High precision $^{176}Hf/^{177}Hf$ measurements in zircons by LA-MC-ICP-MS

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Introduction

The Thermo Scientific™ Neoma™ MC-ICP-MS is the latest MC-ICP-MS from Thermo Fisher Scientific which delivers on performance, with market-leading sensitivity, isotope ratio precision and accuracy. It enables high throughput for routine isotope ratio applications.

Zircon, one of the key minerals in geochronology, contains two chronometers, U-Pb and Hf. One of these complimentary isotope systems, U-Pb, is routinely measured by a variety of analytical techniques including ID-TIMS, SIMS and ICP-MS[1]. Historically, high precision Hf isotope ratio measurements proved challenging by TIMS and SIMS, leading to the development of MC-ICP-MS. Both U-Pb and Hf can be measured in-situ with MC-ICP-MS by using laser ablation (LA) as the sample introduction system.

Here, we demonstrate the benefit of using Thermo Scientific™ Qtegra™ ISDS Software for Neoma MC-ICP-MS, to dramatically improve the ease of LA-MC-ICP-MS analysis of zircons.

Method

An ESL™ NWR™ 193 UC laser ablation system equipped with a TwoVol 2 ablation cell was connected to the Neoma MC-ICP-MS (Figure 1). A He flow rate of 0.8 L/min was applied alongside 4 mL/min of additional N_2. The Neoma MC-ICP-MS was equipped with the Jet Interface using the high sensitivity X-skimmer and Jet sampler cones.

A raster ablation of the reference material NIST® SRM® 610 was used to tune the LA-MC-ICP-MS. The U/Pb cup configuration (Table 1) was used. The Neoma tune parameters were tuned to achieve high sensitivity, a U/Th ratio of approx. 1.07 (1.11), and a low rate of oxide formation ($^{232}Th^{16}O/^{232}Th$ = 0.13%).

The zircon $^{176}Hf/^{177}Hf$ ratio was measured by spot ablation. Each 35 µm circular spot was ablated for 30 seconds with a fluence of 4 J cm^{-2} fired at 10 Hz repetition rate.

Many laser parameters were controlled via the NWR Laser plugin supplied within the Qtegra ISDS Software in the Neoma MC-ICP-MS (Figure 2). This allows bi-directional communication between the two platforms, useful for sharing sample lists, triggering and data processing. Similar plugins for Qtegra Software are available for other laser ablation systems.

Figure 1. ESL NWR193 laser ablation system coupled to the Neoma MC-ICP-MS

Samples and reference materials

The reference material NIST SRM 610 was used to tune and test the overall performance of the LA-MC-ICP-MS. Hf and U-Pb isotope analysis was then carried out for four reference zircons:

- 91500
- Plešovice
- GJ-1
- Mud Tank

A further 14 detrital zircons from the Bengal Basin were subsequently analyzed. Two ablations were performed per zircon except for the final, larger zircon where 4 ablations were used.

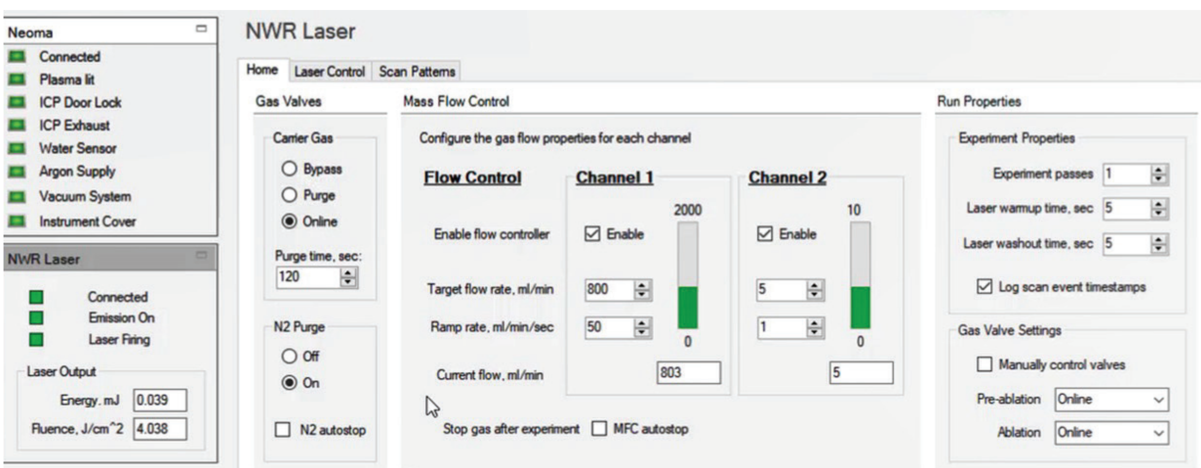

Figure 2. NWR Laser plugin within Qtegra ISDS for Neoma MC-ICP-MS.

Table 1. Hf & U/Pb cup configurations used with the Neoma MC-ICP-MS

Cup	L5	L4	L3	L2	L1	C	H1	H2	H3	H4	H5
Hf	^{171}Yb	^{173}Yb	^{174}Hf	^{175}Lu	^{176}Hf	^{177}Hf	^{178}Hf	^{179}Hf	^{180}Hf	^{182}W	$^{176}Hf^{16}O$
Isotope	^{202}Hg	^{204}Pb	^{206}Pb	^{207}Pb	^{208}Pb		^{232}Th	^{234}U	^{235}U	^{238}U	$^{232}Th^{16}O$
Amplifier	10^{11} Ω	10^{11} Ω	10^{11} Ω	10^{11} Ω	10^{11} Ω	10^{11} Ω	10^{11} Ω	10^{11} Ω	10^{11} Ω	10^{11} Ω	10^{11} Ω

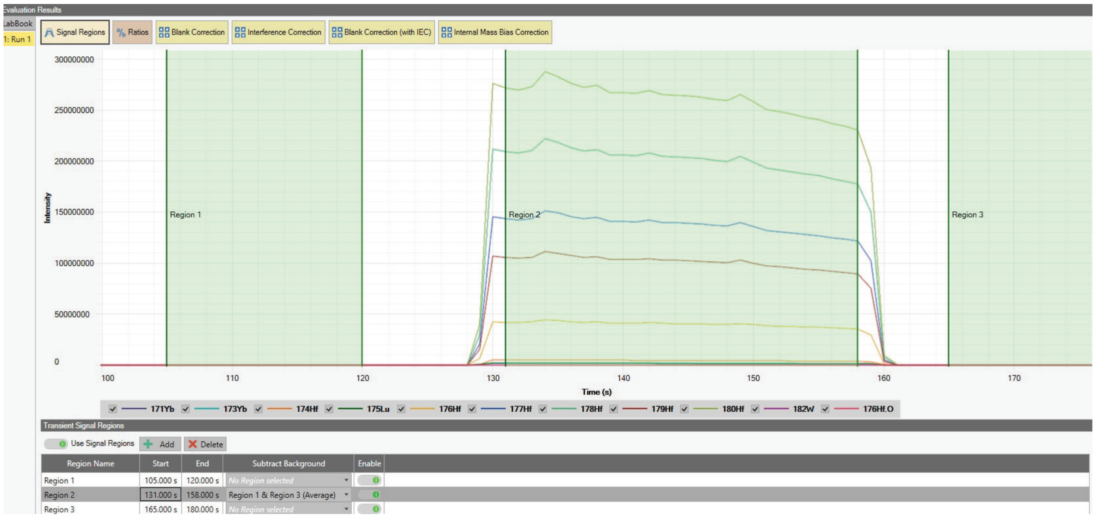

Figure 3. Transient Signal Regions selected for a 30 second zircon ablation. The data for the ablation, region 2, is background corrected for each isotope from the average intensity measured for regions 1 and 2.

Data evaluation

Unlike previous generation MC-ICP-MS[3], the Neoma MC-ICP-MS does not require third-party software to process in-situ Hf isotopic analysis. For each spot ablation the transient signal regions functions of the Qtegra ISDS Software was used to define three regions. Region 1 and 3 were used to background correct the region 2, which captured the ablation of the zircon. Following background correction only the data within region 2 was taken forward into the rest of the data evaluation.

To calculate the $^{176}Hf/^{177}Hf$ isotope ratio, ^{176}Hf requires correction for ^{176}Yb and ^{176}Lu interferences. The ^{176}Yb was corrected via the interference-free ^{173}Yb isotope and mass bias corrected using the $^{173}Yb/^{171}Yb$ ratio. The ^{176}Lu was corrected via the interference-free ^{175}Lu isotope and mass bias corrected using the $^{179}Hf/^{177}Hf$ ratio. The resulting $^{176}Hf/^{177}Hf$ ratio was also mass bias corrected using the $^{179}Hf/^{177}Hf$ ratio.

All required data evaluation was calculated in real time.

Table 2. Total Hf sensitivity and mean $^{176}Hf/^{177}Hf$ for four reference zircons

	Total Hf (V)	$^{176}Hf/^{177}Hf$	SE	RSD (ppm)
91500	12.1	0.282288	0.000007	24.8
Plešovice	22.7	0.282453	0.000014	49.6
GJ-1	13.9	0.282009	0.000010	35.5
Mud tank	21.6	0.282490	0.000009	31.9

Results

The the Neoma MC-ICP-MS with the Jet Interface resulted in high Hf sensitivity for the four reference zircons (Table 2). The $^{176}Hf/^{177}Hf$ reproducibility was better than 50 ppm RSD for all four reference zircons.

For all reference zircons, the mean $^{176}Hf/^{177}Hf$ falls within the range of the accepted values (Figure 4), demonstrating the accuracy of the analysis.

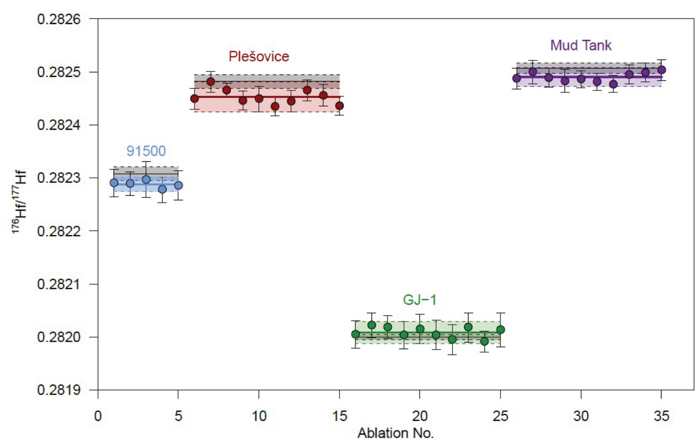

Figure 4. $^{176}Hf/^{177}Hf$ for four reference zircons. The 2σ uncertainty of the accepted value is shown by the grey area[4-6]. The 2σ analytical uncertainty of these measurements is shown by the colored polygon.

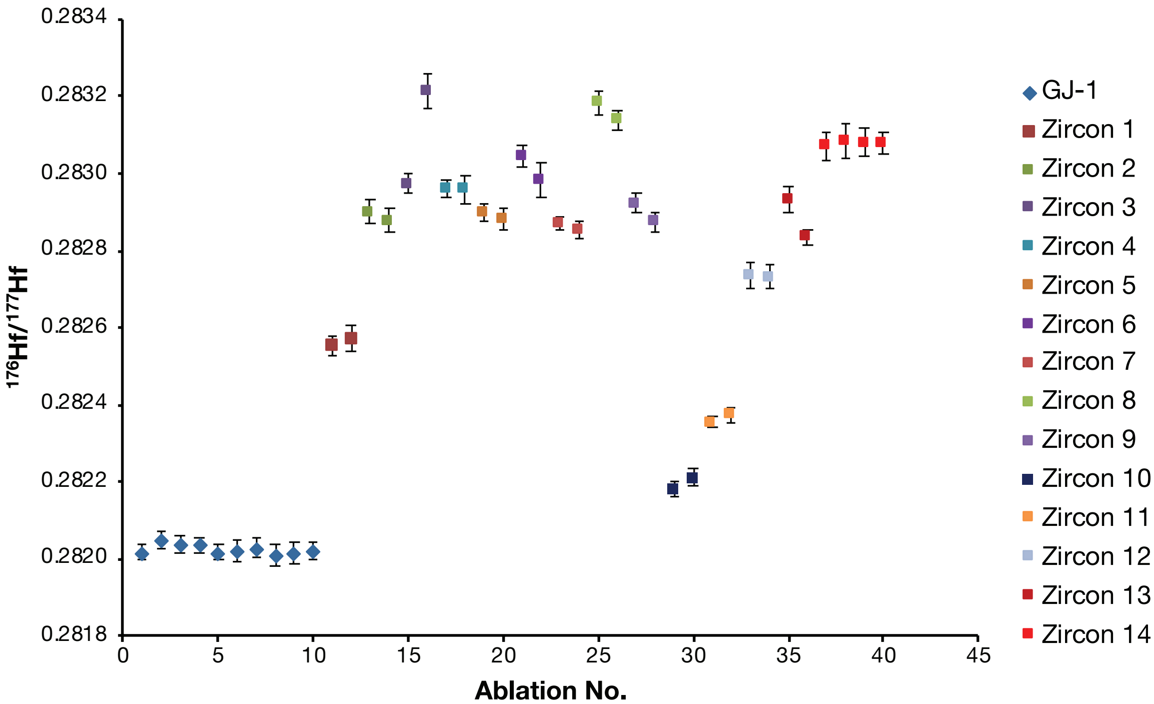

Figure 5. ^{176}Hf/^{177}Hf for 10 replicates of reference zircon GJ-1 and 14 zircons from the Bengal Basin.

The 14 sample zircons from the Bengal Basin have a spread of ^{176}Hf/^{177}Hf ratios between 0.2822 and 0.2832. This variability is evidence of heterogeneity in the processes which shaped these zircons.

Conclusion

The Neoma MC-ICP-MS leverages strong integration with modern laser ablation systems and flexible data evaluation to realize real time determination of in-situ ^{176}Hf/^{177}Hf in zircons.

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