

Uranium-rich accessory minerals in the peraluminous and perphosphorous Belvís de Monroy pluton (Iberian Variscan belt)

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Abstract The strongly peraluminous, perphosphorous (<0.85 wt% P_2O_5) and low-Ca granites from the Belvís de Monroy pluton contain the most U-rich monazite-(Ce) and xenotime known in igneous rocks. Along with these accessory minerals, P-rich zircon occurs, reaching uncommon compositions particularly in the more fractionated units of this zoned pluton. Monazite displays a wide compositional variation of UO_2 (<23.13 wt%) and ThO_2 (<19.58 wt%), positively correlated with Ca, Si, P, Y and REE. Xenotime shows a high UO_2 content (2.37–13.34 wt%) with parallel increases of LREE, Ca and Si. Zircon contains comparatively much lower UO_2 (<1.53 wt%) but high P_2O_5 (<14.91 wt%), Al_2O_3 (<6.96 wt%), FeO (<2.93 wt%) and CaO (<2.24 wt%) contents. The main mechanism of incorporating large U and Th amounts in studied monazite and U in xenotime is the cheralite-type $[(Th,U)^{4+} + Ca^{2+} = 2(Y,REE)^{3+}]$ substitution. Zircon requires several coupled mechanisms to charge balance the P substitution, resulting in non-stoichiometric compositions with low analytical totals. Compositional variations in the studied accessory phases

indicate that the substitution mechanisms during crystal growth depend on the availability of non-formula elements. The strong P-rich character of the studied granites increases monazite crystallization, triggering a progressive impoverishment in Th and LREE in the residual melts, and consequently increasing extraordinarily the U content in monazite and xenotime. This is in marked contrast to other peraluminous (I-type or P-poor S-type) granite series. The P-rich and low-Ca peraluminous melt inhibits uraninite crystallization, so contributing to the U availability for monazite and xenotime.

Keywords Monazite · Xenotime · Zircon · Uranium · Peraluminous granites · Perphosphorous granites

Introduction

Compositional and textural variations in accessory minerals from granitoid rocks have been extensively discussed (e.g. Casillas et al. 1995; Bea 1996; Förster 1998a, b, 1999 and compilations therein; Johan and Johan 2005; Broska and Petrák 2008). Physical, chemical and crystal-chemical parameters determine the crystallization and composition of these minerals (e.g. Cuney and Friedrich 1987), so the accessory mineral paragenesis in granitoids has been used as a petrogenetic indicator (e.g. Fleischer and Altschuler 1969; Harlov and Förster 2007).

In peraluminous P-rich highly fractionated granites, a complex assemblage of phosphate minerals appears in comparison with other felsic magmas (London et al. 1999). Two factors determine the accessory mineral crystallization in this magma type: (1) high alumina saturation index ($ASI = \text{molecular } Al_2O_3 / (CaO + K_2O + Na_2O)$), which depresses the Ca activity. This increases the solubility of

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apatite in the melt promoting the stability of monazite and xenotime, independently of the ASI value (e.g. Rapp and Watson 1986; Pichavant et al. 1992; Montel 1993; Wark and Miller 1993; Wolf and London 1994); and (2) the high P content, which triggers melt depolymerisation, reducing melt viscosity (e.g. Mysen et al. 1981) and enhancing the high field-strength elements (HFSE) solubility (e.g. Wolf and London 1994). In this scenario, HFSE would be available to combine extensively with P, crystallizing a wide spectrum of accessory minerals (Cuney and Friedrich 1987). Monazite $[(\text{LREE})\text{PO}_4]$ and xenotime $[(\text{Y,HREE})\text{PO}_4]$ will crystallize even at low REE contents (Bea 1996), extending their crystallization until the last fractionates. These minerals, along with zircon (ZrSiO_4), are common minerals in those types of granite, which share the ability to incorporate non-formula elements (e.g. U, Th, Ca, Fe, Al, Ti, Mn, Y, REE) in minor or trace contents which may be accompanied by deficient totals (e.g. Pérez-Soba et al. 2007; Hoshino et al. 2012). These three minerals show an “opportunistic” character acquiring anomalous compositions, mainly in low-Ca highly fractionated magmas (Förster et al. 1999; Anderson et al. 2008; Breiter et al. 2014). The relative abundance of these phases in peraluminous felsic granites and the control they exert on the trace element partitioning during magma differentiation makes it important to understand the mechanisms which control their chemical changes.

This study is focused on the occurrence and compositional evolution of monazite, xenotime and zircon in the perphosphorous, peraluminous and Ca-poor granites of the Belvís de Monroy pluton (Central Iberian Zone). The extraordinary high U contents in monazite and xenotime (UO_2 up to 23.13 and 13.34 wt%, respectively) of these granites, and the P-rich composition of associated zircon (P_2O_5 up to 14.91 wt%), along with significant enrichments of other non-formula elements, provides a valuable resource to study the substitution mechanisms of these common granite accessories.

Geological setting, petrology and whole-rock geochemistry

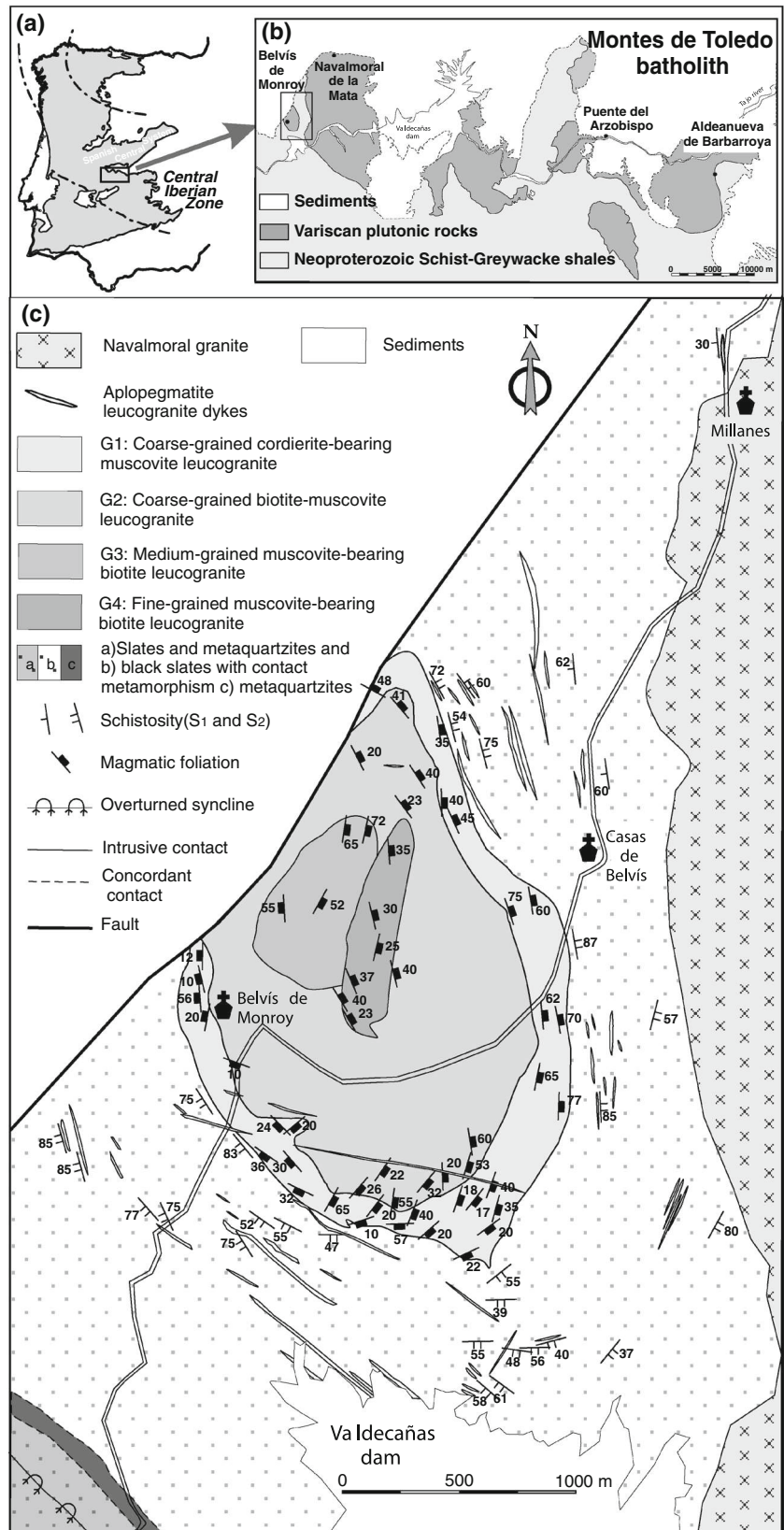
The Belvís de Monroy pluton (Belvís pluton here upon) is located in the Central Iberian Zone (Fig. 1a), the axial domain of the Iberian massif (Julivert et al. 1974). This pluton belongs to the westernmost segment of the Montes de Toledo (MT) batholith, an E–W array of discontinuous post-kinematic Variscan intrusions, mostly granitic in composition (Fig. 1b). The country rocks are metasediments (slates interlayered with minor metagreywackes levels), Precambrian to Ordovician in age, affected by a very low to low-grade metamorphism and folded mainly

during the Variscan orogeny. Most of the plutons cut structures related to the ductile deformation phase (D3) of 320–310 Ma age (e.g. Dias et al. 1998; Valle Aguado et al. 2005), producing a km-size contact metamorphism, reaching high-grade conditions in the inner parts of the aureole ($\text{Kfs} + \text{Sil} + \text{And} + \text{Crd} + \text{Grt}$). The MT batholith is characterized by a marked S-type affinity, which contrasts with the I- and S-type mixed character of the northernmost Spanish Central System batholith (Villaseca et al. 2008) (Fig. 1a).

The Belvís pluton is a NS elongated massif of ca. 3.5 km² (Fig. 1c) intrusive into low-grade Ordovician blackish slates (IGME 1987). A contact metamorphic aureole is developed around this pluton, forming $\text{Ms} + \text{Crd} + \text{Sil} + \text{And} + \text{Bt} + \text{Qtz}$ close to the granite contact. Wall rocks around Belvís pluton display two distinct schistositys, one regional (S1) NNW–SSE, and a secondary foliation (S2) that apparently adapts to the pluton structure, suggesting a relationship with the granite emplacement. A late-Variscan NE–SW fault, reactivated during the Alpine orogeny (IGME 1987), cuts the pluton in the north-western sector and obliterates this part of the original intrusive contact (Fig. 1c). A complex aplopegmatite dyke swarm intrudes in a 1–2 km-wide halo (Fig. 1c), some of them considered of interest for phosphates and Li exploration (Técnicas mineras de santa Marta, S.L. y Tecminsa, S.L. 2009). The Belvís pluton and the aplopegmatite swarm show a spatially homogeneous anisotropic fabric, interpreted as a doming structure (Fig. 1c). The magmatic foliation defined by the preferred orientation of micas and fibrolite in the plutonic units and a pronounced mineral stretching lineation parallel to the orthogonal axes are consistent with an emplacement mechanism close to the free surface, caused by a successive pulse growth. A fairly precise U–Th–Pb isochron age of 314 ± 3 Ma (MSWD = 1.09) obtained in monazite crystals from the G2 unit (Orejana et al. 2012) assigns the Belvís pluton emplacement to the late-to-post-Variscan D3 stage.

Four distinct granite units (G1–G4) can be recognized on the basis of field relationships (Fig. 1c), mineralogy and geochemistry (Supplementary Table 1). Although contact between units cannot be observed because of the unfavourable outcropping conditions, both the tabular shape and the finer-grained texture of the central unit G4 suggest that this was the last pulse in the pluton construction. The outermost G1 unit defines a coarse-grained inequigranular muscovite leucogranite with abundant irregular and cm-size cordierite nodules. In this unit, muscovite stands out by its large euhedral crystals. The G2 unit consists of medium-grained biotite–muscovite granite, with occasional cordierite nodules. The G3 unit is characterized by a fine- to medium-grained biotite > muscovite granite with

Fig. 1 Geological map of the Belvís pluton and position in the Variscan Iberian zone:
a location of the Montes de Toledo (MT) batholith in the Central Iberian zone;
b simplified map of the central and western sectors of the MT batholith, with the Belvís pluton outcropping in the westernmost part;
c detailed geological map of the Belvís pluton, aplopegmatite dykes and their metamorphic host rock



ubiquitous fibrolitic strips in close relationship with biotite. G4 defines a ca. 200-m thick lenticular intrusion of a fine-grained biotite > muscovite granite, both as isolated crystals. Extremely scattered igneous enclaves occur in these plutonic pulses: mesocratic medium-grained granites in G3 and G2, and a micro-augen orthogneiss in the central unit. The main aplopegmatitic dyke swarm shows magmatic foliation cutting the main regional schistosity of the wall rocks (S1). However, these dykes are parallel both to the secondary country-rock schistosity (S2) and to the outermost unit of the pluton, suggesting a pre- to coeval intrusion with the pluton.

The petrography and mineralogy of the Belvís units is synthesized in Table 1 (Supplementary data). The four units are essentially made up of inequigranular interlocking perthitic K-feldspar, quartz and plagioclase. Biotite and muscovite define the foliation along with fibrolitic sillimanite. Sillimanite, in addition, appears wrapped in muscovite, tourmaline and quartz. The accessory minerals occur mainly as isolated grains included in major phases and are only occasionally in contact with each other. The most common magmatic accessory minerals are fluorapatite, monazite, zircon and tourmaline, but other minerals occur in each pulse: G1 includes the exceptional association of gahnite, chrysoberyl and beryl (Merino et al. 2013), cordierite, rutile, eosphorite–childrenite and xenotime; G2 has xenotime and cordierite. In G3 chrysoberyl and beryl appear in small aplite segregates. In G4, no other accessory minerals are present. The aplite–pegmatite dykes also exhibit a wide variety of minerals similar to those of G1 granite: aggregates of cordierite and quartz, rutile, gahnite, chrysoberyl, apatite, zircon, monazite and xenotime. Other minerals commonly cited in perphosphorous leucogranites (e.g. uraninite, columbite–tantalite, cassiterite) have not been found in the Belvís pluton. With respect to mineral chemistry, it is worth noting the high P contents in K-feldspar and plagioclase, typical of P-rich granites (e.g. London et al. 1999; Breiter et al. 2002). The feldspar P_2O_5 content increases towards the most evolved G2 and G1 units (Table 3 of Merino et al. 2013).

The Belvís pluton is the most fractionated intrusion from the MT batholith (Villaseca et al. 2008), and it is characterized by its high P_2O_5 (from 0.47 to 0.85 wt%), and low CaO (0.26–0.56 wt%) contents, and by its strong peraluminous character [ASI (molar $Al_2O_3/(CaO + Na_2O + K_2O) = 1.26–1.32$] (Supplementary Table 1). The chemical composition of this pluton also stands out with its high Rb, Be, F, Li, Nb, Ta, Sn and U (6.8–13.5 ppm) contents (Merino et al. 2013, Supplementary Table 1). The whole-rock composition of the inner units (G4 and G3), which displays high FeO, MgO, K_2O , TiO_2 , Ba, Zr, Hf, Th, Pb, Y and REE contents (Supplementary Fig. 1b–f), points to a less-fractionated origin when compared to the outer

leucogranites (G1 and G2 units). Conversely, G1 and G2 units have high P_2O_5 , Na_2O , Rb, Sr, U, Nb, Ta, F and Li contents (Supplementary Table 1, Supplementary Fig. 1a, e, and Merino et al. 2013). These variations define the pluton as reversely zoned. Merino et al. (2013) interpreted this zoning as a successive emplacement of fractionated magma batches from a deeper magma chamber. In this model, the G1 unit, favoured by its higher volatile content, would have been placed first. They calculate a broad fractional crystallization process involving about 35–50 % Pl, 25–20 % Kfs, 10–5 % Bt and 30–25 % Qtz to explain the whole differentiation from the less to the most evolved units (Supplementary Fig. 1b, c). Nevertheless, the Belvís granites lack a single fractionation trend as illustrated by the U variation (Supplementary Fig. 1e).

Analytical methods

Electron microprobe (EMP) analysis

Monazite, zircon and xenotime crystals from both thin sections and mineral separates of samples from the four Belvís units were analysed with a JEOL Superprobe JXA 8900-M (Centro Nacional de Microscopía Electrónica “Luis Bru”, Universidad Complutense de Madrid) equipped with four wavelength-dispersive mode spectrometers. The acceleration voltage was 20 kV, and the beam current 50 nA, with variable counting times between 10 and 30 s and between 5 and 15 s in the peak and background, respectively; about 15 min was needed for each spot analysis. The beam diameter ranged from 1 to 5 μm to minimize grain damage. Absolute abundances for each element were determined by comparison with albite, kaersutite, almandine, zircon, vanadinite and REE phosphates (Jarosewich et al. 1980; Jarosewich and Boatner 1991), except U and Th, for which commercial glasses were used. An online ZAF program was used for data correction. Analytical precision is 0.5–6 % for oxides with concentrations >0.5 wt% and <10 % for oxides with concentrations <1.5 wt%. Mineral analyses were assisted by appropriate back-scattered electron (BSE) images to ensure that representative and homogeneous points were selected for analysis. Analytical spots were performed avoiding microfissures, where U could be redistributed (Berzina et al. 1974). We have discarded from this study those analyses with total atomic cations substantially deviated from the stoichiometric formulae (>5 %, Linthout 2007).

Scanning electron microscope (SEM)

Some monazite grains were observed using SEM-based techniques to ensure that the high uranium content

Table 1 Representative electron microprobe analyses of monazite from the Belvís pluton

Granite Sample Analysis	G1 N8 3	G1 N8 8	G1 N8 17	G1 N206 18	G1 N206 19	G1 N9 22	G2 N10 32	G2 N10 35	G2 N10 37	G2 N110 45	G3 N204 107	G3 N204 109	G3 N204 116	G3 N316 120	G4 N348 123	G4 N348 138	G4 N348 127	G4 N348 145
P ₂ O ₅	30.14	31.50	30.42	29.59	29.95	30.09	30.30	29.69	29.58	28.34	29.42	28.93	29.94	29.20	29.33	29.83	28.83	30.11
SiO ₂	bdl	bdl	bdl	0.11	0.06	bdl	bdl	0.08	bdl	0.14	0.69	0.23	bdl	bdl	0.15	0.13	0.92	0.02
UO ₂	13.39	8.97	20.14	11.78	18.94	11.02	16.69	3.81	17.05	23.13	14.44	3.46	16.92	12.75	0.37	2.50	0.47	7.92
ThO ₂	0.74	0.10	0.30	16.27	0.11	2.52	6.15	4.60	1.35	1.65	4.28	6.84	13.37	9.10	4.65	3.89	13.11	19.58
Y ₂ O ₃	2.16	4.20	2.56	0.73	3.10	1.83	1.57	1.85	1.96	2.38	0.87	1.46	0.62	0.69	1.09	3.57	0.32	0.35
La ₂ O ₃	8.28	9.19	9.87	8.22	6.06	8.97	9.61	12.35	9.86	6.27	10.08	10.39	10.26	11.55	11.33	10.87	9.71	9.38
Ce ₂ O ₃	20.64	22.82	18.12	13.50	15.92	21.10	17.73	25.56	20.29	16.61	18.87	21.56	14.15	19.63	28.79	25.24	23.77	15.63
Pr ₂ O ₃	2.95	3.07	2.26	1.35	2.29	2.65	1.82	3.18	2.26	1.79	1.86	2.47	1.44	1.93	3.51	3.07	3.25	1.58
Nd ₂ O ₃	10.28	10.39	6.71	4.54	9.39	11.44	7.17	10.94	8.91	7.51	6.49	9.33	4.13	5.36	13.75	11.28	10.94	4.35
Sm ₂ O ₃	3.39	2.94	1.53	0.72	2.3	2.82	1.33	1.95	1.77	1.68	0.98	1.82	0.61	0.73	2.24	2.51	1.10	0.59
Eu ₂ O ₃	0.045	nd	0.027	nd	nd	nd	nd	nd	nd	0.077	nd	nd	nd	nd	nd	nd	nd	nd
Gd ₂ O ₃	2.69	2.68	1.93	1.19	1.80	2.44	1.64	2.31	1.96	1.49	1.61	2.11	1.25	1.58	2.08	2.91	1.17	1.36
Tb ₂ O ₃	0.09	0.10	bdl	bdl	0.07	0.13	bdl	bdl	bdl	0.15	bdl	bdl	bdl	bdl	bdl	0.07	bdl	bdl
Dy ₂ O ₃	1.04	1.42	0.85	0.23	0.93	1.03	0.54	0.86	0.70	0.69	0.30	0.62	0.19	0.16	0.34	1.07	0.10	0.10
Ho ₂ O ₃	bdl	bdl	0.04	bdl	bdl	bdl	bdl	bdl	bdl	0.08	bdl	bdl	bdl	bdl	bdl	0.03	bdl	bdl
Er ₂ O ₃	bdl	0.06	0.08	0.09	0.08	0.09	0.10	0.11	0.11	0.13	nd	nd	nd	nd	nd	nd	nd	nd
Yb ₂ O ₃	0.11	0.14	0.15	bdl	bdl	0.16	0.04	0.04	0.06	0.04	bdl	bdl	0.05	0.08	0.13	0.07	0.08	0.10
Lu ₂ O ₃	0.05	0.10	0.05	0.04	0.17	0.14	0.03	0.04	0.04	bdl	0.05	0.08	bdl	bdl	0.05	0.08	0.06	bdl
CaO	2.98	2.10	4.61	6.48	4.18	2.97	5.37	2.17	4.31	4.34	4.17	2.23	6.85	5.50	0.91	1.85	1.99	4.96
FeO	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.13	bdl	bdl	bdl	bdl	0.02
PbO	0.48	0.38	0.77	0.56	0.75	0.45	0.73	0.21	0.72	0.99	0.62	0.20	0.67	0.53	0.04	0.15	0.08	0.41
Total	99.66	100.71	100.46	95.61	96.68	100.32	100.95	99.95	101.14	97.48	95.79	92.40	100.75	99.18	99.20	99.61	95.99	97.26
Htn	0.000	0.000	0.000	0.004	0.002	0.000	0.000	0.000	0.000	0.000	0.027	0.009	0.000	0.003	0.006	0.005	0.036	0.001
Mnz	0.645	0.680	0.535	0.419	0.527	0.660	0.518	0.752	0.587	0.495	0.583	0.716	0.422	0.717	0.853	0.736	0.750	0.476
Xnt	0.102	0.150	0.094	0.037	0.113	0.094	0.062	0.082	0.076	0.083	0.049	0.079	0.033	0.085	0.062	0.131	0.028	0.039
CrI	0.253	0.169	0.370	0.539	0.358	0.245	0.418	0.164	0.333	0.420	0.341	0.196	0.540	0.193	0.078	0.128	0.185	0.481

bdl below detection limit, *nd* not determined. Symbols of end-member proportions (in molar fraction): *Htn* huttonite, *Mnz* monazite, *Xnt* xenotime, *CrI* cheralite. UCM thin section data collection: *N206* 111,404, *N9* 106,794, *N10* 106,796, *N204* 111,402, *N316* 112,119, *N348* 112,867

analysed by EMP truly corresponded to the monazite lattice and not to micro- or nano-inclusions of other U-rich minerals (as uraninite). Measures were achieved using a JEOL-JSM-7600 F, attached with an Oxford EDX detector (Centro Nacional de Microscopía Electrónica “Luis Bru”, Universidad Complutense de Madrid). The conditions were an accelerating voltage of 10 kV and a working distance of 8 mm, obtaining elemental maps at magnification of 600–30,000 times.

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

The LA-ICP-MS analyses were performed using thin sections of the four units and separate samples of G1 and G2 units. Single-grain trace element analyses of monazite, xenotime and zircon were collected using an Agilent 7500CS ICP-MS coupled to an ESI New Wave UP193 laser source (193 nm ArF excimer laser) at the Natural History Museum in London. 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 laser was 10 Hz, and the fluence 3.5 J cm^{-2} . Spot size varied between 20 and 30 μm in diameter dependent on grain size. Quantitative results for 40 elements were obtained through calibration of relative element sensitivities using the NIST 612 glass standard. Precision was determined to be approximately 2 % or better for most elements. Accuracy was monitored using the USGS basalt glass BCR2-G analysed as an unknown, and data were found to be within the errors associated with the determination of its reference values. Each mineral analysis was normalized by the internal standard method to CaO (monazite, apatite) Y_2O_3 (xenotime) and HfO_2 (zircon), 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 possible contamination from inclusions, fractures and zones of different composition was detected by monitoring several elements and integrating only the relevant part of the signal.

Taking into account that some REE display very high concentrations in monazite (LREE) and xenotime (HREE), falling outside the calibration range allowed by the standards used with the laser equipment, we consider that the EMP analyses for those elements are more accurate. Accordingly, the laser spots have been performed in those mineral domains with EMP data. These spots correspond with the same point or microtextural domain where the EMP analyses were determined. In this manner, we can

combine both techniques to obtain the most complete and accurate REE concentrations. La, Ce, Pr, Nd, Sm and Eu values in monazite, and Eu, Tb, Ho, Yb and Lu in xenotime, which are shown in Tables 1 and 2, have been determined by EMP, whereas contents for the rest of REE that show lower concentrations (close to the detection limit of the EMP), have been obtained by laser ablation. The REE contents in zircon were obtained exclusively by LA-ICP-MS.

Results

Monazite texture and composition

Monazite occurs in the G1, G2 and G3 units preferentially hosted in muscovite, feldspars or along phase boundaries, whereas in G4 it is mostly included in biotite and fibrolitic sillimanite aggregates, oriented along the mica exfoliation planes (Fig. 2a). In thin section, monazite is light greenish in colour, and, when included in feldspars, a brownish orange halo is observed. Some crystals show a pseudomorphic secondary complex aggregate (Fig. 2b) with significant variation in their common main oxides (Al, P, Si, Fe, Ca and REE). Similar coronas in granite monazite have been reported as secondary intergrowths of apatite, allanite and Th–Si phases produced by interaction with high Ca activity fluids (e.g. Negga et al. 1986; Dini et al. 2004; Broska et al. 2005; Petrik et al. 2006).

Monazite and zircon may appear included in the same host crystal, especially in the less differentiated G3 and G4 units. In the G1 and G2 units, monazite appears isolated within the main minerals and exceptionally associated to xenotime (Fig. 2c). Monazite occurs as isometric to short prismatic crystals, euhedral to anhedral in G1 and G2 (Fig. 2b, c, e, g, n), and subhedral to anhedral in G3 and G4 units (Fig. 2a, d, f). Crystal size ranges from 19 to 170 μm in thin sections and up to 260 μm in the separate fraction. Monazite crystal size is higher in the G1 and G2 units. Monazite occasionally contains abundant inclusions of the main minerals, frequently defining an internal foliation (Fig. 2e). Transgressive sectors may occur in monazite crystals of G1 and G2 units (Fig. 2f–h).

The monazite crystals may be fairly homogeneous (Fig. 2e) or display three zoning patterns: (1) concentric oscillatory zoning: in G3 and G4 with darker and euhedral cores which softly contrast with the outer lighter domains (Fig. 2d, g), whereas in G2 and G1 units the zoning is reverse (Fig. 2f, h); (2) sector zoning (Fig. 2i); and (3) extremely irregular patchy zoning (Fig. 2f). U–Pb dating of monazite from G1 unit (Orejana et al. 2012) yielded two age groups which can be associated to different monazite domains: monazite with patchy zoning (type 3) showed an

Table 2 Representative electron microprobe analyses of xenotime from the Belvís pluton

Granite Sample Analysis Spot position	G1 N8 2	G1 N8 3	G1 N8 4	G1 N8 5	G1 N8 6	G1 N8 7	G1 N8 10	G1 N8 11	G1 N8 15	G1 N8 16	G1 N8 17	G1 N8 19	G1 N8 21	G1 N8 22	G1 N8 23	G1 N8 24	G2 N10 25
		c1	r1		r2	c2	c3	r3		c4	r4				r5	c5	
P ₂ O ₅	35.59	32.90	33.58	33.35	34.54	34.44	33.65	34.28	34.31	33.51	32.80	32.83	32.39	33.81	33.77	34.42	33.97
SiO ₂	0.17	0.71	0.39	0.90	bdl	0.02	0.18	0.08	0.14	0.21	0.36	0.51	0.47	0.07	0.24	0.32	0.05
UO ₂	4.73	12.29	9.47	13.34	2.37	3.13	7.05	3.79	4.71	7.33	9.41	10.12	10.7	3.66	7.50	6.15	2.88
ThO ₂	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.03	bdl
Y ₂ O ₃	40.03	36.97	39.51	36.30	42.90	42.23	40.26	42.04	41.66	40.27	37.97	37.76	36.46	42.10	40.48	41.92	44.33
La ₂ O ₃	bdl	0.02	bdl	bdl	0.02	bdl	0.03	bdl	0.02	0.03	0.03	0.02	0.02	bdl	bdl	bdl	0.02
Ce ₂ O ₃	0.11	0.08	0.08	0.05	0.09	0.08	0.10	0.08	0.09	0.13	0.11	0.12	0.12	0.11	0.09	0.07	0.07
Pr ₂ O ₃	0.03	0.03	bdl	0.02	0.04	0.02	0.02	0.02	0.03	0.04	bdl	0.02	0.04	0.02	0.03	0.03	0.04
Nd ₂ O ₃	0.33	0.26	0.33	0.27	0.39	0.43	0.35	0.40	0.45	0.45	0.41	0.43	0.46	0.46	0.32	0.27	0.40
Sm ₂ O ₃	0.24	0.11	0.17	0.53	0.33	0.33	0.16	0.31	0.35	0.23	0.29	0.29	0.33	0.32	0.13	0.09	0.30
Eu ₂ O ₃	nd	0.015	0.017	0.018	0.017	0.016	0.017	0.014	0.014	bdl	bdl	nd	nd	0.016	bdl	bdl	bdl
Gd ₂ O ₃	2.78	1.89	2.31	1.79	3.12	3.08	2.04	2.83	2.61	2.16	2.24	2.27	2.34	2.66	1.91	2.22	2.98
Tb ₂ O ₃	0.85	0.59	0.65	0.62	0.90	0.84	0.68	0.86	0.85	0.65	0.66	0.65	0.70	0.76	0.61	0.68	0.90
Dy ₂ O ₃	6.17	4.83	5.43	4.87	6.38	6.21	5.35	6.19	5.89	5.21	5.22	5.18	5.05	6.01	5.06	5.38	6.06
Ho ₂ O ₃	0.85	0.74	0.74	0.80	0.83	0.83	0.81	0.81	0.76	0.78	0.69	0.74	0.65	0.81	0.75	0.80	0.79
Er ₂ O ₃	2.91	2.89	2.66	2.63	3.10	3.06	2.51	2.81	2.28	2.86	2.67	2.67	2.53	2.75	2.85	3.12	2.93
Yb ₂ O ₃	0.53	1.73	2.11	2.32	1.94	1.86	1.64	1.48	1.65	1.64	1.64	1.68	1.46	1.97	2.13	2.52	1.85
Lu ₂ O ₃	2.03	1.20	1.31	1.18	1.57	1.05	1.30	1.49	1.48	1.27	1.27	1.25	1.22	1.44	1.26	1.36	1.51
CaO	1.42	1.86	1.55	1.92	0.49	0.58	1.25	0.70	0.85	1.27	1.61	1.66	1.70	0.65	1.26	1.36	1.51
PbO	bdl	0.76	0.68	0.76	0.42	0.45	0.61	0.48	0.53	0.60	0.67	0.70	0.71	0.45	0.60	0.52	0.45
Total	99.58	100.40	101.57	102.19	100.03	99.29	98.54	99.27	99.29	99.21	98.60	99.45	97.92	98.64	99.58	101.41	100.26
Mnz	0.009	0.006	0.007	0.010	0.010	0.010	0.008	0.010	0.011	0.011	0.010	0.011	0.012	0.011	0.007	0.006	0.009
Xnt	0.921	0.825	0.862	0.815	0.951	0.942	0.887	0.932	0.918	0.882	0.852	0.845	0.834	0.934	0.885	0.911	0.947
CrI	0.070	0.168	0.131	0.173	0.039	0.048	0.104	0.058	0.071	0.106	0.137	0.143	0.153	0.055	0.107	0.082	0.044

Oxides in wt%, trace elements in ppm, *bdl* below detection limit, *nd* not determined. The huttonite fraction is 0.00 in all the samples included in the table. Symbols of end-member proportions (in molar fraction): *Mnz* monazite, *Xnt* xenotime, *CrI* cheralite spot position: *n1-r1* core (*c*) and rim (*r*) of the same crystal

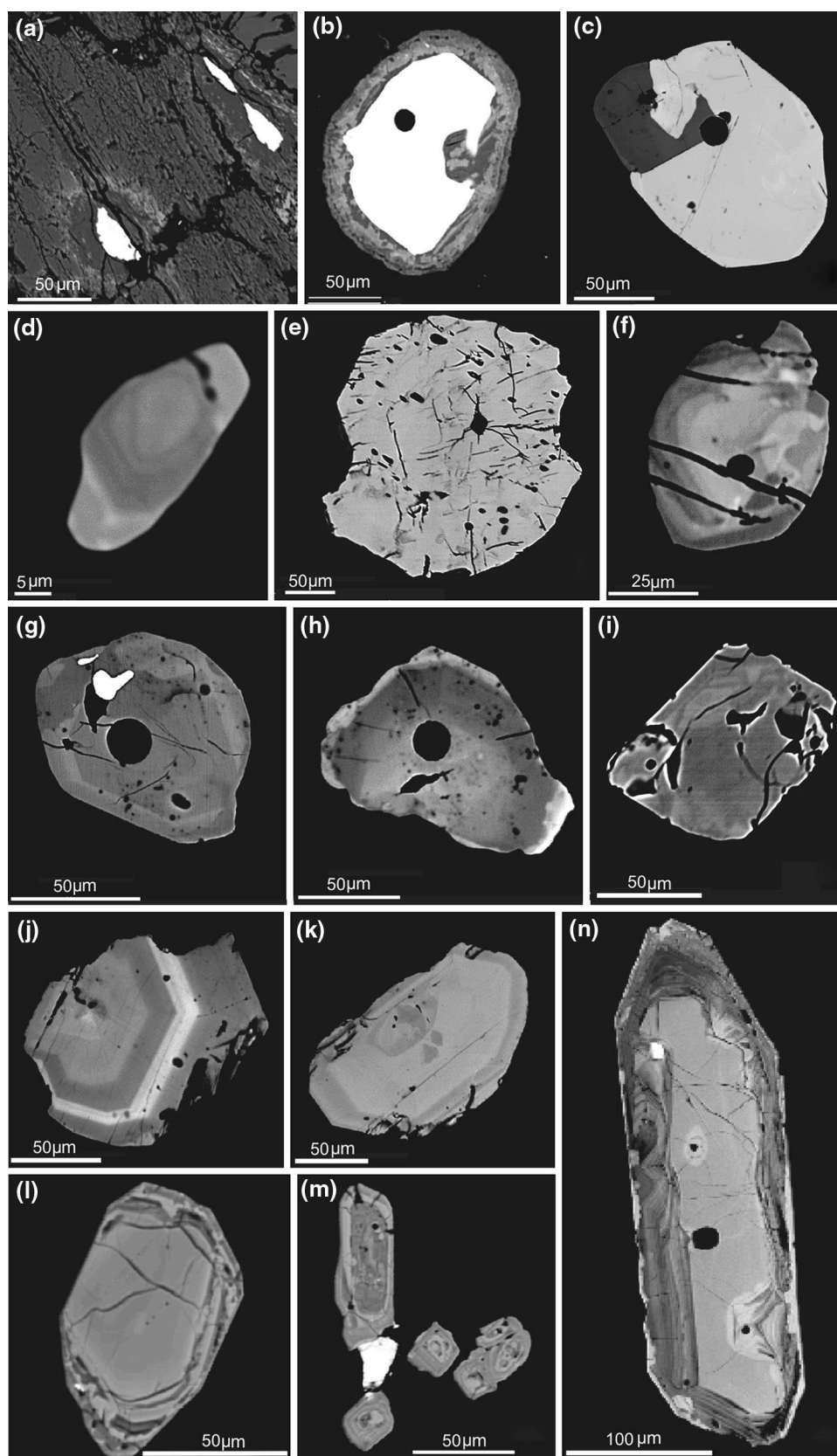


Fig. 2 Representative back-scattered electron images of analysed monazite, xenotime and zircon crystals from the G1 (images B, C, G, J, K), G2 (images E, H, I, L, M, N), G3 (image A) and G4 (images D, F) granitic units of the Belvís pluton: **a** anhedral elongated monazite crystals included in biotite, both defining the magmatic foliation of Belvís pluton. Biotite exhibits a metamictic aureole around these crystals (monazite total actinides = 15.50 wt%); **b** from separate sample, euhedral monazite crystal exhibiting a complex, secondary aureole (BSE image highly contrasted); **c** from separate sample and aggregate of euhedral monazite (*light crystal*) and xenotime (*dark crystal*); **d** hosted in biotite crystal, a subhedral monazite crystal showing oscillatory concentric zoning in two domains: inner and darker ($\text{UO}_2 + \text{ThO}_2 = 0.79 + 9.10$ wt%) and outer and lighter ($7.69 + 10.12$ wt%); **e** from separate sample, a subhedral monazite crystal ($\text{UO}_2 = 13.92 - 20.81$ wt%) exhibiting internal foliation marked by both elongated quartz and alkali feldspar inclusions; **f** subhedral monazite crystal hosted in a muscovite-biotite elongated aggregate. The crystal displays complex zoning, with outer rough oscillatory zoning and inner patchy domains; **g** from separate sample, a subhedral monazite crystal showing concentric zoning (*darker core*), partially truncated by a dark irregular sector in the *upper left* of the magmatic rim. The crystal shows microinclusions and a slight alveolar texture. The inner sector has contents of $\text{UO}_2 + \text{ThO}_2 = 0.79 + 9.10$ wt%; **h** from separate sample, a monazite crystal displaying concentric zoning (*lighter core*) with slight alveolar texture. The lighter core evidences minor resorption prior to rim development; **i** from separate sample, monazite crystal showing contrasted sector zoning, with UO_2 and ThO_2 increase from darker inner domains ($0.02 + 9.27$ wt%) to lighter sectors ($2.67 + 15.19$ wt%); **j** from separate sample, fragment of subhedral xenotime crystal with prominent concentric zoning defining euhedral crystal evolution. The *darker band* shows lower UO_2 abundance (4.44 wt%) compared to the lighter intermediate band (10.12 wt%); **k** from separate sample, subhedral xenotime crystal displaying concentric zoning with a resorbed sector zoning core; **l** hosted in muscovite, euhedral type 1 zircon crystal showing large homogenous core rimmed by irregular concentric and patchy zoning with evidences of resorption; **m** hosted in K-feldspar, cluster of subhedral to anhedral type 2 zircon crystals, displaying a characteristic complex zoning (oscillatory, patchy and resorbed) in concentric bands. *Light crystal* is monazite; **n** from separate sample, euhedral type 1 zircon crystal with homogenous core resorbed by fine and undulating oscillatory-zoned sector which, in turn, is overgrown by an straight oscillatory-zoned rim

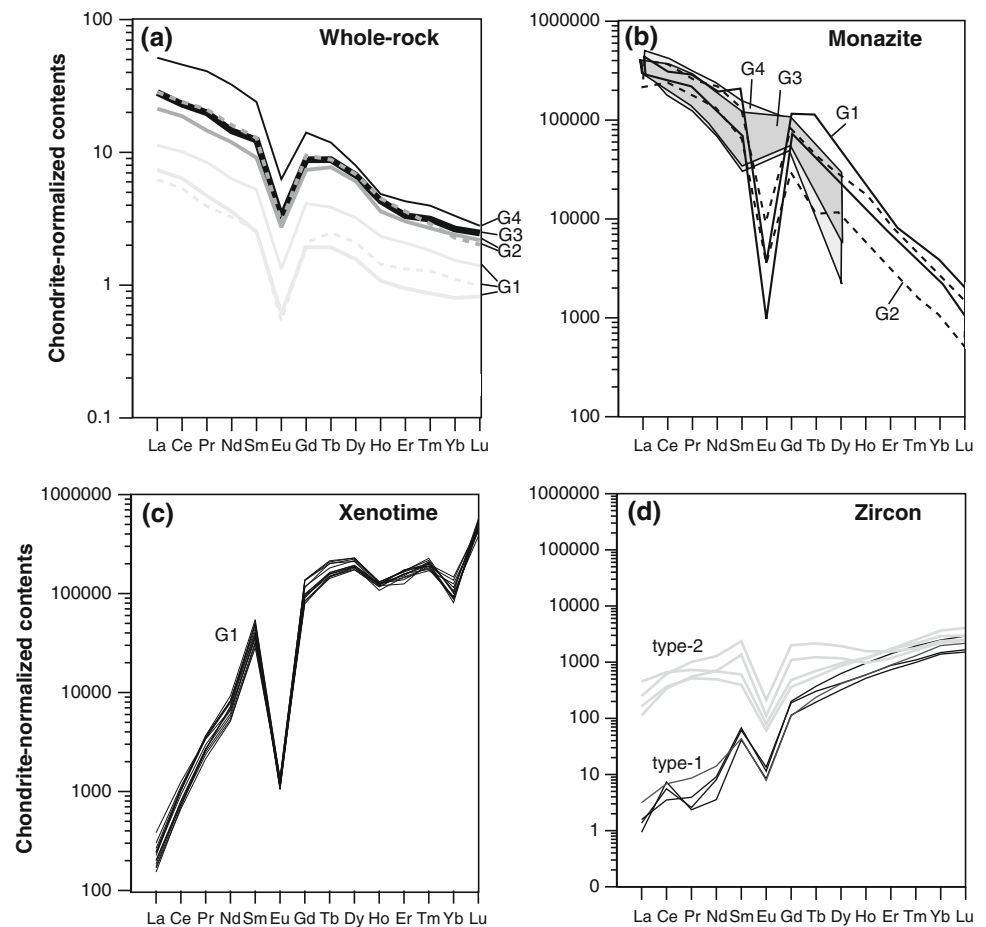
average age of 333 ± 5 Ma, older than type 1 and type 2 zoning, which recorded a mean age of 314 ± 3 Ma. Type 3 zoning is typical of metamorphic monazite (e.g. Crowley et al. 2008). For this reason, type 3 monazite is interpreted as xenocrystic and has not been considered in this study. The light BSE sectors of type 1 and type 2 monazite are systematically enriched in U and Ca, whereas dark sectors are enriched in Y, HREE and Ce (LREE). When plotted in the monazite $[\text{2REEPO}_4]$ —cheralite $[\text{ThCaU(PO}_4)_2]$ —huttonite $[\text{2ThUSiO}_4]$ diagram (Supplementary Fig. 2; after Linthout 2007), the Belvís monazites extend mainly the monazite range, reaching the more uncommon cheralite composition. There is a negligible increase in the huttonite component in some analyses of the less evolved G4 unit. It is noticeable that the combination of both the U and Th in

the cheralite component eliminates any significant decoupling between these two cations and limits the application of this classification. Since all the analyses have $\text{Ce} > (\text{La}, \text{Nd})$, monazite is more specifically classified as (Ce) monazite.

Monazite shows a wide chemical variation within the Belvís granites, with extreme contents in most of the major and trace elements in the most evolved G1 and G2 units (Table 1). The REE contents, in decreasing abundance, are in the following ranges (all in wt%): $\text{Ce}_2\text{O}_3 = 13.50\text{--}28.83$, $\text{La}_2\text{O}_3 = 6.06\text{--}13.51$, $\text{Nd}_2\text{O}_3 = 4.13\text{--}13.75$, $\text{Pr}_2\text{O}_3 = 1.35\text{--}3.51$, $\text{Sm}_2\text{O}_3 = 0.59\text{--}2.82$, $\text{Gd}_2\text{O}_3 = 0.27\text{--}2.91$. Its remarkable the variable ThO_2 (0.10–19.58 wt%, mean of 12.83 wt%) and the high UO_2 (up to 23.13, mean of 11.8 wt%) contents. To our knowledge, this is the highest U content in monazite reported so far, either described from pegmatitic ($\text{UO}_2 = 15.64$ wt%, Gramaccioli and Segastald 1978) or granitic rocks ($\text{UO}_2 = 13.8$ wt%, Bea 1996). In addition, monazite displays high contents of CaO (0.91–6.85 wt%), HREE $_2\text{O}_3$ ($\sum (\text{Tb}\text{--}\text{Lu})_2\text{O}_3 = 0.08\text{--}2.45$ wt%, with Dy as prominent element) and Y_2O_3 (0.32–3.57 wt%), with Y contents close to the highest values reported in granite rocks (4.31 and 4.66 wt%, Förster 1998a). Other trace element contents in monazite show a wide variation (in ppm): Li (3–209), Be (1–56), Zr (93–1,370), Ba (<183) and Hf (1–138), similar or slightly higher than that reported in other monazites (Stepanov et al. 2012). The SiO_2 , FeO and MnO contents are typically low, below or near the detection limit, although SiO_2 and FeO may reach significant contents (up to 0.23 and 0.45 wt%, respectively) in the G3 and G4 units (Table 1). Analytical totals vary considerably, ranging from 92.4 to 103.8 wt% (Table 1).

In the G1 and G2 monazite, the Th/U ratio is typically below 1 and decreases from core to rim in the zoned crystals, whereas in the G3 and G4 units, monazite shows more variable Th/U ratios, generally higher than 1 (Supplementary Fig. 3). High actinide content in monazite has been explained by microinclusion of actinide-rich minerals (Ruschel et al. 2012), sometimes resulting from dissolution–reprecipitation (Hetherington and Harlov 2008). These minerals (e.g. thorite, uraninite) have not been found at any scale in the Belvís granites. The U elemental map at magnification of 30,000 times shows a completely homogenous distribution in the Belvís U-rich ($\text{UO}_2 = 17.67$ wt%) monazite (Supplementary Fig. 4). Furthermore, the U content of the Belvís monazite defines a steady trend in the different coupled substitution mechanism, suggesting that the U is within the mineral lattice. High uranium content in monazite is perfectly plausible according to the experimental work on monazite and actinide orthophosphate stability of Podor and Cuney

Fig. 3 Chondrite-normalized REE spectra for whole-rock samples, monazite, xenotime and zircon from the Belvís granite units (G1–G4). Whole-rock REE data from Villaseca et al. (2008) and Merino et al. (Lithos, in press). Only concentrations above detection limit for each analytical method (LA-ICP-MS or EM) are considered in each part of the REE spectra. In monazite: La–Dy by EM (Table 1), Eu and Ho–Lu by LA-ICP-MS (Supplementary Table 2); in xenotime: La–Eu by LA-ICP-MS (Supplementary Table 3), and Gd to Lu by EM (Table 2); REE abundances of zircon were entirely analysed by LA-ICP-MS (Supplementary Table 4)



(1997), who concluded that partial solid solution of $[(Ca_x^{2+}U_x^{4+}HREE_{1-2x}^{3+})PO_4]$ is stable for $x \approx 0.5$. Those analyses which have U contents in excess of 10 wt% could be more properly classified as (Ce,U)-monazite (Rosenblum and Fleischer 1995).

Chondrite-normalized REE patterns (Fig. 3b) are, in general, typical of monazite from peraluminous granites (Bea 1996; Förster 1998a): a strong fractionation from La to Lu ($La_n/Nd_n = 1.47\text{--}4.76$, mean of 2.37), profound negative Eu anomalies ($Eu/Eu^* < 0.11$ for G1 and G2 monazite) and significant HREE contents (Table 1, Fig. 3b). The comparison of monazite patterns from G4 to G1 shows relatively more pronounced LREE convex-upward patterns and a progressive narrower range of the LREE content. HREE slightly increase from G4 to G1. The negative Eu anomaly (Eu/Eu^*) is more pronounced in G1 (0.012–0.033) than in the G2 (0.043–0.111) monazite. Chondrite-normalized REE patterns show an absence of tetrad effects (TE_1 : La–Nd or TE_3 : Gd–Ho, Bau 1996; Irber 1999), as TE values are below the level of analytical significance ($TE > 0.2$), according to the method of Monecke et al. (2002).

Xenotime texture and composition

This mineral has been found only in the more evolved units (G2 and G1) mainly in mineral concentrates. The euhedral crystals range in size from 60 to 190 μm (mean of 120 μm). The BSE images show a distinctive magmatic oscillatory zoning defined by straight concentric bands, locally with partial resorption (Fig. 2j, k). Xenotime crystals are usually free of inclusions. Xenotime may occur in association with monazite (Fig. 2c) or fluorapatite.

Xenotime (Table 2) shows total $HREE_2O_3$ contents from 12.09 to 15.31 wt% and abundance (all in oxide wt%) of Dy (4.83–6.38) > Er (2.28–3.16) > Gd (1.79–3.12) > Yb (1.46–2.72) > Lu (0.92–1.57) > Ho (0.65–0.85) and Tb (0.59–0.90) > Tm (0.47–0.63). A notable chemical feature is the high and variable U content (2.37–13.34 UO_2 wt%, mean of 6.4 wt%). To the best of our knowledge, this is the highest content reported in xenotime from granites (higher than 9.44 wt% in the Albuquerque granite, also from the Iberian Massif, Bea 1996). Belvís xenotime has Th contents near or below the detection limit

($\text{ThO}_2 < 0.03 \text{ wt\%}$) and $\text{U/Th} > 210$. Unlike observations from other studies (e.g. van Emden et al. 1997), in the Belvís pluton the, U content in xenotime is not higher than that in monazite. The monazite associated with xenotime in the G2 unit (Fig. 2c) shows considerably higher UO_2 (13.39 wt%) when compared to xenotime (4.73 wt%). Other non-formula elements with prominent abundance (all in oxide wt%) are Ca (0.12–1.92), Si (<0.91) and LREE (0.62–1.54), of which Sm (<0.53), Nd (<0.48) and Gd (<3.12) stand out. Mn, Fe and Al are near or below their detection limits, which contrast with their significant contents in monazite or zircon of the same samples. Other elements in appreciable amounts (in ppm) are Zr (265–12,000), Hf (10–800), Li (51–298) and Sc (62–170) (Table 2), with Zr/Hf ratios relatively constant about a mean of 30. Analytical totals range from 97.74 to 102.19 wt% (60 % totals are 100 ± 1).

Xenotime zoning consists of BSE bright sectors with high abundance in U, Ca, Si and LREE (usually crystal cores), alternating with dark domains (generally crystal rims) which are close to a stoichiometric composition. This zoning is similar to other zoned xenotimes in fractionated granites (e.g. Broska et al. 2005). The U compositional variation in a single crystal displays the whole range of xenotime composition in the Belvís units.

Chondrite-normalized REE spectra of the G1 xenotime are fairly homogeneous (Fig. 3c) and characterized by a LREE pronounced positive fractionation (mean $\text{La}_n/\text{Sm}_n = 0.05$), a deep Eu negative anomaly (0.014–0.024) and a gentle positive HREE pattern ($\text{Gd}_n/\text{Lu}_n = 0.22$). The HREE trend shows a well developed TE_3 (from 0.57 to 0.80, exceeding 0.2, the lowest value of significant confidence, Monecke et al. 2002), and a negative kink for Yb. The resulting HREE pattern contrasts with the smoother trends of xenotime in other peraluminous granites (e.g. Bea 1996; Förster 1998b). The whole-rock chondrite-normalized REE patterns of the Belvís pluton show a smooth but significant TE_3 effect (Fig. 5a). This “xenotime signature” suggests that this mineral, although it has not been found in the least evolved units (G3 and G4), might have crystallized from all successive pulses during pluton construction.

Zircon texture and composition

Zircon is a common accessory mineral in the Belvís pluton, although considerably less abundant and smaller than monazite, especially in the more evolved units (G1 and G2). In the G3 and G4 units, zircon occurs included in fibrolitic sillimanite and biotite aggregates, whereas in the G1 and G2 units it mostly occurs included in muscovite and feldspar. Zircon mainly appears as isolated subhedral to euhedral crystals, although in the G3 and G4 units can be

found in contact with monazite or arranged as zircon clusters (Fig. 2m).

Two main zircon typologies have been observed. Type 1 zircon mainly appears in mineral separates of the G1 unit, showing a correlation between the elongation ratio (up to 3.5) and the length of the crystals (120–375 μm) (Supplementary Fig. 5). Zoning in type 1 zircon is characterized by big and homogeneous cores (sometimes partially corroded) surrounded by a complex oscillatory, convolute and patchy rim domain (Fig. 2n). Type 2 zircon is characterized by small (12–75 μm) equant to acicular (elongation ratio up to 5.9) crystals (Supplementary Fig. 5). This second population has been exclusively observed in thin sections and shows complex zoning textures, where patchy, oscillatory and spongy sectors coexist in irregular concentric zones delimited by sharp transgressive boundaries, giving rise to an extremely heterogeneous appearance (Fig. 2l, m).

Type 1 zircons have a near stoichiometric composition, with P, Ca, Fe, Mn, Y and actinides contents near or below detection limits, and HfO_2 content ranging from 1.14 to 1.48 wt% (mean of 1.35 wt%) (Table 3). Type 2 zircons show more variable and significant contents of non-formula elements, reaching the highest values in the G1 and G2 units (in wt%) in P_2O_5 (≤ 14.91), Al_2O_3 (≤ 6.96), FeO (≤ 2.93), CaO (≤ 2.24), MnO (≤ 0.39), UO_2 (≤ 1.53) and TiO_2 (≤ 0.10). This zircon P content is near the highest content reported to date (15.31 wt%, Huang et al. 2000). The Y and REE contents are low, typical of perphosphorous granites (Breiter et al. 2006). G3 and G4 type-2 zircon shows the highest content of Y_2O_3 ($\leq 1.25 \text{ wt\%}$), REE_2O_3 ($\leq 0.91 \text{ wt\%}$) and ThO_2 (≤ 0.08). The HfO_2 content is variable, mostly in the range from 0.93 to 4.85 wt% (mean of 2.09 wt%, mode value 1.65 wt%) (Table 3). In zoned crystals of both types, no significant and systematic variation of Hf content has been detected, and Hf is not correlated with Zr or other significant elements. Indeed, the Zr/Hf ratio values (11–82, mean of 41) almost cover the whole range of common granitic zircon (e.g. Wang et al. 2010). Type 2 zircons mostly display Th/U ratio <0.5, which contrast with the higher values of type 1 zircons (from 0.34 to 2.99). The zircon composition of Belvís is within the common range of zircon from granitic rocks (Hoskin and Schaltegger 2003, and references therein; Breiter et al. 2006; Wang et al. 2010), although those of type 2, are typical of peraluminous and P-rich fractionated granites and pegmatites (Breiter et al. 2006, and cites therein). The REE content of type 2 zircon is within the range of perphosphorous granites (Bea 1996), whereas in type 1 zircons it is even lower than that of zircon from P-poor varieties (Bea 1996). About half of our zircon analyses show deficient totals (down to 90.75 wt%), and cation sums are above the ideal 2 apfu (on the basis of 4 oxygen atoms).

Table 3 Representative electron microprobe analyses of zircon from the Belvís pluton

Granite Sample Analysis	G1 106,792 1	G1 106,793 11	G1 111,404 13	G2 106,795 15	G2 106,795 17	G2 106,795 20	G2 106,795 21	G3 111,402 22	G3 111,402 23	G3 111,402 25	G3 112,110 29	G4 112,867 32	G4 112,867 38	G4 112,866 41	G4 112,866 44
P ₂ O ₅	14.91	0.38	7.28	0.25	7.31	10.09	8.15	0.80	0.77	0.11	0.31	0.15	5.35	4.75	2.69
SiO ₂	14.13	31.07	24.49	32.53	21.73	20.38	22.80	32.46	32.42	32.84	32.94	33.10	24.55	21.47	27.02
ZrO ₂	48.31	64.39	56.77	64.20	53.90	51.55	53.62	63.25	63.77	64.81	63.59	66.14	57.42	53.55	61.33
HfO ₂	2.69	3.19	1.57	2.11	2.20	1.82	1.64	1.75	1.70	1.10	2.21	1.50	1.09	1.69	1.62
UO ₂	1.24	0.20	0.97	0.29	0.66	0.86	1.22	0.88	0.59	bdl	0.22	0.09	0.79	1.34	1.47
ThO ₂	0.02	bdl	0.03	bdl	bdl	bdl	0.03	bdl	0.02	bdl	bdl	0.04	bdl	0.08	0.08
TiO ₂	0.10	bdl	0.05	0.02	0.06	0.06	0.05	bdl	bdl	bdl	bdl	bdl	0.03	0.03	0.08
Al ₂ O ₃	6.96	0.09	1.57	bdl	0.72	3.38	3.22	0.07	0.08	0.03	0.02	0.03	2.07	3.02	1.22
Y ₂ O ₃	0.43	bdl	0.43	0.02	0.20	0.39	0.33	0.43	0.37	0.24	bdl	0.04	1.25	0.51	0.86
Ce ₂ O ₃	0.02	bdl	bdl	0.03	bdl	0.05	0.02	bdl	bdl	bdl	0.02	bdl	0.02	0.21	0.16
Nd ₂ O ₃	bdl	bdl	bdl	0.03	0.03	0.03	bdl	bdl	bdl	0.02	bdl	bdl	0.17	0.24	0.16
Sm ₂ O ₃	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.04	0.07	0.06
Dy ₂ O ₃	0.05	bdl	0.03	bdl	bdl	0.04	0.08	0.08	0.06	0.02	bdl	0.02	0.10	0.07	0.11
Yb ₂ O ₃	0.06	bdl	bdl	bdl	0.02	0.05	0.11	0.05	bdl	0.13	0.07	0.06	0.26	0.16	0.17
CaO	2.24	0.11	1.54	bdl	2.11	1.87	1.52	0.17	bdl	bdl	0.03	0.05	1.02	1.02	1.02
FeO	2.93	0.13	1.12	0.04	1.37	2.20	1.55	0.06	0.11	0.03	0.13	0.03	2.42	2.30	2.07
MnO	0.35	0.05	0.1	bdl	0.31	0.13	0.15	0.02	bdl	bdl	bdl	bdl	0.08	0.08	0.07
PbO	bdl	bdl	bdl	0.02	bdl	0.31	0.13	0.15	0.02	bdl	bdl	bdl	0.02	0.02	0.03
Total	94.64	99.68	96.17	99.57	90.75	93.00	94.55	100.09	100.00	99.39	99.62	101.30	97.01	90.78	100.36

bdl below detection limit

Chondrite-normalized REE patterns of type-1 (from G1) and type-2 (from G3 and G4) zircons are markedly different (Fig. 3d). Type 1 zircon shows a steep positive slope from the LREE to the HREE ($Yb_n/Sm_n = 24\text{--}35$), in accordance with the progressive lower compatibility from HREE to LREE within the Zr site (Hanchar et al. 2001). These patterns show a deeper decrease in the LREE with respect to the MREE when compared to those of common granite zircons (e.g. Bea 1996; Hoskin and Ireland 2000). Their LREE pattern has a positive Ce anomaly ($Ce/Ce^* = 1.3\text{--}4.95$), which contrasts with the smooth LREE profile of zircon from similar P-rich peraluminous granites (Bea 1996). These Ce anomaly values (up to 1.0) are considered as significant (Hoskin and Schaltegger 2003) and typical in zircons from most crustal rocks (e.g. Hoskin and Schaltegger 2003; Schaltegger et al. 1999; Belousova et al. 2002). The HREE branch displays a smooth convex-upward curvature pattern. The chondrite-normalized REE patterns of type-2 zircon have a strong enrichment and lower fractionation of LREE, with no significant Ce anomaly, and a slightly less fractionated to planar HREE branch. This pattern, although more scarce in magmatic zircons (e.g. Bea 1996; Hoskin and Ireland 2000), has been described in some granitoids (Belousova et al. 2002).

Discussion

Substitution mechanisms

The distribution of REE in monazite and xenotime is determined by the atomic arrangement between REE and the oxygen atoms: the REE having larger ionic radii (LREE: La–Gd) in the ninefold-coordinated polyhedron of monazite and smaller REE (HREE: Tb–Lu) accommodated in the eightfold-coordinated polyhedron of xenotime (Ni et al. 1995). Both minerals may incorporate uranium and thorium, although monazite shows a greater ability to incorporate diverse cations than xenotime due to its slightly distorted tetragonal structure (Boatner 2002). Most of the studied accessory minerals are characterized by a significant content of non-formula cations (Tables 1, 2, 3). The incorporation of non-formula elements in the mineral structure is firstly controlled by the difference of effective ionic radii (from Shannon 1976) between substituting and substituted cations (van Emden et al. 1996). Other determining factors are the availability of charge-compensating elements and the structural strain associated with the substitution mechanism (Finch et al. 2001).

Deficient totals have been obtained in a significant percentage of the EMP analyses in the studied accessories, which is relatively common in highly fractionated granites (e.g. Nasdala et al. 2009; Breiter et al. 2006; Pérez-Soba

et al. 2007; Broska and Petřík 2008; Lisowiec et al. 2012). The studied deficient totals are not systematically correlated with alveolar sectors or incomplete analyses (trace element contents checked by LA-ICP-MS in non-stoichiometric monazites only slightly increase the analytical totals). In fact, they have been mainly obtained in oscillatory zoning sectors, evidence of magmatic growth at a low cation diffusivity rate (Wark and Miller 1993). They display a clear correlation with P content in monazite and zircon, suggesting that deficient totals are mainly magmatic in origin.

Pb content in these U-rich minerals could be achieved by both U and Th radiogenic decay in the time elapsed since the granite emplacement and by its incorporation as common Pb^{2+} during crystallization (Quarton et al. 1984; Parrish 1990; Podor and Cuney 1997; Watson et al. 1997). This double origin, magmatic and post-magmatic, leads to the question if Pb content should be, a priori, considered in the substitution mechanisms. Although the radiogenic Pb may initially occupy other sites than those where common Pb enters, in a short time it is incorporated in that of common Pb^{2+} (Cherniak 2010). In this regard, we have decided to exclude the Pb content from the discussion for several reasons: (a) In the study of Orejana et al. (2012), the bulk Pb content in monazite was considered as radiogenic; (b) the very low Pb content in zircon, independently of the origin, would not introduce significant changes in the substitution study; (c) in xenotime, we have not evidence of its origin, but its structure can incorporate very little common Pb because of the large difference between the smaller site and the larger Pb cation (Cherniak 2010).

Monazite

Two main coupled substitution mechanisms have been proposed for monazite and xenotime (Gramaccioli and Segastald 1978), later modified by Franz et al. (1996), van Emden et al. (1997) and Förster (1998a, b):

1. Cheralite substitution (previously *brabantite* substitution, see discussion in Broska and Petřík 2008): $(Th,U)^{4+} + Ca^{2+} = 2(Y,REE)^{3+}$
2. Huttonite substitution: $(Th,U)^{4+} + Si^{4+} = (Y,REE)^{3+} + P^{5+}$

Compositional zoning observed in monazite reflects a combination of the huttonite and cheralite substitution mechanisms. In the Si versus Th and Si versus U plots (Fig. 4a), only a certain group of monazite analyses, those characterized by low U content ($<2.4\text{ UO}_2\text{ wt\%}$), displays the huttonite substitution. This indicates that the huttonite substitution is effective only for Th if the U content is relatively low. Van Emden et al. (1997) also observed that the extent of the huttonite mechanism increases with higher

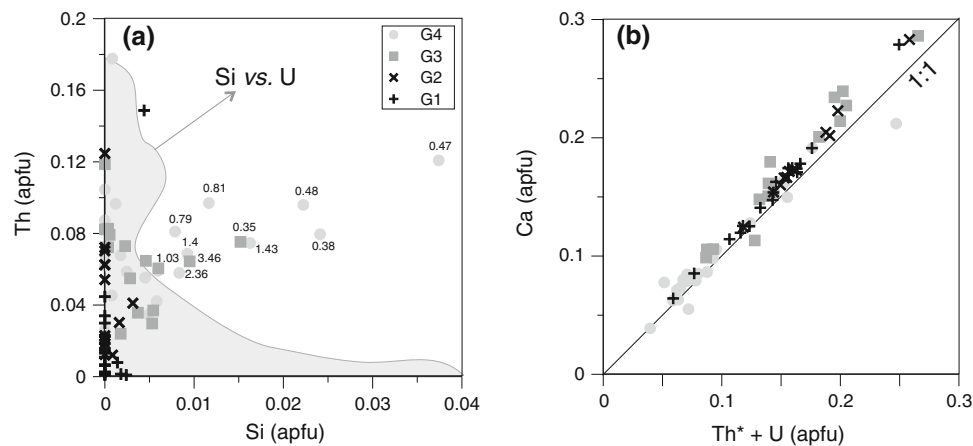


Fig. 4 Plots illustrating the substitution mechanism (on the basis of four oxygen atoms) for monazite of the Belvís pluton: **a** the huttonite substitution: Si versus Th, where the content of UO_2 (in wt%) is indicated for some analysed crystals (see text for explanation), and Si

versus U (in the same scale) with the analyses projection delimited by the shaded area; **b** cheralite substitution. The grey line represents the cheralite substitution vector. Th^* is the Th content after subtracting the equivalent of the Si content (spent in the huttonite substitution)

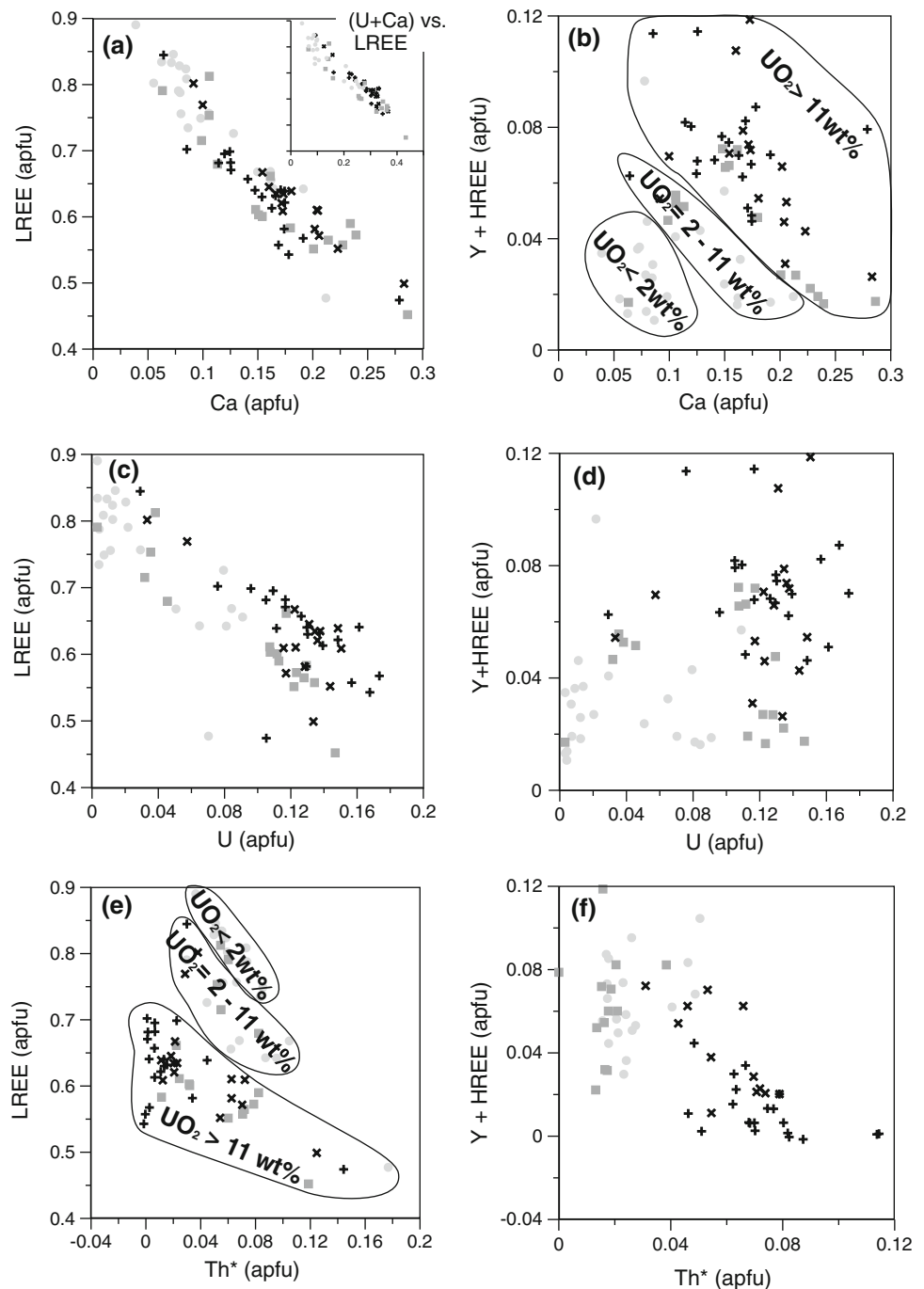
Th contents. As all the Th is incorporated via this mechanism, this content is not considered to evaluate the cheralite substitution. In the Ca^{2+} versus $(\text{U} + \text{Th}^*)^{4+}$ plot (Fig. 4b), monazite shows a strong correlation which suggests that the main compositional variation of the studied crystals is explained by the cheralite substitution, as it would be expected in S-type granites (Förster 1998a, Broska and Petrik 2008, Hoshino et al. 2010). Due to the larger ionic radii of Ca when compared to those of HREE, Ca is incorporated along with U, as their average ionic radii in the ninefold-coordinated state are close to the radius of Gd^{3+} (van Emden et al. 1997). The cheralite mechanism seems to be dominant in G1 and G2 monazite and is only apparent in light BSE domains of G3 and G4 monazite. However, the slope of the best fit (Fig. 4b) is slightly above the substitution vector 1:1, which would evidence either an excess of Ca or a deficiency in $(\text{U} + \text{Th}^*)$. White and Nelen (1987) proposed a complementary substituting mechanism to explain a similar deviation that could charge balance the excess of Ca: $\text{Ca}^{2+} + \text{Ce}^{4+} = 2\text{REE}^{3+}$. This substitution would involve magmatic or post-magmatic oxidation of Ce^{3+} . A lack of positive correlation between excess of Ca ($\text{Ca} - \text{Th}^*$) and the Ce anomaly in the Belvís monazites suggests that the deviation from the 1:1 substitution vector may be better explained by U + Th deficiencies. Significant U (and Th) loss (about 5 %) by radioactive decay after the ~300 Ma from the crystallization of the Belvís granites could partially account for this deficiency. U incorporation in monazite only by cheralite substitution is in agreement with other studies (e.g. Mannucci et al. 1986; Brouand and Cuney 1990; van Emden et al. 1997). It is notable that when considering single LREE cations, La shows the poorest negative correlation with the substituting Ca ($r = 1.18 \text{ \AA}$), Th^*

($r = 1.09 \text{ \AA}$) or U ($r = 1.05 \text{ \AA}$) cations (Supplementary Fig. 6), probably because of its higher ionic radius ($1.216 \text{ \AA}$), indicating a minor participation of La in the total LREE substitution. This observation disagrees with experimental data of Podor and Cuney (1997).

The cheralite substitution has some peculiarities when considering individually the LREE, Y + HREE, U, Ca and Th^* contents (Fig. 5). Ca and LREE display a good negative correlation (Fig. 5a), whereas Ca and Y + HREE correlation is only evident if the analyses are arranged according to their UO_2 content (Fig. 5b). The monazite U content is well correlated with LREE (Fig. 5c), but this is mostly controlled by the good correlation with the Ce content (Fig. 5d). The Th content is correlated with the LREE according to the monazite UO_2 content (Fig. 5e) and displays a rough negative correlation with Y + HREE (Fig. 5f). This can be explained by a similar effective ionic radius between Th and HREE-Y. Actinide incorporation favours substitution of Y and HREE for LREE (Brouand and Cuney 1990). In the Belvís monazite, we observe a positive correlation between LREE and (Y + HREE) according to the U content ($\text{UO}_2 > 11 \text{ wt\%}$, $\text{UO}_2 = 11\text{--}2 \text{ wt\%}$ and $\text{UO}_2 < 2 \text{ wt\%}$), and with different LREE/(Y + HREE) ratios (Fig. 6). The U-poor monazite trend yields a higher LREE/(Y + HREE) value and a shorter REE variation, whereas the opposite features appear in the U-rich monazite. In the same plot, both the Ca content and its range increase from the U-poor monazites to the U-rich group, whereas Th does not define systematic or significant differences between the three groups.

In summary: (1) the bad correlation between U and the individual REE (from Nd to Lu) and Y cations stresses the secondary role of U in the cheralite

Fig. 5 Plots of Ca (a, b), U (c, d) and Th (e, f) versus LREE and (Y + HREE), respectively, for monazite of the Belvís granite units (G1–G4), all of them in atomic proportion (on the basis of 4 oxygen atoms). *Inset* in plot a represents (U + Ca) versus LREE (apfu) from the same monazite analyses, showing a slight better correlation when compared to Ca versus LREE. In b, d and e, several trends are defined according to three different UO_2 ranges (see text)



mechanism, so the Ca substitution for LREE (Ce–Nd) appears to be charge compensated by U and not the reverse; (2) the different substitution trends according to UO_2 ranges (Fig. 5b, e) may record U threshold contents to charge balance the cheralite substitution, in order to minimize the stress introduced in the monazite lattice, similarly to what Finch et al. (2001) proposed for zircon; (3) Th may be preferentially incorporated in monazite

substituting Y + HREE, both via huttonite (Figs. 7a, 8f) and cheralite mechanisms, but this latter is conditioned by the degree of Ca and U substitution for LREE (Figs. 8e, 9). The incorporation of these large cations (i.e. Ca, U or Th) for substituting the smaller HREE and Y cations would be favoured by the lower stress induced in the monazite lattice for these substitutions (Cherniak 2010).

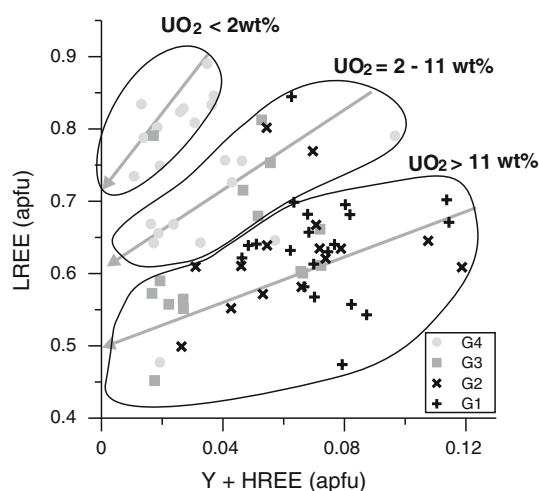


Fig. 6 (Y + HREE) versus LREE contents (apfu on the basis of four oxygen atoms) for monazite of the Belvís granite units (G1–G4). Three groups are defined according to different ranges of monazite UO_2 contents (<2, 2–11 and >11 wt%), which draw three lines of different LREE/(Y + HREE) ratio. Each group, in turn, defines increasing trends of Ca and Th as the LREE/(Y + HREE) ratio decreases (arrows): (i) $\text{UO}_2 < 2$ wt% trend, CaO ranges from 2.3 to 10.9 wt% and ThO_2 from 4.7 to 13.1 wt%; (ii) $\text{UO}_2 = 2\text{--}11$ wt% trend, CaO ranges from 1.6 to 4.6 wt% and ThO_2 from 0.8 to 3.4 wt%; and (iii) $\text{UO}_2 > 11$ wt% trend, CaO ranges from 2.1 to 6.9 wt% and ThO_2 from 0.1 to 13.4 wt%

Xenotime

Xenotime compositions from G1 and G2 units in the Ca versus U plot (Fig. 7a) show a positive trend below the 1:1 vector of the cheralite substitution. This suggests that the U substitution is insufficiently charge balanced by Ca, which is enhanced towards higher U contents. The huttonite substitution is represented in the Si versus U plot (Fig. 7b), showing a positive trend much below the 1:1 vector, with $\text{UO}_2 = 2.8$ wt% at Si = 0 apfu. This, along with the low Si xenotime content (Table 3), suggests that huttonite substitution plays a secondary role, completing the charge balance of the initially favourable and more extensive cheralite substitution. In this way, the U content increases with the progressive higher involvement of the huttonite mechanism. Thus, the U-rich sectors in oscillatory-zoned xenotime would be richer in other non-formula elements (mainly Ca and Si) compared to the U-poor sectors. The Sc, Zr and Hf contents, although significant, show a lack of correlation with the other cations in the octahedral position. Only Sc reaches significant contents in the U-poor sectors.

The uncommon predominance of cheralite over huttonite substitution in xenotime from highly fractionated granites has been reported elsewhere (e.g. Förster 1998b; Broska and Petřík 2008). In the Belvís xenotime, the compositional variation is completely explained by the combination of both mechanisms (Fig. 7c). Similar

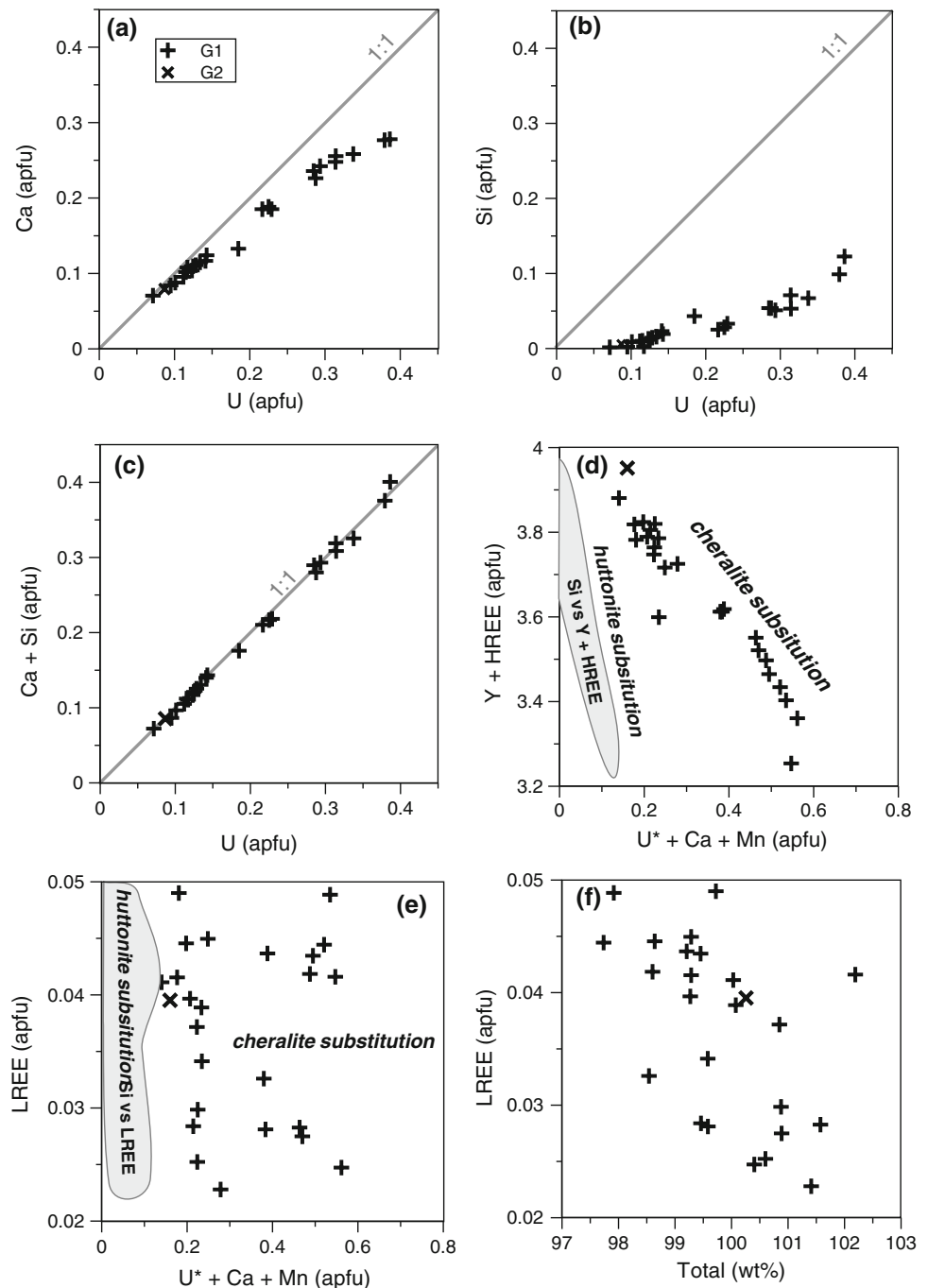
effective ionic radii of (Y + HREE) and (U + Ca + Mn) favour the substitution, as is shown by the strong correlation between them (Fig. 7d). On the contrary, the LREE xenotime content does not appear to be related with the huttonite or cheralite mechanism (Fig. 7e). The LREE content only correlates with the deficient totals (Fig. 7f), and the latter shows a reciprocal behaviour with respect to LREE. This suggests that the low LREE content incorporated in the Belvís xenotime might be controlled by external factors (i.e. monazite crystallization with LREE dragging), but their incorporation to xenotime resulted in the reduction of the analytical totals.

Zircon

The zircon structure consists of highly distorted tetrahedra where HFS cations occupy isolated tetrahedral (Si tetrahedral site) and larger eightfold coordination polyhedron (Zr dodecahedral site), leaving structural voids (4-coordinated channels and 6-coordinated voids) that become potential sites to incorporate impurities for charge balancing without excessive strain (Hoskin et al. 2000; Finch et al. 2001; Finch and Hanchar 2003). Several mechanisms of substitution have been proposed (see compilations of Hoskin and Schaltegger 2003; Cherniak 2010; Bouvier et al. 2012). As type 1 zircon shows nearly stoichiometric composition, we will focus the discussion on the composition of type 2 zircon. The occupation of interstitial sites would involve a significant deviation from the sum of 2 apfu of the stoichiometric zircon (Finch et al. 2001, see discussion in Breiter et al. 2006), as occurs in the studied zircons. Zr and Hf cation define a solid solution (Goldschmidt 1937) and occupy the same site (Wang et al. 2010), so they are considered together in the following discussion.

Type 2 zircon characterized by its P-rich composition may be charge balanced by the incorporation of other non-structural cations (Ca, Fe, Mn, Al, Y, REE, U and Ti) in the Zr site, Si site or interstices. If the P content of Belvís zircon is plotted versus these latter cations, two well-defined positive trends are displayed, respectively, for the G1–G2 and G3–G4 zircon crystals, according to different cation:P ratios (Supplementary Fig. 7a). In addition, positive correlations are observed among pairs of these non-structural cations (e.g. U vs. LREE, similarly to Maas et al. 1992), suggesting that these cations were incorporated into zircon structure during magmatic growth. In the tetrahedral position, P and Al could substitute for Si according to the berlinite substitution: $\text{P}^{5+} + \text{Al}^{3+} = 2\text{Si}^{4+}$. This substitution is represented in the Si versus (P + Al) plot, where type 2 zircon shows a negative correlation according to the 1:1 substitution vector (Supplementary Fig. 7b). Another

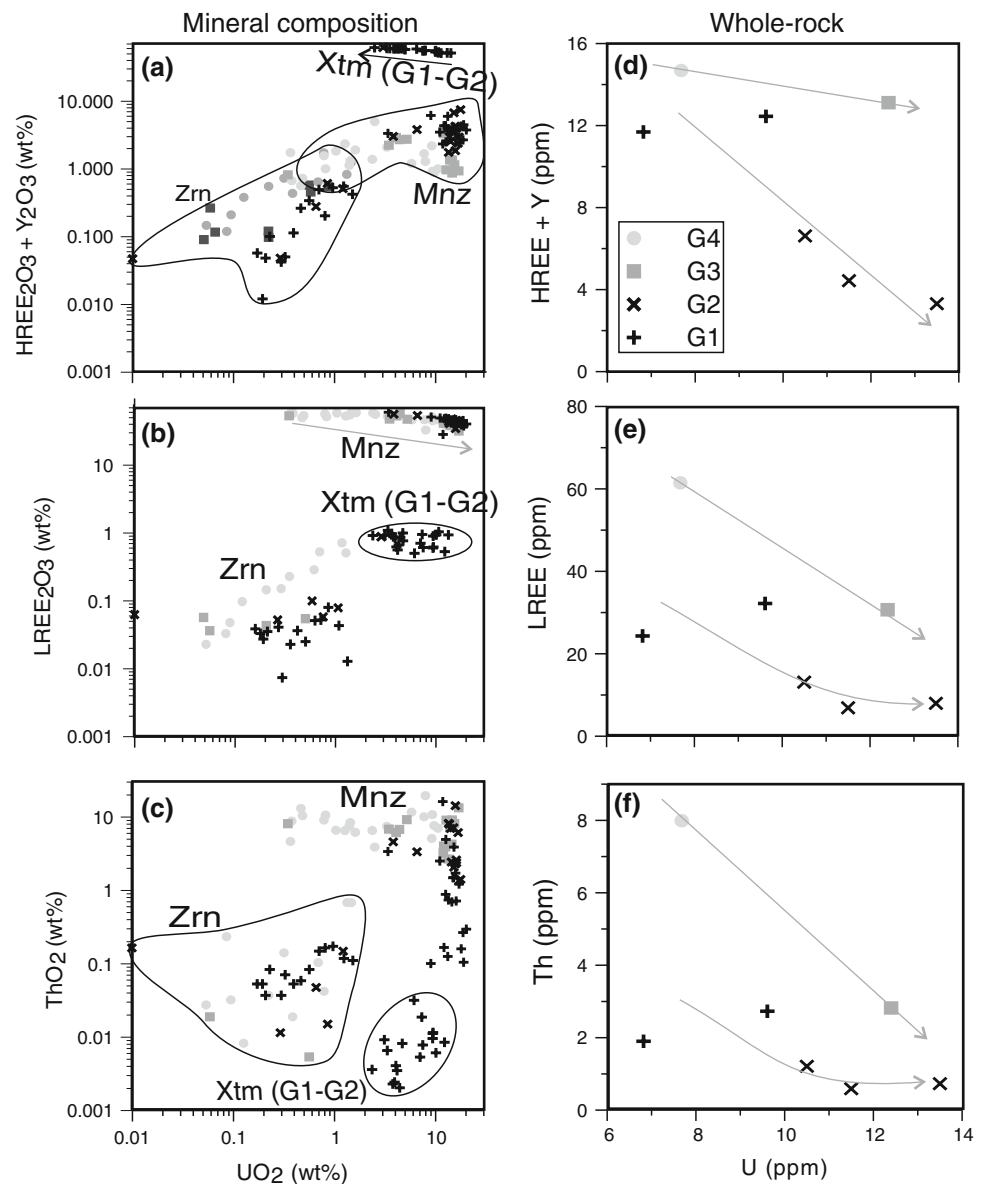
Fig. 7 Plots illustrating the substitution mechanism and other cation relationships (apfu on the basis of 16 oxygen) in the xenotime from the two more evolved units (G1 and G2) of the Belvís granite pluton: **a** U versus Ca (cheralite substitution); **b** U versus Si (huttonite substitution); **c** U versus (Si + Ca) (combination of the cheralite and huttonite substitutions); **d, e** Plots of (U + Ca + Mn) versus (Y + HREE) and LREE, respectively, where the area of the Si (i.e. the U incorporated via huttonite substitution) has been added in both plots for a better visualization; **f** Analytical total (in wt%) versus LREE (apfu). U* is the remaining U content after the huttonite substitution. The grey line (1:1) represents in **a** the cheralite substitution, in **b** the huttonite substitution and in **c** both substitution mechanisms



mechanism to charge balance the high P incorporation is the xenotime substitution $[(Y, REE)^{3+} + P^{5+} = Zr^{4+} + Si^{4+}]$, commonly reported in natural zircon (Speer 1982; Hinton and Upton 1991). If we consider Y along with REE, and the content of P after the berlinite substitution (P^*), in the plot P^* versus (REE + Y), two different positive trends are defined for type 2 zircon from G1–G2 and G3–G4 units (Supplementary Fig. 7a). The more stoichiometric G3 and G4 zircon defines a trend mainly along the substitution vector 1:1, suggesting that charge

balance is achieved by the berlinite and xenotime substitutions. The G1–G2 zircon trend is considerably below the substitution vector 1:1. These different trends suggest that during the magmatic crystallization of zircon, the melt fractions of G1 and G2 granites were very P-rich and, indeed, there were a higher competition for REE and Y with monazite and xenotime. These patterns are also maintained if LREE and HREE are independently considered. So, another substitution mechanism is required for the G1–G2 type 2 zircon. The brabantite substitution

Fig. 8 Variation plots between uranium and the main elements involved in the composition of the U-rich xenotime and U- and Th-rich monazite: **a** UO_2 versus $\text{HREE}_2\text{O}_3 + \text{Y}_2\text{O}_3$, **b** UO_2 versus LREE_2O_3 and **c** UO_2 versus ThO_2 , and their respective evolution in the whole-rock composition: **d** U versus HREE + Y, **e** U versus LREE, **f** U versus Th. The arrows define in each plot the variation of their respective elements within zoned crystals (**a**, **b**, **c**) or among the two trends of evolution defined in the pluton: G1–G2 and G3–G4 (**d**, **e**, **f**)



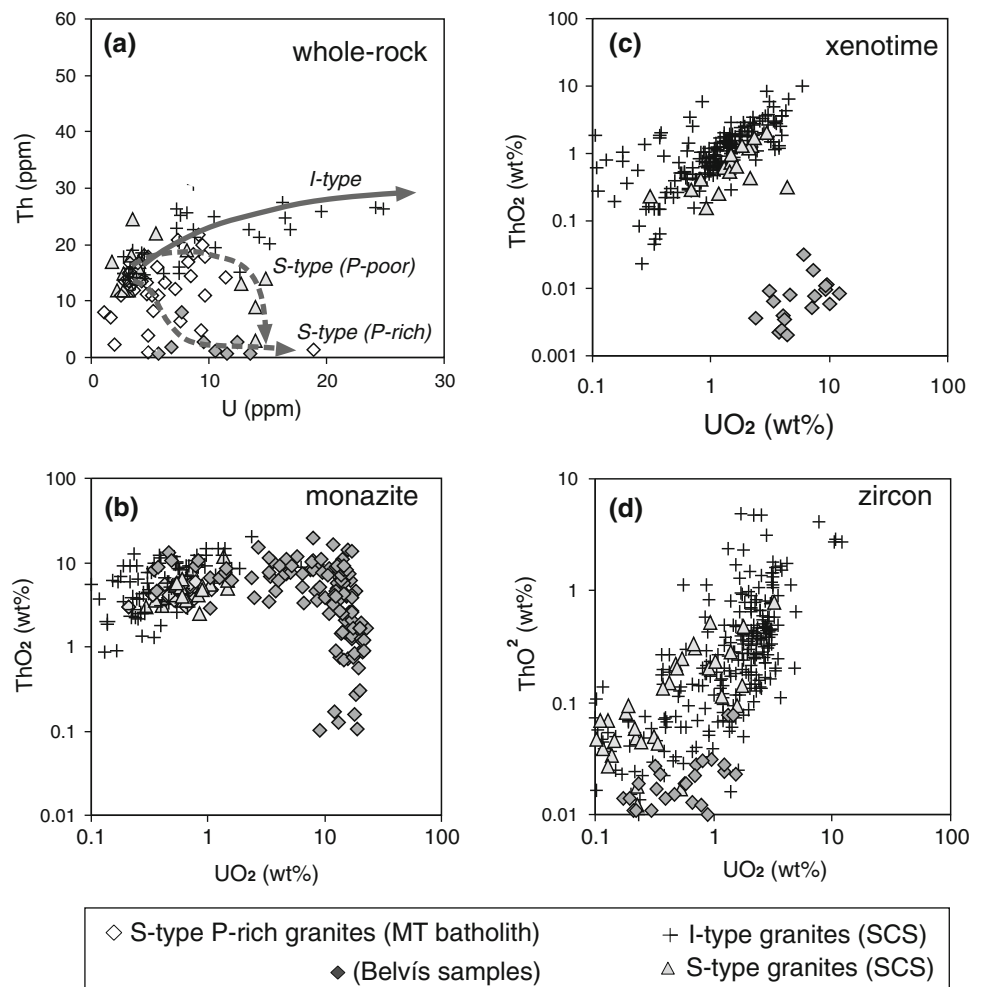
incorporates Ca, U and Th in Zr site, along with P in the Si site $[\text{Ca}^{2+} + (\text{U} + \text{Th})^{4+} + 2\text{P}^{5+} = 2\text{Zr}^{4+} + 2\text{Si}^{4+}]$ (Breiter et al. 2006). This mechanism is illustrated in the P versus (Ca, U, Th) plot for type 2 zircon from G1 to G2 (Supplementary Fig. 7c), showing a positive trend below the 1:1 substitution vector. That substitution is still insufficient to maintain the charge balance of the large P incorporation. The remaining non-formula elements must be incorporated in the zircon structure to complete the charge balance for G1 and G2 type 2 zircon: (1) in the four-coordinated interstitial site (1.84 Å; Finch et al. 2001), the sum of effective ionic radii of Fe^{2+} and O^{2-} is 2.01 Å; (2) Ti^{4+} substitution in Si site results more energetically favourable than in Zr site (Harrison et al. 2005; Cherniak 2010), and (3) Mn cation, with large ionic radii (0.96 Å),

may be incorporated in the octahedral Zr site. The variable and significant contents of non-formula elements in the Belvís type 2 zircon, especially from G1 to G2 units, are explained by several substitution mechanisms which charge balance the P substitution. This final adjustment is expressed in the plot of Fig. 9d.

The Belvís zircons display a good negative correlation between deficient totals and the total content of non-formula elements. As we have noted above, the non-formula cations are well adjusted by substitution mechanisms, so we consider that deficiencies in the analytical total of the P-rich composition of Belvís zircon is magmatic and not a consequence of alteration after metamictization. Similar conclusions are reported in other studies (e.g. Belousova et al. 2002; Breiter et al. 2009).

Fig. 9 U and Th contents in accessory minerals and in whole-rock analyses of granite types from central Spain:

a whole-rock, **b** monazite, **c** xenotime, **d** zircon. Mineral data from the S- and I-type granites of the Spanish Central System (SCS) after Villaseca et al. (2004). Whole-rock composition of I-type granites from Villaseca et al. (1998, 2009) and Pérez-Soba and Villaseca (2010). Composition of P-poor S-type granites from Villaseca et al. (1998). Composition of P-rich S-type granites of the Montes de Toledo (MT) batholith from Villaseca et al. (2008) and Merino et al. (2013, in press)



The zircon Hf content does not show correlation to substitution cations or Zr contents, being always lower than 5 wt% (Table 3). Moreover, it does not seem to be related with core–rim zonation. This would suggest that in the Belvís zircon some structural condition prevents the Hf to be favourably substituted, resulting in a broad range of Zr/Hf ratios. In these cases of zircons with no evident Zr–Hf covariation, the use of the Zr/Hf ratio as differentiation index or tectonic setting characterization (Pupin 1992, Wang et al. 2010) would be meaningless.

Fluid interaction versus magmatic origin of accessory minerals

Although monazite, xenotime and zircon are extremely insoluble and chemically durable under aqueous fluids over a relatively wide pH range (e.g. monazite in Poitrasson et al. 1996, 2004), residual melts or late-to-post-magmatic fluids may interact with them, changing their original magmatic compositions and increasing deficient totals and the content of non-structural elements (e.g. Vavra et al.

1999, Förster 2000; Dini et al. 2004; Broska et al. 2005; Geisler et al. 2007).

In the Belvís fractionated granites, the presence of fluxing and volatile elements (F–Li–B–Be–H₂O) is apparent from: (1) the significant contents of these elements in micas, feldspars and cordierite (Merino et al. 2013); (2) the common occurrence of fluorapatite in the granitic units and pegmatite dykes; (3) the local occurrence of spodumene and lepidolite in associated pegmatite dykes (Junta de Extremadura 2009), and (4) the abundance of tourmaline in the metamorphic contact aureole. However, compositional overprinting by fluids in the granites at different scales is not significant, as we discuss below.

Fluid interaction may be deduced by some chemical parameters of the whole-rock geochemistry. The Y/Ho ratio in the range of 24–34 (29.2–36.5 in the Belvís granites) indicates a magmatic signature (Bau 1996), suggesting that no significant fluid/rock interaction occurred in the studied granites. Significant lanthanide tetrad effects (TE) would reflect the presence of fluids in late-stage magmatic systems (Bau 1996; Irber 1999). In the Belvís granite REE

patterns (Fig. 3a), TE₃ tetrad effect is evident and is also evident in xenotime (Fig. 3c). However, tetrad effects are absent in the Belvís monazites, in clear contradiction with the presence of fluids. The controversial TE has been extensively discussed (e.g. Masau et al. 2000). Experimental studies on monazite and xenotime synthesized in fluid absent conditions have revealed significant differences in the solubility of neighbouring REE as a consequence of different coordination geometry of the melt and the unusual coordination of REE in these phosphates (Tin 2007). In this way, the tetrad effect could not be used as indicator of fluid/melt interaction (Tin 2007), and other origins must be considered.

In studies of actinide-bearing accessory minerals, significant contents of Y, P, Th, U, Ca, Fe and deficient totals have been ascribed to post-magmatic fluid interaction (e.g. see discussion for zircon in Nasdala et al. 2009; Townsend et al. 2000; Broska et al. 2005) or auto-metasomatism (e.g. Hetherington and Harlov 2008). In the Belvís granites, minor alteration has been observed in the main minerals (e.g. feldspars, micas). Most of the monazites and all the xenotimes are completely free of alteration, and the complex type 2 zircons are included in non-altered magmatic minerals. Minor or null accessory mineral alteration is also supported by the absence of typical HFSE-rich secondary phases (e.g. basnäesite, synchysite).

Deficient totals and increased non-structural cations in the Belvís accessory minerals have been explained by substitution mechanism which, in turn, are linked to magmatic textures and melt fractionation. In this respect, we consider as definitive evidence of the magmatic origin of these U-rich minerals, the high U content across the entire unzoned euhedral monazite, not confined to sectors, fissures or rims (Supplementary Fig. 4).

Hence, textural, mineral and geochemical characteristics of Belvís pluton do not evidence significant post-magmatic fluid interactions. The mineral compositional variation is interpreted as magmatic and, as such, considered in the subsequent discussions.

The question of the absence of uraninite

Common accessory minerals in low-Ca peraluminous granites consist of monazite, low-Th uraninite and xenotime (Cuney and Friedrich 1987). In the Belvís samples, excepting monazite, xenotime and, to a lesser degree, zircon, no other U-rich accessory phases have been found. This contrasts with other Variscan peraluminous granites where uraninite has been reported, as in the Central Iberian zone (Brandebourger 1984, Hassan 1996, Gomes and Neiva 2002, Neves 2011), Erzgebirge (Förster et al. 1999), Podlesí (Breiter et al. 1997; Breiter 2002) and Vosges (Pagel 1982), sometimes linked to F-rich melts (Förster

et al. 1999, Förster 1999, Breiter et al. 2006). The uraninite crystallization occurs when uranium is high enough to exceed other U-rich minerals substitution capacity, so the relative abundances of other trace elements determine which U-rich accessory minerals will crystallize (Cuney and Friedrich 1987). In low Th/U magmas with sufficiently high U/REE ratios, the available U in the melt would crystallize as low-Th uraninite (Cuney and Friedrich 1987) if reducing conditions prevailing during the magmatic evolution (Cuney and Friedrich 1987). These two conditions, U-rich magma and reduced oxygen fugacity, occur in the Belvís pluton, so other circumstances are needed to explain the uraninite absence: (1) uraninite has been dissolved in a post-magmatic period by oxidized and acidic solutions (meteoric water or hydrothermal solutions), and (2) low calcium activity in granite melts controls the accessory mineral paragenesis promoting the cheralite substitution in U-rich phosphates. Evidence of the precipitation of remobilized U in reduced microdomains by U-rich minerals coating cracks or forming mineral overgrowths (Finch and Ewing 1992) has not been observed in the Belvís samples. On the other hand, the low Ca, perphosphorous and peraluminous character of the Belvís granites would increase apatite solubility, and the low Th/U ratios in the more evolved melts would enhance incorporation of Ca (i.e. cheralite substitution) to monazite and xenotime during their crystallization, which in turn would consume U (and Th) from the magma to charge balance the mineral structure. The crystallization of a U-rich phase (silicate or oxide) after or coevally with these large uranium consumers would be difficult. In addition, the high whole-rock P₂O₅ content (0.47–0.85 wt%) is over the apatite buffer for this ASI values (about 0.5 wt% for ASI = 1.2, London 1998), so U-rich phosphates crystallization would prevail over that of uranium oxide (uraninite).

Contrasting U and Th evolution in accessory minerals of different peraluminous granite suites

Several chemical and physical factors have been considered for constraining mineral crystallization, although the chemical parameters are the most critical for the accessory minerals in granites (e.g. Cuney and Friedrich 1987), especially “*the availability of other charge-compensating species and the compatibility of such element(s)*” (Hanchar et al. 2001). In the studied minerals, U, Th, Al, Y, Fe, Ca (and REE) are the main *other charge-compensating species* which compete to be incorporated into monazite, xenotime and zircon. Fluorapatite is not considered in this discussion as its U and Th contents are nil or below detection limits, and the REE contents are relative low (up to 4,310 ppm) in the Belvís granites.

Monazite, xenotime and zircon show different U and Th contents in the Belvís granites, reflecting their contrasted mineral partitioning (Fig. 8). Monazite is the main Th-rich accessory mineral, so it chiefly controls the Th and LREE variation in the magma (Fig. 8b, c, e, f). Th decreases from G4 to G3 and from G2 to G1 granites (Fig. 8f), which is consistent with monazite fractionation. This behaviour further evidences that two distinct differentiation trends can be found in the Belvís granites (Fig. 8f). Furthermore, the Belvís granite La/Yb ratio decreases from G4 to G1 units, suggesting a higher amount of monazite than xenotime fractionation with decreasing temperature, i.e. a stronger drop of the LREE saturation over HREE and Y.

Unlike Th, the U content in the Belvís granites increases (Supplementary Fig. 1e) and shows preference (along with Th) firstly for monazite, secondly for xenotime and lastly for zircon (Fig. 8c). The most U-rich monazite occurs in G1–G2 granites, and xenotime is extremely rich in these units (Tables 1, 2). However, according to the effective ionic radius, U should be preferentially partitioned into xenotime (Wark and Miller 1993; van Emden et al. 1997; Förster 1998b) and Th into monazite (Demartin et al. 1991), as reported in other studies (e.g. Wark and Miller 1993; van Emden et al. 1997; Seydoux-Guillaume et al. 2002). This suggests that partition coefficients for U in monazite have been underestimated with respect to those of Th for some granite melts (Franz et al. 1996; Stepanov et al. 2011).

Three different trends for Th and U evolution can be defined for the most common peraluminous granite suites (Fig. 9a). Felsic metaluminous-to-peraluminous I-type granites are characterized by coupled increases of Th and U with crystal fractionation (e.g. Champion and Chappell 1992; Villaseca et al. 1998). Conversely, the two main series of S-type granitoids lack Th enrichment (Fig. 9a) and define contrasted Th–U trends between the common P-poor S-type granites and the unusual P-rich S-types (as the studied Belvís granites).

Decreasing monazite Th/U ratios in highly fractionated granites has been observed in S-type granites, but in the Belvís monazite, this ratio reaches extremely low values (Fig. 9b). This behaviour contrasts with the opposite Th/U evolution in I-type (and A-type) evolved granites, and also in P-poor S-type varieties (Fig. 9a). The high phosphorous content in the studied granite melts significantly increases the amount of monazite crystallization, which controls the chemistry of the residual melts and associated accessories. A greater rate of monazite crystallization triggers the extremely Th impoverishment in the fractionated melts and consequently favour higher monazite/xenotime U partition coefficients in this melt with higher LREE/HREE + Y ratio (Fig. 6). This also enhances the markedly low Th contents of xenotime and zircon in these P-rich peraluminous

granites when compared to those found in other felsic granite types (Fig. 9c, d).

The whole-rock chondrite-normalized REE spectra (Fig. 3a) show the HREE slope gently decreasing from G4 to G1 ($Gd_n/Yb_n = 4.10\text{--}1.25$), whereas monazite HREE patterns increase their slope from G4 to G1 (Fig. 3b). This contrasted behaviour could be explained by the lower abundance of zircon and xenotime in the more fractionated units, so exerting progressively less competition for HREE with monazite. Thus, the LREE/HREE + Y ratio decreases in the more evolved monazites. Ca is always abundant (Tables 2, 3) when compared to the other non-formula elements and defines better evolution trends in the substitution mechanisms in the Belvís granites. Under these conditions, Ca and U would be available, forming a suitable association for charge balance the cheralite mechanism, the most effective mechanism for U substitution in monazite and xenotime, as we have shown above.

Conclusions

1. Highly uranium-rich monazite and xenotime and phosphorous-rich zircon may crystallize from peraluminous, perphosphorous and low-Ca magmas due to the combination of high solubility of apatite, very P-rich melts (up to 0.85 wt% P_2O_5), and the lack of a stronger U-competitor (e.g. uraninite). The low LREE/HREE + Y in the more evolved melts also favours a higher U substitution for LREE to charge balance the Ca incorporation, whereas Th would complete this substitution mechanism (Fig. 6).
2. In these magmas, the cheralite substitution is the most important mechanism to introduce U and Th into monazite and U in xenotime crystals. The huttonite substitution completes the charge balance for U (and Th)-rich compositions. The berlinite, xenotime and brabantite substitutions may be considered, in that order, as the most important to explain the zircon non-stoichiometry in this type of highly felsic magmas.
3. From the studied accessory minerals, monazite stands out as being the only Th-bearing accessory mineral and for the ability to incorporate U preferentially when compared to xenotime and zircon, but showing lower compatibility with respect to other cations (Ti, Al, Mn, Fe). Zircon displays a lower ability to incorporate Th, U, Y and REE if monazite and xenotime are extensively co-crystallizing. However, it incorporates wider spectrum of other non-formula elements (e.g. Al, Ca, Fe, Mn, Ti) coupled with large P abundances, giving rise to deficient totals. The different REE-chondrite-normalized patterns for the two zircon types reinforce its strong dependence of HFSE melt compositions.

4. The extraordinary monazite, xenotime and zircon chemical composition of these highly fractionated P-rich S-type magmas contrasts markedly with the Th and U evolution of these minerals in other peraluminous granite suites (P-poor S-type and I-type granites). The combined extremely low Th and high U contents of studied accessories suggest that this distinctiveness would be used in granite classification schemes.

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