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Attom Note **NA04**

The Attom High Resolution ICP-MS: Laser Ablation U-Pb Geochronology

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Introduction

Modern high resolution ICP-MS (HR-ICP-MS) instruments offer a number of performance advantages compared to more widely used quadrupole ICP-MS instruments, including increased sensitivity, superior detection limits and faster scan speeds. For laser ablation acquisition, rapid peak scanning is a distinct advantage, as it allows for increased temporal resolution of time-resolved data. The advantage of single-collector ICP-MS over multi-collector ICP-MS, is that a wider mass range can be scanned in a single analysis. This means that a range of elemental concentrations can be determined, as well as precise isotope ratios.

Laser ablation sampling coupled to measurement via ICP-MS is an increasingly used tool within earth science, which can be used for determining quantitative trace element concentrations of materials, as well as for isotopic dating of minerals in particular within U-Pb geochronology. Here, we report the use of the Attom for determining U-Th-Pb isotopes in zircon and monazite crystals, whilst demonstrating the ability to combine these isotope ratio measurements with other trace element concentrations using the wide mass range available in rapid peak-scanning mode.

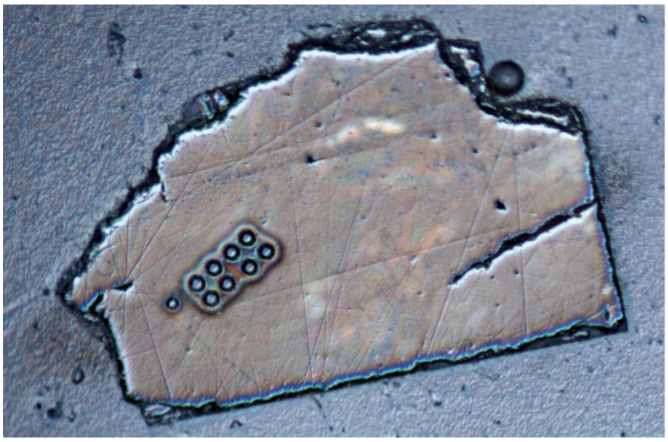


Figure 1: 20 µm diameter ablation pits in Moacyr monazite.

Instrumentation

The Attom is a double-focusing, high-resolution magnetic sector mass spectrometer. The instrument is entirely purpose designed and built to provide the best performance and reliability coupled with flexibility and ease-of-use for precise and accurate elemental and isotope ratio analysis. A unique detector system gives the Attom a large dynamic range, and its electrostatic scanning capability has the widest range in its class (40%). Furthermore, the variable high resolution means that sufficient resolution for isobaric separation can be achieved with minimum compromise in sensitivity.

For the laser ablation work presented here, the Attom was coupled to a New Wave Research UP193FX excimer laser ablation system. Helium was used as a carrier gas, and mixed with argon before entering the ICP-MS. For some experiments a solution was simultaneously aspirated using the Nu Instruments DSN-100 that contained ^{203}Ti, ^{205}Tl, ^{230}Th and ^{236}U; this allows for on-line correction of mass-bias and drift in the inter-element fractionation.

Experiment

Laser ablation analysis used a spot size of 20-35 µm (Figure 1), with a fluence of 1.8 to 2.2 j/cm^2, for 30 seconds of integration. An on-peak zero was measured every 5 to 10 analyses. The Pb-Pb, U-Pb and Th-Pb ratios were normalised to a bracketing primary standard, based on the average measured value of the standard compared to the 'true' value determined by ID-TIMS. The measured masses and dwell time for each of the four experiments are shown in Table 1; also shown are average count rates for the isotopes of interest for the standards shown in the figure. Trace element concentrations are semiquantitative, and use repeat analyses of NIST 612 glass for normalisation.

The Attom can measure large signals by means of an attenuation mechanism; this was used for ^{232}Th which is particularly concentrated in monazite. To measure the degree of attenuation, ^{236}U is introduced via a spike solution and is measured with both a normal and an attenuated signal; the average value of the attenuation/normal signal is then applied to the ^{232}Th offline. Data were collected using the timeresolved-analysis function in the Nu Attolab software; with ratio calculations performed using the Nu calculations editor.

Discussion

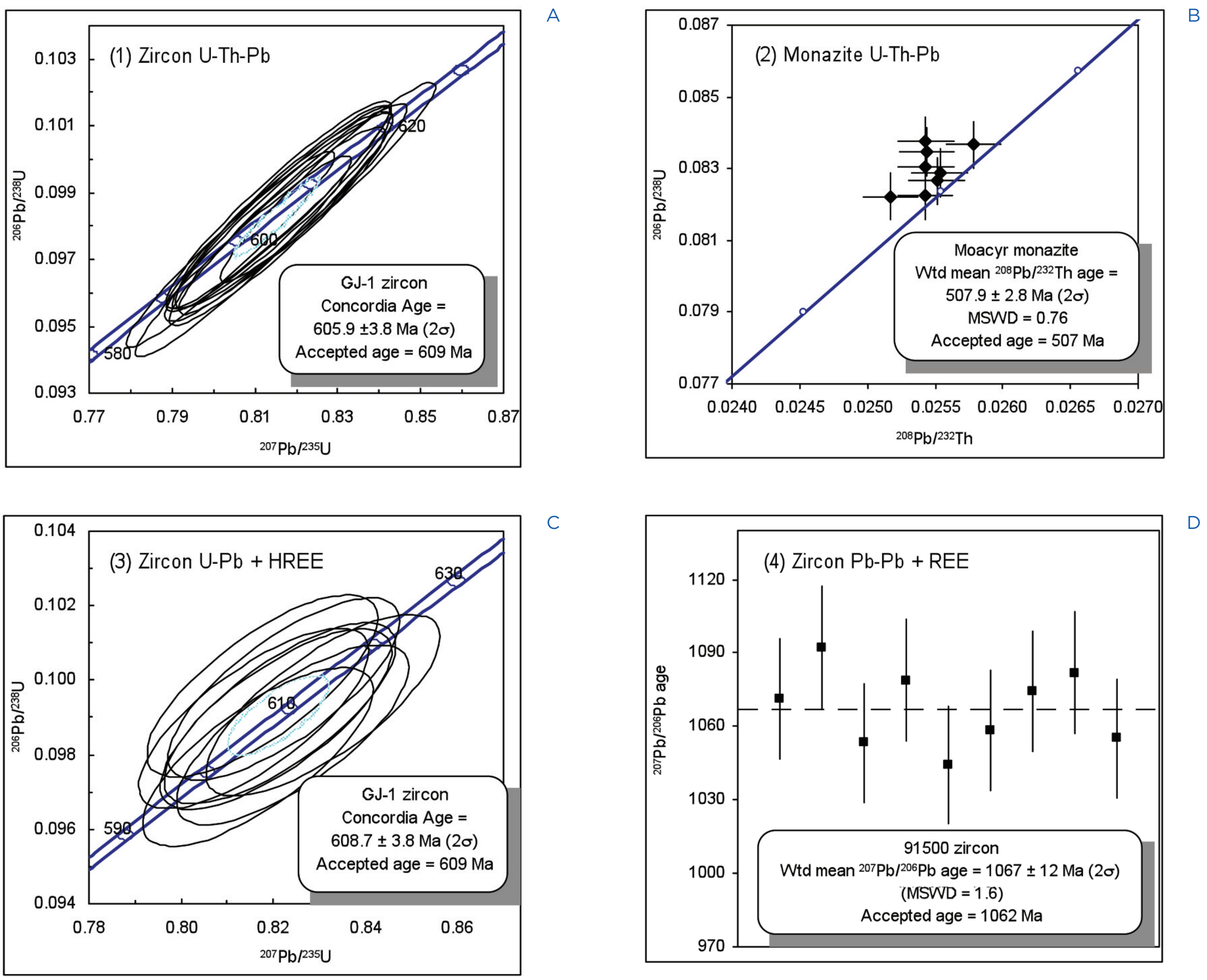
Using typical ablation parameters (20 to 35 µm spot @ 1.5-2.5 j/cm^2), the Attom is capable of measuring ^{207}Pb/^{206}Pb, ^{208}Pb/^{232}Th ^{206}Pb/^{238}U ratios with an external reproducibility of <3% (2σ) after normalisation to a standard, these ratios are accurate to <2% (2σ) (Figure 2). This makes the Attom ideal for U-Th-Pb geochronology of U-bearing accessory minerals such as zircon and monazite. Although not shown, dating of other minerals such as titanite, allanite and apatite is feasible.

To gain the most from U-Th-Pb geochronology it is commonly useful to determine trace element concentrations of the dated minerals. For example, REE patterns in zircon can aid the determination of the coprecipitating mineralogy, and thus whether the dated growth-zone within the zircon represents a magmatic or metamorphic event. Ideally, trace element concentrations will relate to the individual growth zone that has been dated.

This can be done using one ablation for a U-Th-Pb measurement, and a separate ablation for a trace element measurement; however, this assumes that the same zone has been analysed each time. For consumption of less material and allowing a greater spatial resolution, a preferred approach is to analyse U-Th-Pb isotopes and trace elements in one ablation. The large mass range of the Attom allows for certain trace elements to be simultaneously determined along with precise U-Th-Pb isotopic ratios. Experiment 3 shows that $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{238}U$ ratios can be precisely and accurately measured along with determination of the heavy REE content; whilst experiment 4 shows that a complete REE pattern can be determined along with precise and accurate $^{207}Pb/^{206}Pb$ age determinations (Figure 2).

Conclusion

The Attom ICP-MS allows for rapid peak-scanning across a wide mass range. The ability to determine precise and accurate U-Th-Pb isotope ratios, whilst at the same time determining concentrations of other trace elements makes it an ideal tool for geochronological dating of a range of natural materials.



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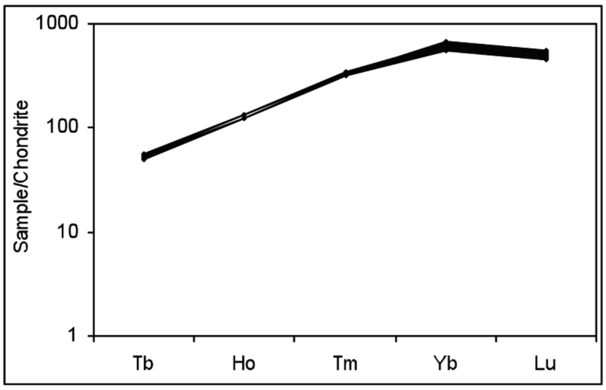

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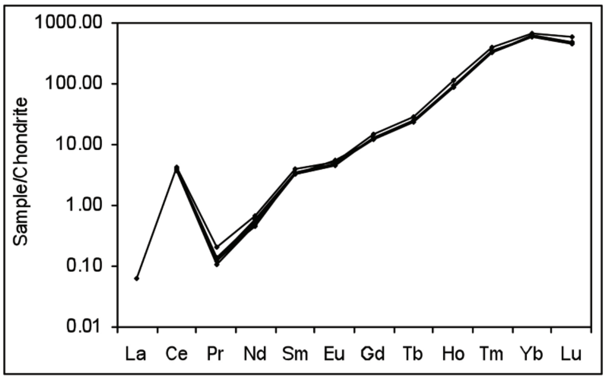

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Figure 2: (A) U-Pb concordia diagram for GJ-1 zircon normalised to 91500 (ellipses are 2σ). (B) Th/Pb vs. U/Pb isochron for Moacyr monazite normalised to Stern monazite (error bars are 2σ). (C) U-Pb Concordia for GJ-1 zircon normalised to 91500, and (D) weighted mean Pb-Pb age of 91500 zircon normalised to Plesovice. (E) Chondrite normalised HREE pattern, and (F) chondrite normalised REE pattern.

(1) 35 µm, ~2.2 j.cm^{-2}, 5 Hz			(2) 20 µm, ~1.8 j.cm^{-2}, 7 Hz			(3) 25 µm, ~1.8 j.cm^{-2}, 7 Hz			(4) 25 µm, ~1.8 j.cm^{-2}, 7 Hz		
peak	dwell (µs)	cps	peak	dwell (µs)	cps	peak	dwell (µs)	cps	peak	dwell (µs)	cps
^{202}Hg	70		^{202}Hg	100		^{159}Tb	100	16600	^{139}La	100	8
^{203}Tl	100		^{203}Tl	100		^{165}Ho	100	56000	^{140}Ce	100	157000
^{204}Hg,Pb	70		^{204}Hg,Pb	100		^{169}Tm	100	63000	^{141}Pr	100	350
^{205}Tl	100		^{205}Tl	100		^{172}Yb	100	164000	^{146}Nd	70	1300
^{206}Pb	200	620000	^{206}Pb	200	650000	^{175}Lu	100	85000	^{147}Sm	70	2600
^{207}Pb	400	38000	^{207}Pb	200	41000	^{206}Pb	200	308000	^{153}Eu	70	7000
^{208}Pb	70		^{208}Pb	200	29000	^{207}Pb	400	19000	^{157}Gd	70	10500
^{230}Th	70		^{230}Th	100		^{235}U	400	26000	^{159}Tb	70	20000
^{232}Th(att)	70		^{232}Th(att)	200	89000				^{165}Ho	70	65000
^{235}U	400	47000	^{235}U	200	65000				^{169}Tm	70	72000
^{236}U	70		^{236}U	100					^{172}Yb	70	185000
^{236}U(att)	70		^{236}U(att)	1000					^{175}Lu	70	95000
									^{206}Pb	250	320000
									^{207}Pb	400	19500

Table 1: Measured masses and dwell times for each of the four experiment.