

# THE NU ATTOM HIGH RESOLUTION ICP-MS: LASER ABLATION U-Pb GEOCHRONOLOGY

Nick M W Roberts<sup>1</sup>, Sabine Pawlig and Matthew Horstwood<sup>1</sup>,

<sup>1</sup>: NERC Isotope Geosciences Laboratory, Keyworth, Nottingham, NG12 5GG

## 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, and 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 Nu Attom for determining U-Th-Pb isotopes in zircon and monazite crystals, and demonstrate the ability to combine these isotope ratio measurements with other trace element concentrations using the wide mass range available in rapid peak-scanning mode.

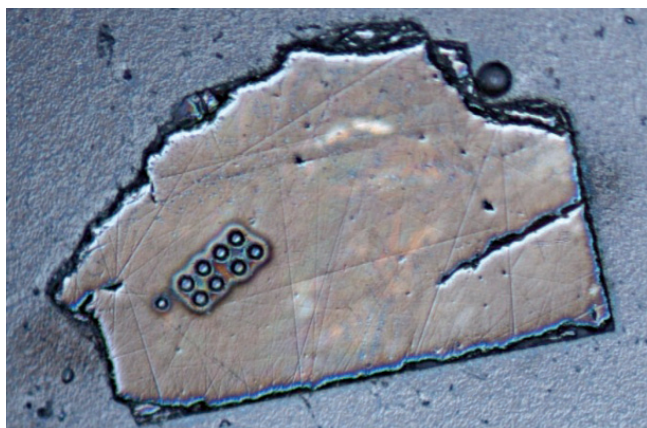


Figure 1: 20 $\mu$ m diameter ablation pits in Moacr monazite.

## Instrumentation

The Nu 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 Nu AttoM a large dynamic range, and its electrostatic scanning capability has the widest range in its class (40%). Furthermore, the continuously 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, a Nu Attom was coupled to a New Wave Research UPI93FX 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 <sup>203,205</sup>Tl, <sup>230</sup>Th and <sup>236</sup>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 $\mu$ m (figure 1), with a fluence of 1.8 to 2.2 J/cm<sup>2</sup>, 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 semi-quantitative, 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 <sup>232</sup>Th which is particularly concentrated in monazite. To measure the degree of attenuation, <sup>236</sup>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 <sup>232</sup>Th offline. Data were collected using the time-resolved-analysis function in the Nu Attolab software; with ratio calculations performed using the Nu calculations editor.

## Discussion

Using typical ablation parameters (20 to 35  $\mu$ m spot @ 1.5-2.5 J/cm<sup>2</sup>), the Nu Attom is capable of measuring <sup>207</sup>Pb/<sup>206</sup>Pb, <sup>208</sup>Pb/<sup>232</sup>Th <sup>206</sup>Pb/<sup>238</sup>U ratios with an external reproducibility of <3% (2SD) after normalisation to a standard, these ratios are accurate to <2% (2SD) (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 co-precipitating 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 Nu Attom allows for certain trace elements to be simultaneously determined along with precise U-Th-Pb isotopic ratios. Experiment 3 shows that <sup>207</sup>Pb/<sup>206</sup>Pb and <sup>206</sup>Pb/<sup>238</sup>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 <sup>207</sup>Pb/<sup>206</sup>Pb age determinations (figure 2).

## Conclusions

The Nu 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.

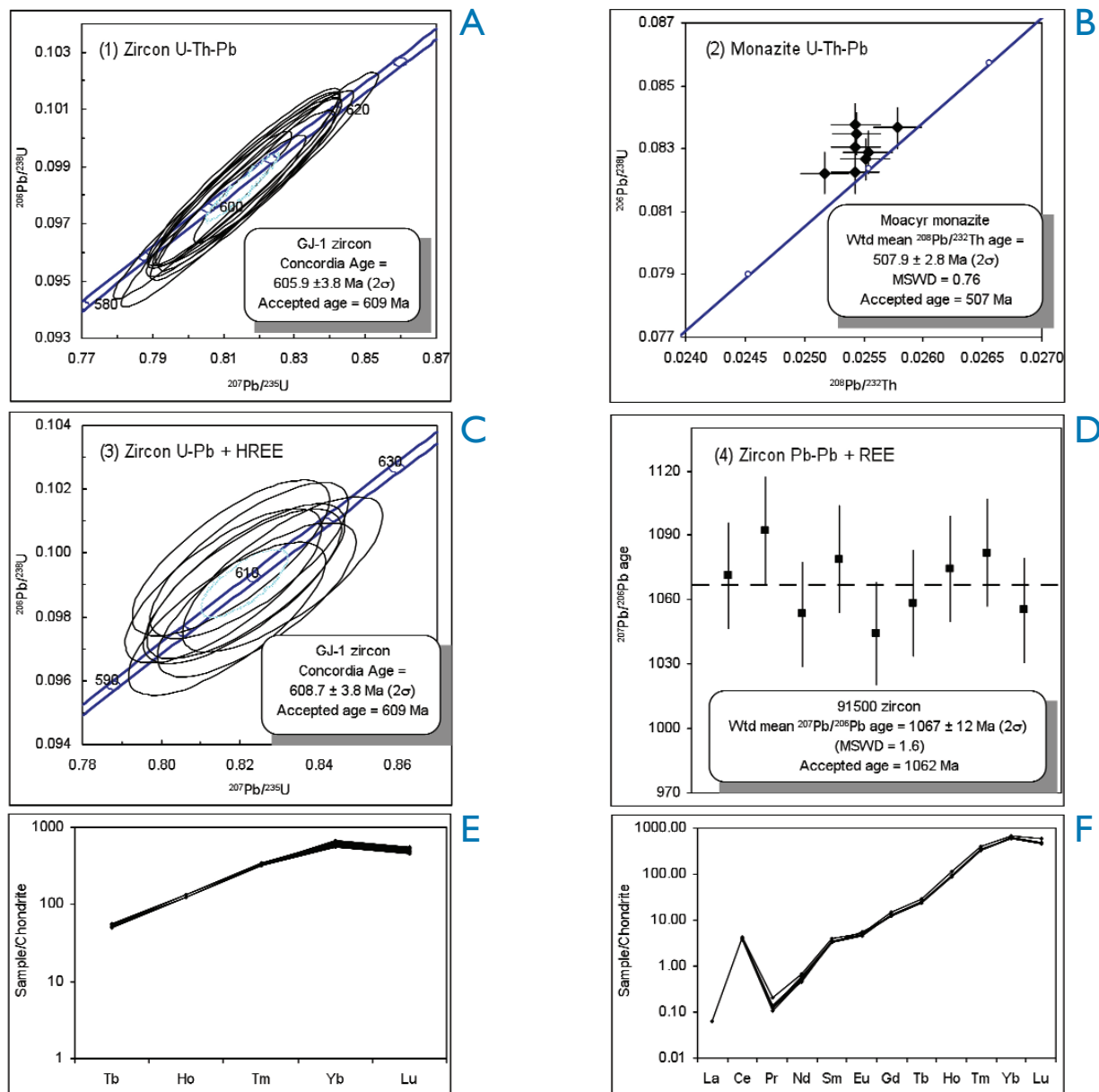


Figure 2: (A) U-Pb concordia diagram for GJ-1 zircon normalised to 91500 (ellipses are  $2\sigma$ ). (B) Th/Pb vs. U/Pb isochron for Moacyr monazite normalised to Stern monazite (error bars are  $2\sigma$ ). (C) U-Pb Concordia for GJ-1 zircon normalised to 91500, and (D) weighted mean Pb-Pb age of 91500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

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

Table 1:

Measured masses and dwell times for each of the four experiments