**Laser Ablation Split Stream (“LASS”) between High Sensitivity SC- and MC-ICP-MS Instruments**

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**Key Words**  
Laser Ablation, MC-ICP-MS, Zircon, U-Pb, Hafnium, Geochronology

**Goal**  
To demonstrate that simultaneous acquisition of U-Pb age and Hf isotopic composition is possible with small ablation spots (30 µm diameter) using the LAS S technique with high-sensitivity ICP-MS instruments.

**Overview**  

**Purpose:** To demonstrate the precision of Hf and U-Pb isotope ratios determinations using laser ablation split stream (“LASS”) with 30 µm diameter ablation spots.

**Methods:** In this research, the ablation output from a Photon Machines Analyte.G2 193 nm laser ablation system was split between a Thermo Scientific™ Neptune Plus™ MC-ICP-MS and an Thermo Scientific™ Element XR™ SC-SF-ICP-MS. A simple, reproducible and reliable two-way split was made to the laser cell output (Figure 1).

**Results:** Both mass spectrometers were configured for enhanced sensitivity, enabling smaller spot sizes (30 µm) to be used for ablation (with 2σ RSD precision better than 1.4 epsilon units for 176Hf/177Hf, and better than 1.2% for 206Pb/238U ages). This reduction of spot size allows analysis of mineral grains that would otherwise be excluded due to size (increasing population sample size and representativity).

**Introduction**  
Laser ablation split-stream (“LASS”) is a technique that allows for the simultaneous analyses of different geochemical systems in mineral samples using two or more mass spectrometers.1 Whereas, conventionally U-Pb and Hf are analyzed in separate sessions from proximal or superimposed LA spots (40–50 µm diameter is typically required for the Hf). LASS allows geochemical information collected by different instruments to be determined from exactly the same ablation volume, avoiding the assumption that serial analyses of neighbouring sites are not affected by heterogeneity (chemical zonation). Further, sample throughput can be increased.

An important application is the determination of the complementary isotopic systems of Lu-Hf and U-Pb (age) which can be determined from the mineral zircon (ZrSiO₄) using MC-ICP-MS and SC-SF-ICP-MS respectively, e.g.² Fisher et al 2014 illustrate the advantages of LASS with respect to interpretation of Hf isotopes, where sequential analyses can lead to incorrect U-Pb age assignments and therefore incorrect assignment of initial Hf isotope compositions.

**Methods**  
**Laser Ablation Split Stream (“LASS”)**

The sample out from a Photon Machines Analyte.G2 (193 nm laser ablation system) was split by a simple Y piece connector (barbed PP fitting). Ar “make-up” gas from each mass spectrometer was added through a further Y piece connector before each injector. The configuration after the initial split was symmetrical and therefore the split is 50:50. This simple configuration was preferred for its reliability.
The Photon Machines Analyte.G2 features a HelEx cell, through which 1.5 L/min He gas was run (for conventional single stream setups 0.9 L/min can be used). Nitrogen gas (11 mL/min) was introduced to the sample gas mixture in order to increase sensitivity as well as reduce oxide formation and elemental fractionation in both mass spectrometers.

The laser ablation parameters for each analysis was 30 µm diameter spot, 10 Hz repetition rate for 60 seconds with ca. 7 J/cm² fluence (moderate settings).

**Mass Spectrometry**
From one split a Neptune Plus MC-ICP-MS was used to measure high-precision Hf isotopes ratios. Multicollector ICP-MS with Faraday cups are required for precise and accurate $^{176}\text{Hf}/^{177}\text{Hf}$ isotope ratio determination. The cup configuration used is shown below and includes two Yb peaks for accurate $^{176}\text{Yb}$ correction.

The second split was used to determine U-Pb isotope ratios with an Element XR SC-SF-ICP-MS. SF-ICP-MS offers higher sensitivity than quadrupole ICP-MS. LA-ICP-MS precision for U-Pb ages is typically limited to % level by standardization, and for common zircon applications multicollector precision and sensitivity is not required. The cross calibration of the triple mode detector of the Element XR was performed once at the beginning of the session and locked for the subsequent analyses.

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<th>L4</th>
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<tr>
<td>$^{171}\text{Yb}$</td>
<td>$^{173}\text{Yb}$</td>
<td>$^{176}\text{Lu}$</td>
<td>$^{177}\text{Hf}$</td>
<td>$^{177}\text{Hf}$</td>
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The gas tuning from one instrument can affect the other, through a change of back-pressures in the shared tubing. In order to achieve high precision Hf isotope determinations using 30 µm spot sizes, the gas tuning was first optimized for the Neptune Plus then for the Element XR and finally re-optimized for the Neptune Plus.

The two sector field ICP-MS instruments share the same interface design and both were fitted with a high-performance interface pump option and high-sensitivity X type skimmer cones. Further sensitivity enhancement can be made using the Jet sample cone.¹

**Data Analysis**
The data outputs from each mass spectrometer were exported to a common (.fin2) format for data reduction by third-party software packages. Iolite v. 2.5² was used for the data reduction of the Hf and U-Pb isotope ratio data. The Hf data are corrected internally and the U-Pb were corrected using the Plešovice reference zircon as a standard. U-PbRedux³ was used for the age calculations and plotting of the U-Pb concordia diagrams.

![Figure 1. Instrumental setup with schematic of the split stream from a Photon Machines Analyte.G2 laser ablation system and Thermo Scientific Neptune Plus MC-ICP-MS and Element XR SC-SF-ICP-MS instruments.](image-url)
Results
Hf and U-Pb Isotope Ratios
The Hf and U-Pb data are plotted in Figure 2. The 2σ RSD for the $^{176}\text{Hf}/^{177}\text{Hf}$ data generally have better than 1.4 epsilon unit repeatability, and the $^{206}\text{Pb}/^{238}\text{U}$ ages are within 1.2%. In each case the data are accurate within uncertainty.

Figure 3. Repeatability of $^{176}\text{Hf}/^{177}\text{Hf}$ isotope ratios for MUNZirc 4. This synthetic zircon is doped with Hf, Yb and other REE. The $^{176}\text{Yb}$ correction on $^{176}\text{Hf}$ is ca. 35%, proving the accuracy of the Yb correction.

Figure 4. Repeatability of $^{176}\text{Hf}/^{177}\text{Hf}$ isotope ratios from 16 analyses of the Plešovice reference zircon. These runs were interspersed by analyses of 4 other reference zircons. The data are in close agreement with reference value (cf. 0.282481 (14)°).

Figure 5. Repeatability of Nd and U-Pb ratios from Memorial University monazite standard “KMO”, as an example of another LASS application. These data were collected at Washington State University using Thermo Scientific Neptune and Element 2 instruments coupled to a New Wave Research UP-213 laser ablation system (7 Hz, 20 μm spot, 8 J/cm²). Note that dispersion in the ‘present day’ $^{143}\text{Nd}/^{144}\text{Nd}$ data can be an effect of $^{143}\text{Nd}$ ingrowth from variable Sm concentrations within the samples. Data plotted using Isoplot.

In order to demonstrate the utility of the LASS technique on other minerals and isotope systems, Figure 5 shows the results of simultaneous measurement U-Pb age and Nd isotope composition in the mineral monazite ($\text{CePO}_4$).
Conclusion
A simple Y piece connector was used to split the output from a laser ablation cell. This configuration produced a 50:50 split to two different instruments: a Neptune Plus MC-ICP-MS for high-precision $^{176}$Hf/$^{177}$Hf isotope ratios, and an Element XR SC-SF-ICP-MS for precise U-Pb age determination.

- Enhanced sensitivity MC-ICP-MS and SC-SF-ICP-MS
- 30 μm diameter ablation spots on zircon for LASS
- LASS for simultaneous U-Pb and Hf isotope ratios
- Better than 1.2% 2σ RSD for $^{206}$Pb/$^{238}$U ages
- Better than 1.4 ε units 2σ RSD for $^{176}$Hf/$^{177}$Hf ratios
- 12.2 V total Hf beam for Plešovice
- 0.92 ε units 2σ RSD for $^{176}$Hf/$^{177}$Hf ratios from Plešovice
- LASS can be extended to other mineral and isotopic systems, for example Nd in monazite.
- Further sensitivity enhancement is available using the ‘Jet’ sample cone.

References
2. Tollstrup et al. (2012). Geochem Geophys, 13(3), 1525–2027
4. Lloyd et al. (2012). Mineral Mag, 76, 2029

Aknowledgements
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