0.37 Ma (2σ)

Table 3 $^{206}Pb/^{238}U$ ratios for zircon Plešovice by LA-ICP-QMS ($n \geq 5$)

Stabilizer type/volume (mL)	Sample no.	$^{206}Pb/^{238}U$ ratio	1σ	Stabilizer type/volume (mL)	Sample no.	$^{206}Pb/^{238}U$ ratio	1σ
Cylinder/21.2	PL-1-1	0.05371	0.00091	Squid/16.3	PL-7-1	0.05453	0.00079
	PL-1-2	0.05372	0.00092		PL-7-2	0.05325	0.00075
	PL-1-3	0.05357	0.00087		PL-7-3	0.05406	0.00080
	PL-1-4	0.05353	0.00081		PL-7-4	0.05345	0.00068
	PL-1-5	0.05261	0.00085		PL-7-5	0.05393	0.00067
	Average	0.05343	0.00087		Average	0.05384	0.00074
Cylinder/25.1	PL-2-1	0.05512	0.00102	Cubic/18.0	PL-8-1	0.05491	0.00094
	PL-2-2	0.05672	0.00113		PL-8-2	0.05450	0.00086
	PL-2-3	0.05800	0.00094		PL-8-3	0.05491	0.00081
	PL-2-4	0.05893	0.00097		PL-8-4	0.05458	0.00081
	PL-2-5	0.05982	0.00099		PL-8-5	0.05414	0.00082
	Average	0.05772	0.00101		Average	0.05461	0.00085
Cylinder/35.3	PL-3-1	0.05453	0.00077	Ball/14.1	PL-9-1	0.05315	0.00078
	PL-3-2	0.05392	0.00090		PL-9-2	0.05361	0.00079
	PL-3-3	0.05438	0.00080		PL-9-3	0.05420	0.00073
	PL-3-4	0.05412	0.00080		PL-9-4	0.05488	0.00063
	PL-3-5	0.05393	0.00074		PL-9-5	0.05523	0.00073
	Average	0.05417	0.00080		Average	0.05421	0.00073
Cylinder/125	PL-4-1	0.05257	0.00072	Without stabilizer/–	PL-10-1	0.05540	0.00101
	PL-4-2	0.05250	0.00072		PL-10-2	0.05435	0.00100
	PL-4-3	0.05356	0.00065		PL-10-3	0.05614	0.00122
	PL-4-4	0.05385	0.00072		PL-10-4	0.05602	0.00111
	PL-4-5	0.05775	0.00084		PL-10-5	0.05549	0.00102
	PL-4-6	0.05592	0.00087		Average	0.05548	0.00107
	Average	0.05472	0.00076		PL-11-1	0.05297	0.00095
Cylinder/21.2 (with 1.0 g stainless wire)	PL-5-1	0.05222	0.00068		PL-11-2	0.05303	0.00096
	PL-5-2	0.05326	0.00074		PL-11-3	0.05305	0.00094
	PL-5-3	0.05324	0.00067		PL-11-4	0.05203	0.00087
	PL-5-4	0.05369	0.00063		PL-11-5	0.05326	0.00079
	PL-5-5	0.05380	0.00078		Average	0.05287	0.00090
	Average	0.05324	0.00070				

Table 4 U–Pb dating results for zircon 91500 by LA-ICP-QMS ($n \geq 5$)

Stabilizer type/volume (mL)	Sample no.	$^{206}Pb/^{238}U$ ratio	1σ	$^{206}Pb/^{238}U$ Age (Ma)	1σ	Concordance (%)	RE%	Average age deviation (%)*
Squid/16.3	91500-1-1	0.17045	0.00305	1014.57	16.81	96	1.66	−4.8
	91500-1-2	0.18828	0.00350	1112.06	18.99	97	1.71	+4.4
	91500-1-3	0.18411	0.00312	1089.40	17.01	99	1.56	+2.3
	91500-1-4	0.17785	0.00370	1055.23	20.23	99	1.92	−0.95
	91500-1-5	0.18113	0.00362	1073.12	19.76	96	1.84	+0.72
	Average	0.18036	0.00340	1068.88	18.56	97	1.74	+0.33
Cylinder/21.2	91500-2-1	0.18008	0.00328	1067.39	17.91	97	1.68	+0.19
	91500-2-2	0.17511	0.00283	1040.20	15.55	98	1.49	−2.4
	91500-2-3	0.18032	0.00297	1068.74	16.20	94	1.52	+0.31
	91500-2-4	0.17841	0.00331	1058.30	18.13	97	1.71	−0.67
	91500-2-5	0.17668	0.00304	1048.82	16.64	94	1.59	−1.56
	Average	0.17812	0.00309	1056.69	16.89	96	1.60	−0.82
Cylinder/25.1	91500-3-1	0.19652	0.00460	1156.62	24.78	48	2.14	+8.6
	91500-3-2	0.50576	0.01620	2638.51	69.38	62	2.63	+148
	91500-3-3	0.19533	0.00368	1150.21	19.87	97	1.73	+8.0
	91500-3-4	0.19407	0.00345	1143.39	18.64	96	1.63	+7.3
	91500-3-5	0.19551	0.00322	1151.16	17.38	98	1.51	+8.1
	Average	0.25744	0.00623	1447.98	30.01	80	1.93	+36
Cylinder/35.3	91500-4-1	0.17666	0.00327	1048.72	17.89	98	1.71	−1.6
	91500-4-2	0.17322	0.00291	1029.85	16.02	98	1.56	−3.3
	91500-4-3	0.16819	0.00303	1002.11	16.74	98	1.67	−5.9
	91500-4-4	0.17241	0.00296	1025.36	16.29	96	1.59	−3.8
	91500-4-5	0.17096	0.00334	1017.42	18.39	97	1.81	−4.5
	Average	0.17229	0.00310	1024.69	17.07	97	1.67	−3.8
Cylinder/21.2 (with 1.0 g stainless wire)	91500-5-1	0.18190	0.00277	1077.32	15.11	96	1.40	+1.1
	91500-5-2	0.17913	0.00271	1062.21	14.82	98	1.40	−0.30
	91500-5-3	0.17830	0.00276	1057.67	15.10	99	1.43	−0.73
	91500-5-4	0.17996	0.00303	1066.73	16.54	97	1.55	+0.12
	91500-5-5	0.18037	0.00298	1069.00	16.30	95	1.52	+0.34
	Average	0.17993	0.00285	1066.59	15.57	97	1.46	+0.11

*The referred $^{206}Pb/^{238}U$ age of zircon 91500 is 1065.4 ± 0.6 Ma (2σ)

error (RE) of a single point of age (1σ) (see in Table 2). As seen in Table 2, the obtained $^{206}Pb/^{238}U$ age (1σ, $n \geq 5$) was 335.53 ± 1.02 Ma (RE: 1.59%), 361.73 ± 5.04 Ma (RE: 1.64%), 340.10 ± 1.98 Ma (RE: 1.46%) and 341.21 ± 5.17 Ma (RE: 1.35%) when using stabilizers with volume of 21.2, 25.1, 35.3 and 125 mL, respectively. Notice that there were no significant differences of the obtained $^{206}Pb/^{238}U$ ages to the referred value of 337.13 ± 0.37 Ma (2σ) (Sláma et al. 2008) except for using 25.1 mL of stabilizer. Currently, the derived + 7.3% deviation of obtained average $^{206}Pb/^{238}U$ age for using 25.1 mL of stabilizer is not clear yet.

The corresponding $^{206}Pb/^{238}U$ ratios were collectively listed in Table 3. Apparently, the average $^{206}Pb/^{238}U$ ratio of zircon Plešovice obtained using 21.2 mL of cylinder stabilizer (0.05343 ± 0.87‰, 1σ, $n = 5$) highly agreed with that using the "squid" signal stabilizer (0.05384 ± 0.74‰, 1σ, $n = 5$). Furthermore, we also compared the $^{206}Pb/^{238}U$ age of zircon 91500 (Wiedenbeck et al. 1995) as an unknown sample using cylinder stabilizers to that using the "squid" signal stabilizer (see in Table 4). It can be seen from Table 4 that the average age deviations were − 0.82%, + 36% and − 3.8% for using cylinder stabilizers of 21.2, 25.1 and 35.3 mL, respectively. Clearly, the analytical property of 21.2 mL of cylinder stabilizer showed no significant difference to that using the "squid" signal stabilizer.

Here, to reach a good compromise on signal rising/washout time, sample throughput and analytical effect on zircon U–Pb dating, the volume of utilized stabilizers was

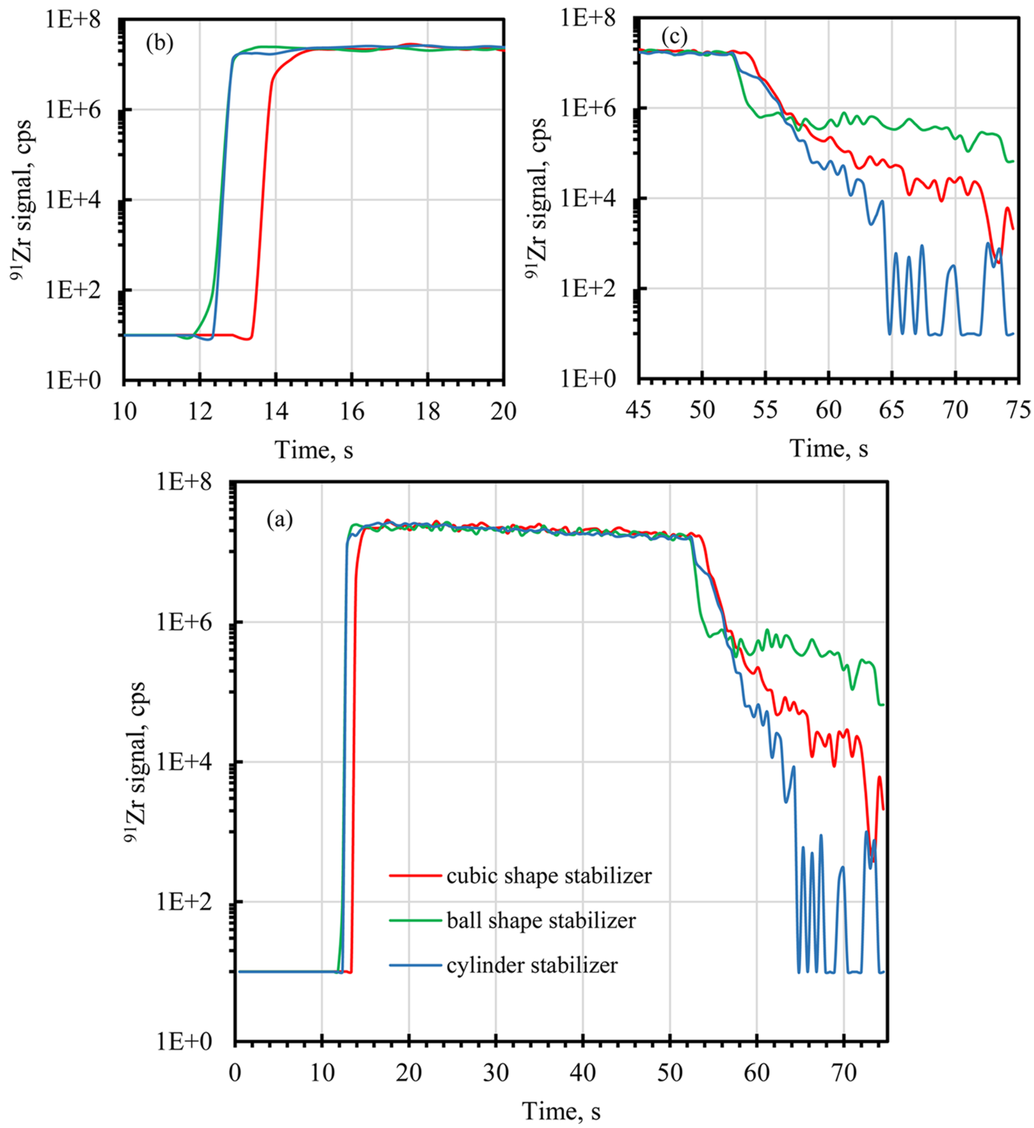

Fig. 3 Transient signal profiles of ^{91}Zr intensity of zircon standard 91500 with 35 μm of spot size and 5 Hz of laser repetition rate using stabilizers with different shapes. **a** Presented the signal profiles of ^{91}Zr versus assay time, while **b**, **c** Showed the signal rising and washout curves when using cylinder, cubic and ball shape stabilizers. The studied volumes for the cylinder, cubic and ball shape stabilizers were 21.2, 18.0 and 14.1 mL, respectively

highly recommended to be controlled less than 21.2 mL in the subsequent LA-ICP-QMS analysis.

Analytical effect for shape of signal stabilizers

Signal variation and signal rising/washout time from stabilizer shape

Since Fig. 2c shows that the signal washout curve using 35.3 mL of stabilizer was distinguished from those using other cylinder stabilizers, the signal variation and signal rising/washout time for stabilizers with cubic shape (18.0 mL), ball shape (14.1 mL) and cylinder shape (21.2 mL) were studied. As shown in Fig. 3a, the transient signals of ^{91}Zr isotope for all the stabilizers were comparable. However, the signal rising time using cubic shape stabilizer was longer than the values using other stabilizers (see in Fig. 3b). Furthermore, despite the volumes of cubic and ball shape stabilizers were smaller than the tested cylinder stabilizer, the signal washout time for using cubic or ball shape stabilizer was found to be longer and at least 270 s was required for the signal dropping to background levels. It was intriguing that the signal washout curve using ball shape stabilizer was similar to that using 35.3 mL of cylinder stabilizer, indicating that the ablated aerosols might have analogue deposition behavior within the two stabilizers.

Analytical influence of stabilizer shape on zircon U–Pb dating

The three stabilizers were further evaluated in the application to U–Pb dating analysis of zircon Plešovice by LA-ICP-QMS, with results summarized in Table 2. The obtained $^{206}Pb/^{238}U$ age was 342.76 ± 2.45 Ma (RE: 1.49%, 1σ, $n=5$) for using cubic shape stabilizer and 340.34 ± 2.36 Ma (RE: 1.68%, 1σ, $n=5$) for using ball shape stabilizer. Compared to the referred $^{206}Pb/^{238}U$ age, the average age deviations were − 0.48%, + 1.7% and + 0.95% for using cylinder, cubic and ball shape stabilizers, respectively. Additionally, the corresponding $^{206}Pb/^{238}U$ ratios using cubic and ball shape stabilizers shown in Table 3 were also comparable to that using 21.2 mL of cylinder stabilizer. Although there was no significant analytical influence on zircon U–Pb dating from the shape of stabilizers, the above discussion showed that signal rising/washout time was greatly affected by the stabilizer shape. Among the three types of stabilizers with volume less than 21.2 mL, cylinder stabilizer was preferred due to reasonable signal rising time of approximately 2.5 s and acceptable signal washout time of less than 20 s.

Particle filter effect of stabilizers

In this work, we also filled the 21.2 mL of cylinder stabilizer with 1.0 g of stainless wire staff (i.e. 47.2 mg/mL) and investigated its influence on signal rising/washout time and zircon U–Pb dating analysis. Results showed that there were no obvious differences for the signal rising times when using cylinder stabilizer with and without stainless wire (Fig. 4a), and the washout time for using "wire" cylinder stabilizer was only slightly longer than that without stabilizer (Fig. 4b) which indicated the addition of stainless wire can efficiently shorten the signal washout time. Here, compared to that without stabilizer, the corresponding signal intensity loss was found to be negligible using "wire" cylinder stabilizer but reached nearly 18% when using empty cylinder stabilizer. However, occasional spiky signals were observed in the transient signal profile of ^{91}Zr isotope when using "wire" cylinder stabilizer (Fig. 4c). This demonstrated that the current "wire" cylinder stabilizer didn't serve as a perfect particle filter despite the average $^{206}Pb/^{238}U$ age deviation was only − 0.81% for zircon Plešovice (see in Table 2) and + 0.11% for zircon 91500 (see in Table 4). Since spiky signals frequently occurred without stabilizer resulting in large variations of the average age deviation of zircon Plešovice within − 1.5 to + 3.3%, such a phenomenon when using "wire" cylinder stabilizer might be attributed to the usage of a nanosecond laser (Kon et al. 2020) and relatively low density of stainless wire (Hu et al. 2012). Hence, it was plausible that the signal smoothing effect by the studied stabilizers without stainless wire was due to the spatial mixture of the generated particles in the stabilizers, and a volume of 21.2 mL of the stabilizer was apparently sufficient to filtrate the large particles by the current nanosecond laser sampling system.

Conclusions

In this current work, we studied the volume and shape effect of stabilizers, which were installed directly after the ablation cell, on zircon U–Pb dating analysis by LA-ICP-QMS in detail. The investigation of cylinder stabilizers with volume in the range of 21.2–125 mL showed that transient signal oscillations were invisible and the signal intensities were comparable with each other, while signal rising time was 2.0-fold and washout time was 27.6-fold for stabilizer with volume of 125 mL to that of 21.2 mL. It was also observed that the transient signal washout curve using 35.3 mL of stabilizer differed from other cylinder stabilizers, showing the signal intensity dropped sharply within the first 3 s and then gradually declined. The average $^{206}Pb/^{238}U$ age deviations for zircon Plešovice to the referred value were generally within − 0.48 to + 1.2%. But for using 25.1 mL of stabilizer, the average $^{206}Pb/^{238}U$ age deviation was found to be high as + 7.3%, for which the reason remains unclear yet. Thus, stabilizers with volume less than 21.2 mL were plausible for the current LA-ICP-QMS configuration.

The further comparison among cylinder, cubic and ball shape stabilizers with volume less than 21.2 mL revealed that there was no significant analytical influence on zircon U–Pb dating from stabilizer shape. However, at least 270 s of signal washout time was required for the signal declining to background levels using cubic/ball shape stabilizer. Clearly, stabilizers with cylinder shape were favorable in this work, giving signal rising time of approximately 2.5 s and acceptable washout time of less than 20 s. Additionally, the particle filter effect discussion showed that the obtained smoothing signals by this nanosecond laser were the results from the spatial mixture of the generated particles in the stabilizers. Considering the comparable signal intensities for using cylinder stabilizers with volume from 21.2 to 125 mL, it can be deduced that a 21.2 mL of stabilizer volume was sufficient to eliminate the spiky signals resulted from large particles by the nanosecond laser in this present study. Furthermore, the obtained average $^{206}Pb/^{238}U$ ratios of zircon Plešovice and 91500 using 21.2 mL of cylinder stabilizer were observed to highly agree with those using the commercially available "squid" signal stabilizer. Thus, an empty stabilizer with volume of 21.2 mL and cylinder shape, which was characterized

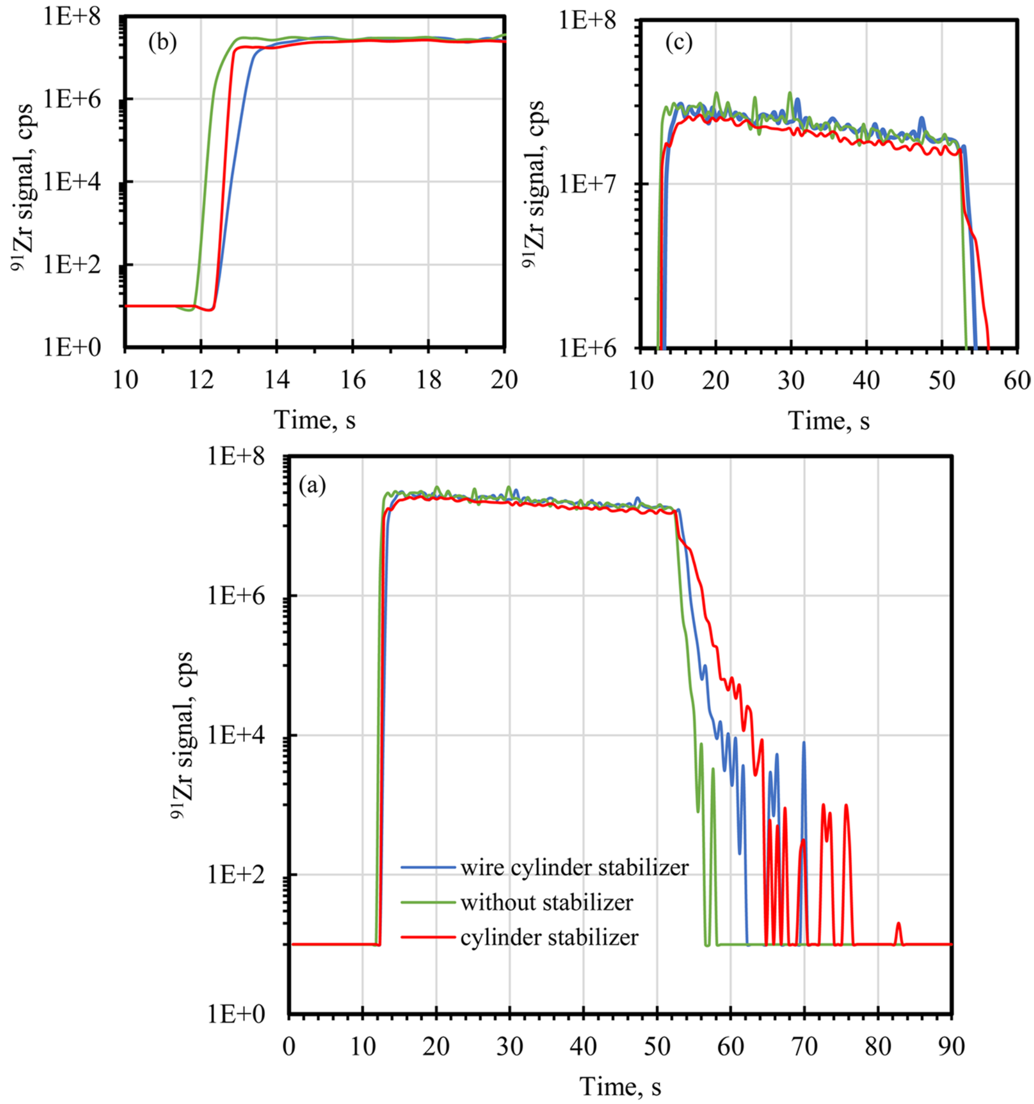

Fig. 4 Transient signal profiles of ^{91}Zr intensity of zircon standard 91500 with 35 µm of spot size and 5 Hz of laser repetition rate without stabilizer, with 21.2 mL of cylinder stabilizer and "wire" cylinder stabilizer. **a** Presented the signal profiles of ^{91}Zr versus assay time, while **b**, **c** Showed the corresponding signal rising and washout curves. Here, the "wire" cylinder stabilizer was assembled by packing 1.0 g of stainless wire into a 21.2 mL of cylinder stabilizer

by easier access and simpler cleaning procedures, was preferred to substitute for the "squid" signal stabilizer producing smoothing signals. The improved analytical accuracy of zircon U–Pb dating ensured the possibility of future application of this proposed stabilizer to trace element analysis by LA-ICP-QMS.

Abbreviations

LA-ICP-QMS: Laser ablation inductively coupled plasma quadrupole mass spectrometry; TIMS: Thermal ionization mass spectrometry; SIMS: Secondary ion mass spectrometry; SHRIMP: Sensitive high resolution ion micro-probe; NIST: National Institute of Standards and Technology; SRM: Standard reference material; PVC: Polyvinylchloride; TRA: Time-resolved analysis.

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Authors contributions

DYX, LFG, CXL, and LW carried out the experimental studies, data collection and analysis. Here, DYX and LFG made the same contribution in this research work. YRL helped to revise the manuscript. XJT designed the research and wrote the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials
Not applicable.

Declarations

Competing interests
The authors declare that they have no competing interests.

Author details
[1]Laboratory of Mineralization and Dynamics, Chang'an University, 126 Yanta Road, Xi'an 710054, China. [2]College of Earth Sciences and Land Resources, Chang'an University, 126 Yanta Road, Xi'an 710054, China.

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