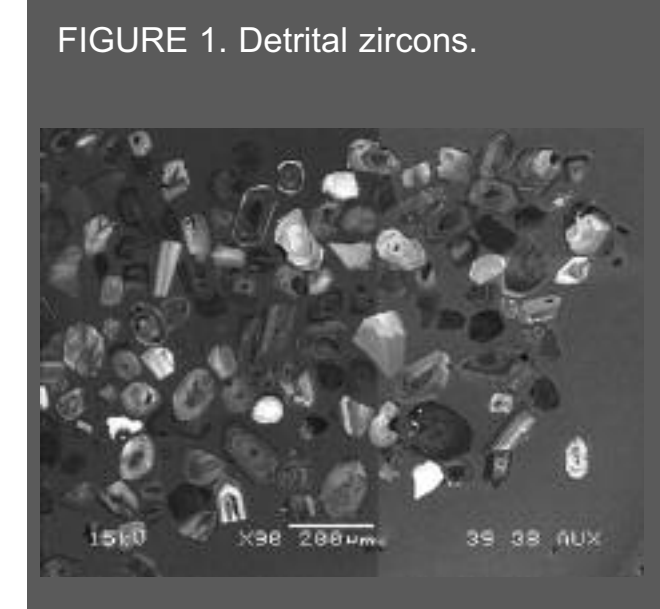


# U-Pb Isotope Ratio Analysis of Zircons by Laser Ablation Coupled to Single Collector Sector Field ICP-MS

Julian D. Wills, Thermo Fisher Scientific (Bremen) GmbH, Hanna Kunath Str. 11, 28199 Bremen, Germany;  
Dirk Frei, GEUS (Geological Survey of Denmark and Greenland), Copenhagen, Denmark (www.geus.dk)  
julian.wills@thermofisher.com

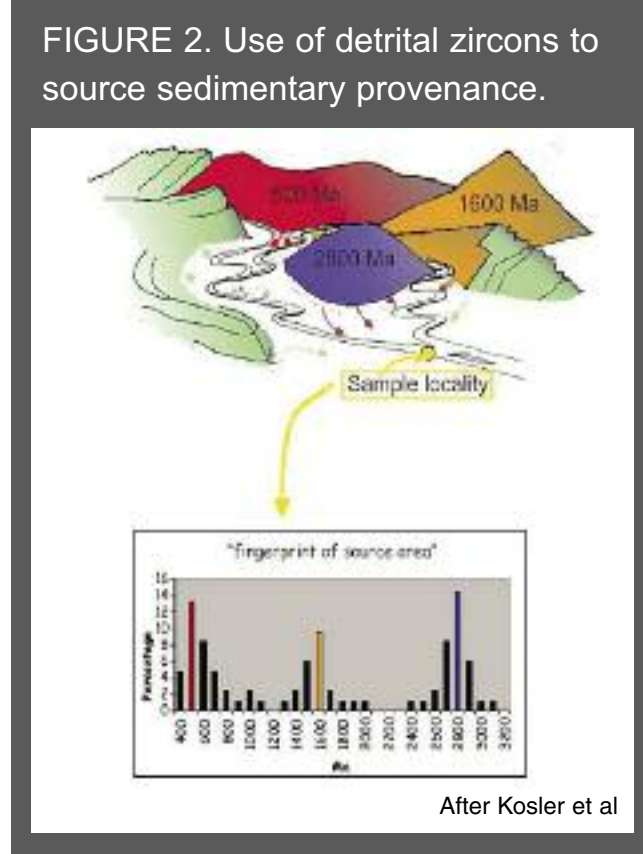
## Introduction

Detrital zircons, since they are highly chemically and mechanically inert, reflect the processes of crustal evolution that their host metamorphic and sedimentary deposits have undergone. The U-Pb isotopic system can be used to date the time of the zircon's crystallization and therefore the age of the body in which they are found.



For the past thirty years SHRIMP (Sensitive High Resolution Ion MicroProbe) has been used for the determination of isotope ratio in minerals (e.g. U-Th-Pb in monazite, zircon etc) for geochronological studies. Its strengths of essentially non destructive sampling and small spot sizes (< 25 µm) have made it the technique of choice but cost and complexity has limited its application with less than 20 instruments installed worldwide.

Access to such instruments is limited due to high purchase/running costs and sample throughput is low with ~ 75 analyses possible per day. By contrast, coupling a laser ablation system with a fast scanning, single collector ICP-MS demonstrates excellent performance for dating analysis of zircons. Sample turn around is very fast and through advanced, flexible hardware and software the laser ablation system can be treated as an autosampler allowing > 300 analyses per day – especially important for the analysis of detrital zircons where statistical limitations demand > 100 individual analyses for a single sediment sample.



## Key Advantages of Sector Field ICP-MS for U-Pb Dating of Zircons

### High Sensitivity

The Thermo Scientific ELEMENT 2 Sector Field ICP-MS is the most sensitive ICP-MS available in solution mode and the same holds true in dry plasma / laser mode. High sensitivities at small laser spot sizes (as shown in Table 1 for NIST 612) are mandatory in detrital zircon studies in order to maximize the number of analyzable zircons in provenance studies. Additionally, since meaningful data can be obtained at smaller spots with such a system, the high lateral & depth resolution available (30 µm spot with ~ 20 µm depth) allows the dating of complex polychronic zircons.

FIGURE 3. Instrument settings and sensitivity obtained for La and Th in NIST 612 with laser sampling parameters shown. Low oxides are maintained with sector field ICP-MS for independence from spectral interferences.

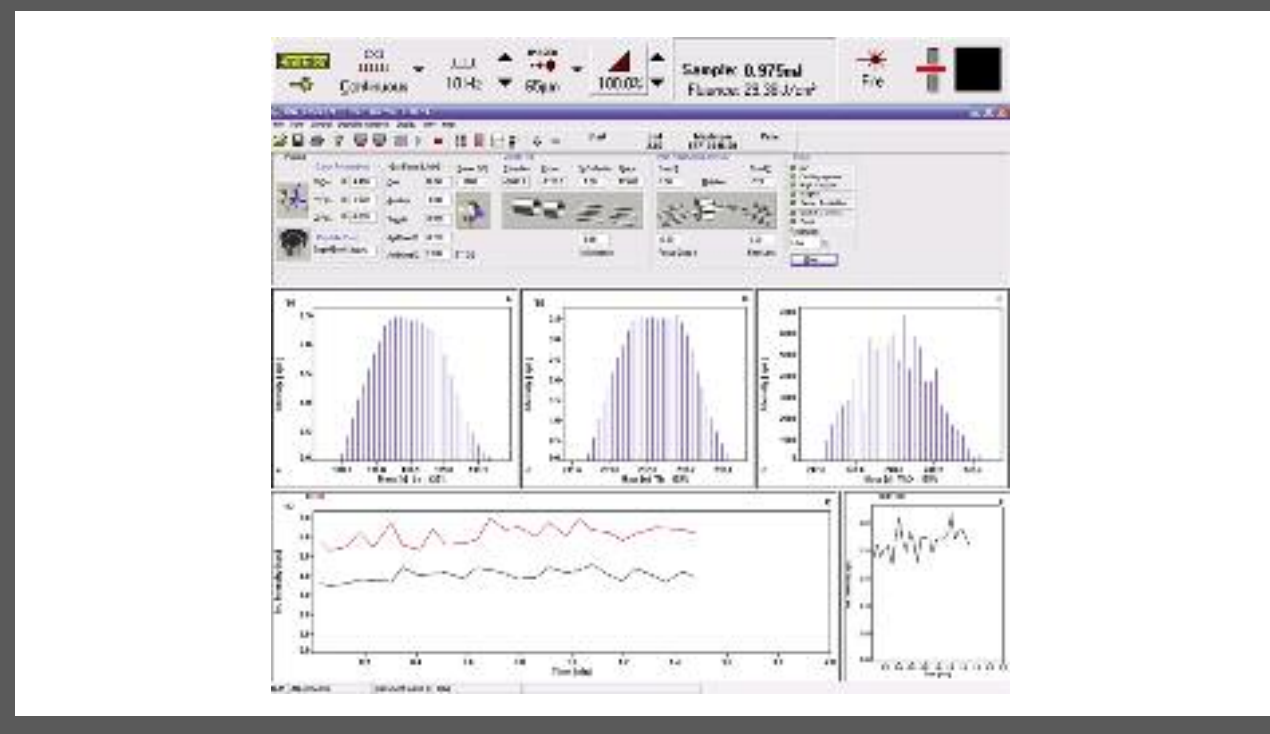


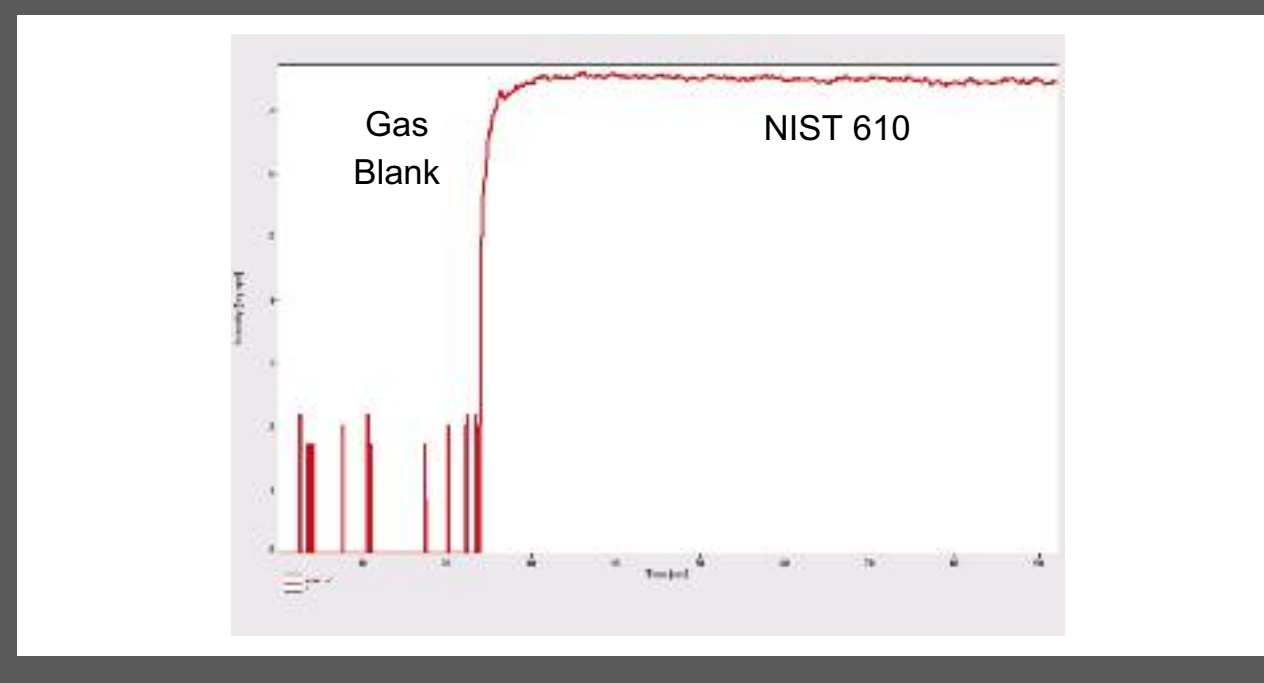
TABLE 1. LA-ICP-MS performance with the ELEMENT 2. All measurements made at a fluence of between 8 - 10 J/cm<sup>2</sup>

	<sup>139</sup> La	<sup>232</sup> Th	<sup>238</sup> U	<sup>232</sup> Th/ <sup>16</sup> O	ThO/Th Ratio
Gas Blank Average (cps)	5	1	2	1	
30 µm NIST 612 (cps)	237796	403393	513949	492	0.12
LoD (ppb)	0.49	0.09	0.17		
BEC (ppb)	0.72	0.06	0.15		
65 µm NIST 612 (cps)	1568101	2536592	3366142	3801	0.15
LoD (ppb)	0.07	0.01	0.03		
BEC (ppb)	0.11	0.01	0.02		

## Advanced Detection System

Through an ingenious detector design a virtual 'BOTH' detector mode provides a seamless crossover over 9 orders of magnitude across counting and analog modes of the dual mode secondary electron multiplier. The ELEMENT 2 detector provides a totally user interaction free, per scan update of the detector's cross calibration factor using a single, mass range independent value.

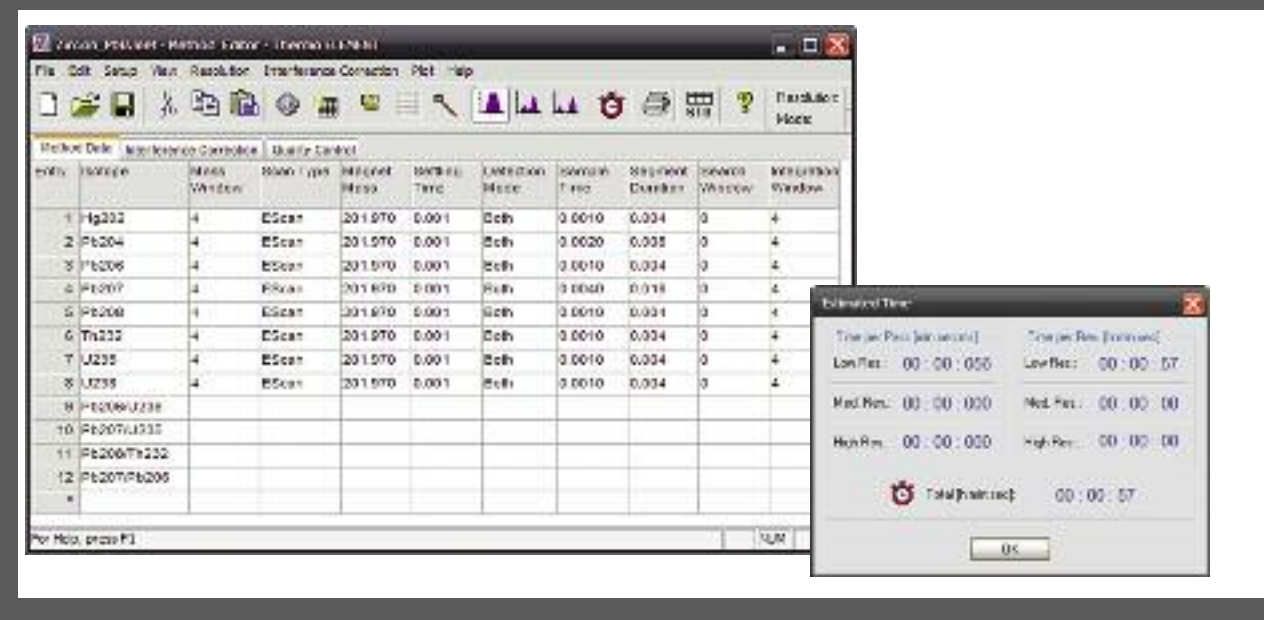
FIGURE 4. Time resolved analysis of <sup>238</sup>U in NIST 610 using a single point per peak in the BOTH detector mode over 7 orders of magnitude.



## High Scan Speed

The ELEMENT 2 analysis Method for the determination of U-Pb ratios as shown in Figure 5 can be summarized as:

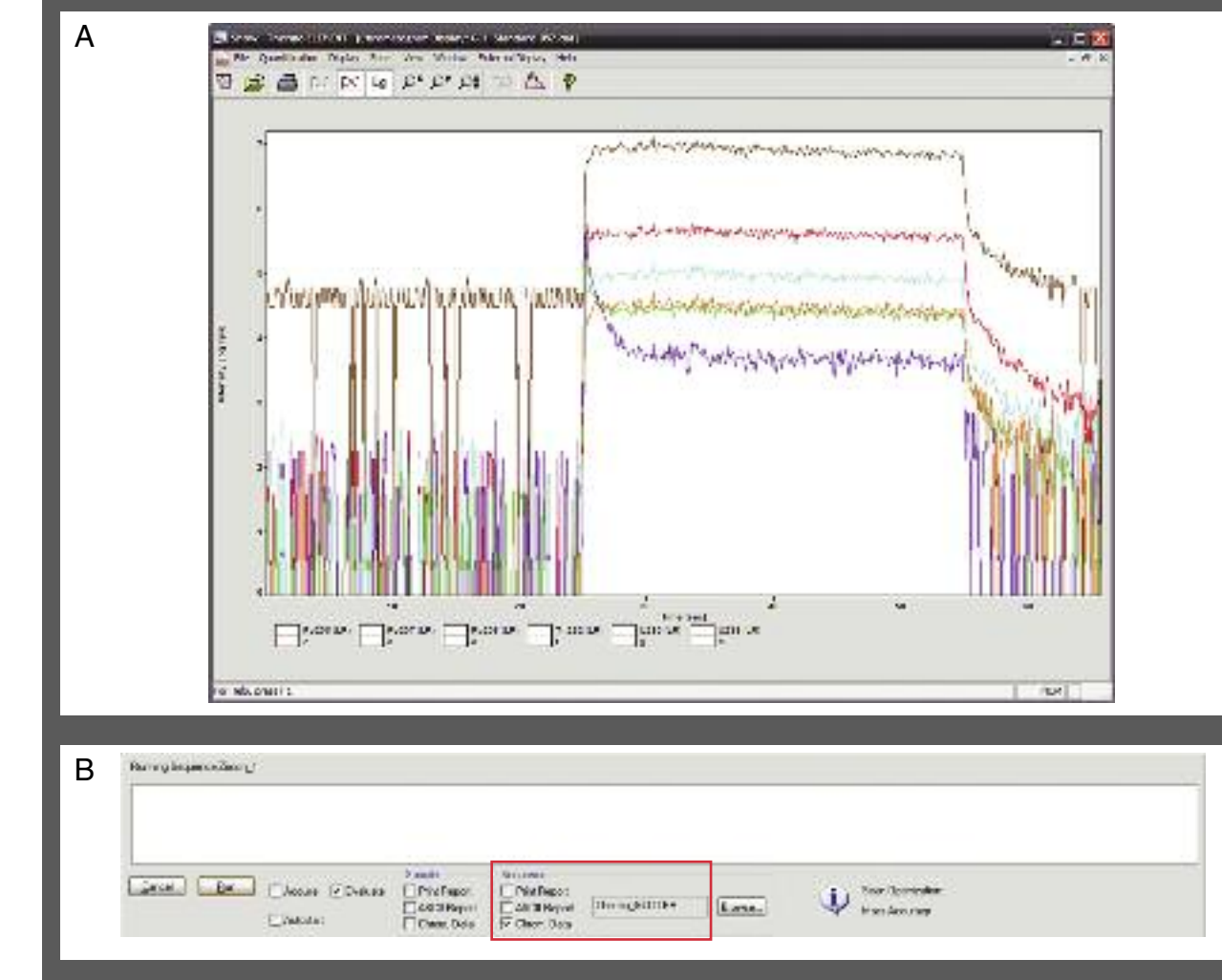
FIGURE 5. ELEMENT 2 Method for U-Pb ratios.



- 1 ms Settling Time for all isotopes
- Acquisition time per isotope of between 4 to 16 ms depending on sensitivity to address Counting Statistics limitations
- 4 data points per isotope (4% Mass Window, 100 Samples per Peak)
- 1000 scans in 57 s
- Time for one scan 56 ms, 48 ms data acquisition; duty cycle: 48/57 = 82%

## Mature Software

FIGURE 6A. TRA display of U-Pb analysis in the GJ-1 zircon. FIGURE 6B. Automated export of data into GLITTER for subsequent data reduction.



## Results

A selection of results from the U-Pb dating facility in GEUS Copenhagen are presented here to illustrate the use of the ELEMENT 2 in routine analysis of provenance zircons.

FIGURE 7A+B. Pb/U ages obtained for the PL zircon standard.

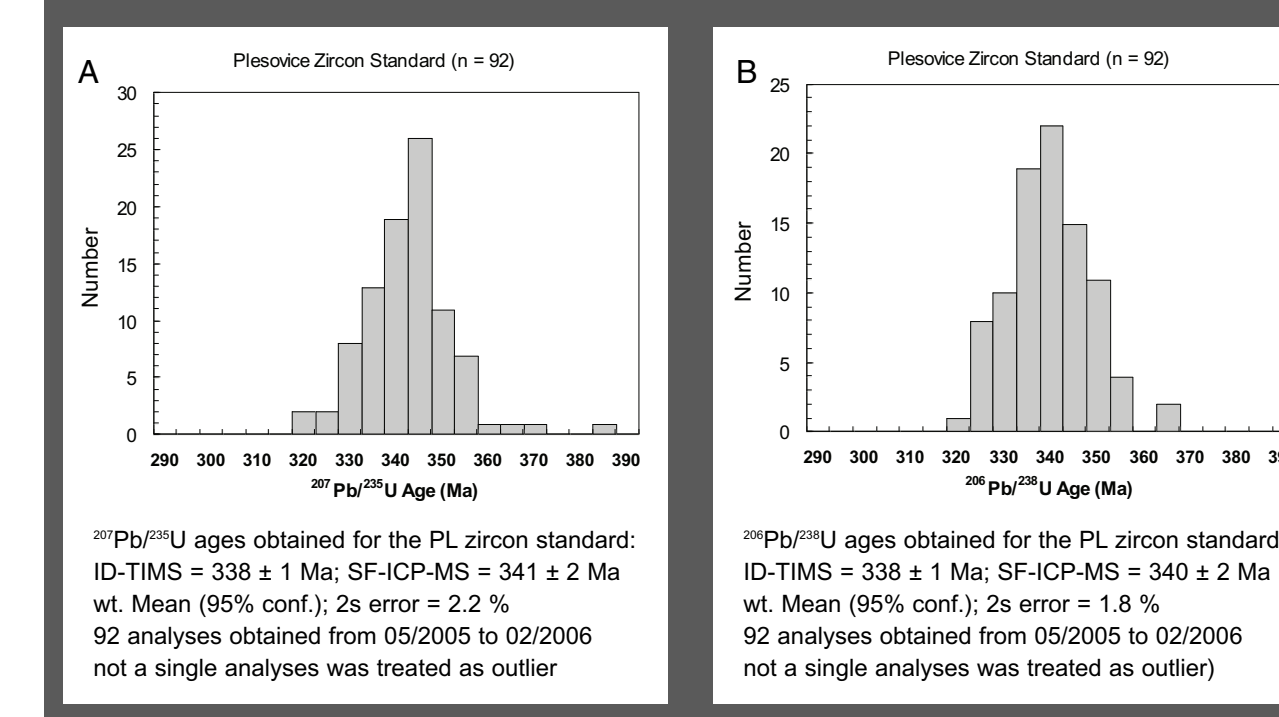


FIGURE 8A. Within-run reproducibility of the Plesovice (PL) zircon standard (ID-TIMS = 338 ± 1 Ma).

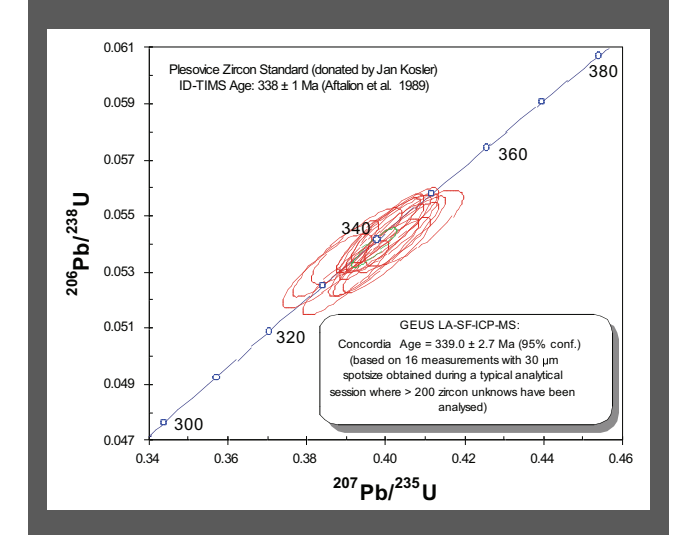


FIGURE 8B. Within-run reproducibility of the 91500 zircon standard (ID-TIMS = 1065 ± 0.4 Ma).

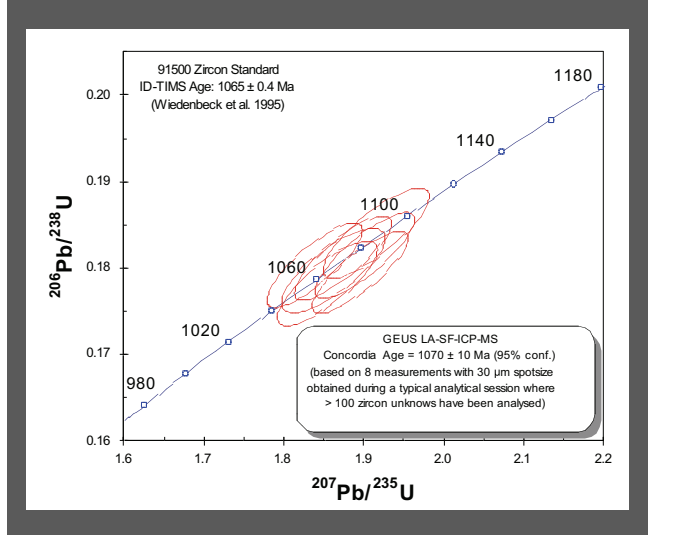
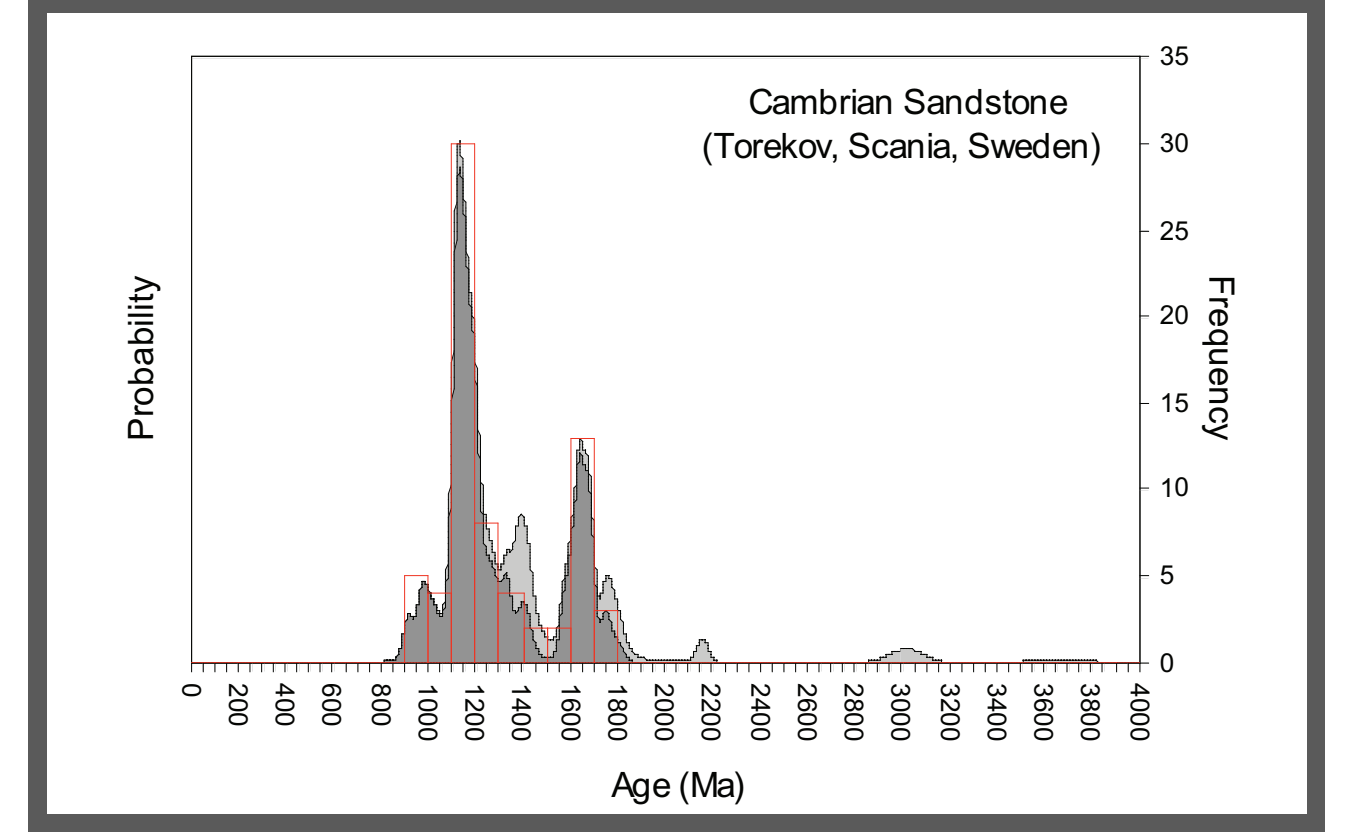


FIGURE 9. Dating of detrital zircons from a Cambrian sandstone (Torekov, Scania, Sweden). Maximum daily sample throughput: > 900 zircon U-Pb age dates.



## Conclusions

Laser ablation coupled with sector field ICP-MS is a low cost and easily accessible alternative to SHRIMP for the analysis of U-Pb ages in zircons and other minerals. The high sensitivity of the Thermo Scientific ELEMENT 2 in dry plasma maximizes the number of analyzable zircons in a sample leading to increased confidence in the U-Pb age obtained. Its fast scanning capabilities enable the high throughput required for the analysis of large numbers of detrital zircons in provenance studies. Through a combination of mature hardware and software, the ELEMENT 2 is the ideal ICP-MS for U-Pb dating simplifying the entire analytical process from automated, unattended interaction with the laser ablation system to data export into dedicated external software packages.