

S4- text: Analytical methods

3.1. Whole-rock geochemistry

Whole-rock geochemistry analyses were performed by means of inductively coupled plasma mass spectrometry (ICP-MS) at the Geochronology and Isotope Geochemistry SGIker facility of the UPV/EHU (Spain) in accordance with procedures set out by [85]. Reagents used were concentrated HF and HNO₃ Merck Pro-Analysis. Deionized water was obtained using a Millipore Elix device and polishing by reverse osmosis (Barnstead EasyPure system) to obtain a resistivity of ≥ 18 MOhm-cm. In and Bi solutions used as an internal standard, multi-elemental solutions for the initial tuning and calibration of the spectrometer were prepared from PerkinElmer multi-element standard solutions for ICP, stabilized in HNO₃ 2 to 6 %. Internal standard was added using an automatic online addition kit to prevent random errors. Weighing to 0.1 mg precision was performed using an electronic balance GRAM SV 205-A. Calcination was performed in two steps, at intervals of one hour at ~ 500 and 1050 °C, in a muffle furnace, to remove H₂O and compounds of C and S. Alkaline fusion of the samples was carried out using an automatic Claisse Fluxy 30 system over butane gas in Pt-Au (95-5) crucibles containing lithium metaborate (LiBO₂) as a fluxer and LiBr as a non-wetting agent. The melt was automatically poured into a polystyrene beaker containing 100 ml of HNO₃ and ~ 0.05 ml HF placed in a magnetic agitator. The solution was gravimetrically diluted to a factor suitable for analysis. Major and trace element concentrations were determined using a Thermo XSeries 2 ICP-MS equipped with a collision cell, an interphase specific for elevated total dissolved solids (Xt cones), a shielded torch, and a gas dilution system. A concentric nebulizer and quartz expansion chamber were used. The results are shown in Table S1 (supplementary material) and Figures. 3, 4, and 5.

3.2. Sm-Nd isotope chemistry

Sm-Nd isotopic analyses were performed at the Geochronology and Isotope Geochemistry Department of the Universidad Complutense de Madrid (Spain) using isotope dilution thermal ionization mass spectrometry (ID-TIMS). Samples were spiked with a mixed ¹⁴⁹Sm-¹⁵⁰Nd tracer and analyzed in an IsotopX-Phoenix spectrometer (TIMS) in single collection and dynamic multi-collection modes for Sm and Nd, respectively. Whole-rock samples, previously weighed in Teflon® vessels along with the mixed-spike solution (¹⁴⁹Sm-¹⁵⁰Nd: Oak Ridge), were dissolved in 5 ml ultrapure HF and 3 ml ultrapure HNO₃ (Merck-Suprapur™) and placed in an oven for 65 h at a temperature of 120°C. After that, vials were evaporated on a hot plate at 120°C. Once the samples were completely dried, 1 ml of HNO₃ (Merck-Suprapur™) was added and the vials were again placed on the hot plate for evaporation at 120°C. Then 4 ml distilled HCL 6N was added to the dried samples and placed inside an oven overnight at a temperature of 120°C. After the cooling of the vials, samples were evaporated at 120°C and the remainder was dissolved in 3 ml of 2.5 N HCl (distilled and titrated). Samples were centrifuged at 4,000 rpm for 10 min to separate the dissolved fraction from the residue, if any. Chromatographic separation of the total group of REE was performed using a previously calibrated cation-exchange resin Dowex 50W-X8 (200-400 mesh). REE fractions recovered from the previous chromatographic stage were dried completely before being dissolved again in 200 μ l HCl 0.18 N and were passed through a new chromatographic resin (Ln Resin™). The result was the total separation of the Nd (using 0.3 N HCl as the eluent) and Sm (using 0.4 N HCl as the eluent) fractions. Dried Sm and Nd fractions were dissolved in 2 μ l of 0.05 M phosphoric acid and loaded onto the side rhenium (Re) filament of a Re-filament triple arrangement. Nd ratios were analyzed in a TIMS-Phoenix™ mass spectrometer, in accordance with a dynamic multi-collection method, through 160 cycles at a stable intensity of 1 V for the ¹⁴⁴Nd mass. In turn, Sm ratios were analyzed using the same spectrometer, in accordance with a single static method, through 112 cycles, maintaining a 1 V intensity for the ¹⁴⁹Sm mass. Along with the samples, reference material BHVO-2 (USGS: [86-87]) was analyzed to test the isotope dilution process. The reference material presented average values of Sm = 5.4 ± 0.8 ppm, Nd = 21.8 ± 3.4 ppm and ¹⁴³Nd/¹⁴⁴Nd = 0.512994 ± 0.000036 . ¹⁴³Nd/¹⁴⁴Nd ratios were corrected for ¹⁴²Ce and ¹⁴⁴Sm interferences, and normalized to ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219 [88] to correct procedural and instrumental mass fractionation. Deviations from the JNdi-1 isotope reference value [87] were corrected by analyzing the

standard along with the samples, yielding an average value of $^{143}\text{Nd}/^{144}\text{Nd} = 0.512106$ for ten replicas, with an internal accuracy rate of ± 0.000008 (2σ). Analytical errors in the $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were estimated at less than 0.1% and 0.006%, respectively, with a total Sm and Nd procedural blank under 0.1 ng. The results are shown in Table S2 (supplementary material) and Figure 6.

3.3. U-Pb zircon geochronology

Zircon separation was performed by means of traditional techniques using gravity separation. Selected crystals were hand-picked using a binocular lens. Zircon concentrates were cast on a 3.5cm diameter epoxy mount, together with zircon standards (TEMORA zircon, SL13 zircon, and GAL zircon), then polished and documented using SEM-CL at the IBERSIMS (University of Granada, Spain). Mount was coated with gold (80-microns thick) and inserted into the SHRIMP for analysis. Each selected spot was hit by the primary beam during 120s before analysis and then analyzed over 6 scans following the isotope peak sequence ^{196}ZrO , ^{204}Pb , 204.1 background, ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{238}U , ^{248}ThO , ^{254}UO . Every peak of each scan was measured sequentially 10 times with the following total counts recorded per scan: 2s for mass 196; 5 s for masses 238, 248, and 254; 15 s for masses 204, 206, and 208; and 20s for mass 207. The primary beam, composed of $^{16}\text{O}^{16}\text{O}^{2+}$, was set to an intensity of 4 to 5nA, using a 120-micron Kohler aperture, which generates 17×20 -micron elliptical spots on the target. The secondary beam exit slit was set at 80-microns, achieving a resolution of about 5000 at 1% peak height. All calibration procedures were performed on the standards included on the same mount. Mass calibration was performed on the GAL zircon (ca. 480 Ma, very high U, Th, and common lead content [90]). Analytical sessions initially involved the measurement of SL13 zircon [91], which was used as a concentration standard (238 ppm U). TEMORA zircon (ca. 417 Ma, [92]), used as isotope ratios standard, was then measured every four unknowns. Data reduction was performed using the SHRIMPTOOLS software specifically developed for the intensity of each measured isotope to be calculated in two steps using the software: i) the STATA letter value display algorithm was used to find outliers in the ten replicates measured at each peak during each scan, discarding them and averaging the rest once they had been normalized to SBM measurements; ii) for each isotope, a robust regression of each scan average versus time, if measured, was performed. The result obtained for each isotope was calculated as the value at the mid-interval of the analysis deriving from a robust regression line. Errors (95% confidence level) were calculated as the standard error of the linear prediction at the midpoint of the analysis. $^{206}\text{Pb}/^{238}\text{U}$ was calculated from measured $^{206}\text{Pb}+^{238}\text{U}+$ and UO^+/U^+ in accordance with the method described by [93]. For high-U zircons ($\text{U} > 2500$ ppm) $^{206}\text{Pb}/^{238}\text{U}$ was further corrected using the algorithm of [94]. Plotted and tabulated analytical uncertainties are 1σ precision estimates. Uncertainties in calculated mean ages were 95% confidence limits ($t\sigma$, where t is the Student's t multiplier) and, for mean $^{206}\text{Pb}/^{238}\text{U}$ ages, including the uncertainty in Pb/U calibration (0.3-0.5 %). Common Pb corrections assumed a model common Pb composition appropriate to the age of each spot [95]. Geochronology data are presented in Table S3 (supplementary material) and Figure 7.