Optimization of the in-situ U–Pb age dating method via LA-Quadrupole-ICP-MS with applications to the timing of U–Zr–Mo mineralization in the Poços de Caldas Alkaline Complex, SE Brazil

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**A R T I C L E   I N F O**

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**A B S T R A C T**

The high spatial resolution of the LA-ICP-MS systems allows rapid extraction of vital isotopic information from individual growth zones of minerals. This paper describes in detail the optimization of a relatively inexpensive LA-ICP-MS system consisting of a UV 213 Laser Ablation and a Quadrupole ICP-MS. The results of optimization take into account laser energy, beam diameter, frequency and ICP-MS gas conditions. The optimized conditions were tested for precision and accuracy on a number of well-characterized zircons, commonly used as primary and secondary quality control standards. The acquisition of the U–Pb data is carried out in automated mode (pre-set points) for up to 12 h/day with only minimal operator presence. Individual U–Pb zircon analysis lasts 80 s. The 2σ uncertainties of the standards ranged between 1.4 and 8.2%, and overall their relative deviations ranged from 0.02 to 0.87%. The results are comparable to techniques that use more complex and time-consuming approaches such as LA-MC-ICP-MS and ion-microprobe. We have applied this method to obtain ages of numerous granitoid rocks from the Southern São Francisco Craton and a well-known Archean granitoid of the Kaapvaal Craton, South Africa. We furthermore provide the first results of U–Pb age dating of U–Zr–Mo mineralization in the Poços de Caldas Alkaline Complex, SE Brazil, with a U–Pb age of 85 ± 3 Ma for zircon-bearing hydrothermal veins.

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1. Introduction

Laser Ablation system (LA) attached to Inductively Coupled Plasma Mass Spectrometer (ICP-MS) is a relatively simple and affordable combination of instruments that is capable of in situ isotope measurements with extremely low detection limits (Fryer et al., 1993). In geochronology, LA-ICP-MS systems are adequate because of sensitivity, high spatial resolution and higher rates of material transference during analysis. Recent advances in gas/solid state laser ablation and in ICP-MS sensitivity has allowed determination of important isotopes (e.g., Hf-, B-, Sr-, Nd-, Pb-) and trace element data from individual growth zones of various minerals such as zircon, monazite, titanite, apatite and tourmaline (e.g., Kinny et al., 1991; Hinton and Upton, 1991; Thirlwall and Walder, 1995; Rubato et al., 2001; Storey et al., 2006; Darlin et al., 2012; Sarkar et al., 2014). Improvements in the through put rates of ICP-MS systems and intelligent automation of laser ablation instruments has allowed acquisition of large datasets in relatively short analytical sections. On the other hand, less sensitive systems such as Quadrupole ICP-MS (Q-ICP-MS) coupled to 213 (or 266)-nm solid-state lasers have to be systematically optimized, in order to avoid recurring problems such as low sensitivity and high elemental fractionation.

The wide dynamic range of Quadrupole-ICP-MS systems permits U–Pb isotopic and trace element analysis of narrow growth zones from a number of minerals such as zircon, monazite and titanite (Jeffries et al., 1998, 2003; Jackson et al., 2004; Storey et al., 2006). Several studies have demonstrated the accuracy and precision of such instruments for U–Pb geochronology (Jackson et al., 2004; Storey et al., 2006) but information about tuning/optimization/data reduction protocols is often scarce. In this paper, we describe the technique and show how a full optimization of the LA-Q-ICP-MS provided optimum results at the end of one year. We
noted that the slightest modifications in the system can result in high counts (especially for the less abundant masses like $^{204}\text{Pb} + ^{206}\text{Hg}$, $^{202}\text{Hg}$ and $^{207}\text{Pb}$), prevent high oxide formation ($\text{ThO} < 1\%$) and produce low elemental fractionation. After systematic normalization against external standards, the system can give ages with high accuracy and acceptable analytical errors. The methodology was tested using five well-characterized zircon standards and a number of magmatic zircons from well-known granitoids in Brazil and South Africa.

As an application to our system, we attempted to estimate the timing of fluid circulation and $\text{Zr} - \text{U} - \text{Mo}$ mineralization in the Poços de Caldas (PC) Alkaline Complex, one of the largest alkaline intrusions in South America (Fig. 1). We provide 34 in situ $\text{U} - \text{Pb}$ analysis from samples of the eastern portion of the PC alkaline complex. These samples came from supergene-enriched deposits of zircon and calcsilicates located a few kilometers west of the Osamu Utsumi uranium mine. Late-stage alkaline fluid activity affected the main body of phonolites and tinguaites and reflects the timing of $\text{U} - \text{Zr} - \text{Mo}$ mineralization in the PC complex. The samples yielded abundant, largely translucent zircons that gave highly concordant and Pb-common free isotopic ($\text{U} - \text{Pb}$) ages.

2. Instrumentation and data acquisition

LA-Q-ICP-MS analyses were carried out in an Agilent 7700x mass spectrometer coupled to a laser system LUV213 (New Wave Research/Merchantek, Nd: YAG). The Agilent 7700x ICP-MS is configured for routine analysis with very low concentrations of elements (0.1–2% relative standard deviations), providing sufficient counts on masses such as $^{202}\text{Hg}$, $^{204}\text{Pb} + ^{206}\text{Hg}$ and $^{207}\text{Pb}$ for $\text{U} - \text{Pb}$ applications in minerals like zircon, monazite and titanite (Lana et al., 2010a,b). The software packages of the Laser Ablation unit and ICP-MS are synchronized via a trigger cable in order to automate the analytical procedure. Individual analyses are produced in less than a minute, and a minimum of 40–50 individual dates can be acquired per hour. The analyses are performed keeping all parameters constant (from laser and ICP-MS) for standards and samples throughout the run. The laser is kept always focused, thus reducing any shifts of the laser beam during ablation. The operating conditions of ICP-MS and laser are specified in Table 1.

Standard and sample mounts are placed in a tear-drop shaped sample chamber that was customized at the University of Stellenbosch (Lana et al., 2013; Romano et al., 2013) (Fig. 2). It has two compartments: one of 1 cm-diameter for standard mounts and one of 2.5 cm-diameter for sample mounts (Fig. 2a). In the path between the ablation cell and ICP-MS, the commonly used Y-tube was replaced by a gas mixer (Squid) in the form of a splitter, with ten PTFE tubes of 3 mm diameter and 80 cm in length (Fig. 2b) for better homogenization of the mixtures. The Squid keeps wash out time short and produces a strikingly smooth signal that is perfect for counting statistics (it eliminates the noise) and consequently gives better averaged signal counts.

The integration times used are 40 ms for $^{207}\text{Pb}$, 15 ms to $^{206}\text{Pb}$ and 10 ms to $^{208}\text{Si}, ^{208}\text{Hg}$, $^{204}\text{Pb} + ^{206}\text{Hg}$, $^{207}\text{Pb}$, $^{232}\text{Th}$ and $^{238}\text{U}$, with a total scan of the masses occurring in 60 s (20 s background/40 s ablation). The relevant isotopic ratios $^{205}\text{Pb}/^{205}\text{Pb}$, $^{207}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{208}\text{Pb}$, $^{208}\text{Pb}/^{232}\text{Th}$, $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ ($^{235}\text{U}$ is calculated from $^{238}\text{U} - ^{238}\text{U}/^{138}\text{U}$) were calculated by the data reduction program Glitter (Van Achterbergh et al., 2001). Background values are measured (20 s) at the beginning of each analysis.

The initial data reduction is done on line via the software Glitter (GEMOC Laser ICP-MS Total Trace Element Reduction), which provides an interactive environment for analytic selection of background and sample signals besides enabling a fast, real-time and online data reduction (Van Achterbergh et al., 2001; Jackson et al., 2004). The program calculates the significant isotopic ratios $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{232}\text{Th}$, $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ which are displayed in time-resolved mode. For our laser system, isotopic ratios generated during the first 5 s of each analysis were discarded. The integration window for the remainder of each analysis is chosen so as to exclude signal segments that were related to inclusions, zones of Pb loss (e.g., fractures), high common Pb or inheritance. Mass bias and drift corrections are based on sets of measured standard ratios that bracket sets of 7–10 analysis of

<table>
<thead>
<tr>
<th>Table 1</th>
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<td>Operating conditions of the LA-Quadrupole-ICP-MS system.</td>
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<td>ThO$^+$ / Th$^+$ (%$</td>
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unknowns. The measured standard ratios are interpolated through a linear regression and the obtained error (1σ) is applied to the bracketed unknowns. Common Pb corrections are done using the interference and background-corrected 204Pb signal in combination with the Pb model composition of Stacey and Kramers (1975). This is done offline with an in-house excel spreadsheet that takes all mass-bias and drift corrected counts exported from Glitter. Relative uncertainties of the 206Pb/207Pb and 206Pb/238U ratios combines the external reproducibility of the primary standard with the within-run uncertainties in the quadrature. A further 1% uncertainty (1σ) is assigned to the measured TIMS values of the isotope ratios for the standard and propagated through the analysis error. The 207Pb/235U ratio is derived from the normalized and error propagated 207Pb/206Pb and 206Pb/238U ratios assuming a 238U/235U natural abundance ratio of 137.88, and the uncertainty is derived by quadratic addition of the propagated uncertainties of both (207Pb/206Pb and 206Pb/238U) ratios. We note that for more than 80% of the analysis, the 206Pb counts were often too low (10–30 cps) and the 206Pb/204Pb ratios are too high for any significant common Pb correction.

3. Samples and quality control standards

In this study the precision (on errors) and accuracy (for validation of results) were monitored through alternating measurements between the primary GJ-1 standard zircon and several secondary (quality control) standards (zircons Plešovec, M127, B89 and 91500). Our GJ-1 standard zircon (Jackson et al., 2004; Elhlou et al., 2006) is a gem-quality yellowish crystal with no apparent zoning in the 206Pb/204Pb ratios are too high for any significant common Pb correction.

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$^{207}\text{Pb}/^{206}\text{Pb}$ ratios increased substantially once the dwell time of the $^{207}\text{Pb}$ mass was modified from 30 ns to 40 ns (Table 2). Tests with 10 Hz frequency, 30 μm-wide beam, and higher ablation times of 50 s, yielded a stable signal but some elemental fractionation affected reproducibility of accepted ages from standards. Moreover, the counts were not satisfactorily high for the purpose of this study. The problem with this last condition is that each individual analysis takes too long, making it difficult to keep a strong stable signal, without significant down-whole fractionation. Tests carried out at 5 Hz, 40 s, and beams of 30 μm and 40 μm, provided very satisfactory analytical signal but with higher analytical errors due to low counts per second of the $^{207}\text{Pb}$ mass. The measured counts per second were 3–4 times lower than those performed in previous conditions A and B.

Table 2 shows results of several runs on the GJ1 zircon for conditions A (30 micron beam) and B (40 micron beam). In both conditions, the instrument gave accurate results within 1% of the accepted age of the GJ1 standard. However, the combination of signal stability, low fractionation (larger crater size) and increased 40 ns dwell time for mass $^{207}\text{Pb}$ (condition B) resulted in much higher precision on all ratios, particularly for the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio. The errors of the $^{207}\text{Pb}/^{206}\text{Pb}$ apparent ages in condition B are 30–40% lower than those of condition A (Table 2). Condition B was proven ideal (giving the Quadrupole performances) for Archean zircons, as the increase in hole size from 30 μm to 40 μm resulted in higher counts, primarily for masses $^{207}\text{Pb}$ and $^{206}\text{Pb}$ (Table 2).

### 4.2. Zircon standards

The precision (on errors) and accuracy (for validation of results) of the LA-ICP-MS system were monitored through alternating measurements between the primary GJ-1 standard zircon and several secondary standards (zircons Plesovice, M127, BB9 and 91500). Table 3 shows all Concordia ages obtained from sessions 1 to 20 (see also electronic supplement). The compiled results for GJ1 show Concordia ages ranging from 607 ± 4 Ma to 610.1 ± 3.8 Ma (with deviations from the accepted age ranging from 0 to 0.35% (Table 2; Fig. 4a), fairly consistent with the TIMS intercept age of 607 Ma. The $^{206}\text{Pb}/^{238}\text{U}$ weighted mean from 746 points gave an age of 608.7 ± 0.47 Ma. The relative deviations for individual ratios were 0.1–3.0% ($^{207}\text{Pb}/^{206}\text{Pb}$), 0.04–2.8% ($^{206}\text{Pb}/^{238}\text{U}$) and 0.4–1.9% ($^{207}\text{Pb}/^{235}\text{U}$). Our Plesovice zircon (sessions 1 to 20 of Table 3; electronic supplement) gave Concordia ages ranging from 337 ± 1.6 Ma to 340 ± 1.3 Ma and a $^{206}\text{Pb}/^{238}\text{U}$ weighted mean of 337.6 ± 0.4 Ma (330 points). Deviations from the accepted value ranged from 0.02 to 0.35%. The relative deviations for individual ratios were 0.4–6.6% ($^{207}\text{Pb}/^{206}\text{Pb}$), 0.15–2.7% ($^{206}\text{Pb}/^{238}\text{U}$) and 0.2–2.42% ($^{207}\text{Pb}/^{235}\text{U}$). Zircon BB9 (sessions 1 through 6 of Table 3; Fig. 4c) gave a range of Concordia ages from 558 ± 2.4 Ma to 566 ± 4.2 Ma and 2σ uncertainties between 2.4 and 4.7%. The $^{206}\text{Pb}/^{238}\text{U}$ weighted mean from 59 points gave an age of 560.8 ± 1.5 Ma. The relative deviations for individual ratios are 0.03–1.7% ($^{206}\text{Pb}/^{238}\text{U}$) and 0.2–1.7% ($^{207}\text{Pb}/^{235}\text{U}$). The analytical sessions for M127 (sessions 1 to 13 of Table 3; Fig. 4d; electronic supplement) yielded Concordia ages ranging from 520 ± 3.5 to 528 ± 3.2 Ma and 2σ uncertainties between 1.4 and 4.3%. Relative deviations for the individual ratios were 0.19–3.2% ($^{207}\text{Pb}/^{206}\text{Pb}$), 0.1–1.0% ($^{206}\text{Pb}/^{238}\text{U}$) and 0.11 to 3.31 ($^{207}\text{Pb}/^{235}\text{U}$)%. The $^{206}\text{Pb}/^{238}\text{U}$ weighted mean from 179 points gave an age of 525 ± 0.82 Ma. The calculated Concordia ages for zircon 91500 (sessions 1 to 10 of Table 3; Fig. 4e; electronic supplement) range from 1062 ± 5.1 Ma and 1070 ± 6.5 Ma. Relative deviations for the individual ratios were 0.04–0.41% ($^{206}\text{Pb}/^{238}\text{U}$), 0.02–0.77% ($^{207}\text{Pb}/^{235}\text{U}$) and 0.06–2.22% ($^{207}\text{Pb}/^{206}\text{Pb}$). The $^{206}\text{Pb}/^{238}\text{U}$ weighted mean from 107 points gave an age of 1064.9 ± 2.2 Ma.

### 4.3. Natural rock samples

Samples of the Kaap Valley pluton were analyzed in two separate runs. The first round provided an upper intercept age of 3227.9 ± 4.6 Ma and a lower intercept age of 498 ± 270 Ma (MSWD = 0.58) (Fig. 5a). The subsequent run provided an upper intercept age of 3229.4 ± 5.1 Ma and a lower intercept age of 461 ± 210 Ma (MSWD = 1.5) (Fig. 5b). The average ages calculated for the $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ ratios were 3199 ± 14 Ma and 3216 ± 6.1 Ma, 3225 ± 18 Ma and 3228 ± 7.6 Ma, and the mean ages of $^{207}\text{Pb}/^{206}\text{Pb}$ ratio were 3227 ± 7 Ma and 3229 ± 11 Ma, respectively.

Zircon ages from the Samambaia Tonalite and Moeda Granodiorite were obtained in the same run. Zircons from the Samambaia tonalite were pink to purple, fairly transparent and made by well defined oscillatory zoning. 32 analyses from these zircons gave concordant points with mean ages of 2785 ± 12 Ma ($^{207}\text{Pb}/^{206}\text{Pb}$), 2777 ± 14 Ma ($^{206}\text{Pb}/^{238}\text{U}$) and 2781.5 ± 6.9 Ma ($^{207}\text{Pb}/^{235}\text{U}$). The same analysis gave a Concordia age of 2782.1 ± 3.7 Ma (Fig. 5c). Most zircons found in the Moeda granodiorite were milky or white and fairly discordant. Only about 20% of the concentrate was sufficient transparent for U–Pb LA-ICP-MS dating. The analyses on the most transparent crystals gave an upper intercept age of 2730.5 ± 6.9 Ma and a lower intercept age of 509 ± 160 Ma (MSWD = 2.2) (Fig. 5d). Average mean ages were found to be 2729 ± 10 Ma for the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio, 2727 ± 13 Ma for the $^{206}\text{Pb}/^{238}\text{U}$ ratio and 2728 ± 6.1 Ma for the $^{207}\text{Pb}/^{235}\text{U}$ ratio.
Table 2
Compilation of runs on standard GJ1 highlighting reproducibility and precision of distinct beam sizes (30 m and 40 um).

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<tr>
<th>Name</th>
<th>Beam Diameter</th>
<th>U238 (CPS)</th>
<th>Pb207 (CPS)</th>
<th>207Pb/206Pb</th>
<th>207Pb/235U</th>
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<td>0.099066</td>
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<td>30 micron beam diameter</td>
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<td>30 micron beam diameter</td>
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<tr>
<td>40 micron beam diameter</td>
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</table>

- **Within-run background-corrected mean** 207Pb signal in counts per second [cps].
- **Corrected for mass-bias by normalizing to reference zircon and common Pb using the model Pb composition of Stacey and Kramers (1975).**
- **207Pb/206Pb calculated using (207Pb/206Pb)/(235U/206Pb*1/137.88).**
- **Average of apparent ages in a single run.**
- **Mean of the error propagated — standard deviation of all (n) analyses within a run.**
- **Standard deviation of apparent ages in a single run.**

Zircons from the Alto Maranhão pluton are pink, euhedral and had conspicuous colors. They gave a TIMS age of 2124 ± 1 Ma (Nose et al., 1998). In this study, we obtained an upper intercept age of 2119 ± 18 Ma, with lower intercept at 591 ± 800 Ma (MSDW = 0.084) (Fig. 5e). Average mean ages from the ratios were 2111 ± 17 Ma (207Pb/206Pb), 2077 ± 16 Ma (206Pb/238U) and 2094 ± 91 Ma (207Pb/235U).

Zircons from the Poços de Caldas Complex phonolite are mm-to cm-wide, and are red to yellow translucent crystals (Fig. 3d). Thirty-three analyses on 12 of these grains gave concordant points with similar 206Pb/238U apparent ages in the range of 80–91 Ma. These points gave 206Pb/238U and 207Pb/235U weighted mean ages of 84.6 ± 1 Ma and 86 ± 3.1 Ma, respectively, whereas a Concordia age of 84.4 ± 1 Ma was given by 23 of the 33 points (Fig. 5f). Identical but more conservative ages of 85 ± 2.8 (0.03% RSD) Ma and 86 ± 3.1 Ma were calculated by averaging the 206Pb/238U and 207Pb/235U apparent ages. All the ages overlap within error and we assume the conservative age of 85 ± 2.8 Ma as the best

### Table 3
Analytical sessions with Concordia ages obtained for the zircon standards in LA-Quadrupole-ICP-MS system, their 2σ errors and relative deviations.

<table>
<thead>
<tr>
<th>Standard</th>
<th>Section 1</th>
<th>Section 2</th>
<th>Section 3</th>
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<tr>
<td></td>
<td>n</td>
<td>Age (Ma)</td>
<td>2σ</td>
</tr>
<tr>
<td>GJ-1</td>
<td>26</td>
<td>608.1</td>
<td>2.3</td>
</tr>
<tr>
<td>Plesioce</td>
<td>16</td>
<td>337</td>
<td>2</td>
</tr>
<tr>
<td>91500</td>
<td>11</td>
<td>1066</td>
<td>4.9</td>
</tr>
<tr>
<td>BB9</td>
<td>15</td>
<td>560</td>
<td>3.3</td>
</tr>
<tr>
<td>M127</td>
<td>14</td>
<td>525</td>
<td>2.9</td>
</tr>
</tbody>
</table>

MSWD: Mean Squares of the Weighted Deviation.
2σ: Analytical error.
n: Number of Analysis.
approximation of the crystallization age of the hydrothermal veins
that crosscut the phonolites and tinguaites in the western part of
the PC complex.

5. Discussion

Optimization tests using a 213 UV Laser Ablation system
coupled to an Agilent 7700x ICP-MS showed a significant
improvement in sensitivity and reproducibility after a series of tests
under varied conditions, including gas flow, laser beam diameter,
laser energy and ablation time. Analysis with 40 μm beam seems
the most suitable for low resolutions systems such as Quadrupole
ICP-MS. We noted that a longer dwell time of 40 ms for 207Pb mass
can sometimes improve counts and drastically improve precision
on the 207Pb/206Pb ratios (Table 2) and ages of Late-Proterozoic and
Archean zircons. With a 30 μm beam (condition A), the counts are
lower but satisfactory; this is verified by similar age reproducibility
observed for conditions A and B (Table 2). Expanding the beam
diameter to 50 μm increases the amount of sampled material but
compromises the spatial resolution and therefore may not be
suitable for complex zircons.

Changing ablation time from 40 s to 50 s improved slightly the
counts, but fractionation increased. Long periods of ablation
translated to deeper craters and again loss of spatial resolution
deep into the crystals. Thus, the crater depth/diameter ratio is an
essential factor for the optimization of quadrupoles, and it is
directly related to the effect of elemental splitting, differential
transport of U and Pb masses during ablation. Increasing this ratio
causes the fractionation of elements, which results in undesirable
age data. When reducing the usual frequency of 10 Hz—5 Hz,
regardless of the diameter of the hole, the analytical error becomes
extremely high due to low counts. Even increasing the ablation
time from 40 s to 50 s, with the aim of supplying the least amount
of material, the laser still does not supply a sufficient quantity of
material to generate satisfactory counts. The analysis performed
under these conditions provides a very unstable analytical signal
and also very high errors. Thus, our preferable conditions are
30 μm, 10 Hz and 40 s of ablation time for Proterozoic zircons and

Fig. 4. Concordia ages for zircon standards (a) GJ-1 (b) Plešovice (c) BR9 (d) M127 and (e) 91500. As in Fig. 4 the cumulative effect of the large number of points resulted in statistically overestimated errors on the calculated ages. These errors should not be more accurate than the external reproducibility of the analysis (see text and Table 3 for details). The diagrams were generated in Isoplot (Ludwig, 2001).
40 μm, 10 Hz and 40 s of ablation time for Archean zircons (depending on the zircon internal complexity).

The signal stability is directly linked to the homogeneity of the gas mixture (He + Ar) and to the material removed by the laser. Compared to the previously used single tube, the Squid increased efficiency by decreasing the dispersion of the spectra. The use of the low-volume sample cell significantly increased the sensitivity of the signal obtained during the analysis and improved accuracy. There was a significant reduction in the washing time and a substantial increase in the rise time of the signal at the beginning of the tests, which in turn reduced the total time spent by the apparatus during the analysis and allowed a greater number of analyses to be conducted daily.

The long term results (using the same conditions) gave adequate reproducibility and acceptable errors. For instance, the GJ-1 zircon gave Concordia age values between 607 ± 4 Ma and 610.1 ± 3.8 Ma, 2σ uncertainties of 2—4%, relative deviations of 0.0—0.4%. For zircon Plešovice we obtained ages ranging from 337 ± 1.6 Ma to 340 ± 1.3 Ma (2σ uncertainties from 1.5 to 2.5%, relative deviations 0.02—0.35%) and uncertainties related with the mean ratios of 1.5—4%. The standard B99 zircon generated Concordia from 558 ± 2.4 Ma to 566 ± 4.2 Ma, with 2σ uncertainties of 2.4—4.7%, relative deviations from 0.19 to 0.87% and uncertainties regarding the means of the ratios from 2.7 to 14%. The standard M127 zircon provided Concordia ages of 520 ± 3.5 Ma to 528 ± 3.4 Ma, 2σ uncertainties of 1.4—4.3%, relative deviations 0.06—0.82%, and uncertainties regarding the means of the ratios between 1.4 and 12%. Finally, zircon 91500 provided a minimum Concordia age of 1062 ± 5.1 Ma and a maximum value of 1070 ± 6.7 Ma, 2σ uncertainties of 4.4—8.2%, relative deviations 0.09—0.46%, and uncertainties of averaged ratios of 8.9—5%.

The method was also successful with older, more complex zircons, from granitoids of a range of ages. For example, for the Kaap Valley tonalite we obtained an upper intercept age of 3227 ± 3 Ma.
and lower intercept age of 447 ± 150 Ma and concordant ages of 3218.3 ± 3.5 Ma to 3227 ± 3.7 Ma for two runs. This is identical, within error, to the U–Pb ages obtained by TIMS and SHRIMP techniques (3226 ± 14 Ma by Armstrong et al., 1990; 3229 ± 5 Ma by Tegtmeyer and Kroner, 1987; 3227 ± 1 Ma by Kamo and Davis, 1994). For the Samambaia tonalite (São Francisco Craton), we have obtained a Concordia age of 2782.1 ± 3.7 Ma, identical to the 2780 ± 3 Ma U–Pb TIMS age of Carneiro (1992). For the Moeda Granodiorite we obtained an upper intercept age of 2730.5 ± 6.9 Ma and a lower intercept age of 609 ± 160 Ma and Concordia age of 2728 ± 3.3 Ma identical to the 2730 ± 7 Ma U–Pb TIMS age of Machado et al. (1992). Finally, the Alto Maranhão Pluton gave an intercept age of 2119 ± 18 Ma (and lower intercept of 591 ± 800 Ma), slightly divergent but within error of the TIMS age of 2124 ± 1 obtained by Noce et al. (1998).

5.1. U–Th mineralization in the Poços de Caldas alkaline complex

The Poços de Caldas is considered the largest known alkaline complex of South America and one of the largest in the world (Wooley, 1987). According to Schorscher and Shea (1992), the petrographic associations of the PC alkaline rocks are potassium-rich phonoaluminous and nepheline-syenitic, consisting broadly of K-feldspar, nepheline, sodic pyroxene and accessory minerals. The complex is marked by large deposits of U, Th and rare-earth elements (REEs) (Schorscher and Shea, 1992) in the form of bauxite, clays, zircon, calcsilite, U–Zr–Mo, F and Th–REE (–Fe). Many of these deposits were caused by a late-stage alkaline fluid alteration (Frayha, 1962; Wedow, 1967; Gorsky and Gorsky, 1974; Putzer, 1976; Santos, 1976; Magno, 1985; Frankenel et al., 1985; Ulbrich and Ulbrich, 1992).

Despite the number of age data accumulated for the PC complex over the last 60 years, there is still a strong disagreement about the emplacement age. Previous studies have pointed out a critical spread in the obtained ages from 54 Ma to 91 Ma (Ulbrich et al., 2002) which in turn cannot be included within one magmatic evolution of an alkaline complex. For instance, whole-rock Rb/Sr isochrons (Kawashita et al., 1984) gave ages of 89.8 ± 2.8 Ma (initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7050 ± 1) from nepheline syenites and 86.3 ± 6.0 Ma (i.r. of 0.7052 ± 1) from lujavrites and kibinites. Other Rb–Sr isochrons based on whole-rock samples of a nepheline syenite yielded an age of 74.2 ± 6.3 Ma (i.r. of 0.70511 ± 1) (Shea, 1992). K–Ar dating of a number of samples gave a substantially large spread in ages ranging from 89.3 to 54.2 Ma (see review in Ulbrich et al., 2002). The variances between the age dating methods may reflect differences in either emplacement ages, cooling of the rock massif and subsequent fluid-flow alteration. A key problem relates to late-stage fluid–host rock interactions. Fluid circulation particularly affects the K–Ar and Rb–Sr systems and therefore the accuracy of the published ages may be compromised by isotopic disturbance. According to Ulbrich et al. (2002) alteration may have added H$_2$O and K to the rocks, and leached out mainly Ca and Mg. Loss of radiogenic Ar is also expected to occur during leaching with the result that the whole rock and K-feldspar ages may be too young. To date, no previous study has attempted to constrain U–Pb ages for the mineralization in the complex.

The U–Pb method is insensitive to chemical alteration and is thus more adequate to constrain the emplacement age of the complex and the timing of fluid circulation. Textures of these rocks are essentially volcanic and suggest that the emplacement should have taken place within a period of a few million years. Our LA–ICP–MS U–Pb zircon age of 88 ± 3 Ma for the zircon–filed cavities and veins in the western part of the PC complex is consistent with most of the older ages (>80 Ma) from whole rock Rb–Sr and some K–Ar in minerals such as biotite (Kawashita et al., 1984; Ulbrich et al., 2002). Our U–Pb age is also within error of the U–Pb (76 ± 12 Ma to 82 ± 11 Ma) ages produced from thorite crystals. These ages indicate that the zircon mineralization took place immediately after the emplacement of the volcanic body of the complex. According to previous studies, fluid alteration and associated mineralization in the PC complex can be compared to those of porphyry copper deposits in granites. The mineralization seems to be a result of both shattering of country rocks followed by extreme boiling fluid circulation in and above the roofs of crystallizing magma chambers. This is followed by cooling through the circulation of hydrothermal cells, mainly composed of supercritical water-rich solutions (e.g., Burnham, 1979; Garda, 1990; Ulbrich and Ulbrich, 1992; Sawkins, 1990). Our U–Pb age is likely to reflect the age of the fluid circulation shortly after the emplacement of the phonolites. The overlapping ages are also consistent with relatively fast cooling shortly after emplacement. Given the regional extent of the host rock, encompassing much of the central and western part of the circular pipe, it is likely that much of the PC alkaline complex was emplaced shortly before 85 ± 3 Ma ago.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jsames.2015.04.007

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Fryer, B.J., Jackson, S.E., Longeicher, H.P., 1993. The application of laser ablation microprobe-inductively coupled plasma-mass spectrometry (LAM-ICP-MS) to the result that the whole rock and K-feldspar ages may be too young. To date, no previous study has attempted to constrain U–Pb ages for the mineralization in the complex. Our U–Pb age is also within error of the U–Pb (76 ± 12 Ma to 82 ± 11 Ma) ages produced from thorite crystals. These ages indicate that the zircon mineralization took place immediately after the emplacement of the volcanic body of the complex. According to previous studies, fluid alteration and associated mineralization in the PC complex can be compared to those of porphyry copper deposits in granites. The mineralization seems to be a result of both shattering of country rocks followed by extreme boiling fluid circulation in and above the roofs of crystallizing magma chambers. This is followed by cooling through the circulation of hydrothermal cells, mainly composed of supercritical water-rich solutions (e.g., Burnham, 1979; Garda, 1990; Ulbrich and Ulbrich, 1992; Sawkins, 1990). Our U–Pb age is likely to reflect the age of the fluid circulation shortly after the emplacement of the phonolites. The overlapping ages are also consistent with relatively fast cooling shortly after emplacement. Given the regional extent of the host rock, encompassing much of the central and western part of the circular pipe, it is likely that much of the PC alkaline complex was emplaced shortly before 85 ± 3 Ma ago.


