DETRITAL ZIRCON GEOCHRONOLOGY BY LASER-ABLATION MULTICOLLECTOR ICPMS AT THE ARIZONA LASERCHRON CENTER

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Abstract—Detrital zircon geochronology is rapidly evolving into a very powerful tool for determining the provenance and maximum depositional age of clastic strata. This rapid evolution is being driven by the increased availability of ion probes and laser ablation ICP mass spectrometers, which are able to generate age determinations rapidly, at moderate to low cost, and of sufficient accuracy for most applications. Improvements in current methods will probably come from enhanced precision/accuracy of age determinations, better tools for extracting critical information from age spectra, abilities to determine other types of information (e.g., REE patterns, O and Hf isotope signatures, and/or cooling ages) from the dated grains, and construction of a database that provides access to detrital zircon age determinations from around the world.

INTRODUCTION

U-Th-Pb geochronology has become a fundamental tool in Earth Science research, with applications that cover the span of structural geology, tectonics, stratigraphy, paleontology, petrology, and geochemistry. Although many U-Th-Pb analytical techniques and applications are well established, emerging technologies are revolutionizing the way that geochronologic information can be acquired and applied. Some of the most exciting advances in the field are being driven by Laser-Ablation Multicollector ICP Mass Spectrometry (LA-MC-ICPMS), which allows for rapid determination of U-Th-Pb ages with micron-scale spatial resolution. These instruments are fundamentally changing the way that geochronologic information is utilized in Earth Science research.

The Arizona LaserChron Center (www.geo.arizona.edu/alc) is built around a Multicollector Inductively Coupled Plasma Mass Spectrometer (GVI Isoprobe) linked to a 193 nm Excimer laser ablation system (New Wave Instruments). These instruments are used for U-Th-Pb geochronology as well as for applications involving the isotope geochemistry of Pb, Sr, Nd, Cu, Fe, U, Th, K, Ca, and REE. Geochronologic applications of the laser-ICPMS have been particularly successful because the instrument:

- Can determine U-Th-Pb ages very efficiently (~40 age determinations per hour) and at low cost ($4 per analysis for NSF-supported users)
- Generates U-Th-Pb ages with an accuracy of ~1% (2-sigma), which is appropriate for most geochronologic problems in Earth Science.
- Offers the potential for development of new U-Th-Pb geochronological techniques and applications
- Is highly amenable to multi-user operation
- Provides an excellent tool for training students and faculty in the generation and interpretation of geochronologic information.

Because of these strengths, the laser-ICPMS laboratory at the University of Arizona is poised to have an important impact on Earth Science research. During the past three years the laboratory has generated over

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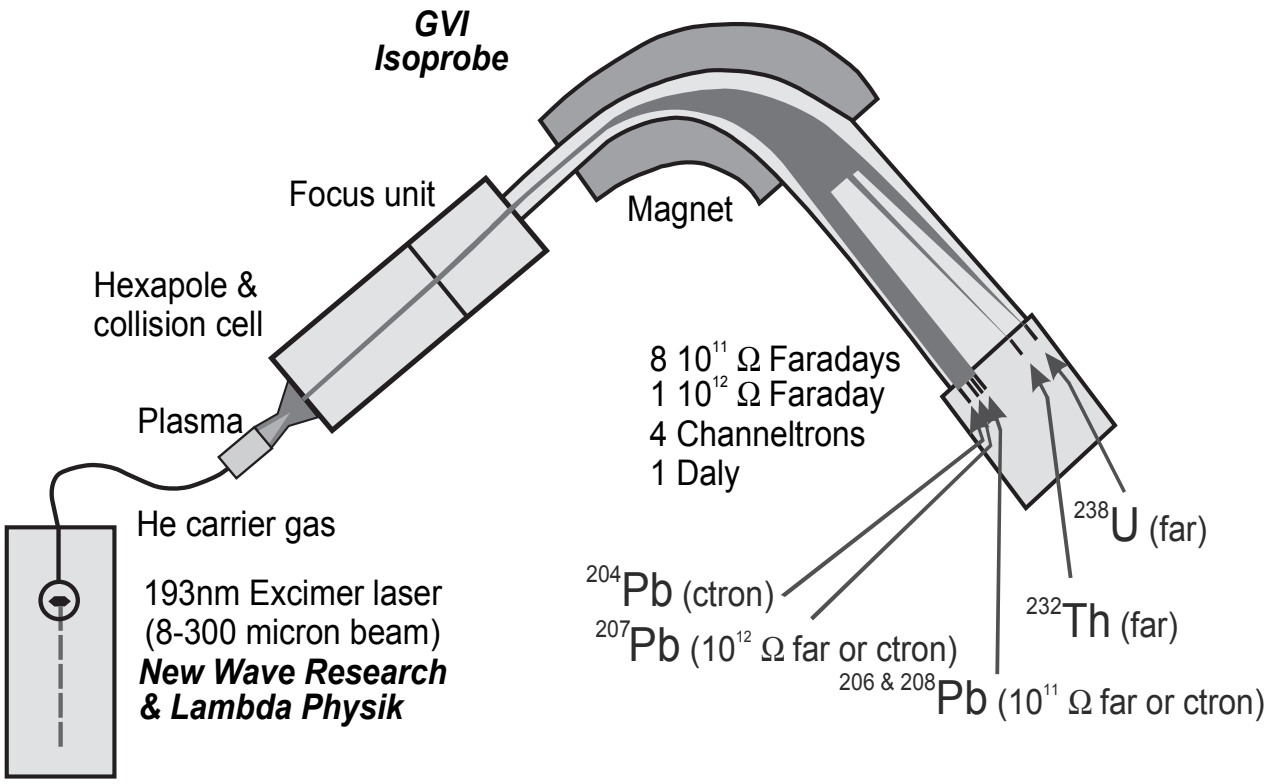

Figure 1—Instrument used for U-Th-Pb geochronology at the Arizona LaserChron Center.

150,000 U-Th-Pb ages, mainly on detrital zircons that were analyzed to determine the provenance and maximum depositional age of sedimentary sequences.

In the following sections we describe the analytical methods used for analyzing detrital zircon grains and the tools that are available for analyzing data.

LA-MC-ICPMS ANALYTICAL METHODS

Geochronologic analyses are conducted by ablating sample material with a laser and analyzing U-Th-Pb isotopes with a multicollector inductively coupled plasma mass spectrometer (Fig. 1). This combination of instruments was first developed in the late 90's, and the fundamental design of the instrumentation has changed little since that time.

Our laser system (ArF Excimer DUV193 from New Wave Instruments, www.new-wave.com) has a wavelength of 193 nm, which couples well with silicate materials and produces well-defined pits, strong ion intensities, and stable elemental (Pb/U and Pb/Th) fractionation. Figure 2 shows the geometry of ablation pits in zircon crystals. For detrital zircon analyses, we generally use a 35 or 25 micron beam diameter and a pit depth of ~15 microns.

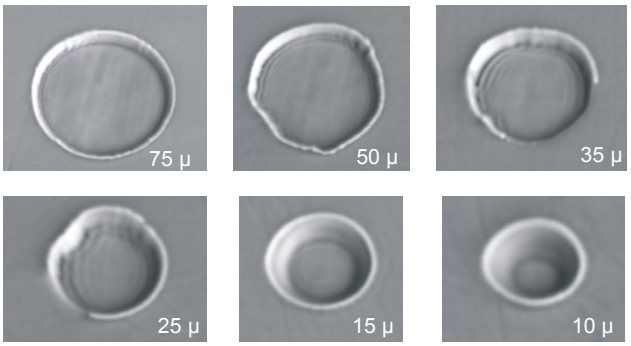

Figure 2—Geometry of ablation pits. Pit depth is ~15 microns.

Samples are generally mounted in 1" diameter epoxy plugs and polished to half-thickness. It is also possible to analyze crystals in situ from the surface of a polished thin section or probe mount, and we have even had success with analysis of loose crystals and crystals exposed on a broken rock surface. Photographic images are made of all samples, and an SEM is used to make BSE and CL images.

The ablated material is carried in helium gas into the plasma source of a multicollector inductively coupled plasma mass spectrometer (Isoprobe, from GV Instruments, www.gvinstruments.co.uk). Figure 1 is a schematic of the Isoprobe showing the main components of the instrument.

This instrument is ideal for U-Th-Pb geochronology because it has a flight tube of sufficient width that U, Th, and Pb isotopes are measured simultaneously, and it is equipped with nine moveable Faraday collectors and four low-side Channeltrons (ion counters). Eight of the Faraday collectors use a 10e11 ohm resistor, whereas the Faraday used for measuring ^{207}Pb is equipped with a 10e12 ohm resistor. This configuration allows static-mode measurement of all isotopes, using 10e11 Faraday detectors for ^{238}U, ^{232}Th, ^{208}Pb, and ^{206}Pb, a 10e12 ohm faraday detector for ^{207}Pb, and an ion-counting channel for ^{204}Pb. Alternatively, for very small signals, all Pb peaks can be analyzed with channeltrons while U and Th are measured with Faraday detectors. The ability to measure in static mode, with reliable determination of ^{206}Pb/^{204}Pb, is essential to the efficiency, precision, and accuracy of U-Th-Pb geochronology by laser-ICPMS.

Each analysis consists of one 20-second integration on peaks with the laser off (for backgrounds), 20 or 12 one-second integrations with the laser firing, and a 30 second delay to purge the previous sample and prepare for the next analysis. This results in a throughput of ~90 seconds per analysis, ~40 analyses per hour, or ~700 analyses per 24 hour session.

Analyses are conducted as described above in an effort to generate signal intensities that are significantly above the on-peak backgrounds that are inherent in an ICP mass spectrometer. Table 1 shows typical intensities for analysis of a 500 Ma zircon analyzed with a 35 micron beam. Of greatest significance are the peak/background ratios for ^{207}Pb and ^{204}Pb, which must be maximized to generate reliable ^{206}Pb/^{207}Pb ages and ^{206}Pb/^{204}Pb common Pb corrections.

Common Pb correction is accomplished by using the measured ^{204}Pb and assuming an initial Pb composition from Stacey and Kramers (1975). Conservative uncertainties of 1.0 for ^{206}Pb/^{204}Pb, 0.3 for ^{207}Pb/^{204}Pb, and 2.0 for ^{208}Pb/^{204}Pb are used for the composition of the common Pb. Measuring ^{204}Pb accurately is a challenge because of the significant amount of ^{204}Hg present in the argon plasma gas. This ^{204}Hg (as well as any background ^{204}Pb or molecular 204) is accounted for by first measuring backgrounds in the 204 mass position, then measuring the peak 204 intensity with the laser firing, and subtracting the background intensity from the peak intensity. We have found that this is significantly more accurate than monitoring ^{202}Hg and correcting for ^{204}Hg by using the natural ^{204}Hg/^{202}Hg. Reducing the background counts in the 204 position is one of our constant challenges!

Our ability to determine ^{206}Pb/^{204}Pb reliably, and thereby to correct for common Pb in a rigorous fashion, is shown on Figure 3. Plotted are LA-ICPMS and ID-TIMS (blank and spike-corrected) determinations of ^{206}Pb/^{204}Pb for various zircons that have been used as standards. The ability to measure ^{206}Pb/^{204}Pb accurately is essential to the generation of robust U-Th-Pb ages. Unfortunately, most single-collector ICP mass spectrometers are not able to measure ^{204}Pb reliably and should not be used for U-Th-Pb geochronology.

Isotope	Peak	Background
^{238}U	29,642,000 cps	110 cps
^{232}Th	4,182,000 cps	480 cps
^{208}Pb	161,000 cps	2050 cps
^{207}Pb	136,000 cps	920 cps
^{206}Pb	2,202,000 cps	1740 cps
^{204}Pb	550 cps	210 cps

Table 1—Intensities on backgrounds and peaks during analysis of a typical 500 Ma zircon.

Fractionation of Pb/U and Pb/Th occurs primarily in the laser pit, and is highly sensitive to the rate of carrier gas flow across the sample surface. To correct for Pb/U and Th/U fractionation, fragments of a large Sri Lanka zircon grain (564 ± 4 Ma at 2-sigma) are analyzed once every 3 to 5 unknowns. The unknowns are corrected for the closest 6 standards using a sliding window average. Figure 4 shows the fractionation factor for $^{206}Pb/^{238}U$ for a zircon sample in which 100 unknowns were analyzed. The diamonds are standard analyses (with 1-sigma errors shown in small dots), gray bars show the position of unknowns between the standards, thick line shows the average fractionation factor applied to the standards, and the thin lines show the standard error of this sliding window average. For comparison, the height of the gray bars shows a 2% error. The error on this fractionation factor is the most significant of the systematic errors, and is generally ~1% (2-sigma) for $^{206}Pb/^{238}U$ ages.

Fractionation of Pb isotopes is minimal, with a maximum of ~3% apparent fractionation of $^{206}Pb/^{207}Pb$. This apparent fractionation is also removed by comparison with standards, using the procedure described above. Figure 5 shows the calibration correction for a typical zircon analysis. The error on this fractionation factor is the most significant of the systematic errors, and is generally ~1% (2-sigma) for $^{206}Pb/^{207}Pb$ ages.

Fractionation affects our analyses in two other important ways. First is the observation that Pb/U and Pb/Th fractionation varies with depth during laser ablation. In most cases, Pb/U and Th/Pb increase by ~5% during an analysis that takes 20 seconds and excavates to a depth of 15 microns. We account for this by monitoring the depth-related fractionation of standards, and then applying a sliding-window depth-related fractionation factor to the unknowns.

Pb/U fractionation also varies by up to several percent depending on position on the mount surface. This is apparently due to variations in the flow rate/pattern of the helium carrier gas across the sample surface. For this reason, we mount all standards and unknowns

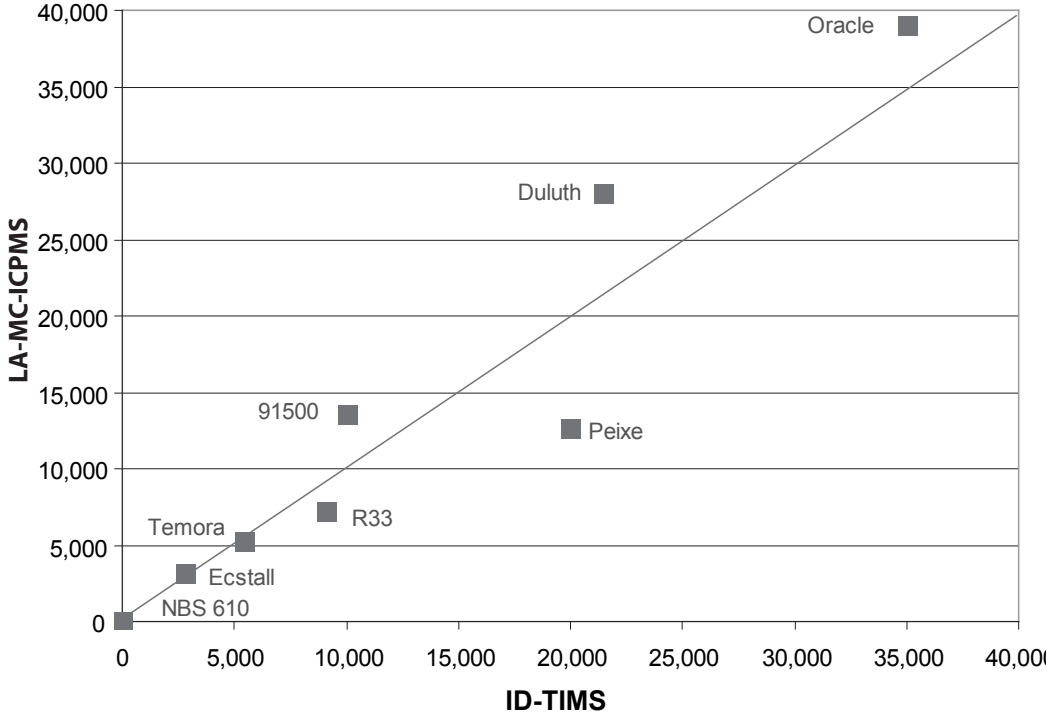

Figure 3—ID-TIMS versus LA-MC-ICPMS analyses of 206Pb/204Pb for well-characterized zircons. This demonstrates that we are able to measure $^{206}Pb/^{204}Pb$ reliably, which is essential to correct for common Pb in a rigorous fashion and thereby to determine reliable U-Th-Pb ages.

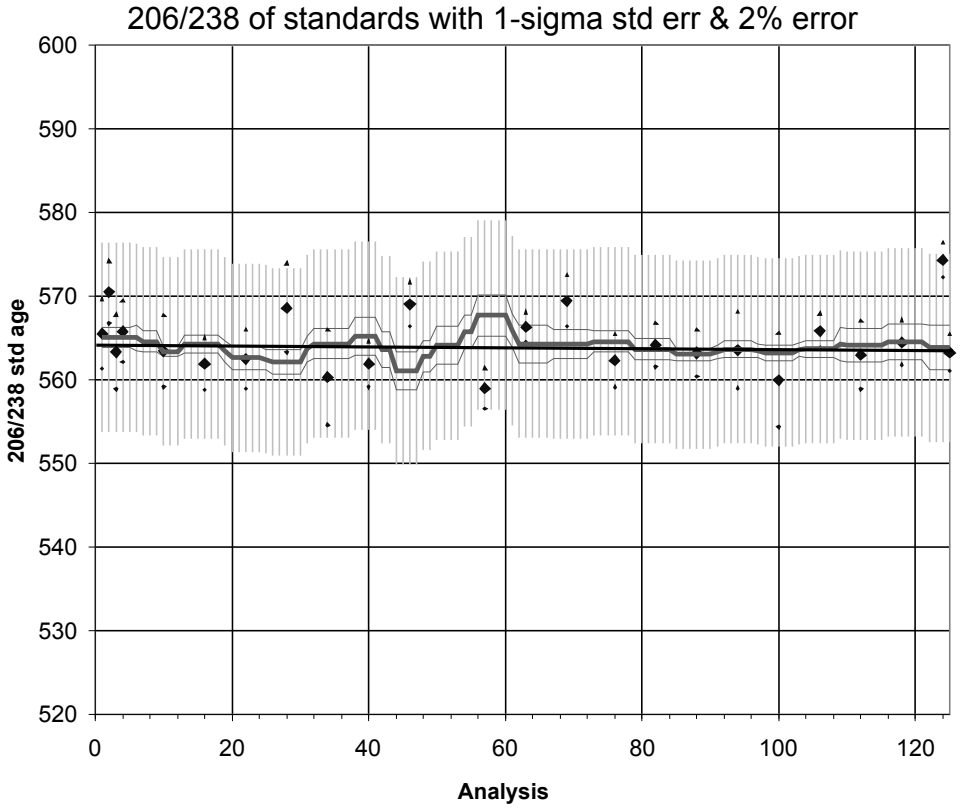

Figure 4—Plot of standards analyzed to calibrate fractionation of $^{206}Pb/^{238}U$.

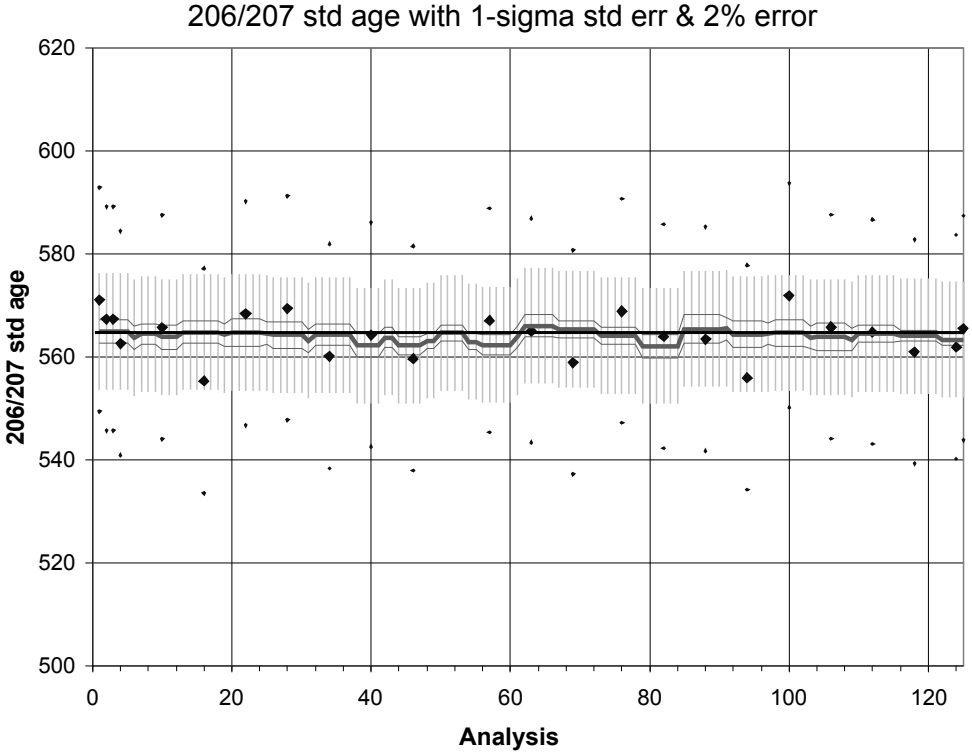

Figure 5—Plot of standards analyzed to calibrate fractionation of $^{206}Pb/^{207}Pb$.

close together in the central portion of each mount.

In order to determine accurate concentrations of U and Th, we analyze fragments of NIST SRM 610 trace element glass with every sample. This glass has ~450 ppm U, Th, and Pb. Comparison with mineral standards indicates that fractionation within the glass is similar to that in zircon, sphene, and monazite. Concentrations are accordingly known to ~20%.

For each zircon analysis, the errors in determination of $^{206}Pb/^{238}U$ and $^{206}Pb/^{204}Pb$ result in a measurement error of ~1-2% (at 2-sigma level) in the $^{206}Pb/^{238}U$ age. The errors in measurement of $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{204}Pb$ also result in ~1-2% (at 2-sigma level) uncertainty in age for grains that are >1.0 Ga, but are substantially larger for younger grains due to low intensity of the ^{207}Pb signal. We refer to errors that arise from the measurement of $^{206}Pb/^{238}U$, $^{206}Pb/^{207}Pb$, and $^{206}Pb/^{204}Pb$ as random (or measurement) errors, for they are different for each analysis. For most analyses, the cross-over in precision of these random errors for $^{206}Pb/^{238}U$ and $^{206}Pb/^{207}Pb$ ages occurs at ~1.0 Ga.

The precision and accuracy of our U-Th-Pb measurements can be evaluated by comparison of LA-ICPMS analyses with ID-TIMS data from zircons that have been used as calibration standards by various laboratories. Figure 6 shows that for these samples, the mean of 10 analyses is generally within 1% of the given ID-TIMS age. This is approximately the same as the accuracy of ion probe analyses (e.g., Black et al., 2004).

METHODOLOGY OF DETRITAL ZIRCON STUDIES

For a detrital zircon study, we generally analyze 100 randomly selected zircon crystals from each sample in an effort to identify each of the main age groups present. Data are filtered according to precision (typically 10% cutoff) and discordance (typically 30% cutoff) and then plotted on Pb/U concordia diagrams and relative age probability plots (Ludwig, 2003). Each relative age probability curve is constructed by (1) calculating a normal distribution for each analysis based on the reported age and uncertainty, (2) summing the probability distributions of all acceptable analyses into a single curve, and (3) if normalized, dividing the area under the curve by the number of analyses. Figure 7 shows a series of relative age probability plots that have been normalized for the number of constituent analyses (area under the curves is the same). Stacked and normalized probability plots can be made with an excel macro that is available from the Arizona LaserChron Center website (www.geo.arizona.edu/alc).

For some applications it is advantageous to show detrital age spectra on a cumulative age probability plot. Figure 8 shows a series of cumulative age probability plots for the same data shown in Figure 7. Cumulative probability plots can be made with an excel macro that is available from the Arizona LaserChron Center website (www.geo.arizona.edu/alc).

Interpretations derived from detrital zircon age spectra are based on the view that only clusters of ages record robust sources ages. This is because a single age determination may be compromised by Pb loss and/or inheritance (even if concordant), whereas it is unlikely

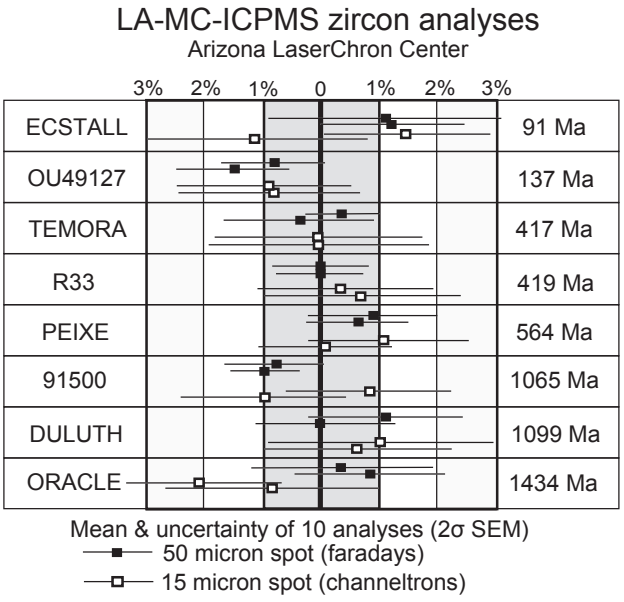

Figure 6—Age-offset plot comparing LA-MC-ICPMS ages with the ID-TIMS age of well-calibrated zircons. This shows that each LA-MC-ICPMS analysis is accurate to within 2-3% and a set of ~10 analyses is accurate to within ~1%.

that three or more grains that have experienced Pb loss and/or inheritance would yield the same age. For most samples, we accordingly attach age significance only to clusters defined by three or more overlapping analyses. This has particular importance for determination of the youngest age component in a detrital zircon sample, which is commonly used as a maximum depositional age. This approach also compromises recent statistical treatments (e.g., Vermeesch, 2004) that report the number of analyses needed for a detrital zircon study, as these treatments assume that a source can be inferred from a single isolated analysis.

Relative age probability curves for two samples can be compared visually, or statistically with the use of the Kolmogorov-Smirnoff (K-S) test. This test compares two distributions to determine if they are statistically different at a specified level of confidence. An excel macro that conducts K-S tests on sets of detrital zircon age spectra is available from the Arizona LaserChron Center website (www.geo.arizona.edu/alc).

COMPLEMENTARY PROVENANCE INFORMATION

Of course, detrital zircon provenance information is most powerful when applied in a solid stratigraphic, sedimentologic, and biostratigraphic framework. It is also becoming apparent that the ability to reconstruct provenance is significantly enhanced if other types of information are available, especially if this information comes from the same grains that have yielded U-Th-Pb ages. For example, the U/Th of a zircon crystal can be used to determine the degree to which metamorphic fluids were present during crystal growth (e.g., Williams, 2001; Rubatto et al., 2001; Rubatto, 2002). Because U/Th is determined during U-Th-Pb geochronologic analysis, a plot of age versus U/Th reveals the main age(s) of metamorphism in the source region(s). For example, Figure 9 shows a suite of zircons (from New Zealand) that clearly record metamorphism at ~ 120 Ma, ~350 Ma, and ~580 Ma. Such information could be very helpful in identifying potential source areas.

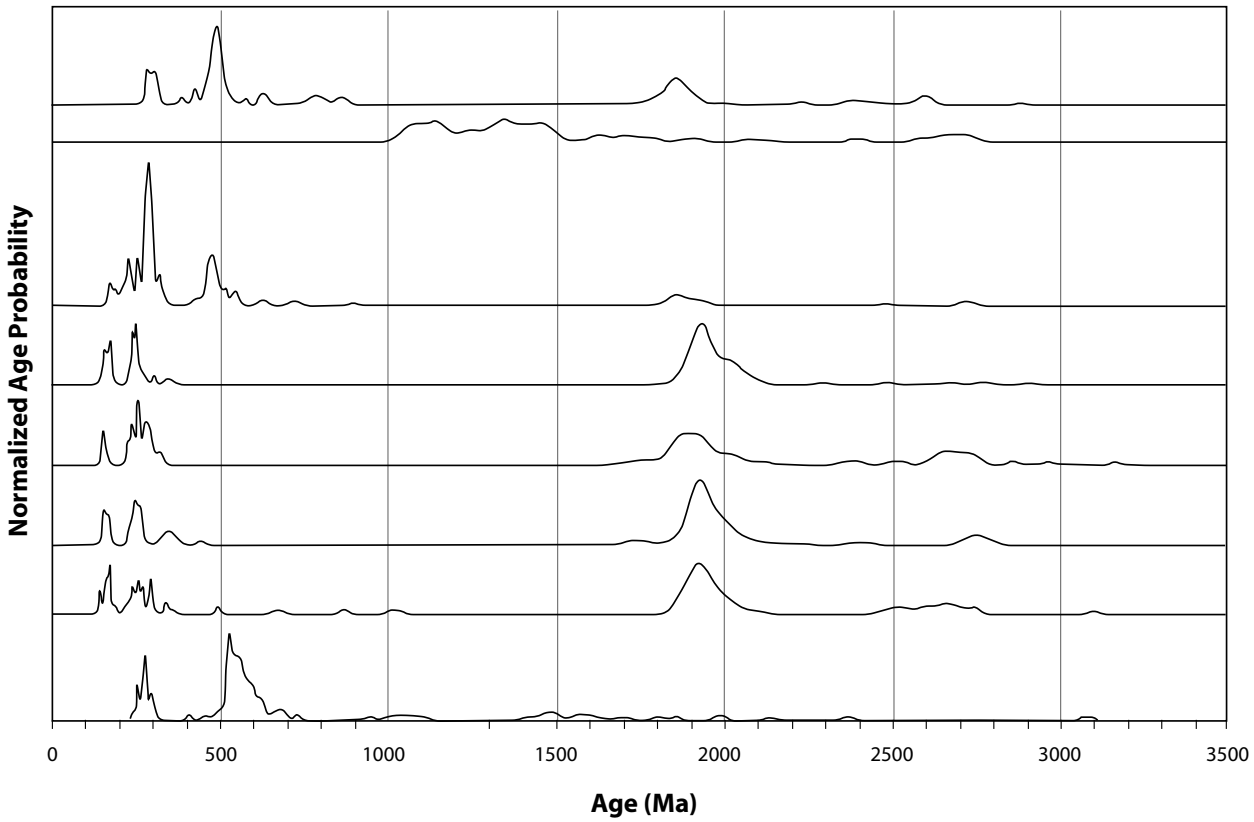

Figure 7—Example of normalized relative age probability plots.

There are many other geochemical and isotopic aspects of zircons that can provide useful provenance constraints. For example, Rahl et al. (2003) have shown that (U-Th)/He cooling ages can be determined on the same grains for which U-Pb ages are known, and that this combination provides a powerful tool for refining provenance interpretations. Other aspects of zircons that may be used to help identify source terranes include REE and Ti concentrations and O and Hf isotope ratios. Exploring these complementary sources of information is one of the most promising areas of provenance research.

MECHANICS OF DETRITAL ZIRCON STUDIES

Sample collection

Samples must be collected in such a way to avoid contamination from other materials (soil, other rocks, concrete, asphalt, etc.). The fresher the rock the better, and make sure to avoid veins and alteration assemblages. Rock fragments should be fist-size or smaller so that they do not need to be broken in the rock crushing lab. Put the collected fragments into well-labeled sample bags, and ship in padded and well-taped boxes or, better yet, in plastic buckets with snap-on lids.

The amount of sample needed for a detrital zircon study depends on the maturity of the sand or sandstone to be analyzed. If quartz (igneous) content is high, zircon abundance will probably also be high and 10-20 pounds is adequate. If quartz content is low, 30-40 pounds is advisable in order to end up with a sufficient zircon yield. We have rarely found detrital zircons in samples that are devoid of detrital quartz.

It is generally advisable to collect the coarsest available sand/sandstone from a sequence in order to maximize the average size and range of sizes of zircons in your sample. But this strategy should be applied cautiously because it will tend to enhance representation of local sources relative to distant sources. If this distinction is important, a reasonable approach would be to collect and analyze samples with a range of grain sizes from the same sequence.

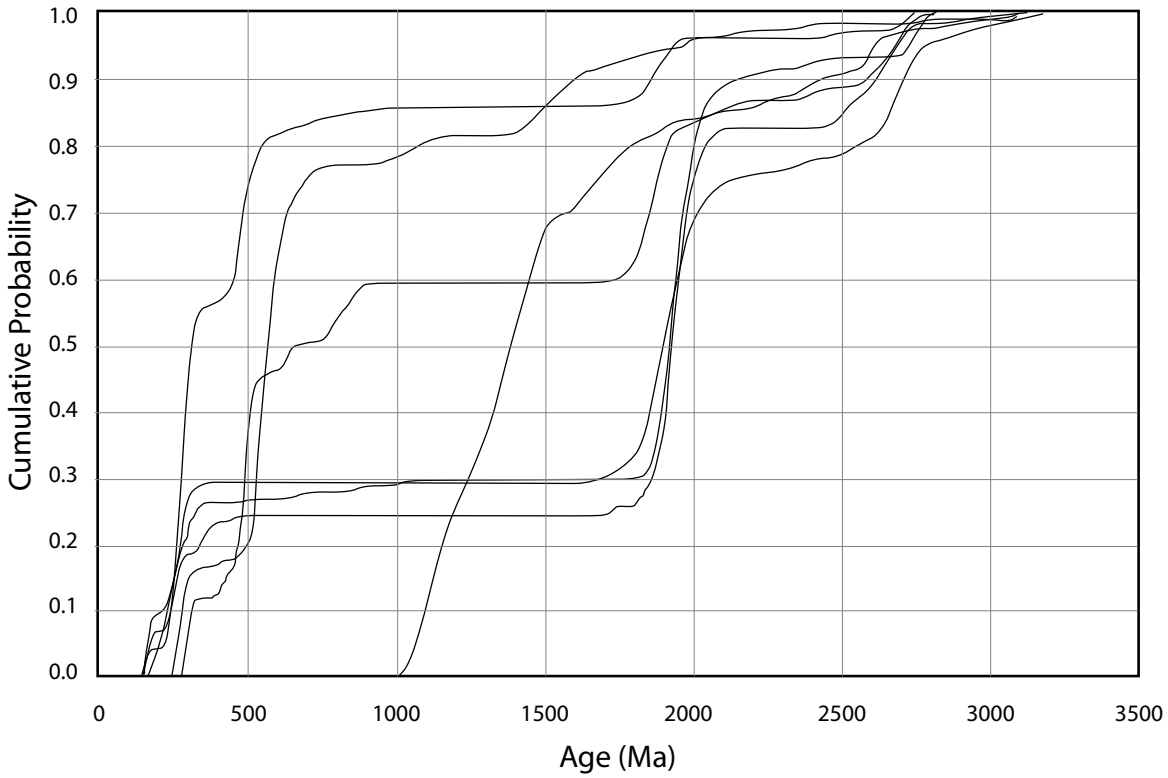

Figure 8—Example of cumulative age probability plots.

Sample processing

Care must be taken to process detrital zircon samples in such a way that the final zircon separate is not biased by size, shape, color, etc. of the grains. This requires extra time and effort, especially when doing density and magnetic separations. Unfortunately, we have found that commercial labs and labs at universities without extensive geochronologic expertise are generally unable to produce high quality mineral separates from detrital zircon samples. Because this compromises the outcome of the study, both in data quality and in achieving an unbiased age spectrum, it is critical that sample processing be done carefully and in a lab with extensive experience separating zircons.

Sample analysis

For a provenance analysis, grains should be mounted without bias according to size or shape, and analyzed by random selection. As described above, we generally analyze 100 detrital zircons from each sample in order to resolve all of the main source areas. Specific grains can selected for analysis based on size, color, or shape to address specific problems, but these data should not be combined with analyses conducted by random selection.

Costs

The cost of analyzing a detrital zircon sample has been reduced in recent years as more ion probes have become available and as new LA-ICPMS facilities have been established. Because the Arizona LaserChron Center is supported by the NSF Instrumentation and Facilities program to serve as a multi-user facility, analytical costs are reduced by ~50% for NSF-supported research. The present cost for an NSF-supported user to analyze 100 detrital zircons is accordingly $400. For researchers who are not supported by NSF, the cost is $800 to analyze 100 detrital zircon grains. To extract zircons from a sample we would charge an additional $300.

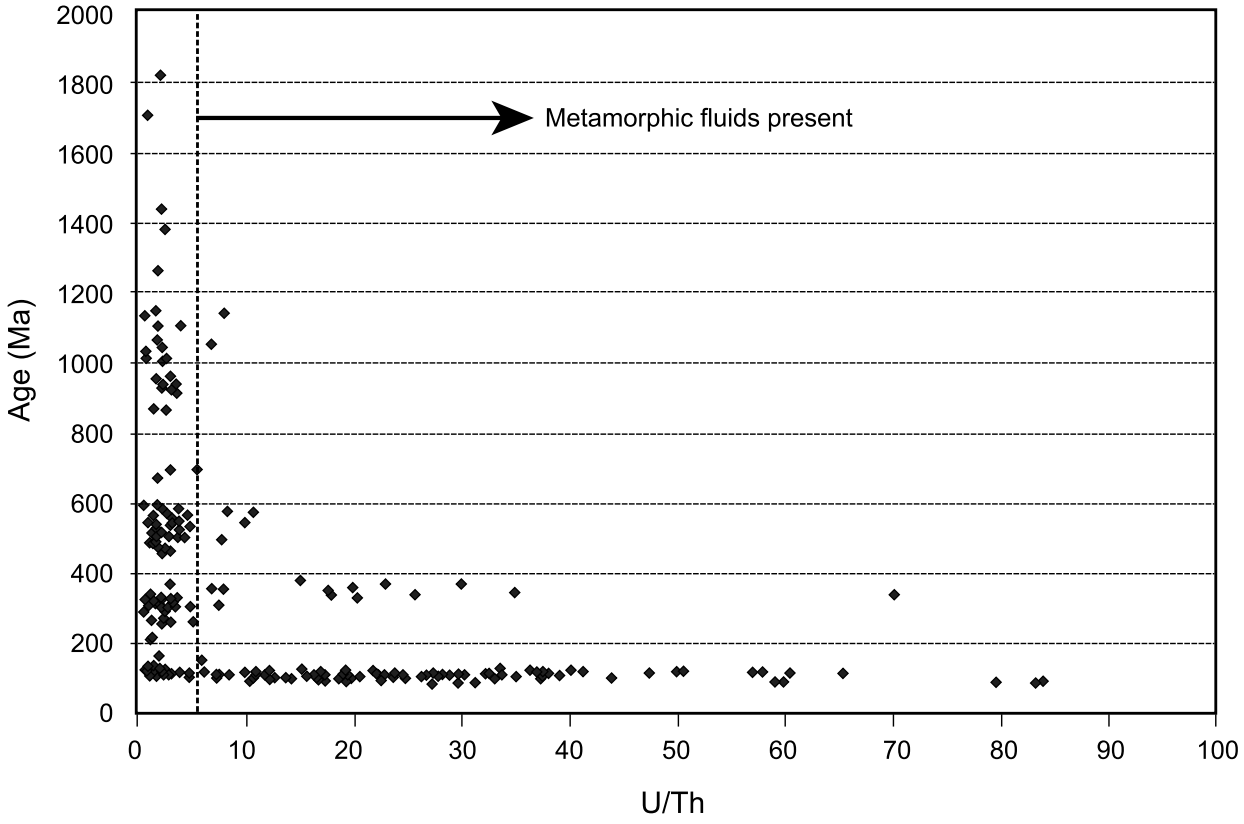

Figure 9—Plot of U/Th versus age for zircons from New Zealand (from Keith Klepeis and Art Goldstein).

The National Science Foundation has also provided funds to subsidize student research at the Arizona LaserChron Center. For students conducting analyses as part of a NSF-funded project, up to $200 per day is available to help cover travel costs as well as lodging and meals while in transit and in Tucson.

CONCLUSIONS

Technological developments have recently made it possible to generate U-Th-Pb ages of detrital zircons rapidly (~40 analyses per hour), at moderate expense ($400 for 100 analyses), and with a precision that is adequate for most provenance studies (1-2% for each analysis). These developments are driving an explosion in the amount of detrital zircon data that is currently being generated and published.

Future challenges in detrital zircon geochronology include:

1. improving the precision and accuracy of analyses to better than 1% (2-sigma)
2. developing techniques that will help users determine reliable maximum depositional ages from a set of detrital zircon ages
3. devising statistical methods that that can be used to reliably determine whether two samples could have been shed from the same source terrane
4. constructing a user-friendly data base that contains detrital zircon age determinations from around the world

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