

U-Pb dating of young zircons by LA-ICP-MS

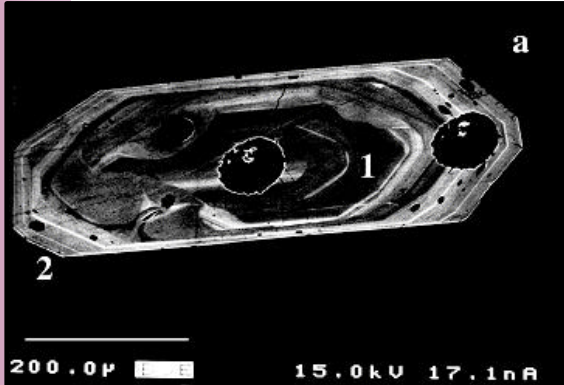


Figure 1: Laser ablation craters in a zircon

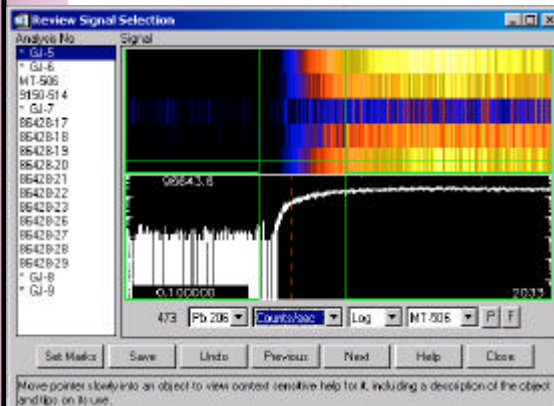


Figure 2: Typical LA-ICP-MS ^{206}Pb signal from a zircon as seen in GLITTER software.

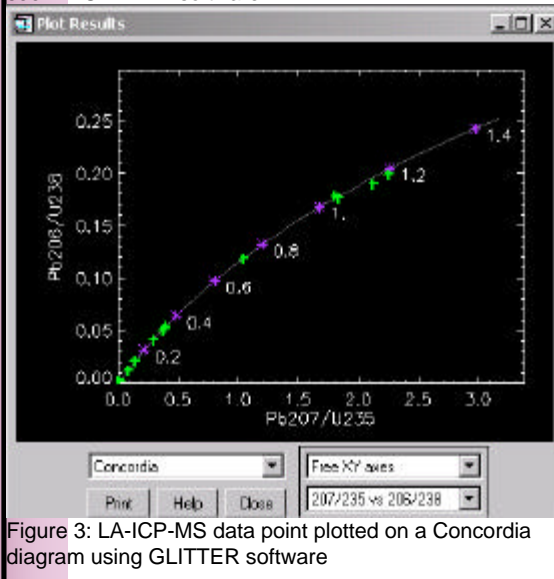


Figure 3: LA-ICP-MS data point plotted on a Concordia diagram using GLITTER software

- Optimised approach for zircon dating
- Successful dating of young zircons
- Good correlation with TIMS data

Introduction

U-Pb geochronology of zircons is a vital chronometer for studying the history of igneous, metamorphic and sedimentary events. $^{207}\text{Pb}/^{235}\text{U}$ and $^{206}\text{Pb}/^{238}\text{U}$ ratios are used to assess concordance and to determine a true age from zircon populations with variable Pb loss from grains or parts thereof.

Laser sampling for ICP-MS analysis (LA-ICP-MS) is increasingly used for U-Pb dating. The LA-ICP-MS procedure involves ablation of zircons, collection of Pb and U signal intensity data, calculation of relevant isotope ratios, and correction of these by calibration against a zircon standard. Figure 1 shows some typical laser craters in a zircon. Figure 2 demonstrates the signal stability for ^{206}Pb in a zircon over the course of a typical analysis using the 213 nm laser wavelength and helium as the ablation gas. The data point is then plotted on a Concordia diagram (Figure 3) using GLITTER, a data reduction software package for LA-ICP-MS. Although LA-ICP-MS cannot match the precision of Thermal Ionisation Mass Spectrometry (TIMS) or the spatial resolution of the Ion Microprobe, its advantages are speed of analysis, low cost and wide availability. At a typical production rate of 50 zircon ages per day, LA-ICP-MS can produce data at a phenomenal rate.

Although application of LA-ICP-MS for zircon dating is growing rapidly, the technique is still widely perceived to have two major limitations:

- fractionation of Pb relative to U during ablation.
- difficulty in common Pb correction, due to a large isobaric interference at mass 204 from Hg.

The aim of this study was to optimise the LA-ICP-MS to perform successful analysis on young zircons, by addressing the fractionation and common Pb correction issues in detail. A New Wave 213 nm laser ablation system and an Agilent ICP-MS were used.



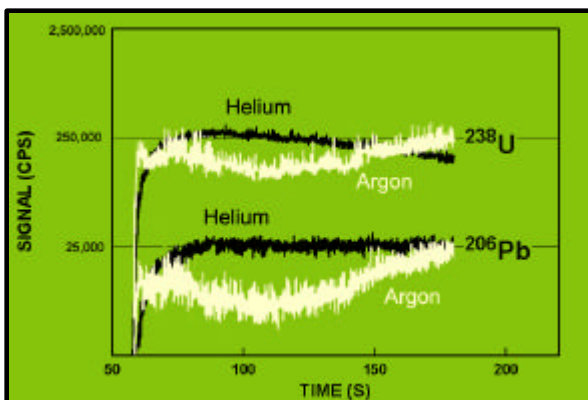


Figure 4: Ablation signals for zircon showing much improved signals and signal stability using He as ablation gas (266 nm laser).

Samples and analytical parameters

Sample and standard zircons were mounted in 2.5 cm diameter grain mounts and polished to reveal surfaces for ablation. Any subsequent surface Pb contamination was removed using 1N nitric acid immediately prior to analysis. Pre-ablation to remove surface contamination was not required.

Crater diameters of 50-80 μm were used for dating by LA-ICP-MS. Approximately 500 ng-1,500 ng of sample were ablated in each acquisition. Ablation was performed in a He carrier gas, to be combined later with Ar in a 30 cm^3 mixing chamber. Figure 4 clearly demonstrates the advantage of using helium as the ablation gas compared to Ar. It is essential to keep the laser parameters constant for all samples and standards in each analytical 'run' (18-22 analyses) to minimise changes in Pb/U fractionation. Conditions were thus dictated by the smallest samples. For large, thick zircons, a 40-60 sec ablation could be used but for small zircons, only 10-20 sec ablations could sometimes be used. All samples and standards were loaded in the sample cell together to avoid opening of the cell and to ensure continuity of laser focus and energy and therefore of Pb/U fractionation characteristics.

Time-resolved analysis was used to record signal intensity data. This allows acquisition of signals as a function of time (ablation depth), and recognition of sample heterogeneity, e.g. zones of radiogenic Pb loss or common Pb contamination related to fractures, inclusions

How to address fractionation

Elemental fractionation is commonly perceived to be a major limitation in LA-ICP-MS zircon dating. When fractionation occurs, there is a change in the Pb/U ratio during ablation. It must be recognised, however, that, provided fractionation is reproducible between analyses, it is straightforward to correct using a zircon standard. The reproducibility of U/Pb fractionation was found to be significantly better when using He as the ablation gas rather than Ar, and a 213 nm laser rather than a 266 nm laser. Improved reproducibility makes fractionation inherently easier to correct. By using fixed analytical parameters, the slope of Pb/U ratio vs time curves for the standard and samples can then be matched. Importantly, because of the time dependence of fractionation, the same analytical time slice, measured from the onset of sampling, must be used for samples and standards. Using this approach, Pb/U ratios can be measured routinely with a precision (1 s) of ca. 1-2%.

How to identify common lead in zircons

Another difficulty for LA-ICP-MS in zircon dating is correction for common Pb using the conventional approach of measuring ^{204}Pb , as it suffers a large interference by ^{204}Hg , a common system contaminant. There are two approaches to the problem:

- (1) If common lead is situated in cracks in samples, it can often be excluded by selectively integrating the time resolved analysis.
- (2) Another way to address this issue is to employ the Tera-Wasserburg diagram.

Common Pb in zircons is commonly distributed around the edge of the grains or in cracks and metamict zones. The latter are common in high-uranium zircons, which suffer alpha-particle damage, making the zircon more porous and susceptible to invasion by common Pb. Polishing the grains prior to analysis will often remove the common Pb at the edge of the zircon. However, during an analysis, a crack containing common Pb might be ablated as the ablation surface penetrates into the sample. As time-resolved analysis records changes in the elemental and isotopic composition of the sample with depth, this will often be accompanied by sudden disturbances in isotopic ratios related to the common Pb. The data for this ablation time interval can then be excluded using the powerful strategy of selective integration of LA-ICP-MS time-resolved signals. In many zircons, domains containing common Pb and/or radiogenic Pb loss, can be identified in analytical data and eliminated easily using appropriate software such as GLITTER, which allows signals and ratios to be displayed and selectively integrated.

In a few cases, data for high-U samples have to be rejected altogether due to pervasively high common Pb. Figure 5 shows the time resolved ratios for such a sample. The resulting data point does not lie near the Concordia (Figure 6) and will be excluded from further interpretation. Given the prodigious speed of the LA-ICP-MS technique, rejection of occasional analyses does not represent a serious limitation of the technique.

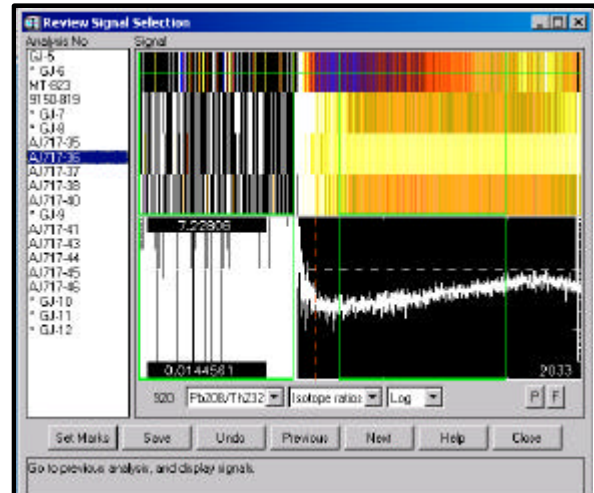


Figure 5: Large variations in $^{208}\text{Pb}/^{232}\text{Pb}$ ratio during an ablation is indicative of common Pb in the zircon.

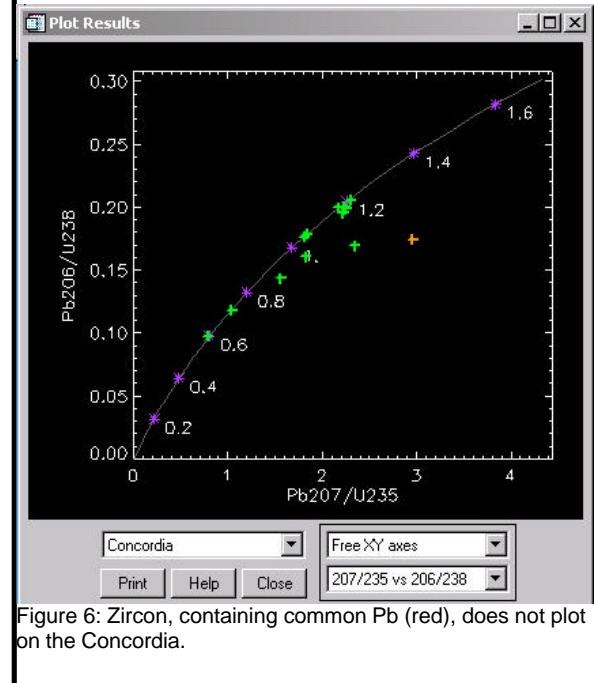


Figure 6: Zircon, containing common Pb (red), does not plot on the Concordia.

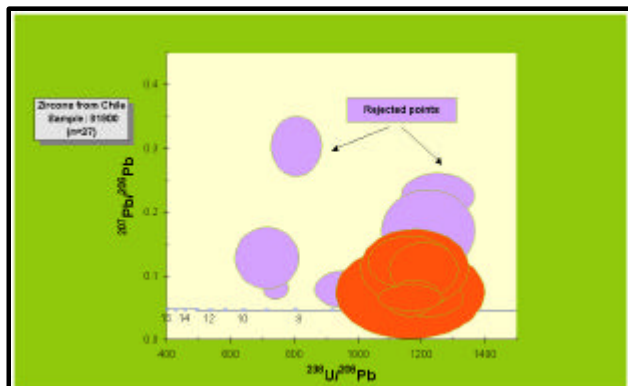


Figure 7: Tera-Wasserburg diagram for young zircon sample 81900

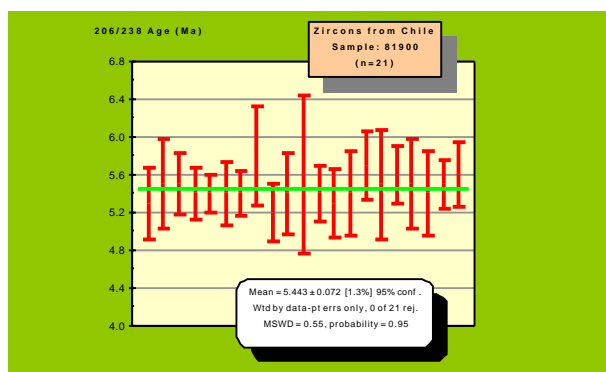


Figure 8: Statistical analysis of LA-ICP-MS data for sample 81900.

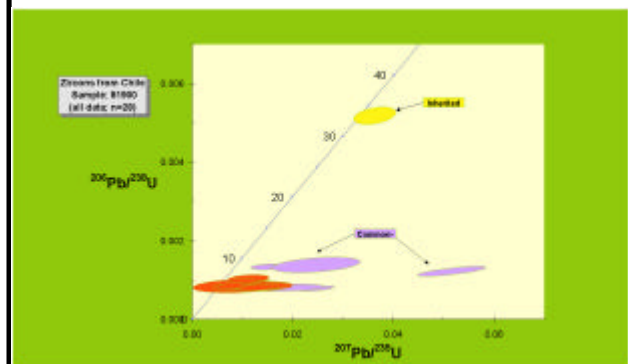


Figure 9: Concordia plot of young zircon sample 81900.

The Tera-Wasserburg diagram is also very useful in identifying common Pb. This diagram plots $^{207}\text{Pb}/^{206}\text{Pb}$ ratio on y-axis against $^{238}\text{U}/^{206}\text{Pb}$ ratio on the x-axis. The $^{207}\text{Pb}/^{206}\text{Pb}$ ratio is very sensitive to the presence of any common lead, particularly in young zircons. Samples containing common Pb will plot above the Concordia line, and can either be excluded or used to construct a regression line to determine a Concordia intercept age. Although there can sometimes be a significant spread on the acquired ratios, determination of the correct gradient is assisted by anchoring the upper end of the line at the composition of common Pb. For young zircons, the isotopic composition of any common Pb can reasonably be assumed to be that of present-day common Pb ($^{207}\text{Pb}/^{206}\text{Pb} \sim 0.836$). The best-fit line can then be drawn much more reliably. This approach works particularly well for young zircons whose concordance is affected significantly by even very small amounts of common Pb.

Dating a young zircon

Multiple grains of a young zircon from Chile, sample 81900, were analysed in runs of 18-22 analyses, which included several analyses of standard zircon, GJ-1, to calibrate elemental fractionation and spectrometer mass discrimination, and two near-concordant zircons run as independent checks of accuracy and reproducibility of the method. The GLITTER software calculated nominated isotope ratios from imported raw ICP-MS data. GLITTER can automatically use the identical integrated time segment for the unknown samples and the standard zircons, eliminating the time-dependence of elemental fractionation.

Figure 7 shows the data from sample 81900 plotted on a Tera-Wasserburg plot. Having removed high-common lead samples, an age of 5.3Ma was determined. Figure 8 shows the statistical data for the same sample.

Figure 9 shows the standard Concordia plot for the same sample. The dark circles lying on the Concordia are the data points to be used in age determination. Using these zircons, the determined age is ca. 5 Ma, which corresponds well with the age determined using the Tera-Wasserburg diagram (Figure 7).

Note that 1 zircon plots on the Concordia at ca. 35 Ma. Zircons generally form in a crystallising melt (magma) and are used to date when the magma crystallized. Sometimes, however, magma genesis will involve partial melting of rocks already containing zircons. Here, the magma has inherited older (35 Ma) zircons.

Conclusions

At crater diameters of 40-80 μm , the use of He ablation gas substantially improved the reproducibility of Pb/U elemental fractionation compared with ablations in Ar. It was the only specific measure employed to reduce the effects of fractionation.

Replicated ablation conditions between samples maintain constant ablation-related elemental fraction of Pb and U. Careful use of the same time segment in time-resolved analysis for all samples and standards is a key component in reproducing and therefore correcting elemental fractionation.

A new zircon standard (GJ-1) has been successfully employed to make instrument mass bias and elemental fractionation corrections. Accurate $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ ratios had 2-sigma values of 1.9% and 3% respectively.

Radiogenic Pb loss and common Pb enrichments can often be eliminated by selection of appropriate analytical time slices of time resolved signals. Tera-Wasserburg diagrams handle more pervasive common Pb contributions, where discrete zones of common Pb enrichment cannot be recognised.

A zircon independently dated at 5Ma was used to demonstrate the accuracy and precision of this overall approach to LA-ICP-MS zircon dating, yielding very good agreement with the accepted age, with precision of the order of 2% to 4%.

The technique is capable of over 40 age determinations per day.

Acknowledgement

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Ref: The application of laser ablation-inductively coupled plasma-mass spectrometry to in situ U-Pb zircon geochronology, Chemical Geology, 211 (2004) 47-69.



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