

Highlights of Analytical Sciences in Switzerland

Division of Analytical Sciences

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Uranium – Lead Geochronology by ID-TIMS at Highest Precision and Reproducibility

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Age determination utilizing the radioactive decay of $^{238,235}\text{U}$ into $^{206,207}\text{Pb}$ is one of the backbones of modern Earth sciences. Precise and accurate temporal correlations are needed to understand the interaction of geosphere, hydrosphere, atmosphere, and life in the geological past. A timely example are periods of dramatic biodiversity loss ('mass extinctions') in the geological past that can be related to largest-scale volcanism (Large Igneous Provinces or LIPs), triggering profound disturbance of the carbon cycle and the climate, and affecting life. The geological record is mostly restricted to marine life, which has repeatedly suffered near-extinction. The most pronounced one at the Permian-Triassic boundary (252 million years ago) coincides with volcanic activity in the Siberian LIP. Precise U-Pb dating of these volcanic products, as well as of volcanic ash beds within marine sedimentary sections, allows for temporal correlation between volcanic activity, changes in biodiversity and marine biomass, and seawater temperature at a precision of a few 10^4 years.

The dating employs isotope-dilution techniques using a $^{202,205}\text{Pb}$ – $^{233,235}\text{U}$ mixed tracer solution, which is distributed by the EARTHTIME consortium. This solution is precisely known for concentration and isotope composition of U, Pb and its U/Pb ratio, and allows for precise Pb, U isotope analysis of individual, 100- μm -sized zircon (ZrSiO_4) crystals through thermal ionization mass spectrometry. One such sample contains 2–5 pg (10^{-12}g) of radiogenic $^{206,207}\text{Pb}$, which is isotopically analyzed in an ultraclean environment at a total procedural background level of 0.1–0.3 pg Pb. However, the U-Pb system in zircon presents two main challenges: (1) zircon crystallized in a magmatic system over several 10^5 years, therefore 10 to 20 analyses of carefully selected zircon grains are needed per sample to identify the youngest products of crystallization; (2) the radioactive alpha-decay of U, Th in zircon creates profound damage of the zircon crystal lattice that no longer behaves as a closed system for radiogenic nuclides. Therefore, an empirical 'chemical abrasion' treatment removes domains that have undergone $>2 \times 10^{18}$ alpha-decays/g prior to dissolution and analysis.

The precision, accuracy and repeatability of a U-Pb laboratory is controlled *via* isotope-dilution analysis of a synthetic EARTHTIME isotope calibration solution, which allows intra- and interlaboratory calibration at the 0.01% level of uncertainty for an apparent $^{206}\text{Pb}/^{238}\text{U}$ date.

Long-term analysis of this calibration solution has confirmed that high-precision $^{206}\text{Pb}/^{238}\text{U}$ dates are reproducible between different laboratories at a precision level of 0.01% (2 σ), providing a temporal resolution of 25'000 years for the correlation of environmental and biotic crisis at the Permian-Triassic boundary 252 million years ago.

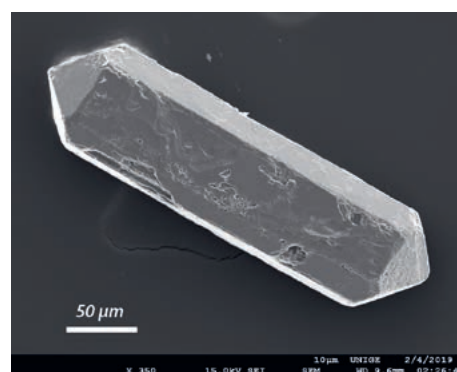


Fig. 1. Secondary electron image of a zircon (ZrSiO_4) in a volcanic ash bed used to date the age of deposition in a sedimentary rock.

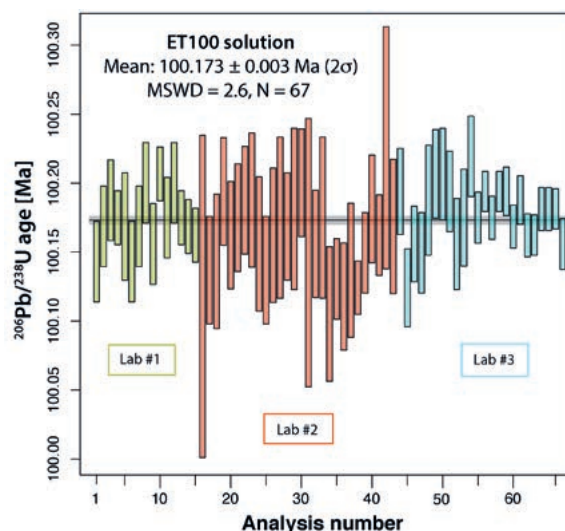


Fig. 2. Measured apparent $^{206}\text{Pb}/^{238}\text{U}$ dates for the EARTHTIME ET100 calibration solution in three laboratories applying identical analytical techniques and using the EARTHTIME $^{202,205}\text{Pb}$ – $^{233,235}\text{U}$ tracer for isotope dilution.

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