APPLICATION NOTE 30785

# ID-TIMS U-Pb geochronology at the 0.1‰ level using $10^{13}$ Ω amplifiers

Authors: J. Roberts[1], Z. Hu[2], J.F. Wotzlaw[3], H. Vollstaedt[1], M.P. Castellanos Melendez[3], C. Bouman[1], C. Chelle-Michou[3], N. Lloyd[1]

[1] Thermo Fisher Scientific, Bremen, Germany;

[2] Thermo Fischer Scientific, China;

[3] Institute of Geochemistry and Petrology, Department of Earth Sciences, ETH Zurich

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## Introduction

Uranium-lead geochronology provides valuable insights into the timing and rates of various geological processes throughout Earth's history. Isotope dilution thermal ionization mass spectrometry is the most precise and accurate technique for U-Pb geochronology. This technique is most commonly applied to single zircon crystals or crystal fragments resulting in small amounts of radiogenic Pb (typically <100 pg) and U (~1 ng) available for analysis. Precise and accurate analysis of such small samples requires sensitive ion detection systems. Here, we document recent advances in U-Pb geochronology using a Thermo Scientific™ Triton™ Plus TIMS equipped with Thermo Scientific™ $10^{13}$ Ω Amplifier Technology™.

## Method

### Samples and tracers

The synthetic EARTHTIME 100 Ma solution (Condon et al. 2008) and natural Archean zircon reference material OG-1 (Stern et al. 2009) were used to document the long-term performance and reproducibility of this technique. Both reference materials were spiked with the EARTHTIME $^{202}Pb$–$^{205}Pb$–$^{233}U$–$^{235}U$ tracer solution (Condon et al., 2015) and processed at ETH Zurich using protocols provided in Wotzlaw et al. (2017).

**Table 1. Cup configuration for Pb and $UO_2$ isotope measurements on the Triton XT TIMS.**

| Cup | T [°C] | L4 | L3 | L2 | L1 | C | H1 | H2 | H3 | H4 |
|---|---|---|---|---|---|---|---|---|---|---|
| Pb | ~1200 | | | | $^{202}Pb$ | $^{204}Pb$ | $^{205}Pb$ | $^{206}Pb$ | $^{207}Pb$ | $^{208}Pb$ |
| $UO_2$ | ~1360 | $^{233}UO_2$ | $^{235}UO_2$ | $^{238}UO_2$ | $^{238}U^{16}O^{18}O$ | | | | | |
| Amp. (Ω) | | $10^{13}$ | $10^{13}$ | $10^{13}$ | $10^{13}$ | SEM | $10^{13}$ | $10^{13}$ | $10^{13}$ | $10^{13}$ |

## Measurement protocols

The Triton Plus TIMS at ETHZ is equipped with one axial MasCom SEM and eight $10^{13}$ Ω amplifiers. Two different measurement protocols for the analysis of Pb isotope ratios were applied:

1. Dynamic peak hopping routine using the axial SEM
2. Static multicollection using $10^{13}$ Ω amplifiers with only $^{204}Pb$ measured in the axial SEM

U ($UO_2$) was always measured using a static multi-collection routine using $10^{13}$ Ω amplifiers. Details of the cup configuration can be found in Table 1.

In the first method, Pb isotopes were collected on the axial SEM by dynamic peak-hopping. After the Pb isotope analysis, the filament was heated up and U isotopes were measured as $UO_2$ employing a static routine on the $10^{13}$ Ω amplifiers.

In the second method, all Pb isotopes except for $^{204}Pb$ were measured statically on $10^{13}$ Ω amplifiers. The SEM yield was determined daily. U isotopes were measured using the same setup as in the first method. With this instrumental setup, it is possible to work with one cup configuration and a dedicated amplifier assignment.

**Table 2. Total measurement time for dynamic vs. static Pb isotope ratio analysis.**

| | Dynamic Pb | Static Pb |
|---|---|---|
| Cycles/block | 11 | 50 |
| Blocks | 30-40* | 12 |
| Integration time | 4.194 s | 4.194 s |
| Total integration on each isotope ratio | 23-31 min | 42 min |
| Measurement time | 330-440 min | 45 min |

*Dependent on signal stability

The detection characteristics were as follows:

$10^{13}$ Ω amplifiers

- Baseline noise (20 min): ± 2.8 x $10^{-18}$ A (2 SD; 0.28 µV, $10^{11}$ Ω scale)
- Inter-channel amplifier gain: ± 9.0 ppm (2 RSD)

Ion counting

- SEM yield stability ($^{204}Pb$): ± 0.4 %/24 h (2 RSD)

## Results

### ET100

Figure 1 shows how the internal precision of the $^{206}Pb/^{205}Pb$ isotope ratio evolves during a ET100 measurement as a function of analysis time, comparing the dynamic and static setup.

With dynamic SEM peak hopping, the internal precision approaches ~0.2 ‰ (2 SE) only after approximately two hours of measurement and gets to 0.15 ‰ after five hours (average intensity of 5.9 mV on $^{206}Pb$). With the static $10^{13}$ Ω measurement, the internal precision reaches the 0.1 ‰ level after 10 minutes of measurement time and settles to 0.08 ‰ (2 SE) after 45 minutes (average intensity of 55 mV on $^{206}Pb$). This comparison emphasizes the rapidity of high-precision Pb isotope data using the static measurement routine with $10^{13}$ Ω amplifiers.

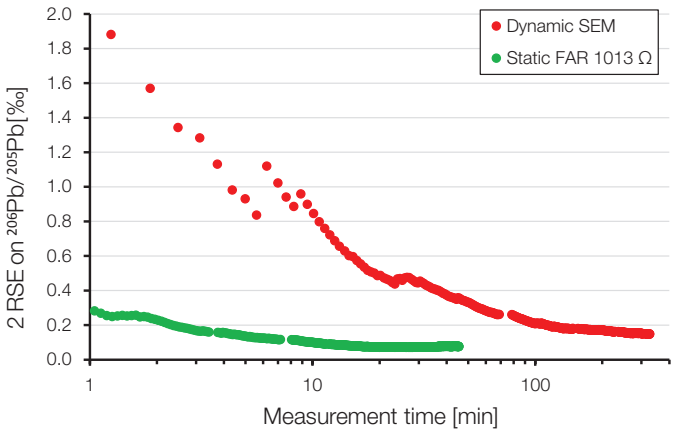


**Figure 1. Internal precision of the $^{206}Pb/^{205}Pb$ (2 S.E.)** as a function of measurement time, for dynamic (SEM peak hopping) and static ($10^{13}$ Ω) measurements.

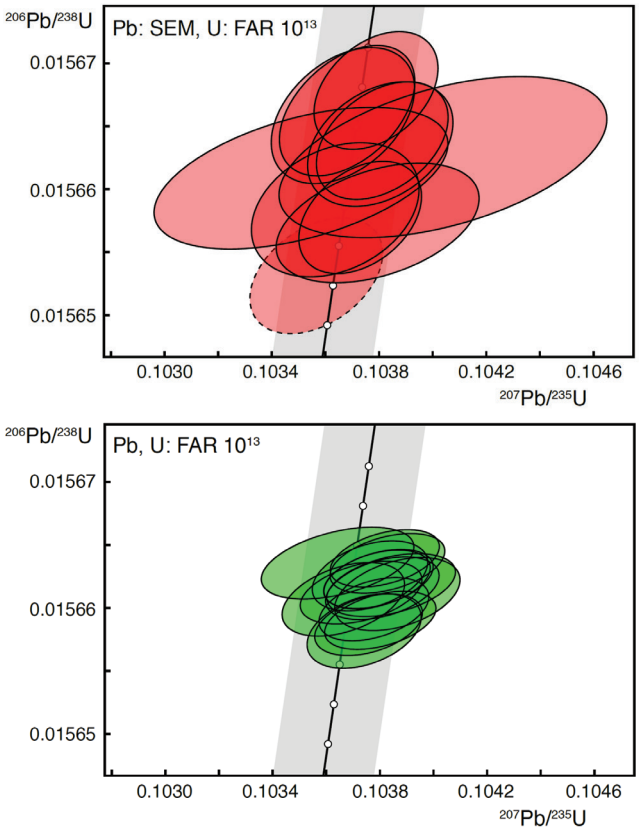


**Figure 2. Concordia diagrams for synthetic ET100 solution measurements using (a) dynamic Pb isotope ratio measurements on the axial SEM and (b) static Pb isotope ratio measurements on $10^{13}$ Ω amplifiers.**

Both setups, dynamic and static, yield precise and accurate results for the ET100 synthetic solution (Figure 2). However the precisions obtained for individual U-Pb dates using the two setups is different.

The static $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$ dates obtained with $10^{13}$ Ω amplifiers are 2-3 more precise than dynamic SEM peak hopping (0.015 ‰, vs 0.03 ‰, 2 SE). Also the external reproducibility is significantly improved using the static $10^{13}$ Ω amplifier setup (0.025 ‰ vs 0.057 ‰, 2RSD). Figure 3 displays the $^{206}Pb/^{238}U$ dates obtained with the two methods, showing the reproducibility and the attainable precision.

Notably, the superior precision of static Pb measurements is most significant for highly radiogenic zircons for which the internal precision of the measurement is the dominant source of uncertainty.

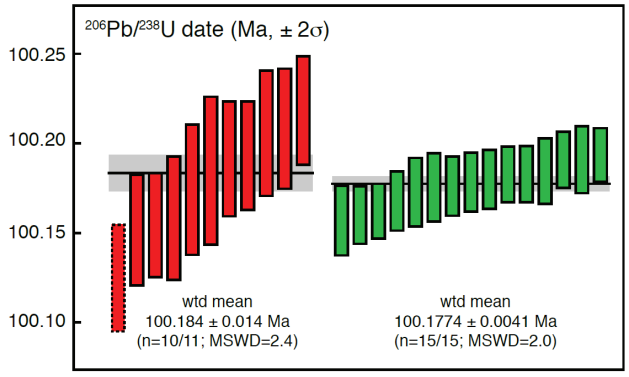


**Figure 3. Comparison of ET100 $^{206}Pb/^{238}U$ dates determined using dynamic SEM (red) and static $10^{13}$ Ω amplifier (green) Pb measurements.**

## OG-1

Both set-ups yield U-Pb data with similar degree of concordance (Figure 4) and the same range of $^{207}Pb/^{206}Pb$ dates. As for ET100, the analytical uncertainties for the static measurements are 2-3 times smaller compared to the dynamic measurements (Figure 4, insert). For OG-1, the higher internal precision of the static measurements results in resolvable differences in single crystal $^{207}Pb/^{206}Pb$ dates that are not resolvable with the SEM method. These differences reflect either a protracted zircon crystallization history or intercrystal U isotope heterogeneity (Tissot et al., 2019).

These results show that the precision of $^{207}Pb/^{206}Pb$ dates of Archean zircons is now primarily limited by the uncertainty on the $^{238}U/^{235}U$ ratio rather than by instrumental limitations.

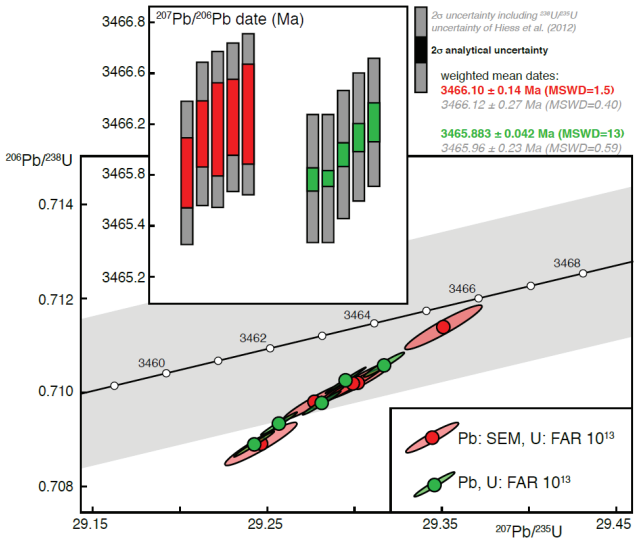


**Figure 4. $^{207}Pb/^{206}Pb$ dates (upper graph) and concordia for OG-1 determined from dynamic SEM (red) and static $10^{13}$ Ω amplifier (green) Pb measurements.** $^{207}Pb/^{206}Pb$ dates are shown with and without the uncertainty on the assumed $^{238}U/^{235}U$ ratio of Hiess et al. (2012).

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## Conclusions

We conducted a comparison of single SEM and static Pb isotope measurements for high-precision U-Pb geochronology using the Triton series TIMS equipped with $10^{13}$ Ω Amplifier Technology.

The static $10^{13}$ Ω amplifier measurements have some clear advantages over dynamic SEM peak hopping:

- Significant reduction in measurement time (up to a factor of 7)
- An extended dynamic range allows for more convenient measurements
- 3 times better precision for U/Pb and $^{207}Pb/^{206}Pb$ dates
- Higher sample throughput at higher precision

The larger dynamic range, higher duty cycle and higher gain stability of $10^{13}$ Ω amplifiers enables more efficient and more precise measurements.

The significant improvement in analytical precision and our results from OG-1 reference zircon point towards potential new avenues for studying crustal magmatism in Archean terranes at a resolution similar to much younger igneous systems.

### References


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