

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

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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™ $10^{13} \Omega$ 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 – ^{206}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 UO₂ 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 10¹³ 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 10¹³ Ω amplifiers with only ²⁰⁴Pb measured in the axial SEM

U (UO₂) was always measured using a static multicollection routine using 10¹³ 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 UO₂ employing a static routine on the 10¹³ Ω amplifiers.

In the second method, all Pb isotopes except for ²⁰⁴Pb were measured statically on 10¹³ 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:

10¹³ Ω amplifiers

- Baseline noise (20 min): ± 2.8 × 10⁻¹⁸ A (2 SD; 0.28 μV, 10¹¹ Ω scale)
- Inter-channel amplifier gain: ± 9.0 ppm (2 RSD)

Ion counting

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

Results

ET100

Figure 1 shows how the internal precision of the ²⁰⁶Pb/²⁰⁵Pb 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 ²⁰⁶Pb). With the static 10¹³ 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 ²⁰⁶Pb). This comparison emphasizes the rapidity of high-precision Pb isotope data using the static measurement routine with 10¹³ Ω amplifiers.

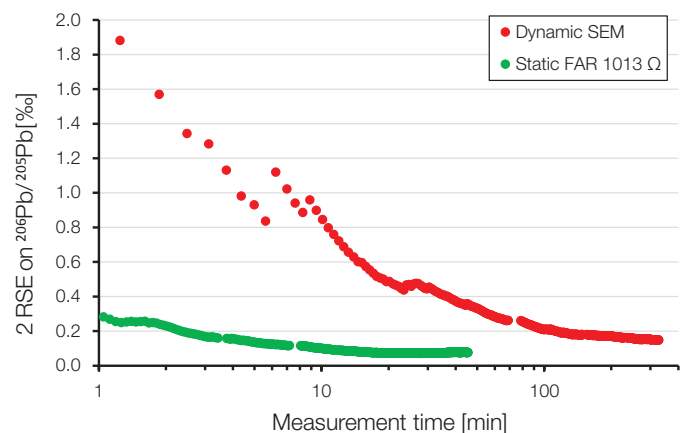


Figure 1. Internal precision of the ²⁰⁶Pb/²⁰⁵Pb (2 S.E.) as a function of measurement time, for dynamic (SEM peak hopping) and static (10¹³ Ω) measurements.

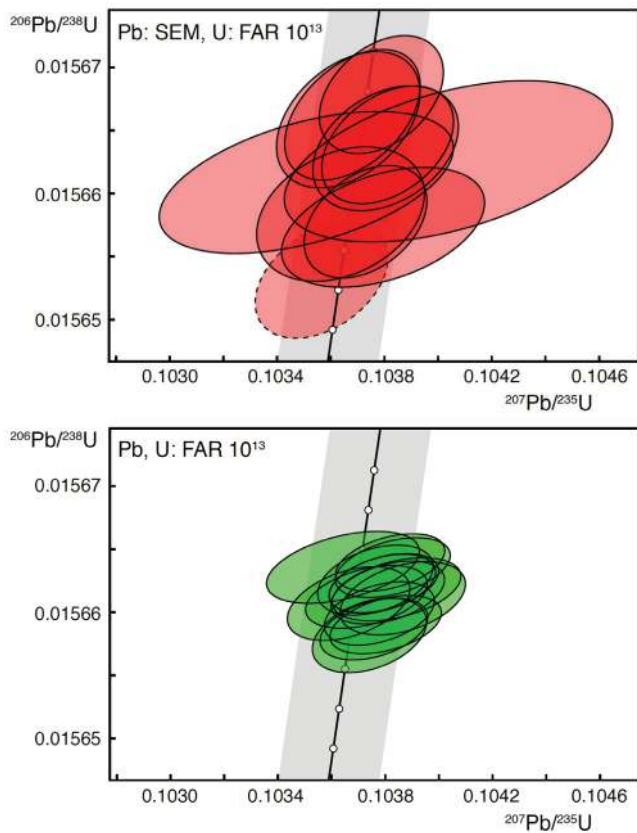


Figure 2. Concordia diagrams for synthetic ET100 solution measurements using (a) dynamic Pb isotope ratio measurements on the axial SEM and (b) static Pb isotope ratio measurements on $10^{13} \Omega$ amplifiers.

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 $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ dates obtained with $10^{13} \Omega$ 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 $10^{13} \Omega$ amplifier setup (0.025 % vs 0.057 %, 2RSD). Figure 3 displays the $^{206}\text{Pb}/^{238}\text{U}$ 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.

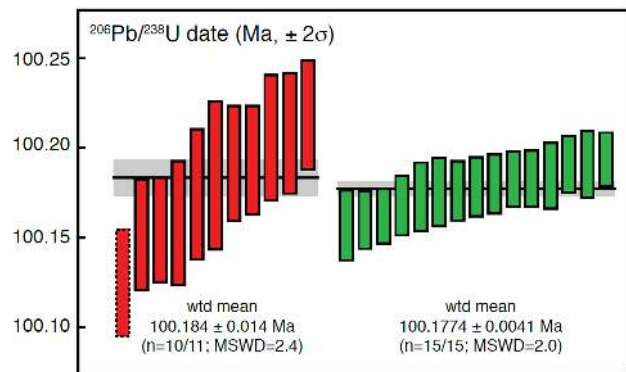


Figure 3. Comparison of ET100 $^{206}\text{Pb}/^{238}\text{U}$ dates determined using dynamic SEM (red) and static $10^{13} \Omega$ amplifier (green) Pb measurements.

OG-1

Both set-ups yield U-Pb data with similar degree of concordance (Figure 4) and the same range of $^{207}\text{Pb}/^{206}\text{Pb}$ 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 $^{207}\text{Pb}/^{206}\text{Pb}$ 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 $^{207}\text{Pb}/^{206}\text{Pb}$ dates of Archean zircons is now primarily limited by the uncertainty on the $^{238}\text{U}/^{235}\text{U}$ ratio rather than by instrumental limitations.

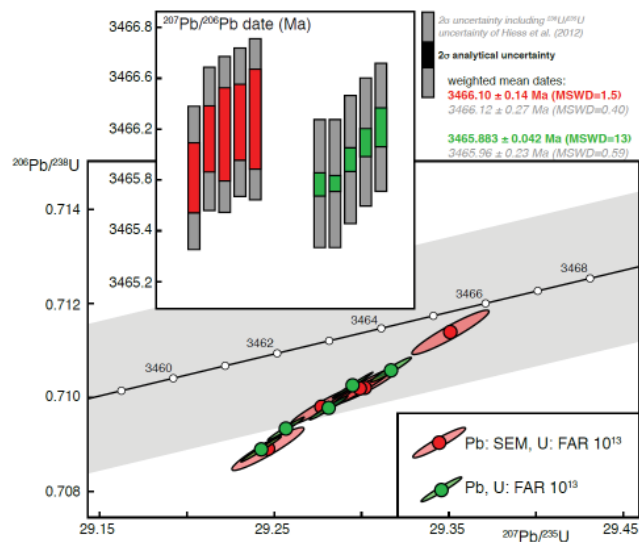


Figure 4. $^{207}\text{Pb}/^{206}\text{Pb}$ dates (upper graph) and concordia for OG-1 determined from dynamic SEM (red) and static $10^{13} \Omega$ amplifier (green) Pb measurements. $^{207}\text{Pb}/^{206}\text{Pb}$ dates are shown with and without the uncertainty on the assumed $^{238}\text{U}/^{235}\text{U}$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

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 $^{207}\text{Pb}/^{206}\text{Pb}$ 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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