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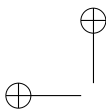
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## High spatial resolution analysis of Pb and U isotopes for geochronology by *laser ablation* multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS)

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### ABSTRACT

Age determinations using the  $^{235}\text{U}$  and  $^{238}\text{U}$  radioactive decay series to the daughter isotopes  $^{207}\text{Pb}$  and  $^{206}\text{Pb}$  respectively, using the mineral zircon ( $\text{ZrSiO}_4$ ), 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 high spatial resolution of ten of microns. The present study describes the analytical set-up and data reduction procedure 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% ( $2\sigma$  SD) and an accuracy of 0.6 to 3.8% ( $2\sigma$  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.

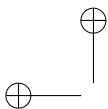
**Key words:** geochronology, U-Pb isotopes, LA-MC-ICP-MS, zircon, age dating.

### 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  $^{235}\text{U}$  and  $^{238}\text{U}$  with half-lives of  $7.04 \times 10^8$  and  $4.47 \times 10^9$  years, and the radiogenic daughter isotopes  $^{207}\text{Pb}$  and  $^{206}\text{Pb}$ ,

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 the characteristics of the abundantly occurring mineral zircon ( $\text{ZrSiO}_4$ ), which is, therefore, the most traditional and widely used mineral for age determinations of various geological formations (e.g. Garbe-Schönberg and Arpe 1997, Kretz *et al.* 2002).

Apart from the improvement in precision, accuracy and mass resolution on the detector side of the



roduction 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 ultra-clean 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 Brasília, 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  $^{238}\text{U}$  and  $^{235}\text{U}$ , the ratios between the stable decay products and the radioactive parent isotopes ( $^{206}\text{Pb}/^{238}\text{U}$  and  $^{207}\text{Pb}/^{235}\text{U}$ ) 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:

$$\frac{^{206}\text{Pb}}{^{238}\text{U}} = \left( \frac{^{207}\text{Pb}}{^{235}\text{U}} + 1 \right) \frac{\lambda_{238}\text{U}/\lambda_{235}\text{U}}{e^{\lambda_{238}\text{U}t} - 1} - 1 \quad (1)$$

age information can be obtained by the  $^{207}\text{Pb}/^{206}\text{Pb}$  age, based on the relationship:

$$\frac{^{207}\text{Pb}}{^{206}\text{Pb}} = \frac{^{235}\text{U}}{^{238}\text{U}} \times \frac{(e^{\lambda_{235}\text{U}t} - 1)}{(e^{\lambda_{238}\text{U}t} - 1)} \quad (2)$$

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

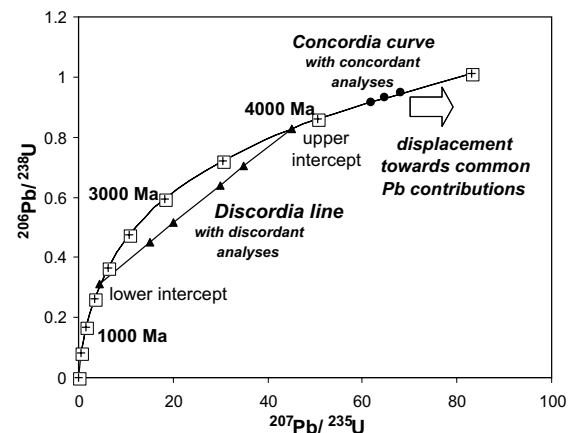
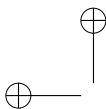


Fig. 1 – Principles of the Concordia diagram  $^{207}\text{Pb}/^{235}\text{U}$  versus  $^{206}\text{Pb}/^{238}\text{U}$ . Concordant analyses fall on the Concordia curve. Minerals with a contribution of common Pb to the bulk Pb content plot below the Concordia curve. Lead loss leads to zircon analyses 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  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{204}\text{Pb}$  compositions. These Pb isotope ratios, however, change with time in terrestrial materials, due to the radiogenic growth of  $^{206}\text{Pb}$  and  $^{207}\text{Pb}$  from the decay of  $^{238}\text{U}$  and  $^{235}\text{U}$ , respectively. The respective, time-dependant isotope ratio used for correction may be calculated from the average crustal Pb isotopic composition.



#### Pb AND U ISOTOPE ANALYSIS BY LA-MC-ICP-MS

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 ( $\text{ZrSiO}_4$ ) or monazite ( $\text{Ce,La,Nd,Th}\text{PO}_4$ ), 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  $\text{Pb}^{2+}$  does not fit the  $\text{Zr}^{4+}$  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.

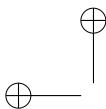
#### METHODOLOGICAL PROGRESS OF Pb-U ISOTOPIC ANALYSIS

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

This technique 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 very high precision of the age determinations (e.g. and Noble 2003, Krymsky et al. 2007). However, the shortcomings of the technique are the need to separate 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 chemical preparation is the Sensitive High Resolution Ion Micro Probe (SHRIMP). It focuses a high-energy ion beam (usually  $\text{O}_2^+$ ) onto an area of usually  $< 10\mu\text{m}$  for *in situ* isotopic analysis of minerals such as zircon. The method reaches a precision and accuracy of  $\pm 1.0\%$  (e.g., Cocherie et al. 2005). The SIMS (Secondary Ion Mass Spectrometry), on the other hand, employs a primary ion beam and analyses the secondary ions. It focuses an  $\text{O}^+$  ion beam of typically  $> 10\mu\text{m}$  in diameter on a solid sample surface, primarily applied to quantify major and trace element contents (for example, Pettke et al. 2004).

Many recent analytical methods, instead, use “Inductively coupled plasma” ionization methods. The sample is introduced into the plasma, 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 ablation system which ablates a solid sample whose vapour 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 micro-collector (MC) arrangements which allow the s



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 gener-

ysed, 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).

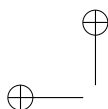
#### SET-UP OF THE LASER ABLATION MC-ICP-MS U-Pb METHOD

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 213 $\mu$ m 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 3 $\mu$ m followed by 1 $\mu$ m diamond



#### Pb AND U ISOTOPE ANALYSIS BY LA-MC-ICP-MS

The mounts are then taken to an ultrasonic bath with 3%  $\text{HNO}_3$ , 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  $^{204}\text{Hg}$  interferes with the  $^{204}\text{Pb}$  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<sup>2</sup>. A small *laser* spot size of say 30  $\mu\text{m}$  applied to a single spot with these *laser* conditions would not produce enough material for a reasonable signal, but at least 40–50  $\mu\text{m}$  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 20  $\mu\text{m}$  spacing. With a 30  $\mu\text{m}$  beam diameter applied here, the sampled area of the zircon is a square of about 70  $\mu\text{m}$  on each side. With a speed of 1  $\mu\text{m}/\text{sec}$ , 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: 40  $\mu\text{m}$  spot size, frequency 10 Hz and 25% *laser* energy.

#### THE ICP-MS AND MULTI-COLLECTOR SET-UP

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 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  $^{238}\text{U}$  in materials with extremely low U content. For the present application, we analyse Pb isotopes on the Faraday cup H4. The other isotopes are collected on the low side. The four ICs on the cup L4 are placed at defined distances referring to: one mass unit between L4 and IC5, one mass unit between IC5 and IC4, one mass unit between IC4 and IC3, and two mass units between IC3 and IC2. The signals collected on the four ICs are:  $^{207}\text{Pb}$  on IC5,  $^{206}\text{Pb}$  on IC4,  $^{204}\text{Hg}/^{204}\text{Pb}$  on IC3, and  $^{202}\text{Hg}$  on IC2. Because of the always present contamination of the He gas with Hg, a correction for the isobaric interference between  $^{204}\text{Hg}$  and  $^{204}\text{Pb}$  has to be applied, using the signal of  $^{202}\text{Hg}$  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 sensitivity. To ensure the optimal operating voltage for the same sensitivity for the ICs, a signal of about 3000 counts per second (cps) is successively directed to the 4 ICs using different analysing lines. We use a signal of  $^{206}\text{Pb}$  for this cross-calibration. Based on the response for each IC, the operating voltage of each IC is adjusted in order to ensure measuring conditions for the same sensitivity for all ICs used.

For standard and sample analysis, the signals are collected in a single block with 40 cycles of 1.0 s 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 4 min and is illustrated in Figure 3. The isotopes  $^{204}(\text{Pb}+\text{Hg})$ ,  $^{206}\text{Pb}$  and  $^{207}\text{Pb}$  are read in counts

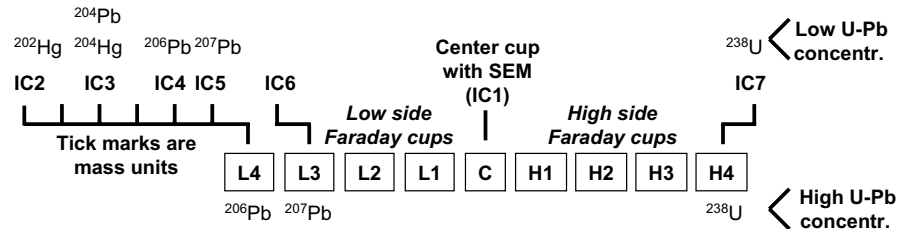
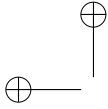


Fig. 2 – Set-up of the cup configurations (Faraday cups and ICs) for low U-Pb and high U-Pb concentrations in zircon with the Thermo Finnigan Neptune MC-ICP-MS.

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

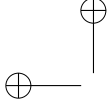
The isotope data of the 40 analysed cycles are transferred into an in-house Excel spreadsheet for data reduction. The isotope ratios of the 40 cycles are evaluated on a  $2\sigma$  standard error rejection basis. The routine then calculates the error correlation value  $\rho$  (rho) for the  $^{206}\text{Pb}/^{238}\text{U}$  and  $^{207}\text{Pb}/^{235}\text{U}$  data. The isobaric contribution of  $^{204}\text{Hg}$  is subtracted from the joint  $^{204}\text{Pb}/^{204}\text{Hg}$  peak by considering the analyzed  $^{202}\text{Hg}/^{204}\text{Hg}$  ratio. The spreadsheet allows to choose between three ways to determine the  $^{202}\text{Hg}/^{204}\text{Hg}$  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  $^{202}\text{Hg}/^{204}\text{Hg}$  ratio of 4.346, which would require an absolutely precise cross-calibration of IC2 and IC3. Because  $^{235}\text{U}$  cannot be analysed with this type of cup configuration, the natural ratio  $^{238}\text{U}/^{235}\text{U}$  of 137.88 is used to calculate the  $^{235}\text{U}$  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

for which  $R_{\text{std}}$  is the true isotopic ratio of the standard ( $^{207}\text{Pb}/^{206}\text{Pb}$  or  $^{206}\text{Pb}/^{238}\text{U}$  ratios, respectively),  $r_{\text{spl}}$  is the analysed isotopic ratio of the sample, and  $r_{\text{std1}}$  and  $r_{\text{std2}}$  are the analysed isotopic ratios of the two standards before and after the samples along the sequence. The variable  $\theta$  (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  $(r_{\text{std1}}^{1-\theta} \times r_{\text{std2}}^{\theta})$  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  $^{206}\text{Pb}/^{238}\text{U}$  and  $^{207}\text{Pb}/^{206}\text{Pb}$  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  $^{206}\text{Pb}/^{238}\text{U}$  and  $^{207}\text{Pb}/^{206}\text{Pb}$  ratios were propagated by quadratic addition of the external reproducibility and the within-run precision, following equation (4):

$$\left( \frac{^{206}\text{Pb}}{^{238}\text{U}} \quad \frac{^{207}\text{Pb}}{^{206}\text{Pb}} \right)$$



Pb AND U ISOTOPE ANALYSIS BY LA-MC-ICP-MS

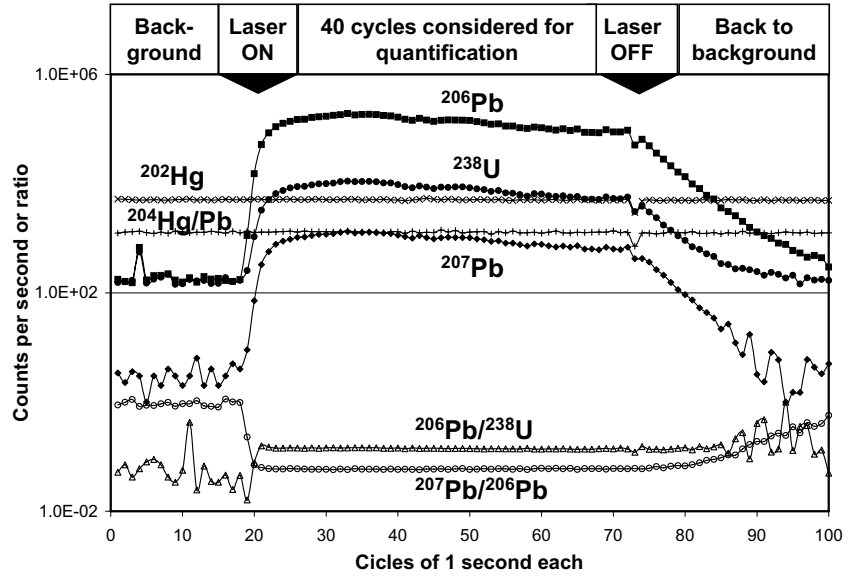


Fig. 3 – Typical signal sequence of a *laser* ablation experiment. Note that the absolute count rates of the isotopes may vary during the ablation process while the isotope ratios remain constant. The signals of  $^{202}\text{Hg}$  and  $^{204}\text{Hg/Pb}$ , in the case of no common  $^{204}\text{Pb}$  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  $\sigma$ :

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

where  $N$  is the number of analyses,  $x_i$  is the value of each individual analyses  $x_1$  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:

$$\text{SE} = \frac{\sigma}{\sqrt{N}} \quad (6)$$

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

Zircon U-Pb isotopic analyses may require a correc-

al. 2003). For minerals with a low common Pb, as, for example, zircon, we use a correction based on the amount of non-radiogenic  $^{204}\text{Pb}$ . The counts per second of  $^{204}\text{Pb}$  (including a correction for  $^{204}\text{Hg}$ ) are used to deduce the amount of non-radiogenic, common Pb, and  $^{207}\text{Pb}$ , given a common Pb composition from the model of Stacey and Kramers (1975). With the fraction  $f_c$  of common  $^{206}\text{Pb}$  and  $^{207}\text{Pb}$  so obtained:

$$f_c = \frac{\text{Pb}_c}{\text{Pb}_t} = \frac{\text{Pb}_c}{\text{Pb}_c + \text{Pb}_r}$$

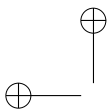
where  $\text{Pb}_c$  is the value (in counts per second) of common Pb,  $\text{Pb}_t$  the total Pb, and  $\text{Pb}_r$  the radiogenic Pb, where  $\text{Pb}_r$  being  $^{206}\text{Pb}$  or  $^{207}\text{Pb}$ , respectively, we use the relationships:

$$\frac{^{206}\text{Pb}}{^{238}\text{U}_{\text{radiogenic}}} = \frac{^{206}\text{Pb}}{^{238}\text{U}_{\text{total}}} \times (1 - f_c),$$

and

$$\frac{^{207}\text{Pb}}{^{235}\text{U}} = \frac{^{207}\text{Pb}}{^{235}\text{U}}$$





of Andersen (2002) to arrive at common Pb-corrected  $^{206}\text{Pb}/^{238}\text{U}$  and  $^{207}\text{Pb}/^{235}\text{U}$  isotopic ratios. The necessity for a correction is judged from the  $^{204}\text{Pb}$  signal intensity. Values smaller than  $\sim 25$  cps (blank-corrected), resulting in  $^{206}\text{Pb}/^{204}\text{Pb}$  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:  $^{207}\text{Pb}/^{206}\text{Pb}$  age =  $608.6 \pm 1.1$  Ma,  $^{206}\text{Pb}/^{238}\text{U}$  age =  $600.4 \pm 1.8$  Ma,  $^{207}\text{Pb}/^{235}\text{U}$  age =  $602.1 \pm 3.0$  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  $\mu\text{m}$  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:  $^{207}\text{Pb}/^{206}\text{Pb}$  age =  $419.1 \pm 9.1$  Ma,  $^{206}\text{Pb}/^{238}\text{U}$  age =  $416.2 \pm 1.1$  Ma,  $^{207}\text{Pb}/^{235}\text{U}$  age =  $416.7 \pm 1.7$  Ma; (iii) FC1 zircon concentrate provided by Richard Armstrong, Australian National University, Canberra, Australia; the crystals have sizes of approximately 50–100  $\mu\text{m}$ , 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:  $^{207}\text{Pb}/^{206}\text{Pb}$  age = 1098.9 Ma,  $^{206}\text{Pb}/^{238}\text{U}$  age = 1099.9 Ma,  $^{207}\text{Pb}/^{235}\text{U}$  age = 1100.0 Ma.

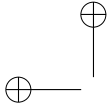
For an additional test of the method, two zircon samples from our own laboratory which had previously

of the Neoproterozoic Goiás magmatic arc which has previously been dated at  $630 \pm 5$  Ma ( $2\sigma$ ) by U-Pb ID-TIMS in our laboratory (Laux et al. 2005). Its average  $^{207}\text{Pb}/^{206}\text{Pb}$  TIMS age is  $633.3 \pm 5.7$  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  $3065 \pm 12$  Ma determined by SHRIMP analysis (Dantas et al. unpublished data).

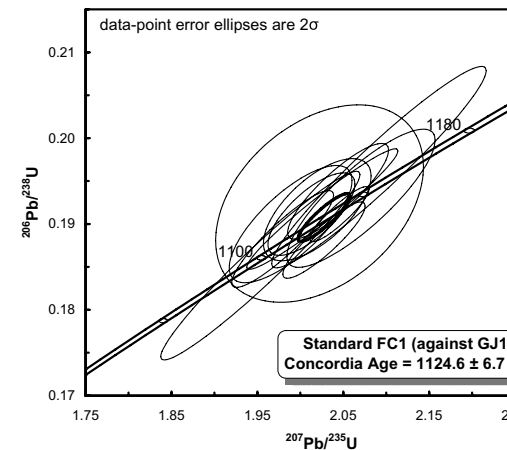
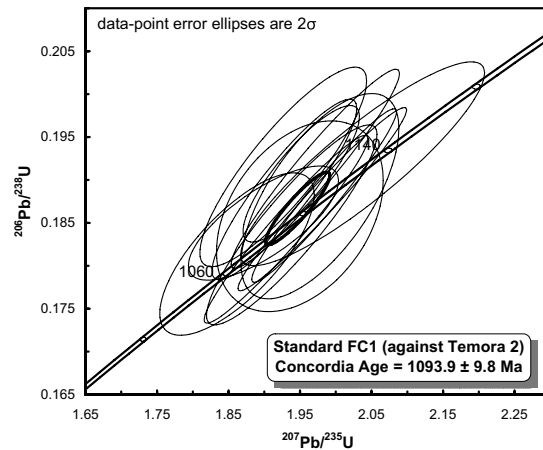
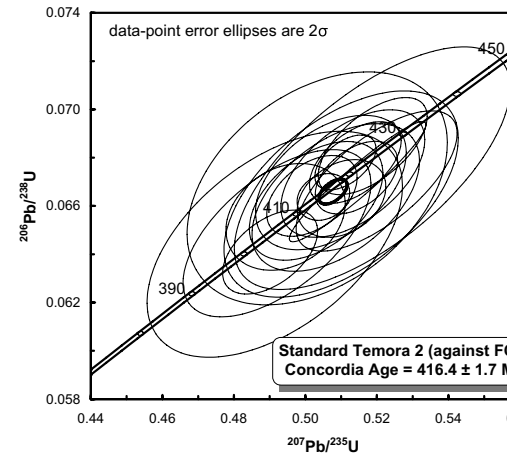
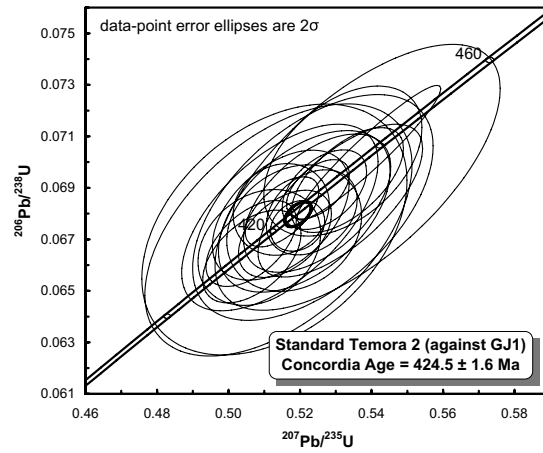
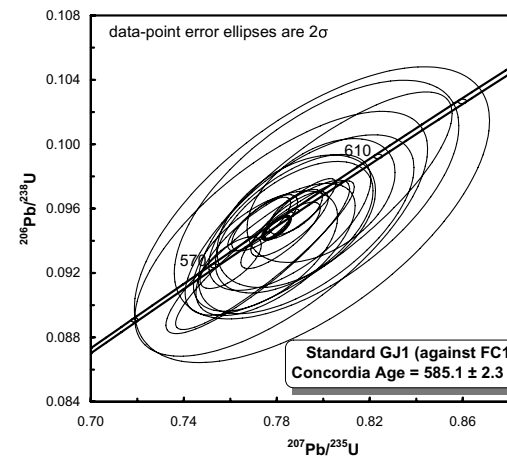
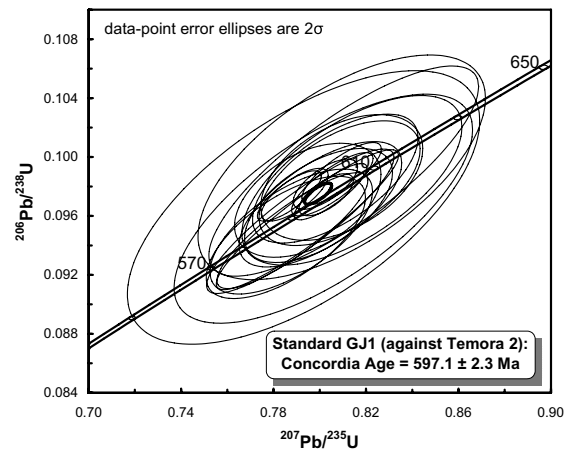
#### RESULTS

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  $^{207}\text{Pb}/^{206}\text{Pb}$ ,  $^{206}\text{Pb}/^{238}\text{U}$  and  $^{207}\text{Pb}/^{235}\text{U}$  age data is well satisfactory. We obtained precisions of 1.9 to 3.7% ( $2\sigma$  standard deviation) for the  $^{207}\text{Pb}/^{206}\text{Pb}$ ,  $^{206}\text{Pb}/^{238}\text{U}$  and  $^{207}\text{Pb}/^{235}\text{U}$  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  $^{207}\text{Pb}/^{206}\text{Pb}$  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  $^{207}\text{Pb}/^{206}\text{Pb}$  age was used. The accuracy so obtained varies between 0.6 and 3.8% ( $2\sigma$  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  $627.6 \pm 1.3$  Ma, which is identical within error to the TIMS age of  $630 \pm 5$  Ma. None of the zir-



Pb AND U ISOTOPE ANALYSIS BY LA-MC-ICP-MS



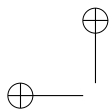


TABLE I  
Referenced and determined ages (by LA-ICP-MS) of the zircon standards GJ1, Temora 2 and FC1.

Sample	Standard	No. of anal.	$^{207}\text{Pb}^*/^{206}\text{Pb}^*$ age (Ma) referenced	Error ( $2\sigma$ ) (Ma)	$^{207}\text{Pb}^*/^{206}\text{Pb}^*$ age (Ma) analysed	Error ( $2\sigma$ ) (Ma)	Prec. ( $2\sigma$ ) (%)	$^{206}\text{Pb}^*/^{238}\text{U}$ age (Ma) referenced	Error ( $2\sigma$ ) (Ma)	$^{206}\text{Pb}^*/^{238}\text{U}$ age (Ma) analysed	Error ( $2\sigma$ ) (Ma)	Prec. ( $2\sigma$ ) (%)
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.	$^{207}\text{Pb}^*/^{235}\text{U}$ age (Ma) referenced	Error ( $2\sigma$ ) (Ma)	$^{207}\text{Pb}^*/^{235}\text{U}$ age (Ma) analysed	Error ( $2\sigma$ ) (Ma)	Prec. ( $2\sigma$ ) (%)	Concordia age (Ma) determined	Error ( $2\sigma$ ) (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.):  $2\sigma$  precision for the number of analyses, “n.r.” = not reported. All errors are  $2\sigma$  standard deviations. Accuracy: Percentage of deviation between analysed concordia age and referenced  $^{207}\text{Pb}/^{206}\text{Pb}$  age.

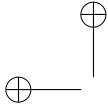
weighted average of 24  $^{207}\text{Pb}/^{206}\text{Pb}$  ages resulted in a  $^{207}\text{Pb}/^{206}\text{Pb}$  age of  $628.7 \pm 6.0$  Ma, compared with the TIMS  $^{207}\text{Pb}/^{206}\text{Pb}$  age of  $633.3 \pm 5.7$  Ma.

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  $3045 \pm 24$  Ma, which agrees within error with the SHRIMP age of  $3065 \pm 12$  Ma. However, various older zircon populations were encountered in the sample. One is defined by 17 discordant zircon analyses which yield an upper

ulations 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  $^{206}\text{Pb}/^{238}\text{U}$  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 confor-

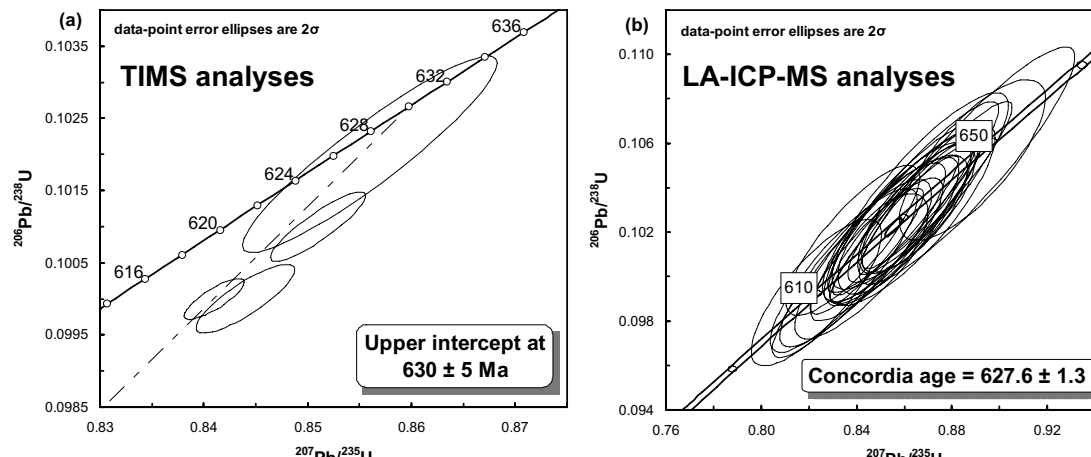


Pb AND U ISOTOPE ANALYSIS BY LA-MC-ICP-MS

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

TIMS															
Analysis	$^{207}\text{Pb}^*/^{206}\text{Pb}^*$	$2\sigma$ error (%)	$^{207}\text{Pb}^*/^{235}\text{U}$	$2\sigma$ error (%)	$^{206}\text{Pb}^*/^{238}\text{U}$	$2\sigma$ error (%)	$\rho$	$^{207}\text{Pb}/^{206}\text{Pb}$ age (Ma)	$2\sigma$ error (Ma)	$^{207}\text{Pb}^*/^{235}\text{U}$ age (Ma)	$2\sigma$ error (Ma)	$^{206}\text{Pb}^*/^{238}\text{U}$ age (Ma)	$2\sigma$ error (Ma)		
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	6.3		
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	15.5		
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	16.3		
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	16.3		
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	12.3		
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	11.3		
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	13.3		
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	14.3		
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	10.3		
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	15.3		
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	11.3		
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	10.3		
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	12.3		
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	12.3		
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	13.3		
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	14.3		
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	14.3		
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	14.3		
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	13.3		
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	10.3		

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



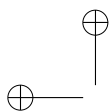


TABLE III  
SHRIMP data of sample EC69A.

Analysis	$^{207}\text{Pb}^*/^{206}\text{Pb}^*$	$1\sigma$ error (%)	$^{207}\text{Pb}^*/^{235}\text{U}$	$1\sigma$ error (%)	$^{206}\text{Pb}^*/^{238}\text{U}$	$1\sigma$ error (%)	$\rho$	$^{207}\text{Pb}/^{206}\text{Pb}$ age	$1\sigma$ error (Ma)	$^{207}\text{Pb}^*/^{235}\text{U}$ age	$1\sigma$ error (Ma)	$^{206}\text{Pb}^*/^{238}\text{U}$ age	$1\sigma$ 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

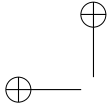
Note that the errors are  $1\sigma$  errors. The majority of shots were taken as single shots on zircon grains.

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

dant 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



Pb AND U ISOTOPE ANALYSIS BY LA-MC-ICP-MS

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

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

Note that the errors are  $2\sigma$  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 serves as well as a precise and for the  $^{207}\text{Pb}/^{206}\text{Pb}$ ,  $^{206}\text{Pb}/^{238}\text{U}$  and  $^{207}\text{Pb}/^{235}\text{U}$  is analyses, the LA-ICP-MS method is a highly con-

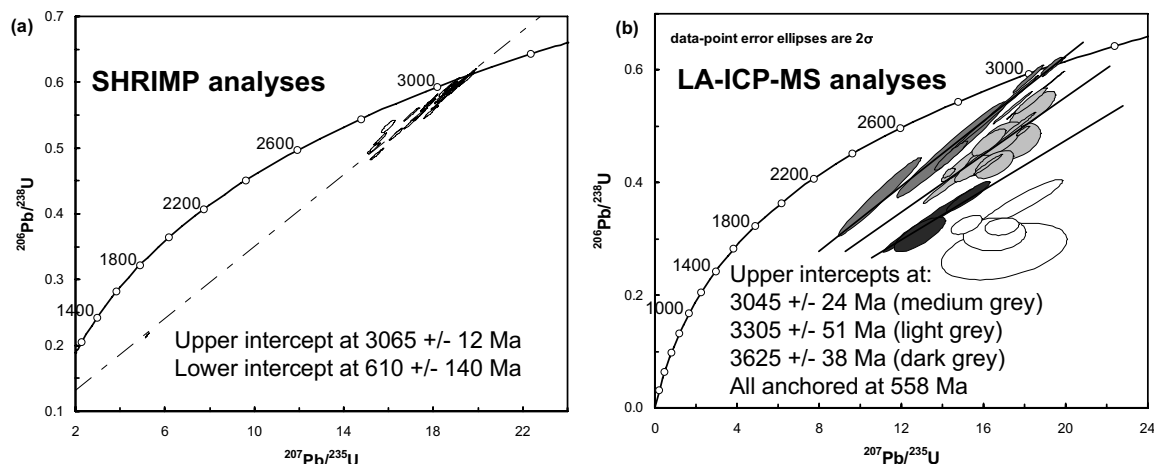
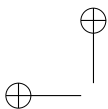


Fig. 6 – Comparison of (a) SHRIMP data (24 analyses from Dantas et al. unpublished data) with (b) 32 LA-ICP-MS analyses of sample EC69A. An upper intercept age of  $3045 \pm 24$  Ma, defined by three concordant and four discordant analyses, is within error of the SHRIMP age of  $3065 \pm 12$  Ma. The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

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#### RESUMO

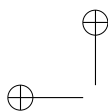
A determinação de idades através do decaimento dos isótopos radioativos  $^{235}\text{U}$  e  $^{238}\text{U}$  para os isótopos radiogênicos  $^{207}\text{Pb}$  e  $^{206}\text{Pb}$ , respectivamente, utilizando o mineral zircão ( $\text{ZrSiO}_4$ ), é amplamente aplicada para decifrar processos geológicos. 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

exatidão de 0,6 a 3,8% ( $2\sigma$  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.

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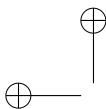
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