

Laser ablation split stream (LASS) between three ICP-MS for zircon petrochronology

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Goal

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

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 need to be measured with a multi-collector ICP-MS; for determination of the rare-earth element (REE) composition, a quadrupole-based instrument is sufficient.

The development of LASS, where the laser aerosol is split between two ICP-MS instruments, has allowed two isotopic (or trace elemental) systems to be measured simultaneously from 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.

Hf isotopes in zircon provide a powerful compliment to U-Pb dates, highlighting different mantle and crustal source contributions to the magma from which the zircon crystallized. In detrital zircon studies, these signatures help discriminate different provenance and mantle source contributions between rocks of similar age and allow interpretation of a richer and more accurate geological evolution. However, these complimentary Lu-Hf and U-Pb isotope systems differ by two orders of magnitude (1% for U-Pb, 0.01% for Lu-Hf) in the degree of uncertainty required for a reliable interpretation. This difference is reflected in the amount of material which needs to be analyzed: LA-MC-ICP-MS of Hf in zircons typically requires much more material than the U-Pb equivalent. The greater amount of material ablated for Hf isotopic determination increases the likelihood the analysis will be affected by sample heterogeneity (chemical zonation). Simultaneous rather than sequential analysis of the Hf and U-Pb isotopic eliminates the possibility of compositions being incorrectly assigned. By adding the simultaneous determination of the REE concentration of the zircon during the same ablation event, cases of sample heterogeneity can be more easily identified.

Here, the LASS analysis of common reference zircons combining three different ICP-MS instruments—Thermo Scientific™ Neptune Plus™ MC-ICP-MS (for Hf), Thermo Scientific™ Element XR™ HR-ICP-MS (for U-Pb), and Thermo Scientific™ iCAP™ RQ ICP-MS (for REE)—is reported. The laser ablation gas stream was split between the three ICP-MS, following the approach outlined by Frick *et al.*², using small diaphragm pumps to control the amount of laser aerosol delivered to each ICP-MS system. The pumps are easy to use, cost effective, and widely available, and as such can be applied for routine LASS analysis.

Experimental

Laser ablation split stream

The output of a Photon Machines™ Analyte G2™ excimer laser ablation system, equipped with a HelEx™ II two-volume ablation cell, was split between three different ICP-MS systems (Figure 1). The majority of the material outflow of the laser ablation system was directed to the Neptune Plus MC-ICP-MS for Hf isotope ratio analysis. A small diaphragm pump (NMP 09, KNF Neuberger™ GmbH, Germany) attached at the arm of a mixing bulb, was used to actively extract part of the main helium

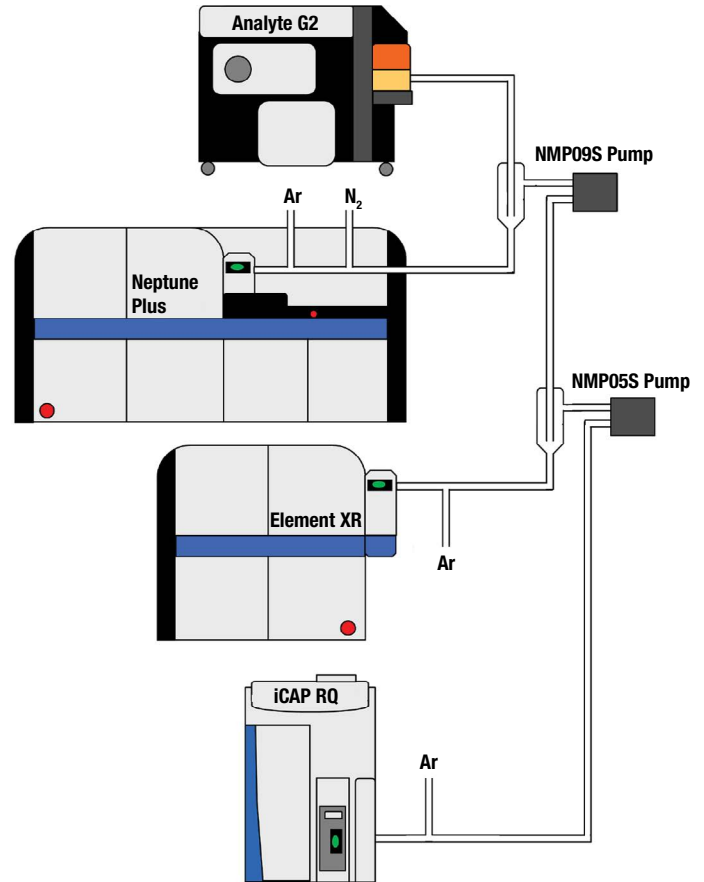


Figure 1. Schematic of LASS to three ICP-MS systems. Approx. 50% of the laser aerosol output was extracted from the primary MC-ICP-MS channel to SF-ICP-MS. Approx. 30% of the SF-ICP-MS channel was extracted to Q-ICP-MS.

stream to an Element XR single collector magnetic sector ICP-MS for U-Pb isotopic analysis. A second, smaller, diaphragm pump (NMP 05, KNF Neuberger GmbH, Germany) was used to extract part of the secondary laser aerosol and transport it to an iCAP RQ quadrupole-based ICP-MS to measure REE concentration.

The compact membrane pumps extracted part of the ablation gas stream from a LA mixing chamber (Figure 1). The percentage of the helium stream and laser aerosol extracted by the compact membrane pumps was dependent on their efficiency. The pumping efficiency of the two pumps could be tuned by altering the DC voltage applied using a variable power supply. For the LASS method used, the applied voltages of 4.4 V (NMP 09) and 4.7 V (NMP 05) were found to supply sufficient signal to each ICP-MS. Consequently:

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

Reference materials

Four reference zircons were analyzed: 91500; Plesovice, GJ-1, and Mud Tank. The synthetic zircon MUNZirc4 was ablated to provide an external mass bias correction for Yb on ^{176}Hf .

Instrumental conditions

A raster ablation of the reference material SRM 610 (National Institute of Science and Technology, USA) was used to tune the conditions on all three mass spectrometers. In LASS, changing the tuning conditions on one mass spectrometer can negatively impact the signal intensity measured on the other. By using the pumps to control the split in the laser aerosol, this effect was significantly reduced but not eliminated. Each instrument was tuned based on three conditions: sensitivity, the Th/U ratio, and a low rate of oxide formation.

Laser ablation

As the laser aerosol was to be split between three ICP-MS systems, a larger circle spot size and faster repetition rate were used than would be expected for an individual analysis (50 μm and 10 Hz respectively). Each ablation site had 600 shots at a fluence of 4 J cm^{-2} . As a result of the split stream analysis, the He flow to the outer cell (0.75 L min^{-1}) and inner cup (0.60 L min^{-1}) were also elevated.

Neptune Plus MC-ICP-MS

Due to the high precision requirements of Hf isotope ratio analysis, approximately 50% of the laser aerosol was directed towards the MC-ICP-MS. After the split, 0.94 L min^{-1} of Ar and 7 mL min^{-1} of N_2 were added. To achieve the highest sensitivity, the X skimmer cone and Jet sample cone were used. The Hf cup configuration is given in Table 1: an integration time of 1.049 s was chosen for all analyses.

Table 1. Cup configuration for LA Hf analysis using the Neptune Plus MC-ICP-MS.

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

Table 2. U-Pb isotopes monitored on Element XR single collector magnetic sector ICP-MS.

The total integration time was 205 ms.

Isotopes Monitored	^{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

Element XR HR-ICP-MS

As for the Neptune Plus ICP-MS, the X skimmer and Jet sampler cones were used in order to achieve the highest possible sensitivity. An Ar flow of 0.81 L min^{-1} was added after the material for the iCAP RQ ICP-MS had been extracted. The segment duration for each isotope monitored are reported in Table 2.

The action of the diaphragm pumps had the effect of adding a small oscillation to the measured signal on all of the ICP-MS systems (Figure 2); however, the position of the Element XR ICP-MS between the two pumps in the LASS setup meant the signal oscillation could be much more prominent. If the oscillations of each pump were in phase, constructive interference would result. Small changes to tubing length, pump efficiency, gas flows, and segment durations³ were all employed to reduce signal oscillation.

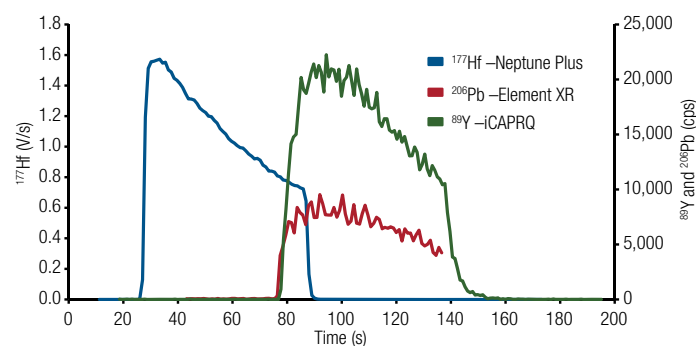


Figure 2. Signal traces for spot ablation of 91500 zircon, LASS to three ICP-MS. Integration times ≈ 1 s. ^{177}Hf (MC-ICP-MS), responded faster than ^{206}Pb (SF-ICP-MS) and ^{89}Y (Q-ICP-MS), reflecting the relative distances from the laser ablation cell.

iCAP RQ ICP-MS

The major isotopes of 17 elements, mostly rare earth elements (REEs), were monitored on the iCAP RQ ICP-MS (Ar gas flow, 1.10 L min⁻¹), with a dwell time of 50 ms on each isotope. The monitored isotopes were ⁸⁹Y, ⁹¹Zr, ⁹³Nb, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵³Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁹Tm, ¹⁷²Yb, ¹⁷⁵Lu, and ¹⁷⁸Hf.

Data processing

All the data analysis was performed within Lolite™ (v3.31), a laser ablation data processing plugin for Igor Pro™ (v6.37). The Hf isotopic analysis was performed using an in-house customized Hf Data Reduction Scheme (DRS). The U-Pb and REE analysis were carried out with DRS supplied with Lolite, U_Pb_Geochronology4 and Trace_Elements_IS, respectively.⁴

Mean ¹⁷⁶Hf/¹⁷⁷Hf, U-Pb ages and REE concentrations were determined for 10 ablation craters. For REE analysis, ⁹¹Zr 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 treated as unknown samples.

Results and discussion

Over the course of the entire LASS experiment, the diaphragm pumps controlled the split of the laser outflow reliably with no evidence of memory effects observed on the baseline. Due to the differences in distance between the laser and each mass spectrometer, a time shift was required to align the ablation signal (Figure 2).

Neptune Plus ICP-MS: ¹⁷⁶Hf/¹⁷⁷Hf isotopic analysis

The average total Hf beam measured on the 91500 zircon standard was 3.8 V and 6.5 V for the higher Hf concentration reference material Plesovice. The ¹⁷⁶Hf/¹⁷⁷Hf isotope ratios for each of the spot ablations are reported in Figures 3, 4, and 5 for Plesovice, GJ-1, and Mud Tank, respectively.

For Plesovice, the measured mean of 0.282455 ± 0.000026 (2σ) was slightly outside the confidence limits of the reported value of 0.282482.⁵ Similar biases have been reported in other LASS analysis of Plesovice grains.⁶ Mud Tank was also biased towards a lower ¹⁷⁶Hf/¹⁷⁷Hf ratio, 0.282435 ± 0.000058 (2σ), than the reported solution analysis value of 0.282507.⁷ GJ-1 however had a determined ¹⁷⁶Hf/¹⁷⁷Hf ratio, 0.282002 ± 0.000044 (2σ), accurate relative to the reported value 0.282003.⁵

Plesovice

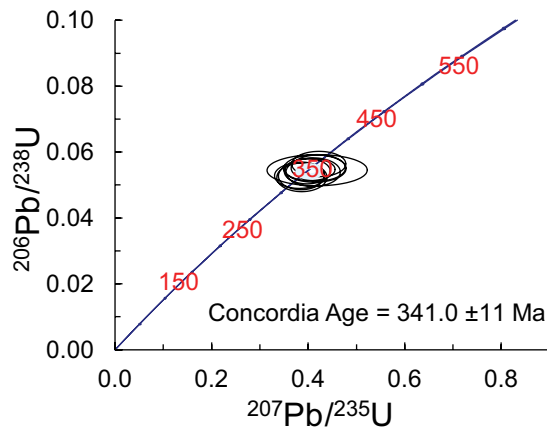
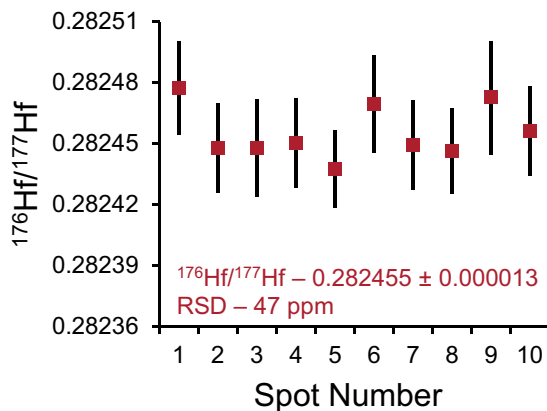


Figure 3. Left: Repeatability of ¹⁷⁶Hf/¹⁷⁷Hf isotope ratio analysis for 10 spot ablations on Plesovice. Error bars are 2SE. Right: U-Pb Concordia for the same 10 spot ablations, ²⁰⁶Pb/²³⁸U Age – 339.9 ± 15.4 Ma (2σ).

GJ-1

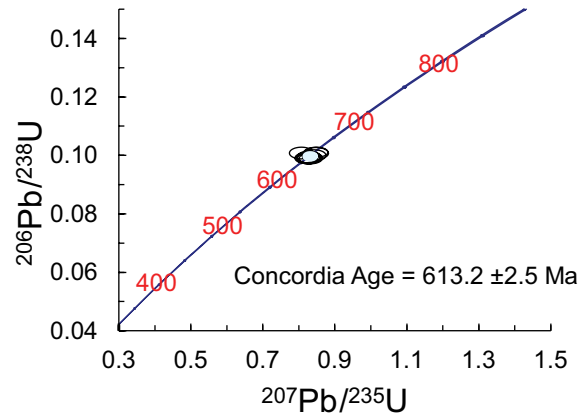
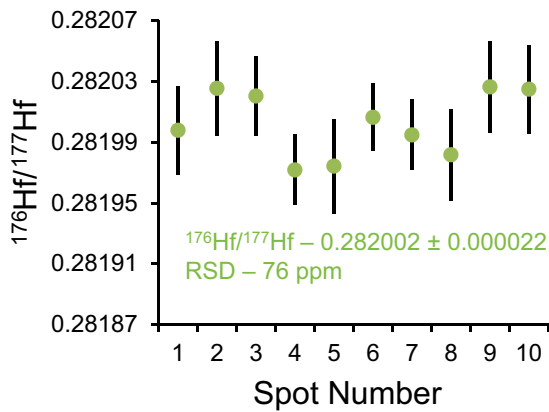


Figure 4. Left: Repeatability of $^{176}\text{Hf}/^{177}\text{Hf}$ isotope ratio analysis for 10 spot ablations on GJ-1. Error bars are 2SE. Right: U-Pb Concordia for the same 10 spot ablations, $^{206}\text{Pb}/^{238}\text{U}$ Age – 612.5 ± 10.0 Ma (2σ).

Mud Tank

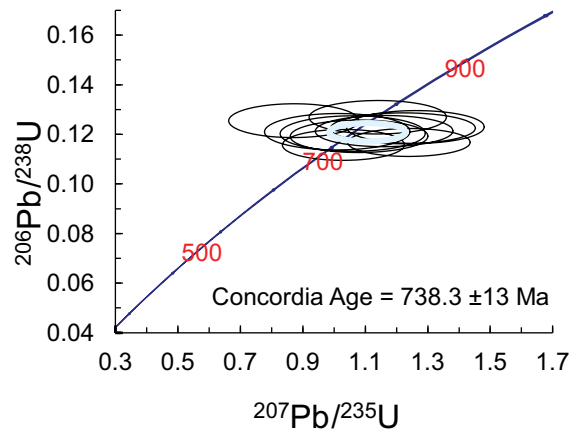
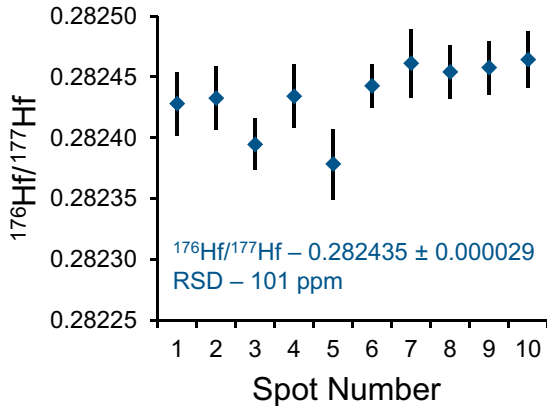


Figure 5. Left: Repeatability of $^{176}\text{Hf}/^{177}\text{Hf}$ isotope ratio analysis for 10 spot ablations on Mud Tank. Error bars are 2SE. Right: U-Pb Concordia for the same 10 spot ablations, $^{206}\text{Pb}/^{238}\text{U}$ Age – 733.3 ± 39.9 Ma (2σ).

Element XR ICP-MS: U-Pb isotopic analysis

For each of the zircons analyzed, the final $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ isotope ratios determined using the U_Pb_Geochronology4 DRS were used to construct U/Pb Concordia using the Microsoft™ Excel™ macro ISOPLOT 4.15.⁸ The Concordia ages (Figures 3, 4, and 5) were then compared to the $^{206}\text{Pb}/^{238}\text{U}$ age.

For all three reference materials analyzed, the $^{206}\text{Pb}/^{238}\text{U}$ and U/Pb Concordia ages were within uncertainty of one another. The $^{206}\text{Pb}/^{238}\text{U}$ ages measured 339.9 ± 15.4 Ma, 612.5 ± 10.0 Ma, and 733.3 ± 39.9 Ma (2σ) for Plesovice, GJ-1, and Mud Tank, respectively. These were within uncertainty of the accepted reference ages (Plesovice 337 Ma,⁵ GJ-1 609 Ma,⁹ Mud Tank 732 Ma¹⁰).

The lower precision achieved on the Mud Tank zircon was a reflection of the lower concentrations of U and Pb measured in the material (Table 3).

Table 3. Concentrations of 20 trace elements determined for three reference zircons. For the 17 isotopes collected on the iCAP RQ ICP-MS, Zr was used as the internal standard, 91500 zircon as the external standard. U, Th, and Pb concentrations were estimated based on the U-Pb isotope data collected on the Element XR ICP-MS.

Element		Plesovice		GJ-1		Mud Tank	
		Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)
Y	ppm	716	4.8	246	0.6	55.6	5.4
Nb	ppm	4.80	17.6	1.52	3.0	0.92	11.2
La	ppm	0.14	162.9	0.01	75.1	0.02	100.0
Ce	ppm	2.52	10.5	16.0	1.1	0.56	9.8
Pr	ppm	0.20	54.9	0.03	14.1	0.02	54.8
Nd	ppm	2.64	18.1	0.60	10.7	0.46	16.0
Sm	ppm	4.67	11.0	1.42	9.1	0.72	20.9
Eu	ppm	1.49	34.8	1.00	8.5	0.62	18.0
Gd	ppm	18.9	8.1	7.08	4.6	3.14	12.8
Tb	ppm	7.46	8.2	1.95	2.9	0.84	6.4
Dy	ppm	76.6	4.9	19.9	1.2	7.83	6.6
Ho	ppm	21.4	5.6	6.80	0.9	2.15	2.8
Er	ppm	75.9	5.7	29.3	0.9	7.31	1.6
Tm	ppm	12.9	7.0	6.24	1.3	1.20	5.9
Yb	ppm	94.1	6.6	62.0	0.7	9.06	3.7
Lu	ppm	13.3	8.8	13.1	0.7	1.49	4.9
Hf	ppm	10733	1.3	6553	0.5	10462	2.2
Pb	ppm	18.9	17.6	4.21	14.0	2.01	23.8
Th	ppm	120	19.3	14.5	16.4	5.78	19.4
U	ppm	1128	19.4	401	14.5	9.46	18.1

iCAP RQ ICP-MS: REE concentration determination

When designing the LASS experiment, it was decided the precision level achieved on the determination of the REE concentrations was less critical than either the Hf or U/Pb isotopic measurements. Consequently, it was decided to assign the iCAP RQ ICP-MS the least amount of laser aerosol. This reduced the number of counts detected sufficiently that elements of low abundance in the reference zircons, such as La and Pr, were near the limit of detection.

However, for more abundant elements (>5 ppm) REE concentrations were determined to a precision level of better than 10% RSD. Plots of the REE concentrations, normalized to chondrite, (Figure 6) in the four reference zircons were in good agreement with REE data collected with other LASS configurations.¹

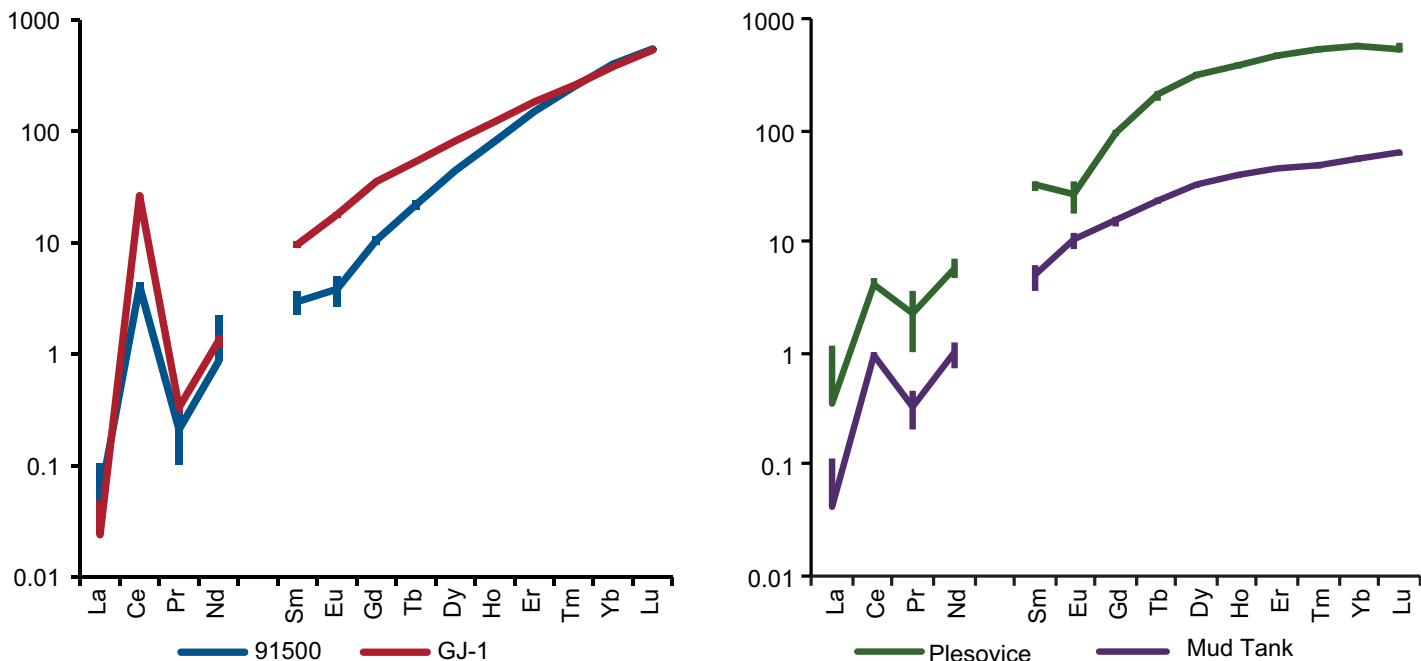


Figure 6. Chondrite-normalized REE concentrations¹¹ (error bars = SD) determined in the four reference zircons on the iCAP RQ ICP-MS in the LASS configuration.

Conclusion

The addition of variable diaphragm pumps to a LASS configuration has been shown to give an extra degree of control over a simple Y piece connector. This extra control has been exploited here to allow the gas outflow stream to be split between three different Thermo Scientific ICP-MS systems. In the resulting LASS configuration, simultaneous U-Pb and Hf isotope ratios were collected, alongside REE concentrations, for a single ablation spot on a zircon. $^{176}\text{Hf}/^{177}\text{Hf}$ ratios were ≈ 100 ppm 1σ RSD for the three sample reference zircons measured. The corresponding U-Pb ages were accurate, within uncertainty, to the accepted values of the reference zircons. The $^{206}\text{Pb}/^{238}\text{U}$ age of GJ-1 was better than 1.7% 2σ , and the Concordia age was better than 0.5% 2σ . REE concentrations could be measured to a precision level of better than 10% RSD and were in agreement with data from previously reported LASS configurations.

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