Evaluation of Pb-Pb and U-Pb Laser Ablation ICP-MS Zircon Dating using Matrix-Matched Calibration Samples with a Frequency Quadrupled (266 nm) Nd-YAG Laser

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This paper reports the successful application of laser ablation (LA) ICP-MS to the in situ analysis of 207Pb/206Pb and 206Pb/238U isotopic ratios on zircon crystals using matrix-matched calibration samples as external calibrators. For 207Pb/206Pb analyses, LA-ICP-MS results on reference materials (UQ-Z1 and G91500) indicated individual precisions in the range 1-10% (2σ), most analyses being better than 6%. The resulting weighted means were associated with errors typically better than 1% with ages of 1148 ± 5 Ma (2σ) and 1069 ± 9 Ma (2σ) respectively. Analyses of well-dated late Archaean granitic rocks from the western margin of the Yilgarn Craton (Australia) are presented and show a close agreement with the reference values. An orthogneiss dated at 2662 ± 4 Ma (2σ) by ion microprobe (SHRIMP) gave a 207Pb/206Pb age of 2657 ± 6 Ma (2σ). A more complex zircon population from a syenite emplaced at 2654 ± 5 Ma containing a ≤ 3.25 Ga inherited component has been investigated using a spot size of approximately 45 µm. LA-ICP-MS provides a 207Pb/206Pb age of 2653 ± 6 Ma with older grains yielding ages of up to 3.23 Ga. Dating of younger rocks (< 1 Ga), however, was limited by poor precision in the measurement of the 207Pb/206Pb isotopic ratios and by inter-element fractionation between Pb and U during the ablation processes. Using a high power density, variations of the 206Pb/238U ratios during one spot analysis appeared to correlate positively with time over the first minute of ablation. A linear fit of the data acquired during this period allowed a 206Pb/238U ratio to be calculated, thus reducing the magnitude of the fractionation and improving precision to around 5% (2σ). Results on the G91500 zircon...
U-Pb zircon geochronology is probably one of the most widely used and reliable dating techniques for the determination of (re)crystallisation age of rocks in a wide variety of environments. This is partly due to the ubiquitous presence of zircon and to the robustness of the U-Th-Pb systems in this mineral, which make it prone to survive anatexis and high-grade metamorphic conditions, as well as to pass through the sedimentary cycle (e.g. Compston and Pidgeon 1986). To date, the different competing techniques capable of dating zircon with reasonable precision are limited to the somewhat expensive SIMS and ID-TIMS analyses. Laser ablation (LA) ICP-MS has been shown to be cheaper and faster than the other two and still has the advantage of in situ analysis at the scale of a few tenths of a micrometre square, thus allowing the determination of parts of grains identified within one crystal. The first work on LA-ICP-MS used a Nd:YAG laser operated at 1064 nm (e.g. Machado and Gauthier 1996), but recent progress in laser technology make it possible to quadrupole and even to quintuple (Jeffries et al. 1998) the fundamental wavelength and to use the fourth (266 nm) and fifth (213 nm) harmonic, so improving absorption of the laser beam by the target material and thus increasing laser efficiency as well as reducing the spot size. The large inter-element fractionation observed during ablation processes (Longerich et al. 1996), however, has hampered the wide use of LA-ICP-MS in U-Pb geochronology. Only few attempts have been successful in obtaining 206Pb/238U ratios and these studies have so far dealt with the evaluation of the method using either international NIST certified reference materials, which are very different from natural zircon crystals (Hirata and Nesbitt 1995, Hirata 1997) or liquid calibrations (Horn et al. 2000). In this study, we chose to investigate the capabilities of a frequency quadrupled Nd:YAG laser in U-Pb zircon geochronology using matrix-matched reference materials (UQ-Z1 and G91500 zircon crystals). The aim of these preliminary experiments was to establish whether an analytical protocol could be proposed that would provide reproducible 206Pb/238U ratios at the precision level expected for a quadrupole ICP-MS.

Keywords: laser ablation, ICP-MS, U-Pb geochronology, zircon, inter-element fractionation.

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Experimental

Apparatus

Ablation experiments were carried out using a Spectraphysic GCR-130 Nd-YAG pulsed laser, operating in the ultraviolet region at 266 nm. The laser was operated in the Q-switched mode at a repetition rate of 10 Hz and a pulse duration of 5 ns. Under these conditions, the maximum laser energy output was 50 mJ per shot at 266 nm. A plano-convex lens was used to focus the laser beam onto the sample surface and the ablation pit diameter for zircon was kept constant at ca. 40-50 µm throughout this study. The ablation cell was made in-house of Teflon with a silica window on top with a total volume of ca. 5 cm³. Samples were placed in the cell and flushed with an argon flow for about fifteen minutes before starting measurements. Sample preparation requirements were minimal. Zircons grains, selected using a binocular microscope from non-magnetic concentrates, were mounted together with chips of reference samples in epoxy resin and slightly polished to expose the top of the grains and to give a reasonably flat surface. The mounts were then carefully washed with tri-distilled water, soap and alcohol and flushed with nitrogen before their introduction into the ablation cell. The laser apparatus was coupled to a VG Plasmaquad II ICP-MS modified by addition of a rotary pump, allowing a two fold decrease of the vacuum in the expansion chamber and, thus, enhancing sensitivity. Before each laser session, initial set-up of the instrument was done using a 5 ng g⁻¹ solution of In, Pb and U, which typically yielded a sensitivity of 100 x 10⁶ cps per µg g⁻¹ of In. The machine was then quickly set to the laser mode by diverting the argon nebuliser gas flow to the ablation cell. Conditions were subsequently refined for dry plasma analysis by ablating a NIST SRM 610 silicate glass CRM containing ca. 500 µg g⁻¹ of Pb and other trace elements. The torch box position, lens setting, gas flows and resolution were optimized and the machine was tuned on ²⁰⁸Pb in order to minimise background and Hg interference. This generally resulted in a loss of sensitivity, but in a more favourable signal/background ratio. Under these conditions, the ICP-MS achieved a typical sensitivity of up to 2000 cps per µg g⁻¹ Pb. Laser and ICP-MS operating parameters are summarized in Table 1.

All laser ablation experiments were conducted in the peak jumping acquisition mode using three points per peak. The dwell time for all peaks was set to 10.24 ms except for ²⁰⁹Hg, ²⁰⁴Pb and ²³²Th, which were counted in 5.12 ms and ²⁰⁷Pb, which was measured for a longer time (20.48 ms). A typical acquisition consisted of five repeats of 10 s each. ²³⁸U was also used to screen the data and repeats with less than 10 000 cps on this isotope were rejected from the calculation in a similar way to that described by Machado and Gauthier (1996). The samples were pre-ablated for 10 s before measurement to avoid the initial signal pulses and to achieve enhanced precision. The typical procedural runs included one gas blank measurement followed by three calibration samples, one gas blank, six unknowns, one gas blank, six unknowns and finally three calibration samples. Blanks were averaged and the values were subtracted from calibration samples and unknowns.

Pb and U-Pb fractionation

Early studies (e.g. Feng et al. 1993, Hirata and Nesbitt 1995) have shown that the main problem in Pb-Pb and U-Pb laser ablation isotopic analyses are related to mass bias, inter-elemental fractionation and interferences that can combine to restrict seriously precision and accuracy of the results. Mass bias is mainly the result of space charge effects taking place in both

Table 1. Laser and ICP-MS operating parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser type</td>
<td>Quadrupled Nd-YAG</td>
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<tr>
<td>Wavelength</td>
<td>266 nm</td>
</tr>
<tr>
<td>Laser mode</td>
<td>Q-switched</td>
</tr>
<tr>
<td>Repetition rate</td>
<td>10 Hz</td>
</tr>
<tr>
<td>Primary output power</td>
<td>50 mJ per pulse at 266 nm</td>
</tr>
<tr>
<td>Pulse width</td>
<td>5 ns</td>
</tr>
<tr>
<td>Ablation cell</td>
<td>Teflon made, 5 cm³ internal volume</td>
</tr>
<tr>
<td>Transportation system</td>
<td>Tygon tube, ca. 3 m total length</td>
</tr>
<tr>
<td>Model</td>
<td>VG PQII+ (with one additional rotary pump)</td>
</tr>
<tr>
<td>Forward power</td>
<td>1350 W</td>
</tr>
<tr>
<td>Reflected power</td>
<td>&lt; 5 W</td>
</tr>
<tr>
<td>Cool gas</td>
<td>14-15 l min⁻¹</td>
</tr>
<tr>
<td>Auxiliary Gas</td>
<td>1-1.1 l min⁻¹</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>1.1 l min⁻¹</td>
</tr>
<tr>
<td>Measured isotopes</td>
<td>²⁰⁸Hg, ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb, ²³²Th, ²³⁸U</td>
</tr>
<tr>
<td>Dwell time per isotope</td>
<td>10.24 ms (20.48 on ²⁰⁷Pb, 5.12 on ²⁰⁹Hg, ²⁰⁸Pb and ²³²Th)</td>
</tr>
<tr>
<td>Quad settle time</td>
<td>10 ms</td>
</tr>
<tr>
<td>Points/peak</td>
<td>3</td>
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<tr>
<td>Pre-ablation time</td>
<td>3.10 s</td>
</tr>
<tr>
<td>Acquisition time</td>
<td>10 s</td>
</tr>
<tr>
<td>No. of repeats</td>
<td>5</td>
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</tbody>
</table>
the plasma and the sampler-skimmer cone interface region (Hirata 1996). This fractionation favours the heavy isotopes, which are preferentially transmitted, while lighter isotopes are more easily dispersed away from their trajectory. In this work, the magnitude of mass bias was evaluated using external calibration procedures either on the silicate glass NIST SRM 610 or on the natural zircon crystals UQZ1 and G91500. Results of these ablation experiments are reported in Figure 1, which shows a series of $^{207}\text{Pb}/^{206}\text{Pb}$ ratio measurements performed within a period of a single day (Figure 1a and 1b) or over a few weeks (Figure 1c). For the NIST SRM 610 glass, the data yielded a weighted mean of $0.9111 \pm 0.0052$ (2s), which gives a mass bias value of 0.16% when compared to the reference value of Walder et al. (1993). Measurements achieved on the G91500 gem crystal (Wiedenbeck et al. 1995) provided a weighted mean of $0.07503 \pm 0.00032$
corresponding to an apparent age of 1069 ± 9 Ma. The calculated mass bias is almost identical to that obtained on the NIST SRM 610 glass reference material, with a value of 0.19%. The zircon reference sample UQZ1 (Machado and Gauthier 1996) was also measured over a period of several months and the results of more than fifty spots gave a weighted mean 207Pb/206Pb ratio of 0.7807 ± 0.00019 (2s), which results in an apparent age of 1148 ± 5 Ma and a mean calculated mass bias of about 0.3%. This slightly higher value is thought to reflect variations in mass bias that are also dependent on the daily operating conditions. In spite of very different optical, thermal, chemical and mineralogical characteristics, the NIST SRM 610 synthetic silicate glass (rhyolitic glass) and natural zircon crystals (light pink zirconium silicates) yielded similar mass bias values, which suggests that, for the nanosecond UV laser, and at the precision level achieved with our apparatus, this parameter is not controlled by properties of the target material. The requirement for matrix matched calibration samples, which is so important for quantitative analyses (Jarvis and Williams 1993), is thus not necessary in Pb-Pb isotopic ratio determination. Based on this observation, the NIST SRM silicate glass or the UQ-Z1 zircon were both used to correct for mass bias, although, taking into account the requirements of sample preparation, it was found easier to include chips of the UQ-Z1 zircon together with “unknown” zircon crystals in the epoxy resin. During a set of measurements (see section above), the mean of the first three calibration samples was used to correct the first six unknowns. The last six unknowns were corrected using the mean of the last three calibration samples. Each ratio was corrected for mass bias following the relationship below:

\[ R_{\text{corr}} = R_{\text{meas}} \cdot (1 + C) \delta m \]  

where \( \delta m \) is the mass difference and \( C \) the mass bias correcting factor determined from measurements on reference samples.

In contrast to Pb/Pb ratios, for which the mass bias correction is straightforward and significantly lower than the individual analytical precision of each spot analysis (between 0.5 and 5% at the 1s level), elemental fractionation between U and Pb is a more serious problem. As a consequence of the very different behaviour of U relative to Pb during ablation, U-Pb ratios evolve during each individual spot analysis. Figure 2a shows the evolution of the 206Pb/238U ratio against time for laser experiments performed with a ca. 30 µm spot on the NIST SRM 610, where each repeat had a 2 s duration. Excluding the 1 s initial pulse, the first part of the diagram (i.e. from 10 to 30 s), yields a regular increase in the 206Pb/238U ratio, which appears to be a linear function of time (see inset in Figure 2a). Using a linear least squares fit, the “initial” 206Pb/238U ratio can be calculated with a precision of around 5% (2s), which compares favourably with the

Figure 2. (a) Evolution of the 206Pb/238U ratio against time for a 30 µm diameter spot (F) drilled in the NIST SRM 610 glass CRM. After the first 10 s, which corresponds to the initial pulse, the 204Pb/238U ratio yielded a linear correlation with time (inset). Defocusing of the laser beam and loss of energy coupled to the sample is responsible for the large increase of the U-Pb ratio observed (main figure). (b) Plot of 206Pb/238U ratio against time for the zircon reference sample UQ-Z1 (Machado and Gauthier 1996) for a spot diameter (F) of ca. 45 µm; slope of best-fit line = 0.0318 ± 0.0060, intercept = 0.3915 ± 0.019, MSWD = 0.29, probability = 0.83. (c) Plot of 206Pb/238U ratio against time for the zircon reference sample G91500 (Wiedenbeck et al. 1995) for a spot diameter (F) of ca. 45 µm; slope of best-fit line = 0.0223 ± 0.0051, intercept = 0.3429 ± 0.016, MSWD = 0.70, probability = 0.55. All error bars represent 2s.
10-15% measurement error. In addition, the magnitude of the inter-element fractionation correction is significantly reduced, thus improving accuracy in the determination of the $^{206}\text{Pb}/^{238}\text{U}$ ratio. The calculated ratio is then used to define the magnitude of the elemental fractionation, and is corrected by comparison with values obtained from a set of measurements performed on a reference material (Figures 2b and c). In the last part of the diagram, the $^{206}\text{Pb}/^{238}\text{U}$ ratio increases significantly and can even reach four times the value of the true ratio. Absorption of the optical energy involves a series of mechanisms that can cause melting, vaporisation, ionisation, ejection of particles (clusters and solid fragments), plasma initiation and expansion. At the laser power density used in this study, we observed that the true isotopic ratio (0.2249 for NIST SRM 610) was approached in the first measurements but ratios were always higher, suggesting that laser ablation is dominated by thermal vaporisation. If ionisation were the main operating mechanism, the $^{206}\text{Pb}/^{238}\text{U}$ ratio would be lower than the true value, since U is easier to ionise (6.194 eV) than Pb (7.417 eV). The regular increase of the $^{206}\text{Pb}/^{238}\text{U}$ ratio is thought to reflect progressive defocusing of the laser beam as it drills through the sample and an associated loss of energy imparted to the sample. This results in a preferential enrichment of Pb in the vapour phase due to an almost two times lower latent heat of vaporisation of Pb than for U. Absorption or scattering of a proportion of the laser energy by the optically dense vapour plume above the ablation crater can further cause a decrease in the amount of energy transferred into the sample and thus contribute to the selective enrichment of Pb in the vapour phase. A plot of the $^{206}\text{Pb}/^{238}\text{U}$ ratio against laser flashlamp voltage (Figure 3) shows that the Pb/U ratios are more reproducible and decrease with increasing laser energy. Decreasing the flashlamp voltage causes a decrease in the laser incident power, which results in lower signal intensity and poorer reproducibility. The Pb/U ratio, however, is significantly different, indicating preferential Pb enrichment and, thus, substantiating the suggestion that a thermal mechanism appears to govern the laser ablation process and could describe the ablation behaviour and inter-element fractionation at low laser power density. Horn et al. (2000) observed a similar positive correlation between Pb/U fractionation and depth with a 15 ns pulse duration excimer laser (193 nm) and proposed that, at this wavelength, a mechanism such as selective condensation of refractory elements (U) on the crater walls successfully describes inter-element fractionation. A less efficient ejection of the particles as the crater deepens can also be invoked at 266 nm and could explain the large increase of the U-Pb ratio in the last part of Figure 2a. From this point of view, it is interesting to note that the relationship between crater aspect ratio (diameter against depth) and fractionation observed by Eggins et al. (1998) is an important parameter and that the best results are obtained with a ratio close to 1. Although the drilling rate should be different in the case of the NIST SRM 610 and natural zircons, it can be seen that the bigger the spot diameter, the longer the linear correlation.

Interference and common lead correction

Using a dry plasma, interferences are generally not a problem except for isobaric interferences of $^{204}\text{Hg}$ on $^{204}\text{Pb}$. Hirata and Nesbitt (1995) suggested that most of the Hg comes from the argon itself and that filtering the gas using charcoal reduced this interference by 30 to 90%. In the course of this study, this interference was corrected by monitoring $^{202}\text{Hg}$ and assuming a $^{204}\text{Hg}/^{202}\text{Hg}$ ratio of 0.2293. The remaining $^{204}\text{Pb}$ was ascribed to common Pb. The difficulty of measuring precisely the small $^{204}\text{Pb}$ isotope generally makes any common lead correction inaccurate and
we used therefore a correction threshold based on the limit of detection (LOD), defined as three times the standard deviation of the intensity in cps of 204Pb in the blank. Most analyses (unknowns and calibration samples) yielded a 204Pb intensity lower than the LOD and, thus, were not corrected for common Pb. For the other analyses, a 204Pb correction was applied, based on an assumed common Pb composition modelled as contemporaneous Pb (Stacey and Kramers 1975). Corrected isotopic ratios and weighted averages were then calculated according to Ludwig (1987). Analytical uncertainties are listed as 1s and uncertainties in ages as 95% confidence levels. Decay constants are those recommended by the IUGS subcommission on geochronology (Steiger and Jäger 1977).

Results

The zircon populations selected for this study have well known ages as they have already been subjected to U-Pb analyses, either by the conventional ID-TIMS method, or by using the SHRIMP, or in some cases by both. The samples come from a wide variety of rocks and cover an age span ranging from late Archaean to Late Palaeozoic. The two first examples are from Archaean rocks of the Jimperding Metamorphic Belt located on the western margin of the Yilgarn Craton (Western Australia) which have been investigated only for 207Pb/206Pb systematics. U-Pb analyses are presented for younger material, i.e. the ca. 1 Ga old G91500 zircon reference sample and Late Palaeozoic zircons from an alkali granite from Corsica (France). In all cases, the UQ-Z1 zircon crystal (Machado and Gauthier 1996) was used as an external calibration sample for evaluating the magnitude of the mass bias and inter-element fractionation.

207Pb/206Pb isotopic measurements

Samples W400 and W395 (Jimpereing Metamorphic Belt, Western Australia): U-Pb ages from these two samples have been obtained previously by ID-TIMS and SHRIMP analyses (see details in Bosch et al. 1996 and Pidgeon et al. 1996). W400 is an orthogneiss for which crystallisation and emplacement has been dated at 2662 ± 4 Ma by SHRIMP (Figure 4a). The zircon population shows a simple behaviour with all points being concordant to slightly discordant. SEM observation of SHRIMP spots showed the occurrence of unzoned recrystallised domains that have statistically younger ages (black symbols in Figure 4a). Recrystallisation is attributed to amphibolite facies regional metamorphism which peaked at ca. 2650 Ma in this area (Nemchin et al. 1994). Laser ablation analyses were performed on non-magnetic zircon crystals selected to be flawless, with no visible fractures or inclusions. The 207Pb/206Pb ratios for thirteen spots on thirteen grains are reported in Table 2. All analyses showed a small amount of 204Pb, but below the LOD (55 cps), except analysis #3, which yielded an unusually high 204Pb intensity (246 cps). The applied correction gave a much younger age than the remainder.

Figure 4. Isotopic results for the W400 orthogneiss (Jimpereing Metamorphic Belt, Western Australia). (a) Concordia diagram for SHRIMP analyses. Polygons represent 1s uncertainties. Unfilled polygons: main euhedral population (2664 ± 4 Ma); black polygons: unzoned domains (2640 ± 16 Ma); grey polygon: core (2684 ± 14 Ma). (b) Laser ablation ICP-MS 207Pb/206Pb diagram, showing a mean value of 0.18050 ± 0.00064 (MSWD = 0.5), giving an age of 2657 ± 6 Ma. Error bars are 2s.
Table 2.
Laser ablation ICP-MS isotopic results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Measured Corrected atomic ratios</th>
<th>Apparent age (Ma)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>204Pb (cps)</td>
<td>206Pb (cps)</td>
</tr>
<tr>
<td>CINQUE FRATI- Alkali granite- Corsica- 286 ± 2 Ma (ref. in Cocherie et al. 1999) Properties: large grains (&gt; 200 µm), euhedral, translucent LOD (204Pb): 46 cps</td>
<td></td>
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<tr>
<td>5FRATI-1</td>
<td>204Pb 1 92647 0.05242 0.6 0.2879 0.344 0.0441 7.9</td>
<td>5FRATI-2 106867 0.05157 0.7 0.2811 0.309 0.0454 8.2</td>
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<tr>
<td>5FRATI-2</td>
<td>5FRATI-3 100047 0.05208 0.5 0.2793 0.305 0.0452 8.0</td>
<td>5FRATI-4 93551 0.05191 1.1 0.2818 0.331 0.0497 17.8</td>
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<tr>
<td>5FRATI-3</td>
<td>205FRATI-5 82964 0.05198 1.6 0.2679 0.294 0.0417 9.3</td>
<td>206FRATI-6 38821 0.05202 0.6 0.2568 0.291 0.0414 9.0</td>
</tr>
<tr>
<td>5FRATI-4</td>
<td>5FRATI-7 1 19464 0.05083 0.6 0.2563 0.291 0.0414 9.0</td>
<td>5FRATI-8 3 43933 0.05098 2.3 0.2430 0.242 0.0472 7.6</td>
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<tr>
<td>5FRATI-5</td>
<td>5FRATI-9 1 47937 0.05303 1.0 0.2924 0.268 0.0446 9.3</td>
<td>Mean: 0.05236 - 0.05236 - 0.0445 - 300.1 -</td>
</tr>
<tr>
<td>5FRATI-6</td>
<td>LOD (1s): 0.00128 - 0.00128 - 0.0033 - 55.0 -</td>
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<tr>
<td>5FRATI-7</td>
<td>G91500- Zircon standard- Canada-1065 ± 1 Ma (ref. in Wiedenbeck et al. 1995) Properties: large fragments (mm), light pink LOD (100Pb): 25 cps</td>
<td></td>
</tr>
<tr>
<td>5FRATI-8</td>
<td>G91500-1 4 31336 0.07500 1.2 0.0989 0.213 0.1818 2.3</td>
<td>5FRATI-9 1 19464 0.05083 0.6 0.2563 0.291 0.0414 9.0</td>
</tr>
<tr>
<td>5FRATI-9</td>
<td>5FRATI-10 1 19464 0.05083 0.6 0.2563 0.291 0.0414 9.0</td>
<td>Mean: 0.05236 - 0.2613 0.281 0.0445 -</td>
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<tr>
<td>5FRATI-10</td>
<td>LOD (1s): 0.00075 - 0.00075 - 0.0064 - 20.4 -</td>
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<tr>
<td>5FRATI-11</td>
<td>W395- Syenite- Western Australia- 2654 ± 5 Ma (ref. in Pidgeon et al. 1996) Properties: small grains (&lt;105-135 µm), euhedral, pink, non magnetic LOD (100Pb): 51 cps</td>
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<tr>
<td>5FRATI-12</td>
<td>W395-1-1 21 224411 0.19282 3.6 0.1135 0.311 - -</td>
<td>W395-1-2 57 226556 0.21508 0.2 0.0938 0.270 - -</td>
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<td>W395-1-4 27 304101 0.25109 2.1 0.0788 0.241 - -</td>
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<td>W395-1-6 3 305002 0.17980 0.2 0.0683 0.263 - -</td>
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<td>5FRATI-16</td>
<td>W395-1-8 3 - - -</td>
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This point was, therefore, discarded from the age calculation. The twelve remaining analyses were combined to give a weighted mean of 0.18050 ± 0.00064 (2σ) corresponding to an age of 2657 ± 6 Ma (Figure 4b). The laser ablation value is very close to the 2662 Ma SHRIMP reference value and shows comparable error margins. Unlike the SHRIMP analyses, LA-ICP-MS analyses were not capable of detecting the younger recrystallised domains, although some young ages would suggest that such domains could have been sampled by the laser beam. The short time span between igneous crystallisation and recrystallisation, and this point was, therefore, discarded from the age calculation. The twelve remaining analyses were combined to give a weighted mean of 0.18050 ± 0.00064 (2σ) corresponding to an age of 2657 ± 6 Ma (Figure 4b). The laser ablation value is very close to the 2662 Ma SHRIMP reference value and shows comparable error margins. Unlike the SHRIMP analyses, LA-ICP-MS analyses were not capable of detecting the younger recrystallised domains, although some young ages would suggest that such domains could have been sampled by the laser beam. The short time span between igneous crystallisation and recrystallisation,
and the low precision of the LA-ICP-MS analyses make the age difference unresolvable.

The syenite W395 outcrops in the same area and was analysed because of a more complex zircon population with evidence of an inherited component in the source region of the magma (Figure 5a). SHRIMP analyses yielded an age of 2654 ± 5 Ma, interpreted as dating emplacement and crystallisation of the syenite. In addition, SHRIMP spot analyses identified an inherited component with ages reaching values of about 3.25 Ga and very discordant analyses between 2660 and 3250 Ma. Seventeen grains were analysed by LA-ICP-MS and were found to contain a small amount of 204Pb, below the LOD, except for two spots (#1-2 and 3-1) for which the beam may have struck a crack in the grain or an inclusion. The 207Pb/206Pb age spectrum, ranges from 2616 ± 88 Ma (2s) to 3233 ± 56 Ma (2s), and confirms the age pattern observed by SHRIMP analyses. A histogram showing the distribution of the 207Pb/206Pb ratios (Figure 5b) indicates that most analyses cluster close to 2650 Ma with a weighted mean of 0.18002 ± 0.00063 (2s), corresponding to an age of 2653 ± 6 Ma. This age is in close agreement with the SHRIMP value of 2654 ± 5 Ma. Another interesting result is the identification of the inherited component, with the oldest LA-ICP-MS value (3233 Ma) being also very close to the oldest SHRIMP value (3250 Ma). Results from grain #6, which was probed in two places, also demonstrate that the spatial resolution available with our laser system has the capability to analyse distinct domains present within one crystal (see Table 2), although the intermediate value of 2848 Ma for the core (#6-2) may indicate that the beam straddled the magmatic growth zone.

206Pb/238U isotopic measurements

Sample G91500 (Ontario, Canada): Fragments of this 238 g zircon crystal are used as a reference sample for the calibration of the U-Pb ratios measured by SIMS on the CAMECA IMS1270 commissioned at the CRPG Nancy (France) and at Stockholm (Sweden). The crystal has been calibrated by different laboratories (see Wiedenbeck et al. 1995) and is known to be homogeneous and concordant at about 1065 Ma with a 207Pb/206Pb of 0.07488 ± 0.00002 (2s) and a 206Pb/238U ratio of 0.1792 ± 0.0002 (2s). Sixteen spots were measured on several fragments of this sample (see Table 2) and were all found to be less than 10% discordant. The measured 206Pb counts were very low (less than 20 cps) in good agreement with the low common lead content of this crystal (see Wiedenbeck et al. 1995). The corrected 206Pb/238U ages range from 1010 ± 30 Ma to 1137 ± 23 Ma. Reported on the concordia diagram (Figure 6), analyses define a discordia line which has an upper intercept age of 1060 ± 36 Ma and a lower intercept not significantly different from zero (300 ± 960 Ma), which is the result of a long extrapolation. All points can be combined to give a 206Pb/238U weighted average of 0.1781 ± 0.0026 (MSWD = 1.13) corresponding to a mean age of 1057 ± 14 Ma (2s). This LA-ICP-MS age is well within the error of the TIMS value of 1062.4 ± 0.4 Ma (Wiedenbeck et al. 1995). Two analyses (#2 and 16) have slightly older 206Pb/238U ages, but can be considered as reversely
discordant (see Table 2). This feature, which is frequently observed during in situ analyses (Williams et al. 1984), can also be ascribed to a quick drift in the U-Pb fractionation.

Sample Cinque Frati: This sample is a Late Palaeozoic alkali granite from Corsica which has been previously dated by ID-TIMS at 286.4 ± 1.8 Ma and by SHRIMP at 284.8 ± 2.3 Ma (Cocherie et al. 1999). The TIMS value corresponds to a \( {^{206}\text{Pb}}/{^{238}\text{U}} \) ratio of 0.0454 ± 0.0003 (2s). Nineteen spots were measured by laser ablation on large, translucent crystals (> 200 µm) devoid of fractures or inclusions. All analyses yielded very low \( {^{204}\text{Pb}} \) counts (< 25 cps) below the LOD and no common lead correction was applied to these measurements. The nineteen analyses plot on or close to the concordia curve (Figure 7) with \( {^{206}\text{Pb}}/{^{238}\text{U}} \) ages ranging from 253 ± 21 Ma to 325 ± 53 Ma (see Table 2). Because of their tight clustering, no discordia can be calculated. A weighted mean for all spots gives a \( {^{206}\text{Pb}}/{^{238}\text{U}} \) ratio of 0.0439 ± 0.0017 (MSWD = 0.53) corresponding to an age of 277 ± 11 Ma (2s). Although slightly younger, the mean LA-ICP-MS age overlaps the more precise TIMS and SHRIMP values.

Discussion and conclusions

The results presented in this study demonstrate that coupling a 266 nm UV laser to a quadrupole ICP-MS can be successfully used to determine in situ \( {^{207}\text{Pb}}/{^{206}\text{Pb}} \) and \( {^{206}\text{Pb}}/{^{238}\text{U}} \) ratios for geochronological purposes. The external calibration can be achieved using either a naturally occurring zircon crystal or a more widely available synthetic glass reference material. Both materials yielded comparable mass bias values and could thus be used to correct the \( {^{207}\text{Pb}}/{^{206}\text{Pb}} \) ratios. Measurements could be routinely achieved on single zircon grains with a spatial resolution of ca. 40-50 µm without the need for matrix matched reference materials. As a single measurement required only 1 minute of data acquisition, a comprehensive study of a zircon population could be achieved within a few hours. This is the case even for heterogeneous zircon populations, such as those from granitic rocks with multiple inherited components and/or sedimentary rocks, which often result from erosion of a wide variety of source rocks, both in terms of ages and compositions. Analysis of the \( {^{207}\text{Pb}}/{^{206}\text{Pb}} \) ratios in these zircon populations can thus provide a wealth of information to pinpoint the deep-seated source regions of magmas or to fingerprint the sources of clastic sediments, both of which may have important geodynamic implications. The high throughput rate of the technique is, in these applications, a major advantage over TIMS or SIMS techniques. Open system behaviour, which is frequently observed on zircon but also on monazite, is a serious drawback but can be minimised by selecting the least
magnetic grains. Potentially discordant analyses can be detected and discarded from age calculation, as they result in a spread of ages towards lower values and skewed $^{207}$Pb/$^{206}$Pb histograms. The $^{204}$Pb isotope cannot be measured accurately by ICP-MS because of both very low counts on this isotope and a significant Hg interference. We are, therefore, generally unable to correct precisely for the common lead contribution using the $^{206}$Pb/$^{204}$Pb ratio (see Table 2). This however does not seem to be a problem for laser ablation analyses and generally we observed that the measured $^{207}$Pb/$^{206}$Pb values were very close to the expected value. This is partly due to the high sensitivity of the ICP-MS, which results in a high count rate on the $^{206}$Pb isotope ($>$ 20 000 cps and up to 400 000 cps) and to the fact that pristine zircons are usually devoid of common lead. For Archaean and Proterozoic zircons, the common lead contribution is generally undetectable.

The external calibration technique used in this study allowed us to control the high inter-element fractionation observed between U and Pb and to correct this fractionation to achieve a precision down to around 5%. This is due to the linear correlation observed between the variation of the $^{206}$Pb/$^{238}$U ratio and time during ablation. The calculated ratio showed a much better precision than the measured ratio. This simple technique allowed the age determination of young material for which the $^{207}$Pb/$^{206}$Pb ratio could not be used. Due to the high sensitivity of the ICP source, this opens up new possibilities in the dating of very young rocks with a precision that should exceed the capabilities of SIMS analyses. In terms of precision and accuracy, analyses performed during the course of this study using matrix matched calibration samples showed comparable or slightly worse results than those obtained by external calibration using a NIST glass CRM (Hirata and Nesbitt 1995) or a liquid calibration (Horn et al. 2000) respectively. Thus, the capability of laser ablation ICP-MS analyses to determine U-Pb ages without the need to use well calibrated naturally occurring gem-quality reference samples constitutes a major advantage over matrix-dependent SIMS analyses, particularly when investigating other accessory minerals for which phase mineral relationships are better documented than for zircon (e.g. sphene, allanite) or even on high U-Pb ratio calcrites or biogenic phosphates.

An important problem inherent to the method is related to the quality of the grains selected for analyses. Several experiments on zircon populations containing fractures or inclusions revealed that catastrophic ablation often occurred, during which grains shattered, even when tightly embedded in epoxy. Ejection of the large fragments led to spiky signals that produced high relative standard deviations. In such cases, the ablation behaviour did not match that of the calibration sample and this precluded any acceptable calibration from being made. Grains must, therefore, be carefully selected from the non-magnetic concentrate, in a similar manner to the conventional isotope dilution method, and the laser beam must be focused on homogeneous grain domains. There is, therefore, a risk of analyses biased towards the highest quality crystals from the zircon population yielding an unrepresentative age spectrum. Shorter wavelength lasers operating in the far UV region have the smoothest ablation behaviour and are expected to reduce this drawback to a significant extent.

The spatial resolution used in this study was about two times worse than that normally achieved by SIMS (20-30 µm), which can be a disadvantage for high spatial resolution studies (overgrowth, recrystallised domains). However, previous studies have shown that, providing sensitivity can be enhanced, comparable (Horn et al. 2000) or even smaller (Hirata and Nesbitt 1995) spot sizes can be achieved. Our results, obtained on Palaeozoic and Precambrian zircons, show that high precision age measurements can be obtained by LA-ICP-MS instrumentation that is more widely available than high resolution secondary ion microprobes.

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