

Samples and analytical methods

The granite mineral assemblage has been previously characterized by Villaseca et al. (2008), Merino et al. (2013) and Pérez-Soba et al. (2014). Apatite crystals were selected during the petrographic study on thin section and mineral concentrated mounts of the four granite units of the Belvís pluton, and characterized by means of electron microscopy: electron microprobe (EMP), scanning electron microscopy (SEM) equipped for microanalysis, and laser ablation inductively coupled plasma mass (LA-ICP-MS) analyses. A total of ca. 270 spots were made on apatite crystals from 41 thin sections and 3 mineral concentrates of a total of 17 rock samples from the four granite units. The structural formula of apatite is calculated for 10-M-site cations according to Ketcham (2015). Analyses are considered acceptable when the cation sums do not deviate more than ± 0.2 from the ideal 16 apfu (MacDonald et al. 2008). A significant number of analyses have totals below 98.00 wt%, typically considered as the lower limit for acceptable analyses results. We have extended this criterion to those analyses with significant content of non structural elements, since in these cases low analytical totals are common, as in other accessory minerals (e.g., zircon, monazite, e.g., Nasdala et al. 2009).

Electron microprobe (EMP) analysis

EMP analyses were done on a JEOL Superprobe JXA 8900-M, equipped with five wavelength dispersive spectrometers, at the Centro Nacional de Microscopía Electrónica (Universidad Complutense, Madrid). The acceleration voltage was 20 kV with a 5 μm spot size at a 20 nA current, with variable counting times between 10 and 60 seconds and between 5 and 30 seconds in the peak and background, respectively. (These characteristics

determine a beam exposure of about 15 minutes) synchronous mode analysis was used in order to avoid damages in the samples. Absolute abundances for each element were determined by comparison with albite, kaersutite, almandine, zircon, vanadinite, REE phosphates and P&H Development glasses. An on-line ZAF program was used for data correction. Error limits for each element depend strongly on the absolute concentration in each phase, but could be estimated significantly for the < 1 wt% level (with error >10 %). Concentrations below 0.2 wt% are quoted, but considered qualitative. Mineral analyses were assisted by appropriate back-scattered electron (BSE) images to ensure that representative and homogeneous points were selected for analysis. To corroborate the presence of OH⁻ in the apatite structure, total oxygen content of selected fluorapatite crystals was analyzed by electron microprobe with two different multilayer crystals.

The crystallographic orientation of apatite affects the X-ray flux, so EMP analyses can vary considerably introducing analytical errors, especially in F contents (Stormer et al. 1993; Pyle et al. 2002; Webster and Piccoli 2015). The tardi-magmatic character of most of the apatite analyzed (anhedral sections) strongly limits the selection of appropriate sections to be analyzed. Therefore, in this study F content in Table 1 may be considered as an upper limit of true F concentration (Henderson 2011). However, we consider that the large number of analyses carried out in each apatite type defines enough significant trends to discuss the compositional results.

Images and chemical characterization of graphite

To characterize graphite inclusions different electron microscopes were used at the Centro Nacional de Microscopía Electrónica and the CAI “Técnicas geológicas” (Universidad Complutense, Madrid). Graphite included in type 2 apatite was difficult to observe with detail during EMP sessions due to its small size. To better characterize the

morphological features of the graphite inclusions and to ensure the carbonaceous nature of this acicular inclusions, imaging and qualitative analyses were taken with two scanning electron microscopes (SEM): JEO JSM 6335F and JEOL JSM 7600, this last configured with a high resolution semi in-lens SEM with an EDX detector. The samples were fragments of graphite-bearing apatite grains extracted from both epoxy mounts and thin sections, and subsequently coated with gold layer. Semi-quantitative elemental composition (C, P, Ca and F) was determined along line profiles in longitudinal and transversal sections of graphite filaments for which a goniometer was used.

Laser ablation multicollector inductively coupled plasma mass spectrometry (LA-ICP-MS)

In order to characterize trace element composition of the apatite types LA-MC-ICP-MS analyses were collected at the Core Research laboratories of the Natural History Museum of London, using an Agilent 7500CS ICP-MS coupled to a New Wave UP213 laser source (213 nm frequency-quadrupled Nd–YAG laser). The counting time for one analysis was typically 90 s (36 s measuring gas blank to establish the background and 54 s for the remainder of the analysis). The frequency of the analyses was 10 Hz, the rotation 30%, and the fluency between 3 and 4 J·cm⁻² with a variable 20 - 30 µm in diameter spot size. Quantitative results for 40 elements were obtained through calibration of relative element sensitivities using the NIST 612 and BCR2-G glass standards. Precision was determined to be approximately 2% or better for most elements. Accuracy was monitored using the basalt glass BCR2-G analyzed as an unknown and data were found to be within the errors associated with the determination of its reference values. Analysis was normalized to Ca wt% carried out by EMP. The NIST 612 and BCR2G glass standards were used to calibrate relative element sensitivities for the mineral analyses. Each analysis was normalized to

CaO, using the concentrations previously determined by electron microprobe in these minerals. In those cases where analyses were carried out in thin sections (33 μm) the depth and the timing used for the analyses were enough for the detection and the acquisition of reliable trace element counts. During the time-resolved analysis of minerals, the contamination from inclusions, fractures and zones of different composition was detected by monitoring several elements and integrating only the relevant part of the signal.

Part of the apatite trace element analyses were conducted by LA-ICP-MS at the Geochronology and Isotope Geochemistry-SGIker facility of the University of the Basque Country (UPV/EHU, Bilbao, Spain) using the method described by García de Madinabeitia et al. (2013). The analyses involved the ablation of minerals in ca. 90 μm thick petrographic sections with a NewWave UP213 Nd:YAG laser ablation system coupled to a Thermo Fisher Scientific XSeries 2 quadrupole ICP-MS instrument with enhanced sensitivity through a dual pumping system. Spot diameters of ca. 40 μm associated to repetition rates of 10 Hz and laser fluency at the target of ca. 5 J/cm^2 were used for the analysis. Counting time and data acquisition were similar in both routines but, in this laboratory, B, Li and Be were not analyzed. The NIST 614 silicate glass and Durango apatite were used as standards for quality control of the major and trace element results. Raw data were processed using Glitter 4.4.2 (van Achterbergh et al. 2001; Jackson et al. 2004) and the Ca values obtained by electron microprobe on the same spots.

Electron energy-loss spectroscopy (EELS)

EELS is a technique capable of giving structural and chemical information with high spatial resolution, even down the atomic level, more if considered the low thickness of the particles required (Egerton 1996). To obtain thin specimens to take high-resolution images (a point resolution of 0.17 nm) of apatite crystals, these were previously removed from

epoxy mount and thin sections and crushed in agate mortar. EELS spectra were obtained in a JEOL (JEM3000F) microscope operating at 300 kV, attached with an x-ray emission spectrometer. The dispersion was 0.5 eV/channel and entrance aperture of 2 mm was used. The spectra were recorded in diffraction mode at 12 cm camera length. All crystals were selected to be well away from a Bragg condition prior to the recording of the spectra. The microscope has a dispersive X-ray spectroscopy (EDX) detector, so analyses of elemental composition were carried out.

Carbon isotopes

Carbon isotope analyses of graphite were performed in the Stable Isotope Laboratories of the University of Salamanca. The extremely low carbon contents of the igneous samples required a considerable higher weight (about 41 mgr) in order to obtain a good signal. The determination of isotope $^{13}\text{C}/^{12}\text{C}$ ratios in graphite was performed by combustion in an elemental analyzer EA3000 Eurovector coupled online to a mass spectrometer Isoprime (TM) in “continuous flow.” The results (the mean value of triplicate analysis ± 1 standard deviation) are reported in δ ‰ relative to the PDB standard for carbon. Laboratory machine standard CO_2 gas measurements gave in the standard samples a reproducibility better than 0.16 ‰ ($n = 3$).