

Analytical methodology

U-Pb zircon geochronology: SHRIMP methodology

Zircon grains from the new four samples of Purrido amphibolites samples were separated at the Universidad Complutense (Madrid) following conventional gravimetric and magnetic techniques. At the Stanford-US Geological Survey micro analytical center (SUMAC), the zircon obtained was handpicked under a binocular microscope and mounted on a double-sided adhesive on glass slides in 1 x 6 mm parallel rows together with some chips of zircon standard R33 (Black *et al.* 2004; *Chemical Geology*, 205, 115-140). After being set in epoxy resin, the zircon crystals were ground down to expose their central portions by using 1500 grit wet sandpaper, and polished with 6 μm and 1 μm diamond abrasive on a lap wheel. Prior to isotopic analysis, the internal structure, inclusions, fractures and physical defects were identified with transmitted and reflected light on a petrographic microscope, and with cathodoluminescence (CL) on a JEOL JSM 5600 electron microscope. After the analysis, secondary electron images were taken to locate the exact position of the spots.

U-Th-Pb analyses of zircon were conducted on the Bay SHRIMP-RG (Sensitive High Resolution Ion Microprobe-Reverse Geometry) operated by the SUMAC facility (USGS-Stanford University) during three analytical sessions on July 2008. U-Th-Pb analytical procedures for zircon dating followed methods described by Williams (1997; *Economic Geology*, 7, 1-35). Secondary ions were generated from the target spot with an O^{2-} primary ion beam varying from 4-6 nA. The primary ion beam produced a spot with a diameter of ~25 microns and a depth of 1-2 microns for an analysis time of 12-13 minutes. Data for each spot were collected utilizing six-cycle runs through the mass stations, and the counting time for

^{206}Pb was increased according to the Paleozoic age of the samples and the low uranium content to improve counting statistics and precision of the $^{206}\text{Pb}/^{238}\text{U}$ age. The isotopic compositions were calibrated against R33 ($^{206}\text{Pb}/^{238}\text{U} = 0.06716$, equivalent to an age of 419 Ma; Black *et al.* 2004; *Chemical Geology*, 205, 115-140) which was analyzed every four analyses of the unknowns. Data reduction was carried out using Squid software (v. 1.08; Ludwig 2002; Berkeley Geochronology Center Special Publication, 2, 17p) which follows the methods described by Williams (1997; *Economic Geology*, 7, 1-35), and Ireland & Williams (2003; *Reviews in Mineralogy and Geochemistry*, 53, 215-241), and Isoplot software (v. 3.41c; Ludwig 2003; Berkeley Geochronology Center Special Publication, 4, 71p) was used to create the graphs. All the ages are reported based on $^{206}\text{Pb}/^{238}\text{U}$ ratios corrected from common Pb using the ^{207}Pb method. The Pb composition used for initial Pb corrections ($^{204}\text{Pb}/^{206}\text{Pb}=0.0554$, $^{207}\text{Pb}/^{206}\text{Pb}=0.864$ and $^{208}\text{Pb}/^{206}\text{Pb}=2.097$) was estimated from Stacey & Kramers (1975; *Earth Planetary Science Letters*, 196, 17-33). Analytical results are presented in Table 1 (supplementary material).

U-Pb zircon geochronology: LA-ICP-MS methodology

The U-Th-Pb analyses of zircon were carried out at the Goethe University Frankfurt (GUF) during one analytical session in March 2009 using a Thermo-Scientific Element sector field ICP-MS coupled to a New Wave Research UP-213 ultraviolet laser system with a teardrop low-volume ablation cell (Janousek *et al.* 2006; *Journal of Petrology*, 47, 705-744; Frei & Gerdes 2009; *Chemical Geology*, 261, 261-270), following the method of Gerdes & Zeh (2006; *Earth and Planetary Science Letters*, 249, 47-61) and Gerdes & Zeh (2009; *Chemical Geology*, 261, 230-243). Previous to the analysis, the old mount (Sánchez Martínez *et al.* 2006; *Journal of the Geological Society*, London, 163, 737-740) was slightly

re-polished, exposing grains that were not analyzed before, and the internal structure of all of them was investigated by cathodoluminescence (CL) imaging in order to ensure the analysis of discrete domains. Isotope data were acquired in time resolved – peak jumping – pulse counting mode over 810 mass scans during 19 second background measurement followed by 30 second of sample ablation, using a 20 μm spot-size with a typical penetration depth of $\sim 15\text{-}20$ μm . The laser was fired with a repetition rate of 10 Hz and an energy of ~ 0.025 mJ/pulse (laser fluence of ~ 2 J.cm⁻²). Signal was tuned for maximum sensitivity for Pb and U while keeping oxide production, monitored as $^{254}\text{UO}/^{238}\text{U}$, well below 1%. Raw data were corrected offline for background signal, common Pb, laser induced elemental fractionation, instrumental mass discrimination, and time-dependent elemental fractionation of Pb/U using an in-house MS Excel© spread-sheet program (Gerdes & Zeh 2006; Earth and Planetary Science Letters, 249, 47-61). No common Pb correction has been applied as the interference- and background-corrected ^{204}Pb signal was generally very low. The interference of ^{204}Hg (mean = 375 ± 119 cps; counts per second) on mass 204 was estimated using a $^{204}\text{Hg}/^{202}\text{Hg}$ ratio of 0.2299 and measured ^{202}Hg . Laser-induced elemental fractionation and instrumental mass discrimination were corrected by normalization to the reference zircon GJ-1 for the analytical session. Prior to this normalization, the drift in inter-elemental fractionation (Pb/U) during 30s of sample ablation was corrected for the individual analysis. The correction was done by applying a linear regression through all measured ratios, excluding the outliers (± 2 standard deviation; 2SD), and using the intercept with the y-axis as the initial ratio. The total offset of the measured drift-corrected $^{206}\text{Pb}/^{238}\text{U}$ ratio from the “true” ID-TIMS value (0.0986 ± 0.0004 ; ID-TIMS JWG value) of the analyzed GJ-1 grain was typically around 3-10%. Reported uncertainties (2σ) of the $^{206}\text{Pb}/^{238}\text{U}$ ratio were propagated by quadratic addition of the external reproducibility (2 SD %) obtained from the standard zircon GJ-1 ($n = 9$; 2 SD $\sim 1.2\%$) during the analytical session (sequence) and the within-run precision of each analysis

after correction for the intraelemental fractionation (2 SE %; standard error). In case of the $^{207}\text{Pb}/^{206}\text{Pb}$, we used a ^{207}Pb signal-dependent uncertainty propagation (Gerdes & Zeh 2009; *Chemical Geology*, 261, 230-243). Twelve spot analyses on 4 grains of the Plesovice zircon analysed as unknown yielded a concordia age of 337.6 ± 1.1 Ma, which is in perfect agreement with the data of Slama *et al.* (2008; *Chemical Geology*, 249, 1-35). Age calculations and the creation of Concordia plots were performed using Isoplot software (Ludwig 2003). Analytical results are presented in Table 2 (supplementary material).

Lu-Hf zircon isotope geochemistry: LA-MC-ICP-MS methodology.

Hafnium isotope measurements in zircons corresponding to samples G03-8, G07-1 and G07-2 were performed with ThermoScientific Neptune multicollector (MS) ICP-MS at Goethe University of Frankfurt coupled to the same laser ablation system and cell as described for the U-Pb analyses of sample G03-8. Data were collected in static mode (^{172}Yb , ^{173}Yb , ^{175}Lu , ^{176}Hf -Yb-Lu, ^{177}Hf , ^{178}Hf , ^{179}Hf , ^{180}Hf) during 55 s of laser ablation. The “Lu–Hf laser spot” of 40 or 30 μm diameter (as the grain size allowed it) was commonly drilled directly beside the “U–Pb laser/SHRIMP spot”, or in the same domain this was located, according to the CL images. Nitrogen (~ 0.005 L/min) was introduced into the Ar sample carrier gas via a Cetac Aridus nebulisation system, without aspirating any solution, in order to enhance the signal sensitivity (~ 10 – 20%) and to reduce oxide formation in the plasma. The use of the Aridus system allowed bracketing of laser ablation analyses with solution mode analyses. Analytical protocols were the same for laser ablation and solution mode analyses. Solution mode data were acquired with 60 integration cycles over a period of 2 min, followed by 8 min of washout with a mixture of 2% HNO_3 –0.5 N HF. Data were corrected and normalized following the procedure of the laser ablation analyses. The isotopes ^{172}Yb , ^{173}Yb

and ^{175}Lu were simultaneously monitored during each analysis step to allow the correction of isobaric interferences between Lu and Yb isotopes on mass 176. The ^{176}Lu and ^{176}Yb were calculated using $^{176}\text{Lu}/^{175}\text{Lu}$ of 0.02658 and $^{176}\text{Yb}/^{173}\text{Yb}$ of 0.795015 (both JWG in-house values), and by taking into account the instrumental mass fractionation of each individual analysis. The second of the above mentioned values is identical to the mean of the values given by Chu *et al.* (2002; *Journal of Analytical Atomic Spectrometry*, 17, 1567-1574) and Segal *et al.* (2003; *Journal of Analytical Atomic Spectrometry*, 18, 1217-1223). For a more detailed description of the data acquisition and processing, see Gerdes & Zeh (2006; *Earth and Planetary Science Letters*, 249, 47-61) and Gerdes & Zeh (2009; *Chemical Geology*, 261, 230-243) and Zeh *et al.* (2007a; *Journal of Petrology*, 48, 1605-1639) and Zeh *et al.* (2007b; *Geochimica et Cosmochimica Acta*, 72, 5304-5329).

The values of $^{176}\text{Lu}/^{177}\text{Hf}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ corresponding to the chondritic uniform reservoir (CHUR) according to Bouvier *et al.* (2008; *Earth and Planetary Science Letters*, 273, 48-57) and a decay constant of 1.867×10^{-11} (Scherer *et al.* 2001; *Science*, 293, 683-687; Söderlund *et al.* 2004; *Earth and Planetary Science Letters*, 219, 311-324) were used for calculation of the epsilon Hf (ϵHf_t) value for each analysis. Initial $^{176}\text{Hf}/^{177}\text{Hf}_t$ and ϵHf_t ($^{176}\text{Hf}/^{177}\text{Hf}_{\text{int}}$ and $\epsilon\text{Hf}_{\text{int}}$) for all analysed zircon domains were calculated using the apparent ages ($^{206}\text{Pb}/^{238}\text{U}$ or Pb-Pb for zircons younger or older than 1.0 Ga, respectively) obtained for the respective domains. Analytical results are presented in Table 3 (supplementary material).

Sm-Nd isotope geochemistry: TIMS methodology.

The Sm-Nd analyses were performed at the Memorial University of Newfoundland, using the following analytical procedures. Approximately 0.05 to 0.2 g of rock powder is

dissolved in Savilex Teflon beakers using a mixture of concentrate HF – HNO₃ acids. A mixed ¹⁵⁰Nd/¹⁴⁹Sm spike is added to each sample prior to acid digestion. Both sample and spike are weighed on a high-precision balance. After five days of digestion, the solution is evaporated to dryness and then taken up in 6 N HCl acid for two days. The solution is then dried and taken up in 2.5N HCl and loaded on cationic exchange chromatography using AG50W – X8 resin to collect the REE fractions. The REE fractions are then purified and Sm and Nd are isolated using a secondary column loaded with Eichrom Ln resin. All reagents are purified in order to insure a low contamination level. The measured total chemical blanks range between 40 and 90 pg for Nd and are considered negligible.

Sm and Nd concentrations and Nd isotopic compositions were analyzed using a multicollector Finnigan Mat 262 mass spectrometer in static mode. Nd isotopic ratios are normalized to ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219. The reported ¹⁴³Nd/¹⁴⁴Nd values were adjusted to the JNdi-1 standard (¹⁴³Nd/¹⁴⁴Nd = 0.512115, Tanaka *et al.* 2000; *Chemical Geology*, 168, 279-281). During the course of data acquisition, replicates of the standard give a mean value of ¹⁴³Nd/¹⁴⁴Nd = 0.512130 ± 12 (Std Dev, n=85). The in-run precisions on Nd isotopic ratio are given at 95% confidence level. Errors on Nd isotopic compositions are <0.002% and errors on the ¹⁴⁷Sm/¹⁴⁴Nd ratio are estimated to be lower than 0.1%. The εNd values are calculated using ¹⁴⁷Sm/¹⁴⁴Nd = 0.1967 and ¹⁴³Nd/¹⁴⁴Nd = 0.512638 values for the present day chondrite uniform reservoir (CHUR). ¹⁴⁷Sm decay constant is 6.54 10⁻¹² y⁻¹ (Steiger & Jäger 1977; *Earth and Planetary Science Letters*, 36, 359-362). Considering the zircon population that appear in the amphibolites εNd(t) values for all samples were also calculated at t = 400 Ma, 1100 Ma and 1600 Ma. Moreover, f_{Sm/Nd} values have been also calculated. Analytical results are presented in Table 4 (supplementary material).