New data on nodular monazite from Monfortinho (Idanha-a-Nova, Portugal)

Novos dados acerca da monazite nodular de Monfortinho (Idanha-a-Nova, Portugal)

Salgueiro, R.[1*]; Inverno, C.[1]; de Oliveira, D.[1]; Guimarães, F.[2]

[1] Laboratório Nacional de Energia e Geologia (LNEG), Unidade de Recursos Minerais e Geofísica, Estrada da Portela, Bairro do Zambujal, Apartado 7586-Alfragide, 2610-999 Amadora, Portugal; *rute.salgueiro@lneg.pt

[2] Laboratório Nacional de Energia e Geologia (LNEG), Unidade de Ciência e Tecnologia Mineral, Rua da Amieira, Apartado 1089 S. Mamede de Infesta, Portugal.

Abstract

The alluvial nodular monazite of the Monfortinho region (Idanha-a-Nova, Portugal) presents physical and chemical characteristics identical to other mineral specimens occurring in other parts of the world. In particular its geochemical signature, showing zonation in the distribution of REE contents within grains (i.e. an increase of La and Ce towards the rim, and of Nd, Eu, Gd and Sm towards the core), and relatively high Eu_2O_3 (up to 0.74 wt%) and low ThO_2 (≤ 2.16 wt%) values, that distinguishes it from igneous monazites. Conditions for its formation, under temperature up to ≈300ºC in presence of phosphate, would have occurred in the Monfortinho region in the course of the sedimentary and/or metamorphic (regional greenschist facies or thermometamorphic) processes experienced by Proterozoic marine sequences (Slate-Greywacke Complex) and Ordovician (Penha Garcia - Canãveral syncline) during the Variscan orogeny. Mineral inclusions (quartz, apatite and rutile), already identified in the Monfortinho nodular monazite, are important indications for unraveling the source rock(s) and support the hypothesis of that source might be the Ordovician (radioactive) quartzite.

Keywords: Nodular monazite, REE, Central-Iberian Zone, Monfortinho-Portugal.

Resumo

A monazite nodular aluvionar da região de Monfortinho (Idanha-a-Nova, Portugal) apresenta características físicas e químicas idênticas a outros exemplares da mesma espécie mineral ocorrentes em diversos locais do mundo. Em particular a sua assinatura geoquímica evidencia zonalidade na distribuição dos conteúdos em REE no interior do nódulo (i.e. incremento de La e Ce no bordo e de Nd, Eu, Gd e Sm no núcleo) e conteúdos relativamente elevados em Eu_2O_3 (até 0.74 wt%) e baixos em ThO_2 (≤ 2.16 wt%), distinguindo-as das monazites ígneas. Condições necessárias à sua formação, com temperatura até ≈ 300ºC e disponibilidade de ião fosfato, terão ocorrido na região de Monfortinho, no decorrer do processo sedimentar e/ou metamórfico (regional de fácies de xistos verdes, ou de contacto) experimentados pelas sequências marinhas Proterozóicas (Complexo Xisto-Grauváquico) e Ordovícicas (sinclinal de Penha Garcia – Canãveral) durante a orogenia Varisca. As inclusões minerais já identificadas (quartzo, apatite e rútilo) na monazite nodular de Monfortinho constituem pistas relevantes para a descoberta da(s) rocha(s) onde tiveram origem, e suportam a hipótese de esta ter sido os quartzitos (radioactivos) Ordovícicos.

Palavras-chave: Monazite nodular, Terras raras, Zona Centro-Ibérica, Monfortinho-Portugal.

Introduction

Rare earth elements (REE) are on the top of Europe's critical minerals list. Eu-rich monazite, also known as nodular monazite (NM) because of its nodule form, is a REE phosphate [(Ce, La, Ca, Th, Y) PO_4)], chemically, morphologically and optically distinct from igneous monazite (e.g. Read et al., 1987), and has been mostly interpreted as a metamorphic or diagenetic mineral phase (Rosenblum and Mosier, 1983; Alipour-Asll et al., 2012). Some studies about the geochemical signature of NM have revealed essential data to better understand its formation (e.g. Rosenblum and Mosier, 1983; Read et al., 1987; Alipour-Asll et al., 2012). The reconnaissance survey targeted at the identification of REE minerals/deposits in central-eastern Portugal (Inverno et al., 2007) made possible the identification of xenotime, igneous monazite and NM in alluvial samples. In particular, Inverno et al. (2007) recognised that NM is abundant (up to 75% of the magnetic fraction) in 188 alluvial samples from Monfortinho and that its possible original provenance is from Ordovician (radioactive) quartzites. The present study aims to follow-up the previous studies (e.g. Lencastre, 1999) on these NM grains from Monfortinho and contributes to understand its formation.

Geological setting

The study area (Fig. 1) is located in part of the region covered by the 1:25000 topographic sheet, n.º271, Monfortinho and the 1:50000 geological map, n.º 25-B, Salvaterra do Extremo (Sequeira et al., 1999a) and are included in the Central-Iberian Zone. This region is dominated by slates and greywackes of Neoproterozoic age, known as Slate-Greywacke Complex (SGC; Sequeira, 2011). The SGC is cut by several intermediate-mafic tholeiitic and felsic dykes; the Variscan intrusions, Batão de Baixo tonalite and Salvaterra do Extremo granite (both to the south of Fig. 1 area) generated contact metamorphism in the SGC rocks (Sequeira et al., 1999b).

This complex surrounds the Ordovician rocks that define the Penha Garcia – Canãveral syncline which includes a sequence of metaconglomerates, quartzites (including radioactive quartzites) and slates covered by Cenozoic sedimentary formations (Fig. 1; Sequeira et al., 1999a).

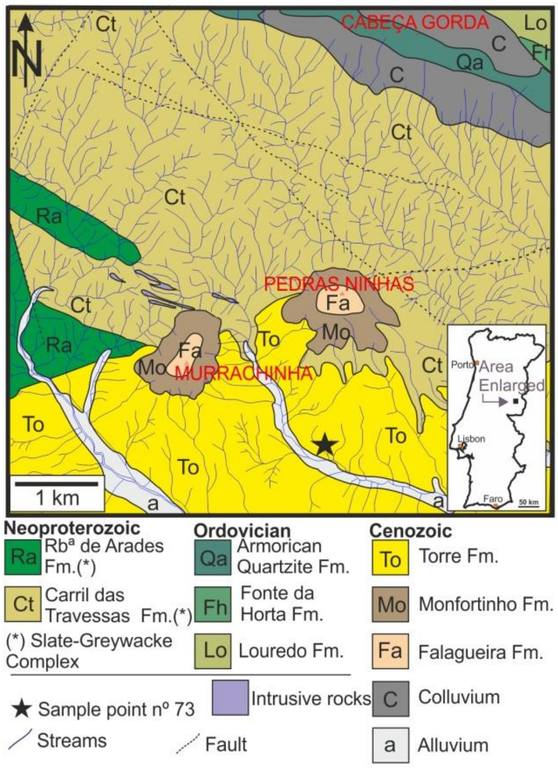

Fig. 1 – Geological setting sketch map with the sample point location (adapted from Sequeira et al., 1999a).

Methodology and analytical methods

The alluvial NM and respective thin polished section used in the present study were part of the reconnaissance survey conducted by Inverno et al. (2007) mentioned above. The NM grains were hand picked from alluvial heavy minerals collected in catchments draining from Cenozoic sedimentary rocks (sample n.º73; Fig. 1). For the present work, the NM grains were analysed under a binocular microscope. To determine the NM chemistry, microanalyses were carried out, using a JEOL JXA-8500F microprobe.

Nodular monazite physical properties

The grains of NM observed are generally flattened ellipsoidal to discoidal, but some have irregular form. They have short and long axes size of 0.1 to 0.3 mm and 0.15 to 0.6 mm, respectively, and some regular borders (Fig. 2). Their color is variable from white, grey, reddish-grey, red and light-brown to brown. The grains contain several (sub)microscopic mineral inclusions (Fig. 2), that turned out to be at least rutile, apatite and (abundant) quartz, identified with microprobe.

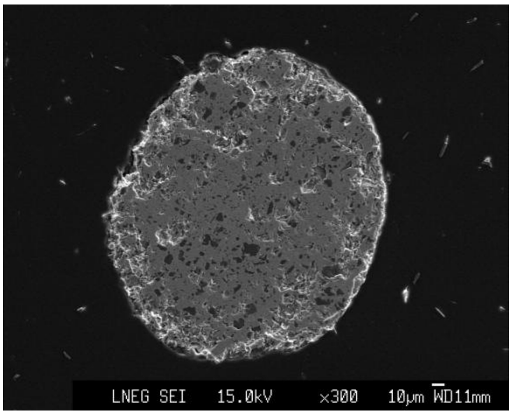

Fig. 2 – Secondary electron image of nodular monazite (grain 3) with some regular borders and several mineral inclusions (black dots).

Nodular monazite geochemistry

Nine analyses from four NM grains are shown in Table 1. Results confirm that it corresponds to a phosphate (average value of 27.65 wt% P_2O_5) with REE oxide concentrations dominated by Ce_2O_3 (≤ 33.83 wt%), Nd_2O_3 (≤ 25.37 wt%) and La_2O_3 (≤ 26.64 wt%); further includes Sm, Pr, Gd Eu and Dy oxide in minor concentrations, the last two, occasionally below their detection limits. Eu_2O_3, ThO_2, Y_2O_3 and UO_2 content reach 0.74, 2.16, 0.71 and 0.35 wt%, respectively. The normalized REE (Gromet et al., 1984) patterns clearly illustrate the enrichment of these elements in the studied grains relatively to NASC (Fig. 3). The REE distribution in the grains shows a consistent zonation (Table 1; Fig. 3) with gradual enrichment of La and less obvious of Ce towards the rim, and enrichment of Nd, Eu, Sm and Gd towards the core. Tb, Dy and Pr (local enrichment in the Grain 2 rim; Table 1) appear trendless.

Table 1 – Point analyses of alluvial nodular monazite grains from Monfortinho. (-) Below the detection limit.

Grain	1	2	2	3	3	3	4	4	4
Location	Rim	Core	Rim	Core	Interm.	Rim	Core	Interm.	Rim
Oxide (wt%)									
SiO_2	3.56	-	0.15	-	-	-	-	-	-
PbO	0.00	0.11	-	-	-	0.02	0.04	-	0.06
ThO_2	0.08	-	2.16	0.01	-	1.89	-	-	0.55
UO_2	0.14	-	0.26	0.30	0.02	0.35	-	0.01	-
Al_2O_3	0.26	-	-	0.00	0.03	0.01	0.06	-	-
Nd_2O_3	12.67	17.12	14.06	21.80	18.77	14.30	25.37	15.65	9.87
Y_2O_3	-	0.21	-	0.71	0.18	0.25	0.43	0.21	0.41
P_2O_5	27.19	27.18	27.46	27.79	28.44	27.04	27.63	27.94	28.18
MgO	-	-	-	-	-	-	-	-	-
CaO	0.13	0.09	0.30	0.12	0.03	0.18	0.08	0.04	0.19
Pr_2O_3	2.08	2.71	9.88	2.93	3.62	2.94	3.59	2.64	2.54
TiO_2	-	-	-	0.06	-	0.19	0.08	-	-
Sm_2O_3	0.83	2.33	1.44	3.22	2.23	1.04	8.04	0.82	0.38
FeO	-	-	-	-	-	-	-	-	-
Ce_2O_3	36.07	35.07	33.45	31.03	35.74	36.34	24.65	37.29	34.83
Gd_2O_3	0.95	1.54	1.05	1.73	1.01	1.01	3.08	0.51	0.12
La_2O_3	14.73	10.71	12.03	8.06	9.79	12.77	3.34	12.94	20.64
Eu_2O_3	0.30	0.55	-	0.66	0.16	0.10	0.74	0.29	-
Tb_2O_3	0.01	0.02	-	-	0.01	0.01	-	-	-
Dy_2O_3	0.28	0.16	0.16	0.13	0.27	0.06	0.27	0.22	0.21
Total	99.29	97.80	102.41	98.55	100.31	98.51	97.39	98.55	97.98

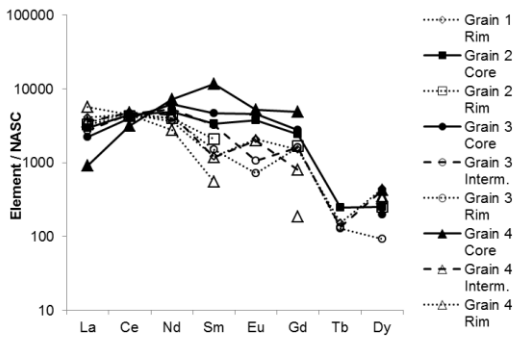

Fig. 3 – NASC-normalized REE (Gromet et al., 1984) patterns for nodular monazite from Monfortinho, illustrating the REE enrichment and the core/rim grains zonation (enrichment of La, Ce in rims and Nd, Sm, Eu and Gd in cores). Concentrations below the detection limit were not plotted.

Discussion and conclusions

The studied monazites were collected from alluvial deposits in the Monfortinho region that comprise detrital fractions derived from Cenozoic sedimentary rocks, which in turn were sourced from the dismantling of Variscan substrate. The regular borders of monazites suggest mechanical abrasion, possibly initiated during its transport to the Cenozoic sedimentary basin. Besides the distinct morphological features, the REE zoning in the monazite grains (La and Ce enriched rim and Nd, Sm, Eu and Gd enriched core), low ThO_2 contents (≤ 2.16 wt%) and Eu_2O_3 content (up to 0.74 wt%) are similar to those found by other studies (e.g. Rosenblum and Mosier, 1983; Alipour et al., 2012); and are distinct from those of igneous origin, that are poor in Eu and have ThO_2 contents up to 31.5 wt% (Deer et al., 1962; Kucha, 1980). The genetic models proposed for nodular monazite consider the involvement of contact metamorphic processes, REE precipitation followed by formation of authigenic nodular monazite in a sedimentary or metamorphic environment and diagenetic nucleation of the REE of the detrital monazite into nodules (Read et al., 1987). The low Th contents in monazite grains are indicative of relative low temperatures; such is the temperature of its formation (up to ≈ 300ºC; e.g. Read et al., 1987). This is compatible with the temperature of the contact metamorphism and regional low-grade metamorphism (not above the greenschist facies conditions), that affected the pre-Mesozoic formations, during the Variscan orogeny, in Monfortinho region (Sequeira et al., 1999b). Regarding the availability of phosphate ion required for the formation of nodular monazite (Rosenblum and Mosier, 1983) it should be noted that either the SGC or the Ordovician sequence include rocks formed in marine environments (Sequeira, 2011). In both sequences is admitted the presence of phosphate conglomerates, namely Cabeço das Popas (Neoproterozoic; Sequeira, 2011) and Fonte da Horta (Ordovician) formations (Sequeira et al., 1999b). The mineral inclusions of the nodular monazite are good indicators of their environment of formation since they are indistinguishable from the minerals of the host rock (Rosemblum and Mosier, 1983; Read et al., 1987; Alipour-Asll et al., 2012). The abundant quartz inclusions identified in the grains suggest a siliceous source rock. The REE zonation in the authigenic nodular monazite is a consequence of REE contribution from distinct sources to the mineralizing fluids and/or changes in the degree of their mobility (Alipour-Asll et al., 2012). Therefore, the apatite inclusions are another potential source of P and contributor to REE zonation; and rutile inclusions suggest the availability of Ti. Since all these elements show high or anomalous contents in the Ordovician (radioactive) quartzites (Inverno et al., 2007), these rocks are the most probable original source of the Monfortinho alluvial nodular monazite, as proposed by the cited authors.

Acknowledgments

Part of this study was carried out within the framework of a project funded by the European Union Cross-border INTERREG II program. João Fernandes (LNEG) is thanked for helping in map preparation.

References

Alipour-Asll, M., Mirnejad, H., Milodowski, A.E., 2012. Occurrence and paragenesis of diagenetic monazite in the upper Triassic black shales of the Marvast region, South Yazd, Iran. *Miner. Petrol*., 104, 197-210.

Deer, W.A., Howie, R.A., Zussman, J., 1962. *Rock Forming Minerals. Nonsilicates*. Longman, London. vol. 5, 371 pp.

Gromet, L.P., Dymek R.F., Haskin L.A., Korotev R.L, 1984. The "North American Shale Composite": its compilation, major and trace element characteristics. *Geoch. et Cosmoch. Acta*, 48, 2469-2482.

Inverno, C.M.C., Oliveira, D.P.S., Rodrigues, L., (collaboration from: Viegas, L., Matos, J., Martins, L., Salgueiro, R., Lencastre, J., Farinha, J., Rosa, D., Chichorro, M., Santana, H., Oliveira, V., Fernandes, J., Pateiro, R.), 2007. Inventariação e prospecção de terras raras nas regiões fronteiriças da Beira Baixa e do Norte Alentejo. INETI Report, Alfragide, 2982 pp.

Kucha, H., 1880. Continuity in the monazite-huttonite series. *Mineral. Magaz*., 43, 1031-1034.

Lencastre, J., 1999. Estudo Preliminar da Monazite Nodular de Monfortinho, Portugal. *Est. Notas e Trabalhos*, 42, 97-119.

Read, D., Cooper, D.C., MCArthur, J.M., 1987. The composition and distribution of nodular monazite in the Lower Palaeozoic rocks of Great Britain. *Mineral. Magaz*., 51, 271-280.

Rosenblum, S., Mosier, E.L., 1983. Mineralogy and occurrence of europium-rich dark monazite. *In*: U.S. Geol. Surv. Prof. Paper 1181, U.S. Govern. Print. Office, Washington, 67 pp.

Sequeira, A.J.D., 2011. Microfósseis do Grupo das Beiras (Monfortinho – Salvaterra do Extremo, Beira Baixa, Portugal Central). *Comun. Geológicas*, 98, 55-60.

Sequeira, A.J.D., Cunha, P. Proença, Ribeiro, M.L., 1999a. Carta Geológica de Portugal à escala 1/50 000, Folha 25-B (Salvaterra do Extremo). IGM, Lisboa.

Sequeira, A.J.D., Cunha, P.Proença., Ribeiro, M.L., 1999b. Notícia Explicativa da Folha 25-B (Salvaterra do Extremo) da Carta Geológica de Portugal à escala 1/50 000. IGM, Lisboa 47 pp.