Laser Ablation Split Stream (LASS) Between Three Inductively Coupled Plasma Mass Spectrometers for Zircon Petrochronology

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Overview

Purpose: To evaluate the effectiveness of laser ablation split stream (LASS) between three different inductively coupled plasma mass spectrometers (ICP-MS) for zircon geochronology.

Methods: LASS was achieved using disposable membrane pumps. Hf, U-Pb and rare earth element (REE) data were measured simultaneously by multicollector (MC), sector field (SF), and quadrupole (Q) ICP-MS respectively.

Results: Hf and U-Pb isotope ratios, and REE concentrations were determined successfully for four reference materials.

Introduction

In laser ablation analysis the choice of which type of ICP-MS to use is dependent on the application. Chronometers requiring epsilon level precision are measured on multi-collector ICP-MS: for determination of the rare earth composition a quadrupole based instrument is sufficient. The development of LASS, where the laser aerosol is split between two ICP-MS, has allowed two isotopic (or trace elemental) systems to be measured simultaneously on a single ablation site. A primary LASS application is zircon and monazite petrochronology[1], for which two separate chronometers, U-Pb and Hf, and REE concentration, are often collected. By determining both the chronometers and the elemental composition for a single ablation site, a direct link between each can be established.

LASS analysis of common reference zircons and monazites combining three different Thermo Scientific™ ICP-MS, the Neptune *Plus*™ (for Hf), Element XR™ (for U-Pb) and iCAP™ RQ (for REE) is reported. The laser ablation gas steam was split between the three ICP-MS, following the approach was outlined by Frick *et al*[2].

Methods

Sample Reference Materials

- NIST SRM® 610
- 4 reference zircons and monazites
  - 91500
  - Plesovice
  - GJ-1
  - Mud Tank
- MUN artificial zircon - external Yb correction of Hf.

Laser Ablation

The LA system used was a Teledyne Photon Machines Analyte G2™ equipped with a HelEx II ablation cell.

- Spot Size – 50 µm
- Repetition Rate - 10 Hz
- Fluence – 4J cm^{-2}
- Shot Count – 600
- He Outer Cell – 0.75 L min^{-1}
- He Cup Flow – 0.60 L min^{-1}

Thermo Scientific™ NEPTUNE *Plus*™

1.049 s integration time was used for all analyses. The Hf cup configurations was:

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

Thermo Scientific™ Element *XR*™

Isotopes	^{202}Hg	^{204}Pb	^{206}Pb	^{207}Pb	^{208}Pb	^{232}Th	^{235}U	^{238}U
Segment Duration	5 ms	5 ms	26 ms	48 ms	26 ms	26 ms	26 ms	26 ms

Thermo Scientific™ iCAP™ *RQ*

Monitored Isotopes (Dwell time – 50 ms)

- ^{89}Y, ^{91}Zr, ^{93}Nb, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{169}Tm, ^{172}Yb, ^{175}Lu, ^{178}Hf

LASS

Compact membrane pumps were used to perform each split, extracting ablated material from the central LA-MC-ICP-MS channel to the other ICP-MS. The membrane pumps extracted part of the ablation gas steam from a LA mixing chamber (Figure 1). The amount of material extracted could be varied for each pump.

- Split 1 – 0.75 L min^{-1} pump at 88% efficiency.
- Split 2 – 0.40 L min^{-1} pump at 94% efficiency.

Data Analysis

All data analysis was performed within Iolite v3.31[3] (Igor Pro™ v6.37) using appropriate Data Reduction Schemes.

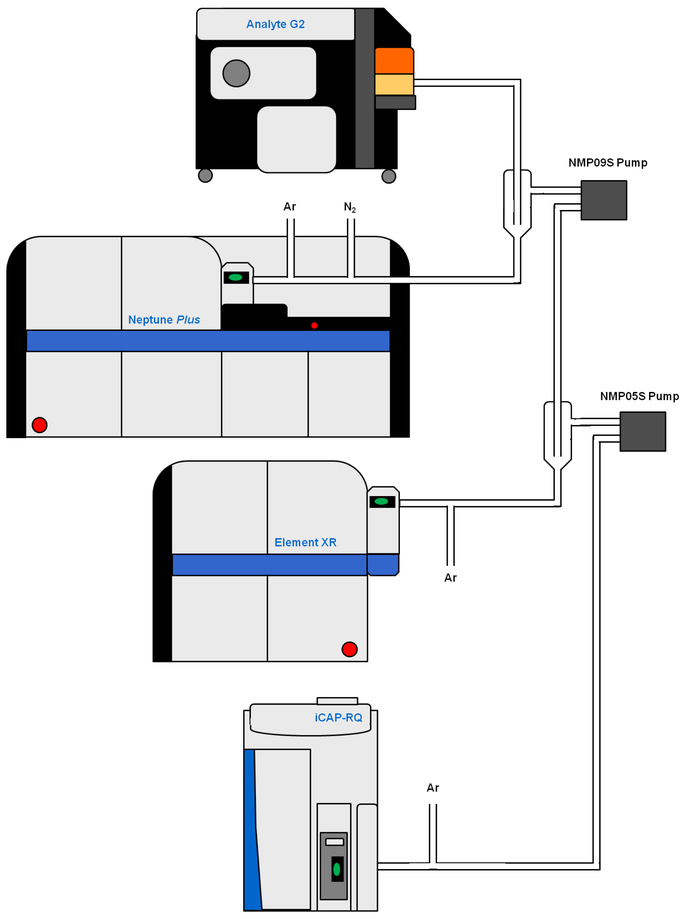


FIGURE 1. Schematic of LASS to three ICP-MS. Approx. 50% of the laser output was extracted from the primary MC-ICP-MS channel to SF-ICP-MS. Approx. 30% of the SF-ICP-MS channel extracted to Q-ICP-MS.

Results

Experimental

Each ICP-MS was tuned for high sensitivity, a U/Th ratio of approximately 1 and low oxides. The split was controlled via the pumps to supply sufficient signal on each ICP-MS during tuning.

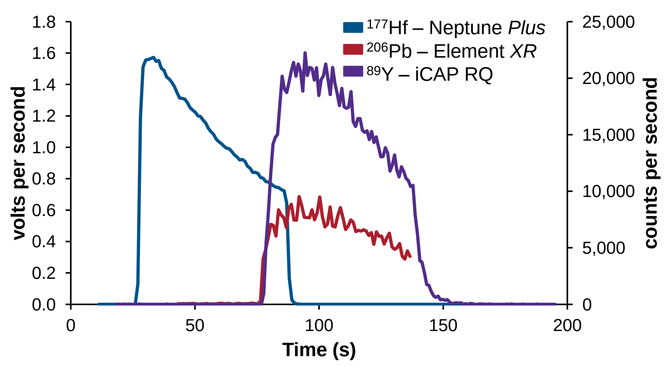


FIGURE 2. Signal traces for spot ablation of 91500 zircon, LASS to three ICP-MS. Integration time ≈ 1s. ^{177}Hf (MC-ICP-MS), responded faster than ^{206}Pb (SF-ICP-MS) and ^{89}Y (Q-ICP-MS), reflecting the relative distances from the laser ablation cell.

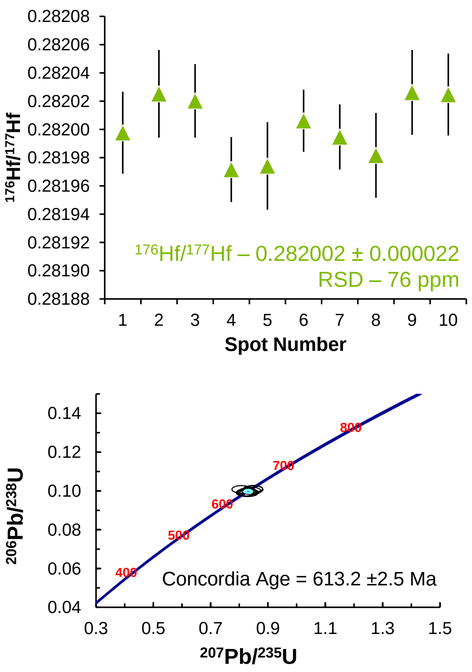
Mean ^{176}Hf/^{177}Hf, U-Pb ages and REE concentrations were determined for 10 ablation craters. For REE analysis ^{91}Zr was used as the internal standard. The 91500 zircon was used as an external standard, employing the sample-standard bracketing model. The other three reference materials, Plesovice, GJ-1 and Mud Tank, were used as unknown samples.

Plesovice

		Plesovice	
		Mean	RSD
Y	ppm	716	4.8
Nb	ppm	4.80	17.6
La	ppm	0.14	162.9
Ce	ppm	2.52	10.5
Pr	ppm	0.20	54.9
Nd	ppm	2.64	18.1
Sm	ppm	4.67	11.0
Eu	ppm	1.49	34.8
Gd	ppm	18.9	8.1
Tb	ppm	7.46	8.2
Dy	ppm	76.6	4.9
Ho	ppm	21.4	5.6
Er	ppm	75.9	5.7
Tm	ppm	12.9	7.0
Yb	ppm	94.1	6.6
Lu	ppm	13.3	8.8
Hf	ppm	10733	1.3
Pb	ppm	18.9	17.6
Th	ppm	120	19.3
U	ppm	1128	19.4

FIGURE 3. LASS results for Plesovice. ^{206}Pb/^{238}U Age – 339.9 ± 15.4 Ma (2σ).

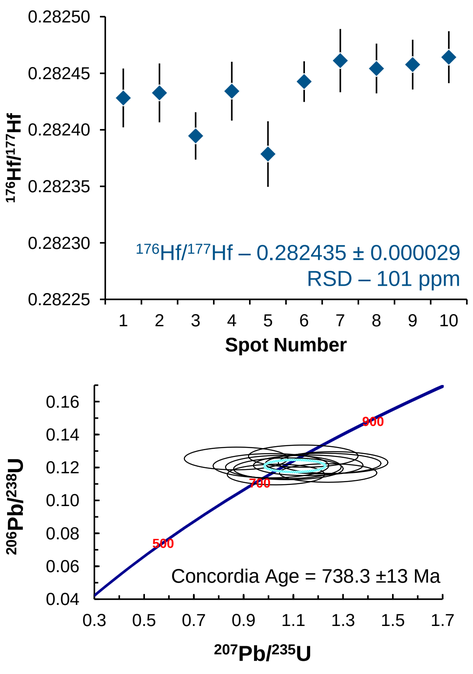
GJ-1



		GJ-1	
		Mean	RSD
Y	ppm	246	0.6
Nb	ppm	1.52	3.0
La	ppm	0.01	75.1
Ce	ppm	16.0	1.1
Pr	ppm	0.03	14.1
Nd	ppm	0.60	10.7
Sm	ppm	1.42	9.1
Eu	ppm	1.00	8.5
Gd	ppm	7.08	4.6
Tb	ppm	1.95	2.9
Dy	ppm	19.9	1.2
Ho	ppm	6.80	0.9
Er	ppm	29.3	0.9
Tm	ppm	6.24	1.3
Yb	ppm	62.0	0.7
Lu	ppm	13.1	0.7
Hf	ppm	6553	0.5
Pb	ppm	4.21	14.0
Th	ppm	14.5	16.4
U	ppm	401	14.5

FIGURE 4. LASS results for GJ-1. ^{206}Pb/^{238}U Age – 612.5 ± 10.0 Ma (2σ).

Mud Tank



		Mud Tank	
		Mean	RSD
Y	ppm	55.6	5.4
Nb	ppm	0.92	11.2
La	ppm	0.02	100.0
Ce	ppm	0.56	9.8
Pr	ppm	0.02	54.8
Nd	ppm	0.46	16.0
Sm	ppm	0.72	20.9
Eu	ppm	0.62	18.0
Gd	ppm	3.14	12.8
Tb	ppm	0.84	6.4
Dy	ppm	7.83	6.6
Ho	ppm	2.15	2.8
Er	ppm	7.31	1.6
Tm	ppm	1.20	5.9
Yb	ppm	9.06	3.7
Lu	ppm	1.49	4.9
Hf	ppm	10462	2.2
Pb	ppm	2.01	23.8
Th	ppm	5.78	19.4
U	ppm	9.46	18.1

FIGURE 5. LASS results for Mud Tank. ^{206}Pb/^{238}U Age – 733.3 ± 39.9 Ma (2σ).

Hf

^{176}Hf/^{177}Hf ratios with RSD ≈ 100 ppm were achieved for all three sample reference materials.

U-Pb

The corresponding U-Pb ages were accurate, within uncertainty, to accepted values.

REE

The REE precision obtained varied depending on concentration and heterogeneity of the sample material.

Conclusion

The gas stream from a laser ablation system can be split between three ICP-MS.

- Membrane pumps can control the split to each ICP-MS
- Simultaneous Hf, U-Pb and REE determination

References

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2. D. Frick, J. Schuessler, J. Buhk, F. von Blankenburg, *Goldschmidt Abstracts*, 2015, **947**
3. C. Paton, J. Hellstrom, B. Paul, J. Woodhead, J. Hergt, *J. Anal, At, Spectrom.*, **2011**, 26, 2508-2518

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