Simultaneous *in-situ* Laser Ablation Analysis of Pb-U and Lu-Hf Isotope Ratios in Zircons Using MC-ICPMS

J.B. Schwieters, C. Bouman, M. Deerberg, Thermo Fisher Scientific, Bremen, Germany

Key Words
NEPTUNE, NEPTUNE *Plus*, Laser Ablation, Lu-Hf, U-Pb

Introduction

Laser Ablation ICP-MS is a powerful technique for producing high quality zircon age data from U-Pb isotopic studies. To assess growth and alteration processes in these zircons, it is mandatory to analyse Lu-Hf isotopes in conjunction with U-Pb.

Since zircons have much lower contents of Pb and U than Hf, simultaneous analysis of U-Pb and Lu-Hf isotope ratios requires different detection systems. The amount of Lu-Hf in zircons is sufficient for producing ion beam intensities to be measured in Faraday cup detectors, whereas Pb and U isotopes require ion counting detectors.

In this study, we present U-Pb and Lu-Hf isotope ratios in the zircon 91500 obtained using the Thermo Scientific™ NEPTUNE™ MC-ICPMS. The mass spectrometer was run in a combined mode of static Faraday cup measurements and rapid dynamic peak jumping: For high precision Lu-Hf measurements we used static Faraday cup measurements alternating with rapid peak jumping of the U and Pb isotopes on the axial ion counter.

Method

The NEPTUNE MC-ICPMS was coupled to a laser (UP213 SA, New Wave Research Inc.). The NEPTUNE instrument is equipped with 9 Faraday cups, enabling the analysis of all Hf isotopes, including the Yb, Lu and W interferences. During the analysis, all Pb isotopes, as well as Hg and U isotopes are measured in peak jumping mode in the secondary electron multiplier. The cup configuration is listed in Table 1. It enables the analysis of the Pb-U and the Lu-Hf isotopes systems within the same spot.

Table 1. Cup configuration.

	Far-L4	Far-L3	Far-L2	Far-L2	Center Far/SEM	Far-H1	Far-H2	Far-H3	Far-H4
Line 1	^{172}Yb	^{174}Hf	^{175}Lu	^{176}Hf	^{177}Hf	^{178}Hf	^{179}Hf	^{180}Hf	^{82}W
Line 2					^{238}U				
Line 3					^{208}Pb				
Line 4					^{207}Pb				
Line 5					^{206}Pb				
Line 6					^{204}Pb				
Line 7					^{202}Hg				

Thermo SCIENTIFIC

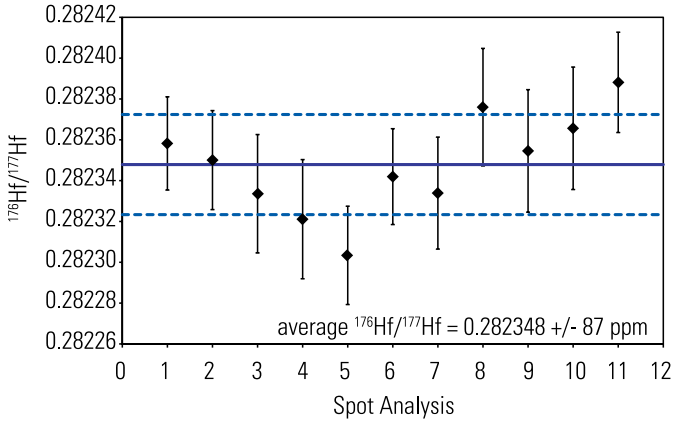


Figure 1. Hf isotope composition of zircon 91500.

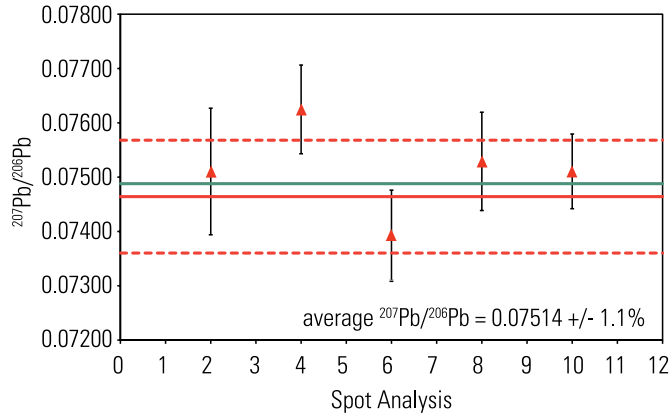


Figure 2a. $^{207}Pb/^{206}Pb$ isotope ratios.

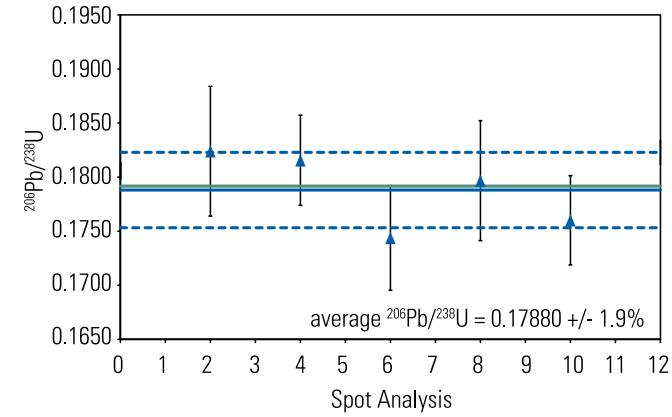


Figure 2b. $^{206}Pb/^{238}U$ isotope ratios.

Results and Discussion

Lu-Hf

Figure 1 shows $^{176}Hf/^{177}Hf$ isotope ratios for single spot analyses of reference standard zircon 91500. The mean value for $^{176}Hf/^{177}Hf$ is 0.282348 +/- 85 ppm. This value is well within published values for this zircon.[3, 4]

Pb-U

Figures 2a and 2b show $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{238}U$ for 5 single spot analyses of reference standard zircon 91500. The green lines represent the true values for $^{207}Pb/^{206}Pb$ (0.07488) and $^{206}Pb/^{238}U$ (0.17917).

Internal and external precisions are around 1% for $^{207}Pb/^{206}Pb$. As expected, this is comparable to what is obtained on a single collector magnetic sector ICP-MS (Thermo Scientific ELEMENT 2™).[5] The precision for $^{206}Pb/^{238}U$ obtained in this study is a little lower, but can be explained by the fact that only 5 spot analyses were taken and no internal correction for U-Pb fractionation was applied as was done by Frei *et al.* (2009).[5]

Multi-Ion-Counting (MIC) measurements on the NEPTUNE MC-ICPMS have shown a factor of 2 to 3 or better precisions for both $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{238}U$.[1, 2]

Summary

This study described a method to obtain Lu-Hf and Pb-U isotope ratios in one single laser event. Lu-Hf were measured simultaneously in Faraday cups. U-Pb were measured in single collector mode using a peak jumping routine on the axial electron multiplier. Precisions on $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{238}U$ obtained in this study are comparable with those of other single collector techniques. Moreover, for high precision in-situ analysis of U-Pb by laser ablation, multicollection is absolutely necessary. Previous studies have shown the capability of Multi Ion Counters (MICs) on the NEPTUNE MC-ICPMS to obtain highly precise U-Pb isotopes ratios in zircons.[1, 2]

Table 2. Precisions obtained for $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{238}U$ in zircon 91500 using different techniques.

$^{207}Pb/^{206}Pb$, 1σ	$^{206}Pb/^{238}U$, 1σ	Method	Reference
1.1%	1.9%	Single collector peak jumping on NEPTUNE	this study
1.1%	1.3%	Single collector peak jumping on ELEMENT 2	5
0.4%	0.7%	Multi-Ion-Counting on NEPTUNE	1, 2

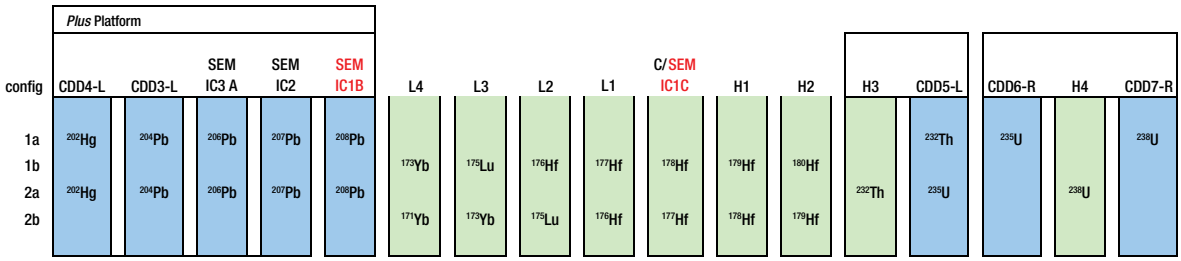
NEPTUNE *Plus*: No Compromise Packages for Zircon Analysis

The new Thermo Scientific NEPTUNE *Plus* features new ion counters, which give the same dynamic range up to 1.4 Mcps and the same performance as standard-sized discrete dynode multipliers. These new Compact Discrete Dynode multipliers enable simultaneous analysis of all U, Th and Pb isotopes in a multicollector setup. Compared to a single collector approach, where all ion beams are measured sequentially on the same ion counter, the Multi-Ion-Counting approach offers ultimate detection efficiency because of the parallel detection of all isotopes.

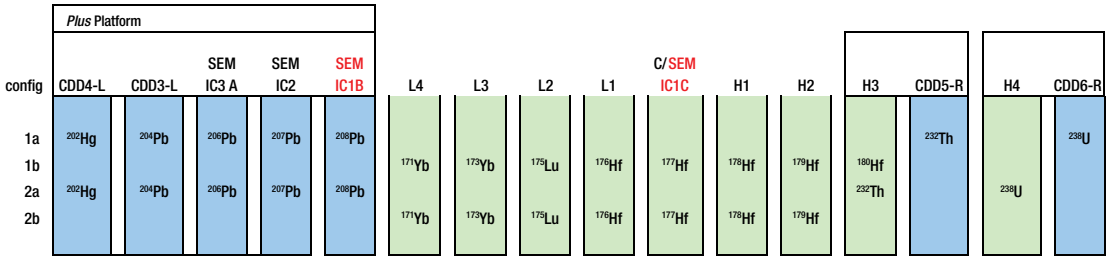
The NEPTUNE *Plus* offers various no compromise packages for the simultaneous analysis of Lu-Hf and Pb-U in zircons using these new Compact Discrete Dynode multipliers.

Table 3. U-Pb configurations NEPTUNE *Plus* MC-ICPMS.

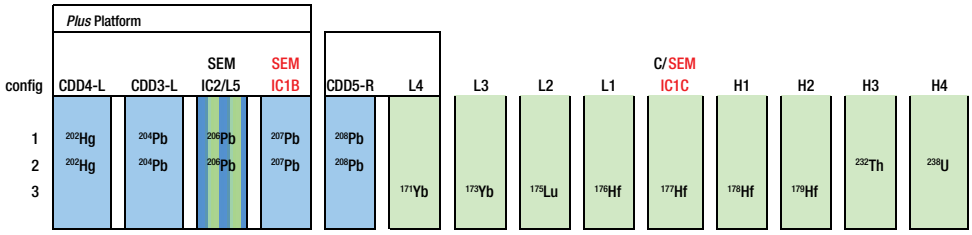
PN1361910 U-Pb Package 1 NEPTUNE *Plus* MC-ICPMS



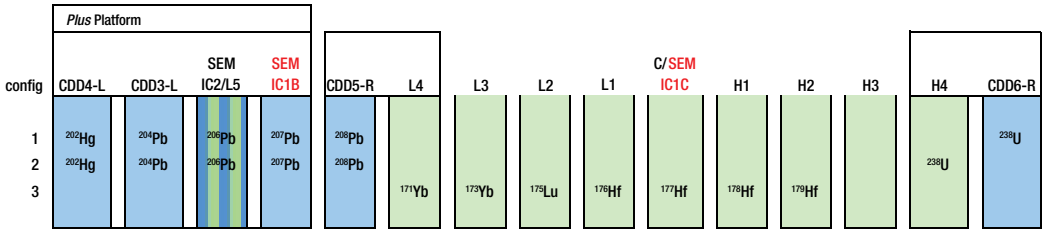
PN1361920 U-Pb Package 2 NEPTUNE *Plus*



PN1361930 U-Pb Package 3 NEPTUNE *Plus*



PN1361940 U-Pb Package 4 NEPTUNE *Plus*



References

1. Cocherie, A. et al (**2009**) LA-MC-ICPMS and SHRIMP U-Pb dating of complex zircons from Quartenary tephras from the French Massif Central: Magma residence time and geochemical implications. *Geochimica et Cosmochimica Acta,* 73, 1095-1108.
2. Application Note Thermo Scientific AN30012: *In-Situ* U-Pb Zircon Dating Using Laser Ablation-Multi Ion Counting-ICP-MS (LA-MIC-ICP-MS).
3. Woodhead, J.D. and Hergt, J.M. (**2005**) A preliminary appraisal of seven natural zircon reference materials for in situ Hf isotope determination. *Geostandards and Geoanalytical Research*, 29 (2), 183–195.
4. Andersen, T. et al (**2009**) Granitic magmatism by melting of juvenile continental crust: new constraints on the source of Palaeoproterozoic granitoids in Fennoscandia from Hf isotopes in zircons. *Journal of the Geological Society, London*, 166, 233-247.
5. Frei, D. and Gerdes, A. (**2009**) Precise and accurate in situ U–Pb dating of zircon with high sample throughput by automated LA-SF-ICP-MS. *Chemical Geology*, 261, 261-270.

Acknowledgements

We would like to thank Alain Cocherie very much for providing the zircon picture.

thermofisher.com/NEPTUNE*Plus*

©2016 Thermo Fisher Scientific Inc. All rights reserved. NEW WAVE RESEARCH is a trademark of New Wave Research Inc. All other trademarks are the property of Thermo Fisher Scientific Inc. and its subsidiaries. Specifications, terms and pricing are subject to change. Not all products are available in all countries. Please consult your local sales representative for details.

Africa +43 1 333 50 34 0
Australia +61 3 9757 4300
Austria +43 810 282 206
Belgium +32 53 73 42 41
Canada +1 800 530 8447
China 800 810 5118 (free call domestic) 400 650 5118
Denmark +45 70 23 62 60
Europe-Other +43 1 333 50 34 0
Finland +358 9 3291 0200
France +33 1 60 92 48 00
Germany +49 6103 408 1014
India +91 22 6742 9494
Italy +39 02 950 591
Japan +81 45 453 9100
Korea +82 2 3420 8600
Latin America +1 561 688 8700
Middle East +43 1 333 50 34 0
Netherlands +31 76 579 55 55
New Zealand +64 9 980 6700
Norway +46 8 556 468 00
Russia/CIS +43 1 333 50 34 0
Singapore +65 6289 1190
Spain +34 914 845 965
Sweden +46 8 556 468 00
Switzerland +41 61 716 77 00
UK +44 1442 233555
USA +1 800 532 4752

Thermo SCIENTIFIC
A Thermo Fisher Scientific Brand

AN30191-EN 11/16S