Non-matrix-matched 9 μm U-Pb Dating of Zircon Using Excimer Laser Ablation ICP-MS

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ABSTRACT: U-Pb dating geochronology by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has been widely applied in geological research as a low-cost and high-efficient in situ micro-analytical tool. Currently, quantitative analysis using LA-ICP-MS requires matrix-matched external standards to correct for elemental fractionation. Since natural standard minerals are often limited in supply or not available, non-matrix-matched calibration methods using synthetic glasses as the calibration standards have attracted attention. In addition, access to a higher spatial resolution capability of $<10\ \mu\text{m}$ spot size has been driven by the interest in studying the temporal records of fine mineral grains or rims compared to the conventional $>20\ \mu\text{m}$ laser ablation spots used in most LA-ICP-MS laboratories for zircon dating. In this study, we present an LA-ICP-MS analytical procedure for non-matrix-matched U-Pb zircon dating using a $9\ \mu\text{m}$ laser ablation spot size and a synthetic silicate glass (NIST SRM 610) as the external standard. The elemental fractionation between the NIST SRM 610 glass and zircons can be significantly reduced by using a low laser frequency (2 Hz) and energy density ($3\ \text{J}/\text{cm}^2$). To minimize the matrix effect on matrix-mismatched calibration between samples and standards, the effect of adding a small amount of water vapor or hydrogen into the carrier gas was investigated. A small amount (about $1.9\ \mu\text{L}/\text{min}$) of water vapor added into the sample cell can reduce the Pb/U ratios of the NIST SRM 610 up to 14% during a 40 s ablation time at a small spot size. However, by adding water vapor after the sample cell can achieve an accuracy and precision of better than 2.3% for the weighted average $^{206}\text{Pb}/^{238}\text{U}$ ages using a $9\ \mu\text{m}$ spot size. In addition, the laser-ablated crater depth needs to be less than $4.3\ \mu\text{m}$ to control the down-hole fractionation during laser ablation.

INTRODUCTION

In situ U-Pb dating of zircon using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is one of the most widely applied geochronological analytical tools in the earth sciences.¹⁻⁸ Compared with isotope dilution thermal ionization mass spectrometry (ID-TIMS), LA-ICP-MS is more commonly used due to its simple sample preparation, high spatial resolution, high throughput and acceptable precision.^{1,6} The spatial resolution of single-spot ablation used in LA-ICP-MS is

normally larger than $20\ \mu\text{m}$, and most of the U-Pb age accuracy is within 2-4%.^{8,9} Although many U-Pb dating obstacles by using LA-ICP-MS have in the interim been solved, information regarding the age or the chemical features in specific domains, such as fine-grained zircons and/or zircons with complex zonation, are indistinguishable at these scales. Thus, the demand for higher spatial resolution at a scale of less than $10\ \mu\text{m}$ has been driven by many geologists.^{7,10,11} However, zircon U-Pb dating using LA-ICP-MS has challenges when the spot size is less than $20\ \mu\text{m}$. Different elemental fractionation between Pb and U

occurs during a thermal effect induced by laser ablation sampling, and the particles with different sizes and compositions yielded by phase separation.¹² These lead to different transport efficiency and ionization zones within the plasma and result in observed U/Pb fractionation. Furthermore, the U and Pb fractionations evolve significantly with the increasing aspect ratio (depth/width) of the ablation crater, which is commonly referred to as down-hole fractionation (DHF). Matrix-matched reference materials are normally used to quantify the trend of DHF, and then the correction factor to unknown samples to yield reliable Pb/U ratio is applied. This method is based on the assumption that the samples and the calibration standards have the same elemental fractionation patterns.¹³ However, DHF is not only time-related but also matrix-dependent, so the elemental fractionation in different matrices is affected by their physical and chemical properties^{13,14} even the same species is unlikely to share the same trait in elemental fractionation.^{7,14,15} Previous research suggests that DHF can be alleviated by using a larger diameter spot size, shorter ablation time,⁷ or by carefully adjusting the laser parameters such as fluence, repetition rate or laser wavelength which determines the aspect ratio. Several studies suggested that DHF could be calibrated using mathematical models.^{15,16}

Significant matrix effects often occur in U-Pb isotope measurements using LA-ICP-MS. Previous U-Th-Pb isotope studies have reported systematic errors from 4.9% up to 28.8% higher than the reference ages obtained by using zircon as the non-matrix-matched reference material to calibrate allanites,⁴ which necessitates the use of external matrix-matched standards.

Fig. 1 Schematic diagram of the experimental setup. (a) Adding additional gas after sample cell. (b) Adding additional gas before the sample cell. (c) Water introduction system (homemade). The diameter of the quartz bottle is 65 mm. The glass bottle was designed with a heat preservation cover to control the temperature.

However, other investigations suggest that the matrix effect can be minimized by optimizing the laser ablation mode and the instrumental operating conditions.^{3,17} Although laser-induced elemental fractionation can be minimized by optimizing the laser parameters, ICP-induced elemental fractionation and the matrix effects related to the sample composition may still persist.¹⁸ The non-matrix-matched standardization mentioned above suggests that particle size, mass load, and ionization efficiency are the dominant issues in restraining elemental fractionation in ICP.¹⁷ Furthermore, adding moisture or so-called wet plasma conditions has been demonstrated to suppress the matrix effect in isotope analysis significantly.^{19,20}

In this work, we investigated zircon U-Pb dating by using NIST SRM 610 as the non-matrix-matched external standard at 9 μm spot size and 193 nm laser ablation-ICP-MS. The enhancement and matrix effects by introducing additional H₂O and H₂ into the carrier gas were systematically investigated. The precision and accuracy of this analytical protocol were verified by examining the results obtained using five international zircon standards.

EXPERIMENTAL

Instrumentation and operating conditions

A 193 nm ArF excimer laser ablation (LA) system was used in this study. The LA system consists of a Coherent ExciStar XS 200 laser, with the beam delivery system and operating software provided by Beijing HLG Instrument LTD. The pulse width of the laser system was about 5 ns, and the repetition rate varied between 1 to 200 Hz. This laser ablation system was equipped with a customized small rectangular sample cell, six mounts with a diameter of 16 mm which can be placed in a linear array in one run. The sample cell was flushed with helium gas during laser ablation, and the ablated aerosol flushed out from the sample cell was first mixed with 0.9 L/min argon via a Y-junction, then passed through a homemade on-line mercury removing and signal smoothing device² before reaching the ICP-MS.

Minor additional gases (hydrogen or water vapor) were introduced into the carrier gas (helium) before or after the sample cell. Hydrogen was supplied by electrolyzing ultrapure water with a hydrogen generator (QL-500, Shandong Saikesaisi Hydrogen Energy Co., Ltd.), and the gas flows were controlled using an external mass flow controller (1-10 mL/min) (Fig. 1). The stable introduction of water vapor was performed using an in-house system (Fig. 1c) and consisted of a quartz glass bottle filled with ultrapure water (18.2 M Ω ·cm, Millipore Corporation, USA). A constant helium gas flow (20 mL/min) was introduced into this system which carried an extremely small amount of water vapor (about 1.9 $\mu\text{L}/\text{min}$) that spontaneously evaporated in this container as the helium gas passed through the water surface ($A \approx 33 \text{ cm}^2$) at room temperature (22 $^{\circ}\text{C}$). This system can

Table 1. Instrumental Parameters Used in this Work

ICP-MS model: Jena PQ-MS Elite	
RF power	1.6 kW
Plasma Flow	9.5 L min ⁻¹
Auxiliary Flow	1.5 L min ⁻¹
Nebulizer Flow	0.80–0.90 L min ⁻¹
Trace elements measured	⁷ Li, ⁹ Be, ²⁹ Si, ⁴⁴ Ca, ⁴⁵ Sc, ⁴⁹ Ti, ⁵¹ V, ⁵³ Cr, ⁵⁵ Mn, ⁵⁷ Fe, ⁵⁹ Co, ⁶⁰ Ni, ⁶³ Cu, ⁶⁶ Zn, ⁶⁹ Ga, ⁷² Ge, ⁸⁵ Rb, ⁸⁸ Sr, ⁸⁹ Y, ⁹⁰ Zr, ⁹³ Nb, ⁹⁵ Mo, ¹³³ Cs, ¹³⁷ Ba, ¹³⁹ La, ¹⁴⁰ Ce, ¹⁴¹ Pr, ¹⁴⁶ Nd, ¹⁴⁷ Sm, ¹⁵³ Eu, ¹⁵⁷ Gd, ¹⁵⁹ Tb, ¹⁶³ Dy, ¹⁶⁵ Ho, ¹⁶⁶ Er, ¹⁶⁹ Tm, ¹⁷² Yb, ¹⁷⁵ Lu, ¹⁷⁸ Hf, ¹⁸¹ Ta, ¹⁸² W, ²⁰² Hg, ²⁰⁴ Pb, ²⁰⁵ Tl, ²⁰⁶ Pb, ²⁰⁷ Pb, ²⁰⁸ Pb, ²⁰⁹ Bi, ²³² Th, ²³⁸ U
Detector mode	Pulse counting
Laser ablation system	
Laser	Coherent ExciStar XS excimer laser
Wavelength	193 nm
Pulse width	5 ns
Fluence	2–5 J/cm ²
Repetition rate	2–5 Hz
Carrier gas (He)	500 mL/min
Spot size	9 µm
Dwell time	10ms for ²⁰⁴ Pb, ²⁰⁶ Pb, ²⁰⁷ Pb, ²⁰⁸ Pb, ²³² Th, ²³⁵ U, ²³⁸ U; 6ms for other isotopes

Table 2. Five Zircon Reference Materials with Preferred ID-TIMS Ages and U Concentration Ranges

Sample	ID-TIMS Ages (Ma, ±2σ)		²⁰⁶ Pb/ ²³⁸ U ratio	U range (µg/g)	References
	²⁰⁶ Pb/ ²³⁸ U	²⁰⁷ Pb/ ²⁰⁶ Pb			
91500	1062.4±0.4	1065.4±0.3	0.17917	71–86	31
GJ-1	599.8±1.7	602.1±1.6	0.09761	212–422	5
Plešovice	337.13±0.37	337.23±0.18	0.05368	465–3084	32
Qinghu	159.38±0.12	159.68±0.22	0.02516	684–2413	33
Temora-2	416.78±0.33	416.99±0.24	0.06679	61–389	34

provide a stable amount of H₂O to the ICP and can alter the water vapor introduction rate by changing the helium gas flow rate and water temperature.

A model PlasmaQuant MS ICP-MS was used for the experiments (Analytik Jena, Germany). This instrument was operated in high-sensitivity mode with 1390 million counts per second/ppm for ¹¹⁵In in the solution nebulization mode. The ICP-MS was optimized for stability and sensitivity in the solution mode before being connected to the laser ablation system. The plasma was kept lit during removal of the spray chamber and its connection to the laser ablation system. We used the line-scan mode to tune the operating parameters of the ICP-MS and used the NIST SRM 610 glass as reference material. The nebulizer gas flow rate and the ion optics were optimized to maximize the sensitivity and to make sure the ²³²Th¹⁶O⁺/²³²Th⁺ ratios were below 0.3% and the ratios of ²³⁸U/²³²Th between 0.96–1.00. After adding water vapor or hydrogen, the oxide formation was slightly increased, and the gas flow rate was retuned to keep the ²³²Th¹⁶O⁺/²³²Th⁺ ratios below 0.8%. All measurements for the ²³⁸U, ²³²Th, ^{208,207,206,204}Pb, and ²⁰²Hg isotopes were collected in peak jumping mode. Mass 204 was measured to monitor the presence of common Pb in the zircon grains, and ²⁰²Hg was measured in order to correct for the isobaric interference of ²⁰⁴Hg on ²⁰⁴Pb. The details of the instrumental operating conditions and parameters used in this study are summarized in Table 1. The

instrument was warmed up for at least one hour prior to the start of sample analysis.

Reference samples

In this study, five zircon standards were used as the unknown samples, i.e., 91500, GJ-1, Plešovice, Temora-2, and Qinghu, all of which have well-characterized U–Pb ID-TIMS ages (Table 2). These zircon reference materials cover a wide range of U concentrations and ages and were used to assess the precision and accuracy of the analytical protocol proposed in this study. The synthetic glass NIST SRM 610, one of the most commonly used reference materials in LA-ICP-MS analysis, was used as an external standard to calibrate the zircon U–Pb ages. The external standard was measured twice between every six samples to calibrate the instrumental drift. The U concentration of NIST SRM 610 is 475 µg/g.²¹ The reference ²⁰⁶Pb/²³⁸U ratio of NIST SRM 610 is 0.2236±0.015 (2σ),²² and the working value of ²⁰⁷Pb/²³⁵U ratio is 28.1753±0.016 (2σ) as calculated by Horn et al. (2007) and assuming ²³⁸U/²³⁵U = 137.818.²³ Fragments of the zircon grains and the NIST SRM 610 glass were mounted into 16-mm diameter round epoxy mounts and polished with one-micron diamond paper until 1/3 of each zircon was exposed.

Data reduction

The U–Pb dating raw data were calculated using the ICPMSDataCal software, and the detailed calculations for the

U-Th-Pb isotopic ratios and the correction method used were as reported by Liu *et al.* (2009).²⁴ Non-matrix-matched U-Pb dating standardization requires similar elemental fractionation between standard and sample. The observed elemental fractionation during analysis can occur in various processes, including ionization and atomization within the plasma,¹⁸ aerosol transportation, and at the ablation site.^{12,14} The fractionation factor was used here to indicate the elemental fractionation (Eq. 1):

$$f_{206/238} = \left(\frac{{}^{206}\text{Pb}}{{}^{238}\text{U}} \right)_{0-\left(\frac{t}{2}\right)s} / \left(\frac{{}^{206}\text{Pb}}{{}^{238}\text{U}} \right)_{\left(\frac{t}{2}\right)-t s} \quad (\text{Eq. 1})$$

where t is the total integration time. The fractionation factor (f) of ${}^{206}\text{Pb}/{}^{238}\text{U}$ ratio should be around 1 if little fractionation occurs. Fig. 2 illustrates the fractionation factor of the ${}^{206}\text{Pb}/{}^{238}\text{U}$ ratios for the five zircon standards and NIST SRM 610 glass at 9 μm spot size (2 Hz, 3 J/cm²) using different integration intervals. With a deepening of the ablation pit, the fractionation factor of NIST 610 is basically around 1, indicating little effect of the DHF on the U/Pb ratios of NIST 610. However, the U/Pb ratios of the zircons increased with a deepening of the ablation pit, and the fractionation factors of the zircon samples were all significantly higher than those of the NIST SRM 610 when using 40 s integration intervals (Fig. 2b), which indicates a severe influence from the DHF. In addition, when ablation takes place on the sample surface at the beginning, there was a relatively high U/Pb ratio in the first 5 s, even higher than the U/Pb ratio which is affected by DHF in the later stage of laser ablation (Fig. 2a and 2c), indicating elemental fractionation occurred before an increase of the aspect ratio. This suggests a volatile/refractory element fractionation within the plasma and/or along the particle transportation efficiency between the sample cell and the plasma. The laser ablation process produces larger particles in the initial several seconds for single-hole ablation.²⁵ The refractory elements are preferentially enriched in large particles,²⁶ resulting in higher ${}^{206}\text{Pb}/{}^{238}\text{U}$ ratios. The data reduction should avoid the part where fractionation displays distinctively different trends. Accordingly, for all of the 9 μm non-matrix-matched calibrations in this study, the data reduction was processed by using 20 s intervals (i.e., 40 laser shots) and by carefully masking the first 5 seconds to acquire reliable results. The fractionation factor of the NIST SRM 610 and the zircons was almost identical and close to 1 when masking the initial 5 seconds (10 pulses) and limiting the ablation intervals within 20 s (Fig. 2d). The depth of the laser ablation craters were 4.3 μm after 25 s, which was obtained using a confocal laser scanning profilometer (OLS4100, Olympus) (Fig. 3). Thus, the elemental fractionation could be reduced by controlling the depth of the ablation pit to less than 4.3 μm for a 9 μm laser spot during non-matrix-matched standardization. Furthermore, because the signal-to-noise ratios of ${}^{207}\text{Pb}$ of some natural zircons were not enough to obtain a reasonable value under the conditions of low frequency, low fluence and small beam spot, only the ${}^{206}\text{Pb}/{}^{238}\text{U}$ ages are discussed in this study.

Fig. 2 Fractionation factor of ${}^{206}\text{Pb}/{}^{238}\text{U}$ ratios of NIST SRM 610 and five zircon standards using 2 Hz and 3 J/cm. (a) Using 40s integration intervals; (b) Using 40s integration intervals and masking the initial 5s; (c) Using 20s integration intervals; (d) Using 20s integration intervals and masking the initial 5s.

Fig. 3 Depth of laser ablation crater with 50 pulses of laser shots.

RESULTS AND DISCUSSION

Elemental fractionation of laser ablation

The U/Pb ratios of zircons display an increasing trend with ablation time. This phenomenon can be accelerated in analyses involving a small diameter laser spot size ($\leq 20 \mu\text{m}$) due to the increased aspect (depth/width) ratios of the ablation crater, i.e., the DHF. Thus, the laser beam should be set at a low repetition rate and low fluence to restrain elemental fractionation at the 9 μm spot size.

Besides the aspect ratios, DHF is also known as matrix-dependent and shows different patterns among different matrices, even among zircons.^{7,14} The normalized ${}^{206}\text{Pb}/{}^{238}\text{U}$ ratios (relative to their reference ${}^{206}\text{Pb}/{}^{238}\text{U}$ values) for the reference zircon Plesovice and NIST SRM 610 glass analyzed in this study are illustrated in Fig. 4. In order to compare the ratios of the different matrices, the raw data of ${}^{206}\text{Pb}/{}^{238}\text{U}$ was normalized to their reported ID-TIMS ratios. All of the normalized ratios increased with the ablation time at 5 Hz and 5 J/cm² ablation conditions (Fig. 4a), suggesting both the zircon and the glass were affected by the DHF as the ablation pits deepened. The trend of the ${}^{206}\text{Pb}/{}^{238}\text{U}$ ratios for NIST SRM 610 was relatively flat, while the trend for zircon tended to show a more significant increase. Therefore, we used 2 Hz and 3 J/cm² on 9 μm spot

Fig. 4 The trend of element fractionation of zircon and NIST SRM 610 in 9 μm . (a) Zircon Plesovice and NIST SRM 610 were analyzed using 5 Hz and 5 J/cm^2 . (b) Zircon Plesovice and NIST SRM 610 were analyzed using 2 Hz and 3 J/cm^2 . The measured $^{206}\text{Pb}/^{238}\text{U}$ ratios were normalized to ID-TIMS result (Table 2).

Fig. 5 The effect of a smoothing device on signal intensity. The laser frequency is 2 Hz.

analysis for non-matrix-matched calibration. Compared with the routine laser ablation conditions (5 Hz and 5 J/cm^2 , Fig. 4a) for zircon dating, the difference between the trend of the normalized $^{206}\text{Pb}/^{238}\text{U}$ ratios of zircon and NIST SRM 610 was reduced when mild laser ablation conditions (2 Hz, 3 J/cm^2 , Fig. 4b) were applied.

A smoothing device was used before the sample aerosol reached the plasma (Fig. 1 a and b) to obtain a stable signal under such low laser repetition rates (Fig. 5). Under mild conditions (3 J/cm^2 , 2 Hz), the net mean intensity of ^{238}U on the NIST SRM 610 glass was 1.85×10^4 counts per second (cps) for 9 μm spot ablation. The U-Pb ages obtained by a laser of 5 Hz and 5 J/cm^2 in 9 μm with NIST SRM 610 as the external standard were 13–19% above the relative ID-TIMS reference ages, while the age offsets of 9 μm U-Pb dating using a laser of 2 Hz and 3 J/cm^2 were less than 2.8% (Table 3).

Therefore, the laser-induced elemental fractionation, which was suggested as the dominant factor of fractionation,²⁷ can be manifestly alleviated by lowering the repetition rate and the laser fluence. However, various processes may lead to matrix effect and elemental fractionation during laser ablation and ionization

or atomization within the plasma, which means even the laser-induced fractionation can be alleviated with a lower repetition rate and fluence, yet the matrix effect still exists within the ICP. Thus, the hydrogen and the water introduction systems were employed to further investigate the suppression effect of the ICP-induced matrix effect by attaching them to the front and the rear of the sample cell.

Effects of hydrogen and water vapor

1) Effect on signal sensitivity

Fifty elements of the NIST SRM 610 were analyzed to identify the signal enhancement by adding an extra stream of gas into the helium carrier gas (Fig. 6d). The signal intensities for all elements measured in the NIST SRM 610 glass showed significant enhancement by adding hydrogen into the carrier gas. The enhancement factor depends on the amount of extra gas and the elements. The relative signal enhancement of several selected elements during the gradual increase of hydrogen (0–5 mL/min) is illustrated in Fig. 6b. For each hydrogen gas flow rate, the nebulizer gas was optimized to acquire the highest sensitivities. The increase factor of 2.0–4.6 for all of the elements was investigated in this study. In general, optimal U-Th-Pb sensitivity can be obtained by adding 3 mL/min hydrogen into the carrier gas (Fig. 6b). The sensitivity enhancement can be partly attributed to the higher electron temperature of the plasma with a constant supply of a small amount of hydrogen, which therefore provides higher ionization efficiency.²⁸

The water vapor is carried into the ICP by a stream of helium gas, split from the carrier gas by a Y-junction. In order to get a constant and adjustable gas flow rate, the separated stream of helium gas was first connected to a mass flow controller, then passed through a home-made water-filled gas-wash bottle (Fig. 1c). An amount of 5–50 mL/min helium gas was introduced into this home-made glass bottle which passed over the water's surface to achieve water vapor at around 0.3–4.6 $\mu\text{L}/\text{min}$. The

Table 3. Weighted Average $^{206}\text{Pb}/^{238}\text{U}$ Ages at 9 μm Spot Size Under Different Analytical Conditions

Ablation Parameter	Zircon	n	$^{206}\text{Pb}/^{238}\text{U}$ age (Ma)	$\pm 2\text{SE}$	%2SE	Age offset (%)
9 μm	91500	6	1231.0	20	1.6	15.7
5 Hz, 5 J/cm²	GJ-1	6	713.8	9.1	1.3	19.0
	Plešovice	6	387.6	9	2.3	15.0
	Temora	3	471.0	13	2.7	13.0
	QingHu	6	184.3	2.6	1.4	15.5
9 μm	91500	15	1078.0	22	2.1	1.47
2 Hz, 3 J/cm²	GJ-1	10	585.0	12	2.0	-2.47
	Plešovice	10	327.6	5.8	1.8	-2.82
	Temora	10	406.0	24	5.8	-2.59
	QingHu	10	159.3	3.3	2.1	-0.13
9 μm	91500	7	1145.0	21	1.8	7.77
2 Hz, 3 J/cm²	GJ-1	10	628.1	8.6	1.7	4.72
adding H₂	Plešovice	7	341.2	5.3	1.5	1.22
before sample cell	Temora	7	433.0	11	2.5	3.89
	QingHu	7	166.3	2.6	1.9	4.26
9 μm	91500	7	1140.0	20	1.3	7.30
2 Hz, 3 J/cm²	GJ-1	6	620.0	11	1.2	3.37
adding H₂O	Plešovice	7	350.0	3.9	1.0	3.83
before sample cell	Temora	7	442.8	7.5	2.6	6.24
	QingHu	7	164.9	3.1	1.2	3.39
9 μm	91500	14	1079.0	18	1.7	1.56
2 Hz, 3 J/cm²	GJ-1	15	607.8	7.8	1.3	1.33
adding H₂	Plešovice	10	341.5	6.2	1.8	1.31
after sample cell	Temora	10	419.8	9.9	2.4	0.72
	QingHu	10	163.2	3.0	1.8	2.32
9 μm	91500	15	1057.0	19	1.8	-0.51
2 Hz, 3 J/cm²	GJ-1	15	594.2	9.1	1.5	-0.93
adding H₂O	Plešovice	10	336.9	5.2	1.6	-0.06
after sample cell	Temora	10	419.6	9.7	2.3	0.67
	QingHu	10	161.1	3	1.9	1.00

results show that adding such a small amount of water vapor into the carrier gas increased the sensitivity of all investigated elements by a factor of 1.3–4.2. The optimal additional helium gas flow rate for introducing water vapor was 1.9 $\mu\text{L}/\text{min}$ (introduced using 20 mL/min helium) for U, Th, Pb (Fig. 6a).

We also investigated the signal enhancement by introducing a small amount of hydrogen and a fixed flow of water vapor (1.9 $\mu\text{L}/\text{min}$) at the same time (Fig. 6c). The results showed that adding hydrogen based on the optimized signal by adding 1.9 $\mu\text{L}/\text{min}$ water vapor had limited enhancement on the signal. Adding 1 mL/min of hydrogen and 1.9 $\mu\text{L}/\text{min}$ water vapor simultaneously increased the sensitivity by 20% compared with only adding 1.9 $\mu\text{L}/\text{min}$ water vapor. However, by increasing the amount of hydrogen (> 1 mL/min), the sensitivity decreased continuously. Furthermore, introducing water vapor and hydrogen into the sample cell at the same time increases the oxide formation rate from 3×10^{-3} to 7×10^{-3} and the Th/U ratio from around 0.97 up to 1.1.

2) Effect of adding water vapor or hydrogen before sample cell on 9 μm U–Pb dating analysis using non-matrix-matched calibration

In order to achieve accurate and precise zircon U–Pb ages and further alleviate the matrix effect, we investigated whether adding water vapor and hydrogen into the carrier gas affects the accuracy of U–Pb dating analysis by using non-matrix-matched calibration.

For a small spot size, introducing a small amount of water vapor into the sample cell dramatically decreased the $^{206}\text{Pb}/^{238}\text{U}$ ratios of NIST SRM 610 up to 14% during 40 s ablation (Fig. 7b). However, the $^{206}\text{Pb}/^{238}\text{U}$ ratios of zircon increased about 1% (Fig. 7b). The trend of the $^{206}\text{Pb}/^{238}\text{U}$ ratios of NIST SRM 610 was distinctively different from that of zircon with water vapor present in the sample cell. When adding extra water vapor before the sample cell, the age offsets for five standard zircons increased from 1.47% to 7.30% by using mild laser ablation conditions of 9 μm (2 Hz and 3 J/cm², Table 3). After adding water vapor before the sample cell, the ages in 9 μm using non-matrix-matched calibration get worse and much higher than the reference ID-TIMS ages (Table 3, Fig. 9). In addition, adding an extra 3 mL/min of hydrogen before the ablation cell also did not show obvious suppression on the matrix effect in non-matrix-matched calibration in 9 μm spot size (Table 3, Fig. 9).

Fig. 6 The sensitivity enhancement factors for seven selected elements in the presence of additional gases (e.g., hydrogen and water vapor) into carrier gas relative to normal ablation mode by 193 nm laser ablation of NIST SRM 610 at a spot size of 35 μm , 5 Hz and 3 J/cm^2 . (a) Water vapor was introduced with helium gas range from 5–50 mL/min; the net signal was relative to the signal of normal ablation without additional gas. (b) Hydrogen was introduced ranging from 1–5 mL/min; the net signal was relative to the signal of normal ablation without additional gas. (c) On the optimal condition of introducing water vapor (1.9 mL/min), introducing a small amount of hydrogen ranging from 1–5 mL/min, the net signal was relative to the signal of adding water at 1.9 mL/min. (d) the sensitivity enhancement of 50 elements with the presence of additional gases.

Fig. 7 The trend of elemental fractionation of zircon and NIST SRM 610 in 9 μm . Zircon Plešovice and NIST SRM 610 glass were analyzed using 2 Hz, 3 J/cm^2 . (a) Water vapor was introduced into carrier gas at 20 mL/min helium after sample cell. (b) Water vapor was introduced into carrier gas at 20 mL/min helium before sample cell.

However, it should be noted that the addition of water vapor before the sample cell significantly alleviates down-hole fractionation. To investigate the suppression effect of DHF, NIST SRM 610 glass and five zircon standards were analyzed at 5 J/cm^2 and 5 Hz using the 9 μm laser spot size, which resulted in a significant DHF. The raw $^{206}\text{Pb}/^{238}\text{U}$ ratios were normalized to their ID-TIMS values and plotted versus the ablation time (Fig. 8). The slopes of time-dependent Pb/U fractionation of different

matrices showed a significant decrease after adding humid gas into the sample cell. Although the elemental fractionation was not completely eliminated, after adding water vapor using 20 mL/min helium, the $^{206}\text{Pb}/^{238}\text{U}$ ratios of NIST SRM 610, 91500, Plešovice, QingHu, Temora, and GJ-1 decreased within the first 25 s by 23.7%, 9.8%, 2.2%, 5.3%, 7.4% and 3.1%, respectively. The fractionation factor of the $^{206}\text{Pb}/^{238}\text{U}$ ratios for NIST SRM 610 and the zircon references also declined when adding water

Fig. 8 Normalized $^{206}\text{Pb}/^{238}\text{U}$ ratios of NIST SRM 610 and five zircons using He or He + H_2O carrier gases at $9\text{ }\mu\text{m}$, 5 Hz , $5\text{ J}/\text{cm}^2$ laser ablation conditions. Each curve was normalized to the accepted ID-TIMS $^{206}\text{Pb}/^{238}\text{U}$ ratio (Table 2), the water was added before the sample cell using $20\text{ mL}/\text{min}$ helium gas. f_c refers to the fractionation factor of $^{206}\text{Pb}/^{238}\text{U}$ ratios under common ablation mode without additional water vapor, f_w refers to the fractionation factor of $^{206}\text{Pb}/^{238}\text{U}$ ratios with water vapor addition.

Fig. 9 The offsets (%) of the weighted mean $^{206}\text{Pb}/^{238}\text{U}$ ages of five reference zircons (at $9\text{ }\mu\text{m}$, 2 Hz , $3\text{ J}/\text{cm}^2$) compared with respective ID-TIMS $^{206}\text{Pb}/^{238}\text{U}$ ages. Vertical bar represents the 2-standard error (2SE%) uncertainty.

vapor into the ablation cell, but the extent of the decrease depends on the matrix.

These results suggest that the existence of water vapor in the sample cell can partially suppress the elemental fractionation that occurred during the laser drilling process. However, the apparent alleviation of Pb/U fractionation by adding water vapor did not improve the accuracy of the U-Pb age at $9\text{ }\mu\text{m}$ spot size, neither by using NIST SRM 610 glass nor GJ-1 zircon for calibration. On the contrary, the presence of water vapor shifted the $^{206}\text{Pb}/^{238}\text{U}$ ratios of the samples, and the degree of this shifting depends on the amount of water vapor and the type of matrix. Even if only a very small amount of humid gas (e.g., $0.3\text{ }\mu\text{L}/\text{min}$ water) was introduced, the $^{206}\text{Pb}/^{238}\text{U}$ ratios of the NIST SRM 610 glass reduced by about 10%, which ultimately affects the

zircon U-Pb age calibrated against the NIST SRM 610 glass.

3) Effect of adding water vapor or hydrogen after the sample cell on $9\text{ }\mu\text{m}$ U-Pb dating analysis using non-matrix-matched calibration

Introducing a small amount of water vapor after the sample cell could alleviate the matrix effect on $9\text{ }\mu\text{m}$ spot U-Pb dating using NIST SRM 610 glass as a calibration standard and resulted in improving both the accuracy and the precision of the $^{206}\text{Pb}/^{238}\text{U}$ ages (Fig. 9). The weighted average $^{206}\text{Pb}/^{238}\text{U}$ ages of 91500, GJ-1, Plešovice, QingHu, and Temora are summarized in Table 3 and Fig. 10. The net mean signal intensity of ^{238}U was 3.32×10^4 counts per second (cps) for NIST SRM 610 glass using a supply of humid gas after the sample cell. In addition, the background signal increased from 5.5×10^4 cps to 4.5×10^5 cps for ^{29}Si .

Fig. 10 Weighted average $^{206}\text{Pb}/^{238}\text{U}$ ages of five reference zircons (91500, GJ-1, Plesovice, Temora, Qinghu) analyzed using NIST SRM 610 as external standard. All samples were analyzed using a 193 nm laser ablation with a repetition rate of 2 Hz, fluence of 3 J/cm² and a spot size of 9 μm.

However, the background signal of U and Pb did not change. Moreover, by adding a small amount of water vapor after the sample cell, the oxide formation rate ($^{232}\text{Th}^{16}\text{O}^+ / ^{232}\text{Th}^+$) increased from 2×10^{-3} in the normal ablation mode to 8×10^{-3} .

Introducing hydrogen into the carrier gas after the sample cell increased the signal intensity by 80% on 9 μm spot size analysis, and thus increased the precision of the dating results. However, the $^{206}\text{Pb}/^{238}\text{U}$ ages of zircon after hydrogen addition are systematically higher than the preferred values, while the accuracy of the U-Pb age calibrated by non-matrix-matched standards was not improved. This suggested that the effect of water vapor on the matrix effect does not directly come from the effect of hydrogen ions.

The matrix effect suppression by adding water vapor after the sample cell is probably caused by the higher temperature of the plasma because the addition of water vapor leads to more complete atomization and ionization of the sample within the plasma.²⁰ In addition, considering the different suppressions resulting from the different positions of the water vapor introduction experiments, the presence of humid gas within the sample cell plays an important role in alleviating the matrix effect caused by the laser ablation process. Previous studies suggest that the rate of laser-induced fractionation and the deposition on the ablation pit wall would significantly evolve, and consequently shift the U-Pb age, when other active gases, such as N₂, O₂ or atmospheric air, are present in the helium carrier gas during the ablation processes.^{27,29,30} The presence of water vapor in the sample cell may also have an effect on the particle deposition and

drilling rate of the materials. Besides, the moisture of the gas present in the sample cell may affect the size distribution of the ablated particles. Furthermore, the amount of water introduced is also important for the optimization of the non-matrix-matched U-Pb dating, since the introduction of excessive water vapor could lead to systematic deviation.³⁰ Comparatively, no obvious reduction of matrix effects by adding hydrogen into the ablation system (no matter before or after the sample cell) suggests that the mechanism for eliminating the matrix effect by water vapor is not entirely related to hydrogen atoms. The addition of oxygen was also considered not to have a significant improvement on the $^{206}\text{Pb}/^{238}\text{U}$ ages of the zircons.³⁰ Further research is required to explain the suppression of matrix effects by adding moisture into carrier gas in terms of physical and chemical property changes during both plasma ionization and the laser ablation process.

CONCLUSIONS

In this paper, we presented an LA-ICP-MS analytical procedure for zircon U-Pb dating using the 9 μm laser spot size without reliance on a matrix-matched zircon reference material. The U-Pb data were acquired using NIST SRM 610 glass as the primary non-matrix-matched standard reference material and the ICPMSDataCAL software for offline data reduction. The results obtained from five reference zircons indicated that the non-matrix-matched calibration in high spatial resolution (9 μm) LA-ICP-MS U-Pb dating can be successfully applied at low frequency (2 Hz) and low fluence (3 J/cm²).

The plasma-induced matrix effect on zircon U-Pb dating can be improved by introducing additional humid gas after the sample cell. The accuracy and precision of the U-Pb ages using a 9 μm ablation spot are better than 2.3%. Our data also show that the presence of water vapor in the sample cell can significantly suppress the DHF observed at a small diameter spot size. System bias was found in shifting the $^{206}\text{Pb}/^{238}\text{U}$ ratios in the presence of a small amount of water vapor in the sample cell at 9 μm spot dating when calibrating the zircon U-Pb ages against NIST SRM 610. Moreover, for small diameter ablation pits, using shorter ablation intervals (15–20 s, i.e., 30–40 pulse) on data reduction can also limit the difference of temporal changed $^{206}\text{Pb}/^{238}\text{U}$ ratios between the different matrices. Controlling the depth of the ablation craters to less than 4.3 μm could also limit the degree of fractionation. Alleviating the mismatches of the different matrices can broaden the range of minerals accessible for geochronology investigation and enable the use of well-characterized synthetic external standards, which are more uniform than natural minerals. Therefore, our in situ non-matrix-matched U-Pb dating methodology supports the use of NIST SRM 610 as a reliable external standard for zircon U-Pb geochronology with the advantages of obtaining simple, low cost, and high spatial resolution.

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Notes

The authors declare no competing financial interest.

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