CHARACTERIZATION OF REE(+/-BA)-BEARING MINERALS FROM GRANITIC ROCKS (CENTRAL PORTUGAL) AND METASOMATIC ROCKS (BAYAN OBO, CHINA)

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ABSTRACT

Detailed characterization of REE-bearing minerals in granitoid rocks from the Idanha-a-Nova and Castelo Branco plutons (Central Portugal) and in a few metasomatic rocks associated to the Bayan Obo Fe-REE-Nb mineralization (Inner Mongolia, China) provided an interesting basis for the interpretation of the bulk-rock REE patterns.

Of the REE-bearing minerals analysed in the granitoid rocks, monazite exhibits the highest total REE contents and a LREE-enriched pattern which explains the bulk-rock LREE enrichment, and is quite distinct from the REE patterns obtained for zircon and xenotime, which probably occur in lower modal concentrations. In the Bayan Obo rocks, monazite and fluorcarbonates (bastnäsite and/or Nd-cebaite) are the main REE-bearing minerals, both exhibiting very high REE contents and pronounced LREE-enrichment quite matching that of the bulk-rocks, while REE contents in pyrochlore and in minerals of the hejtmanite-bafertisite group are much lower.

Keywords: REE, Monazite, Fluorcarbonates, Zircon, Pyrochlore

1. INTRODUCTION

Rare-earth elements (REE) have great importance in present-day economics (e.g. in high-tech technology) and science, such as in understanding the different sources and evolution of parental magmas and distinguishing post-magmatic hydrothermal alteration.

The main focus of this study has been to characterize and interpret REE distribution patterns in several REE-bearing minerals, in order to ascertain their individual contribution to the bulk-rock REE patterns of their host-rocks, of either granitic or metasomatic nature.

2. GEOLOGICAL SETTINGS

2.1. GRANITOID ROCKS FROM THE IDANHA-A-NOVA AND CASTELO BRANCO PLUTONS

The Oledo-Idanha-a-Nova and Castelo Branco granitic plutons, located in the Portuguese side of the Central Iberian Zone of the Variscan Massif, are intrusive in the Schist-Greywacke Complex (Sousa, 1985).

The Oledo-Idanha-a-Nova pluton is ante-orogenic and includes several granitoid facies, with ages 479-480 Ma (Antunes et al., 2009). The Idanha-a-Nova muscovite-biotite granite constitutes the most abundant facies, and is considered an I-type or hybrid granite (Antunes, 2006).

The Castelo Branco pluton is a composite massif formed by S-type granites which include several facies, with U-Pb-Th ages ranging from 303 ± 3 Ma in the central and northern facies (G1 and G5: late-D3 granites; e.g., Ferreira et al., 1987; Castro et al., 1999) to 301 ± 4Ma, for the G2 facies, 300 ± 4 Ma, for the G3 facies, and 297 ± 3 Ma, for the G4 facies (Antunes, 2006).

2.2. METASOMATIC ROCKS FROM BAYAN OBO

Bayan Obo is the largest known Fe-REE-Nb deposit, producing more than 80% of LREE (Zhi Li & Yang, 2014).

The Bayan Obo deposit is located in a mesoproterozoic rift zone, on the northern border of the Northern China Craton (NCC). The Fe-REE-Nb deposits are hosted by paleo- and mesoproterozoic sediments, mostly dolomites, and limestones, quartzites and phyllites. The main mineralization is located in the Kuangou synclinal, in a region of important tectonic activity. The genesis of these deposits is still controversial, the two main hypothesis defending either that the deposits are associated to carbonatitic magmatism, or that they result from hydrothermal alteration of carbonate sedimentary sequences (Yang et al., 2008; Fan et al., 2015).

3. SAMPLING AND ANALYTICAL PROCEDURES

Samples used for the petrographic and analytical study included:
- 8 granitoid rocks from Central Portugal: 1 sample of the Idanha-a-Nova muscovite-biotite granite (sample IDN-1); and 7 samples of the distinct Castelo Branco granite facies: G1 (two-mica granite:

samples CALT and GCL-7), G2 (biotite-muscovite granite: samples GIN and GIN-4), G3 (biotite-muscovite granite: sample BCAL), G4 (two-mica granite: sample GR-1), and G5 (two-mica granite: sample LARDO-1);

- and 6 samples of distinct metasomatic rocks from the Bayan Obo area (Ribeiro da Costa & Barriga, 2013): banded Fe-oxide+Na-amphibole+fluorite -bearing rocks (samples BO-9B, BO-11); fine-grained foliated Fe-oxide + sulphide ores ± carbonate, fluorcarbonates, phlogopite, Na-amphibole and fluorite (sample BO-14); fine-grained massive pyrrothite ore ± sphalerite and late carbonates (sample BO-16); Fe sulphide + Fe oxide ore ± sphalerite, carbonate and Na-amphibole (sample BO-20); fine-grained quartz rock, containing minor amounts of carbonate, plagioclase, Na-amphibole, phlogopite and Fe sulphides (sample BO-23A).

The analytical work was carried out on a JEOL-JXA-8200 electron microprobe (Geology Department, FCUL; Lisboa, Portugal). Analytical conditions for this study were: beam diameter 5 µm for most minerals, 9 µm for fluorcarbonates; beam current 10nA, 5nA for fluorcarbonates; accelerating voltage 15 kV; and measuring times of 20s in the analytical peaks, and 5s in the backgrounds. Elements were measured against natural and synthetic mineral standards: REE 1 (Eu, Gd, Tb, Tm), REE 2 (Sm, Yb, Lu), REE 4 (Dy, Ho, Er), REE 6 (Nd) monazite (La, Ce, Pr, Th), apatite (F, P), LiNbO3 (Nb), LiTaO3 (Ta), zirconia (Zr, Y), m32 (Hf), benitoite (Ba, Ti), pyrope (Mg), almandine (Fe, Al), bustamite (Mn), diopside (Ca.Si), jadeite (Na), sanidine (K), celestite (Sr), Vmetal (V), galena (Pb), stibnite (S), Ga arsenate (As), UO2 (U) and tugtupite (Cl).

Bulk-rock REE data were provided by previous works: REE contents for the granitoid rocks were obtained by ICP-MS, in the facilities of the SGS-Mineral Services, Canada, and of the Southampton Oceanography Centre, UK (Antunes, 2006); REE contents for the Bayan Obo rocks were analysed by ICPAES-MS, in the USGS laboratories.

The C1-chondrite (McDonough & Sun, 1995) was used for REE normalization in rocks and minerals.

4. RESULTS AND DISCUSSION

The REE-bearing minerals selected for analysis were: monazite, zircon and xenotime, in the granitoid rocks, and monazite, fluorcarbonates (bastnäsite and Nd-cebaite), pyrochlore and minerals of the hejtmanite-bafertisite group, in the Bayan Obo rocks. Fairly consistent data and REE patterns were obtained for each mineral population (Fig. 1 & 2). Table 1 presents the most significant features of the studied rocks and respective REE-bearing minerals.

TABLE 1 - BULK-ROCK AND MINERAL REE DATA FOR THE CENTRAL PORTUGAL AND BAYAN OBO ROCKS

Rock samples and Minerals	Total REE (ppm)	(La/Lu)N	Eu*
Granitoid rocks (Central Portugal)			
IDN1	16	6.0	0.76
GCL7	82	33.2	0.37
CALT	76	21.7	0.36
GIN	195	22.4	0.61
GIN4	196	28.3	0.60
BCAL	131	22.9	0.46
GR	106	18.2	0.53
GM	86	20.1	0.44
LARDO	58	6.9	0.36
Bayan Obo Rocks			
BO-9B	22522	252.8	0.71
BO-11	110498	2646.8	0.81
BO-14	48906	1497.3	0.65
BO-16	6647	280.3	0.56
BO-20	6214	228.4	0.60
BO-23A	501	13.0	0.99
Monazites (CB granitoids)	414754 - 536728	2.6 - 163.7	0.01 - 0.06
Monazites (Bayan Obo)	524334 - 617689	1.4 - 56.8 (81.5 - 236.7)	0.01 - 0.78; 3.01 - 26.20
Zircons (IDN1+CB granitoids)	20729 - 22309; 2204 - 17194	0.001 - 0.70	0.13 - 0.73; 1.12 - 33.13
Zircons (Bayan Obo)	4594 - 5170	0.02 - 0.03	3.01 - 21.7
Xenotime (IDN1 granitoid)	163129 - 192836	0.001 - 0.003	0.004 - 0.007
Bastnäsites (Bayan Obo)	466746 - 627696	1.2 - 248.6	0.02 - 0.98; 2.85 - 3.01
Nd-Cebaites (Bayan Obo)	247293 - 366848	0.1 - 50.5	0.01 - 0.96; 1.33 - 3.75
Pyrochlore (Bayan Obo)	409606 - 415386	0.001 - 0.024	0.59 - 0.67
Hejtmanite-Bafertisite (Bayan Obo)	5064 - 8329	0.003 - 0.335	2.36 - 7.26

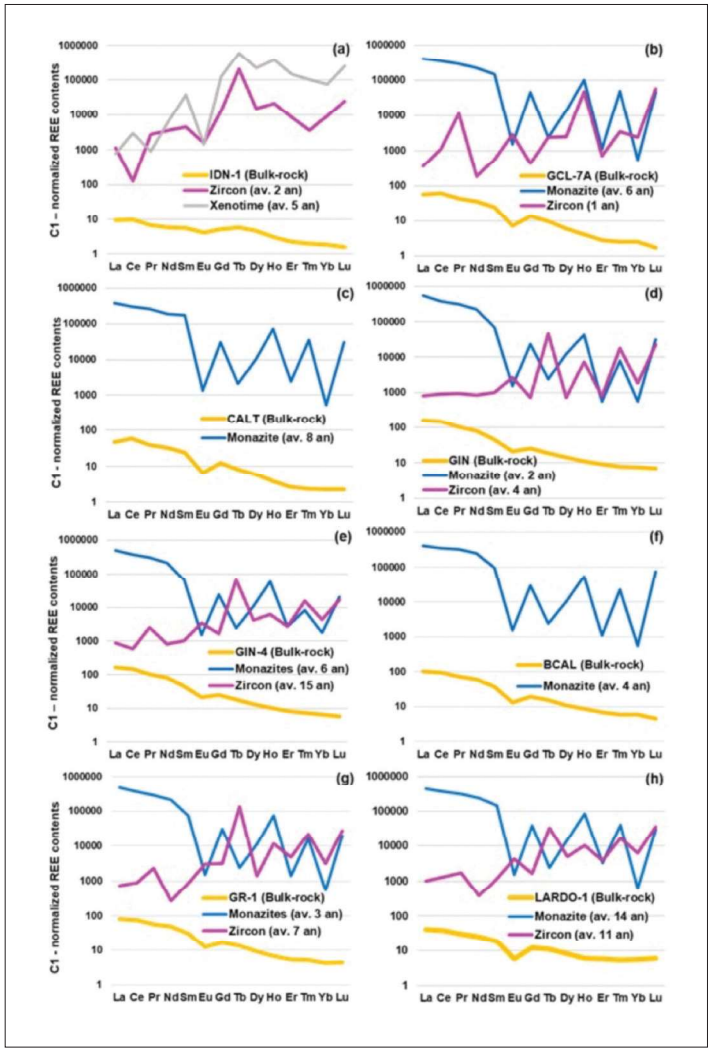

Figure 1 – REE patterns for the Central Portugal granitoids and their REE-bearing minerals.

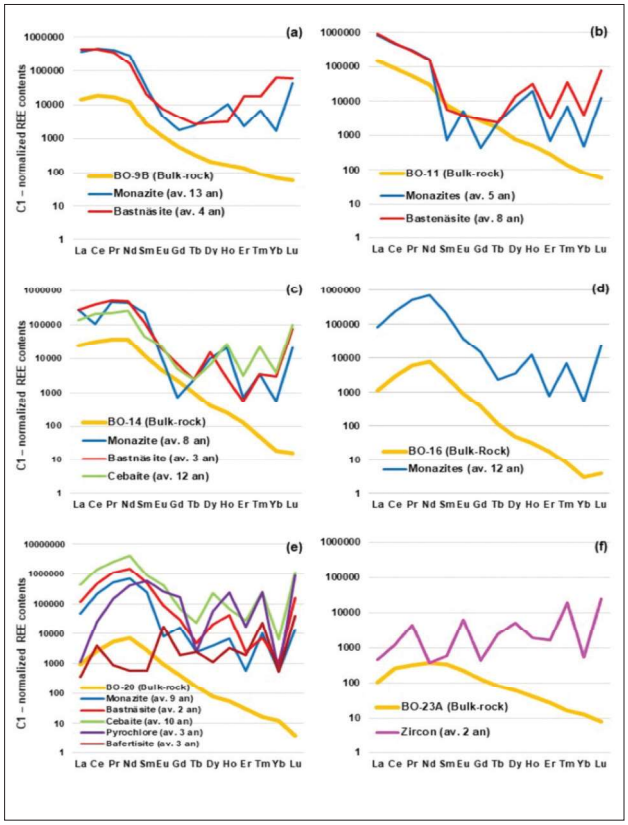

Figure 2 – REE patterns for the Bayan Obo metasomatic rocks and their REE-bearing minerals.

4.1. Granitic rocks from Central Portugal

Bulk-rock REE patterns for each granitoid rock and for each metasomatic rock, accompanied by the average REE patterns of their REE-bearing minerals, are displayed in Figures 1 and 2.

Contrasting with the I-type Idanha-a-Nova granite, which shows significantly lower REE contents and little LREE-enrichment (Fig. 1a), bulk-rock REE patterns for the Castelo Branco granitoids are typically enriched in LREE (Figs. 1b-h). These REE patterns evidence a marked contribution from monazite, not only indicating that this is the main REE-bearing mineral in these rocks, exhibiting much higher REE contents than zircon, but also suggesting that monazite probably occurs in higher modal concentrations (~ 0.1 %) in these granitoid rocks. Although no monazite was identified in the Idanha-a-Nova granite, the REE pattern for this rock does not match the patterns for either zircon or xenotime, implying that some other REE-bearing mineral phase may be present in this rock. The Eu anomaly of the Idanha-a-Nova granite is also less distinct than in the other granitoids, probably due to the presence of greater amount of Eu^{2+}-bearing plagioclase, therefore evidencing the more reduced character of the original magma.

4.2. REE-rich rocks from Bayan Obo (Inner Mongolia, China)

REE contents are much higher in the Bayan Obo metasomatic rocks (Table 1), especially in samples BO-9B, BO-11 and BO-14. Although REE patterns display some differences (Fig. 2), all of them show strong LREE enrichment, particularly evident in samples BO-11 and BO-14.

Monazite and fluorcarbonates (bastnäsite and Nd-cebaíte) are the most important REE-bearing minerals in these rocks (Table 1), probably corresponding to as much as approx. 1% of their modal contents, and therefore being the most significant to their bulk REE patterns (Figs. 2a-e).

Pyrochlore, identified only in sample BO-20, also shows preferential LREE enrichment, though it presents a peak in Sm, against the Nd maximum typical of monazite, fluorcarbonates and the rocks themselves (Fig. 2e). Minerals of the hejtmanite-bafertisite group, also identified in sample BO-20, show much lower REE contents (Table 1), therefore their REE pattern, contrastingly different from those of monazite, fluorcarbonates or pyrochlore (Fig. 2e), does not seem to contribute in the least to the bulk-rock pattern.

The REE pattern for sample BO-23A shows less pronounced LREE enrichment (Fig. 2f) and no REE-bearing minerals were identified which match this pattern, as the rock zircons exhibit their typical HREE-enriched patterns.

Comparison of the monazites and bastnäsites analysed in these metasomatic rocks with equivalent data provided by previous

Bayan Obo studies (e.g., Smith et al., 2000) has indicated that samples BO-11 and BO-9B may correspond to the "aegirine alteration and veins" and "fluorite" episodes in the paragenetic sequence proposed by Chao et al. (1992, 1993, 1997) for the Bayan Obo mineralization.

5. CONCLUSIONS

A few relevant conclusions could be gathered from this study:
(i) The most relevant minerals for the bulk-rock REE pattern of the studied rocks are monazite, in the granitoid rocks, and monazite and fluorcarbonates, in the Bayan Obo metasomatic rocks. Zircon, xenotime, pyrochlore and minerals of the hejtmanite-bafertisite group display much lower REE contents and usually occur in much lower modal proportions, therefore hardly contributing to the bulk-rock REE patterns.
(ii) Monazites and fluorcarbonates (bastnäsite and Nd-cebaíte) display significant LREE enrichment and are responsible for the similarly pronounced LREE enrichment observed in their host-rocks, particularly in the Bayan Obo rocks where both mineral species occur and exhibit much higher modal proportions.
(iii) REE patterns for the studied minerals closely match published data for the same minerals in similar rocks. The REE patterns of monazites and bastnäsites of a few Bayan Obo samples indicate they may have formed during the "aegirine alteration and veins" and "fluorite" episodes within the paragenetic sequence established for the Bayan Obo deposit by Chao et al. (1992, 1993, 1997).
(iv) The marked irregularities observed in the REE or HREE patterns of the studied minerals are mostly due to the fact that some REE contents are close to the electron microprobe detection limits and analytical error. Moreover, LREE/HREE fractionation has often been over-estimated (Table 1), whenever Lu2O3 contents were close to 0.01 wt.%. Electron microprobe analysis is therefore an unsatisfactory method for REE2O3 concentrations below 0.02 wt.%.

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