In Situ U-Pb Zircon Dating Using Laser Ablation-Multi Ion Counting-ICP-MS (LA-MIC-ICP-MS)

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Key Words
Neptune, Laser Ablation, Multicollector ICP-MS, Multi Ion Counting, U-Pb Dating, Zircons

In-Situ Analysis of Zircons

The systematics of U and Pb in zircons serve as one of the most important dating tools available in the geosciences. Until now, most zircon analyses are performed by secondary ion mass spectrometry (SIMS) or thermal ionization mass spectrometry (TIMS). SIMS offers the possibility of in-situ analysis of single crystals at high spatial resolution. TIMS relies on micro-drilling in order to achieve spatial resolution, with subsequent chemical separation required to extract U and Pb. A new technique for in-situ U-Pb analysis in zircons is ICP-MS in combination with laser ablation. However, the sample volumes are small and concentrations of U and Pb can be very low, necessitating an ion detection system with very high sensitivity and low noise. Because laser ablation produces transient signals, multicollection is the method of choice. In order to fulfill these requirements, we have developed miniaturized ion counters, which are fully integrated into the multicollector array of the Thermo Scientific™ NEPTUNE™ MC-ICP-MS.

The U-Pb Clock

The U-Pb dating method uses the characteristics of U-decay to Pb. The uranium isotopes ^{235}U and ^{238}U decay in several steps to the lead isotopes ^{207}Pb and ^{206}Pb, respectively. The decay schemes are as follows:

$^{238}U \rightarrow {}^{206}Pb + 8\,{}^{4}He + 6\,\beta$	$\lambda_{238} = 1.55125 \times 10^{-10}/yr$
	$t_{1/2} = 4.47$ Ga
$^{235}U \rightarrow {}^{207}Pb + 7\,{}^{4}He + 4\,\beta$	$\lambda_{235} = 9.8485 \times 10^{-10}/yr$
	$t_{1/2} = 0.704$ Ga

where $t_{1/2}$= half life of the parent isotope and λ = decay constant. The equilibrium value of the present $^{238}U/^{235}U$ ratio is 137.88.

The equilibrium value of the present $^{238}U/^{235}U$ ratio was taken to be 137.88 (Rosman and Taylor, 1998). From recent publications, e.g. Weyer et al. (2008), it is well-known that this ratio is variable to ~1 permil. It is beyond the scope of this note to discuss the effects on U-Pb age dating.

Natural lead has four isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb) of which ^{204}Pb is the only non-radiogenic isotope. Because it is not a daughter product of the radioactive decay of uranium, ^{204}Pb can thus be used to correct for the initial lead content in the sample and/or analytical blank, which does not originate from radioactive decay of uranium. The isotopic composition of this initial lead content or the analytical blank is assumed to be "common" (i.e. non-radiogenic) lead. This common lead correction is very important for precise and accurate dating, particularly of young zircons.

From the U-Pb system, it is possible to obtain two isochron equations and thus two independent ages:

$$\frac{^{206}Pb}{^{204}Pb_t} = \frac{^{206}Pb}{^{204}Pb_0} = \frac{^{238}U}{^{204}Pb_0}\,(e^{\lambda_{238}t} - 1)$$

$$\frac{^{207}Pb}{^{204}Pb_t} = \frac{^{207}Pb}{^{204}Pb_0} = \frac{^{235}U}{^{204}Pb_0}\,(e^{\lambda_{235}t} - 1)$$

If these two ages are the same, the data are concordant.

A Concordia diagram is constructed by plotting $^{206}Pb/^{238}U$ on the y-axis and $^{207}Pb/^{235}U$ on the x-axis. If the two ages obtained from the above equations are consistent, they plot on the so-called Concordia curve. This curve can be calculated by the equation:

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

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For example, when a zircon crystal crystallizes from a magma and remains a closed system (thus no loss or gain of U and Pb) from the time of crystallization to the present, then the $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$ ratios in the zircon will plot on the Concordia and the age of the zircon can be determined from the position on the curve.

This $^{207}Pb/^{206}Pb$ model age of the zircon is given by:

$$\frac{^{207}Pb}{^{206}Pb} = \frac{1}{137.88} \times \frac{(e^{\lambda_{235}t} - 1)}{(e^{\lambda_{238}t} - 1)}$$

Why Multi Ion Counting?

Low signal intensities are produced by laser ablation when high spatial resolution is required, when the total sample amount is limited, and/or when U and Pb contents of zircons are low. The signal to noise level of Faraday detectors is too low to obtain high precision data. This is illustrated in Figure 1, which shows simultaneous peak scans of the ^{206}Pb and ^{207}Pb isotopes of SRM 981 standard. The intensities of both isotopes are about 1 mV, however, compared to the Faraday detector the noise on the ion counting channel is significantly reduced. Ion counters are used to extend the sensitivity of the instrument by several orders of magnitude. In addition, because laser ablation sampling can produce erratic transient signals, static multicollection is an absolute must when high precision is required. This points to the need for a flexible multicollector with ion counting detectors instead of Faraday cups.

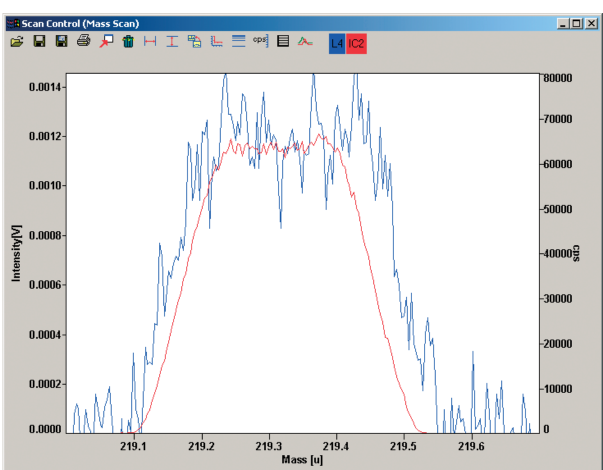


Figure 1. Multicollector measurement of the isotopes ^{206}Pb and ^{207}Pb from a SRM 981 standard at 200 ppt concentration. Signal intensities of both isotopes are similar and yield about 1.2 mV on Faraday cup L4 (blue), respectively 65,000 cps on ion counter IC2 (red).

Materials

Four zircons with different ages were used to evaluate the potential of Multi Ion Counting-ICP-MS combined with laser ablation. These include: 91500, PMA7, CN92 (UQ-Z1) and 5FRATI. 91500 is a well known zircon and was used in this study for mass bias correction and correction for U-Pb fractionation.

Method

A New Wave Research NWR UP-213 laser (wavelength 213 nm) was used and the laser parameters were as follows:

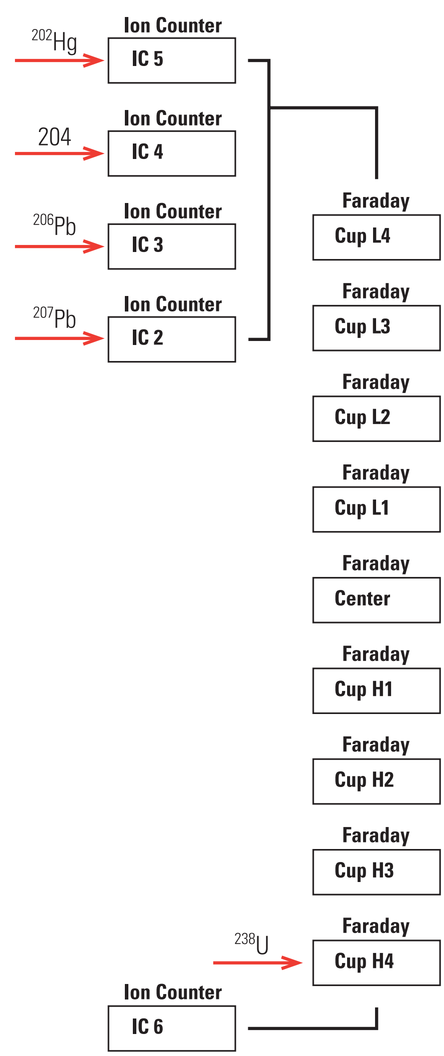
Table 1. Laser parameters.

Spot Size	20 µm
Energy	25 J/cm2 (85%)
Rep. Rate	10 Hz
Ar	0.825 L/min
He	0.65 L/min

Table 2. Typical blank levels.

^{202}Hg	~2,000 cps
^{204}Hg	~460 cps
^{204}Pb	~20–30 cps
^{206}Pb	~250 cps
^{207}Pb	~350 cps

A gold trap was integrated into the He and Ar gas lines in order to reduce the Hg blank level. Mercury is a common contaminant in He and Ar gas and ^{204}Hg interferes on ^{204}Pb, typical blank levels were as listed in Table 2.



Note that the Pb isotope composition of the blank resembles that of common lead.

The following cup configuration was used:

^{202}Hg, mass ^{204} (^{204}Pb + ^{204}Hg) and the Pb isotopes ^{206}Pb and ^{207}Pb were detected on the ion counters. It is important to measure ^{202}Hg simultaneously with the Pb isotopes in order to monitor and correct for the isobaric interference of ^{204}Hg on ^{204}Pb. ^{238}U was measured in Faraday cup H4 because the U contents in the zircons were too high for the dynamic range of the ion counters. However, in cases where the ^{238}U signal is too small for the Faraday detector, it can be measured using ion counter IC6.

Before measurements with the laser, the ion counters were cross-calibrated. The cross calibration factors were derived by direct comparison of the detector response by peak jumping of the same ^{206}Pb signal across all ion counters involved in the measurement (Table 3). The precision of this dynamic peak jumping method very much depends on the signal stability and in order to achieve best precision Pb was introduced into the ICP by aspirating a very dilute solution of a Pb standard (200 ppt).

Table 3. Multi-dynamic method for cross calibration of the ion counters.

IC5	IC4	IC3	IC2	
Line 1	201	203	205	
Line 2	202	204	**^{206}Pb**	
Line 3	204	**^{206}Pb**	208	209
Line 4	**^{206}Pb**	208	210	211

Typical peak shape and peak overlap of U and Pb detected on the ion counters (obtained in wet plasma conditions) is shown in Figure 2.

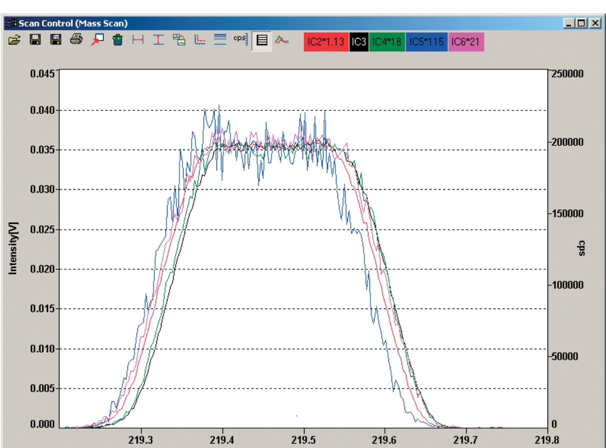


Figure 2. Typical peak shape and peak overlap of the U and Pb isotope signals detected on the ion counters.

Data Acquisition

1 block
180 cycles/block
1-second integration time
total analysis time: 180 seconds

Both the 91500 zircon standard and the samples were placed in one mount. Thus, the ablation chamber could remain closed during sample-standard analyses and all measurements could be performed under exactly the same analytical conditions. It was assumed that mass bias and U-Pb fractionation during the ablation process were similar for both the 91500 zircon standard and the samples. Data were evaluated using a type of standard sample bracketing method. Individual spot analyses of several grains of 91500 were averaged and this mean ratio was used to normalize the unknowns. An example of such a sequence is shown in Figure 3.

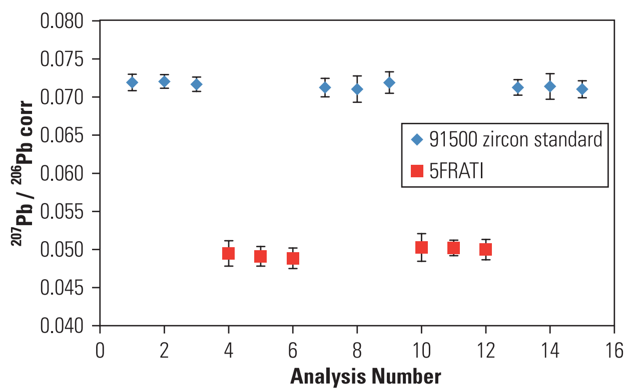


Figure 3. Example of an analysis sequence. The nine analyses of the standard are averaged and this average value is taken to normalize the six individual analyses of the unknown (in this case 5FRATI).

The full control of the common lead contribution from the sample itself as well as from the instrument blank (see Table 1) was very important. Blanks were measured in between standards and samples. From the measured ^{207}Pb/^{206}Pb ratio of the blank, one can conclude that the blank was very similar to common lead. Therefore the ^{204}Pb contribution on the measured mass 204 was calculated directly from the known ^{206}Pb/^{204}Pb of the common lead. After peak stripping of the ^{204}Pb common lead blank contribution from mass 204 one can calculate the ^{202}Hg/^{204}Hg of the blank. The value of this isotope ratio was used for accurate peak stripping of the ^{204}Hg intensity from the 204 signal measured during ablation of the zircon. This procedure enabled us to accurately correct the measured ^{207}Pb/^{206}Pb and ^{206}Pb/^{238}U of the zircons for the contribution coming from the common lead.

Results

In general, the analyzed grains were very small (less than 200 µm) and very thin. Figure 4 shows an image of one analyzed grain of the 91500 standard.

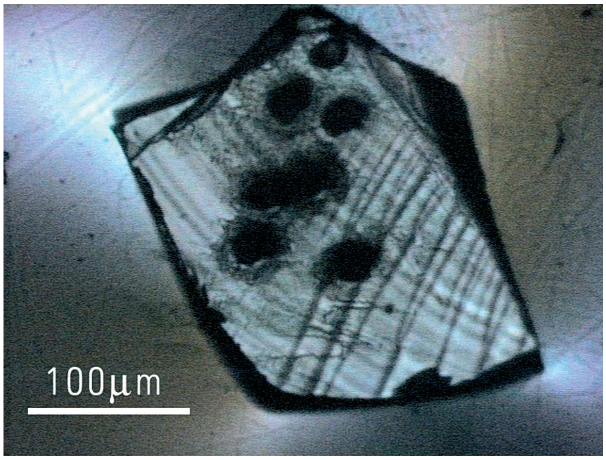


Figure 4. Image of a 91500 grain.

Reproducibility of Several Spot Analyses

Figure 5 shows the reproducibility of $^{207}Pb/^{206}Pb$ (corrected for common Pb) ratios of 6 individual spot analyses of the same 91500 grain (see Figure 4).

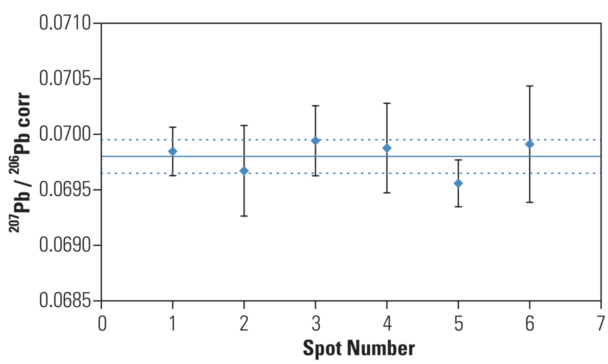


Figure 5. Reproducibility of $^{207}Pb/^{206}Pb$ (corrected for common lead) of 6 spot analyses of 91500. Average $^{207}Pb/^{206}Pbcorr$ = 0.069801 (1 s.d. = 0.22%, n = 6).

Single Spot Analysis

Because the majority of the zircon grains were very thin, the laser often penetrated the zircons after 60 to 120 seconds of ablation. Figure 6a shows a typical intensity profile during ablation of the 91500 zircon standard. The stability of the $^{207}Pb/^{206}Pb$ ratio (corrected for common Pb) is better than 0.5% (Figure 6b).

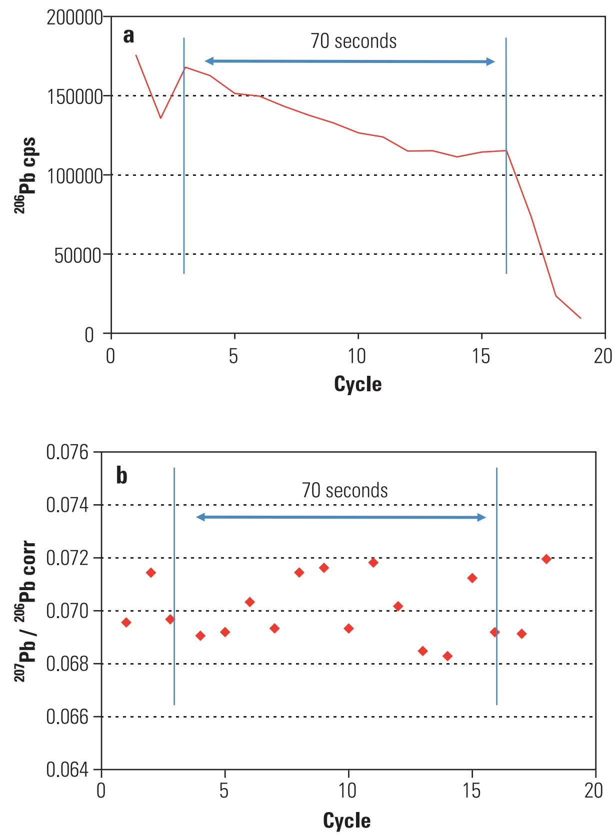


Figure 6a. Intensity profile of ^{206}Pb during ablation of 91500. Figure 6b. Stability of $^{207}Pb/^{206}Pb$ (corrected for common Pb) during the ablation process. The average ^{207}Pb/206Pbcorr = 0.069942 (1 s.e. = 0.45%).

Measured U-Pb Ages for the Three Zircons

The three zircons analyzed were of different ages and have previously been determined by TIMS and ion microprobe techniques. The age of the oldest sample, PMA7, is not well known and is probably not always concordant. The same is true for CN92 (UQ-Z1). This could be due to Pb and/or U loss. The Concordia diagrams of Figures 7a and 7b were created by Alain Cocherie using the ISOPLOT program of Ken Ludwig.

PMA7

The recommended age of this zircon comes from SHRIMP analyses (Menot et al., 1993, 1994; Peucat and Fanning, unpublished data, referred to in Hirata and Nesbitt, 1995). The mean $^{207}Pb/^{206}Pb$ age for this zircon is 2430±8 Ma (2σ), with $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$ ages of 2378±40 Ma and 2401±20 Ma, respectively. The $^{207}Pb/^{206}Pb$ age obtained in this study by laser ablation ICP-MS is 2390±55Ma (2σ) (Figure 7a).

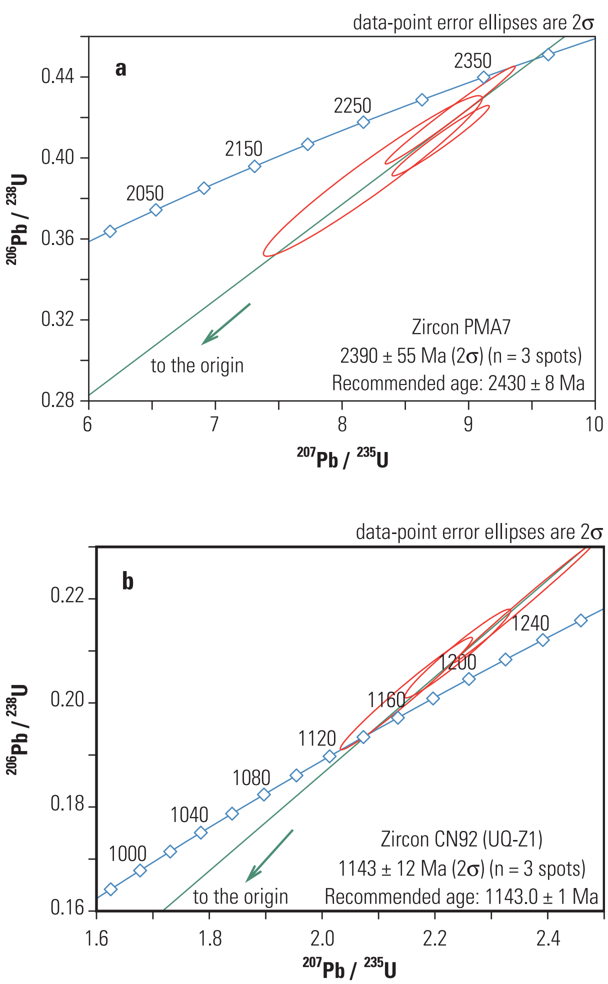


Figure 7. Concordia diagrams of PMA7 (a) and CN92 (UQ-Z1) (b).

CN92 (UQ-Z1)

The recommended U-Pb age for this zircon is 1143±1Ma (2σ) and comes from TIMS analyses (Feng et al., 1993; Machado and Gauthier, 1996). The $^{207}Pb/^{206}Pb$ age obtained here for CN92 is exactly the same as the recommended age (1143 Ma) and even the uncertainty is small (12 Ma, 2σ) (Figure 7b).

5FRATI

5FRATI is a relatively young sample. For this zircon, three methods have been used to define the age. TIMS gave a $^{207}Pb/^{206}Pb$ age of 286.4±1.8 Ma (2σ). The Pb-evaporation method gave an age of 291.8±5.3 Ma (2σ) and the SHRIMP gave an age of 284.8±2.3 Ma (2σ). Details of these methods and obtained ages can be found in Cocherie et al. (1999) and Cocherie et al. (2005, in press). For young zircons (Figure 8), due to the larger uncertainty on $^{206}Pb/^{204}Pb$ measurement, it is more suitable to use the inverse Concordia diagram (i.e. Tera and Wasserburg, 1972). For this 5FRATI zircon we obtained a $^{206}Pb/^{238}U$ age of 292±14Ma (2σ) by laser ablation MC-ICP-MS. This is well within uncertainty of the recommended age obtained by other methods (see above). Moreover, Figure 8 also shows that the common Pb correction works very well, as the measured U-Pb ratios plot on the Concordia curve. This would not have been the case if we would have under- or overcorrected the measured $^{207}Pb/^{206}Pb$ ratio.

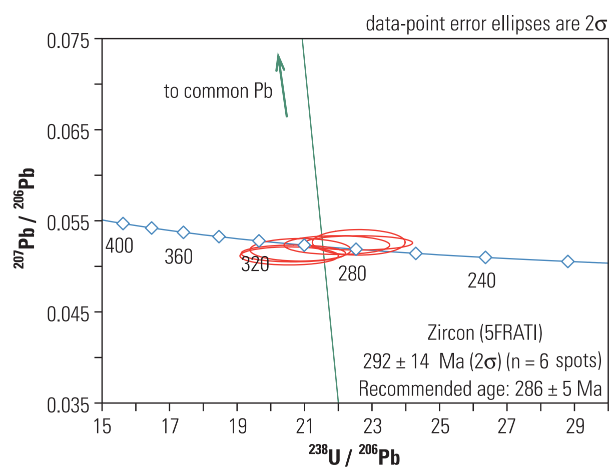


Figure 8. Terra-Wasserburg diagram showing the U-Pb age of 5FRATI.

Conclusions

Laser Ablation-Multi Ion Counting-ICP-MS has been shown to be capable of:

- Precise and accurate U-Pb age dating of zircons at high spatial resolution (20 µm).
- Realizing internal and external precisions of $^{207}Pb/^{206}Pb$ better than 1% (common Pb corrected).
- Measuring U-Pb ages similar to recommended ages within error for three analyzed zircons (5FRATI, CN92 (UQ-Z1), PMA7).

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AN30021_E 02/14S