Anais da Academia Brasileira de Ciências (2009) 81(1): 99-114
(Annals of the Brazilian Academy of Sciences)
ISSN 0001-3765
www.scielo.br/aabc

High spatial resolution analysis of Pb and U isotopes for geochronology by *laser ablation* multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS)

BERNHARD BÜHN, MÁRCIO M. PIMENTEL, MASSIMO MATTEINI and ELTON L. DANTAS

Instituto de Geociências, Universidade de Brasília, Campus Universitário Darcy Ribeiro, Asa Norte, 70910-900 Brasília, DF, Brasil

Manuscript received on March 13, 2008; accepted for publication on July 15, 2008;
contributed by MARCIO M. PIMENTEL*

ABSTRACT

Age determinations using the ^{235}U and ^{238}U radioactive decay series to the daughter isotopes ^{207}Pb and ^{206}Pb, respectively, using the mineral zircon ($ZrSiO_4$), are widely used to decipher geological processes. A new method developed in the last couple of years, the *laser* ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS), overcomes previous laborious sample preparation, and yields isotopic ratios and age data with a high spatial resolution of ten of microns. The present study describes the analytical set-up and data reduction process as presently applied at the Laboratory for Geochronology of the University of Brasília. It explores the precision and accuracy of the method by cross-analysing three international zircon standards. We arrive at a precision of 1.9 to 3.7% (2σ SD) and an accuracy of 0.6 to 3.8% (2σ SD) for and U isotopic ratios of the standards. We also apply the method to two natural zircon samples, which have previously been dated by other analytical methods. A comparison of the results shows a good conformity of the age data, being within the error limits. The data demonstrate the great analytical potential of the method for rapid, precise and accurate U-Pb isotopic analyses on the micron scale.

Key words: geochronology, U-Pb isotopes, LA-MC-ICP-MS, zircon, age dating.

INTRODUCTION

Absolute age determinations in the geosciences serve for a variety of applications including geotectonic studies, sedimentation ages and sediment provenance, as well as dating of igneous and metamorphic rocks. They use the decay of a radioactive isotope in a natural mineral with a half-life favourable for the expected age of the material or process investigated. Many of these applications are conducted in materials of considerable age (millions to billions of years), which suggests the use of the radioactive uranium isotopes ^{235}U and ^{238}U with half-lifes of 7.04×10^8 and 4.47×10^9 years, and the radiogenic daughter isotopes ^{207}Pb and ^{206}Pb, respectively. Analysis of the parent and daughter isotopes allows the determination of the crystallization age of the mineral. The mineral analysed should show certain physicochemically favourable characteristics, such as high resistance to chemical exchange and recrystallization, and reasonably high U and radiogenic Pb contents for analysis, amongst others. These are met by the abundantly occurring mineral zircon ($ZrSiO_4$) which is, therefore, the most traditional and widely used mineral for age determinations of various geological applications (e.g. Garbe-Schönberg and Arpe 1997, Košler et al. 2002).

Apart from the improvement in precision, accuracy and mass resolution on the detector side of the instrumental set-up, a new method of material sampling is gaining more and more importance. Instead of the in-

---

*Member Academia Brasileira de Ciências
Correspondence to: Bernhard Bühn
E-mail: berbu@unb.br

troduction of the sample in aqueous solution, a *laser* microprobe for sampling of solid material on the micron scale is connected to an ionization cell, which ionizes the sampled material in an inductively coupled plasma (ICP) and supplies single-charged ions to a magnetic sector or quadrupole mass spectrometer. The technique is referred to as "*laser* ablation inductively coupled mass spectrometry" (LA-ICP-MS). It avoids the laborious sample cleaning, dissolution and element separation in an ultraclean laboratory environment required by the traditional isotope dilution thermal ionization mass spectrometry (ID-TIMS). Since the pioneering work by Feng et al. (1993) and Hirata and Nesbitt (1995), significant analytical progress of the LA-ICP-MS method was achieved (see Vanhaecke and Moens 1999, Günther et al. 2000, Horn et al. 2000, Stirling et al. 2000, Simonetti et al. 2006, Paquette and Tiepolo 2007, Simon et al. 2007).

In this study, advances of this particular dating method, the multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) coupled to a *laser* microprobe, which has recently been set up at the Geochronology Laboratory of the University of Brasilia, are reported. We present results of three international zircon standards cross-calibrated one against the other, and two natural zircon samples which have previously been analysed by other analytical methods. The data demonstrate the capacity of the method in terms of rapid, precise and accurate U and Pb isotope analyses with high spatial resolution.

RATIONALE

For the case of two radioactive isotopes of a single element, as for the decay systems of ^{238}U and ^{235}U, the ratios between the stable decay products and the radioactive parent isotopes (^{206}Pb/^{238}U and ^{207}Pb/^{235}U) are interrelated. Given closed-system conditions, they plot on a curve which extends from today towards the formation of the Earth and the solar system at approximately 4.53 Ga ago (Fig. 1). The ratios have to concord one to the other following the relationship:

$$\frac{^{206}\mathrm{Pb}}{^{238}\mathrm{U}} = \left(\frac{^{207}\mathrm{Pb}}{^{235}\mathrm{U}} + 1\right)^{\lambda 238\mathrm{U}/\lambda 235\mathrm{U}} - 1 \qquad (1)$$

and define the "Concordia curve", with λ being the decay constant of the respective radioactive isotope. Another age information can be obtained by the ^{207}Pb/^{206}Pb age, based on the relationship:

$$\frac{^{207}\mathrm{Pb}}{^{206}\mathrm{Pb}} = \frac{^{235}\mathrm{U}}{^{238}\mathrm{U}} \times \frac{(e^{\lambda 235\mathrm{U}\times t} - 1)}{(e^{\lambda 238\mathrm{U}\times t} - 1)} \qquad (2)$$

With the constant present-day ^{238}U/^{235}U ratio of 137.88, this age information considers only the daughter isotopes. Hence, the more accurate and valid age information is obtained from the ^{206}Pb/^{238}U and ^{207}Pb/^{235}U isotope ratios.

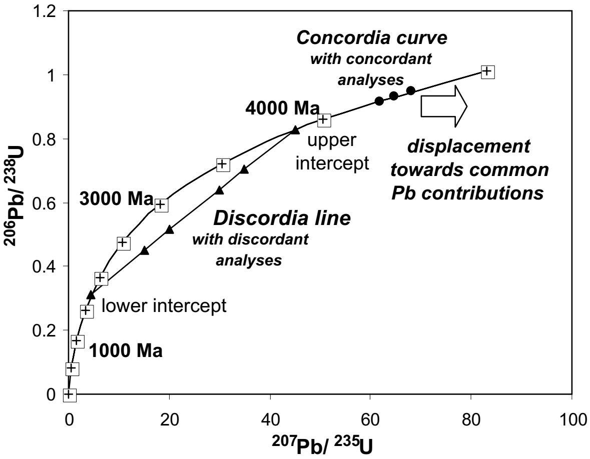

Fig. 1 – Principles of the Concordia diagram ^{207}Pb/^{235}U *versus* ^{206}Pb/^{238}U. Concordant analyses fall on the Concordia curve. Minerals with a contribution of common Pb to the bulk Pb content plot below the Concordia curve. Lead loss leads to zircon analyses plotting on a Discordia line with the upper intercept indicating the age of crystallization.

There are two fundamental problems with this method. Firstly, the material analysed may contain initial common Pb of non-radiogenic origin. The non-radiogenic Pb fraction displaces the isotope analyses towards values below the Concordia curve (Fig. 1). The problem of this "common Pb" content can be resolved by correction procedures using crustal ^{206}Pb/^{204}Pb and ^{207}Pb/^{204}Pb compositions. These Pb isotope ratios, however, change with time in terrestrial materials, due to the radiogenic growth of ^{206}Pb and ^{207}Pb from the decay of ^{238}U and ^{235}U, respectively. The respective, time-dependant isotope ratio used for correction may be calculated from the average crustal Pb isotopic composition, or may directly be analysed in cogenetic minerals which contain predominantly common, and little radiogenic Pb.

In order to avoid these corrections, it is always more effective to analyse minerals which, due to their crystal lattice characteristics, contain sufficient U to analyse the parent and the daughter isotope but, on the other hand, do not accommodate common Pb in the structure, because of the mismatch between ionic charge and effective ionic radius (Shannon 1976). These are, for example, zircon ($ZrSiO_4$) or monazite $(Ce,La,Nd,Th)PO_4$, which generally contain sufficient U to be analysed, ranging from 1 to > 10000 ppm for zircon and 282 to > 50000 ppm for monazite (Heaman and Parish 1991). The common Pb content of the two minerals is generally (but not always) very low.

Secondly, the system must have been closed to the gain or loss of the parent and daughter isotopes. In most cases, we deal with a loss of radiogenic lead which can be easily mobilized by geological processes because, as in the case of zircon, radiogenic Pb^{2+} does not fit the Zr^{4+} ion characteristics (Mezger and Krogstad 1997). The result is that the isotopic analyses plot on a "Discordia line" which intersects the Concordia curve twice (Fig. 1): the upper intercept generally represents the time of crystallization of the mineral; the lower intercept may, in cases, be interpreted as the geological event when the crystal lost part of his radiogenic lead. Mineral standards for isotopic analyses by LA-ICP-MS or ion microprobe should meet these two requirements, i.e. they should be concordant, and void of common lead.

METHOLOGICAL PROGRESS OF Pb-U ISOTOPIC ANALYSIS

Conventional Pb-U analyses for absolute age determination of geological materials commonly use the technique of ID-TIMS (Isotope Dilution Thermal Ionization Mass Spectrometry). Sample preparation is laborious (e.g. Nebel-Jacobsen et al. 2005, Amelin and Davis 2006). The minerals have to be separated from the rock matrix, cleaned and sometimes abraded if the outer margins show alteration features (Mattinson 2005). The minerals are dissolved, and the Pb and U isotopes separated by resin columns in an ultra-clean laboratory to allow sub-nanogram Pb isotopic analysis. The solutions are deposited on rhenium filaments for thermal ionization and introduction of the ionized species into a magnetic sector mass spectrometer.

This techniques has been successfully applied for decades and is still commonly used for U-Pb age determinations and other isotopic geochemical applications worldwide. Low-blank laboratories normally achieve a very high precision of the age determinations (Parrish and Noble 2003, Krymsky et al. 2007). However, shortcomings of the technique are the need to separate the minerals from the matrix, the lack of spatial resolution of the analyses, and the laborious wet chemical preparation under ultra-clean laboratory conditions. On the other hand, the quality of the analyses is excellent, reaching precisions down to $\leq 0.1\%$ for the Pb/U isotopic ratios (e.g., Mattinson 2005).

Another method which overcomes the need for wet chemical preparation is the Sensitive High Resolution Ion Micro Probe (SHRIMP). It focuses a high-energy ion beam (usually O_2^-) onto an area of usually $< 30\mu m$ for *in situ* isotopic analysis of minerals such as zircon. The method reaches a precision and accuracy of about 1.0% (e.g., Cocherie et al. 2005). The SIMS method (Secondary Ion Mass Spectrometry), on the other hand, employs a primary ion beam and analyses the ejected secondary ions. It focuses an O^- ion beam of typically $> 10\mu m$ in diameter on a solid sample surface, and is primarily applied to quantify major and trace element contents (for example, Pettke et al. 2004).

Many recent analytical methods, instead, use an "Inductively coupled plasma" ionization method (ICP) of the sample, generating a fine aerosol which is ionized in an Ar plasma (Horn et al. 2000). With Ar having a high first ionization potential of 15.759 V, the plasma ionizes all other elements to single-charged ions except for He, F and Ne. The method was developed in the early 1980s for introduction of dissolved samples. Likewise, the ICP array may be connected to a *laser* system which ablates a solid sample whose vaporized material is then transported by a He gas flow into the ICP unit. This method overcomes the need of ultra-clean laboratory conditions and allows the selective sampling of solid material on the micrometer scale. On the detector side, the recent technology came up with multi-collector (MC) arrangements which allow the simultaneous detection of the relative abundance of various isotopes (see Simonetti et al. 2005). The conventional Faraday cup detectors (normally 9 in a line) may be equipped with additional multichannel ion counters (MICs) for high-sensitivity isotope analyses. The equipment with additional MICs is only a spatial problem within the Faraday cup arrangement and, generally, 6–8 MICs may easily be accommodated, allowing the simultaneous analysis of about 15 isotopes.

The shortcomings of the *laser* ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) relative to SHRIMP or conventional TIMS analyses have been its lower precision. The *laser* ablation process is not as stable as the SHRIMP method, or as the introduction of the sample in solution as in the case of TIMS. Firstly, this is due to the fragmentation and vaporization process of the solid material ablated. The *laser* beam may ablate parts of the mineral which are slightly fractured, altered or otherwise physically weakened or inhomogenized by previous geological processes, including the destruction of the mineral lattice by the proper radioactive radiation. The result is that the ablation and vaporization process of the material may vary in efficiency and completeness and, thus, the material transport to the plasma may not be continuous. Secondly, the carrier gas flux, normally ultrapure He, has an appreciable effect on the stability of the gas flow. Hence, the *laser* settings, such as *laser* intensity, *laser* frequency and beam diameter, together with the gas flow parameters, are fundamental for a reasonably stable signal reaching the detectors.

With the more recent developments, however, the analytical uncertainties are getting closer to those of SHRIMP (see Willigers et al. 2002). Bruguier et al. (2001) arrived at 6%, Horn et al. (2000) at 2%, Chang et al. (2006) at 4%, and Gerdes and Zeh (2006) at 3–4% precision or accuracy for U-Pb isotope ratios of natural materials. These values depend very much on the nature of the material analysed, such as its composition, presence of fractures, inclusions and heterogeneities. The LA-ICP-MS analyses may be even more precise for synthetic glass standards which are chemically and isotopically homogeneous (Bernal et al. 2005). Often, the largest uncertainty is given by the analysis of the standards (Chang et al. 2006) which are generally natural minerals including all the potential pitfalls. With a precision of that magnitude, however, with the control of the spatial resolution of the material analysed, and with the relatively easy preparation of the samples, the *laser* ablation MC-ICP mass spectrometry certainly is the method of choice for the coming years for isotopic analysis of solid materials in the geo- and environmental sciences (Willigers et al. 2002, Košler and Sylvester 2003).

SET-UP OF THE LASER ABLATION MC-ICP-MS U-Pb METHOD

The analytical equipment used in this study was installed at the "Laboratório de estudos geocronológicos, geodinâmicos e ambientais" of the Geosciences Institute of the University of Brasília, Brasília, Brazil, by initiative of Petróleo Brasileiro S/A – PETROBRAS and the "Ministério de Minas e Energia". The laboratory is part of the "Rede de Estudos Geodinâmicos e Ambientais – GEOCHRONOS". It was inaugurated in December 2006 and consists, apart from other installations and instrumentation, of a Thermo Finnigan *Neptune* multi-collector inductively coupled plasma mass spectrometer. Attached to this is a New Wave 213μm Nd-YAG solid state *laser* which provides the ablated material to the mass spectrometer.

SAMPLE PREPARATION

Sample preparation is straightforward. The minerals of interest, in this case zircon, are separated from the rock matrix by crushing the rock, concentrating the heavy mineral fraction by panning, separating the zircon grains by a Frantz magnetic separator, and final hand-picking of individual zircon grains. *In situ* analysis directly on a rock slab or thin section is also possible. However, it was found that the procedure of pre-concentration largely facilitates the measurements and localization of the zircons, so that it is worthwhile to be done.

The zircon grains are then located under the binocular one by one on a glass wafer covered with a double-sided tape in order to secure the grains. A 9 mm diameter plastic ring is placed on the tape around the zircons, and filled with two-compound epoxy. After 1-2 days of drying, the mounts are removed from the tape. Polishing of the mounts is done with 3μm followed by 1 μm diamond paste in order to expose unaltered and clean zircon surfaces. It is advisable to locate the grains on existing flat crystal surfaces (if present) to avoid excessive polishing.

The mounts are then taken to an ultrasonic bath with 3% HNO_3, and then cleaned with distilled water. A Nylon sample holder which takes three mounts was especially constructed. The three sites may be occupied with one standard and two samples, or with two standards and one sample.

THE LASER SET-UP

The sample chamber is flushed with He gas of analytical quality, which samples the ablated and vaporized material to be transported via Tygon tubes into the ICP. Before entering the *laser* sample chamber, the He passes through a glass tube filled with gold-coated quartz crystals (gold trap) to remove the largest part of mercury (Hg) whose isotope ^{204}Hg interferes with the ^{204}Pb isotope analysed to apply the common Pb correction. The He gas flux is commonly 0.35–0.45 L/min.

The *laser* is run at a frequency of 7–10 Hz and an energy of 30–36%, resulting in a *laser* energy of ca. 0.5 to 1.2 J/cm^2. A small *laser* spot size of say 30μm applied to a single spot with these *laser* conditions would not produce enough material for a reasonable signal, but at least 40–50μm would be required, with the signal intensity deteriorating along duration of the analysis because of the deepening of the *laser* pit. This suggested the use of a raster scheme of the *laser* which samples only the surface of the zircon. The raster is composed of two parallel and a connecting line with a 20μm spacing. With a 30μm beam diameter applied here, the sampled area of the zircon is a square of about 70μm on each side. With a speed of 1μm/sec, the propagating *laser* spot takes about 1 min to pass the raster, which is enough time to collect the signal. This setting also avoids the prominent down-hole fractionation of isotopes which would require an additional correction, and a significantly higher *laser* energy to drill the zircon. Before signal collection, a pre-ablation run along the raster is applied to clean the mineral surface. The running conditions of this cleaning run are: 40μm spot size, frequency 10 Hz and 25% *laser* energy.

THE ICP-MS AND MULTI-COLLECTOR SET-UP

Before entering the plasma, the He gas coming from the *laser* with the ablated material, is combined with Ar gas of analytical quality which sustains the plasma. The detector arrangement consists of a central Faraday cup and 4 Faraday cups each on the high side and low side of the centre cup (Fig. 2). For high-sensitivity analyses of the Pb and U isotopes, the mass spectrometer is equipped with 6 ion counters (ICs, or multichannel ion counters MICs). Four of them are fixed on the outermost Faraday cup of the low side (cup L4), one on the third cup of the low side (cup L3), and one on the outermost Faraday cup on the high side (cup H4). The latter is used only for the analysis of ^{238}U in materials with extremely low U content. For the present application, we analysed ^{238}U on the Faraday cup H4. The other isotopes are collected on the low side. The four ICs on the cup L4 are fixed at defined distances referring to: one mass unit between L4 and IC5, one mass unit between IC5 and IC4, two mass units between IC4 and IC3, and two mass units between IC3 and IC2. The signals collected on the four ICs are: ^{207}Pb on IC5, ^{206}Pb on IC4, ^{204}Hg/^{204}Pb on IC3, and ^{202}Hg on IC2. Because of the always present contamination of the He gas with Hg, a correction for the isobaric interference between ^{204}Hg and ^{204}Pb has to be applied, using the signal of ^{202}Hg collected on IC2.

DATA COLLECTION

With this collector set-up, five isotopes are analysed simultaneously. Before analysis, the Faraday cups are calibrated for baseline and gain, and the ICs for their yield. To ensure the optimal operating voltage and the same sensitivity for the ICs, a signal of about 300,000 counts per second (cps) is successively directed into the 4 ICs using different analysing lines. We use a solution of ^{206}Pb for this cross-calibration. Based on the signal response for each IC, the operating voltage of each IC is adjusted in order to ensure measuring conditions with the same sensitivity for all ICs used.

For standard and sample analysis, the signals are collected in a single block with 40 cycles of 1.049 sec. each. The *laser* is started and, when the signal at the detectors has reached its maximum, the 40 cycles are taken. A typical analysis therefore takes about 1 min and is illustrated in Figure 3. The isotopes ^{202}Hg, ^{204}(Pb+Hg), ^{206}Pb and ^{207}Pb are read in counts per second (cps), and ^{235}U in mV, which is transferred into cps by multiplication by a factor of 62,500. We apply a standard-sample bracketing technique, analysing

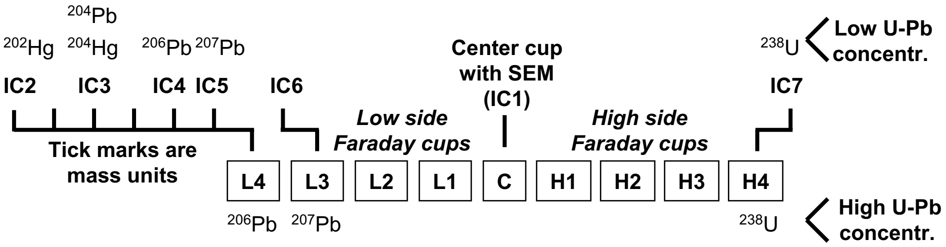

Fig. 2 – Set-up of the cup configurations (Faraday cups and ICs) for low U-Pb and high U-Pb concentrations in zircon with the Thermo Finnigan *Neptune* MC-ICP-MS.

a blank, a standard, and three samples, blank, standard, and so on. The method accounts for the drift of the instrument, and eliminates the need to correct for the mass bias of individual isotopes.

DATA REDUCTION

The isotope data of the 40 analysed cycles are transferred into an in-house Excel spreadsheet for data reduction. The isotope ratios of the 40 cycles are evaluated on a 2σ standard error rejection basis. The routine then calculates the error correlation value ρ (rho) for the ^{206}Pb/^{238}U and ^{207}Pb/^{235}U data. The isobaric contribution of ^{204}Hg is subtracted from the joint ^{204}Pb/^{204}Hg peak by considering the analyzed ^{202}Hg/^{204}Hg ratio. The spreadsheet allows to chose between three ways to determine the ^{202}Hg/^{204}Hg value which is applied for correction: (i) from the mean of the two bracketing blanks, (ii) from the mean of the two bracketing (common Pb-free) standards, or (iii) from the mean of the four. Normally, the difference between the three determinations is minor. We consider this more favourable than applying the natural ^{202}Hg/^{204}Hg ratio of 4.346, which would require an absolutely precise cross-calibration of IC2 and IC3. Because ^{235}U cannot be analysed with this type of cup configuration, the natural ratio ^{238}U/^{235}U of 137.88 is used to calculate the ^{235}U intensity.

The correction for instrumental drift and mass bias is done by considering the two standards analysed before and after the samples, and the two blank analyses run before and after the samples, respectively, after applying a blank correction for all isotopes analysed. The normalization of the isotopic ratios of the samples (R_{spl}) follows the formula of Albarède et al. (2004):

$$R_{spl} = \frac{R_{std} \times r_{spl}}{\left(r_{std1}^{1-\theta} \times r_{std2}^{\theta}\right)} \qquad (3)$$

for which R_{std} is the true isotopic ratio of the standard (^{207}Pb/^{206}Pb or ^{206}Pb/^{238}U ratios, respectively), r_{spl} is the analysed isotopic ratio of the sample, and r_{std1} and r_{std2} are the analysed isotopic ratios of the two standards before and after the samples along the sequence. The variable θ (theta) is a time factor (Albarède et al. 2004) or, in other words, gives respective weight to the two standard measurements. It depends on the location of the samples within the analysing sequence, and takes values between 0 and 1. For example, three successive analyses run between two standards and two blanks suggest $\theta = 0.25$, 0.50 and 0.75 for samples 1, 2 and 3, respectively. The term $\left(r_{std1}^{1-\theta} \times r_{std2}^{\theta}\right)$ is a linear interpolation of the logarithms of the isotopic ratios, which accounts for the generally exponential instrumental drift. The same algorithm is applied to correct for the drift in the blank analyses. An alternative would be to inject a diluted thallium (Tl) solution to determine the mass bias of the Pb isotopes (e.g., Horn et al. 2000) which, however, does not allow the correction of U mass bias. The standard-sample bracketing approach applied here, therefore, certainly bears the least error for that analytical method, as it does not require intensive mass bias corrections.

The corrected ^{206}Pb/^{238}U and ^{207}Pb/^{206}Pb ratios so obtained are transferred into absolute age information using the software of Ludwig (2003). The software was also used to plot the Concordia diagrams. The errors of the ^{206}Pb/^{238}U and ^{207}Pb/^{206}Pb ratios were propagated by quadratic addition of the external reproducibility and the within-run precision, following equation (4):

$$2\sigma\left(\frac{^{206}\mathrm{Pb}}{^{238}\mathrm{U}}, \text{ or } \frac{^{207}\mathrm{Pb}}{^{206}\mathrm{Pb}}\right)_{\text{propagated}} \qquad (4)$$

$$= \left(2\mathrm{SD}^{\wedge 2}_{\text{analysed}} + 2\mathrm{SE}^{\wedge 2}_{\text{analysed}}\right)^{1/2}$$

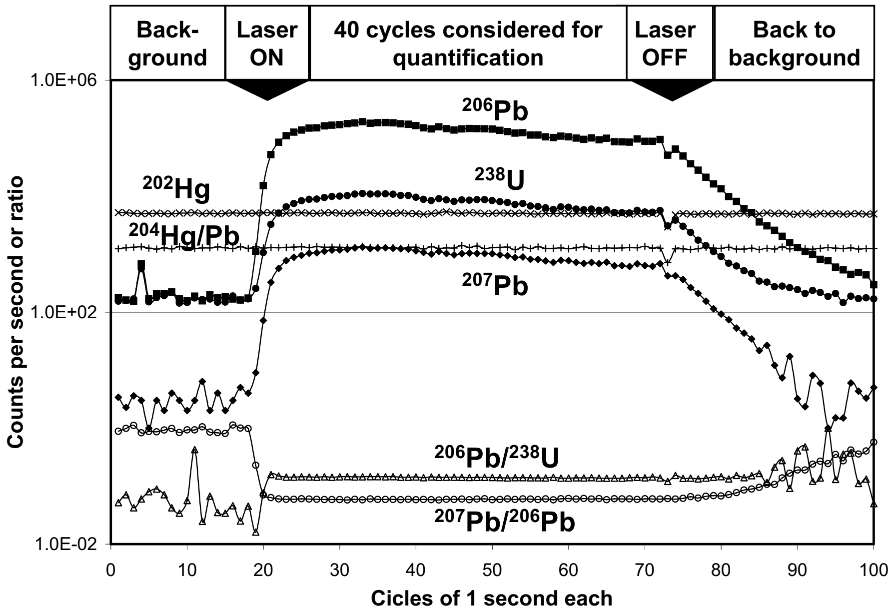

Fig. 3 – Typical signal sequence of a *laser* ablation experiment. Note that the absolute count rates of the isotopes may vary during the ablation process while the isotope ratios remain constant. The signals of ^{202}Hg and ^{204}Hg/Pb, in the case of no common ^{204}Pb present in the ablated sample, come solely from the Hg contents in the Ar gas, and are therefore not influenced by the ablation process.

with SD being the sample standard deviation σ:

$$\sigma = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(x_i - x_m\right)^2} \tag{5}$$

where N is the number of analyses, x_i is the value of each individual analyses x_i to x_N, and x_m is the arithmetic mean of all analyses. Whereas the SD is independent of the number of analyses, the standard error SE:

$$SE = \frac{\sigma}{\sqrt{N}} \tag{6}$$

decreases with the number of analyses N taken. The external reproducibility (2 $SD^{\wedge 2}_{analysed}$) is represented by the standard deviation obtained by repeated analysis of standard zircon GJ-1 which were run during the analytical session (generally ~0.8% for ^{207}Pb/^{206}Pb, and ~1% for ^{206}Pb/^{238}U). The within-run precision (2 $SE^{\wedge 2}_{analysed}$) is the standard error calculated for each analysis. The resulting errors are 2σ standard deviations.

Zircon U-Pb isotopic analyses may require a correction for the common lead contribution to the total ^{206}Pb and ^{207}Pb signals. There are a couple of methods to do this in the literature (see Andersen 2002, Horstwood et al. 2003). For minerals with a low common Pb content as, for example, zircon, we use a correction based on the amount of non-radiogenic ^{204}Pb. The counts per second of ^{204}Pb (including a correction for ^{204}Hg) are used to deduce the amount of non-radiogenic, common ^{206}Pb and ^{207}Pb, given a common Pb composition following the model of Stacey and Kramers (1975). With the fraction f_c of common ^{206}Pb and ^{207}Pb so obtained:

$$f_c = \frac{Pb_c}{Pb_t} = \frac{Pb_c}{Pb_c + Pb_r} \tag{7}$$

where Pb_c is the value (in counts per second) of common Pb, Pb_t the total Pb, and Pb_r the radiogenic Pb, with Pb being ^{206}Pb or ^{207}Pb, respectively, we use the relationships:

$$\frac{^{206}Pb}{^{238}U_{radiogenic}} = \frac{^{206}Pb}{^{238}U_{total}} \times (1 - f_c), \tag{8}$$

and

$$\frac{^{207}Pb}{^{235}U_{radiogenic}} = \frac{^{207}Pb}{^{235}U_{total}} - \left(\frac{^{206}Pb}{^{238}U_{total}} \times \frac{^{207}Pb}{^{206}Pb_{common}} \times \frac{^{238}U}{^{235}U} \times f_c\right) \tag{9}$$

of Andersen (2002) to arrive at common Pb-corrected ^{206}Pb/^{238}U and ^{207}Pb/^{235}U isotopic ratios. The necessity for a correction is judged from the ^{204}Pb signal intensity. Values smaller than ~25 cps (blank-corrected), resulting in ^{206}Pb/^{204}Pb ratios well beyond 3000, suggest an insignificant common Pb content which would not recognizably effect the calculated ages. All zircons analysed in this study met this condition, and therefore did not require a correction.

STANDARDS AND SAMPLES

Three international zircon standards were analysed, using each one as an external standard and correcting the remaining two against it. This yields a set of 6 isotope ratio and age data which are compared with the certified values of the standards (see Table I). The standards are: (i) GJ-1 zircon standard provided by the ARC National Key Centre for Geochemical Evolution and Metallogeny of Continents (GEMOC), Australia. This is a gem-quality zircon crystal of about 0.7 cm in diameter which was broken and prepared for analysis. Its reference age after Jackson et al. (2004) is: ^{207}Pb/^{206}Pb age = 608.6 ± 1.1 Ma, ^{206}Pb/^{238}U age = 600.4 ± 1.8 Ma, ^{207}Pb/^{235}U age = 602.1 ± 3.0 Ma; (ii) Temora 2, provided by Lance Black, Geoscience Australia, Australia, which comes from the Middledale gabbroic diorite in eastern Australia; the zircon crystals have a size of about 300–500 μm and, prior to sample preparation, the concentrate was hand-picked to obtain a high-purity zircon concentrate. Its reference age after Black et al. (2004) is: ^{207}Pb/^{206}Pb age = 419.1 ± 9.1 Ma, ^{206}Pb/^{238}U age = 416.2 ± 1.1 Ma, ^{207}Pb/^{235}U age = 416.7 ± 1.7 Ma; (iii) FC1 zircon concentrate provided by Richard Armstrong, Australian National University, Canberra, Australia; the crystals have sizes of approximately 50–100μm, and were hand-picked prior to sample preparation; they were extracted from the Duluth Complex in the U.S.A. Its reference age (Paces and Miller 1993) is: ^{207}Pb/^{206}Pb age = 1098.9 Ma, ^{206}Pb/^{238}U age = 1099.9 Ma, ^{207}Pb/^{235}U age = 1100.0 Ma.

For an additional test of the method, two zircon samples from our own laboratory which had previously been dated by other analytical methods were also investigated here. One is a relatively young zircon concentrate (sample HD66) from a hornblende-bearing orthogneiss of the Neoproterozoic Goiás magmatic arc which has previously been dated at 630 ± 5 Ma (2σ) by U-Pb ID-TIMS in our laboratory (Laux et al. 2005). Its average ^{207}Pb/^{206}Pb TIMS age is 633.3±5.7 Ma. The other sample (EC69A) has much older zircon crystals and went through a more complex geological history. They were extracted from a migmatized hornblende- and biotite-bearing tonalite from an Archean nucleus of the São José do Campestre Massif in the Borborema Province, NE Brazil. The zircons yielded an upper intercept age of 3065 ± 12 Ma determined by SHRIMP analysis (Dantas et al. unpublished data).

RESULTS

Between 13 and 23 analyses were run for the standards GJ1, Temora 2 and FC1. Figure 4 shows the ages obtained for each standard normalized against one another in a Concordia diagram, and Table I summarizes the data obtained. The concordance between the values obtained and the referenced standard data of the ^{207}Pb/^{206}Pb, ^{206}Pb/^{238}U and ^{207}Pb/^{235}U age data is well satisfactory. We obtained precisions of 1.9 to 3.7% (2σ standard deviation) for the ^{207}Pb/^{206}Pb, ^{206}Pb/^{238}U and ^{207}Pb/^{235}U age data, depending on the isotope system and on the particular standard. The accuracy was calculated as the percentage of deviation between the analysed Concordia age and the referenced ^{207}Pb/^{206}Pb age. The Concordia age, following Ludwig (2003) is, "the most-probable age for a data-point (or weighted-mean data-point) on a Concordia diagram, where the true location of the data point is assumed to fall precisely on the Concordia curve". Because not all referenced standards provide the error correlation coefficient to calculate that age, their referenced ^{207}Pb/^{206}Pb age was used. The accuracy so obtained varies between 0.6 and 3.8% (2σ standard deviation).

The majority of the 23 analyses obtained for the natural sample HD66 (Table II) were taken as multiple analyses on different localities of individual grains. They are all concordant (Fig. 5), yielding a Concordia age of 627.6 ± 1.3 Ma, which is identical within error to the TIMS age of 630 ± 5 Ma. None of the zircons required a common Pb correction. The ^{204}Hg-corrected ^{204}Pb signal was 30 cps at most, yielding calculated ^{206}Pb/^{204}Pb ratios between 3000 and 50000. The

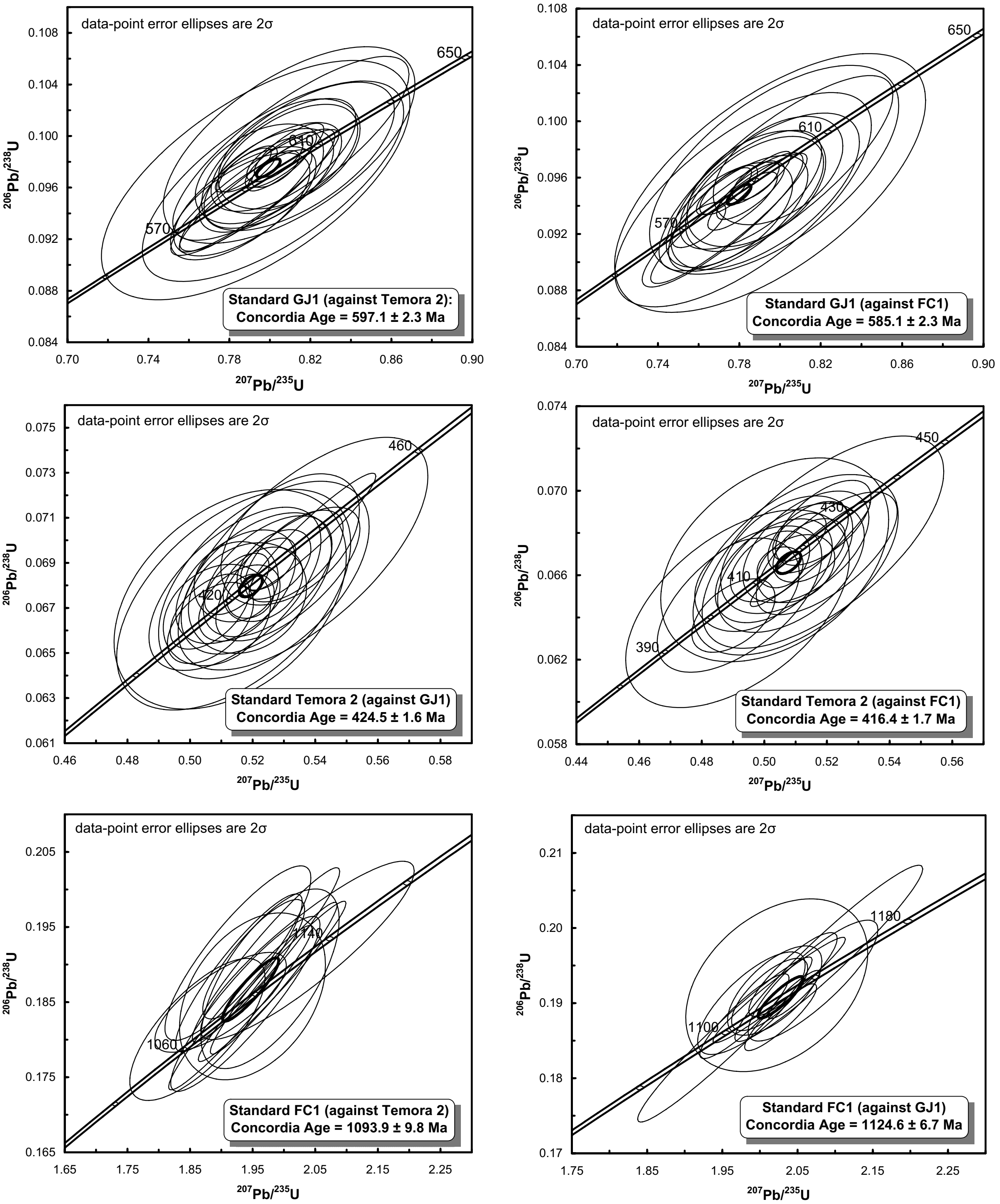

Fig. 4 – Concordia diagrams of LA-ICP-MS analyses of standards GJ1, Temora 2 and FC1. See Table I for the full data set. The Concordia line is shown as a Concordia band considering the 2σ decay constant errors for ^{235}U and ^{238}U of Ludwig (2003).

TABLE I
Referenced and determined ages (by LA-ICP-MS) of the zircon standards GJ1, Temora 2 and FC1.

Sample	Standard	No. of anal.	^{207}Pb*/ ^{206}Pb* age (Ma) referenced	Error (2σ) (Ma)	^{207}Pb*/ ^{206}Pb* age (Ma) analysed	Error (2σ) (Ma)	Prec. (2σ) (%)	^{206}Pb*/ ^{238}U age (Ma) referenced	Error (2σ) (Ma)	^{206}Pb*/ ^{238}U age (Ma) analysed	Error (2σ) (Ma)	Prec. (2σ) (%)
GJ1	Temora 2	23	608.6	1.1	598.4	6.3	2.8	600.4	1.8	598.3	20.2	2.7
GJ1	FC1	20	608.6	1.1	583.7	6.1	2.4	600.4	1.8	584.0	19.8	2.3
Temora 2	GJ1	23	419.1	9.1	424.8	16.5	2.9	416.2	1.1	424.9	12.9	2.8
Temora 2	FC1	20	419.1	9.1	414.9	16.6	3.5	416.2	1.1	414.9	12.6	3.5
FC1	Temora 2	13	1098.9	n.r.	1111.6	5.5	3.7	1099.9	n.r.	1109.9	30.4	3.4
FC1	GJ1	13	1098.9	n.r.	1127.8	4.8	2.9	1099.9	n.r.	1127.2	25.5	2.7

Sample	Standard	No. of anal.	^{207}Pb*/ ^{235}U age (Ma) referenced	Error (2σ) (Ma)	^{207}Pb*/ ^{235}U age (Ma) analysed	Error (2σ) (Ma)	Prec. (2σ) (%)	Concordia age (Ma) determined	Error (2σ) (Ma)	Accuracy (%)
GJ1	Temora 2	23	602.1	3.0	596.7	15.9	1.6	597.1	2.3	1.9
GJ1	FC1	20	602.1	3.0	587.7	15.7	1.9	585.1	2.3	3.9
Temora 2	GJ1	23	416.7	1.7	426.6	10.8	2.8	424.5	1.6	1.3
Temora 2	FC1	20	416.7	1.7	415.9	10.6	3.7	416.4	1.7	0.6
FC1	Temora 2	13	1100.0	n.r.	1098.0	24.7	2.6	1093.9	9.8	0.5
FC1	GJ1	13	1100.0	n.r.	1123.3	21.9	2.2	1124.6	6.7	2.3

Referenced values from: GJ1 (Jackson et al. 2004), Temora 2 (Black et al. 2004), FC1 (Paces and Miller 1993). Precision (Prec.): 2σ precision for the number of analyses, "n.r." = not reported. All errors are 2σ standard deviations. Accuracy: Percentage of deviation between analysed concordia age and referenced ^{207}Pb/^{206}Pb age.

weighted average of 24 ^{207}Pb/^{206}Pb ages resulted in a ^{207}Pb/^{206}Pb age of 628.7 ± 6.0 Ma, compared with the TIMS ^{207}Pb/^{206}Pb age of 633.3 ± 5.7 Ma.

Sample EC69A shows a more complex zircon population, as seen from 24 SHRIMP (Table III) and 35 LA-ICP-MS analyses (Table IV). Most of the LA-ICP-MS analyses were taken as multiple shots on individual zircon grains. None of the zircons required a common Pb correction. The ICP-MS analyses display various groups of zircons plotting on supposedly different Discordia lines (Fig. 6). The youngest upper intercept age, defined by four discordant and three concordant analytical points, yields the age of 3045 ± 24 Ma, which agrees within error with the SHRIMP age of 3065 ± 12 Ma. However, various older zircon populations were encountered in the sample. One is defined by 17 discordant zircon analyses which yield an upper intercept age of 3305 ± 51 Ma. A minor population composed of three discordant analyses gives an upper intercept age of 3625 ± 38 Ma. The two latter populations may relate to 3.4–3.5 Ga ages reported from the same area by Dantas et al. (2004). Another group of five highly discordant zircon analyses with extremely low ^{206}Pb/^{238}U ratios may represent still another, even older geological event. Three analyses on grain 14 (see Table IV, but not included in Fig. 6) yielded one concordant and two nearly concordant data with ages between 540 and 570 Ma. They represent another event of resetting of the isotope system during the Neoproterozoic/Cambrian Brasiliano cycle. Therefore, the Discordias of all older zircon populations were anchored to 558 Ma, which is the mean of these three analyses.

DISCUSSION AND CONCLUSIONS

A comparison of the LA-ICP-MS results of the natural sample HD66 with TIMS analyses shows a fine conformity even within the limits of error, yielding 627.6 ± 1.3 Ma for LA-ICP-MS and 630 ± 5 Ma for the TIMS analyses. Moreover, the LA-ICP-MS analyses indicate

TABLE II
TIMS and LA-ICP-MS analyses of sample HD66.

Analysis	$^{207}Pb^*/^{206}Pb^*$	2σ error (%)	$^{207}Pb^*/^{235}U$	2σ error (%)	$^{206}Pb^*/^{238}U$	2σ error (%)	ρ	$^{207}Pb/^{206}Pb$ age	2σ error (Ma)	$^{207}Pb^*/^{235}U$ age	2σ error (Ma)	$^{206}Pb^*/^{238}U$ age	2σ error (Ma)
TIMS													
1	0.0609	0.16	0.841	0.28	0.100	0.23	0.82	637.0	3.5	619.7	1.3	614.4	1.3
2	0.0609	0.24	0.844	0.46	0.100	0.39	0.84	636.0	5.3	621.4	2.1	614.4	2.3
3	0.0608	0.20	0.851	0.44	0.101	0.39	0.89	634.0	4.3	625.2	2.1	620.3	2.3
4	0.0606	0.44	0.856	1.17	0.102	1.09	0.93	626.0	9.5	627.9	5.5	626.1	6.5
LA-ICP-MS													
1	0.06112	1.6	0.8864	2.5	0.10499	2.5	0.91	643.5	33.9	644.4	11.9	643.6	15.4
2	0.06054	2.2	0.8511	1.6	0.10147	1.6	0.63	622.8	46.3	625.2	7.4	623.0	9.5
3a	0.06068	1.0	0.8566	2.8	0.10230	2.8	0.94	627.9	22.4	628.2	12.9	627.9	16.5
3b	0.06054	1.2	0.8474	2.7	0.10147	2.7	0.93	623.0	26.1	623.2	12.5	623.0	16.1
3c	0.06082	1.1	0.8658	2.0	0.10316	2.0	0.90	632.8	22.5	633.3	9.5	632.9	12.2
4	0.06116	1.5	0.8885	1.9	0.10525	1.9	0.76	645.0	31.2	645.5	9.2	645.1	11.9
5a	0.06094	2.0	0.8666	2.2	0.10385	2.2	0.86	637.2	42.8	633.7	10.5	636.9	13.5
5b	0.06090	1.7	0.8637	2.4	0.10358	2.4	0.92	635.7	37.2	632.1	11.0	635.3	14.3
6a	0.06080	1.9	0.8653	2.3	0.10303	2.3	0.77	632.1	39.7	633.0	10.9	632.2	14.0
6b	0.06076	1.6	0.8642	1.7	0.10283	1.7	0.75	630.8	33.1	632.4	7.8	631.0	10.0
6c	0.06077	2.0	0.8632	2.5	0.10284	2.5	0.82	630.9	41.9	631.8	11.8	631.0	15.2
7a	0.06085	1.0	0.8671	1.9	0.10333	1.9	0.94	633.9	21.0	634.0	8.9	633.9	11.4
7b	0.06079	1.1	0.8637	1.7	0.10296	1.7	0.87	631.7	24.0	632.1	7.9	631.7	10.1
7c	0.06083	1.2	0.8662	1.6	0.10319	1.6	0.89	633.1	26.6	633.5	7.6	633.1	9.7
8a	0.06049	1.1	0.8441	2.1	0.10114	2.1	0.90	621.0	23.5	621.4	9.5	621.1	12.1
8b	0.06059	1.3	0.8657	2.2	0.10188	2.2	0.83	624.6	27.7	633.2	10.1	625.4	12.8
8c	0.06069	1.7	0.8571	2.2	0.10236	2.2	0.82	628.2	35.9	628.6	10.1	628.2	13.0
9	0.06056	1.6	0.8524	2.5	0.10161	2.5	0.83	623.6	34.3	626.0	11.4	623.8	14.6
10a	0.06018	2.1	0.8231	2.6	0.09928	2.6	0.80	610.2	44.8	609.8	11.7	610.2	14.9
10b	0.06046	1.8	0.8424	2.4	0.10097	2.4	0.88	620.0	38.4	620.5	10.9	620.1	14.0
10c	0.06051	2.1	0.8484	2.9	0.10127	2.9	0.85	621.7	45.7	623.8	13.5	621.9	17.3
11a	0.06035	1.4	0.8346	2.3	0.10028	2.3	0.86	616.1	29.3	616.1	10.7	616.1	13.6
11b	0.06057	1.4	0.8485	1.8	0.10162	1.8	0.76	623.9	30.3	623.8	8.4	623.9	10.7

Note: Analyses with letters (a, b, c) indicate analyses on the same zircon grain. All errors are 2σ standard deviations.

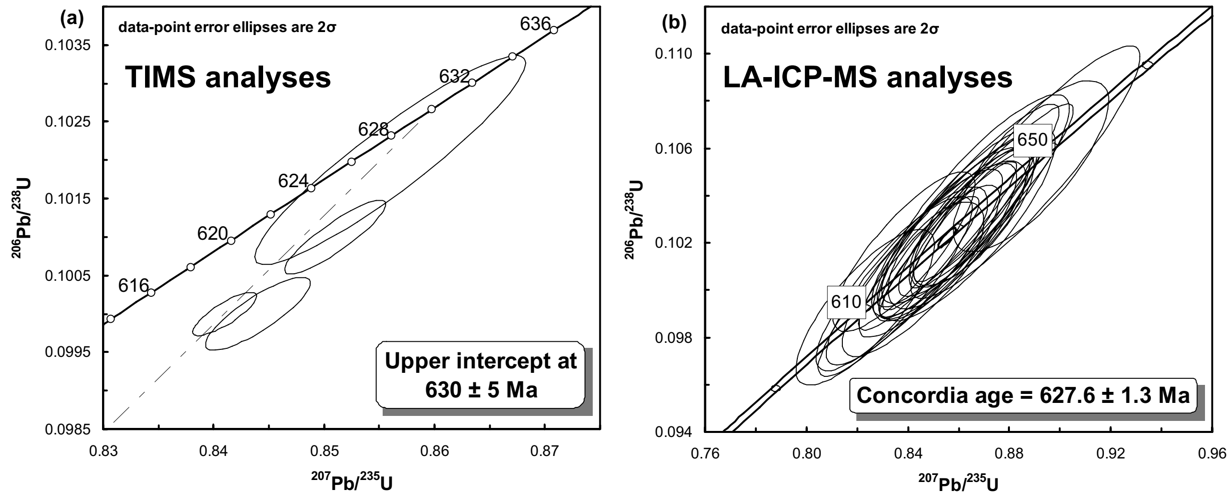

Fig. 5 – Comparison of (a) TIMS data (4 analyses from Laux et al. 2005) with (b) 24 LA-ICP-MS analyses of sample HD66. The Concordia age of 627.6 ± 1.3 Ma obtained by LA-ICP-MS falls well within the error range on the TIMS age of 630 ± 5 Ma. See Table II for full analyses.

TABLE III
SHRIMP data of sample EC69A.

Analysis	^{207}Pb*/ ^{206}Pb*	1σ error (%)	^{207}Pb*/ ^{235}U	1σ error (%)	^{206}Pb*/ ^{238}U	1σ error (%)	ρ	^{207}Pb/ ^{206}Pb age	1σ error (Ma)	^{207}Pb*/ ^{235}U age	1σ error (Ma)	^{206}Pb*/ ^{238}U age	1σ error (Ma)
1	0.23187	0.16	18.88	1.4	0.5904	1.4	0.99	3065	2.6	3036	13.6	2991	34
2	0.22398	0.26	17.02	1.6	0.5512	1.5	0.99	3010	4.2	2936	15.5	2830	34
3	0.22960	0.59	18.61	1.6	0.5877	1.4	0.92	3049	9.6	3022	15.5	2980	33
4a	0.17531	0.17	5.20	1.5	0.2153	1.5	0.99	2609	2.8	1853	12.9	1257	17
4b	0.23401	0.24	17.90	1.5	0.5547	1.5	0.99	3080	3.9	2984	14.5	2845	35
5	0.22896	0.20	18.83	1.5	0.5964	1.4	0.99	3045	3.2	3033	14.6	3015	33
6	0.23269	0.11	18.40	1.4	0.5734	1.4	1.00	3071	1.7	3011	13.6	2922	33
7	0.22065	0.33	15.63	1.5	0.5139	1.5	0.98	2986	5.4	2854	14.4	2673	33
8a	0.22995	0.22	18.74	1.5	0.5909	1.4	0.99	3052	3.5	3029	14.6	2993	34
8b	0.23278	0.20	19.57	1.4	0.6098	1.4	0.99	3071	3.2	3070	13.6	3069	34
9	0.22789	0.36	17.77	1.5	0.5654	1.4	0.97	3037	5.8	2977	14.5	2889	33
10	0.22748	0.34	16.34	1.5	0.5210	1.4	0.97	3034	5.5	2897	14.5	2703	31
11	0.23340	0.41	19.46	1.6	0.6047	1.5	0.96	3076	6.6	3065	15.6	3049	37
12	0.22859	0.26	15.47	1.5	0.4907	1.4	0.98	3042	4.2	2845	14.4	2574	30
13	0.22691	0.13	17.89	1.4	0.5719	1.4	1.00	3030	2.1	2984	13.6	2915	32
14	0.23221	0.14	19.22	1.4	0.6003	1.4	1.00	3067	2.2	3053	13.6	3031	34
15	0.22759	0.23	17.75	1.5	0.5655	1.5	0.99	3035	3.7	2976	14.5	2889	35
16	0.23251	0.09	18.21	1.4	0.5680	1.4	1.00	3069	1.4	3001	13.6	2900	33
17	0.23087	0.12	18.37	1.4	0.5772	1.4	1.00	3058	1.9	3009	13.6	2937	33
18	0.22915	0.32	17.01	1.5	0.5382	1.4	0.98	3046	5.1	2935	14.5	2776	32
19	0.21750	0.68	15.98	1.6	0.5327	1.5	0.91	2962	11	2876	15.4	2753	34
20	0.22271	0.44	15.34	1.5	0.4996	1.4	0.96	3000	7.1	2837	14.4	2612	30
21	0.23329	0.19	19.00	1.4	0.5906	1.4	0.99	3075	3.1	3042	13.6	2992	34
22	0.22929	0.10	17.43	1.4	0.5513	1.4	1.00	3047	1.6	2959	13.5	2830	32

Note that the errors are 1σ errors. The majority of shots were taken as single shots on zircon grains.

that there was no Pb loss in the zircons (no discordant zircons), in contrast to three out of four TIMS analyses (Fig. 5a). It is most probable, that weathered or otherwise isotopically disturbed surfaces of the zircons are responsible for the discordant U-Pb TIMS data, since the zircons were not abraded before digestion to remove possible alterations or disturbances. The LA-ICP-MS method avoids this by polishing of the zircon grains before analysis, and by a *laser* pre-ablation which cleans the uppermost part of the mineral surface.

The LA-ICP-MS analyses of the natural sample EC69A show a complex history of zircon growth and lead loss. Three concordant zircon analyses, together with 4 other analyses, define an upper intercept age of 3045 ± 24 Ma (Fig. 6) which agrees, within error, with the 3065 ± 12 Ma SHRIMP age. There are other discordant zircon analyses which, although being discordant, indicate a complex history of crystallization and partial resetting. In that particular case, the internal structure of the zircons would have to be imaged by cathodoluminescence or back-scattered electron techniques prior to analysis, for ensuring an unequivocal interpretation of the various age populations. The analyses presented here show, nevertheless, that it is possible to detect an even complex geological history from a set of only 10–15 zircon grains, by high spatial resolution LA-ICP-MS analysis.

The LA-MC-ICP-MS method presented here is designed for rapid analysis of large sample sets, which often are needed in sediment provenance or other regional geological studies. It overcomes extensive sample preparation and careful wet chemical isotope separation,

TABLE IV
LA-ICP-MS data of sample EC69A.

Analysis	^{207}Pb*/ ^{206}Pb*	2σ error (%)	^{207}Pb*/ ^{235}U	2σ error (%)	^{206}Pb*/ ^{238}U	2σ error (%)	ρ	^{207}Pb/ ^{206}Pb age	2σ error (Ma)	^{207}Pb*/ ^{235}U age	2σ error (Ma)	^{206}Pb*/ ^{238}U age	2σ error (Ma)
1	0.18772	0.4	18.40	6.2	0.55912	6.2	0.99	2722	7.2	3011	57.9	2863	141
2a	0.12520	1.7	15.34	12.8	0.43386	12.8	0.99	2032	29.4	2836	115	2323	245
2b	0.13026	2.3	15.21	7.3	0.44414	7.3	0.96	2101	40.1	2828	67.6	2369	144
3a	0.14210	2.6	16.13	4.2	0.47461	4.2	0.82	2253	44.5	2885	39.0	2504	85.7
3b	0.11516	13.4	10.85	15.2	0.37785	15.2	0.98	1882	224	2510	133	2066	264
3c	0.15040	1.5	17.38	4.8	0.49850	4.8	0.99	2351	24.9	2956	44.9	2607	102
4a	0.17586	0.8	17.33	4.5	0.53625	4.5	0.99	2614	12.6	2953	42.0	2768	99.7
4b	0.17187	1.6	16.36	10.7	0.52396	10.7	0.98	2576	26.4	2898	97.7	2716	233
5	0.14147	6.7	14.30	15.0	0.46184	15.0	0.98	2245	111	2770	133	2448	299
6	0.13705	6.1	17.42	5.8	0.47611	5.8	0.43	2190	102	2958	53.8	2510	119
7a	0.10342	7.7	15.16	5.8	0.37870	5.8	0.93	1686	136	2825	53.6	2070	102
7b	0.12225	0.9	16.12	3.6	0.43484	3.6	0.98	1989	16.4	2884	34.1	2328	70.4
7c	0.12528	4.6	15.74	6.5	0.43896	6.5	0.92	2033	79.9	2861	60.3	2346	127
8a	0.16852	3.5	18.26	5.1	0.53185	5.1	0.80	2543	57.0	3003	47.8	2749	113
8b	0.14777	1.2	17.80	1.5	0.49492	1.5	0.92	2320	20.7	2979	14.2	2592	31.8
8c	0.09571	2.3	13.34	14.1	0.33741	14.1	0.99	1542	42.7	2704	125	1874	226
9a	0.09655	7.2	17.69	9.3	0.36624	9.3	0.93	1559	129	2973	85.7	2012	159
9b	0.07537	13.3	16.89	14.7	0.28108	14.7	0.41	1078	246	2929	132	1597	205
9c	0.08637	4.9	16.78	4.0	0.32480	4.0	0.25	1346	91.0	2922	38.0	1813	63.6
9d	0.08336	8.0	16.41	7.6	0.31092	7.6	0.11	1278	148	2901	70.4	1745	115
10a	0.23273	1.0	19.28	2.5	0.60829	2.5	0.98	3071	15.8	3056	23.4	3063	59.5
10b	0.23732	0.9	19.18	2.1	0.61117	2.1	0.96	3102	14.4	3051	20.3	3075	51.8
10c	0.21793	1.7	18.07	3.4	0.58752	3.4	0.98	2965	26.9	2993	32.1	2979	80.4
11a	0.13695	3.3	14.30	4.7	0.45064	4.7	0.95	2189	55.6	2770	43.3	2398	92.6
11b	0.14320	1.6	16.17	8.6	0.47580	8.6	0.99	2266	27.5	2887	78.8	2509	176
11c	0.18069	1.5	18.19	3.5	0.54860	3.5	0.96	2659	23.9	3000	33.0	2819	79.0
12a	0.09062	3.6	15.42	4.1	0.33203	4.1	0.57	1439	67.9	2842	38.3	1848	65.5
12b	0.12647	1.2	15.27	1.7	0.43256	1.7	0.76	2049	20.3	2832	15.8	2317	32.4
12c	0.09022	9.4	13.17	8.0	0.31563	8.0	0.78	1430	170	2692	73.0	1768	123
13a	0.12573	3.9	16.94	4.6	0.44200	4.6	0.61	2039	66.8	2931	42.7	2360	89.3
13b	0.14744	3.8	17.27	5.1	0.48892	5.1	0.65	2316	63.4	2950	48.1	2566	108
13c	0.13245	4.5	16.69	6.4	0.45527	6.4	0.78	2131	75.9	2917	59.4	2419	128
14a	0.05842	0.8	0.7476	6.4	0.08864	6.4	0.99	545.7	16.9	566.8	27.6	547.5	33.7
14b	0.05902	1.1	0.7526	2.9	0.09212	2.9	0.97	567.9	23.8	569.8	12.5	568.0	15.6
14c	0.05882	0.8	0.7486	1.5	0.09090	1.5	0.93	560.3	17.8	567.4	6.6	560.9	8.2

Note that the errors are 2σ errors. The majority of shots were taken as multiple shots on zircon grains.

which may always be a source of sample contamination. Apart from that, however, it serve as well as a precise and accurate geochronological tool. With a precision of 1.9 to 3.7% (2σ SD) and an accuracy of 0.6 to 3.8% (2σ SD) for the ^{207}Pb/^{206}Pb, ^{206}Pb/^{238}U and ^{207}Pb/^{235}U isotopic analyses, the LA-ICP-MS method is a highly competitive method for rapid but nonetheless high-quality analyses of geological materials.

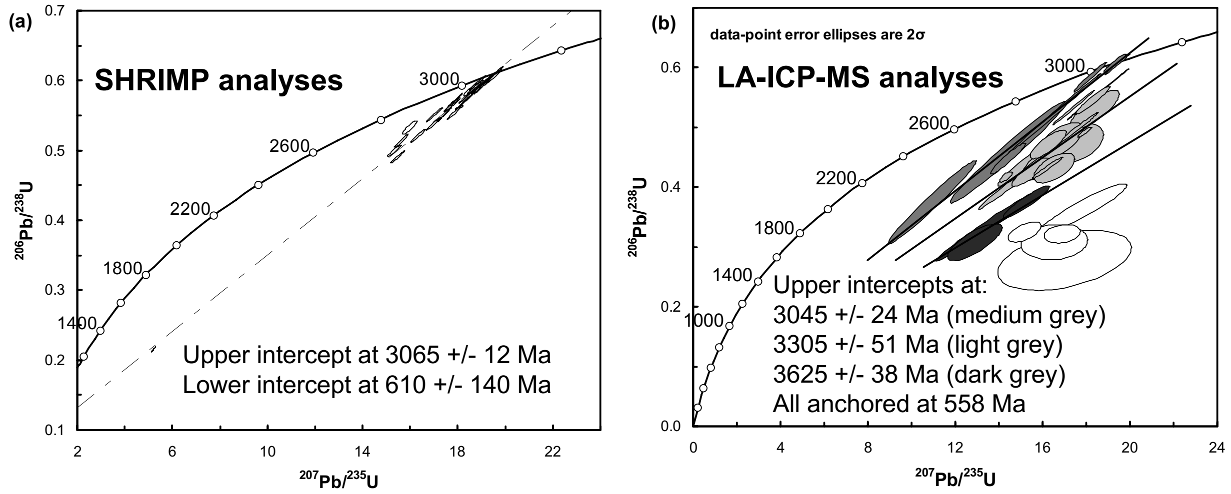

Fig. 6 – Comparison of (a) SHRIMP data (24 analyses from Dantas et al. unpublished data) with (b) 32 LA-ICP-MS analyses of sample EC69A. An upper intercept age of 3045 ± 24 Ma, defined by three concordant and four discordant analyses, is within error of the SHRIMP age of 3065 ± 12 Ma. The Discordia lines obtained by LA-ICP-MS are archored at 558 Ma. See Tables III and IV for full analyses.

ACKNOWLEDGMENTS

The LA-ICP-MS facility was installed at the Universidade de Brasília with funds provided by PETROBRAS and the Ministério de Minas e Energia do Brasil, which are gratefully acknowledged. Thanks go to Lance Black, Elena Belousova and Richard Armstrong for providing the zircon standards. We also thank the three anonymous journal referees for valuable and clarifying comments and suggestions.

RESUMO

A determinação de idades através do decaimento dos isótopos radioativos ^{235}U e ^{238}U para os isótopos radiogênicos ^{207}Pb e ^{206}Pb, respectivamente, utilizando o mineral zircão ($ZrSiO_4$), é amplamente aplicada para decifrar processos geológicos. Um novo método tem sido desenvolvido nos últimos anos, a ablação a *laser* multi-coletor espectrometria de massas com plasma indutivamente acoplado (LA-MC-ICP-MS), superando o laborioso trabalho anteriormente necessário em outros métodos, na preparação de amostras, e permite obtenção de razões isotópicas com alta resolução espacial de micrômetros. O presente estudo descreve os procedimentos analíticos e os métodos usados na redução de dados que estão sendo aplicados no Laboratório de Geocronologia da Universidade de Brasília. Explora-se a precisão e exatidão do método através da análise de três padrões internacionais de zircão. Observa-se uma precisão entre 1,9 a 3,7% (2σ desvio padrão) e uma exatidão de 0,6 a 3,8% (2σ desvio padrão) para as razões isotópicas de Pb e U dos padrões. Também foram obtidas idades pelo método LA-ICP-MS de duas amostras de zircões naturais, que já foram datadas anteriormente por outros métodos analíticos. A comparação dos resultados mostra uma boa conformidade das idades obtidas, dentro dos limites de erro. Os dados demonstram o grande potencial do método analítico para análises isotópicas rápidas, precisas e exatas de U-Pb, numa escala de micrômetros.

Palavras-chave: geocronologia, isótopos U-Pb, LA-MC-ICP-MS, zircão, datação.

REFERENCES

Albarède F, Telouk P, Blichert-Toft J, Boyet M, Agranier A and Nelson B. 2004. Precise and accurate isotopic measurements using multiple-collector ICPMS. Geochim Cosmochim Acta 68: 2725–2744.

Amelin Y and Davis WJ. 2006. Isotope analysis of lead in sub-nanogram quantities by TIMS using a ^{202}Pb-^{205}Pb spike. J Anal Atom Spectrom 21: 1053–1061.

Andersen T. 2002. Correction of common lead in U-Pb analyses that do no report ^{204}Pb. Chem Geol 192: 59–79.

Bernal JP, Eggins SM and McCulloch MT. 2005. Accurate *in situ* ^{238}U-^{234}U-^{232}Th-^{230}Th analysis of silicate glasses and iron oxides by laser-ablation MC-ICP-MS. J Anal Atom Spectrom 20: 1240–1249.

Black LP et al. 2004. Improved ^{206}Pb/^{238}U microprobe geochronology by the monitoring of a trace-element-related matrix effect: SHRIMP, ID-TIMS, ELA-ICP-MS and oxygen isotope documentation for a series of zircon standards. Chem Geol 205: 115–140.

BRUGUIER O, TÉLOUK P, COCHERIE A, FOUILLAC AM AND ALBARÈDE F. 2001. 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. Geostandard Newslett 25: 361–373.

CHANG Z, VERVOORT JD, MCCLELLAND WC AND KNAACK C. 2006. U-Pb dating of zircon by LA-ICP-MS. Geochem Geophy Geosy 7, Doi:10.1029/2005GC001100.

COCHERIE A, ROSSI P, FANNING CM AND GUERROT C. 2005. Comparative use of TIMS and SHRIMP for U-Pb zircon dating of A-type granites and mafic tholeiitic layered complexes and dykes from the Corsian Batholith (France). Lithos 82: 185–219.

DANTAS EL, VAN SCHMUS WR, HACKSPACHER PC, BRITO NEVES BB AND CORDANI UG. 2004. The 3.4–3.5 Ga São Jose do Campestre Massif, NE Brazil. Remmants of the oldest crust in South America. Precambrian Res 130: 113–137.

FENG R, MACHADO N AND LUDDEN J. 1993. Lead geochronology of zircon by Laser-Probe-inductively coupled plasma mass spectrometry (LP-ICPMS). Geochim Cosmochim Acta 57: 3479–3486.

GARBE-SCHÖNBERG CD AND ARPE T. 1997. High-resolution ICPMS in fast scanning mode: application for laser ablation analysis of zircon. Fresen J Anal Chem 359: 462–464.

GERDES A AND ZEH A. 2006. Combined U-Pb and Hf isotope LA-(MC-)ICP-MS analyses of detrital zircons: Comparison with SHRIMP and new constraints for the provenance and age of an Armorican metasediment in Central Germany. Earth Planet Sc Lett 249: 47–61.

GÜNTHER D, HORN I AND HATTENDORF B. 2000. Recent trends and developments in laser ablation ICP mass spectrometry. Fresen J Anal Chem 368: 4–14.

HEAMAN L AND PARRISH R. 1991. U-Pb geochronology of accessory minerals. In: HEAMAN L AND LUDDEN JN (Eds.) Short course handbook on applications on isotope systems to problems in geology. Mineral Ass Canada, Toronto, p. 59–102.

HIRATA T AND NESBITT RW. 1995. U-Pb isotope geochronology of zircon: evaluation of the laser probe – inductively coupled plasma mass spectrometry technique. Geochim Cosmochim Acta 59: 2491–2500.

HORN I, RUDNICK RL AND MCDONOUGH WF. 2000. Precise elemental and isotope ratio determination by simultaneous solution nebulization and laser ablation-ICP-MS: application to U-Pb geochronology. Chem Geol 164: 281–301.

HORSTWOOD MSA, FOSTER GL, PARRISH RR, NOBLE SR AND NOWELL GM. 2003. Common-Pb corrected *in situ* U-Pb accessory mineral geochronology by LA-MC-ICP-MS. J Anal Atom Spectrom 18: 837–846.

JACKSON SE, PEARSON NJ, GRIFFIN WL AND BELOUSOVA EA. 2004. The application of laser ablation inductively coupled plasma mass spectrometry to *in situ* U-Pb zircon geochronology. Chem Geol 211: 47–69.

KOŠLER J AND SYLVESTER P. 2003. Present trends and the future of zircon in geochronology: laser ablation ICPMS. Rev Mineral Geochem 53: 243–275.

KOŠLER J, FONNELAND H, SYLVESTER P, TUBRETT M AND PEDERSEN RB. 2002. U-Pb dating of detrital zircons for sediment provenance studies – a comparison of laser ablation ICMPS and SIMS techniques. Chem Geol 182: 605–618.

KRYMSKY RS, MACABIRA MJB, LAFON JM AND ESTUMANO GS. 2007. Uranium-lead dating method at the Pará-Iso isotope geology laboratory, UFPA, Belém – Brazil. An Acad Bras Cienc 79: 115–128.

LAUX JH, PIMENTEL MM, DANTAS EL, ARMSTRONG R AND JUNGES SL. 2005. Two Neoproterozoic crustal accretion events in the Brasília belt, central Brazil. J S Am Earth Sci 18: 183–198.

LUDWIG KR. 2003. Isoplot 3.00: A geochronological toolkit for Microsoft Excel. Berkeley Geochronological Center, Spec Publ No. 4, 70 pp.

MATTINSON JM. 2005. Zircon U-Pb chemical abrasion ("CA-TIMS") method: Combined annealing and multi-step partial dissolution analysis for improved precision and accuracy of zircon ages. Chem Geol 220: 47–66.

MEZGER K AND KROGSTAD EJ. 1997. Interpretation of discordant U-Pb zircon ages: An evaluation. J Metamorph Geol 15: 127–140.

NEBEL-JACOBSEN Y, SCHERER EE, MÜNKER C AND MEZGER K. 2005. Separation of U, Pb, Lu, and Hf from single zircons for combined U-Pb dating and Hf isotope measurements by TIMS and MC-ICPMS. Chem Geol 220: 105–120.

PACES JB AND MILLER JD. 1993. Precise U-Pb ages of Duluth Complex and related mafic intrusions, northeastern Minnesota: geochronological insights into physical, petrogenetic, paleomagnetic and tectonomagmatic process associated with the 1.1 Ga midcontinental system. J Geophys Res 98: 13997–14013.

PAQUETTE JL AND TIEPOLO M. 2007. High resolution (5μm) U-Th-Pb isotope dating of monazite with excimer laser ablation (ELA)-ICPMS. Chem Geol 240: 222–237.

PARRISH RR AND NOBLE SR. 2003. Zircon U-Th-Pb geochronology by Isotope Dilution – Thermal Ionization Mass Spectrometry (ID-TIMS). Rev Mineral Geochem 53: 183–213.

PETTKE T, HALTER WE, WEBSTER JD, AIGNER-TORRES M AND HEINRICH CA. 2004. Accurate quantification of melt inclusion chemistry by LA-ICPMS: a comparison with EMP and SIMS and advantages and possible limitations of these methods. Lithos 78: 333–361.

SHANNON RD. 1976. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Cystallogr A32: 751–767.

SIMON JI, REID MR AND YOUNG ED. 2007. Lead isotopes by LA-MC-ICPMS: Tracking the emergence of mantle signatures in an evolving silicic magma system. Geochim Cosmochim Acta 71: 2014–2035.

SIMONETTI A, HEAMAN LM, HARTLAUB RP, CREASER RA, MACHATTIE TG AND BOHM C. 2005. U-Pb zircon dating by laser ablation MC-ICP-MS using a new multiple ion counting Faraday collector array. J Anal Atom Spectrom J 20: 677–686.

SIMONETTI A, HEAMAN LM, CHACKO T AND BANERJEE NR. 2006. *In situ* petrographic thin section U-Pb dating of zircon, monazite, and titanite using laser ablation MC-ICP-MS. Int J Mass Spectrom 253: 87–97.

STACEY JS AND KRAMERS JD. 1975. Approximation of terrestrial lead isotope evolution by a two-stage model. Earth Planet Sc Lett 26: 207–221.

STIRLING CH, LEE DC, CHRISTENSEN JN AND HALLIDAY NA. 2000. High-precision *in situ* ^{238}U-^{234}U-^{230}Th isotopic analysis using laser ablation multiple collector ICPMS. Geochim Cosmochim Acta 64: 3737–3750.

VANHAECKE F AND MOENS L. 1999. Recent trends in trace element determination and speciation using inductively coupled plasma mass spectrometry. Fresen J Anal Chem 364: 440–451.

WILLIGERS BJA, BAKER JA, KROGSTAD EJ AND PEATE DW. 2002. Precise and accurate *in situ* Pb-Pb dating of apatite, monazite, and sphene by laser ablation multiple-collector ICP-MS. Geochim Cosmochim Acta 66: 1051–1066.