Low volume multi-shot LA-ICP-MS

[1,2]Corbett E., [1]Simonetti A., [3]Shaw P., [1]Corcoran L., [2]Crowley Q., [2]Hoare B.C.

[1]Univeristy of Notre Dame, USA.; [2]Trinity College Dublin, Ireland; [3]Nu Instruments, UK.

*contact: corbetep@tcd.ie

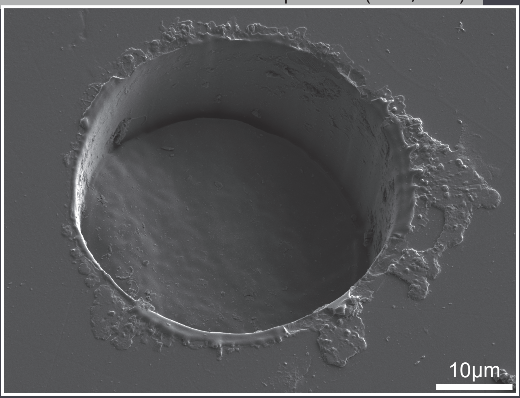
Introduction

The interaction of incident laser radiation and sample substrate is complex and difficult to predict. Natural zircons are often both structurally and chemically heterogeneous in 3-dimensional space. Encountering growth-related, structural micro-heterogeneities, inclusions and chemical complexities is almost inevitable when employing 'conventional' static, high-frequency laser sampling protocols often lasting several tens of seconds at a time.

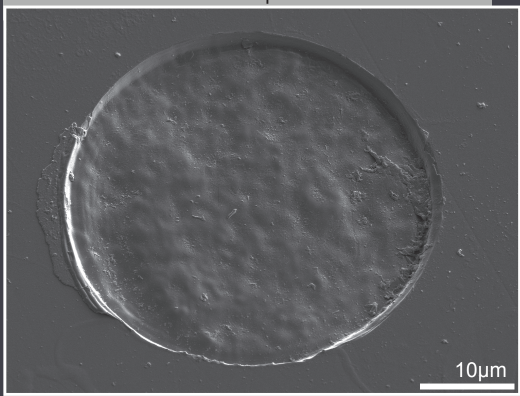
A multi-shot approach to laser ablation by contrast reduces sample exposure time to incident laser radiation by applying multiple 1 Hz shots in delayed succession to a single sampling site. This process can be conceptualised as a "slowing down" of a high-frequency (10-20 Hz) static Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) analysis. Each laser pulse to strike the sample, produces signal peak which is distinct albeit transient. The ability to integrate and collate signal pulses for a small number of consecutive laser shots (in this case,10 or 30 shots), as opposed to continuously pulsing the laser, produces precise age determinations (<1% reproducibility, 2σ level) on small sample volumes (~698µm³ on 91500 zircon standard). The multi-shot LA-ICP-MS protocol employed here effectively eliminates 'downhole' fractionation as the resultant craters are extremely shallow (as shallow as ~555nm on 91500 zircon standard) and maintain an aspect ratio of <<1. Further benefits include minimal sample destruction, a reduced probability of signal mixing (with depth) in a heterogeneous sample, as well as a reduced likelihood of plasma loading effects.

Pit depth

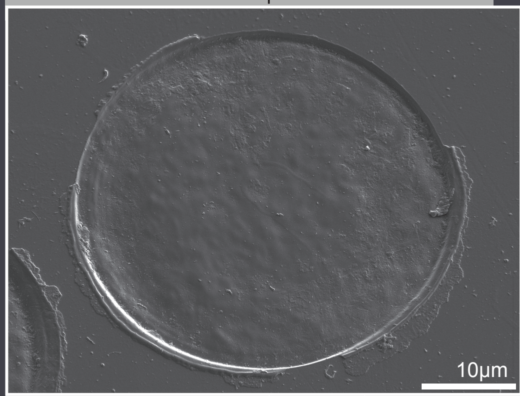
Resultant ablation crater in 91500 zircon following a 'conventional' static ablation protocol (5 Hz, 20 s)



The same 91500 zircon fragment analysed using a multi-shot static ablation protocol of **30 shots**.

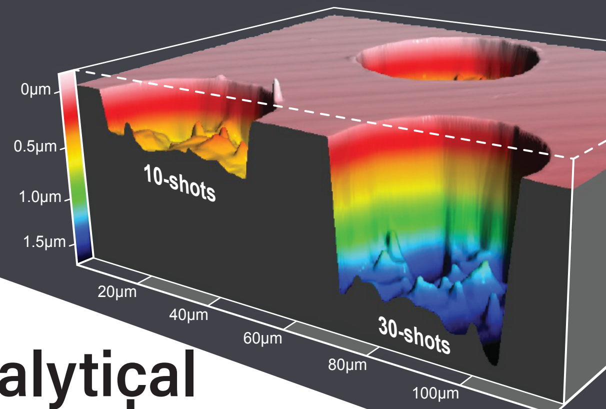


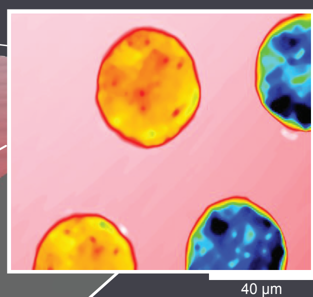
The same 91500 zircon fragment analysed using a multi-shot static ablation protocol of **10 shots**.



	91500 (30-shots)	91500 (10-shots)	Plešovice (30-shots)	Plešovice (10-shots)
Mean crater depth (µm)	1.41 ± 0.03	0.56 ± 0.02	1.67 ± 0.10	0.62 ± 0.01
Mean crater volume (µm³)	1770 ± 120	704 ± 23	2100 ± 420	779 ± 17
Crater aspect ratio	0.04	0.01	0.04	0.02

Below left: 3-D rendering of crater morphologies resulting from 30 and 10 shot analyses of Plešovice zircon (measured by white light interferometry and exaggerated in its vertical dimension. **Below right:** top-down view of the same sample surface





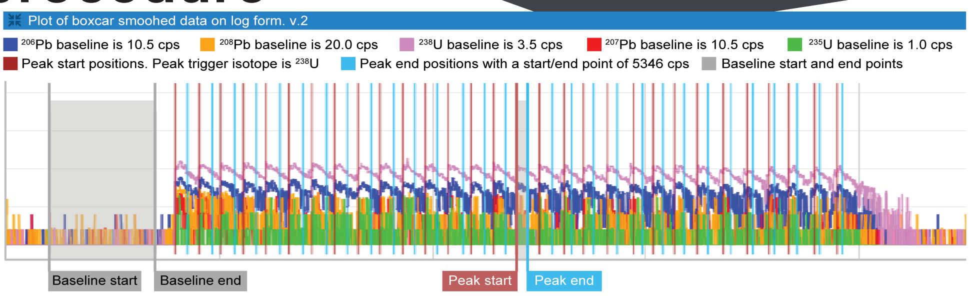
Instrumentation

Laser ablation system	
Make, model and type	ESI/New Wave Research, UP-213, solid state
Wavelength (λ)	213 nm Nd:YAG
Pulse width	3 ns
Fluence	3 Jcm^{-2}
Repetition rate	1 Hz
Spot size	40 µm
Shot count	30 and 10
Sampling mode/pattern	Sequential single shot, static spot ablation
Washout interval	3 s

ICP-MS instrument	
Make, model and type	Nu Instruments, Nu Plasma Attom HR-ICP-MS, fast-switching magnetic sector
Detector mode	Static/parked magnet, peak jump detector mode, combined with FastScan Ion optics
Forward RF power	1300 W
Reflected power	≤3 W
Sweeps	10
Cycles	10000 cycles for 30 shots 2500 cycles for 10 shots
Dwell time	500 µs on each mass
Measured masses	202, 204, **206**, 207, 208, 235, 238
Parked mass	206
Gas blank duration	30 s

Transport regime and sweep gas flow	
Laser cell design	standard 'quick-change drawer' cell (~8cm³)
Transport tubing	2m x 4.8mm (ID) of Teflon-lined Tygon® tubing
Cell atmosphere and transport gas composition	100% He in cell, Ar auxiliary gas combined via a 'Y'-style connection 20 cm before entry into the ICP
Sweep gas flow	1 Lmin^{-1} He
Auxiliary gas flow	2-3 Lmin^{-1} Ar at 110°C, maintainted by a CETAC Aridus II Desolvating Nebuliser (DSN)

Analytical procedure

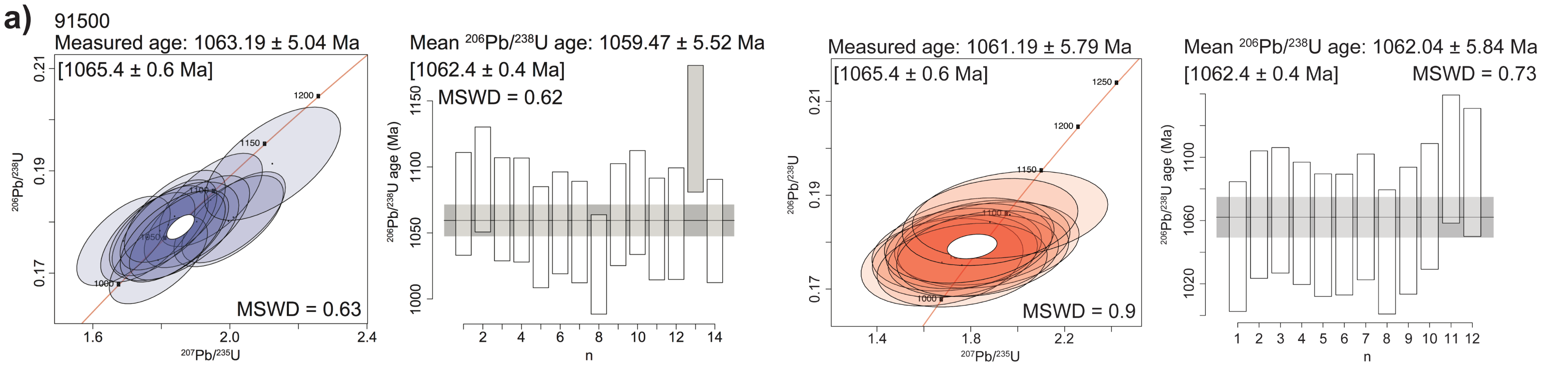


Representative 30-shot analysis of 91500 zircon, as displayed (with annotation) within the NICE script add-on to the Nu-Quant data processing software. A time-resolved analysis (TRA), begins with a determination of baseline of at least 30 s (highlighted in grey), during which time the laser-head is 'warmed-up'. This baseline continuum measurement informs all subsequent baseline subtraction calculations. Singal peaks as illustrated above represent a single laser shot, seperated by a partial washout in each case. The relatively large volume of the standard ablation cell (~8 cm³) is utilised in concert with a short washout duration (3 s) allows for the maintainance of elevated signal intensities throughout an analysis. A portion of the peak-top signal which satisfies user defined threshold parameters is integrated following baseline subtraction *i.e.* the portion between 'peak start' (red) and 'peak end' (blue) vertical bars. Cycles not satidfying the user-defined threshold parameters are ignored. The resulting integrations are collated and combined for a total of either 30 or 10 shots and constitute a single analysis.

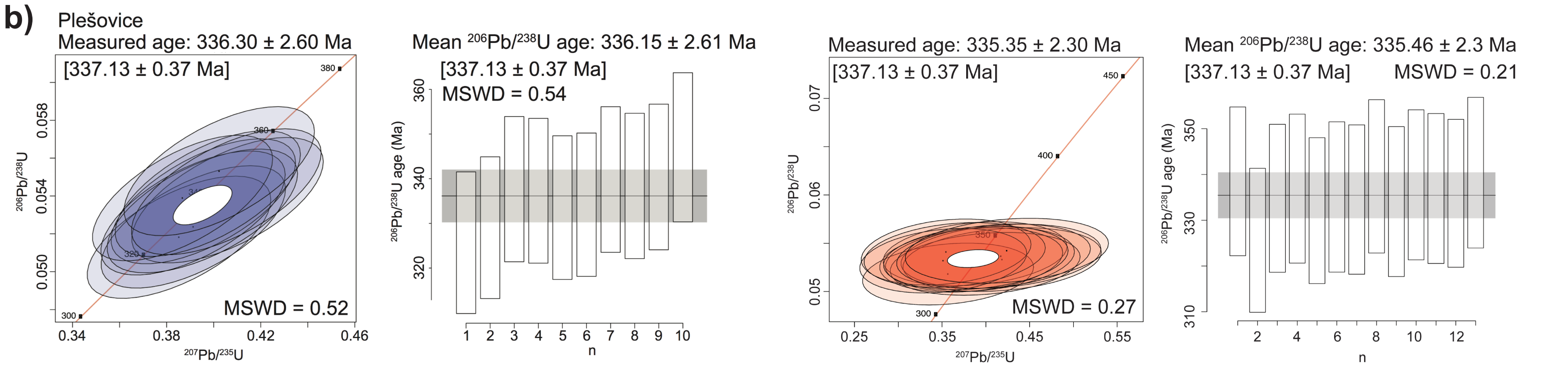
30-shot age data

10-shot age data

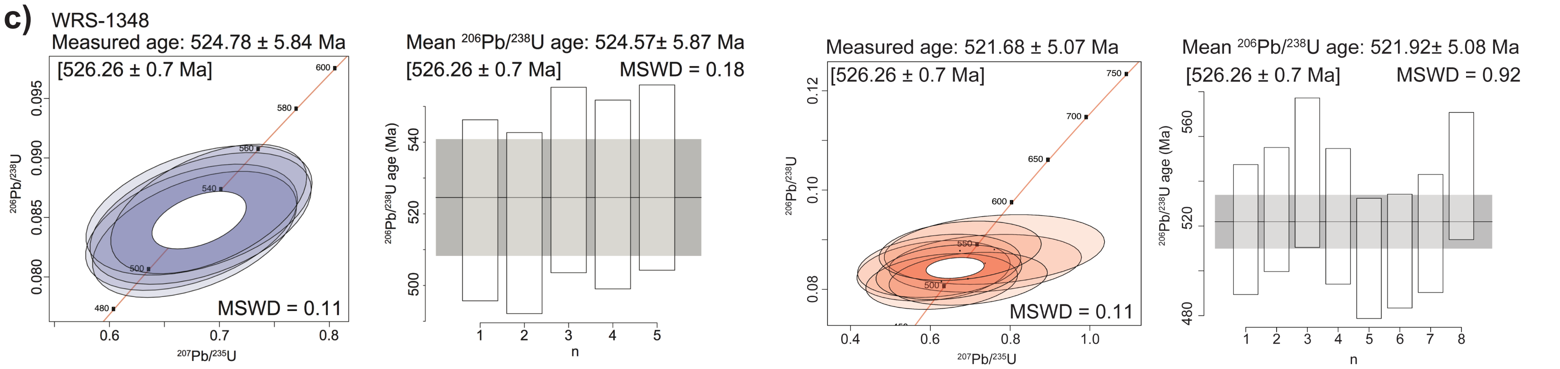
a)



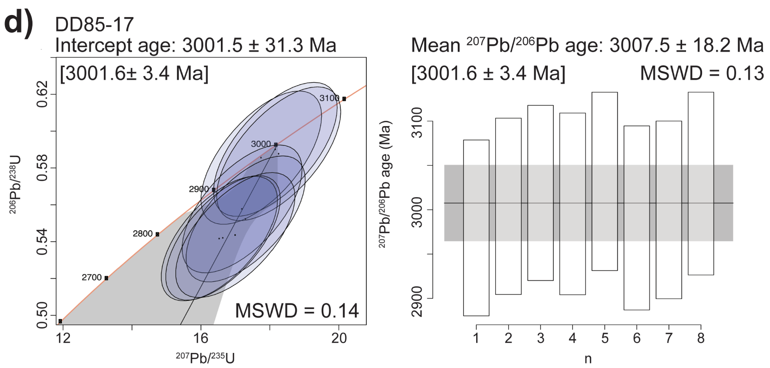
b)



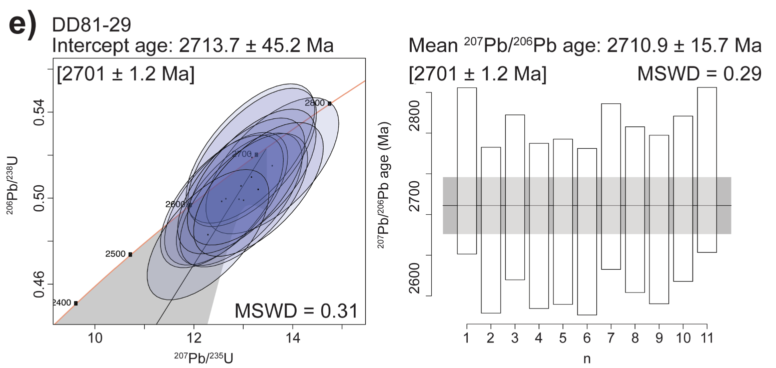
c)



d)



e)



Age data are displayed both in Wetherill Concordia space and as weighted mean age plots. Uncertainties are quoted at a 2σ level (95% con dence). Plots were generated using IsoplotR (Vermeesch, 2018). The samples used in this study have all had their ages independently verified by benchmark ID-TIMS. All the samples analysed are consistently reproducible to within 1% of their accepted age and are within an acceptable range of MSWD values.

The data reduction in terms of linear drift correction and uncertainty propagation were carried out in Mircosoft Excel®. Processed data were rejected within the same spreadsheet based upon both Rho error correlation (>1) and a discordance % threshold (usually >20%).

Conclusion

A multi-shot approach to U-Pb age determinations by LA-ICP-MS allows for precise and often indistinguishable ages compared to those determined by ID-TIMS for the same zircon standards and unknowns. The instrumental set-up requires no modification of the standard equipment for both the UP213 laser ablation system and Attom HR-ICP-MS employed here. Moreover, the standard ablation cell allows for the maintenance of elevated signal intensities when utilised in conjunction with a short washout interval between shots. The shallow ablation depths achieved by multi-shot analysis allow for precise age determinations to be made both on the micron to sub-micron scale (with depth) whilst negating the need to apply a 'downhole' inter-elemental fractionation correction.

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Working copies of the NICE script add-on software, can be acquired from the online data repository associated with the above article, or by contacting Nu.attomservice@ ametek.com directly.