

ELECTRONIC SUPPLEMENT

American Mineralogist FebMar 2015, AM-15-103, Schaltegger et al.

ANALYTICAL TECHNIQUES

Scanning electron microscopy:

Crystals ZFG2b and c were imaged for their cathodoluminescence using a CamScan MV2300 scanning electron microscope at the University of Lausanne, in order to document their internal structure, overgrowths and zonation. From some mineral fillings in the ubiquitous cracks, semi-quantitative EDS analyses were carried out using a JEOL JSM7001F scanning electron microscope, equipped with a JED2300 EDS system at the University of Geneva.

Electron backscatter diffraction (EBSD):

The surface of the epoxy-mounted crystals ZFG2b and c was polished down to 0.25 μm with successive grades of diamond paste followed by a further two-hour polishing with 25 nm colloidal silica suspension (pH 9.8) on a Buehler Phoenix 4000 polisher. The sample surface was kept uncoated in order to maximize the backscattered signal and ensure good EBSD pattern quality. Electron backscattered diffraction (EBSD) was carried out at the University of Lausanne using a Tescan Mira LMU SEM operated at 20 kV acceleration voltage, ~ 1.5 nA probe current, 23 mm working distance and 70° sample tilt, and equipped with a Nordlys S detector. EBSD patterns were collected using Oxford Instruments Channel 5.10 software package and indexed with the match unit *Zircon 5260* recommended by Reddy et al. (2008). As EBSD was performed over a large area, a combination of beam and stage scan modes was used. The raw EBSD map was noise reduced using the standard wildspike correction method and a six-neighbor zero solution extrapolation.

Trace element composition:

The trace element abundances in zircon were analyzed by laser ablation ICPMS using a Perkin-Elmer ELAN 6100 DRC quadrupole mass spectrometer interfaced to a GeoLas 193 nm excimer ablation system (Lambda Physik, Germany) at the University of Lausanne. The ablation system was operated at a 10 Hz repetition rate, 60 μm pit size, and c. 10 J/cm^2 on-sample energy density. Helium was used as a carrier gas. Background and signal were measured for 60-70 and ~ 25 s, respectively. The NIST SRM 610 synthetic glass served for external standardization; average element abundances in it were taken from Pearce et al. (1997). The raw data were reduced using LAMTRACE, a Lotus 1-2-3 based spreadsheet program written by S.E. Jackson (Macquarie University, Sidney).

LA-ICP-MS U-Pb dating:

A 3020 μm long transect from core to rim in crystal ZFG2b was studied for U-Pb age distribution, analyzing a total of 72 spots. Isotopic measurements were done using a 193 nm Excimer laser (New Wave) coupled to an ELEMENT2 XR sector-field, single-collector ICP-MS

at the University of Lausanne. Operating conditions were largely identical to those described in Ulianov et al. (2012) and included a 35 μm spot size combined with a relatively low on-sample energy density of 2.2-2.3 J/cm² and a repetition rate of 5 Hz to minimize the fractionation. Helium was used as a carrier gas (1.07 L min⁻¹). Synthetic glass SRM 612 from NIST was used to maximize the sensitivity and to control the oxide and doubly charged ion production rate during the instrument optimisation. The instrument mass bias was calibrated by repeated measurements of one grain of reference zircon material GJ-1 (CA-ID-TIMS ²⁰⁶Pb/²³⁸U age of 600.5 \pm 0.4 Ma; Schaltegger et al., unpublished, in Boekhout et al. 2012). The calibration was repeatedly controlled using Carnegie zircon 91500 as a secondary standard (²⁰⁶Pb/²³⁸U age of 1065.4 \pm 0.3 Ma; Wiedenbeck et al. 1995); 20 out of 24 analyses carried out in parallel with the profile through ZFG2b yielded a mean ²⁰⁶Pb/²³⁸U age of 1058.7 \pm 2.4 Ma (MSWD=2.0). No common lead correction was applied due to the presence of ²⁰⁴Hg in the system.

CA-ID-TIMS U-Pb dating:

The zircon fragments of ZFG1 were mechanically abraded and analyzed in 1999 on a Thermo Finnigan MAT262 mass spectrometer at the ETH Zürich in ion counting mode, using a ²⁰⁵Pb-²³⁵U tracer solution. The used techniques are summarized in Schaltegger and Brack (2007). The selected fragments of sample ZFG2a and b as well as the grains of ZFG3 were chemically abraded after Mattinson (2005) and analyzed using the EARTHTIME ²⁰⁵Pb-²³³U-²³⁵U tracer solution. The methodology used for samples ZFG2 and 3 for zircon annealing and leaching, dissolution and chemical separation of Pb and U, isotopic analysis and data treatment, follows Schoene et al. (2010). Isotopic analyses were performed at the University of Geneva on a Thermo Scientific TRITON mass spectrometer equipped with a MasCom electron multiplier in ion counting mode. The U-Pb data are plotted as 2 σ error ellipses in concordia diagrams.

Hf isotope determinations:

Hf isotopic compositions were measured on the exact same volume of zircon dated by CA-ID-TIMS techniques. This involves retaining the usually discarded solution obtained as a product of ion exchange chemistry. The dried residue was dissolved in at least 1000 μl 2% HNO_{3(aq)} without any further element separation and introduced into the plasma with an Aridus II desolvating nebulizer connected to a Thermo-Scientific Neptune multi-collector ICP-MS at JWG University Frankfurt. To correct for isobaric interferences of Lu and Yb on mass 176 the isotopes ¹⁷²Yb, ¹⁷³Yb and ¹⁷⁵Lu were simultaneously monitored. The ¹⁷⁶Yb and ¹⁷⁶Lu were calculated using a ¹⁷⁶Yb/¹⁷³Yb of 0.796218 (Chu et al. 2002) and ¹⁷⁶Lu/¹⁷⁵Lu of 0.02658 (JWG in-house value). The instrumental mass bias for Hf isotopes was corrected using an exponential law and a ¹⁷⁹Hf/¹⁷⁷Hf value of 0.7325. In case of Yb isotopes the mass bias was corrected using the Hf mass bias of the individual integration step multiplied by a daily $\beta\text{Hf}/\beta\text{Yb}$ offset factor (Slama et al. 2008; Gerdes and Zeh 2008). All zircon LA-MC ICP-MS analyses were adjusted relative to the JMC 475 ¹⁷⁶Hf/¹⁷⁷Hf ratio of 0.282160. Every three unknowns were bracketed by one JMC475 standard measurement. The standard measurements did not indicate any systematic instrumental drift over the analysis time.

Oxygen isotope analysis:

The oxygen isotope composition (^{16}O , ^{18}O) of the samples were measured at the University of Lausanne, using a method adapted after Rumble and Hoering (1994) and described in more detail in Kasemann et al. (2001). Between 0.5 to 2 mg of sample was loaded onto a small Pt-sample holder and pumped out to a vacuum of about 10^{-6} mbar. After prefluorination of the sample chamber for 2 x 20 minutes, the samples were heated with a CO_2 -laser at 50 mbar of pure F_2 . Excess F_2 is separated from the O_2 produced by conversion to Cl_2 using KCl held at 150°C . The extracted O_2 is collected on a molecular sieve (5A) and subsequently expanded into the inlet of a Finnigan MAT 253 isotope ratio mass spectrometer. Oxygen isotope compositions are given in the standard δ -notation, expressed relative to VSMOW in permil (‰). Replicate oxygen isotope analyses of the standard used (NBS-28 quartz; $n = 4$) for the two runs had an average precision of ± 0.05 ‰ for $\delta^{18}\text{O}$. The accuracy of $\delta^{18}\text{O}$ values is better than 0.2 ‰ compared to accepted $\delta^{18}\text{O}$ values for NBS-28 of 9.64 ‰.

Diffusion calculations

The diffusion calculations used the equations from Crank (1975). The equations used determine how much daughter isotope would have formed over time t , and what % of daughter isotope would be lost over the same duration. The equations are only valid for a square heat pulse at constant temperature T , for a duration t and therefore do not resolve diffusional daughter isotope loss during increments shorter than time t . In the present diffusion calculations, t has been set to 100 ka, the model thus calculates the radiogenic ingrowth during 100 ka as well as the partial loss over the same duration. We have assumed spherical geometry for zircon, since we are not aware of any demonstration of anisotropic diffusional behaviour of Pb in zircon. The values for radiogenic Pb diffusivity through the zircon lattice have been taken from Cherniak and Watson (2001), which are $D_0 = 7.76 \cdot 10^{-2} \text{ m}^2/\text{s}$, and the activation energy $E = 545000 \text{ J/mol}$.

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Figures

Figure S1. Laser ablation ICP-MS $^{206}\text{Pb}/^{238}\text{U}$ results from 20 analyses of 91500 standard zircon, analyzed as secondary standard during the analytical session of ZFG2b. The MSWD of 2.0 for $N=20$ indicates a source of analytical error not accounted for during the data treatment (mass bias non-stationarity, see Ulianov et al., submitted)

Tables

Table S1. Laser ablation ICP-MS analyses of trace elements along the profile in crystal ZFG2b

Table S2. Laser ablation ICP-MS U–Pb data on crystal ZFG 2b

Table S3. U–Pb isotopic data acquired using CA-ID-TIMS and Hf isotope determinations on crystals ZFG 1, ZFG2a, b and ZFG3

Table S4. Oxygen isotope analyses on fragments of crystals ZFG 2a and b

