Zr-REE-Y-Rich Accessory Minerals from Peraluminous Granites of the Montes de Toledo Batholith (Iberian Hercynian Belt)

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INTRODUCTION.

The study of compositional and textural characteristics of accessory minerals in granitoid rocks may provide a broad register of the origin and compositional evolution of magmas. The discussion on petrogenesis of these minerals being either residual, or early- to late-magmatic phases, together with the lack of widespread re-equilibration processes, are the clues for reconstructions of magmatic evolution.

The Hercynian Montes de Toledo Batholith (MTB) is a discontinuous E-W outcrop made up by late- to post-tectonic granite plutons from Madridejos (Toledo) to Belvís de Monroy (Cáceres). This large batholith is characterized by a marked S-type affinity which contrasts with the more complex I- and S-type character of the granite plutons of the Spanish Central System (SCS). Compositional variations have been distinguished along the MTB suggesting a segmented batholith (Villaseca et al., 2008): the slightly lower CaO and higher P_2O_5 contents of the western-sector granitoids led to a stronger peraluminous character of this part of the MTB. The studied plutons belong to this western segment. Cordierite, sillimanite, andalusite, muscovite, tourmaline, ilmenite, apatite, zircon monazite and spinel, may occur as magmatic accessory minerals in these plutons. Specifically, zircon and monazite show higher ability to accept not essential structural trace elements (ESC), what makes them interesting as magmatic evolution recorders. We have studied the Zr-REE-Y-rich phases from representative units of some plutons (Belvís de Monroy, Navalmoral, Peraleda and Aldeanueva plutons) which cover the compositional range.

The Belvís de Monroy pluton consists of the most felsic leucogranites (SiO_2 = 74.51 wt.%), with higher P_2O_5 contents (mainly concentrated in the albite plagioclase and K-feldspars by the berlinite substitution), and high F content in the magmatic muscovite and biotite (Villaseca et al., 2008). Some granites from the Peraleda pluton show the higher peraluminosity character and the less evolved composition (SiO_2 = 68.67 wt.%). This whole-rock compositional spectre is reflected in the geochemistry of the Zr-REE-Y-rich accessory phases.

RESULTS.

About 95 quantitative electron-microprobe analyses of zircon and REE phosphates in 9 characteristic granite samples were conducted using a Jeol JXA-8900 M electron microprobe, in the "Centro de Microscopía Electrónica Luis Bru" (Complutense University of Madrid). The crystal size is usually too small to allow a representative number of core-rim analyses to assess variation on this scale.

Three main types of zircon can be defined in the studied MTB samples: (1) subhedral to euhedral crystals, unzoned or showing two-zoned irregular sectors, with sizes below 100 μm and aspect ratios between 2 and 5. They are hosted by biotite. Their composition is very poor in not ESC. They are the only zircon type in the restite-rich tonalite of the Aldeanueva pluton, but also appear in the less fractionated units of the other studied plutons (Aldeanueva, Peraleda and Navalmoral). This variety could be interpreted as relict zircon. (2) Magmatic zoned zircon, where it is possible to distinguish three subtypes: (2a) large euhedral and fine scale oscillatory zoned crystals (with aspect ratios up to 4); (2b) is the more widespread and abundant zircon variety, occurring not only in less evolved units, but also, and exclusively, in the more evolved studied units of the four plutons studied; the crystals are equant (aspect ratios between 2 and 3), showing homogeneous cores (sometimes rounded, relict cores?), with rims displaying a coarse oscillatory zoning with frequent transgresive internal margins, suggesting resorption vs. crystallization processes; and (2c) scarce and small equant grains with diffuse oscillatory zoning. (3) Magmatic subhedral to anhedral small zircon crystals (< 50μm), with a characteristic spongy texture and an irregular patchy zoning. This type has been observed exclusively in the most fractionated unit of the Belvís pluton. The subtypes 2a and 2c (i.e. with more or less clear oscillatory zoning) only occur in the microgranites, which outcrop in the Peraleda and Navalmoral plutons.

The zircon types 1 and 2 display a compositional range (including core-rim analyses) rather homogeneous (near to stequiometric zircon composition). On the contrary, zircon type 3, from the most fractionated granite of the Belvís pluton, shows significant contents of not ESC (Ca, Fe, Al, Mn, Y, Ti, P), accompanied by deficient totals and the highest HfO_2 contents (1.8 to 7.1 wt.%). Similarly to other highly evolved granites (e.g. Nasdala et al., 2009), the deficient total increase displayed by Zr-poor zircon is associated with progressively higher Al, Ca, Fe, Mn and P contents, reaching high values (in wt.%) of P_2O_5 14.9, Al_2O_3 < 7.0, CaO < 2.2, FeO < 2.9 and MnO < 0.4. Composition of zircon type-3 is explained partially by the berlinite-type sustitution $P^{5+} + Al^{3+} \leftrightarrow 2Si^{4+}$, and brabantite-type substitution $Ca^{2+} (U+Th)^{4+} + 2P^{5+} \leftrightarrow 2Zr^{4+} + 2Si^{4+}$ (Fig. 1).

The parallel enrichment of Y-REE with P (xenotime-type substitution) is only found in zircon subtypes 2a and 2c described above. Zircon types 2b and 3 plot below this substitution line in the diagram P vs. (Y + HREE), which is

palabras clave: Minerales accesorios, Granitos peralumínicos tipo-S, Leucogranitos perfosfóricos, Cinturón Hercínico

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typical of peraluminous and P-rich fractionated leucogranites (Breiter et al., 2006, and cites therein). Finally, some zircon type-3 crystals included in apatite reach high Ca-P-Y-Th-U-Ti contents compared to the rest of varieties (excepting zircon from the leucogranite of the Belvís pluton). These compositions can be explained by coupled brabantite-xenotime substitution.

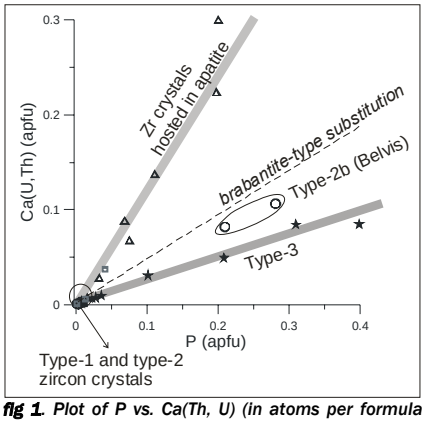

***fig 1**. Plot of P vs. Ca(Th, U) (in atoms per formula unit). Lines represent different substitution trends defined by: i) zircon type-3 (leucogranite of the Belvís pluton), and ii) zircon type-2 hosted in large apatite crystals. Brabantite-type substitution line is plotted for comparison.*

Monazite-(Ce) tends to occur as small (< 30 μm) and equant subhedral crystals, showing diffuse zoning. Monazite is associated to apatite (in Navalmoral pluton) or less frequently to zircon. In the Belvís pluton, exceptionally large monazite crystals of circa 100 μm appear. Monazite-(Ce) in restite-rich granites occurs as large crystals, sometimes acicular, mainly unzoned and occasionally rich in inclusions.

Monazite compositional range is (in wt.%): ThO_2=1.41 to 14.3; UO_2 = 0.11 to 17.67; Y_2O_3 = 0.2 to 15.05; La_2O_3 = 1.43 to 15.05, and Ce_2O_3 = 16,74 to 32.26. Cheralite compositions are restricted to the most fractionated plutons, displaying the highest U content (up to 17.67 wt.%) in the leucogranites of the Belvís pluton. The Ce contents of cheralite from the Belvís pluton are clearly lower than the other studied crystals. These variations are explained by monazite-cheralite substitution, as is shown by the similar atomic abundance of (Th + U) and (Si + Ca) (Fig. 2). Only those monazite crystals included in large crystals of apatite display a distinct excess of Ca, similarly to those ones described by Harlov et al. (2008), which are interpreted as magmatic in origin. The huttonite mole fraction in monazite is practically zero in the studied plutons.

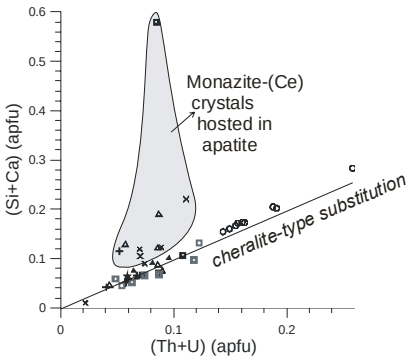

***fig 2**. Plot of (Th + U) vs. (Si + Ca) (in atoms per formula unit). The vector represents the cheralite-type substitution. The cheralite crystals hosted in large apatite crystals display an excess of Ca, compared to the (Th + U) content.*

Xenotime-(Y) has been exclusively found in the restite-rich tonalite from the Aldeanueva pluton. The crystals are small (less than 50 μm), with rounded margin and unzoned, lacking significant compositional variations (in wt.%): Y_2O_3 = 41.6 to 43.18; $HREE_2O_3$ = 19.65 to 19.82; ThO_2=0.19 to 0.35; UO_2 = 1.07 to 1.24. These characteristics suggest a restite origin.

CONCLUSIONS.

1) Zircon composition is very similar in all granites excepting in the more perphosphorous granite of the Belvís pluton, where the zircon type-3 shows berlinite- and brabantite- substitutions, which would be explained as zircon being practically the only Y-REE-Zr accessory mineral in this unit. The typical oscillatory zoned crystals (type-2a and 2c), with short range of composition, are indicative of stable growth conditions in the microgranites units where they have been found. On the contrary, the type-2b and 3 suggest changing saturation levels of these elements during the zircon growing.

2) Monazite compositions reflect more clearly the magmatic evolution of magmas.

(3) The absence of magmatic xenotime is consistent with the poorness of Y-HREE in these peraluminous magmas (Y ≤ 23 ppm, HREE ≤ 16.2 ppm) (Villaseca et al., 2008). Even in the more evolved sectors, appropriate saturation levels of these elements are not reached, which determines that these elements are incorporated both in the structure of zircon and/or monazite.

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