LA-ICP-MS U/Pb dating of CA-treated zircons: improved technique for accurate geological interpretation

LA-ICP-MS U/Pb датиране на химично абразирани циркони: усъвършенствана техника за коректна геоложка интерпретация

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Introduction

Chemical Abrasion (CA) technique (Mattinson, 2005) is applied routinely to zircons that are analyzed by Isotope Dilution-Thermal Ionization Mass Spectrometry (ID-TIMS). CA-ID-TIMS is known as a high precision method (2σ uncertainties <0.1%) for resolving lead loss and improving the interpretation of U/Pb zircon age data (e.g. Schaltegger et al., 2009; Von Quadt et al., 2011). Here, we argue that combining CA with the widely applied Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) also improves the precision and accuracy of zircon dates, while removing the substantial parts with lead loss and reducing data scatter. As a consequence, the technique improves the precision of age dating and allows the correct interpretation of geological data (Von Quadt et al., 2014).

Samples, analytical methods and results

For present study we choose magmatic samples of different age (Paleozoic, Mesozoic and Cenozoic), as well as one metamorphic sample of Neoproterozoic/Cadomian age. All zircon separates are analyzed by LA-ICP-MS before and after CA, and age data are in most cases compared with the CA-ID-TIMS $^{206}Pb/^{238}U$ dates that are considered as the most accurate age.

LA-ICP-MS U-Th-Pb isotope zircon analyses are carried out using a New Wave Research (NWR) 193 nm excimer laser UP-193FX attached to a Perkin-Elmer ELAN DRC-e quadrupole Inductively Coupled Plasma-Mass Spectrometer (LA-ICP-MS) at the Geological Institute, Bulgarian Academy of Science in Sofia. An in-laboratory designed ablation cell with lowered position effects, "squid" smoothing device, energy density on sample ca. 8.8 J/cm^{-2} and repetition rate of 8 are used. Ablation craters are 35 μm. The second equipment is PerkinElmer Elan 6100 ICP-MS coupled to 193 nm ArF-Excimer laser ablation system similar to a Geolas system at the Institute of Geochemistry and Petrology, ETH-Zurich. The laser was operated at 10 Hz, spot size 40 μm and fluence of 4 J/cm^{-2}. All experiments were performed using He as carrier gas. Preliminary selection of the background, analysis signal intensities, instrumental drift correction and data calculation was performed using the Glitter (Van Achterberg et al., 2001) and Iolite (Paton et al., 2011) software. Concordia age calculation and plotting were performed using the Isoplot/Ex rev. 2.49 (Ludwig, 2001).

The Cenozoic sample represents an andesite (029-5) of the Cu-Au porphyry deposit at Buchim, Macedonia. The zircons are characterized by high uranium concentrations between 834 ppm and 2298 ppm and dated at 24.480 ± 0.048 Ma by CA-ID-TIMS. The obtained LA-ICP-MS $^{206}Pb/^{238}U$ average age of the CA-treated zircons is 24.41 ± 0.21 Ma and they overlap perfectly with the ID-TIMS data, whereas the non-CA-treated zircons yield an age of 23.50 ± 0.25 Ma. An important observation is that CA treatment appears to reduce age scatter. Scatter of the $^{206}Pb/^{238}U$ ages of 0.29 Ma for CA-treated zircons is lower, compared to a greater scatter (0.73 Ma) for non-CA zircons.

The Mesozoic sample DG026 represents a granodiorite from the Romanian part of the >1600 km long Cretaceous magmatic belt in Eastern Europe. Uranium concentrations vary between 498 ppm and 682 ppm and no inherited lead components were found. U-Pb zircon CA-ID-TIMS yields a concordia age of

76.413 ± 0.088 Ma. Sample DG026 clearly shows the difference in $^{206}Pb/^{238}U$ ages acquired from non-CA and CA treated zircons. The obtained $^{206}Pb/^{238}U$ ages are 74.14 ± 0.65 Ma and 76.13 ± 0.45 Ma (95% conf.) reveal a clear deference in timing of the magmatism. The obtained LA-ICP-MS ages of CA-treated zircons coincide within error with the ages ID-TIMS method. A second, granitic sample from the North American Cordillera with uranium-rich zircons reveals also clear younging of >3% in the non-CA treated zircons, showing an $^{206}Pb/^{238}U$ age 147.4 ± 1.6 Ma, compared with 152.3 ± 1.7 Ma of the CA-treated zircons.

The granite sample AvQ244 belongs to the basement in Tran region, Western Bulgaria (Dyulgerov et al., 2010). The magmatic zircons have high uranium concentration mainly between 890 and 2170 ppm. Four out of seven zircons define a Variscan CA-ID-TIMS age of 333.60 ± 0.66 Ma. Two of the measured zircons are slightly younger, but they were more gently CA-treaded and obviously the shorter chemical abrasion has failed to entirely eradicate zones with Pb loss. From the other side the CL-imaging show inherited cores in some grains. For the age calculations we have taken only data for the magmatic rims/grains. The CA-LA-ICP-MS $^{206}Pb/^{238}U$ average age of 331.8 ± 4.7 Ma coincides with the CA-ID-TIMS concordia age within error. Non-CA treated zircons of sample AvQ244 yield a considerably younger mean $^{206}Pb/^{238}U$ age 306 ± 10 Ma and the data scatter is wider (280–340 Ma).

Finally, a low-grade orthometamorphic sample – a metadiorite from the Struma Diorite Formation near the village of Topolnitsa in western Bulgaria was analyzed using only LA-ICP-MS method. Uranium content in the zircons is estimated to vary between 40 and 370 ppm. Again, a clear deference in CA- and non-CA treated zircons appears, combined with a wider spread of data for the non-treated grains. Non-CA treated zircons have individual $^{206}Pb/^{238}U$ ages between 551 ± 20 Ma and 628 ± 23 Ma (2σ uncertainties), the majority of data being younger than 600 Ma. An average age of 566 ± 4 Ma is calculated using 25 concordant zircons. The $^{206}Pb/^{238}U$ average age and the uncertainty increase to 575 ± 7 Ma, when using all 30 zircon analyses (including the outlier with an age >610 Ma). CA-treated zircons yield a concordia age of 590 ± 4 Ma, whereas the individual zircons are older than 570 Ma ($^{206}Pb/^{238}U$ age from 574 ± 16 Ma to 604 ± 16 Ma).

Conclusion

All LA-ICP-MS analyses on CA-treated zircon crystals show up to 50% less data scatter compared to the non-CA treated zircon grains and thus a reduction of the calculated errors is apparent. The obtained weighted average LA-ICP-MS $^{206}Pb/^{238}U$ ages of the CA-treated zircon grains are up to 4–6% higher/older than those of the non-CA treated crystals, exceeding the analytical uncertainties of the LA-ICP-MS dating technique of 1–2%. The differences of the $^{206}Pb/^{238}U$ weighted mean ages are suggested to correlate with the U and Th contents in zircons (Allen, Campbell, 2012). Crystal radiation damage increases with time, more substantially in zircon grains with higher content of radioactive elements. The damaged crystal parts are removed by the CA technique, so that we can exclude lead loss as a reason for younging during geological interpretations. CA-LA-ICP-MS age data are in good agreement with the CA-ID-TIMS dates and suggest advantages of using it to define accurate ages in magmatic and orthometamorphic rocks.

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