Optimization of ablation protocol for 200 nm UV femtosecond laser in precise U–Pb age dating coupled to multi-collector ICP mass spectrometry

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The ablation protocols for 200 nm ultra violet-femtosecond laser ablation (200FsLA)—inductively coupled plasma mass spectrometry (ICPMS) have been examined using a quadrupole ICPMS and applied to zircon U–Pb age dating coupled to a multiple collector (MC)-ICPMS. As high spatial resolution is often required in small natural zircons, the following ablation protocols were examined: (1) a $\sim 30\ \mu\text{m}$ circular spot crater with 5 Hz repetition rate, and (2) a $\sim 30\ \mu\text{m}$ circular crater formed by rotation raster (a $\sim 20\ \mu\text{m}$ beam rotated along the circumference of a circle with a radius of $8\ \mu\text{m}$) at 10 Hz. A line raster with a $\sim 30\ \mu\text{m}$ crater at 5 Hz was also examined for comparison. The repetition rates were set in order to achieve the necessary signal intensity for zircon dating. During the spot and the rotation raster analyses there was almost no down-hole fractionation of $^{207}\text{Pb}/^{206}\text{Pb}$, $^{206}\text{Pb}/^{238}\text{U}$, and additionally $^{232}\text{Th}/^{238}\text{U}$. Therefore, precise zircon U–Pb chronology, that does not require a down-hole fractionation correction, is possible using optimized protocols for 200FsLA. However, absolute $^{206}\text{Pb}/^{238}\text{U}$ ratios deviated from the natural ratios in zircon by 1.4% for 200FsLA when using synthetic glass as a standard. This indicates that a standard with a matrix that matches the sample or close monitoring of the correction factor is still recommended.

Keywords: laser ablation, UV-femtosecond, zircon, U–Pb dating

INTRODUCTION

Development of Laser Ablation with less element fractionation

Ultra violet femtosecond (fs) laser ablation (UVFsLA) was introduced in order to broaden the applications of laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) (Horn and Blanckenburg, 2007; Pisonero and Günther, 2008). The short pulse beam minimizes the thermal effects, and the UV light can generate finer particles of silicate and, especially, metal samples (Koch *et al.*, 2004, 2006; Liu *et al.*, 2003; Poitrasson *et al.*, 2003; Russo *et al.*, 2004).

Prior to the introduction of UVFsLA systems, element fractionation was minimized using nanosecond (ns) UV laser systems (Eggins *et al.*, 1998; Guillong *et al.*, 2003; Horn *et al.*, 2000). The minimization was interpreted to be due to the shallow penetration of the laser into the sample, owing to the opacity of the sample materials to UV light (Guillong *et al.*, 2003; Horn *et al.*, 2000; Koch *et al.*, 2006) and the resultant smaller particles generated because of limited ablation depth by single laser pulse

(Horn and Günther, 2003; Russo *et al.*, 2004). Excimer laser (ExLA) or frequency multiplied Nd-YAG laser sources have been used for UV ablation. Ablation properties were improved as shorter wave-length laser systems such as, 266, 213, 193 (Guillong *et al.*, 2003), and even 157 nm, were introduced (Telouk *et al.*, 2003). As element fractionation was still an issue with these UV lasers (Guillong *et al.*, 2003; Horn and Blanckenburg, 2007; Poitrasson *et al.*, 2003), attention moved to the pulse duration of these lasers.

An ultra short pulse laser was introduced with the infra-red (IR) fundamental wavelength ($\sim 800\ \text{nm}$) of Ti-sapphire fs laser. This system minimized elemental fractionation for most of the elements in silicate materials due to a reduction in the thermal fractionation effect at the ablation region (Claverie *et al.*, 2009) and smaller particle sizes in the ablation aerosol (Koch *et al.*, 2004). However, fractionation between elements with different physico-chemical properties still occurred. Frequency tripled ($\sim 266\ \text{nm}$) or quadrupled ($\sim 200\ \text{nm}$) UVFsLA beams have become available (Horn and Blanckenburg, 2007; Pisonero and Günther, 2008), which theoretically should minimize element fractionation (Koch *et al.*, 2004). Minimization of elemental fractionation, however, has only been achieved at the level of a few percent to ten percent drift during single hole ablation, or between difficult elements, such as U, Th, and Pb (Koch *et al.*, 2006).

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Fractionation between transition metals, such as Cu and Zn, and other lithophile elements is still high (Koch *et al.*, 2006).

The effect of the laser fluence of UVFsLA was then investigated as a factor controlling the element fractionation (Claverie *et al.*, 2009; Koch *et al.*, 2006; Russo *et al.*, 2004). Additionally, responses of the ICP plasma against particle size and mass loading of the laser aerosols are also regarded as sources of mass fractionation (Aeschliman *et al.*, 2003; Krosiakova and Günther, 2007). These fractionation factors are interrelated (e.g., laser fluence, particle size, mass loading, etc.); therefore, their optimization has become the focus of research on UVFsLA mass spectrometry.

Application of LA-ICPMS to dating rocks and the associated problems

One of the most important fields of research in geosciences that LA-ICPMS is applied to is chronology. Using the radiogenic U–Pb decay system enables ages to be determined using U-rich Pb-free minerals such as zircon. The method was first introduced using thermal ionization mass spectrometry (TIMS) and has become popular with the development of *in-situ* micro-beam analysis using high resolution high sensitivity secondary ion mass spectrometry (HR-SIMS) (Wiedenbeck *et al.*, 1995). Only after high sensitivity quadrupole (Q)-ICPMS and UV (266 nm) laser ablation systems became available was LA-ICPMS used for U–Pb dating (Hirata and Nesbitt, 1995). The deep-UV 193 nm excimer or 193/213 nm solid state YAG lasers reduced fractionation and more efficiently ablated elements, while sector field ICPMS (Tiepolo, 2003) improved spatial resolution by providing ultra-high sensitivity. Together these developments enabled higher precision U–Pb dating using LA-ICPMS (Eggins *et al.*, 1998; Horn *et al.*, 2000; Jackson *et al.*, 2004; Tiepolo, 2003). In addition, the use of a multiple collector (MC)-ICPMS improves the precision of the ages obtained from small sample volumes (Cocherie *et al.*, 2009; Simonetti *et al.*, 2005).

Despite these instrumental developments over the last decade, elemental fractionation remains a problem in determining accurate zircon U–Pb ages (Cocherie *et al.*, 2009; Horn and Günther, 2003; Iizuka and Hirata, 2004; Jackson *et al.*, 2004; Paton *et al.*, 2010). Element pairs between volatile and refractory, such as Pb and U, fractionate at the ablation site (Horn and Günther, 2003; Jackson *et al.*, 2004). Element pairs with different ionization potentials, such as Th and U, also present problems, with fractionation most likely to be occurring in the ICP plasma. This is induced by mass loading of the laser aerosols (Krosiakova and Günther, 2007) or by larger particle sizes in the aerosol (Guillong *et al.*, 2003), which both cause insufficient ionization of Th. This affects the

new application fields in zircon chronology using the $^{208}\text{Pb}/^{232}\text{Th}$ – $^{206}\text{Pb}/^{238}\text{U}$ – $^{207}\text{Pb}/^{235}\text{U}$ system (Paquette and Tiepolo, 2007) and ^{238}U – ^{230}Th disequilibrium (Bacon and Lowenstern, 2005). Even for ordinary zircon U–Pb dating, young zircons require correction for the short-lived ^{230}Th nuclide, which affects ^{206}Pb , by measuring Th/U ratio (Cocherie *et al.*, 2009). Elemental fractionation between U, Th, and Pb should be carefully examined and the ablation protocols optimized. This is our motivation for organizing experiments using a 200 nm UVFsLA (hereafter 200FsLA) laser source with various ablation protocols, such as variable spot and raster modes.

Element fractionation that affects age dating is two fold. Firstly there is down-hole fractionation of U–Th–Pb during ablation of a single spot. This is obvious with 193ExLA and the properties have been investigated intensively (Cocherie *et al.*, 2009; Guillong *et al.*, 2003; Hirata and Nesbitt, 1995; Horn and Günther, 2003; Iizuka and Hirata, 2004; Jackson *et al.*, 2004; Paton *et al.*, 2010). Although some experiments, using low fluence 193 nm YAG laser, do not show significant down-hole fractionation between U and Pb (Guillong *et al.*, 2003), down-hole fractionation is still a major issue in zircon dating (Horn and Günther, 2003; Jackson *et al.*, 2004; Paton *et al.*, 2010). Indeed, currently efforts are underway to develop models to correct for down-hole fractionation (Paton *et al.*, 2010). Recently studies with <200 nm UVFsLA showed that down-hole fractionation is less than with 193ExLA (Garcia *et al.*, 2008; Poitrasson *et al.*, 2003). However, further investigations are required. Secondly, U–Th–Pb fractionation occurs between materials that have a different matrix. Using a synthetic glass standard to date zircons is only possible when the element fractionation factor between the glass and zircon can be closely monitored (Hirata and Nesbitt, 1995; Iizuka and Hirata, 2004). Use of a matrix matched zircon standard has been recommended for robust and accurate U–Pb age determinations (Jackson *et al.*, 2004; Paton *et al.*, 2010). The effect of different laser ablation protocols on the absolute element fractionation factors have not previously been examined in detail. Therefore this study will systematically examine the element fractionation caused by the different ablation settings.

Research objectives and approach

In this paper we explore down-hole and absolute element fractionations, especially between Pb, Th, and U, during U–Pb age analyses using 200FsLA on silicate glass standard SRM 610/612 and zircon age standard 91500 and TEMORA 2. We focus on the optimization of ablation protocols by comparing spot and various raster ablation methods for the laser source. Finally, the optimized protocol for 200FsLA is used and evaluated in zircon U–Pb dating using MC-ICPMS.

a. Laser ablation system set up

b. Rotation raster ablation setting

c. Laser craters

Fig. 1. (a) 200–266 nm femtosecond laser ablation system, and (b) configuration of ablation crater with sample stage rotation for “rotation raster” ablation. (c) The left three plates of the laser craters showing laser microscope photomicrographs of 200FsLA craters created by spot ablation (upper), rotation raster (middle) and close up of the crater walls and fringes formed by 200FsLA (low). The right three plates are craters by 193ExLA generated with the same fluence, beam diameter, and repetition rate for comparison. White lines (center of upper and middle photos) indicate locations of cross sections and lower white lines with numbers are profiles across the bottom of the craters. Numbers are in μm for depth scale. Dotted profiles for spot craters are from observations by optical microscope in order to amend the poor reproducibility of the laser microscope in craters with steep walls and deep bottoms. Craters generated by 200FsLA have sharp edges and almost no debris. Crater diameters are approximately 30 μm except for close up photos (see scales on the plates). Quench cracks on the crater walls and fringe are not observed on the 200FsLA crater walls, where the walls are smooth and have a sharp fringe, indicating that no melting occurred. In contrast, quench cracks are observed on the 193ExLA crater walls and fringes.

EXPERIMENTAL

Laser ablation system

Laser ablation sample cell: Our 200FsLA system uses the sample cell, which has an inner volume of $\sim 12.5 \text{ cm}^3$, with the dimensions 1 cm (height) $\times$ 2.5 cm (width) $\times$ 5 cm (length). He gas enters the sample cell through six small nozzles, 1 mm in diameter, set at 4 mm intervals, producing a laminar flow regime inside the sample cell.

200FsLA system: The fs laser source used in this study is a Spectra-Physics (Santa Clara, CA, USA) Solstice one-box Ti-sapphire regenerative amplifier with 3.5 mJ pulse energy, $<100 \text{ fs}$ pulse duration, and 800 nm wavelength. It is equipped with a MaiTai Ti-sapphire laser source and an Empower Nd-YAG green pump laser. The pulse rate is adjustable between a single shot, and 4 and 1000 Hz.

The wavelength of the output IR fs laser pulses are tripled and then quadrupled by a third harmonic generator (THG: Spectra-Physics TP-THG-HA-E) and a fourth harmonic generator (FHG: Spectra-Physics TP-FHG-HA-E) obtaining 270 μJ at 266 nm, and 60 μJ at 200 nm wavelengths. Pulse widths in the UV regions are assumed to be $<300 \text{ fs}$. The two UV wavelength fs laser beams are switched over by flipping-in re-direction mirrors (Fig. 1). Due to energy loss at optical surfaces and in the optical elements, final laser energies delivered onto the sample surface are 200 μJ at 266 nm, and 40 μJ at 200 nm wavelengths. Because of the change in temperature of the beta-BaB₂O₄ (BBO) nonlinear optical crystal, in both the THG and FHG units, beam energy optimization is performed by re-positioning the BBO crystals for high (1000–100 Hz) and low (100–4 Hz) repetition conditions.

In order to reduce energy absorption in the laser focusing optics, our laser optics possess only one ultra-pure grade fused silica plano-convex objective lens for each of the 266 and 200 nm wavelengths (OK-FS1000, OK Laboratory, Mitaka, Tokyo, Japan). These objective lenses are motor driven and switched over at the same time with the flip-in re-direction motorized mirrors for both 266 and 200 nm beam lines. The laser beam focused by the objective lenses are re-directed at 90 degrees by 266 and 200 nm kick-down mirrors placed immediately above the sample ablation cell. The viewing optics is aligned to look through the kick-down mirrors (Fig. 1a). Focusing for the UV laser beams and viewing optics can be adjusted separately, which provides the flexibility of enabling laser fluence to be optimized (Horn *et al.*, 2000; Koch *et al.*, 2006). Laser beam size can be adjusted by changing a set of apertures upstream of the laser objective lens. We used 200FsLA at $\sim 6 \text{ J/cm}^2$ fluence, which allows a 20–30 μm crater to be ablated.

Laser ablation protocols: spot, rotation raster, line raster

In order to provide sufficient spatial resolution for microanalysis, a spot crater with a diameter of 20–30 μm was used for age determinations. This crater size is required to obtain the required sensitivity and ion count for counting statistics. Precise isotope ratio measurements also depend on a stable signal intensity during ablation. Signal intensity normally decreases with time due to defocusing of the laser beam. The degree of defocusing is also a factor of the laser repetition rate. With a crater of 20–30 μm , a rapid decrease in the signal is inevitable at a repetition rate of 5–10 Hz.

We evaluated spot, rotation raster, and line raster protocols. The line raster was evaluated only for the purpose of comparison, because, in practice, a line raster is not applicable to tiny zircon grains, smaller than few tens of microns in diameter, from natural samples and a spatial resolution better than 30 μm is required to analyze zoned zircon crystals.

Ablated craters were inspected using a laser microscope (VK-9700, KEYENCE, Osaka, Japan) and an optical microscope. Observations with an optical microscope were undertaken in order to view the near cylindrical deep craters more clearly, as these are not well reproduced by a laser microscope cross section profile, due to the low reflectivity of the vertical walls and the deep crater bottom in a crater of small diameter (Fig. 1b).

Spot ablation: With 200FsLA, an ablation crater with a diameter of $\sim 30 \mu\text{m}$ is achievable at a fluence of $\sim 6 \text{ J/cm}^2$ (see Fig. 1c). In contrast to 193ExLA with a flat-top beam energy profile, 200FsLA has a Gaussian beam energy profile and defocuses quickly then lose more than half of their signal intensity after 60 s at a repetition rate of 5 Hz.

Rotation raster: The second ablation mode used was a laser raster rotated along the circumference of a circle with a radius of 8 μm (Fig. 1c). We hereafter call this method “rotation raster”. A $\sim 20 \mu\text{m}$ beam with a fluence of $\sim 6 \text{ J/cm}^2$ at a repetition rate of 10 Hz was used in order to maintain a signal intensity that is consistent with other ablation modes. For the rotation raster, the sample was rotated using programmable X-Y axis stepping motors at a velocity of 5 $\mu\text{m/s}$. This approach has previously been applied in low energy IRfsLA using a beam scanning device (Claverie *et al.*, 2009). Using the rotation raster permits the sample to be observed at high spatial resolution, which is often required for zircon age dating (Fig. 1c). Resultant craters were $\sim 30 \mu\text{m}$ in diameter, and a flat signal was obtained for over a minute using 200FsLA (see below).

Line raster: Line raster has previously been used to overcome the signal decay problem. Line raster allows a new sample surface to be exposed by the laser throughout ablation. In our experiments, a laser beam with a fluence of $\sim 6 \text{ J/cm}^2$ and a diameter of $\sim 30 \mu\text{m}$ was used. A 5 Hz repetition rate was used for the line raster analysis.

Mass spectrometer settings

Two ICP-MS machines were used in this study; a PQ-3 (VG Elemental, now part of Thermo Fisher Scientific; Bremen, Germany) and a Neptune (Thermo Fisher Scientific, Bremen, Germany). The Neptune is equipped with four multiple ion counters (MIC) along with Faraday cups. Small Pb signals in natural zircons are acquired by the MICs simultaneously. Use of the MIC system does not improve analytical precision greatly compared to the peak jumping analysis using a full-size single IC system. This is because of the strong time dependent drift of the small MICs (Cocherie *et al.*, 2009). However, the benefit of the MIC system is in its simultaneous detection, which reduces the sample volume required to achieve the necessary counting statistics. As with the advantage of using the rotation raster over line raster, a reduced sample surface area allows improved spatial resolution. We therefore explore the performance of a MIC system for zircon age dating. The 200FsLA system is evaluated using the PQ-3 with a stable full-size single IC. In both the PQ-3 and the Neptune, sensitivity has been improved through modifications to the ICP-MS instruments, as follows.

PQ-3 settings: The PQ-3 uses S-option, a high efficiency interface rotary pump, for greater sensitivity. The typical sensitivity with solution analysis using a desolvating nebulizer, Aridus II (CETAC Technologies, Omaha, Nebraska, USA), is 2–3 Gcps/ppm. The PQ-3 was used to evaluate ablation fractionation of Pb–Th–U on glass standard SRM 610 (Kent, 2008) and zircon standard TEMORA 2 (Black *et al.*, 2004). This instrument pos-

Table 1. MC-ICPMS, Q-ICPMS, and laser ablation settings used for 200FsLA-MC(Q)-ICPMS for U–Pb age dating

Experimental settings	
Laser system/Beam delivery	
Femtosecond laser	
Source wave length/pulse width	800 nm/100 fs
Energy:	
at 800 nm	3500 μ J
at 266 nm	270 μ J
at 200 nm	60 μ J
Focusing lens	Single planoconvex/f = 5.0 cm
Spot size	17 and 30 μ m
Fluence at laser spot	6 J/cm ²
Q-ICPMS	
RF-power	1370 W
Carrier gas (Ar)	~0.6 L/min
Laser carrier gas (He)	~1.0 L/min
Measurement mode	Peak jumping (3 points per peak)
Dwell time	10.25 ms
MC-ICPMS	
RF-power	1200 W
Sampling cone	JET sample cone
Skimmer cone	X skimmer cone
Carrier gas (Ar)	~1.3 L/min
Laser carrier gas (He)	~1.0 L/min
Interface vacuum using big rotory pump	1.2 mbar with He carrier gas
Integration time	66 ms
Acquisition time for background/signal	60s/40s
Detector setting	
²⁰² Hg	Ion Counter (IC) 1
²⁰⁴ Pb	IC2
²⁰⁶ Pb	IC3
²⁰⁷ Pb	IC4
²⁰⁸ Pb	L4-Faraday cup (FC)
²³² Th	H2-FC
²³⁸ U	H4-FC

sesses a large single multiple-dynode ion counter that maintains isotope ratios at stable values over several weeks of measurements. Mass scans between ²⁰²Hg, ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb, ²³²Th, and ²³⁸U were performed by peak jumping using 3 points per peak with 10.25 ms dwell time on each peak (Table 1).

Neptune settings: The Neptune is modified by the addition of a high efficiency expansion rotary pump (E2M80; Edwards, Crawley, West Sussex, UK). This increases the sensitivity by about 5–7 times when used with an X skimmer and JET sample cones. The typical sensitivity with solution analysis using Aridus II is 150–180 Gcps/ppm. Mass fractionation caused by the JET sample cone is insignificant at the high mass ranges and precisions required in this study. The modified Neptune has an extremely high sensitivity and thus provides greater signals at a given sample volume. This is a real benefit for precise U–Pb age determination at high spatial resolutions.

Neptune uses four small multiple ion counters (MIC) and three Faraday cups (FC). Mass assignments were IC1: ²⁰²Hg, IC2: ²⁰⁴Pb, IC3: ²⁰⁶Pb, IC4: ²⁰⁷Pb, L4-FC: ²⁰⁸Pb, H2-FC: ²³²Th, and H4-FC: ²³⁸U (Table 1). Due to rapid consumption of the small dynodes, the ion count yields of MICs degrade rapidly (Cocherie *et al.*, 2009). This is inappropriate for the examination of element fractionation at the laser ablation site and in the ICP-MS instrument. Therefore, the Neptune was only used to apply the optimized ablation protocol (200FsLA, rotation raster ablation) to U–Pb age dating. A standard bracketing method was used to correct for the time dependent drift of the MIC detectors (see details below).

Laser ablation gas line settings: For any combination of 200FsLA laser and PQ-3 and Neptune ICPMSs, He gas (~1.0 L/min) was used as the ablation gas (Eggins *et al.*, 1998; Horn and Günther, 2003). Although there are a few reports that suggest He has no effect on element sen-

sitivity (Paton *et al.*, 2010), we confirmed that He gas does reduce the surface deposition of ablated particles significantly. This indicates better sample transport with less element fractionation (Eggins *et al.*, 1998; Horn and Günther, 2003), and as a result He gas was used for ablation in all our experiments. He gas was mixed with Ar carrier gas (0.7–1.3 L/min) in a cylindrical mixing chamber (70 cm³ inner volume) immediately before reaching the ICP torch. Pulsed signals at low laser repetition rate were sufficiently smoothed out and the washout time using this mixing device was about 20 s, short enough for normal operations.

RESULTS AND DISCUSSION

We now examine the laser ablation profiles obtained by the three different ablation methods with 200Fs laser source and evaluate the (1) crater profiles, (2) elemental and isotopic fractionation on glass and (3) zircon, and (4) apply the most versatile ablation protocol, 200FsLA with rotation raster, to the measurement of zircon U–Pb ages by MC-ICPMS.

Laser crater profiles

Crater profiles ablated from SRM 610 glass and zircon standard TEMORA 2 during spot and rotation raster were inspected. Figure 1c shows examples of the craters generated on the zircon. 193ExLA crater photos are also presented for comparison. These were generated by our in house 193ExLA system. The ablation conditions, laser fluence, beam diameter, repetition rate, etc. are same with those in 200FsLA apart from 20 ns 193 nm laser source.

Spot ablation: Craters produced by 200FsLA in the spot form are quasi-cylindrical in shape with relatively flat bottoms (see Fig. 1c). The 200FsLA crater walls were less steep than by 193ExLA (see Fig. 1c top panels). This is due to Gaussian beam profile for 200FsLA. Any molten layer was not observed on the walls of the crater generated by 200FsLA (see Fig. 1c left bottom panel). Molten wall is usually not observed on the crater walls generated in synthetic glasses by 193ExLA laser ablation but is observed in zircons as shown by small quench cracks developed on the walls and the fringes of the craters (see Fig. 1c right bottom panel). Zircons (ZrSiO₄) has different ablation properties (Kuhn *et al.*, 2010) and the molten walls may be due to selective ablation of SiO₂, with ZrO₂ being left over as reported elsewhere (Eggins *et al.*, 1998). Such the molten wall was not observed for 200FsLA, only smooth surfaces were formed on and around the crater walls and fringes (see the crater wall close up in Fig. 1c bottom panel), indicating better ablation properties.

Rotation raster ablation: Craters generated by rotation raster for 200FsLA have more gently sloping sides than

those generated by spot laser and concave up bottoms (see middle panel in Fig. 1c). Crater depths by 10 Hz were comparable to those of spot analyses using a repetition rate of 5 Hz. As with the spot analysis, molten crater walls and crater rim fringes were not observed and aerosol deposits were comparable to that by spot analysis.

Ablated deposits around the crater were finer and thinner from 200FsLA than from 193ExLA. Deposits from 200FsLA do pile up after long ablation (see Fig. 1c), but their color in reflected light under the microscope indicates that they are thinner than those of 193ExLA at the same repetition rate and laser fluence with the same crater volume (see comparison in Fig. 1c middle panels). Therefore the difference does not reflect ablation volume, but rather the smaller ablation particles generated by 200FsLA. Small (~0.5 μm) fluffy particles were dispersed around craters generated by 200FsLA (see Fig. 1c). These are presumably re-ablated thin films of ablation deposits. They were observed for both spot and rotation raster ablation (see Fig. 1c).

Line raster ablation: The 5 Hz line raster generated grooves with flat bottoms and depths of less than 1 μm for 200FsLA (images of ablated areas not shown). Ablation deposits occurred along both side of the raster lines, and were again thinner for than for 200FsLA than for 193ExLA.

Fractionation profiles on NIST 610 glass standard

Signal intensity profile: Analytical results of down-hole profiles over 60 s after signal stabilization from 200FsLA are shown in Figs. 2a and 2b. Each signal profile shows from 40 to 100 s time interval after 30 s of gas blank measurement and 10 s of signal stabilization so that almost entire profile usable for laser ablation is shown. Examples are shown for changes in signal intensities monitored by ²⁰⁷Pb/1000 (cps). Each panel in Fig. 2 shows 10 separate analyses with a stacked average, except for the line raster, which used a single run.

Signal intensities gradually decrease to about 40% of their initial values during spot analysis protocol (Fig. 2a). In contrast, an almost flat signal was achieved using rotation raster 200FsLA for up to 60 s, but the signal intensity was less (Fig. 2b). The origin of this lower signal intensity is perhaps due to the Gaussian beam profile of the 200FsLA, which results in gently dipping crater walls compared to the steeper crater walls generated by spot analysis. The line raster (Fig. 2c) showed stronger signal intensities and flat signals. This is due to continuous focusing of the laser beams on the fresh sample surface.

²⁰⁶Pb/²³⁸U ratios: Unlike many other reports using 193ExLA (Cocherie *et al.*, 2009; Guillong *et al.*, 2003; Hirata and Nesbitt, 1995; Horn and Günther, 2003; Iizuka and Hirata, 2004; Jackson *et al.*, 2004; Paton *et al.*, 2010), the ²⁰⁶Pb/²³⁸U ratios are almost flat over 60 s in all abla-

a. Femtosecond 200, 30 μ m beam spot, 5 Hz

b. Femtosecond 200, 20 μ m beam spot, 30 μ m rotation raster, 10 Hz

c. Femtosecond 200, 30 μ m beam spot, line raster, 5 Hz

Fig. 2. Down-hole profiles of ablation signal intensity and key isotope ratios measured for NIST SRM610 glass using 200FsLA. Results are given for (a) spot, (b) rotation raster, and (c) line raster protocols. $^{207}\text{Pb}/1000$ diagrams show signal intensities on ^{207}Pb cps over 60 s. $^{206}\text{Pb}/^{238}\text{U}$ and $^{232}\text{Th}/^{238}\text{U}$ are shown in the middle and right columns. Ten separate runs are plotted with thin lines, while stacked averages are shown by thick solid lines, except for line raster (bottom) whose results are from single run. Literature isotope ratios, determined by solution analyses, are denoted by thick white lines for $^{206}\text{Pb}/^{238}\text{U}$ and thick solid lines for $^{232}\text{Th}/^{238}\text{U}$ and shown for comparison. Ground average (avg.) values are also given in each panel except for $^{207}\text{Pb}/1000$.

tion conditions indicating little down-hole fractionation. Isotope ratio scatter is almost identical between spot and rotation raster protocols although signal intensity is less in the early half of the rotation raster profile (Fig. 2). The line raster results are stable in terms of signal intensity and isotope ratio scatter. These compare well to those measured by 200FsLA rotation raster (Figs. 2b and 2c). The minimized down-hole fractionation feature is somewhat similar to 193 nm YAG laser results (4 ns pulse at 4.2 J/cm²) (Guillong *et al.*, 2003), probably due to the lower laser fluence used in this study (~ 6 mJ/cm²), which resulted in shallow craters with low aspect ratios that prevented element fractionation occurring on the walls (Horn

et al., 2000).

Spot analyses gave the highest average $^{206}\text{Pb}/^{238}\text{U}$ value (0.2515), line raster the lowest (0.2161), with values from rotation raster intermediate (0.2439), although the values stick around the reported value by 193ExLA (e.g., 0.2249 by ExLA-ICP-QMS; Iizuka and Hirata, 2004). $^{206}\text{Pb}/^{238}\text{U}$ ratio change day by day basis dependent on instrumental settings; however, these results were obtained by the same condition within a day. Therefore the observed difference is valid. We interpret that thermal fractionation between Pb and U is smallest during the line raster, slightly higher during the rotation raster, and is highest during spot analyses. This may reflect the

Table 2. Fractionation index during down-hole ablation on SRM 610 glass standard for 200F s laser ablation

Laser type	Ablation mode	Crater diameter (μm)	Laser fluence (J/cm^2)	Repetition rate (Hz)	40 s fractionation index* (%)			60 s fractionation index* (%)				
					$^{207}\text{Pb}/^{206}\text{Pb}$	$^{206}\text{Pb}/^{238}\text{U}$	$^{232}\text{Th}/^{238}\text{U}$	$^{208}\text{Pb}/^{232}\text{Th}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{206}\text{Pb}/^{238}\text{U}$	$^{232}\text{Th}/^{238}\text{U}$	$^{208}\text{Pb}/^{232}\text{Th}$
Fs200	Line**	20	6	10	-1.2	0.6	-0.2	0.8	-0.3	2.0	1.2	0.9
Fs200	Spot	30	6	5	-0.3	-0.5	-3.7	3.2	0.6	-0.5	-1.7	1.2
Fs200	Rotation	30 (20)	6	10	-0.8	0.1	0.8	-0.7	-0.2	1.3	1.1	0.2

*Fractionation index is denoted by $[(\text{"average of first } 30 \text{ s"} - 1) \times 100 (\% \text{ deviation}) \text{ for } 60 \text{ s and } [(\text{"average of first } 20 \text{ s"} - 1) \times 100 \text{ for } 40 \text{ s}.$

**Line raster is performed at a velocity of 1 micrometer per second.

Table 3. Absolute isotopes and elemental fractionations of SRM610 glass standard and TEMORA 2 zircon standards

Standard	Method	Crater diameter/ Repetition rate	$^{207}\text{Pb}/^{206}\text{Pb}$	%RD	%RD*	$^{206}\text{Pb}/^{238}\text{U}$	%RD	%RD*	$^{232}\text{Th}/^{238}\text{U}$	%RD	%RD*	$^{208}\text{Pb}/^{232}\text{Th}$	%RD
[Synthetic glass] SRM610 solution	Fs200		0.90998			0.22817			1.01108			0.56042	
	Line	30 $\mu\text{m}/5 \text{ Hz}$	0.917	0.8	—	0.216	-5.3	—	0.713	-29.5	—	0.658	17.4
	Spot	30 $\mu\text{m}/5 \text{ Hz}$	0.920	1.1	—	0.252	10.4	—	0.606	-40.1	—	0.901	60.8
	Rotation	30 $\mu\text{m}/10 \text{ Hz}$	0.914	0.4	—	0.244	6.9	—	0.713	-29.5	—	0.743	32.6
[Zircon] TEMORA 2 solution	Fs200		0.05517			0.06684							
	Line	30 $\mu\text{m}/5 \text{ Hz}$	0.0564	2.2	1.4	0.0614	-8.1	-2.8	—	—	—	—	—
	Spot	30 $\mu\text{m}/5 \text{ Hz}$	0.0560	1.5	0.4	0.0742	11.0	0.6	—	—	—	—	—
	Rotation	30 $\mu\text{m}/10 \text{ Hz}$	0.0556	0.8	0.4	0.0704	5.3	1.4	—	—	—	—	—

SRM 610 solution data are calculated based on isotope data of Kent (2008) and Pb, Th, and U element abundances determined by the authors. TEMORA 2 solution data are ID-TIMS results from AMU (Black *et al.*, 2004). 200F-sLA data are calculated from raw count data obtained in this study. Note that no calibrations were made for the purpose of comparison of absolute element fractionation between different settings. The rotation raster always gives less elemental fractionation in Th/U. %RD: relative difference from solution values. %RD*: relative difference between glass and zircon. Note that mass fractionation in the solution based ICP-QMS is on the level of a few percent. Isotopic and elemental fractionations greater than a few percent are due to elemental fractionation caused by the laser ablation or by the mass loading in the ICP plasma due to coarse particle sizes in the laser aerosols.

aspect ratios of the craters generated by the different modes.

$^{232}\text{Th}/^{238}\text{U}$ ratios: The $^{232}\text{Th}/^{238}\text{U}$ results are more variable than in $^{206}\text{Pb}/^{238}\text{U}$. The values measured using spot 193ExLA sometimes show sigmoidal increase over time as reported elsewhere (e.g., Paton *et al.*, 2010). This was interpreted due to a decrease in particle size as laser craters deepened leading to progressively more efficient Th ionization in the ICP plasma (Kroslakova and Günther, 2007). $^{232}\text{Th}/^{238}\text{U}$ by 200FsLA shows excellent stability over 60 s for both spot and rotation raster protocols. Linear raster 200FsLA also produced stable result. However, measured SRM 610 values by 200FsLA are significantly lower (0.6055–0.7127) than in solution (normally about 1 by our PQ-3) or in natural value (~ 1.01108 see below), irrespective of ablation mode, perhaps indicating that Th ionization is less efficient for the laser particle generated even by 200FsLA.

Down-hole fractionation index (FI): Fractionation indices (Koch *et al.*, 2006) (a modified notation of the % deviation between the average element ratio for the last half of the measurements with that from the first half) over 40 s and 60 s from the ablation profiles (Fig. 2) are calculated and shown in Table 2. Briefly, element fractionation indices (FI) for $^{206}\text{Pb}/^{238}\text{U}$ over 60 s are less than 2.0% for all 200FsLA protocols, which are comparable to, or slightly larger than, the statistical limit shown by $^{207}\text{Pb}/^{206}\text{Pb}$ (FI < 1.2%). For $^{232}\text{Th}/^{238}\text{U}$ measured for 200FsLA are all less than 3.7% but greater than other ratios. Absolute FI for $^{208}\text{Pb}/^{232}\text{Th}$ are reciprocal to those of $^{232}\text{Th}/^{238}\text{U}$ (see Table 2), indicating Th suppression is the common cause. The FI for the line raster are minimal in agreement with previous reports (Horn and Blanckenburg, 2007).

Advantages of 200FsLA with rotation raster protocols: There are three advantages to using 200FsLA rotation raster; (1) generation of finer particles, (2) less down-hole fractionation, and (3) less fractionation in ICP plasma. The major advantage of using 200Fs as the laser source is that it generates finer particles (see above crater observations). As a result, 200FsLA provides the best performance in determining U–Th–Pb element and isotope ratios, especially in terms of Th down-hole fractionation. Therefore, 200FsLA potentially becomes a proper tool for U–Th age dating and for U–Pb dating of young zircons where precise Th/U determination is required. In the case of ordinary U–Pb dating, down-hole element fractionation of 200FsLA is comparable to or even better than 193ExLA or other nano-second LA.

In terms of the analytical protocol when using 200FsLA source, rotation raster has the benefit over spot ablation in determining isotope ratios more accurately. Rotation raster analyses yielded stable signal intensity over 60 s. This is an advantage in maintaining a stable

mass loading to the ICP plasma as mass loading and coarse aerosol loading are the sources of element fractionation for weakly ionized elements, including Th (Kroslakova and Günther, 2007; Russo *et al.*, 2004). Our observations of down-hole fractionation indirectly support this conclusion. Down-hole fractionation of $^{232}\text{Th}/^{238}\text{U}$ and $^{208}\text{Pb}/^{232}\text{Th}$ are minimal with rotation raster 200FsLA, rivaling line raster (FI < 1.1% over 60 s for all isotope ratios compared to FI < 3.7% by spot; see Table 2).

Observed absolute $^{232}\text{Th}/^{238}\text{U}$ also provides evidence for less element fractionation by rotation raster 200FsLA. All analyzed $^{232}\text{Th}/^{238}\text{U}$ are lower than the natural value for SRM 610 ($^{232}\text{Th}/^{238}\text{U} = 1.01108$ calculated by element abundances Pb = 414.6, Th = 432.7, and U = 442.3 ppm measured by solution based PQ3 analysis for the half-cut of the SRM 610 wafer used in our 200FsLA analyses; Table 3) supporting poorer ionization of Th in the ICP plasma when LA is used. Relative fractionation factor by line and rotation raster protocols (%RD = –29.5) were less than that of spot analysis (%RD = –40.1%). Other deviations from natural isotope ratios, e.g., $^{207}\text{Pb}/^{206}\text{Pb}$ (Kent, 2008) and $^{206}\text{Pb}/^{238}\text{U}$ (calculated by Pb and U abundances above and Pb isotope ratios of Kent, 2008), are also minimal in rotation raster providing support of the versatility of this protocol (Table 3).

Fractionation profiles on zircon standard TEMORA 2

The analytical results measured on the standard zircon TEMORA 2 (Black *et al.*, 2003, 2004) using spot, rotation raster, and line raster with 200FsLA are shown in Fig. 3 (profiles obtained between 40 and 100 s after 30 s gas blank measurement and signal stabilization for 10 s same as in Fig. 2). Absolute isotope ratios are also shown and compared to reference values measured by isotope dilution thermal ionization mass spectrometry (ID-TIMS) (Black *et al.*, 2003, 2004) in Table 3. A natural zircon standard was analyzed because the matrix effects might differ from those in synthetic glass. $^{232}\text{Th}/^{238}\text{U}$ was analyzed but not shown, because TEMORA 2 exhibits significant zoning in this ratio as reported elsewhere (Black *et al.*, 2004).

Down-hole fractionation in TEMORA 2: Firstly, $^{207}\text{Pb}/^{206}\text{Pb}$ shows almost no down-hole fractionation for 200FsLA (see Fig. 3a). $^{206}\text{Pb}/^{238}\text{U}$ measured by 200FsLA is identical for spot and rotation raster and are constant over 60 s indicating almost no down-hole fractionation (see Fig. 3b). Stable ablation is maintained in zircon analysis using 200FsLA.

$^{207}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{238}\text{U}$ fractionation from TIMS results: Solution TIMS measured $^{207}\text{Pb}/^{206}\text{Pb} = 0.05517$ for TEMORA 2 (Black *et al.*, 2004), while for 200FsLA $^{207}\text{Pb}/^{206}\text{Pb} = 0.0560$ – 0.0564 (Table 3). Thus, the analysis by LA causes slight shifts in the absolute isotope ratios (0.8 to 2.2%RD). ID-TIMS measured TEMORA 2

Fig. 3. Down-hole fractionation profiles on zircon standard TEMORA 2. Comparison between (a) 200FsLA for spot, rotation and line raster protocols are shown for $^{207}\text{Pb}/^{206}\text{Pb}$, while (b) show the same comparison for $^{206}\text{Pb}/^{238}\text{U}$. Left panels indicate observed isotope ratios over 60 s and right panels show histograms. Legend for all panels is shown in (b). Filled triangles are isotope ratios determined by solution TIMS (Black *et al.*, 2004).

$^{206}\text{Pb}/^{238}\text{U} = 0.06684$ (Black *et al.*, 2004), those for 200FsLA was $0.0614\text{--}0.0742$ (-8 to 11.2% RD). $^{207}\text{Pb}/^{206}\text{Pb}$ in TEMORA 2 zircon varies $<0.47\%$ in measurements by SIMS (Black *et al.*, 2004), so the large mass discrimination for 200FsLA (up to 2.2% RD) is not due to heterogeneities in the standard. Although rotation raster gave the closest isotopic ratios, the different degree of shift between $^{207}\text{Pb}/^{206}\text{Pb}$ (0.8% RD) and $^{206}\text{Pb}/^{238}\text{U}$ (5.3% RD) does not allow immediate use of the measured isotope ratios for age determination by 200FsLA. These shifts should originate both at the LA site and in the ICP mass spectrometer as has been discussed intensively over several decades for other LA systems.

TEMORA 2 measurement with SRM 610 normalization: Calibration using a standard glass for zircon dating has been used; however, immediate use of a glass standard for zircon age determination is not advisable unless the fractionation factor between glass and zircon is carefully monitored (Jackson *et al.*, 2004). The relative isotopic fractionations between SRM 610 glass and TEMORA 2 zircon by 200FsLA is compared using $\%RD^*$ ($RD\%^* = RD\% (\text{SRM 610}) - RD\% (\text{TEMORA 2})$; Table 3). The $\%RD^*$ differs by 1.4% for $^{207}\text{Pb}/^{206}\text{Pb}$, by -2.8% for $^{206}\text{Pb}/^{238}\text{U}$ using line raster (Table 3). In contrast, both spot and rotation raster provide less than $0.4\%RD^*$ for $^{207}\text{Pb}/^{206}\text{Pb}$ and 0.6 to $1.4\%RD^*$ for $^{206}\text{Pb}/^{238}\text{U}$, the dif-

Fig. 4. An example of standard bracketing analysis for $^{206}\text{Pb}/^{238}\text{U}$ ratio analyzed by 200FsLA on SRM612 glass. Note that the steep decrease in the analyzed ratio is a result of a change in the condition of the ion counter (IC) used in the MC-ICPMS for ^{206}Pb against the Faraday detector used for ^{238}U . Analytical precision is still within one percent for the key isotope ratios used in determining U–Pb ages.

ference between the two protocols are within or closer to typical statistical errors supporting small fractionation between different matrix by 200FsLA (also see Horn and Blanckenburg, 2007). This confirms versatility of 200FsLA for U–Pb zircon dating.

U–Pb dating

Hereafter we examine the applicability of rotation raster 200FsLA to determine the U–Pb zircon ages. The reasons why spot and line raster are not chosen are that although the spot ablation fractionates U/Pb similarly but Th/U more than the rotation raster does in glass analysis (see SRM 610 result Table 3), and the line raster cannot provide sufficient spatial resolution for zircon U–Pb age dating for smaller zircon crystals. Additional factor is the rapid decrease in signal intensity by spot analysis (Fig. 2), which may cause change in mass loading to the ICP plasma potentially introducing more down-hole fractionation as evidenced by the worst FIs in $^{232}\text{Th}/^{238}\text{U}$ shown by the spot glass analysis (Table 2). Following examination uses a 91500 zircon as external standard in dating TEMORA 2 zircon. Inter-calibration between high quality age standards provides the best test for the ablation protocol. Before examining the dating results, we examine optimization of the analytical protocol using Neptune multiple ion counters.

Analytical precision of U–Th–Pb isotope ratios using

Table 4. Comparison between 200 nm femtosecond laser ablation analytical results for a 30 μm crater over 40 seconds, using a 20 μm laser spot, $\sim 6 \text{ J/cm}^2$ laser fluence at 10 Hz laser pulse with rotation raster. Laser results are the average of nine bracketing runs on SRM612 glass, with odd number runs on the standard and even number runs on the unknown.

Sample	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{206}\text{Pb}/^{238}\text{U}$	$^{232}\text{Th}/^{238}\text{U}$	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$
SRM612 solution	0.90745	0.29336	1.01503	17.098	15.516
	average of Woodhead and Hergt (2001) and Baker <i>et al.</i> (2004)				
Femtosecond 200 nm	0.90875	0.29483	1.01716	17.123	15.534
SD% ($n = 9$)	0.11	0.73	0.74	0.49	0.28
Diff%	0.14	-0.50	-0.21	0.08	0.10

Table 5. Analytical results for ages of zircon standard TEMORA 2. SHRIMP values are from Black *et al.* (2004) for comparison.

Spot No.	Atomic ratio				Apparent age (Ma)			
	$^{206}\text{Pb}/^{238}\text{U}$	2SE	$^{207}\text{Pb}/^{206}\text{Pb}$	2SE	$^{206}\text{Pb}/^{238}\text{U}$	2SE	$^{207}\text{Pb}/^{206}\text{Pb}$	2SE
1	14.944	0.474	0.05516	0.00025	417.5	13.2	418.6	1.9
2	15.017	0.421	0.05514	0.00027	415.6	11.7	417.9	2.0
3	15.067	0.427	0.05481	0.00026	414.3	11.7	404.4	1.9
4	15.035	0.534	0.05524	0.00022	415.1	14.7	421.9	1.7
5	15.012	0.311	0.05524	0.00021	415.7	8.6	422.0	1.6
6	15.020	0.518	0.05512	0.00034	415.5	14.3	417.2	2.6
7	15.091	0.476	0.05499	0.00027	413.6	13.1	411.6	2.0
8	15.031	0.435	0.05501	0.00028	415.2	12.0	412.5	2.1
9	14.839	0.489	0.05477	0.00038	420.4	13.9	402.8	2.8
10	14.779	0.628	0.05432	0.00046	422.1	17.9	384.3	3.2
11	14.873	0.401	0.05536	0.00033	419.5	11.3	426.6	2.5
12	14.891	0.393	0.05540	0.00037	419.0	11.0	428.5	2.9
13	14.891	0.293	0.05535	0.00029	419.0	8.3	426.2	2.2
14	14.913	0.352	0.05527	0.00038	418.4	9.9	423.2	2.9
15	14.972	0.509	0.05505	0.00037	416.8	14.2	414.2	2.8
Arithmetic mean*	14.958	0.182	0.05508	0.00056	417.2	4.9	415.5	23.0
SHRIMP*	14.984	0.035	0.05517	0.00012	416.5	1.0	419.0	4.7

*Errors in arithmetic mean and SHRIMP are given as 2 SD.

the bracketing method: As the main goal of this study is to optimize the analytical protocol for U–Pb age dating using Neptune MC-ICPMS, we have investigated the reproducibility of relevant isotope ratios in the NIST SRM612 glass. Low concentration glass was used because of the greater sensitivity of the Neptune. The Neptune is equipped with four ion counters (IC) and three Faraday cups (FC). The efficiencies of the ion count yields from the small multiple-IC (MIC) drift significantly between runs due to the consumption of a small dynode, unlike when big secondary electron multipliers are used (Simonetti *et al.*, 2005). This effect is shown in Fig. 4, indicated by a decrease in $^{206}\text{Pb}(\text{IC3})/^{238}\text{U}(\text{H4-FC})$ ratios from 0.33 to 0.19 during 36 runs due to a change in the condition of IC3 alone. This also happens between ICs, where it is reflected in changes in $^{207}\text{Pb}(\text{IC4})/^{206}\text{Pb}(\text{IC3})$,

$^{206}\text{Pb}(\text{IC3})/^{204}\text{Pb}(\text{IC2})$, and $^{207}\text{Pb}(\text{IC4})/^{204}\text{Pb}(\text{IC2})$. The IC1 on ^{202}Hg is no exception and the error requires a ^{204}Hg isobaric overlap correction factor. The rapid changes in ICs do not make any internal correction possible. If a stable signal is available, such as during solution analysis, an inter-IC-FC efficiency calibration is possible by analyzing the same isotope signal, such as ^{207}Pb , by sequential flipping of the same ion beam from IC1 to IC4 and L4-FC. Subsequently, simultaneous isotope ratio analyses are performed by applying the inter cup efficiency correction factors that have been determined. However, it is not recommended for LA analyses as chemical zoning is usually encountered in the natural samples during analysis, preventing a stable ion beam signal being maintained.

Instead, we applied a bracketing correction method,

Fig. 5. Down-hole ablation profiles for the 91500 and TEMORA 2 zircon standards using the optimized analytical protocol. Use of a 5 Hz repetition rate gives prolonged stable signals. Note that the high ^{207}Pb intensity and $^{207}\text{Pb}/^{206}\text{Pb}$ ratio in the first 300 scans (~ 20 s) are due to the sample surface being contaminated by Pb. This time range is used for pre-ablation. All isotope ratios are fairly stable in the down-hole profile after pre-ablation.

as proposed elsewhere (Cocherie *et al.*, 2009), using frequent sample-standard analyses. To test this method, odd number runs analyzed the standard SRM 612, while even number runs analyzed the unknowns. Gas blanks were measured on the peak without laser aerosols for 120 s. Although changes in absolute $^{206}\text{Pb}/^{238}\text{U}$ were about 25%, corrected results for 19 unknowns were within 0.92% of the standard deviation (SD) (Fig. 4). Other isotope ratios were also within 0.74% ($n = 9$) of the SD for a different run on a different day from those shown in Fig. 3 and Table 4. These results are comparable, or even better, than those obtained using the 213 nm UV-YAG laser and the same MIC system equipped in a Neptune (Cocherie *et al.*, 2009).

Fig. 6. Analytical results of zircon standard TEMORA 2 using 91500 zircon as bracketing standards. The concordia age given when the zircon is used as the standard indicate no isotopic and elemental fractionation occurred during analysis. Age calculations were undertaken using IsoPlot ver. 2.2 (Ludwig, 2001). A two-stage model (Stacey and Kramers, 1975) was assumed to calculate intercept age.

Reproducibilities better than 1.0 SD% (% 1-standard deviation) for all isotope ratios used in U–Pb age determination provide sufficient precision (Cocherie *et al.*, 2009; Jackson *et al.*, 2004; Simonetti *et al.*, 2005). These are obtained from a sample containing 38.00 ppm Pb, 35.86 ppm Th, and 36.51 ppm U (concentrations measured by solution-based PQ3 analysis for half-cut of the same wafer used in 200FsLA analyses). Considering the abundance of elements in natural zircon crystals, typically >5 ppm Pb, >100 ppm Th, and >100 ppm U, the signal intensity of U and Th should be sufficient. Pb ion count on ^{204}Pb and ^{206}Pb – ^{207}Pb are typically >400 and >5000 cps/ppm, which would result in 2000 and 25000 cps for 5 ppm of Pb, respectively. Statistically, these counts would result in $<0.9\%$ error for $^{206}\text{Pb}/^{207}\text{Pb}$ and $<3.0\%$ errors for $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ analyzed on a single spot, which is sufficient for U–Pb age determination. This will be verified in the next section where results from natural zircon crystals are discussed. If larger signals are required, the rotation radius and repetition rate of the laser can be increased. However, it is important that the ablation conditions for the standard and unknown are the same, because of the number of factors (e.g., mass loading) affecting ablation properties as discussed above.

Analysis of zircon standards for U–Pb age dating: We have applied our optimized analytical protocols for 200FsLA-MC-ICPMS to the determination of U–Pb ages using zircon standards 91500 (Wiedenbeck *et al.*, 1995) and TEMORA 2 (Black *et al.*, 2003, 2004). The zircon grains were mounted in epoxy and polished to expose internal surfaces. The zircon standards have been used as bracketing standards for the purpose of matrix matched

analysis. Although fractionation factor in $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{238}\text{U}$ between SRM 610 and TEMORA 2 are small enough by 200FsLA in a level of less than 1.4% (see Table 3), the matrix matched analysis has an advantage for precise U–Pb age dating (Cocherie *et al.*, 2009; Jackson *et al.*, 2004; Simonetti *et al.*, 2005). This is also useful for the test of the versatility of the rotation raster protocol by eliminating any errors introduced from difference in the matrix. For the analysis of natural zircon standards, the repetition rate of the laser was reduced to 5 Hz in order to achieve a sufficient signal, while the rotation velocity remained unchanged at 5 $\mu\text{m/s}$. These conditions still resulted in the generation of a circular crater with a near-flat bottom. Craters were $\sim 30\ \mu\text{m}$ in diameter and $\sim 15\ \mu\text{m}$ deep after $\sim 60\ \text{s}$ ablation.

First, down-hole ablation profiles for 91500 and TEMORA 2 zircons were evaluated. The results indicate stable ablation similar to those observed in SRM612 glass (Fig. 5). For the first 300 scans ($\sim 20\ \text{s}$), ^{207}Pb intensity and $^{207}\text{Pb}/^{206}\text{Pb}$ are both high, gradually decrease, then become stable. This is due to surface contamination of Pb. The required pre-ablation time of $\sim 20\ \text{s}$ originates from the washout time of the signal smoothing chamber set in the sample introduction system (see above). Data acquisitions followed after the pre-ablation for 650 scans ($\sim 40\ \text{s}$) (see shaded area in Fig. 5). Cleaning the sample surface with hexane and diluted hydrochloric acid can reduce Pb contamination but pre-ablation is still recommended. As shown in the Fig. 5a, $^{207}\text{Pb}/^{206}\text{Pb}$, $^{206}\text{Pb}/^{238}\text{U}$, and $^{232}\text{Th}/^{238}\text{U}$ do not show significant changes using rotation raster 200FsLA for 91500 zircon (FI = -1.1 , 3.5 , and -0.2% respectively). In particular, ^{232}Th and ^{238}U were both analyzed by Faraday Cup with minimal down-hole fractionation between Th and U by 200FsLA suggesting no significant change in laser aerosol particle size. Confirmation of negligible down-hole fractionation in the zircons is again provided by the analysis of the two zircon standards (Fig. 5).

Analytical results of relevant isotope ratios and ages for the zircon standard TEMORA 2 are summarized in Table 5. Tera-Wasserburg concordia plots are shown in Fig. 6. The zircon standard TEMORA 2, with the 91500 zircon as standard, showed a concordia age of $417.1 \pm 2.5\ \text{Ma}$ (Fig. 6), which is in good agreement with the age of $416.78 \pm 0.33\ \text{Ma}$ obtained by the ID-TIMS method (Black *et al.*, 2004). Reverse dating on the 91500 by TEMORA 2 gave a concordia age of $1067.1 \pm 11\ \text{Ma}$, consistent with $1062.4 \pm 0.8\ \text{Ma}$ (Wiedenbeck *et al.*, 1995) obtained by ID-TIMS confirming the versatility of the analytical protocol.

CONCLUSION

Evaluation of UV (200 nm)-FsLA properties have made it clear that rotation raster minimizes down-hole

element fractionation during the ablation of silicate glass and zircon crystals. Under the condition element fractionation between Pb, U, and Th was not observed in the down-hole ablation profiles over 60 s on glasses and zircons. This minimizes uncertainties originated from the down-hole fractionation affecting precise determinations of elemental ratios. U–Pb elemental fractionation between glass and zircon with different matrix is minimal (less than 1.4%), whereas U–Th and Th–Pb fractionations still present. Applying this ablation protocol to U–Pb age dating of zircons was examined. Dating of zircon using a zircon standard provided excellent accuracy and precision. Although element fractionation in Th is still larger than those in U and Pb and more investigation is needed, rotation raster-200FsLA-MC-ICPMS can be a versatile tool for U–Pb dating.

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