

## Title Case Must be Used: Avoiding Abbreviations Where Possible

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Various zircons of Proterozoic to Oligocene ages (1060-31 Ma) were analysed by laser ablation-inductively coupled plasma-mass spectrometry. Calibration was performed using Harvard reference zircon 91500 or Australian National University reference zircon TEMORA 1 as external calibrant. The results agree with those obtained by SIMS within 2s error. Twenty-four trace and rare earth elements (P, Ti, Cr, Y, Nb, fourteen REE, Hf, Ta, Pb, Th and U) were analysed on four fragments of zircon 91500. NIST SRM 610 was used as the reference material and <sup>29</sup>Si was used as internal calibrant. Based on determinations of four fragments, this zircon shows significant intra- and inter-fragment variations in the range from 10% to 85% on a scale of 120 μm, with the variation of REE concentrations up to 38.7%, although the chondrite-normalised REE distributions are very similar. In contrast, the determined age values for zircon 91500 agree with TIMS data and are homogeneous within 8.7 Ma (2s). A two-stage ablation strategy was developed for optimising U-Pb age determinations with satisfactory trace element and REE results. The first cycle of ablation was used to collect data for age determination only, which was followed by continuous ablation on the same spot to determine REE and trace element concentrations. Based on this procedure, it was possible to measure zircon ages as low as 30.37 ± 0.39 Ma (MSWD = 1.4; 2s). Other examples for older zircons are also given.

Keywords: LA-ICP-MS, excimer laser, zircon, geochronology, trace elements.

Zircon ( $\text{ZrSiO}_4$ ) is one of the most widely used minerals for determining the age, origin and thermal history of rocks by U-Th-Pb geochronology. This is because of its high closure temperature and resistance to late disturbance (Lee *et al.* 1997, Cherniak and Watson 2001), high concentration of parent element uranium, but negligible incorporation of daughter element Pb during crystallisation, and the possible use of two geochronometers based on uranium ( $^{235}\text{U}$  and  $^{238}\text{U}$ ) decay, which can test the concordance of the determined age. Zircon frequently exhibits a complicated growth history that causes zonation on a single-grain scale particularly for minerals originating from metamorphic rocks, mandating the *in situ* microanalysis of U-Pb isotopes in such cases. On the other hand, cathodoluminescence (CL) and backscattered electron (BSE) imaging can be used to assist in the interpretation of the geological significance of multiple zircon ages. Recent studies have shown that trace element data and, in particular, the rare earth elements (REE) are helpful in clarifying the significance of age (Belousova *et al.* 2002, Hidaka *et al.* 2002, Rubatto 2002). Therefore, simultaneous *in situ* determination of U-Pb isotopes combined with trace elements is important for zircon geochronology. Although large geometry SIMS instruments (e.g., the Sensitive High Resolution Ion Micro-Probe: SHRIMP) are powerful tools for this purpose, this method suffers from a number of shortcomings including cost, access to instrumentation and SIMS's sensitivity to so-called matrix effects. Due to recent improvements in instrumentation and methodology, laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) has become a powerful alternative method, providing age dates and trace element data comparable to those of SIMS in both accuracy and precision but with significantly higher throughputs for Archaean to Tertiary zircons (Horn *et al.* 2000, Belousova *et al.* 2001, Li *et al.* 2001, Ballard *et al.* 2001, Kosler *et al.* 2002).

## Experimental

### Instrumentation

The experiments were carried out at the LA-ICP-MS laboratory of Northwest University. The ICP-MS used was an Elan 6100 DRC (Dynamic Reaction Cell) from Perkin Elmer/SCIEX (ON, Canada), which could be operated in the normal mode as a standard ICP-MS instrument or in the dynamic reaction cell (DRC) mode. In this study, determinations were carried out in the normal mode only. Therefore, details of the DRC are

not discussed here. The instrument offered a sensitivity of ca. 90 million counts per second (cps) for  $1 \mu\text{g ml}^{-1}$  of In used in standard solution nebulisation mode (Meinhard concentric nebuliser and cyclonic spray chamber). Background intensities were usually less than a few cps for elements above  $m/z = 85$  (Rb), except Sn and Pb, which might reach 100-200 cps due to a persistent memory effect (Gao *et al.* 2002).

All gas flow rates, including nebuliser, auxiliary, plasma and carrier, were optimised by ablation of NIST SRM 610 at  $80 \mu\text{m}$ , 4 Hz and  $28 \text{ J cm}^{-2}$  for maximum sensitivity for  $^{206}\text{Pb}$  while keeping  $\text{ThO}^+/\text{Th}^+$  ratios at low production ( $< 0.5\%$ ). The AutoLens was turned off during U-Pb isotopic analysis. Both calibrants and samples were arranged on the gas-line in order to improve transfer efficiency and reduce elemental fractionation. All the gas lines were purged for over one hour prior to each analytical stage to remove Pb on the gas line walls such that  $^{204}\text{Pb}$  was less than 50 cps in the gas blank. The operating parameters of the instrumentation used for U-Pb age and trace element determination are summarised in Table 1.

### Data acquisition

All LA-ICP-MS measurements were carried out using time resolved analysis (TRA) that operated in a fast, peak hopping sequence in DUAL detector mode (Table 1).

**Trace elements:** Twenty-five isotopes ( $^{29}\text{Si}$ ,  $^{31}\text{P}$ ,  $^{49}\text{Ti}$ ,  $^{53}\text{Cr}$ ,  $^{89}\text{Y}$ ,  $^{93}\text{Nb}$ ,  $^{139}\text{La}$ ,  $^{140}\text{Ce}$ ,  $^{141}\text{Pr}$ ,  $^{143}\text{Nd}$ ,  $^{147}\text{Sm}$ ,  $^{151}\text{Eu}$ ,  $^{157}\text{Gd}$ ,  $^{159}\text{Tb}$ ,  $^{163}\text{Dy}$ ,  $^{165}\text{Ho}$ ,  $^{166}\text{Er}$ ,  $^{169}\text{Tm}$ ,  $^{173}\text{Yb}$ ,  $^{175}\text{Lu}$ ,  $^{178}\text{Hf}$ ,  $^{181}\text{Ta}$ ,  $^{208}\text{Pb}$ ,  $^{232}\text{Th}$  and  $^{238}\text{U}$ ) were analysed. Each analysis consisted of approximately 30 s background acquisition (gas blank) followed by 40 s data acquisition for the twenty-five isotopes.

**U-Pb age:** Raw count rates for  $^{29}\text{Si}$ ,  $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ ,  $^{208}\text{Pb}$ ,  $^{232}\text{Th}$  and  $^{238}\text{U}$  were collected for age determination.  $^{202}\text{Hg}$  was  $< 10$  cps in the gas blank and the ablation signal in most cases. Therefore, contribution of  $^{204}\text{Hg}$  to  $^{204}\text{Pb}$  was negligible and not considered to increase the sampling efficiency of other isotopes. The integration time for the four Pb isotopes was 62.76 ms (7.31 ms for  $^{204}\text{Pb}$ , 21.74 ms for  $^{206}\text{Pb}$ , 23.71 ms for  $^{207}\text{Pb}$ , and 10 ms for  $^{208}\text{Pb}$ ), whereas for  $^{29}\text{Si}$ ,  $^{232}\text{Th}$  and  $^{238}\text{U}$  it was 10 ms for each of them. Data were acquired for 30 s with the laser off and 40 s with the laser on, giving ca. 340 (= 170 reading/replicate  $\times$  2 sweeps) mass scans for a penetration depth of ca.  $20 \mu\text{m}$ .

**Table 1.**  
**LA-ICP-MS operating conditions**

<b>Perkin-Elmer Sciex ELAN 6100DRC</b>	
Forward Power	1350-1400 W
Gas flow rate	
Nebuliser	0.60-0.80 l min <sup>-1</sup>
Auxiliary	0.80-1.10 l min <sup>-1</sup>
Plasma	14.2-15.0 l min <sup>-1</sup>
Lens Voltage	7.75-10.5 V
Auto Lens	
Trace element analysis	ON (6.5-11.25V)
U-Pb age analysis	OFF
Oxide ThO <sup>+</sup> /Th <sup>+</sup>	< 0.5%
<b>GeoLas 200M laser ablation system</b>	
Wavelength	193 nm
Energy (26-30 kV, 10 Hz)	100-110 mJ
Laser frequency	
Two stage U-Pb age and trace element analysis	10 Hz
Trace element analysis of 91500	12 Hz
Spot size	
U-Pb age analysis	30 μm
Trace element analysis	30-120 μm
He carrier gas flow	0.67 l min <sup>-1</sup>
Pulse duration	20 ns
<b>Data acquisition</b>	
Data acquisition protocol	Time Resolved Analysis (TRA)
Scanning mode	Peak hopping, 1 point per peak
Dwell time per isotope	
Trace element analysis	10 ms
U-Pb age analysis	
<sup>29</sup> Si	10 ms
<sup>204</sup> Pb+ <sup>206</sup> Pb+ <sup>207</sup> Pb+ <sup>208</sup> Pb	62.76 ms (7.31+21.74+23.71+10)
<sup>232</sup> Th	10 ms
<sup>238</sup> U	10 ms
Quadruple settling time	1 ms
Analytical time	~ 30 s gas blank and ~ 40 s ablation.
Sweeps	2
Reading/Replicate	450 (150 for blank + 200 for ablation signal + 100 for monitoring memory effect)
Replicates	1

The averaged gas blank was typically < 4000 cps for <sup>29</sup>Si; < 1000 cps for <sup>31</sup>P and <sup>53</sup>Cr; < 500 cps for <sup>49</sup>Ti; < 10 cps for <sup>89</sup>Y, <sup>93</sup>Nb, <sup>139</sup>La, <sup>169</sup>Tm, <sup>175</sup>Lu, <sup>202</sup>Hg, <sup>204</sup>Pb, <sup>206</sup>Pb, <sup>207</sup>Pb and <sup>208</sup>Pb; < 1 cps for <sup>141</sup>Pr, <sup>140</sup>Ce, <sup>143</sup>Nd, <sup>147</sup>Sm, <sup>151</sup>Eu, <sup>157</sup>Gd, <sup>159</sup>Tb, <sup>163</sup>Dy, <sup>165</sup>Ho, <sup>166</sup>Er, <sup>173</sup>Yb, <sup>179</sup>Hf, <sup>181</sup>Ta, <sup>232</sup>Th and <sup>238</sup>U.

### Data reduction and quantification

**Trace elements:** Calibration was performed using NIST SRM 610 as external calibrant in conjunction with internal standardisation using <sup>29</sup>Si according to Anczkiewicz *et al.* (2001). Data reduction was made using GLITTER 4.0 software (Macquarie University). Concentration values of NIST SRM 610 used for external calibration were taken from Pearce *et al.* (1997). Internal standardisation was used to correct for differences in the ablation rates between sample and reference material. Additionally, it also partially corrected

for matrix effects and signal drift in the ICP-MS (Longerich *et al.* 1996a, Günther *et al.* 1999). Previous work indicates that the 193 nm excimer laser shows a much smaller time-dependent elemental fractionation in comparison to other lasers (Günther *et al.* 1997).

**U-Pb age:** U, Th and Pb concentrations were calibrated by using <sup>29</sup>Si as internal calibrant and NIST SRM 610 as reference material. <sup>207</sup>Pb/<sup>206</sup>Pb and <sup>206</sup>Pb/<sup>238</sup>U ratios were calculated using GLITTER 4.0, which were then corrected using the Harvard zircon 91500 as external calibrant. The Australian National University zircon reference material TEMORA 1 (TEM) was used as external calibrant in the case of age determination of zircon 91500. According to Ballard *et al.* (2001), measured <sup>207</sup>Pb/<sup>206</sup>Pb, <sup>206</sup>Pb/<sup>238</sup>U, and <sup>208</sup>Pb/<sup>232</sup>Th ratios in zircon 91500 were averaged over the course of the analytical session and used to calculate correction factors. These correction factors were then applied to each sample to correct for both

instrumental mass bias and depth-dependent elemental and isotopic fractionation. Since the intensities of  $^{204}\text{Pb}$  were lower than 50 cps in most cases, common Pb was not subtracted in this work because of the large determination uncertainty in  $^{204}\text{Pb}$ , as already noted in other works (Belousova *et al.* 2001, Andersen 2002).

The  $^{207}\text{Pb}/^{206}\text{Pb}$  isotopic system is well suited to the dating of Mesoproterozoic and older samples. Unfortunately, low relative levels of  $^{207}\text{Pb}$  (a consequence of the relatively short half-life of its  $^{235}\text{U}$  parent) generally render this method unsuitable for precise dating of comparatively young (particularly Phanerozoic) zircon (Black *et al.* 2003). We therefore used the  $^{207}\text{Pb}/^{206}\text{Pb}$  age for zircons older than 1100 Ma and the  $^{206}\text{Pb}/^{238}\text{U}$  age for younger ones.

The U-Pb isotopic ratios of the zircon 91500 used for the calibration were the weighted means of Wiedenbeck *et al.* (1995). The  $^{207}\text{Pb}/^{235}\text{U}$  ratio was calculated from the formula:

$$^{207}\text{Pb}/^{235}\text{U} = (^{207}\text{Pb}/^{206}\text{Pb}) \times (^{206}\text{Pb}/^{238}\text{U}) \times 137.88 \quad (1)$$

according to the constant ratio of  $^{238}\text{U}/^{235}\text{U} = 137.88$  (Jaffey *et al.* 1971). U-Pb age and concordia figures were calculated using ISOPLOT (rev.3) (Ludwig 2003).

## Sample preparation

Reference materials (NIST SRM 610, 612 and 614, USGS BCR-2G and BHVO-1G glasses, and Harvard zircon 91500) and handpicked zircons were mounted on double-sided tape, cast in epoxy resin and polished to expose surfaces suitable for LA-ICP-MS analysis. The surface of the grain mounts was acid-washed in dilute  $\text{HNO}_3$  and pure ethanol to suppress lead contamination. The height of sample mounts was fixed at 7 mm to allow the jet of helium carrier gas to be properly centred. Twelve to twenty-four spots per sample were analysed for age dating with every fifth spot being conducted on zircon 91500. For trace element determination, every eighteenth, nineteenth and twentieth measurement was made on NIST SRM 610, BCR-2G and BIR-1G, respectively.

## U-Pb age

### ANU reference zircon TEMORA 1(TEM)

This reference zircon was prepared by the Australian

National University (ANU) and provided by L.P. Black and D.Y. Liu. The reference TIMS  $^{206}\text{Pb}/^{238}\text{U}$  age of this zircon is  $416.75 \pm 0.24$  Ma (95% confidence limits) (Black *et al.* 2003). Calculated from the data of Black *et al.* (2003), fifty analyses of this zircon gave a  $^{206}\text{Pb}/^{238}\text{U}$  age of  $416.8 \pm 1.1$  Ma (2s). Our twenty-four analyses of zircon TEM with a spot size of 30  $\mu\text{m}$  are illustrated in Figures 1a and 2a. The obtained intercept age and weighted average  $^{206}\text{Pb}/^{238}\text{U}$  age were  $415.0 \pm 4.5$  Ma (2s) and  $415.2 \pm 4.1$  Ma (2s), respectively.

### Harvard reference zircon 91500

Zircon 91500 is one of three frequently used natural zircon reference samples. Wiedenbeck *et al.* (1995) reported TIMS ages and selected trace element compositions of this zircon with  $^{207}\text{Pb}/^{206}\text{Pb}$  and  $^{206}\text{Pb}/^{238}\text{U}$  ages being  $1062.4 \pm 0.8$  Ma (2s) and  $1065.4 \pm 0.6$  Ma (2s), respectively. Horn *et al.* (2000) dated zircon 91500 by LA-ICP-MS using a spot size of 35-125  $\mu\text{m}$  and gave  $^{207}\text{Pb}/^{206}\text{Pb}$  age =  $1074 \pm 8$  Ma (2s) and  $^{206}\text{Pb}/^{238}\text{U}$  age =  $1061 \pm 4$  Ma (2s).

Our fragment of zircon 91500 was provided by C.A. Francis from the Harvard Mineral Museum. Twenty analyses of this zircon were made as an unknown using ANU reference zircon TEM as external calibration and a spot size of 30  $\mu\text{m}$ . The results yielded an intercept age of  $1063.3 \pm 8.7$  Ma (2s), and a weighted  $^{206}\text{Pb}/^{238}\text{U}$  age of  $1063.1 \pm 8.1$  Ma (2s) and  $^{207}\text{Pb}/^{206}\text{Pb}$  age of  $1075 \pm 16$  Ma (2s) (Figures 1b and 2b). The intercept and  $^{206}\text{Pb}/^{238}\text{U}$  ages agree well with the TIMS age of Wiedenbeck *et al.* (1995) and LA-ICP-MS age of Horn *et al.* (2000). Although the  $^{207}\text{Pb}/^{206}\text{Pb}$  age is 13 Ma older with a larger uncertainty, it is still consistent with the TIMS value within error. Additionally, our results indicate the general age homogeneity of this zircon at the scale of 30  $\mu\text{m}$ .

### Zircon 9921-4

Zircon 9921-4 is from an Oligocene nepheline syenite located along the northern margin of the North China Craton. SHRIMP analysis of this sample gives a weighted average  $^{206}\text{Pb}/^{238}\text{U}$  age of  $31.6 \pm 1.3$  Ma (2s) (Wu *et al.* 2001). Our LA-ICP-MS analysis of twenty spots yielded identical intercept and weighted average  $^{206}\text{Pb}/^{238}\text{U}$  ages of  $31.05 \pm 0.84$  Ma (2s) and  $31.08 \pm 0.42$  Ma (2s) (Figures 1d and 2d). The shift of data off the concordia curve towards a higher  $^{207}\text{Pb}/^{235}\text{U}$  ratio (Figure 1d) is not due to common Pb (although a 450 count was found

when a large spot size of 60  $\mu\text{m}$  was used, the average  $^{204}\text{Pb}$  was always less than 10 cps for 30  $\mu\text{m}$ ) and the reason for this shift is still not clear. However, if correction for the common Pb is made according to the method of Andersen (2002), most of the analyses fall on the concordia (Figure 1e), but this has little effect on the derived intercept and  $^{206}\text{Pb}/^{238}\text{U}$  ages. The corrected intercept and  $^{206}\text{Pb}/^{238}\text{U}$  ages were  $31.41 \pm 0.72$  Ma (2s) and  $30.37 \pm 0.39$  Ma (2s), respectively (Figures 1e and 2e).

### Zircon SK10-2

Zircon SK10-2 is from a gabbro, which occurs in the same area as the Oligocene nepheline syenite 9914-2. The gabbro intrudes a 120 Ma granite and thus must be younger than the granite. Thirteen analyses of this zircon showed that the age is concordant. Both the intercept and weighted average  $^{206}\text{Pb}/^{238}\text{U}$  ages were the same ( $32.10 \pm 0.49$  Ma, 2s) (Figures 1f and 2f). The spread in  $^{207}\text{Pb}/^{235}\text{U}$  is due to very low intensities of  $^{207}\text{Pb}$  (average 358 cps).

### Trace elements of Harvard zircon 91500

As one of the three widely used zircon reference samples, the isotopic composition and age of zircon 91500 are well characterised (Wiedenbeck *et al.* 1995). However, its trace element and REE compositions are less well known. Wiedenbeck *et al.* (1995) report the trace and REE compositions of this zircon determined by various methods. The results show variations of up to one order of magnitude. Although average compositions from later studies (Hoskin 1998, Belousova *et al.* 2002, Whitehouse and Platt 2003) (Table 2) are much less variable, the variations are still significant. For example, La, Nd, Eu, and Dy show > 60%, Ce, Pr, Sm, Er ~ 30%, Gd, Yb, Lu 15-17%, and Tb, Ho, Tm 6-7% variations between the averages of Hoskin (1998), Belousova *et al.* (2002) and Whitehouse and Platt (2003). The large variations of La and Pr apparently suffer from the low concentrations (< 0.1  $\mu\text{g g}^{-1}$ ) of these two elements. However, other elements have concentrations greater than 0.2  $\mu\text{g g}^{-1}$ , which are well above the limit of detection (LOD) for LA-ICP-MS and ion probe (Hoskin 1998, Belousova *et al.* 2002, Whitehouse and Platt 2003).

We analysed four different fragments of zircon 91500. Because our analyses using a spot size of 60  $\mu\text{m}$  showed that the La content of the zircon 91500 is close to the LOD, the experiments were done using a

larger spot size of 120  $\mu\text{m}$  and a high laser frequency of 12 Hz. In order to eliminate possible changes due to instrumental drift in the course of measurements, all analyses on the four fragments were carried out during the same run. The analysis cycle consisted of nine four-spot cycles with one spot on each fragment in one cycle. Data obtained during the experiments for NIST SRM 612 and 614 and USGS glasses BIR-1G and BCR-2G are also given in Table 2. It can be seen that results on these glasses agree with their recommended values (Gao *et al.* 2002 and references therein) within 1s uncertainty for NIST SRM 612, NIST SRM 614 and BCR-2G and within 2s for BIR-1G, which has lower incompatible element concentrations than BCR-2G. Data on zircon 91500 obtained with a spot size of 60  $\mu\text{m}$  during a period of 4 months are also shown in Table 2. Except for P, La, and Pr, Nd, Hf and Ta, the two sets of results using 120 and 60  $\mu\text{m}$  spots showed generally good agreement with relative errors of less than 30%. As illustrated in Table 2 and Figure 3, our 120  $\mu\text{m}$  spot analyses also demonstrated significant intra- and inter-fragment compositional variations in zircon 91500. For example, the relative standard deviation of La and Pr in Fragment 1, Cr and La in Fragment 2, La in Fragment 3, and La and Lu in Fragment 4 varied from 20 to 35%. Taken together, all 120  $\mu\text{m}$  spot analyses showed variations between 8 and 23%, except La, which was 38.7%. These variations exceed the 2s error of the weighted mean (Figure 3). Although the large variations of La and Pr may suffer from the low concentrations of these two elements, other elements have concentrations well above the LOD (Table 2). It is thus concluded that significant compositional heterogeneities exist on the 120  $\mu\text{m}$  scale. However, the rare earth element distributions are quite similar (Figure 4).

### Two-stage ablation analysis of U-Pb age and trace elements

As described above, trace and particularly rare earth element compositions of zircon are helpful in interpreting age significance (Belousova *et al.* 2002, Hidaka *et al.* 2002, Rubatto 2002). Therefore, the quasi-simultaneous analysis of U-Pb age and trace element and REE compositions on the same spot is desirable. However, due to the shorter acquisition time for data for U-Pb ages if determined at the same time as the REE, this approach will lead to reduced precision of obtained ages compared to results of age analysis only. To optimise age determinations, we adopted a two-stage ablation strategy. The first cycle of ablation

**Table 2.**

 Trace and rare earth element concentrations ( $\mu\text{g g}^{-1}$ ) of four different fragments of zircon 91500, USGS reference material glasses BIR-1G, BCR-2G and NIST SRM 612 and 614

	P	Ti	Cr	Y	Nb	La	Ce	Pr	Nd	Sm	Eu	Gd
LOD	4.4	0.10	1.7	4.00E-04	1.54	3.00E-04	3.00E-04	3.00E-04	0.002	1.00E-03	2.00E-04	1.00E-03
	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	Pb	Th	U
LOD	8.00E-05	7.00E-04	1.00E-06	1.00E-03	5.00E-04	1.00E-05	3.00E-04	5.00E-03	2.00E-04	7.00E-03	2.00E-04	2.00E-04

  

91500 fragment M, 120 $\mu\text{m}$												
	P	Ti	Cr	Y	Nb	La	Ce	Pr	Nd	Sm	Eu	Gd
F-1-1	26.2	9.9	1.61	213	0.939	0.0024	2.84	0.0149	0.280	0.623	0.285	3.71
F-1-2	27.5	5.8	1.50	194	0.924	0.0020	2.74	0.0263	0.264	0.559	0.294	3.65
F-1-3	25.6	7.5	1.51	194	0.952	0.0017	2.70	0.0133	0.261	0.527	0.258	3.25
F-1-4	27.4	7.1	1.5	171	0.801	0.0030	2.84	0.0107	0.220	0.504	0.280	3.11
F-1-5	24.9	6.8	1.42	176	0.893	0.0013	2.79	0.0119	0.196	0.484	0.244	2.97
F-1-6	26.2	5.8	1.39	171	0.864	0.0007	2.72	0.0141	0.254	0.479	0.222	2.95
F-1-7	26.6	6.0	1.77	180	0.920	0.0017	2.68	0.0111	0.239	0.495	0.264	2.35
F-1-8	25.6	6.5	2.1	196	0.840	0.0020	2.84	0.0129	0.265	0.519	0.249	2.50
F-1-9	26.3	7.8	1.69	198	0.852	0.0023	2.89	0.0150	0.264	0.534	0.281	2.68
WAv	26.2	6.84	1.59	186	0.888	0.0016	2.778	0.0137	0.246	0.521	0.261	3.00
s	2.1	0.77	0.58	11	0.041	0.0011	0.068	0.0025	0.032	0.044	0.017	0.35
	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	Pb	Th	U
F-1-1	1.218	17.41	7.06	36.9	10.47	109.7	16.39	5777	0.718	16.7	40.6	78.4
F-1-2	1.188	16.16	6.37	32.5	9.53	100.9	15.39	5352	0.625	16.3	36.9	75.2
F-1-3	1.061	15.04	6.07	31.1	8.89	91.7	14.99	5135	0.644	16.5	36.5	77.9
F-1-4	0.991	13.45	5.42	27.6	7.77	83.6	13.29	4469	0.482	17.3	32.4	81.8
F-1-5	0.964	13.73	5.59	28.8	8.05	84.6	13.59	4724	0.518	16.9	33.6	80.8
F-1-6	0.969	13.81	5.37	28.3	7.91	84.7	13.44	4647	0.501	16.7	32.8	80.1
F-1-7	0.976	14.22	5.60	29.0	8.22	87.9	14.18	4920	0.602	17.2	34.9	81.7
F-1-8	1.097	15.00	6.08	31.0	8.86	94.7	15.21	5400	0.575	17.4	38.2	84.1
F-1-9	1.130	15.84	6.14	32.3	9.15	94.7	15.70	5357	0.563	18.0	39.7	87.4
WAv	1.054	14.79	5.90	30.4	8.62	91.2	14.54	5024	0.570	17.0	35.7	80.5
s	0.074	0.96	0.40	2.2	0.64	6.2	0.83	330	0.057	1.1	2.2	2.7

  

91500 fragment N, 120 $\mu\text{m}$												
	P	Ti	Cr	Y	Nb	La	Ce	Pr	Nd	Sm	Eu	Gd
F-2-1	23.7	6.2	1.64	198.9	0.855	0.0023	2.576	0.0133	0.248	0.495	0.228	3.19
F-2-2	21.1	6.7	2.62	182.7	0.992	0.0018	2.570	0.0136	0.204	0.463	0.217	3.12
F-2-3	20.4	7.8	1.50	171.8	0.843	0.0017	2.524	0.0108	0.212	0.453	0.219	2.66
F-2-4	25.9	5.5	1.43	155.2	0.783	0.0017	2.606	0.0127	0.192	0.430	0.188	2.63
F-2-5	23.2	6.5	1.44	167.4	0.814	0.0018	2.697	0.0105	0.219	0.437	0.232	2.76
F-2-6	23.9	6.2	1.41	153.2	0.786	0.0012	2.71	0.0107	0.182	0.415	0.200	2.53
F-2-7	23.6	5.4	2.1	167.0	0.825	0.0011	2.65	0.0107	0.177	0.448	0.207	2.03
F-2-8	23.9	6.4	2.2	168.7	0.842	0.0015	2.55	0.0115	0.218	0.424	0.195	2.17
F-2-9	27.6	6.0	2.01	165.9	0.934	0.0015	2.535	0.0098	0.214	0.400	0.194	2.00
WAv	23.5	6.25	1.77	168	0.846	0.0016	2.600	0.0114	0.205	0.438	0.208	2.55
s	1.9	0.73	0.60	10	0.039	0.0011	0.064	0.0023	0.029	0.040	0.015	0.31
	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	Pb	Th	U
F-2-1	1.059	15.24	6.47	34.1	9.76	100.1	16.64	6572	0.659	14.03	33.9	66.4
F-2-2	1.038	14.50	5.89	30.7	8.69	91.7	14.25	5638	0.616	13.89	31.0	65.3
F-2-3	0.864	12.92	5.40	28.9	8.12	86.4	14.27	5598	0.578	13.99	29.5	66.5
F-2-4	0.870	12.26	4.99	25.1	7.21	77.6	11.96	4706	0.501	14.07	27.1	68.1
F-2-5	0.893	13.26	5.26	27.2	7.77	80.9	13.44	4632	0.441	15.40	30.7	73.8
F-2-6	0.825	12.29	4.93	26.0	7.45	79.2	12.31	4958	0.574	14.35	27.3	70.3
F-2-7	0.939	12.84	5.10	27.3	7.60	82.3	13.03	5359	0.584	14.92	29.7	70.7
F-2-8	0.860	12.73	5.15	27.5	7.78	83.1	14.07	5610	0.569	14.33	30.3	70.3
F-2-9	0.881	12.45	5.04	26.8	7.85	82.0	13.33	5646	0.598	14.16	29.2	68.5
WAv	0.903	13.05	5.19	27.3	7.77	82.5	13.23	5301	0.555	14.4	29.6	68.7
s	0.058	0.73	0.25	1.4	0.36	3.5	0.74	440	0.053	1.0	1.5	1.4

was used to collect data (including U, Th and Pb concentrations) for age determination, which was followed by continuous ablation on the same spot to determine REE and other trace element concentrations (except U, Th and Pb) in the second cycle of ablation. As the laser focal plane becomes higher than the ablation site after the first cycle of ablation, it was necessary to refocus the laser beam to the bottom of the ablated hole simply by lifting the ablation cell before the second cycle of ablation. The first and second cycles of ablation used the same methods for U-Pb age dating and trace element determination alone, as described above. This can be achieved simply by switching between the method menus. In this way U-Pb fractionation, which increases with the crater depth (Horn *et al.* 2000), is minimised. As the REE behave similarly during ablation, the depth-related fractionation is expected to be minimal. Table 2 and Figure 4b compare REE results for zircon 91500 using this approach with a spot size of 30  $\mu\text{m}$  and those using the conventional single stage ablation method. Although the 30  $\mu\text{m}$  results are systematically lower, their REE patterns agree with that of 120  $\mu\text{m}$ .

## Conclusions

As already documented by previous studies, laser ablation ICP-MS provides a powerful tool for determinations of U-Pb age and trace element and REE compositions of zircon. Our results show that by simple external calibration using the reference zircons 91500 and TEMORA 1, this technique yielded age dates of Proterozoic to Oligocene zircons that are comparable with SIMS ages in both accuracy and precision.

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