

APPENDIX 1: ANALYTICAL METHODS

1 GEOCHEMICAL METHODS

The majority of the whole-rock analyses were carried out by Labtium Ltd. All of these samples were analysed using X-ray fluorescence (XRF) (Labtium codes 175X and 176X) on pressed pellets. Methods 175X and 176X differ in the automatic sample preparation of the latter, contrary to the manual preparation used in 175X. Samples were first crushed with a jaw crusher (Mn-steel jaws) and ground using a tungsten carbide vessel. In XRF, samples are analysed for the following: major elements Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P and trace elements As, Ba, Bi, Ce, Cl, Cr, Cu, Ga, La, Mo, Nb, Ni, Pb, Rb, S, Sb, Sc, Sn, Sr, Th, U, V, Y, Zn and Zr. According to the normal convention, the main elements are listed as wt% of oxides and trace elements as elements in ppm in the Electronic Appendix. Total carbon was analysed with a carbon analyser (Labtium method 811L).

In certain samples, additional trace elements (Ce, Co, Dy, Er, Eu, Gd, Hf, Ho, La, Lu, Nb, Nd, Pr, Rb, Sc, Sm, Ta, Tb, Th, Tm, U, V, Y, Yb and Zr) were analysed by inductively coupled plasma mass spectrometry (ICP-MS) using Labtium method 308PM. For this method, the grinding was carried out using a carbide steel vessel. Total dissolution

of the samples was performed using perchloric acid.

Aqua regia partial leaching followed by analysis with inductively coupled plasma optical emission spectroscopy (ICP-OES) (Labtium code 511PM) was carried out on a limited number of sulphide-bearing samples. The elements analysed were Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Se, Sn, Sr, Te, Th, Ti, U, V, W, Y and Zn.

Gold, platinum and palladium analysis was performed with Labtium methods 703P, 704P and 705P, respectively, with the methods differing in the size of the sample (10 g, 25 g and 50 g, respectively). In this method, samples are prepared with the Pb-fire assay method and analysed using ICP-OES. For a detailed description of the analytical methods, see Rasilainen et al. (2007) and the website of Labtium Ltd (www.labtium.fi).

For those samples in which REE elements were determined in the Reactor Laboratory of the Technical Research Centre of Finland (VTT), the instrumental neutron activation analysis (INAA) method was applied following the procedure of Rosenberg et al. (1982).

2 MINERAL CHEMISTRY

A Jeol JXA-8200 electron microprobe analyser (EPMA) at the Centre of Microscopy and Nanotechnology of the University of Oulu, in wavelength dispersive X-ray spectrometer mode, was used to determine mineral compositions from thin sections. The acceleration voltage was 15 kV and the current of the electron beam 15 nA. The diameter of the beam was normally 10 µm, and 5 µm when

analysing the finest grained minerals. Oxide minerals were analysed for the following components: SiO₂, TiO₂, Al₂O₃, Cr₂O₃, Fe₂O₃, MgO, CaO, MnO, FeO, Na₂O, K₂O, BaO, PbO and ZnO. Sulphide minerals were analysed for Se, S, Co, As, Cd, Ni, Pb, Fe, Cu, Ag, Zn, Bi, Sb, Ti, V, Mn and Hg. Excel spreadsheets of AGTSoft and GabbroSoft[©] were utilised in processing the analytical data.

3 U–PB GEOCHRONOLOGY

3.1 Sample preparation

Samples weighting 5–20 kg were washed, crushed, washed using a Wilfley table, and treated with methylene iodide and Clerici® solutions for the separation of the heavy minerals. Non-magnetic heavy fractions were separated using a Frantz isodynamic separator, and zircons were finally selected by hand-picking for analyses. The grains were mounted in epoxy resin and sectioned approxi-

mately in half and polished. Back-scattered electron images (BSE) and/or cathodoluminescence (CL) images were prepared for the zircons to select the spot analysis sites. For certain samples, U–Pb dating was carried out *in situ* from thin sections. For these analyses, the samples were initially scanned using a secondary electron microscope (SEM) to locate the zircons and monazites.

3.2 TIMS

The decomposition of minerals and extraction of U and Pb for multigrain TIMS (thermal ionisation decoupled multicollector mass spectrometer) analyses followed the procedure described by Krogh (1973, 1982). Before analysis, zircons were treated using the chemical abrasion (CA) method of Mattinson (2005). ^{235}U – ^{208}Pb -spiked and unspiked isotopic ratios were measured using GTK's VG Sector 54 TIMS in Espoo. The measured lead and uranium

isotopic ratios were normalized to the accepted values of SRM 981 and U500 standards. Common lead corrections were carried out using the age-related Pb isotope composition of the model of Stacey and Kramers (1975) and errors of 0.2 (for $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$) and 0.1 ($^{207}\text{Pb}/^{204}\text{Pb}$). The U–Pb age calculations were performed using the PbDat program (Ludwig 1991) and the fitting of the discordia line using the Isoplot/Ex program (Ludwig 2003).

3.3 Nu Plasma HR multicollector ICPMS

U–Pb dating analyses were performed using a Nu Plasma HR multicollector ICPMS at the Geological Survey of Finland in Espoo. The technique was very similar to that of Rosa et al. (2009), except that a Photon Machine Analyte G2 laser microprobe was used. Samples were ablated in He gas (gas flows = 0.4 and 0.1 l/min) within a HelEx ablation cell (Müller et al. 2009). The He aerosol was mixed with Ar (gas flow = 0.8 l/min) prior to entry into the plasma. The gas mixture was optimized daily for maximum sensitivity. All analyses were carried out in static ablation mode. Normal ablation conditions were: beam diameter 20 μm , pulse frequency 5 Hz and beam energy density 0.55 J/cm². A single U–Pb measurement included 30 s of on-mass background measurement, followed by 60 s of ablation with a stationary beam. Masses 204, 206 and 207 were measured in secondary electron multipliers, and 238 in an extra high mass Faraday collector. The geometry of the collector block does not allow simultaneous measurement of ^{208}Pb and ^{232}Th . Ion counts were converted and reported as volts by the Nu Plasma time-resolved analysis software. ^{235}U was calculated from the signal at mass 238 using a natural $^{238}\text{U}/^{235}\text{U} = 137.88$. Mass number 204 was used as

a monitor for common ^{204}Pb . In ICPMS analysis, ^{204}Hg mainly originates from the He supply. The observed background counting rate on mass 204 was ca. 1200 (ca. 1.3×10^{-5} V) and had been stable at that level over the year before the analysis reported here. The contribution of ^{204}Hg from the plasma was eliminated by on-mass background measurement prior to each analysis. Age-related common lead (Stacey & Kramers 1975) correction was used when the analysis showed common lead contents above the detection limit. Signal strengths on mass 206 were typically $>10^{-3}$ V, depending on the uranium content and age of the zircon. Two calibration standards were run in duplicate at the beginning and end of each analytical session, and at regular intervals during the sessions. Raw data were corrected for the background, laser-induced elemental fractionation, mass discrimination and drift in ion counter gains and reduced to U–Pb isotope ratios by calibration to concordant reference zircons of known age, using protocols adapted from Andersen et al. (2004) and Jackson et al. (2004).

Standard zircons GJ-01 (609 \pm 1 Ma; Belousova et al. 2006) and an in-house standard A1772 (2712 \pm 1 Ma; Huhma et al. 2012) were used for calibration. The

calculations were performed off-line using an interactive spreadsheet program written in Microsoft Excel/VBA by T. Andersen (Rosa et al. 2009). To minimize the effects of laser-induced elemental fractionation, the depth-to-diameter ratio of the ablation pit was kept low, and isotopically homogeneous segments of the time-resolved traces were calibrated against the corresponding time interval for each mass in the reference zircon. To compen-

sate for drift in instrument sensitivity and Faraday vs. electron multiplier gain during an analytical session, a correlation of signal vs. time was assumed for the reference zircons. The algorithms used are described in Rosa et al. (2009). The concordant age offset from ID-TIMS ages for several samples including zircon 91500 (1066 Ma) and A382 (1877 ± 2 Ma; Patchett & Kouvo 1986, Huhma et al. 2012) does not exceed 0.5%.

3.4 Nu Plasma AttoM single collector ICPMS

U–Pb dating analyses were performed using a Nu Plasma AttoM single collector ICPMS at the Geological Survey of Finland in Espoo connected to a Photon Machine Excite laser ablation system. Samples were ablated in He gas (gas flows = 0.4 and 0.1 l/min) within a HelEx ablation cell (Müller et al. 2009). The He aerosol was mixed with Ar (gas flow = 0.8 l/min) prior to entry into the plasma. The gas mixture was optimized daily for maximum sensitivity. Typical ablation conditions were: beam diameter 25 μm , pulse frequency 5 Hz and beam energy density 2 J/cm². A single U–Pb measurement included a short pre-ablation, 10 s of on-mass background measurement, followed by 30 s of ablation with a stationary beam. ²³⁵U was calculated from the signal at mass 238 using a natural ²³⁸U/²³⁵U = 137.88. Mass number 204 was used as a monitor for common ²⁰⁴Pb. In ICPMS analysis, ²⁰⁴Hg mainly originates from the He supply. The observed background counting rate on mass 204 was 150–200 cps and had been stable at that level over the previous two years. The contribution of ²⁰⁴Hg from the plasma was eliminated by on-mass background measurement prior to each analysis. Age-related common lead (Stacey & Kramers 1975) correction was used when the analysis showed common lead contents significantly above the detection limit (i.e., >50 cps). Signal strengths on mass 206

were typically 100 000 cps, depending on the uranium content and age of the zircon.

Calibration standard GJ-1 (609 ± 1 Ma; Belousova et al. 2006) or in-house standard A382 (1877 ± 2 Ma; Huhma et al. 2012) was run at the beginning and end of each analytical session, and at regular intervals during the sessions. Raw data were corrected for the background, laser-induced elemental fractionation, mass discrimination and drift in ion counter gains and reduced to U–Pb isotope ratios by calibration to concordant reference zircons, using the program Glitter (Van Achterbergh et al. 2001). Further data reduction, including common lead correction and error propagation, was performed using an Excel spreadsheet written by Y. Lahaye and H. O'Brien. Errors include measured within-run errors (SD) and quadratic addition of reproducibility of the standard (SE). To minimize the effects of laser-induced elemental fractionation, the depth-to-diameter ratio of the ablation pit was kept low, and isotopically homogeneous segments of the time-resolved traces were calibrated against the corresponding time interval for each mass in the reference zircon. The concordant age offset from ID-TIMS ages for several samples, including zircon 91500 (1066 Ma) and A382 (1877 ± 2 Ma; Patchett & Kouvo 1986, Huhma et al. 2012), did not exceed 0.5%.

3.5 Nordic Cameca IMS 1270 secondary ion mass spectrometer (SIMS)

Single-grain analyses of zircons were performed with a Nordic Cameca IMS 1270 secondary ion mass spectrometer (SIMS) at the Swedish Museum of Natural History in Stockholm (NORDSIM facility). The spot diameter of the primary O₂⁻ beam was 20 μm . The instrument was operated in monocollection peak-hopping mode using an ion-counting electron multiplier detector. Pb, Th and U isotopes

from each spot were measured for 12 cycles following automated centring, mass calibration and adjustment of energy offset. Pb/U ratios were calibrated against regularly interspersed analyses of the 1065 Ma Geostandards zircon 91500 (Wiedenbeck et al. 1995). Correction for modern common lead was carried out using the isotope composition model of Stacey and Kramers (1975) assuming modern

surface contamination. The detailed analytical procedures are essentially the same as those described

by Whitehouse et al. (1999) and Whitehouse & Kamber (2005).

3.6 Data plotting

Plotting of the U–Pb isotopic data and age calculations were performed using the Isoplot/Ex program version 4.15 (Ludwig 2003). All the ages were cal-

culated with 2σ errors and without decay constants errors. Data-point error ellipses in the figures are at the 2σ level.

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