

Analytical Techniques

Laser-ablation (LA)-ICP-MS method

Hand-picked zircon grains were mounted in 25 mm-diameter circular epoxy mounts and polished to expose a section at their inner core. Prior to their analysis, the grains were examined using cathodoluminescence (CL) imaging in order to recognize their internal structure and to identify cracks and mineral inclusions. Zircon U–Pb isotope analysis was performed by LA-ICP-MS technique using a Thermo-Finnigan Element II sector field ICPMS attached to a New Wave LUV213 laser ablation system ($\lambda=213$ nm). Ablation was carried out in a He carrier gas in a low volume (2.5 cm³) cell; laser beam parameters used were 30 μ m diameter; 5 Hz repetition rate 75% power output. Isotope data were acquired in peak-jumping mode on eight masses; ²⁰²Hg, ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb, ²³⁵U and ²³⁸U. Background and ablation data for each analysis were collected over 90 s, with background measurements (carrier gas, no ablation) being taken over the first 30 s prior to initiation of ablation. Data were collected at time-resolved mode allowing acquisition of the signal as a function of time (ablation depth), and subsequently recognition of isotopic heterogeneities within the ablated volume. Raw data were processed offline using an Excel® spreadsheet program (Frei and Gerdes 2008). Mass discrimination of the MS, and elemental fractionation during laser ablation were corrected by calibration against the GJ-1 zircon standard (Jackson et al. 2004), which was analyzed routinely during analytical sessions (three standard analyses at the beginning and end of every session of 33 unknowns, and two standard analyses every 10 unknowns). Prior to this correction, the change of elemental fractionation (e.g. Pb/U and Pb/Th ratios as function of ablation time and thus depth) was corrected for each set of isotope ratios by applying a linear regression through all measured ratios versus time, excluding some outliers (>2 s.e.), and taking the intercept t=0 as the correct ratio. Changes in isotopic ratios arising from laser drilling into domains of distinct Pb/U ratio (core/rim), mineral inclusions, and zones affected by Pb loss (metamictization/cracks), can usually be detected by careful monitoring of the time-resolved signal, such analyses are normally rejected. Common Pb correction was applied only when the interference- and background-corrected ²⁰⁴Pb signal was significantly higher than the detection limit of about 20 cps. The latter is limited by the amount of Hg in the carrier gas and the accuracy to which the ²⁰²Hg and thus the interfering ²⁰⁴Hg can be monitored. Corrections made were based on model common lead composition of Stacey and Kramers (1975). Data presentation was made with Isoplot (Ludwig 2001). In order to monitor the reproducibility and accuracy of our analytical procedure, the standard zircon 91500 (Wiedenbeck et al. 1995) has been reproduced with an age of 1063 \pm 3 Ma.

Isotopic dilution-thermion mass spectrometer (CA-ID-TIMS) method

Samples for ID-TIMS were processed using standard mineral separation techniques. These include crushing and sieving, before concentration of heavy minerals by heavy liquids (bromoform, methyleniodide) and magnetic-separation with a Frantz isodynamic separator. Zircon grains with the size of 100 μm to 180 μm were handpicked from the > 1.6 Amp fraction of the heavy mineral separate for ID-TIMS. The zircons were put over night into an oven at 900°C (Annealing, Mattison 2005). After cooling down they were washed with 6 N hydrochloric acid (HCl) and acetone ($\text{C}_3\text{H}_6\text{O}$). The zircon grains were weighted, transferred to small Savillex beakers (Parrish 1987) and put with 24 N hydrofluoric acid (HF) for 6 to 12 h into a Parr bomb at 180 °C. HF was decanted and the vials loaded again with 24 N HF and a mixed $^{205}\text{Pb}/^{235}\text{U}$ -spike. The Savillex vials were then placed into a Parr bomb. After dissolution at 180 °C for 96 h and subsequent evaporation to dryness at ca. 80 °C on a hotplate, the samples were converted into chloride by adding 0.2 ml 3 N HCl. Chemical separation of lead (Pb) and uranium (U) on 200 μl columns (ion-exchange resin AG 1 \times 8, 100–200 mesh) followed the method of Krogh (1973). U and Pb isotope ratios of zircon were obtained using a Finnigan MAT 261 mass spectrometer in static multicollector mode with simultaneous ion counting of ^{204}Pb (Dörr et al. 2002). All isotopic ratios were corrected for mass fractionation (1.0 ± 0.3 ‰/a.m.u), blank (appx. 1-3 pg) and initial lead using the Stacey and Kramers (1975) model lead composition. Zircon standard GJ-1 (Jackson et al. 2004) and M257 (Nasdala et al. 2008) were repeatedly analysed under the same conditions as the samples in order to monitor the reproducibility and accuracy. It yielded a concordia age at 607 ± 2 Ma ($n = 5$) and 562.6 ± 0.6 Ma ($n = 4$), respectively. U–Pb data were calculated using the program PBDAT (Ludwig 1980) and isotope ratios were plotted using Isoplot (Ludwig 2001), with error ellipses reflecting 2σ uncertainties.