SHRIMP IIe/mc (IBERSIMS, UGR): U-Th-Pb geochronology

Hand-picked zircons from the studied samples, several grains of the TEMORA-1 standard (for isotope ratios; Black et al., 2003), one grain of the SL13 zircon standard (for U concentration, Claoué-Long et al., 1995), plus a few grain of the REG zircon (plenty of common lead, for calibrating the masses) are set in a 3.5 cm diameter epoxy mount (megamount), polished and documented using optical (reflected and transmitted light) and scanning electron microscopy (secondary electrons and cathodoluminescence). After extensive cleaning, mounts are coated with ultra pure gold (8 - 10 nanometers thick) and inserted into the SHRIMP for analysis. The analytical method follows that described by Williams and Claesson (1987). Each selected spot is rastered with the primary beam for 120 s prior to the analysis, and then analysed in 6 scans, following the isotope peak sequence $^{196}Zr_2O$, ^{204}Pb, $^{204.1}background$, ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{238}U, ^{248}ThO, ^{254}UO. Every peak of every scan is measured sequentially 10 times with the following total counting times per scan: 2 s for mass 196; 5 s for masses 238, 248 and 254; 25 s for masses 204, 206, 207 and 208. The primary beam, composed of $^{16}O^{16}O^-$, is set to an intensity of about 5 nA, with a 120 microns Kohler aperture, which generates 17 x 20 micron elliptical spots on the target. The secondary beam exit slit is fixed at 80 microns, achieving a resolution of about 5000 at 1% peak height.

All calibration procedures are performed on the standards included on the same mount. Mass calibration is done on the REG zircon (ca. 2.5 Ga, very high U, Th and common lead content). Every analytical session starts by measuring the SL13 zircon, which is used as a concentration standard (238 ppm U). The TEMORA-1 zircon (416.8 ± 1.1 Ma), used as isotope ratios standard, is then measured every 4 unknowns.

Data reduction is done with the SHRIMPTOOLS software (available from www.ugr.es/~fbea), specifically developed for IBERSIMS by F. Bea. This software is a new implementation of the original PRAWN software developed for the SHRIMP, and has been extensively checked against PRAWN and Ludwig's SQUID. SHRIMPTOOLS is platform-independent and runs on any Windows, Mac or Unix computer regardless of language, time, and date system settings. It has been written in the programming language of the STATA commercial package which implements powerful algorithms for robust regression, outlier detection and time-series analysis. The software calculates the intensity of each measured isotope in two steps. First, it uses the STATA letter-value display algorithm to find outliers in the ten replicates measured in each peak during each scan, discarding them and averaging the rest. Then, the blank, measured at 204.1 mass is subtracted from each peak. This may produce negative values in mass 204 when it recorded next to zero counts. Once normalised to the SBM measurements, the software calculates the 204/206, 207/206, 208/206, 254/238 ratios using Dodson's (1978) double linear interpolation method. The 206/238, 206/195, 238/195, and 248/254 ratios are calculated by dividing the value at the mid-time of the analysis of each isotope calculated from the robust regression lines of the peak average of each scan vs the time at which it was measured. Errors for Dodson interpolated ratios are calculated as the standard error of the (scans-1) interpolations for each ratio. Errors for the isotope ratios calculated by regression result from propagating accordingly the standard error of the linear

prediction at the mid-point of the analysis. The $^{206}Pb/^{238}U$ ratio is calculated from the measured $^{206}Pb^{+}/^{238}U^{+}$ and UO^{+}/U^{+} following the method described by Williams (1998). The error reported for $^{206}Pb/^{238}U$ includes (1) the error in UO^{+}/U^{+} (2) the error in the regression line $\ln(UO^{+}/U^{+})$ vs $\ln(^{206}Pb/^{238}U)$ (3) the standard error in the replicate measurements of the TEMORA zircon. For high-U zircons (U > 2500 ppm) $^{206}Pb/^{238}U$ is further corrected using the algorithm of Williams and Hergt (2000). Though seldom necessary, the software also permits correction for instrumental drift with time using the sequence of replicate measurements of the TEMORA zircon.

Negative ^{204}Pb values may arise from subtracting the blank from the 204 peak measurement when the later is very low, zero, one or two counts per 10 seconds. Zero counts on 204 and 1 count on 204.06 (the blank) result in negative 204/206 ratios. Despite negative isotope ratios having no physical meaning, there is a general agreement in the SHRIMP users community that negative 204 values should be kept for (1) balancing averages between different measurements (2) to counter-effect anomalously high blank measurements. Given that the blank is subtracted from masses 206 and 207, the negative 204 helps approximating the correct 207/206 ratio.

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SHRIMP IIe/mc (IBERSIMS, UGR): oxygen isotopes

Once analysed for U-Th-Pb, the megamounts are cleaned, re-polished, and coated with a 30 nm thick gold layer for oxygen isotope analyses. To this end the SHRIMP primary ion optics was set with a 120 µm Kohler aperture to produce a ~18 µm diameter spot on the mount surface. The Cs gun was set to yield a ~8 nA Cs+ beam. The e-gun to neutralise Cs ions on non conductive materials was set to an intensity of about 1 µA. Spots to be analysed were burned for about 5

minutes before measurements began. During this time the secondary beam and the e-gun were fully optimised to maximise the ^{16}O signal. Measurements were done in 2 sets of 10 scans each. The scans were of 10 seconds each so that the real data collection time was 200 seconds per spot. The electron induced secondary ion emission (EISIE) background was recorded for 10 s before and after each set, and subtracted from the ^{18}O and ^{16}O counts. As a standard we used the TEMORA-II zircon measured every four unknowns and cross-checked again the 91500 zircon every 20 unknowns. The reproducibility of the standards was excellent: $\partial^{18}O$ = 8.17 ± 0.34 (2s) for the TEMORA and $\partial^{18}O$ = 9.98 ± 0.26 (2s) respectively. Data reduction was done with the POXY program developed by P. Lanc and P. Holden at the Australian National University.

Perkin Elmer NexION 350X ICP-MS (UGR): trace elements

Zircon trace element analyses were done at the CIC-UGR LA-ICPMS laboratory using a Perkin Elmer NexION 350X ICP-MS coupled to a New Wave Research NR 213 laser ablation system. The analyses were performed on the different mounts than used for U-Th-Pb isotope analyses using the NIST-610 glass as external standard, which was measured every six unknowns. Spots to be analysed were pre-ablated for 15 seconds with a laser fluency of 2.5 Jcm-2, and then ablated during 60 seconds with a laser fluency of 7.5 Jcm-2. Every measurement was preceded by a blank, measured in the same conditions but with zero laser energy. Data reduction was done with the LA-ICPMS software written in the STATA™ programming language (available from F. Bea upon reasonable request).

ThermoScientific Neptune Plus MC-ICP-MS (BGS, Keyworth, United Kingdom): Hf isotopes

Laser ablation Hf isotopes were determined using a ThermoScientific Neptune Plus MC-ICP-MS equipped with a Jet sampler and X-skimmer cone to maximise sensitivity, coupled to an Elemental Scientific Lasers NWR193UC 193nm excimer laser ablation system. Ar make-up gas was introduced using a TeledyneCETAC Technologies Aridus II desolvating nebuliser and combined with the 0.8l/min He sample gas approximately halfway between the ablation cell and the plasma torch. This instrumental set-up was tuned and performance checked by measurement of JMC475 Hf reference material assuming 176Hf/177Hf = 0.282160 (Nowell et al 1998). Data were processed as time-resolved using the 'Iolite' software (v.3, Paton et al 2011) using a modified data reduction scheme to enable correction for 176Yb using either Yb mass bias or Hf mass bias calibrated to Yb (see Bauer & Horstwood 2018). 176Hf/177Hf and 176Lu/177Hf data were normalised to 91500 zircon (Woodhead & Hergt, 2005) with GJ1 and Temora 2 used as validation (Morel et al 2008 and Woodhead & Hergt (2005) respectively). After normalisation and propagation to the scatter of 91500, GJ1 and Temora 2 176Hf/177Hf were 0.282035 +/- 0.0051% (95% conf., MSWD = 0.57, n = 12) and 0.282684 +/- 0.0046% (95% conf., MSWD = 1.09, n=15) respectively. All 178Hf/177Hf and 180Hf/177Hf were considered accurate with little or no scatter. After normalisation and propagation to 91500, sample OD zircons demonstrated single or near-single Hf isotope compositions with near identical weighted mean 176Hf/177Hf compositions. 176Hf/177Hf data translate to εHf = -3.7 +/- 0.7 propagated for age and Hf model components using the calculations and spreadsheet of Ickert (2013).

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