U-Pb isotopic age dating by LAM ICP-MS, INCO Innovation Centre, Memorial University: Sample preparation methodology and analytical techniques

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ABSTRACT

This contribution reports on sample preparation methods and Laser Ablation Microprobe Inductively Coupled Plasma Mass Spectrometry (LAM ICP-MS) analytical techniques routinely used to acquire U-Pb isotopic age data at the INCO Innovation Centre, Memorial University. Four concordant zircon reference materials that span from Miocene to Archean in age (9.52 Ma, 337.15 Ma, 1066.3 Ma and 2674.3 Ma) were recently analysed during a data collection session in which U-Pb isotopic data for 11 suspected Cretaceous plutonic rocks were being acquired. Final U-Pb age calculations determined for the four zircon reference materials are in excellent agreement with the corresponding known and/or published ID TIMS ages and demonstrate the reproducibility, accuracy and precision of the LAM ICP-MS technique. Furthermore, data collected for sample GP-09-02 demonstrate the applicability of the LAM ICP-MS technique for dating zircon populations as young as Miocene.

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INTRODUCTION

The intent of this contribution is to outline the sample preparation and analytical methodology employed during the recent acquisition of U-Pb isotopic datasets on Cretaceous-age plutonic rocks through Laser Ablation Microprobe Inductively Coupled Plasma Mass Spectrometry (LAM ICP-MS). The LAM ICP-MS instrumentation used comprises part of the Micro Analytical Facility within the INCO Innovation Centre at Memorial University. Geochronology using ICP-MS techniques has been carried at Memorial University since at least 1993, when initial experiments indicated that analysis of $^{206}Pb/^{207}Pb$ ratios could be performed *in situ* on zircon grains when the ICP-MS was coupled to a laser ablation sample introduction system (Fryer *et al.*, 1993; Jackson *et al.,* 2004.). Since the initial experiments, the methodology has consistently evolved and improved, such that data currently produced are sufficiently accurate and precise to unravel complex geological histories from at least the Miocene onwards. We report the analytical conditions and sample preparation techniques that were employed to complete U-Pb dating of 11 Cretaceous plutonic rocks collected throughout Yukon during the summer of 2009 (presented elsewhere in this volume). Additionally, we present U-Pb isotopic data for four zircon reference materials that were routinely analysed during data collection.

ANALYTICAL METHODS

Zircon separates were extracted using standard crushing techniques, and heavy mineral concentrates were produced using a Wilfley™ table, heavy liquids and a Frantz™ isodynamic separator before hand-picking in ethanol under a binocular microscope. All extraction and analyses were conducted at Memorial University, Department of Earth Sciences and INCO Innovation Centre.

Subdivision of zircon populations was initially carried out using a binocular microscope and standard optical criteria (*i.e.*, colour, morphology and inclusion characteristics). A subset (average of n = 20-30 per population) of grains selected from each zircon population identified using optical criteria were isolated, photographed in transmitted light and subsequently mounted in epoxy resin and polished to expose grain cores. Grain mounts were then carbon coated and imaged using backscattered electron (BSE) and cathodoluminescence (CL) image analysis. The number of zircon grains imaged per sample ranged between 60 and 100 depending on the complexity of the zircon populations. Thorough characterization of the magmatic zircon populations is crucial for correct selection of grains that will yield the most accurate estimate of the crystallization age. Additionally, a clear understanding of zircon epitaxial relationships (core *vs.* rim) occurring within an unknown population assists intragrain placement of the laser beam, which ensures analysis of single discrete age domains rather than overlapping age domains. Analysis of multiple age domains within a single zircon grain produces isotopically heterogeneous data which, typically, is a significant contributor to U-Pb discordance using the LAM ICP-MS technique.

Zircon unknowns and reference materials were polished to a 0.25 μm finish using an automated Struers Tegrasytem™ polisher. Grain mounts were washed in ethyl alcohol and placed in an ultrasonic bath of deionized water for 2-5 minutes between polishing steps and after the final 0.25 μm polish was attained. Immediately prior to loading grain mounts into the laser sample cell, unknowns and reference materials were repolished for 3 minutes to 0.25 μm, washed in ethyl alcohol and placed in an ultrasonic bath of deionized water for 2-5 minutes. Grain mounts were then dried and transferred to a reflected-light microscope, where a cotton swab soaked in acetone was used to gently scrub grain surfaces and remove any dirt or other particles. Each grain mount was viewed under the reflected light microscope to ensure the sample surface was clean of particles and free of scratches.

U/Pb and Pb/Pb isotopic ratios of the unknown samples and four zircon reference materials analysed for data quality control purposes were measured using a Finnigan ELEMENT XR double focusing magnetic sector field ICP-MS coupled to Geolas 193 nm excimer laser. Zircon grains previously imaged by BSE and CL techniques were ablated using two ablation methods:

Method 1: a 10 μm laser beam was rastered over the sample surface at a velocity of 10 $\mu m/s^{-1}$ to create a 40 x 40 μm square spot (Fig. 1a,b). Laser energy was set at 5 J/cm^2 with a laser repetition rate of 10 Hz.

Method 2: 10 μm and 20 μm diameter line rasters were employed (Fig. 1c-f) where either zircon epitaxial relationships required sampling of thin magmatic rims (10 μm lines) or, where increased precision was required (20 μm lines). In each situation, the laser beam was programmed to create a linear ablation within

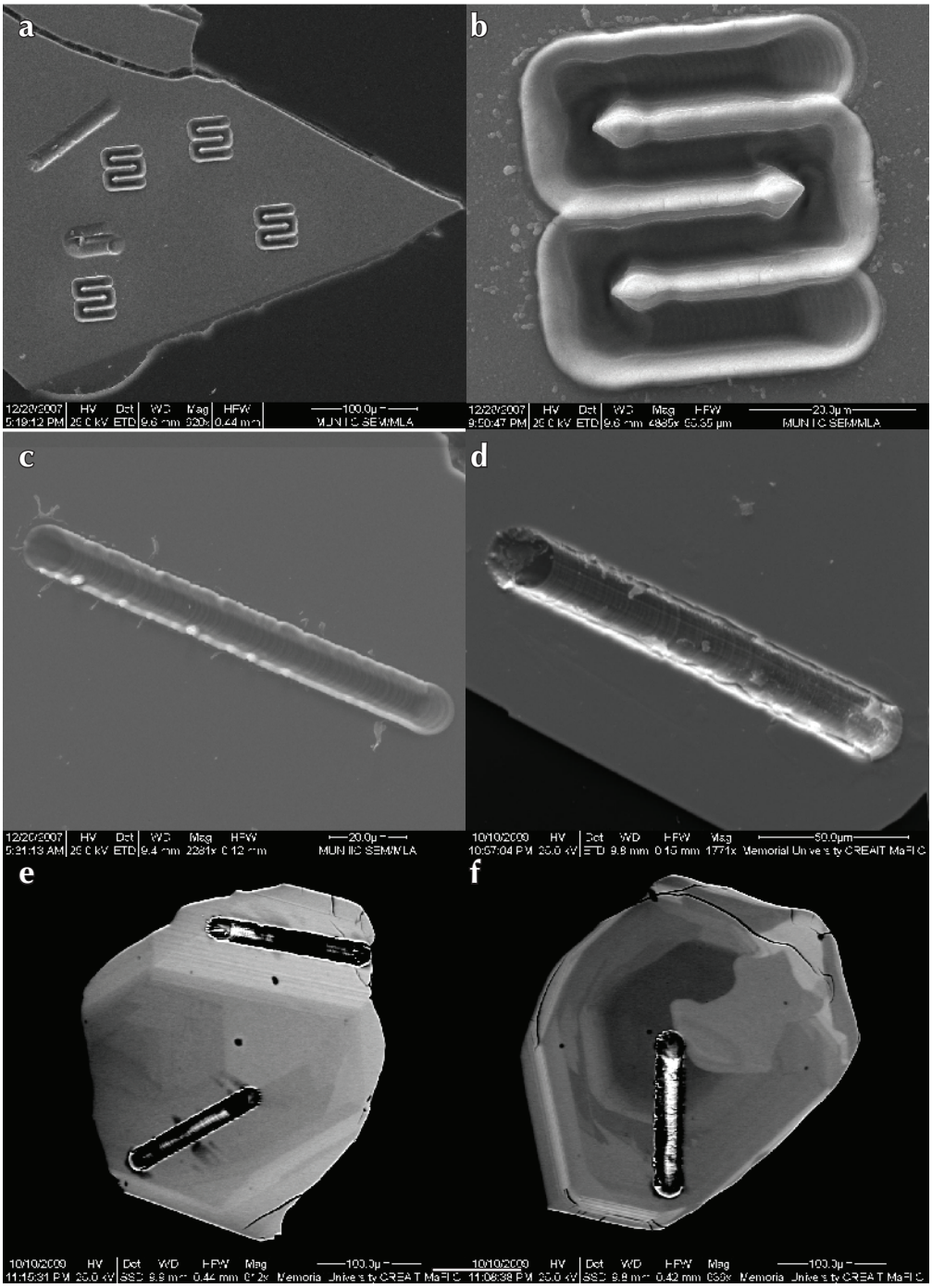

Figure 1. *Representative LAM ICP-MS pit images of ablated zircon.* ***(a)*** *Secondary electron (SE) image enlargement of 40 x 40 μm raster ablation pit in Plešovice zircon.* ***(b)*** *SE image of 40 x 40 μm raster ablation pit morphology.* ***(c)*** *Secondary electron image illustrating pit morphology of 10 μm line raster.* ***(d)*** *SE image illustrating pit morphology of 20 μm line raster.* ***(e)*** *and* ***(f)*** *Representative backscattered electron images illustrating location of 20 μm pits associated with core and rim analysis performed on complex zircon populations.*

zones of interest. Laser energy was set at 5 J/cm^2 with a laser repetition rate of 5 Hz and the stage was moved along the desired path at 1 μm/s^{-1}. Prior to data collection using linear ablation, the grain was pre-ablated by firing 5-10 shots of the laser beam (60-100 μm diameter; 5 J/cm^2 energy) onto the grain surface to remove surface contamination.

The sample introduction system enabled simultaneous nebulization of an internal standard tracer solution and laser ablation of the solid sample. The tracer solution, consisting of a mixture of natural Tl (^{205}Tl/^{203}Tl = 2.3871), ^{209}Bi and enriched ^{233}U, and ^{237}Np (concentrations of ~1 ppb per isotope) transported in a mixed Ar-He carrier gas, was employed to correct for instrumental mass bias. The various isotopic compositions of the aspirated solution were calibrated against a variety of well-characterized zircon reference materials. These zircons have a wide range of ages and U and Pb concentrations and hence, provide enough variation in isotopic ratios to cover the isotopic range of unknown zircons analysed.

Time-resolved data acquisitions (120-205 s experiments) consisted of N 20-30 s measurement of the Ar-He gas blank and aspirated tracer solution prior to introduction of ablated material.

Data were collected on unknown zircon samples and four zircon reference materials, GP-09-02 (*ca.* 9.52 Ma), Plešovice (*ca.* 337 Ma), 91500 (*ca.* 1065 Ma) and VB165 (*ca.* 2674 Ma), whose U-Pb and Pb-Pb ages had been previously determined by Isotope Dilution Thermal Ionization Mass Spectrometry (ID TIMS). Typically 10 unknowns were collected for every 6-8 analyses of the reference materials. Analysis and treatment of zircon reference materials as unknowns is a robust quality control procedure that allows assessment of the accuracy and precision of the technique during an analytical session. This approach ensures the efficiency of the mass bias correction as well as the correction for laser-induced fractionation. Additionally, the choice of zircon reference materials that encompass a range of geological time (Miocene to Archean) ensures that the accuracy of all three measured isotopic ratios, ^{207}Pb/^{235}U, ^{206}Pb/^{238}U and ^{207}Pb/^{207}Pb are monitored. Typically Archean material produces precise ^{207}Pb/^{207}Pb ages and less precise ^{207}Pb/^{235}U and ^{206}Pb/^{238}U ages. In contrast, analysis of Phanerozoic material results in precise ^{207}Pb/^{235}U and ^{206}Pb/^{238}U ages, but generally imprecise ^{207}Pb/^{207}Pb ages. This is particularly useful when analysing inherited or detrital zircon populations, which are typically characterized by a wide range of ages.

During ablation, U and Pb isotopes and tracer solution signals were acquired in time-resolved peak-jumping, pulse-counting mode with one point measured per peak. The range of masses measured for each analysis was: ^{202}(Hg) (flyback or settling mass), ^{204}(Hg), ^{203}(Tl), ^{205}(Tl), ^{206}(Pb), ^{207}(Pb), ^{209}(Bi), ^{232}(Th), ^{233}(U), ^{237}(Np) and ^{238}(U). Three oxide masses ^{249}(^{233}U^{16}O), ^{253}(^{237}Np^{16}O) and ^{254}(^{238}U^{16}O) were measured to correct for oxide formation by adding signal intensities at masses 249, 253 and 254 to the intensities at masses 233, 237 and 238, respectively. Raw data were corrected for dead time (20 ns) of the electron multiplier and processed off line in an Excel spreadsheet-based program (LAMdate - Košler *et al.*, 2002). For detailed description of the technique, see Košler *et al.* (2002) and Cox *et al.* (2003). Data reduction for ablation method 1 included correction for gas blank, laser-induced elemental fractionation of Pb and U via the intercept method after Sylvester and Ghaderi (1997) and instrument mass bias. The mass bias correction utilized the power law and the ratio measurements of the isotopic tracer solution (Horn *et al.*, 2000; Košler *et al.*, 2002).

The intercept method of Sylvester and Ghaderi (1997) was not readily applicable to the line raster analyses performed with ablation method 2 due to the minimization of elemental fractionation at the ablation site when utilizing a 1 μm/s^{-1}raster speed. In these cases, average isotopic ratios were used rather than intercept ratios.

No common Pb correction was applied to the data, however, mass 204 was monitored as an indirect assessment of common Pb concentrations. For any individual analysis, where 204 levels exceeded acceptable background levels, the data were rejected from the final dataset. Th and U concentrations for the unknown zircons were calibrated against analyses of zircon 91500. Isoplot *vs.* 2.06 of Ludwig (1999), in conjunction with the LAMdate Excel spreadsheet program was used to calculate final U-Pb ages of unknowns, and present data in graphical format (Košler *et al.,* 2002).

Final interpreted crystallization ages of both unknown and reference materials are based on calculation of concordia ages from individual U-Pb isotopic analyses that have a probability of concordance greater than 0.20. Age calculations include U decay constant uncertainties, which are plotted graphically on concordia plots. A concordia age that includes U decay constant uncertainties is considered the best estimate of the crystallization age of a sample.

ANALYSES OF REFERENCE MATERIALS AND TREATMENT OF DATA

Routine analysis of four zircon reference materials was carried out during a recent session of U-Pb isotopic data collection (October 14-19, 2009). As mentioned above, reference material analysis is a necessary quality control procedure that ensures production of geologically accurate and precise isotopic data. In addition to the two internationally recognized zircon reference materials, Plešovice (weighted mean $^{206}Pb/^{238}U$ = 337.13 ± 0.37 Ma; Slama *et al.*, 2008) and 91500 (weighted mean $^{207}Pb/^{206}Pb$ = 1066.4 ± 0.3 Ma; Schoene *et al.*, 2006), we used two internal reference materials with ID TIMS ages, GP-09-02 and VB165. GP-09-02 has a weighted mean $^{206}Pb/^{238}U$ date of 9.520 Ma (n = 7, MSWD = 0.5) with a total combined error (internal, tracer solution calibration and decay constant error) of ± 0.022 Ma (unpublished data, Boise State University Isotope Geology Laboratory). This age was corrected for initial Th/U disequilibrium. A Th/U ratio for the melt of 3 was used in the correction and resulted in increasing the $^{206}Pb/^{238}U$ date by *ca.* 70 ka. VB165 has a weighted mean $^{207}Pb/^{206}Pb$ age of 2674.3 ± 0.8 Ma (not including decay constant errors; n = 4, MSWD = 0.42; Bennett *et al.*, 2005) and a concordia age of 2671 ± 3 Ma (U decay constant uncertainties included).

Representative CL and BSE images, U-Pb concordia and weighted mean plots for LAM ICP-MS analyses collected for the four reference materials are shown in Figures 2-5. Table 1 summarizes the final calculated LAM ICP-MS ages for each sample and the accepted ID TIMS age for each zircon reference material. Uncertainties reported for all

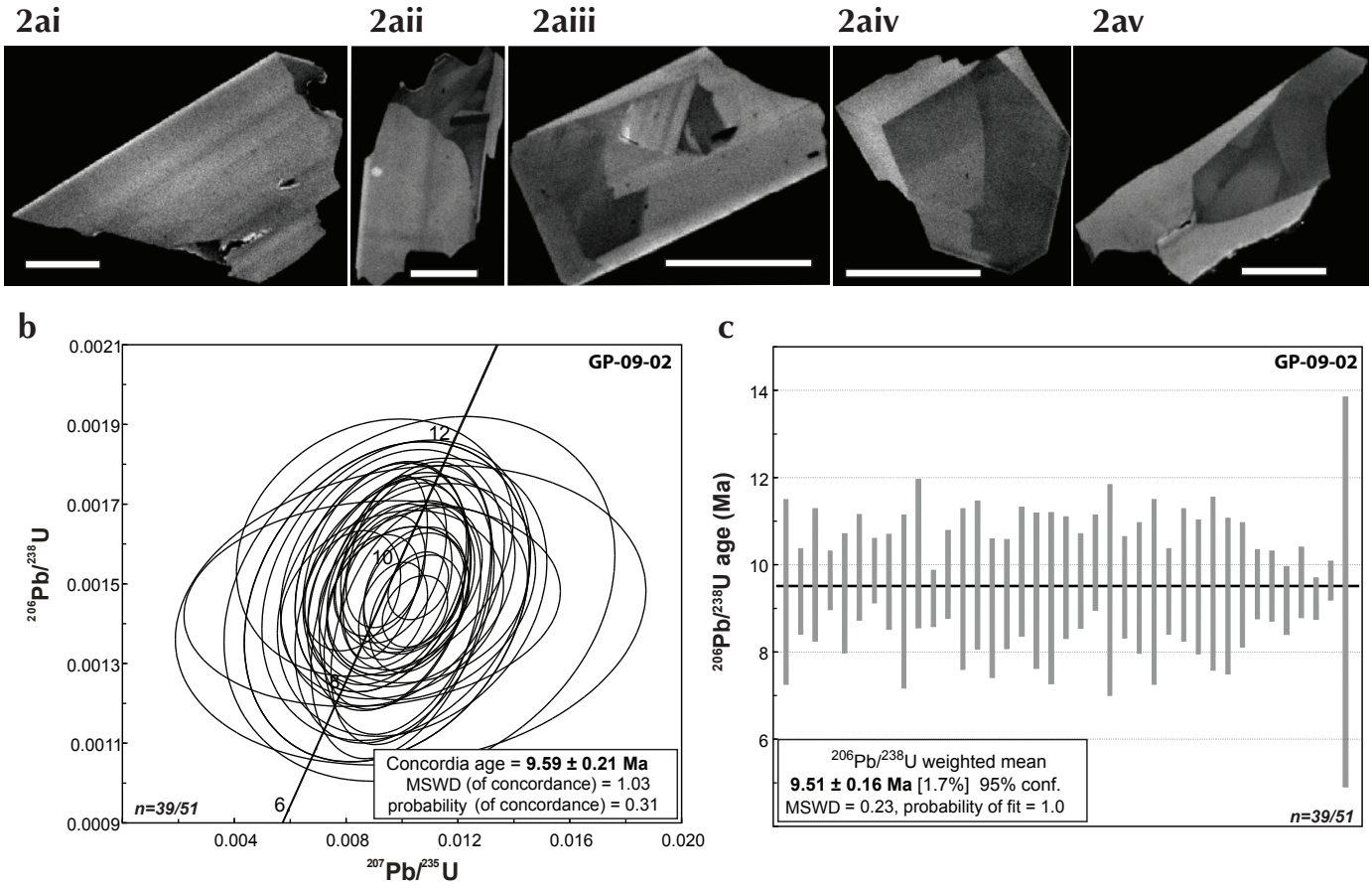

Figure 2. (a) *Representative CL images of zircon grains from reference material GP-09-02. Scale bar represents 50 μm.* ***(b)*** *Concordia diagram for U-Pb analyses from reference material GP-09-02.* ***(c)*** *Plot of weighted mean $^{206}Pb/^{238}U$ ages from GP-09-02. A total of 51 analyses of GP-09-02 were collected during data acquisition. Of the total dataset, 39 analyses have a probability of concordance greater than 0.2 and only these are used to calculate final concordia and weighted mean $^{206}Pb/^{238}U$ ages.*

calculated ages given in Table 1 and plotted on associated concordia and weighted mean diagrams are at the 2σ uncertainty level unless stated otherwise. Final age calculations include U decay constant uncertainties. Decay constant uncertainties are plotted graphically on concordia plots. The concordia age that includes U decay constant uncertainties is considered the best estimate of the crystallization age of a sample when analysed by ICP-MS. Initial filtering of data involves discarding analyses where data have been affected by instrument drift, surface contamination, ablation irregularities or high common Pb contents (*e.g.*, inclusion phases). Final age calculations involve a second filtering of data to include analyses with a probability of concordance greater than 0.20. This subset of data are then used to calculate weighted mean $^{206}Pb/^{238}U$ and $^{207}Pb/^{206}Pb$ ages (which do not include U decay constant uncertainties).

The U-Pb concordia and the weighted mean age calculations for all four reference materials analysed during this study are in excellent agreement with the corresponding ID TIMS ages (Table 1). Importantly, LAM ICP-MS isotopic data collected for sample GP-09-02 demonstrate the applicability of the technique to zircon populations as young as Miocene. A final concordia age of 9.59 ± 0.21 Ma (decay constant uncertainties included) and a $^{206}Pb/^{238}U$ weighted mean age of 9.51 ± 0.16 Ma (decay constant uncertainties not included) are in excellent agreement with the highly precise ID TIMS age of 9.520 ± 0.022 Ma. Concentration data calculated from GP-09-02 show a variation in U concentrations from 141-1325 ppm for zircon grains from sample GP-09-02. The excellent agreement between datasets for zircon reference materials of widely varying geological age, demonstrate that the LAM ICP-MS results are both precise and accurate.

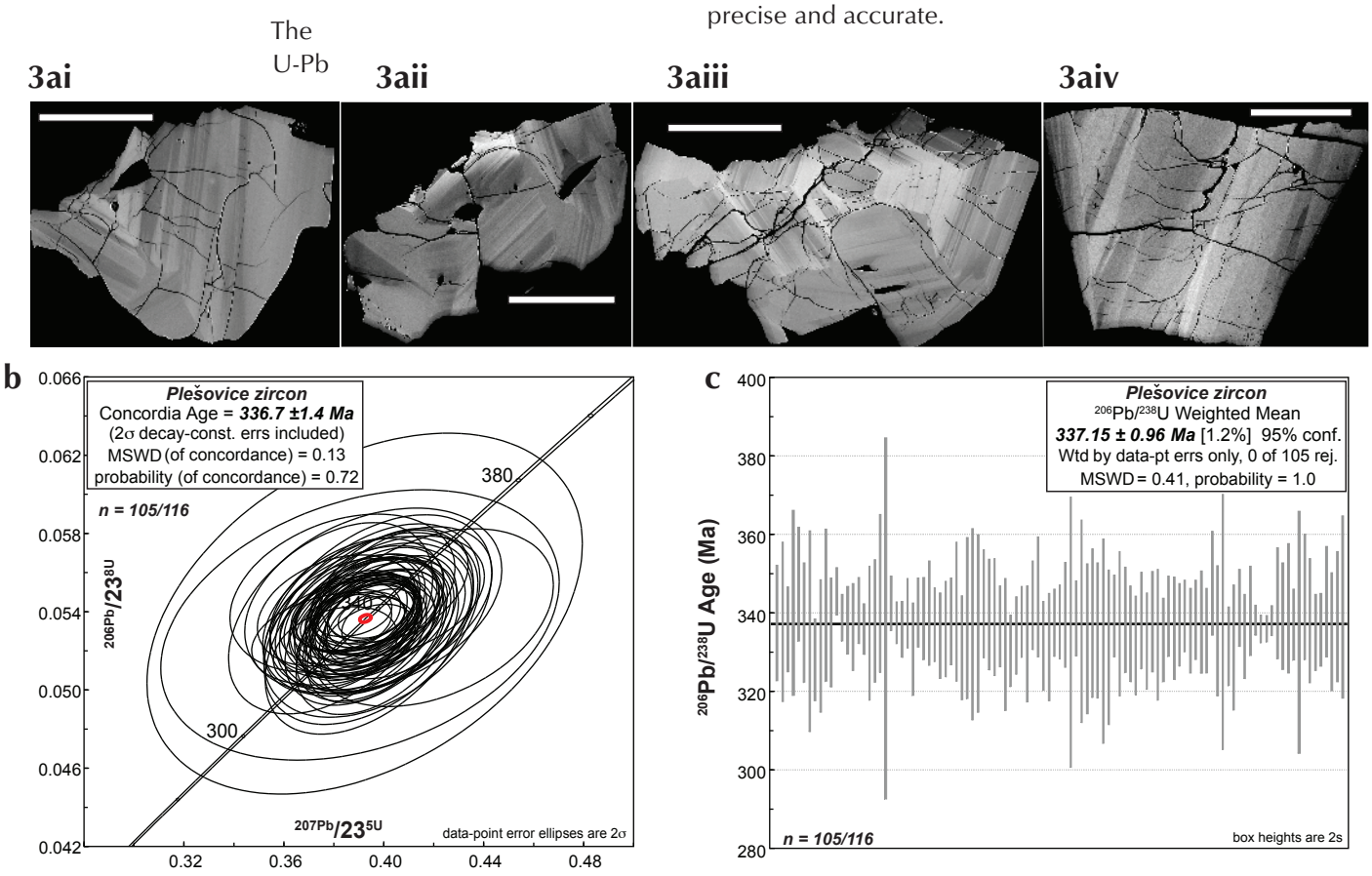

Figure 3. ***(a)*** *Representative BSE images of Plešovice zircon reference material. Scale bar represents 500 μm.* ***(b)*** *Concordia diagram for U-Pb analyses from Plešovice zircon reference material.* ***(c)*** *Plot of weighted mean $^{206}Pb/^{238}U$ ages from Plešovice zircon standard. A total of 116 analyses of the Plešovice zircon reference material were collected during data acquisition. Of the total dataset, 105 analyses had a probability of concordance greater than 0.2 and only these are used to calculate final concordia and weighted mean $^{206}Pb/^{238}U$ ages.*

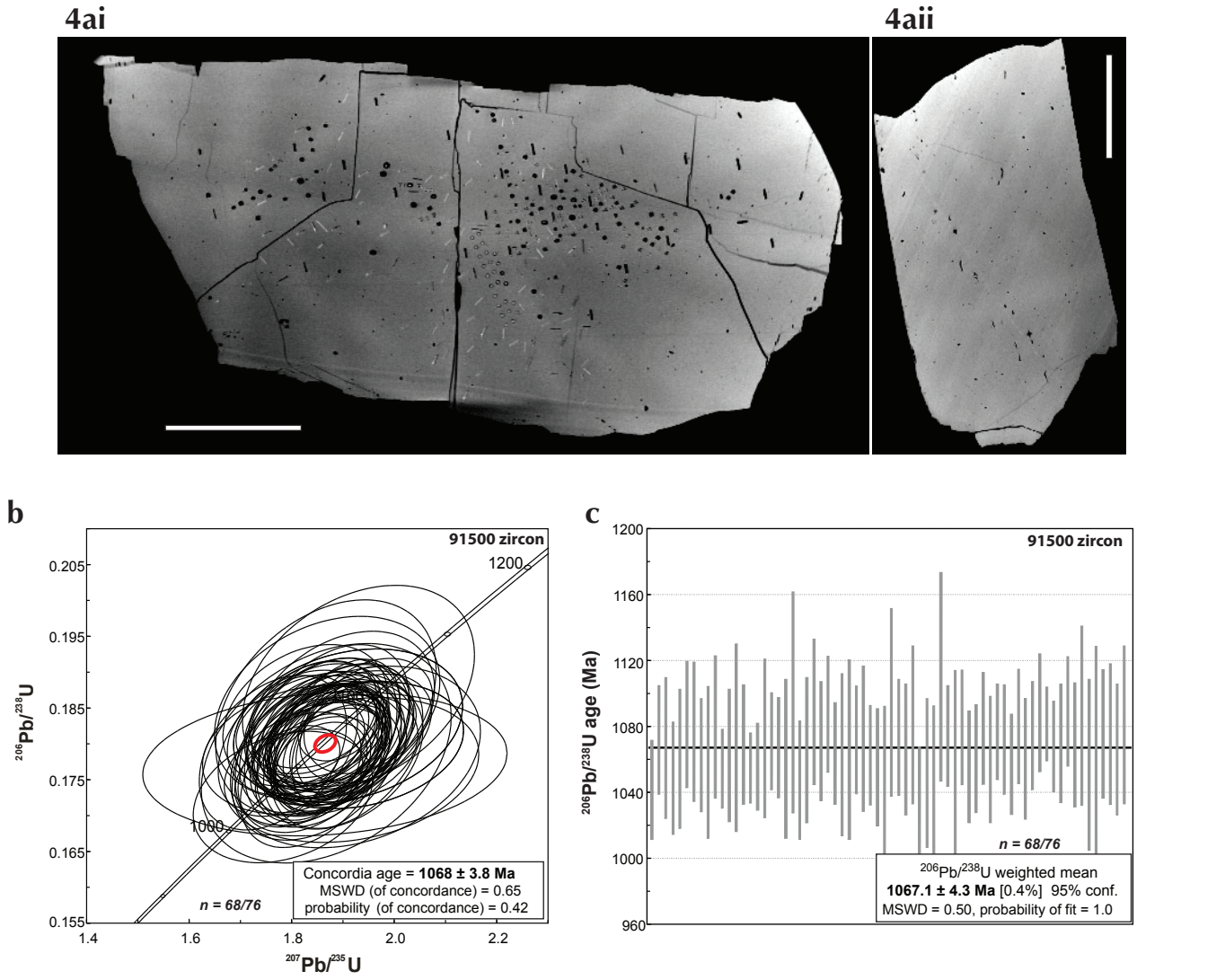

Figure 4. ***(a)*** *Representative BSE images of 91500 zircon reference material. Scale bar represents 2 mm.* ***(b)*** *Concordia diagram for U-Pb analyses from 91500 zircon reference material.* ***(c)*** *Plot of weighted mean $^{206}Pb/^{238}U$ ages from 91500 zircon reference material. A total of 76 analyses of the 91500 zircon reference material were collected during data acquisition. Of the total dataset, 68 analyses have a probability of concordance greater than 0.2 and only these are used to calculate final concordia and weighted mean $^{206}Pb/^{238}U$ ages.*

Table 1. *Summary calculated ages.*

	LAM ICP-MS		ID TIMS
	Concordia Age (2σ)	**Weighted $^{206}Pb/^{238}U$ (2σ)**	**Weighted $^{206}Pb/^{238}U$ (2σ)**
GP-09-02	9.59 ± 0.21 Ma	9.51 ± 0.16 Ma	9.520 ± 0.022 Ma
Plešovice	336.7 ± 1.4 Ma	337.15 ± 0.96 Ma	337.13 ± 0.37 Ma
91500	1068.0 ± 3.8 Ma	1067.1 ± 4.3 Ma	1065.x ± 0.4 Ma

	Concordia Age		**Weighted $^{207}Pb/^{206}Pb$**
vb165	2676.2 ± 5.7 Ma	2672.8 ± 2.3 Ma	2674.3 ± 0.8 Ma

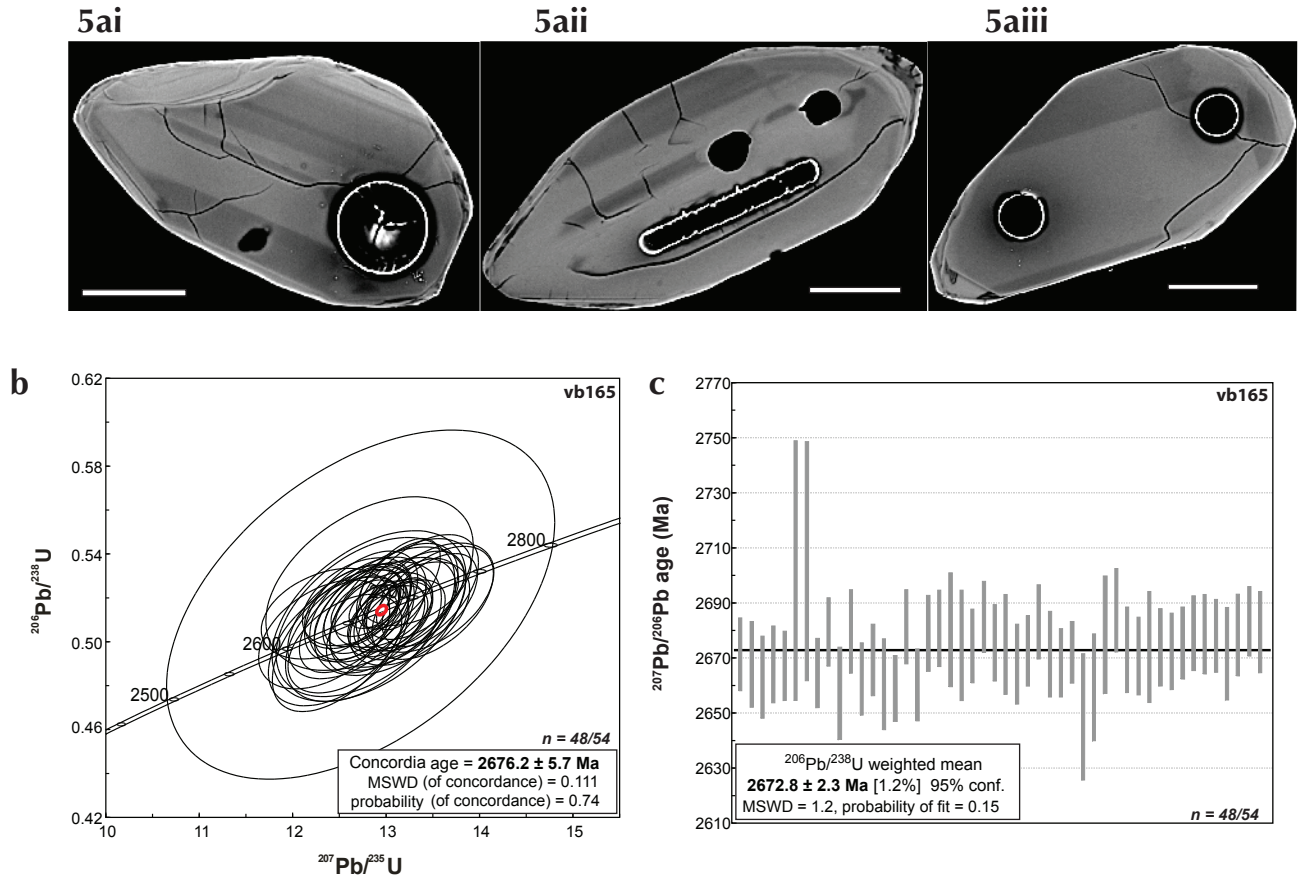

Figure 5. ***(a)*** *Representative BSE images of zircon grains from reference material vb165. Scale bar represents 50 μm.* ***(b)*** *Concordia diagram for U-Pb analyses from reference material, vb165.* ***(c)*** *Plot of weighted mean $^{207}Pb/^{206}Pb$ ages from reference material, vb165. A total of 54 analyses of the vb165 zircon reference material were collected during data acquisition. Of the total dataset, 48 analyses have a probability of concordance greater than 0.2 and only these are used to calculate final concordia and weighted mean $^{206}Pb/^{238}U$ ages.*

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