thermo scientific

TECHNICAL NOTE

No. 30654

Optimizing methodologies for Hf and U-Pb analysis of zircons by MC-ICP-MS using ultrafast laser ablation technology

Authors: G. Craig[1], R. Hutchinson[2], D. N. Douglas[2], C. O'Connor[2], M. P. Field[3] and N. S. Lloyd[1]
[1]Thermo Fisher Scientific, Bremen, Germany; [2]Elemental Scientific Lasers LLC. Bozeman, MT, USA; [3]Elemental Scientific Inc. Omaha, NE, USA

Keywords: Geochronology, hafnium, laser ablation, MC-ICP-MS, U-Pb, zircon

Goal

To demonstrate the utility of ultrafast laser ablation technology for high precision isotope ratio geochronology by MC-ICP-MS.

Abstract

Measuring two chronometers, Hf and U-Pb for a single location on a sample zircon by laser ablation multicollector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) is a commonly used analytical technique in geosciences. These complimentary isotope systems differ significantly in the degree of uncertainty (1% for U-Pb, 0.01% for Hf) required for reliable interpretation. This difference is echoed in the amount of material required for analysis: LA-MC-ICP-MS of Hf in zircons typically requires much more material than the U-Pb equivalent. This extra material is partially delivered by enlarging the spot size for Hf analysis relative to U-Pb, which can be problematic for interpretation in complex zoned materials.

ThermoFisher SCIENTIFIC

Developments to improve sensitivity in LA-MC-ICP-MS has led to reductions in the spot size required for precision Hf analysis to 25 µm[1], approaching values used for U-Pb (≥20 µm). Rapid response, high efficiency laser ablation systems, designed for bioimaging applications[2,3], have recently been shown to double LA-MC-ICP-MS sensitivity[4]. Here we report on using one such ablation system, the Elemental Scientific Lasers™ DCI™ combined with the Thermo Scientific™ Neptune XT™ MC-ICP-MS in order to maximize efficiency for zircon analysis. By doing so, we proportionally reduced the volume of material necessary for complimentary Hf and U-Pb isotopic analysis: demonstrated by ablation of a series of reference and zoned sample zircons.

Introduction

Simultaneous rather than sequential analysis of the Hf and U-Pb isotopic systems by laser ablation split stream (LASS) eliminates the possibility of compositions being incorrectly assigned. However, this system can lack for sensitivity and therefore more efficient sample utilization methods are available. This may be especially true with the introduction of rapid response, high efficiency laser ablation systems to MC-ICP-MS which can double sensitivity[4] but are incompatible with LASS.

Here a series of reference zircons were analyzed for Hf and U-Pb using one such rapid response, high efficiency laser ablation system. A NWR193 laser ablation system (Elemental Scientific Lasers) was directly connected to a Dual Concentric Injector (DCI) fitted in the semi-demountable torch of a Neptune XT MC-ICP-MS (Thermo Scientific, Figure 1). The Jet Interface of the Neptune XT MC-ICP-MS was used to maximize sensitivity.

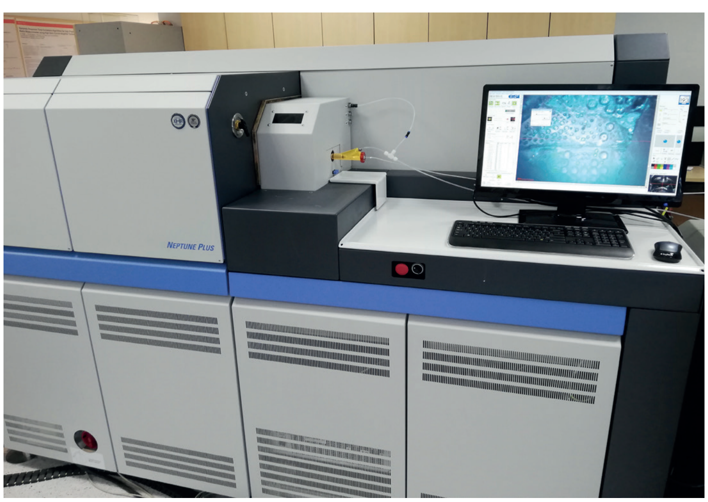

Figure 1. NWR193 laser ablation system coupled to the Neptune XT MC-ICP-MS via the Dual Concentric Injector (DCI).

Materials and methods

Sample reference materials

The reference materials NIST SRMR 610 and SRMR 612 were used to tune and test the overall performance of the LA-MC-ICP-MS. Hf and U-Pb isotopic analysis was then carried out for four reference zircons:

- 91500
- Plešovice
- GJ-1
- Mud Tank

A fifth, unknown, zircon was also analyzed. The MUN-4 artificial zircon was ablated for external Yb correction of Hf.

Table 1. Laser and MC-ICP-MS settings used in this study.

NWR193 settings	
Fluence	4 J/cm^2
Spot size	25 µm
Repetition rate	20 Hz
He sample gas	600 mL/min
N_2 plasma gas	9 mL/min
Neptune XT settings	
Nebuliser Ar gas	0.67 L/min
RF power	1250 W
Cooling gas	16 L/min
Auxiliary gas	0.70 L/min
Z torch position	-1.0 mm

LA-MC-ICP-MS

All analyses were of 30 second duration. An integration time of 262 ms was used for Hf and 131 ms for U-Pb. ^{206}Pb, ^{207}Pb and ^{208}Pb were measured with 10^{13} Ω amplifiers, not multi ion counting, which would have substantially reduced the spot size required.

Table 2. Cup configuration for Hf and U-Pb isotopes on the Neptune XT 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	
^{206}Pb	^{207}Pb	^{208}Pb				^{232}Th	^{235}U	^{238}U

Data analysis

All data analysis was performed within Iolite v2.5 (Igor Pro™ v6.37) using appropriate Data Reduction Schemes.

Results

Optimization

The LA-MC-ICP-MS was tuned for high efficiency at the same time as balancing the U/Th ratio and maintaining a low UO/U ratio. With these conditions baseline separation between laser ablation pulses could be achieved at ≤10 Hz for both the SEM and Faraday detectors (Figure 2). Therefore, the optimum repetition rate required for the analysis of the zircons would be greater than 10 Hz.

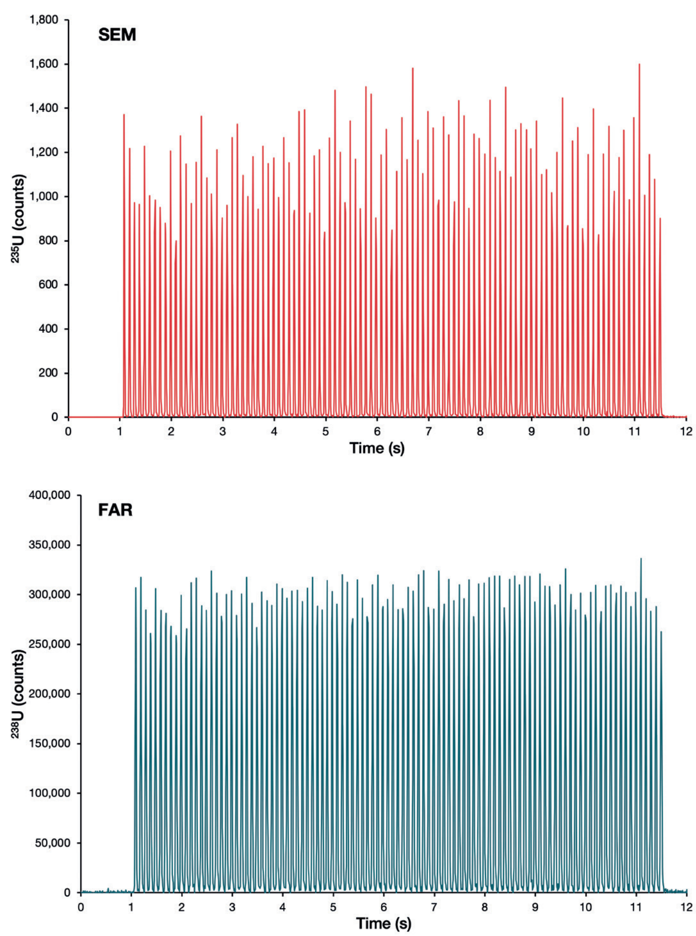

Figure 2. Baseline separation of individual laser ablation pulses on SRM610 reference glass using both the central SEM and Faraday detector equipped with 10^{13} Ω amplifier (tau corrected).

Hf

With excellent signal/noise ratio and sensitivity confirmed by ablating the reference glasses the same laser conditions were then used for 30 spot ablations of each zircon material, 20 for Hf and 10 for U-Pb analysis. A spot size of 25 µm proved sufficient for a ^{176}Hf/^{177}Hf ratio reproducibility better than 100 ppm 2RSD on the four reference zircons (Table 3, Figure 3). The reproducibility for the unknown zircon was <150 ppm due to its low Hf concentration.

Table 3. ^{176}Hf/^{177}Hf isotope ratios for 20 spot ablations on four reference zircons, one unknown zircon and the MUN-4 artificial zircon.

	^{176}Hf/ ^{177}Hf	Int. 2SE	Int. 2RSE	Ext. 2SD	Ext. RSD
91500	0.282270	0.000028	101 ppm	0.000022	78 ppm
Plešovice	0.282440	0.000017	60 ppm	0.000016	58 ppm
Mud Tank	0.282475	0.000018	64 ppm	0.000019	67 ppm
GJ-1	0.281980	0.000024	87 ppm	0.000026	91 ppm
MUN-4	0.282120	0.000029	102 ppm	0.000036	128 ppm
Unknown	0.282257	0.000045	159 ppm	0.000037	133 ppm

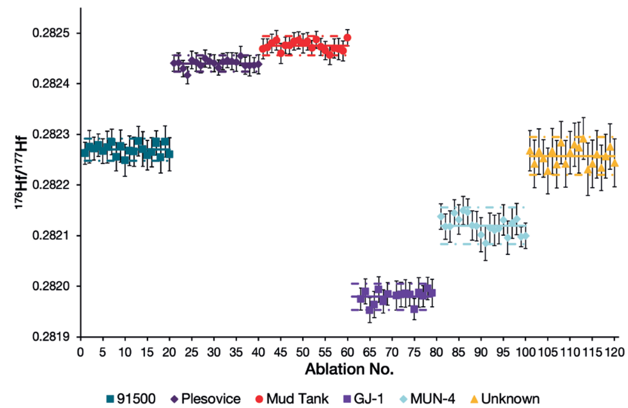

Figure 3. Repeatability of ^{176}Hf/^{177}Hf isotope ratio analysis for 20 spot ablations on four reference zircons, one unknown zircon and the MUN-4 artificial zircon. Internal error bars are 2SE, external error bars are 2SD.

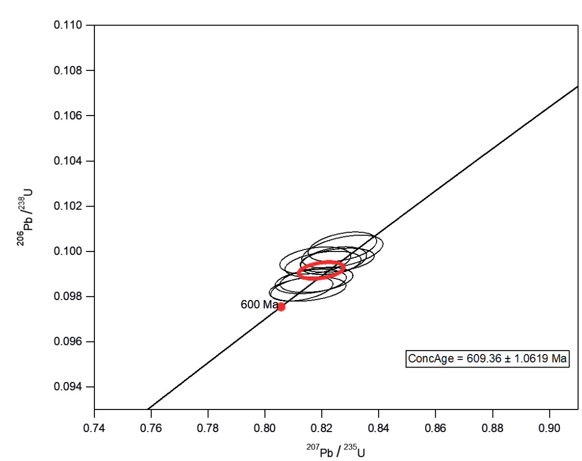

Figure 4. GJ-1. U-Pb Concordia for 10 spot ablations. Error bars are 2SE. ^{206}Pb/^{238}U Age – 610.0 ± 4.0 Ma (2σ).

thermo scientific

U-Pb

Reproducibility on the $^{206}Pb/^{238}U$ age was better than 1% 2RSD for the four reference zircons (Table 4). There was more scatter on the age for the unknown zircon (Figure 5): the average was close to that of the reference zircon 91500.

Table 4. $^{206}Pb/^{238}U$ ages for 10 spot ablations of zircons with estimated Pb and U concentrations. 91500 was used as the standard. Reproducibility better than 1% 2RSD for the four reference zircons.

	Pb	U	$^{206}Pb/^{238}U$ Age	Int. 2RSE	Ext. 2RSD
91500	7.7 ppm	80 ppm	1062.4 Ma	0.9%	0.3%
Plešovice	13 ppm	740 ppm	350.0 Ma	0.6%	0.7%
Mud Tank	1.7 ppm	8.4 ppm	719.2 Ma	2.0%	0.9%
GJ-1	2.8 ppm	270 ppm	610.0 Ma	0.6%	0.7%
Unknown	6.7 ppm	36 ppm	1032.6 Ma	1.0%	3.0%

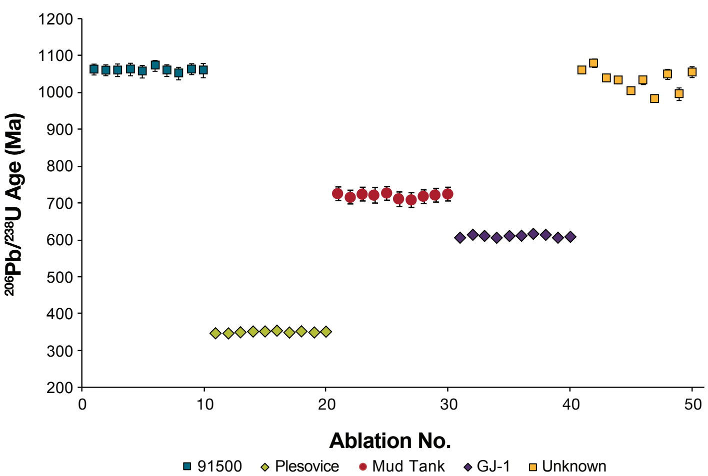

Figure 5. Repeatability of $^{206}Pb/^{238}U$ ages for 10 spot ablations. Error bars are 2SE.

Comparison to LASS

Previous reported results for LASS for zircons between a Neptune Plus MC-ICP-MS and a Thermo Scientific™ Element XR™ HR-ICP- MS[5] used the same number of laser ablation pulses with the same laser fluence as this study. However, as the spot size, 50 µm, used for LASS was double that reported here the total volume ablated for Hf and U-Pb analysis was also double.

In the previous study the average total Hf beam measured on the 91500 zircon standard was 3.8 V, here we achieved a total Hf beam of 13.4 V for the same standard. Consequently, the $^{176}Hf/^{177}Hf$ isotope ratio had 2-3 times less uncertainty for a similar number of spot ablations using ultrafast laser ablation technology than LASS.

Conclusions

The use of ESI Lasers Bloodhound and DCI ultrafast laser ablation technology with the Thermo Scientific Neptune XT MC-ICP-MS leads to excellent signal/noise ratio and sensitivity which is highly beneficial to zircon petrochronology. Using this system sacrifices the possibility of simultaneous measurement of Hf and U-Pb by LASS, however the increase in performance means two sequential, separate, measurements of Hf and U-Pb can achieve significantly better analytical results for less total volume ablated.

References

1. Bauer, A. M. & Horstwood, M. S. A., Chem. Geol. 476, 85–99 (2018).
2. Van Malderen, S. J. M., Managh, A. J., Sharp, B. L. & Vanhaecke, F., J. Anal. At. Spectrom. 31, 423–439 (2016).
3. Douglas, D. N., Managh, A. J., Reid, H. J. & Sharp, B. L., Anal. Chem. 87, 11285–11294 (2015).
4. Craig, G., Managh, A. J., Stremtan, C., Lloyd, N. S. & Horstwood, M. S. A., Anal. Chem. 90, 11564–11571 (2018).
5. Craig, G., Frick, D. A., Bouman, C. & Lloyd, N., *Thermo Fish. Sci. Tech. Note 30415.*

Data shown here are not specifications.

Find out more at **thermofisher.com/ICP-MS**

ThermoFisher SCIENTIFIC