High Sensitivity Laser Ablation MC-ICP MS

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Goal
This application note demonstrates that high precision $^{176}Hf/^{177}Hf$ isotope ratios can now be obtained from 25 µm diameter laser ablation spots.

Thermo Scientific NEPTUNE *Plus* MC-ICPMS and Photon Machines Analyte.G2 193 nm LA system.

Introduction
High precision Hf isotope ratios can be obtained by simultaneous collection of Hf, Yb and Lu isotopes on Faraday cups. Typically LA spot sizes of 50 µm diameter are required to achieve targets of better than 100 ppm (epsilon unit) external precision (2RSD).

However, improved sensitivity would allow small detrital zircon gains to be analyzed, larger zircon crystals to be mapped for heterogeneity, or other accessory minerals with lower analyte concentrations to be analyzed.

The Jet Interface is an option on the Thermo Scientific™ NEPTUNE™ and NEPTUNE *Plus*™ MC-ICP MS; it is also available on the Thermo Scientific ELEMENT 2/XR™ SC-SF-ICP MS. Previously it has been shown to deliver breakthrough ICP-MS sensitivity for solution samples.[1]

A 25 µm diameter spot covers just ¼ of the area of a conventional 50 µm diameter spot. In this application note, we demonstrate that precise and accurate Hf isotope ratios can be obtained from the zircon 91500 standard using a 25 µm diameter laser ablation spot size.

Methods
Laser Ablation
A Photon Machines Analyte.G2 laser ablation system with HelEx two-volume cell was run at 7 Hz and 6 J/cm^2 fluence (moderate settings) with a dwell time of 60 seconds for each spot. The excimer laser has a 193 nm wavelength and short pulse-width (ca. 4 ns). 0.9–1.0 L/min He was passed through the LA cell as a carrier gas.

Mass Spectrometry
A NEPTUNE *Plus* MC-ICP MS was equipped with the Jet Interface option for increased sensitivity. The Jet Interface option comprises a high performance interface pump and high sensitivity cones. For desolvated solutions more than 2% of uranium ions can be detected;[1] accurate and precise Hf and Pb isotopes can be acquired for sub-ng solution samples.[2] 0.4–0.6 L/min Ar gas was mixed with the He carrier gas before the injector.

The collector configuration in Table 1 is possible with the standard NEPTUNE/NEPTUNE *Plus* MC-ICP-MS moveable Faraday collector array. By measuring $^{173}Yb/^{171}Yb$, the ^{176}Yb interference can be accurately corrected ($\beta_{Yb} \neq \beta_{Hf}$).[3]

Table 1. Example cup-configuration for Hf isotopes on the NEPTUNE/NEPTUNE *Plus* MC-ICP MS. $^{173}Yb/^{171}Yb$ is measured for accurate ^{176}Yb correction.

L4	L3	L2	L1	C	H1	H2	H3	H4
^{171}Yb	^{173}Yb	^{175}Lu	^{176}Hf	^{177}Hf	^{178}Hf	^{179}Hf	^{180}Hf	

Data were collected with 1.049 s integration times from Faraday cups equipped with 10^{11} Ohm amplifiers (and precisely matched time constants). 1350 W RF power was used, and tuning was either for maximum LA Hf sensitivity or for lower oxide ratios (e.g. 1% UO/U).

Nitrogen Addition

Nitrogen add gas at a rate of 7–11 mL/min was introduced by a mass flow controller installed in the NEPTUNE *Plus* MC-ICP MS. Nitrogen gas addition has previously been shown to increase LA sensitivity for most elements.[4]

Data Analysis

Signal data were exported from the Thermo Scientific *multicollector* software and imported into the *Iolite* software package.[5] A Hf data reduction scheme was modified so that an external Yb fractionation factor could be used. The Yb fractionation factor was taken as the median value of $^{173}Yb/^{171}Yb$ measured from all runs within each ablation session, as this is more precise than using an internal cycle-by-cycle correction from the low intensity Yb peaks (normalizing ratios[6,7]).

Results

Effect of N_2 Addition

N_2 addition increased LA Hf sensitivity by a factor of 2.4 on average. N_2 addition increased LA Hf sensitivity for both standard cones and for the high sensitivity cones. The optimal rate of N_2 addition was 7–11 mL/min, dependent on tune conditions.

Effect of X Type Skimmer Cone

The X type skimmer cone increased LA Hf sensitivity by another factor of 1.5.

Effect of Jet Type Sample Cone

The Jet type sample cone increased LA Hf sensitivity by another factor of 2.

Cumulative Sensitivity Increase

The cumulative sensitivity increase from N_2 addition and the high sensitivity X type skimmer cone and Jet sample cone is shown in Figure 3. A sensitivity increase of 7.2 times is possible for Hf ions using this combination. The increase is slightly larger for U-Pb.

Matrix Tolerance at High Sensitivity

Figure 1 shows a plot of measured $^{179}Hf/^{177}Hf$ ratios for two different spot sizes. There is no difference in Hf mass fractionation between the 25 and 50 µm diameter spot sizes, corresponding to an increase in matrix loading of 400%.

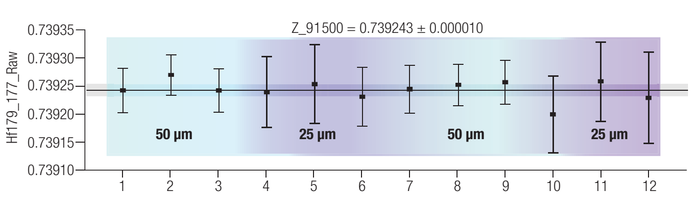

Figure 1. Raw $^{179}Hf/^{177}Hf$ ratios measured from zircon 91500 using two different spot sizes. There is no difference in Hf mass fractionation between the 25 and 50 µm diameter spot sizes (48 ppm 2RSD for one population).

Effect of High Sensitivity on Accuracy and Precision

Figure 2 shows the repeatability of $^{176}Hf/^{177}Hf$ measurements using a 25 µm diameter spot. The results are precise and accurate, with a scatter of 86 ppm (2RSD).

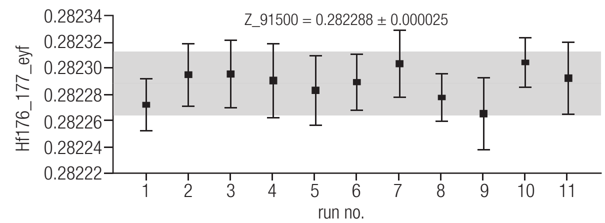

Figure 2. Plot of $^{176}Hf/^{177}Hf$ ratios from the zircon standard 91500 using a 25 µm diameter LA spot size. The 2RSD repeatability was 86 ppm, the results are accurate within uncertainty to accepted literature values.

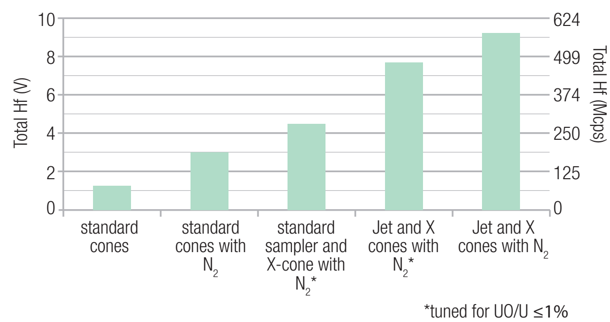

Figure 3. Plot of LA Hf sensitivity with and without N_2 addition and high sensitivity cones.

Conclusions

- N_2 addition increases LA Hf sensitivity on the NEPTUNE *Plus* MC-ICP MS by a factor of 2.4.
- The Jet Interface option further increases sensitivity for LA Hf by a factor of 3.
- A cumulative sensitivity increase of 7.2 times is possible, whilst maintaining $^{176}Hf/^{177}Hf$ accuracy.
- This increased sensitivity uniquely allows precise and accurate $^{176}Hf/^{177}Hf$ ratios to be obtained from zircons using 25 µm diameter LA spots.

References

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