Application Note: 30170

Simultaneous in situ Analysis of U-Pb Age and Hf Isotopes of Zircon by Laser Ablation Sector-Field (MC-) ICP-MS

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Key Words

- ELEMENT XR
- NEPTUNE
- Isotope Ratio
- Laser Ablation
- Zircon

Introduction

The combination of laser ablation with multicollector inductively coupled plasma mass spectrometers (LA-MC-ICP-MS) has been shown to produce high quality zircon age data from U-Th-Pb isotopic studies. These results however may not correctly indicate the number of zircon forming events, especially those arising from multiple growth and alteration processes. This limitation can be overcome by combining results from Pb-U and Lu-Hf analyses made on small, well defined zircon areas.

Static measurements of Pb-U and Lu-Hf can not be achieved in a single MC-ICP-MS analysis due to the large mass range that would need to be scanned. This has previously meant sequential analyses of the Pb-U and the Lu-Hf systems at the same zircon site[1], e.g. an initial Pb-U analysis by laser ablation coupled to sector-field ICP-MS (LA-ICP-SFMS) and a subsequent LA-MC-ICP-MS analysis for Lu-Hf[2]. The sequential analyses were made as closely as possible in the same area (growth domain) of the zircon, for example a 40 µm Lu-Hf spot was drilled on top of a 30 µm U-Pb spot)[2].

In order to overcome the limitations of sequential sampling of U-Th-Pb and Hf isotopes from different sites in zircons, a fast scanning single collector and a multicollector inductive coupled plasma mass spectrometer have been coupled in parallel to a New Wave UP213 213 nm UV laser ablation system. A low volume laser ablation sample chamber with fast response (< 1 s) and rapid washout time was fitted instead of the standard sample chamber in order to enable sequential sampling of heterogeneous grains during time-resolved data acquisition on both instruments. The ablated material was transported in helium, split after the ablation cell via a Y-shaped connector and introduced simultaneously into the two mass spectrometers, the Thermo Scientific ELEMENT XR for U-Th-Pb analysis and Thermo Scientific NEPTUNE for high precision Hf isotope analysis.

For accurate age dating of zircons the control of common lead contaminations is essential. This can be done by monitoring mass ^{204}Pb which is not part of the U-Pb decay scheme. Since the natural abundance of ^{204}Pb is so small every common lead contribution measured on ^{204}Pb is magnified by about a factor of 15 to 18 on ^{206}Pb and ^{207}Pb intensities. This means the small ^{204}Pb signal has to be measured precisely and therefore the highest sensitivity is required to achieve the smallest statistical error. In comparison to quadrupole ICP-MS instruments[3] the ELEMENT XR sector-field ICP-MS is at least one order of magnitude more sensitive and as a consequence the statistical uncertainty on ^{204}Pb is significantly improved.

Instrumentation

	U-Th-Pb analysis	Hf isotope analysis
Instrument	ELEMENT XR	NEPTUNE
Scan mode	E-Scan	Static
Scanned masses	202, 204, 206, 207, 208, 235, 232, 238	171, 173, 175, 176, 177, 178, 179, 180
Mass resolution	300	300
Dead time	18 ns	20 ns
Dwell time/isotope	4 ms	1 s
Settling time/isotope	1 ms	–
Number of scans	1080	50
Integration time	1 s (= 15 scans)	1 s
Background	20 s	
Ablation time	50 s	50 s
Carrier gas	0.5 L/min He (+1.1 L/min Ar)	
Laser	UP213 SA (New Wave Research; Nd:YAG, 213 nm)	
Spot size	55 to 80 µm	
Laser settings	5 Hz	
Laser fluence	~ 3 J/cm²	
Drill speed	0.6 µm/s	

Table 1: Operating conditions and instrument settings.

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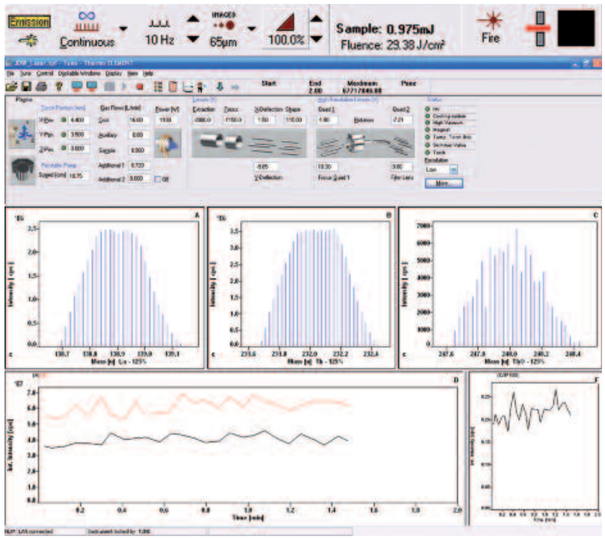


Figure 1: Screenshot from the ELEMENT software showing instrument settings and sensitivity obtained for La and Th in NIST 612 using the laser sampling parameters as shown.

The primary advantages of ICP-SFMS offers over other ICP-MS instrumentation for U-Th-Pb analyses are shown in Figure 1 and can be summarized as:

- The characteristic flat-top peaks of sector-field mass spectrometers in low mass resolution allow the reliable use of single point per peak analyses.
- The high sensitivity of ICP-SFMS allows for increased accuracy on the common lead correction that is made when measuring ^{202}Hg as well as ^{204}Pb+Hg. With less sensitive instrumentation small common lead contaminations detected at mass 204 would be otherwise magnified on masses ^{206}Pb and ^{207}Pb, leading to worsened Pb-U dating accuracy.

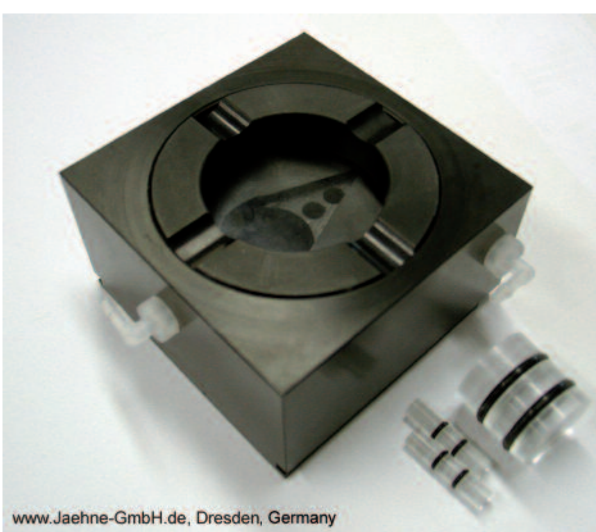
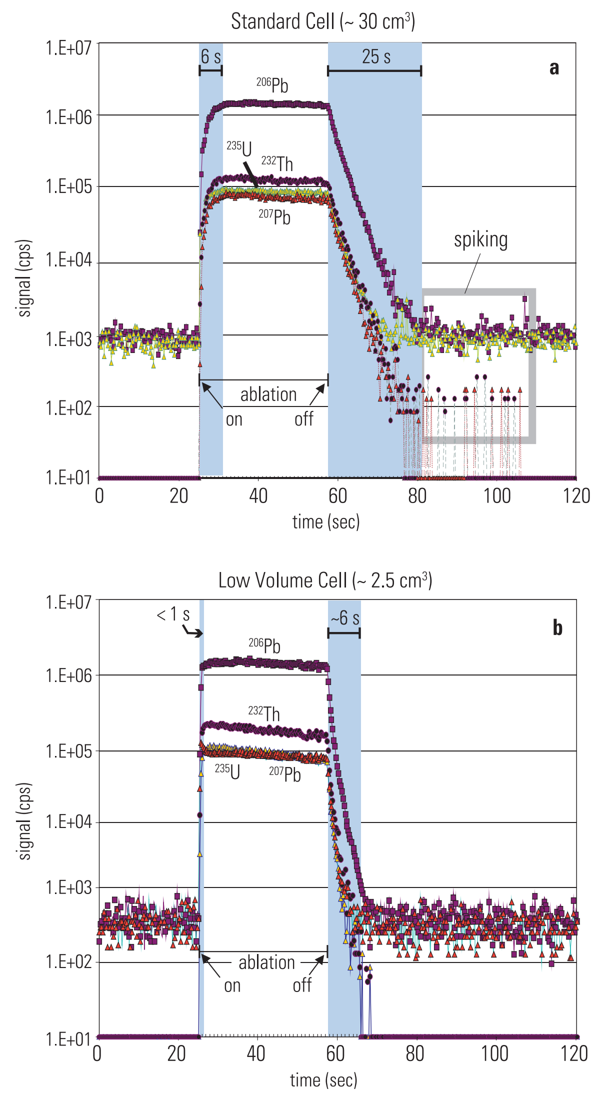


Figure 2: Low volume laser sample chamber used in all analyses.

The advantages of the low volume laser chamber[4] (Figure 2) for discrete laser sampling can be seen in Figure 3. Uptake delays of 1 s were achievable with the low volume cell, compared to 6 s with the standard sample cell. In the low volume cell, signal intensities after the end of the ablation dropped by 2 orders of magnitude in less than 4 s and 3 orders in about 6 s. In comparison, the signal from the standard cell needs more than 3 times longer (13 s and 25 s respectively) to drop to the same levels. Spiking is still observed in the standard cell up to 50 s after the end of ablation, while the low volume cell shows no spiking.



Frei & Gerdes, Chem. Geol. in press

Figure 3: Improvement in sample uptake and washout when using the low volume laser sample chamber.

Results

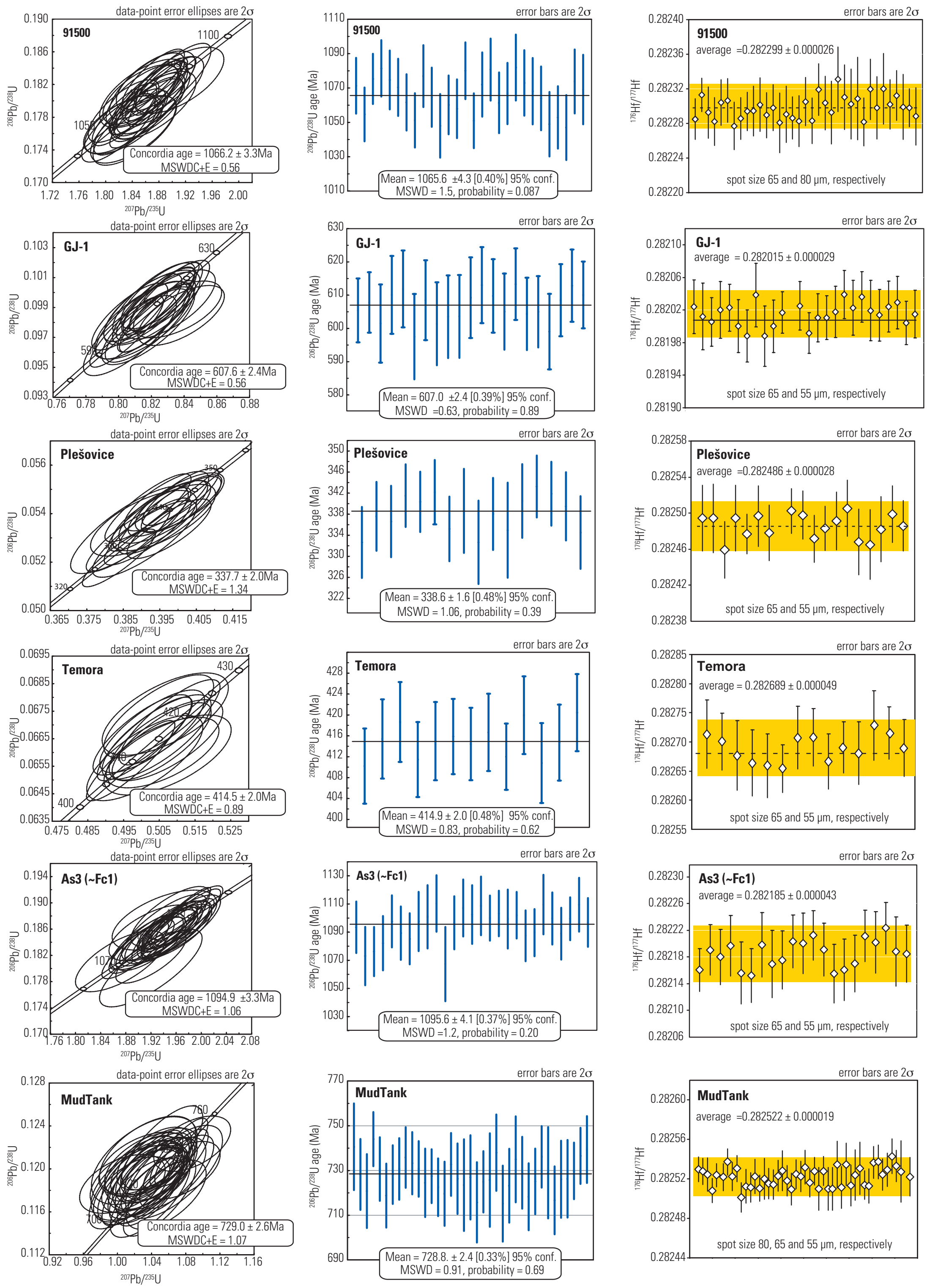


Figure 4: Simultaneous U-Pb and Hf isotope analyses in zircon.

	U-Pb age	$^{176}Hf/^{177}Hf$
91500:	1065 Ma[5]	0.282306 ± 0.000008[8]
GJ-1:	607 Ma[2]	0.282103 ± 0.000008[1] (unpublished)
Plešovice:	337.1 Ma[6]	0.282484 ± 0.000008[6]
Temora 2:	417 Ma[7]	0.282686 ± 0.000006[8]
AS3 (~FC1):	1099 Ma[9]	0.282184 ± 0.000016[7]
MudTank:	732 Ma[10]	0.282507 ± 0.000006[8]

Table 2: Reference U-Pb age and Hf isotope data for the zircons analyzed in Figure 4.

Conclusions

Coupling the Thermo Scientific ELEMENT XR and the NEPTUNE to the laser ablation system was easy to achieve and demonstrated to be a powerful instrumental solution for the simultaneous analysis of U-Th-Pb and Hf isotope ratios in small zircons. The low volume laser cell used in this study demonstrated fast sample uptake and fast washout, resulting in low backgrounds without spiking signals. U-Pb ages and Hf isotope ratios of all zircons obtained in this study are in very good agreement with the published data.

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