Small-Volume U–Pb Zircon Geochronology by Laser Ablation–Multicollector–ICP–MS

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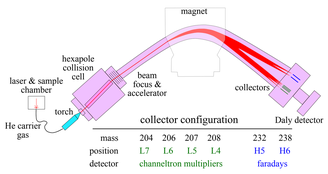
Abstract

U–Pb zircon geochronology is hampered by problems acquiring meaningful geologic ages on zoned grains that retain isotope signatures from multiple growth or thermal events. We present a new method at the University of Arizona LaserChron Center using laser ablation–multicollector–inductively coupled plasma–mass spectrometry to overcome complications associated with intricately zoned zircon crystals through in situ sampling of zircon volumes as small as 12–14 µm in diameter by 4–5 µm in depth (<3 ng of zircon). Using Channeltron multipliers to monitor Pb intensities in conjunction with a total count counting method and errors calculated a as function of the number of counts, the small-volume technique reproduced published ages on eight Mesoproterozoic–Cretaceous secondary zircon standards accurate and precise within 2%, and an age only ~1 Ma too young on a Miocene-aged grain. Two initial applications of the small-volume technique—the detrital zircon provenance of fine-grained mudstones and shales and the creation of zircon U–Pb age maps to investigate the detrital and metamorphic history of a granulite-facies paragneiss—demonstrate the utility of this technique to a wide variety of geologic problems and confirm the viability of laser ablation–multicollector–inductively coupled plasma–mass spectrometry as a tool for high-resolution U–Pb geochronology.

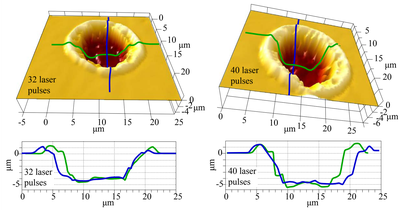
Data acquisition

1. ICP setup:



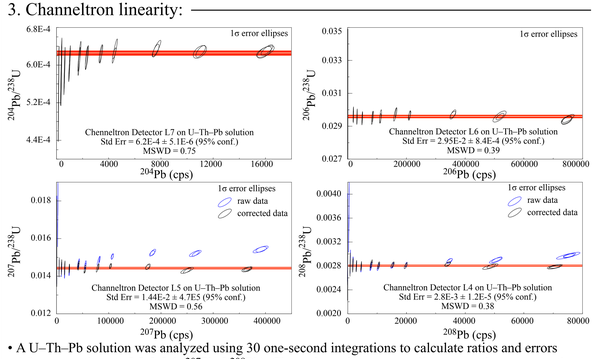
- GV Instruments Isoprobe with S-option interface
- Intermediate gas = 1.0 mL/min
- Ar coolant gas = 14.0 L/min
- Hexapole Ar gas = 0.24 mL/min
- Accelerating voltage ~6 kV
- Operated under wet plasma conditions (50 µL/min miliQ water + 0.340 mL/min Ar gas)

2. Laser setup:



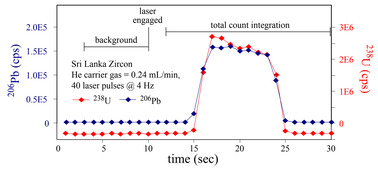
- New Wave Instruments 193 nm ArF excimer laser
- operated at 23.5 kV with 4 beam attenuator plates
- 10 µm beam
- 32–40 pulses at 2–8 hz (typically 40 pulses at 4 hz)
- ablation rate of 0.12 µm/laser pulse
- He carrier gas = 0.2–0.36 mL/min (typically 0.24 mL/min)

3. Channeltron linearity:



- A U–Th–Pb solution was analyzed using 30 one-second integrations to calculate ratios and errors
- After corrections to L5 & L4 (^{207}Pb &^{208}Pb), Channeltron detectors are linear over the concentrations typically observed in zircon

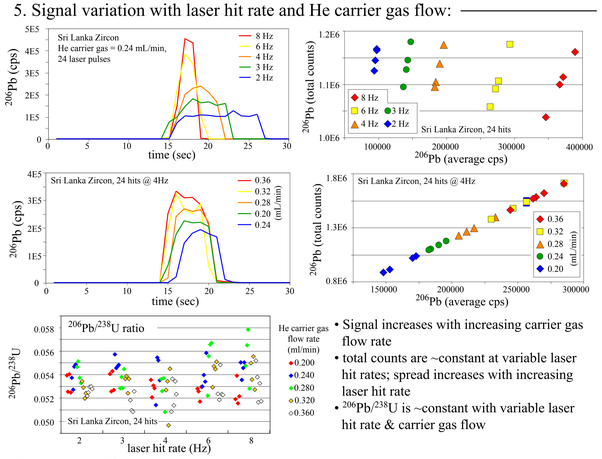
4. Acquisition routine:



- Background, n_{bg}, is characterized as the average of timesteps 3–10
- Sample signal, N, is the sum of the laser signal, n_s, minus n_{bg} over timesteps 12–30:

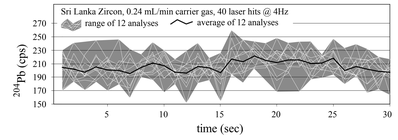
$$N = \sum_{12}^{30} (n_s - n_{bg})$$

5. Signal variation with laser hit rate and He carrier gas flow:



- Signal increases with increasing carrier gas flow rate
- total counts are ~constant at variable laser hit rates; spread increases with increasing laser hit rate
- ^{206}Pb/^{238}U is ~constant with variable laser hit rate & carrier gas flow

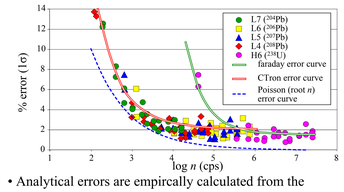
6. Common Pb:



- ^{204}Pb is typically <50cps above background, and yields values that are not significantly different from zero
- none of the data presented here common Pb corrected

Error propagation and fractionation

1. Analytical errors:

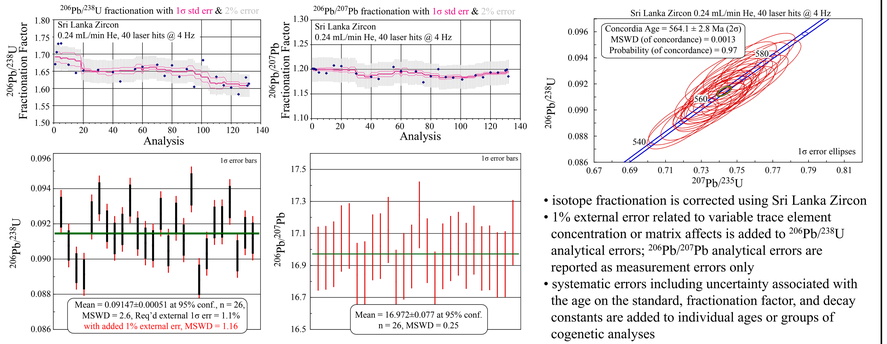


- Analytical errors are empirically calculated from the linearity experiments and are proportional to n_s and normalized to the student's t distribution
- $\sigma_{s,\ Channeltron} = 1.02[(n_s+200)0.45+0.02(n_s+200)]$
- $\sigma_{s,\ faraday} = 1.02[(n_s+100000)0.5+0.015(n_s+100000)]$
- Then, following the law of combination of errors:

$$\sigma_{N,\ Channeltron} = \sqrt{\sum_{12}^{30} (\sigma_{s,\ Channeltron}^2 - \sigma_{bg}^2)}\text{, and}$$

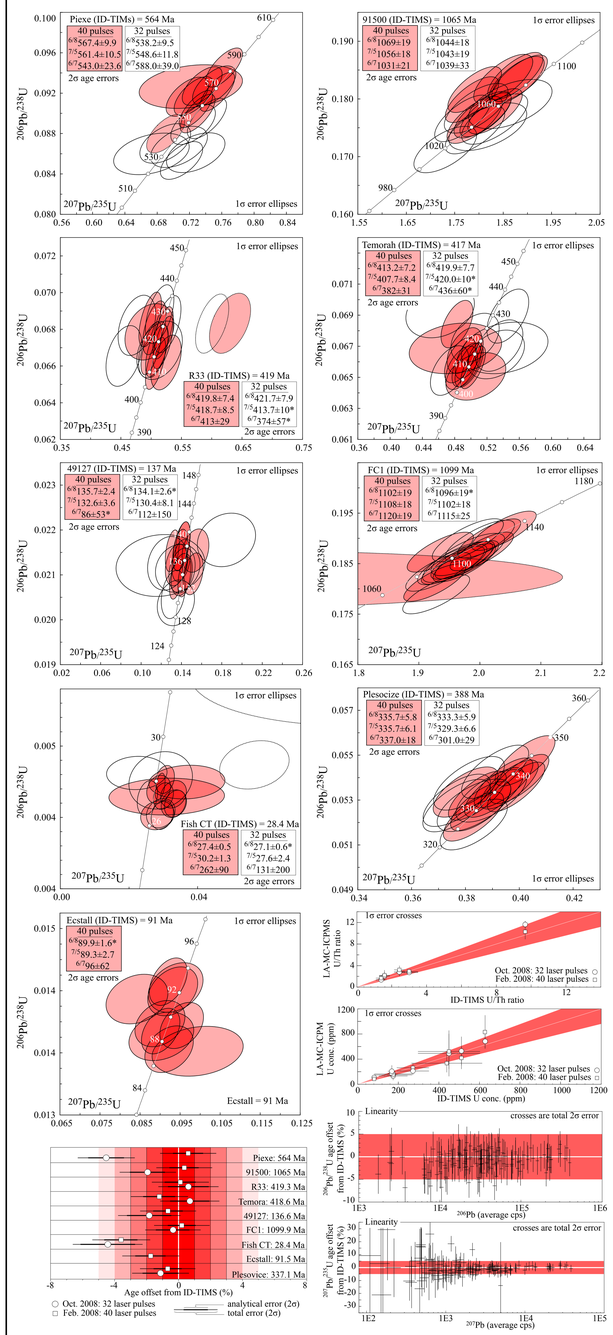
$$\sigma_{N,\ faraday} = \sqrt{\sum_{12}^{30} (\sigma_{s,\ faraday}^2 - \sigma_{bg}^2)}$$

2. Fractionation and systematic errors:



- isotope fractionation is corrected using Sri Lanka Zircon
- 1% external error related to variable trace element concentration or matrix affects is added to ^{206}Pb/^{238}U analytical errors; ^{206}Pb/^{207}Pb analytical errors are reported as measurement errors only
- systematic errors including uncertainty associated with the age on the standard, fractionation factor, and decay constants are added to individual ages or groups of cogenetic analyses

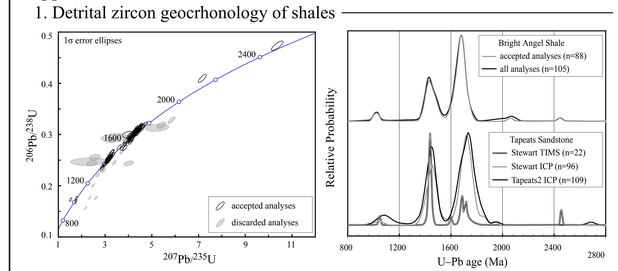
Results: secondary zircon standards



- Nine zircon standards of Mesoproterozoic–Miocene age were used to test the small-volume technique
- Ages are precise and accurate to 2% in 8 samples and within 1.5 Ma in one Miocene-aged sample
- Measured U concentration and U/Th are within 20% of ID-TIMS values
- Age offsets are linear with respect to ^{206}Pb and ^{207}Pb concentrations

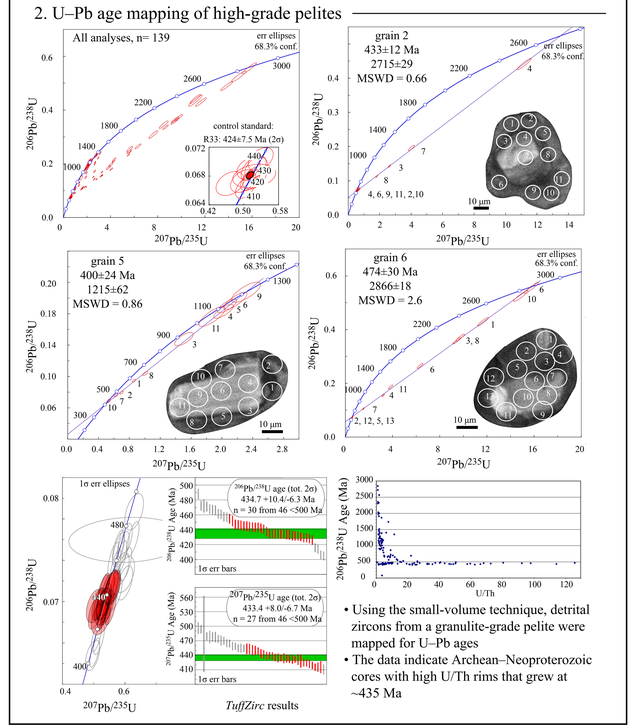
Applications

1. Detrital zircon geochronology of shales



- Detrital zircons analyzed from the Bright Angel Shale with an average grain size of 20–30 µm
- Calculated probability distribution matches distributions from the underlying Tapeats Sandstone

2. U–Pb age mapping of high-grade pelites



- Using the small-volume technique, detrital zircons from a granulite-grade pelite were mapped for U–Pb ages
- The data indicate Archean–Neoproterozoic cores with high U/Th rims that grew at ~435 Ma

Conclusions

The small-volume U–Pb geochronology technique at the Arizona LaserChron Center microsamples and dates zircon volumes as small as 12–14 µm in diameter by 4–5 µm in depth, comparable to sample volumes for U–Pb geochronology by secondary ion mass spectrometry. Low Pb yields produced by the small laser spot diameter and a slow laser pulse rate require using Channeltron detectors to monitor all Pb peaks coupled with a total count integration counting method to calculate U and Pb peaks and isotope ratios. Measurement errors are calculated as a function of the number of counts and observed 206Pb/238U scatter on Sri Lanka standard zircon. Using this technique, precise and accurate ages on eight Mesoproterozoic–Cretaceous-aged secondary zircon standards were reproduced within 2% of published ID-TIMS ages; a ninth Miocene-aged standard produced an age ~1 Ma, or 3–4%, too young. In addition to the small spot diameter, the shallow pit depth is essential to the utility of the small-volume technique because it ensures that the sampled volume corresponds directly to chemical zones observed in CL and minimizes the probability that multiple chemical zones will be sampled at greater depths within the sample. The ability of this method to overcome difficulties associated with acquiring meaningful U–Pb ages on complexly zoned zircons by targeting single age domains <15 µm, combined with the rapid rate of data collection (~60 analyses per hour) and non-destructive nature of the technique, should prove useful for a wide variety of geologic applications, and confirms the utility of LA–MC–ICP–MS as a tool for high-resolution U–Pb zircon geochronology.

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