

The Pedregal granite (Portugal): petrographic and geochemical characterization of a peculiar granitoid

El granito de Pedregal (Portugal): caracterización petrográfica y geoquímica de un granitoide peculiar

J.A. Ferreira¹, M.A. Ribeiro¹, H.C.B. Martins¹

¹ Geology Centre/Department of Geosciences, Environment and Spatial Planning, Faculty of Sciences, Porto University, Rua do Campo Alegre, 4169-007 Porto, Portugal. Email: joana.alexandra.ferreira@gmail.com

ABSTRACT

The Pedregal granite outcrops in the Central Iberian Zone, northern Portugal, in the eastern border of a synorogenic variscan granite-migmatite complex sub-concordant with the regional metamorphic structures. It is a granitoid (ca. 3 km²) with an elongated NW-SE shape intruded in staurolite-micaschist and banded gneiss-migmatite rocks, with local igneous breccias in the contact. The country rocks belong to a metapelitic and metasammitic sequence of Edicarian-Cambrian age, known as the "Complexo Xisto-Grauváquico" (CXG) which shows a main regional foliation with a NW-SE to NNW-SSE direction. The Pedregal granite is peraluminous (its A/CNK parameter ranges from 1.18 to 1.62), with a magnesian and alkali to alkali-calcic signature. The peculiar features of the granite are high contents of Zr (389 to 435 ppm) and a LREE flat pattern, which are uncommon characteristics for granitic rocks, as well as the corroded shape of the biotite, and the large amount of secondary muscovite. These peculiar features distinguish it from the adjacent synorogenic granites.

The field, petrographical and chemical features of the Pedregal granite are in accordance with a second phase of partial melting of a residuum, depleted by melt segregation during a first melting episode with the involvement of peritectic garnet and abundant residual biotite with LREE- and Zr-bearing accessory minerals. Besides, the intrusive character of the granite, and the presence of metasedimentary xenoliths point out to a secondary diatexite.

Keywords: Variscan granites; anatexis; geochemistry; rare earth elements

RESUMEN

El granito de Pedregal aflora en la Zona Centro-Ibérica, en el norte de Portugal, en el borde oriental de un complejo granito-migmatítico sinorogénico varisco, subconcordante con las estructuras metamórficas regionales. Es un granitoide (ca. 3 km²) de forma elongada NW-SE, que intruye en micaesquistos estaurolíticos y en rocas gneissico-migmatíticas bandeadas, con brechas ígneas locales en el contacto. Las rocas encajantes pertenecen a una secuencia metapelítica-metasamítica de edad Ediacariense - Cámbrico, conocida como el "Complejo Esquisto-Grauváquico" (CEG), que muestra una foliación regional principal NW-SE a NNW- SSE. El granito de Pedregal es peralumínico (el parámetro A/CNK oscila desde 1.18 hasta 1.62), con una composición magnesiana, entre alcalina y alcalino-cálcica. Sus características peculiares son el alto contenido de Zr (389–435 ppm) y de tierras

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raras ligeras (LREE) que presentan un patrón plano, la forma corroída de la biotita, y la gran cantidad de moscovita secundaria. Estas características peculiares lo distinguen de los otros granitos sinorogénicos adyacentes.

Las características de campo, petrográficas y químicas del granito de Pedregal parecen apuntar a una segunda fase de fusión parcial de un residuo, empobrecido por la segregación de fundido durante una primera fase de fusión con participación de granate peritéctico y abundante biotita residual con minerales accesorios portadores de LREE y Zr. Además, el carácter intrusivo del granito, y la presencia de xenolitos metasedimentarios sugieren una diatexita secundaria.

Palabras Clave: Granitos variscos; anatexia; geoquímica; tierras raras

Introduction

The occurrence of S-type granitic rocks associated with thermal gneiss migmatitic domes in orogenic context is demonstrated by several authors for example at the Appalachians (Maine, USA) (Solar & Brown, 2001), Armorican Massif (St. Malo, France) (Milorde *et al.*, 2001) and Bohemian Massif (Austria) (Vanderhaeghe, 2009). The existence of these thermal domes has a relation of cause-effect with syn-orogenic magmatism and metamorphism, The association of isochronous lateral thermal gradients more significantly by advective rather than by conductive heat transport is proved in this kind of orogenic context (Lux *et al.*, 1986; Lancaster *et al.*, 2008). This advection could be related with ascension of fluids, melts or magmas.

In the Iberian Massif some works have been developed about this theme (Viruete *et al.*, 2000; Alcock *et al.*, 2009; Díez Fernández *et al.*, 2012). Since the 80's, multiple publications put in evidence the association of anatetic granites with gneiss-migmatite rocks at the Portuguese Variscan Orogeny (Holtz & Barbey, 1991; Moita *et al.*, 2009; Bento dos Santos *et al.*, 2010; Valle Aguado *et al.*, 2010; Ribeiro *et al.*, 2011; Areias *et al.*, 2012; Ferreira, 2013; Ferreira *et al.*, 2013).

Regarding the NW sector of Portugal, during the 1950/60's decades Carlos Teixeira referred the existence of migmatitic rocks associated to the "Oporto Granite" which is a two-mica syntectonic granite (Carríngton da Costa & Teixeira, 1957). In the last decades the granites outcropping in the eastern border of Porto Massif were described and dated taking in account their relation with variscan deformation phases, namely D_2 and D_3 (Pinto *et al.*, 1987; Pereira *et al.*, 1992; Mendes, 1967/1968; Martins *et al.*, 2001).

The objective of this study is the geological, mineralogical and geochemical characterization of the Pedregal granite and its relation with surrounding magmatic and metamorphic rocks. The aim is to contribute to a better understanding of the relationship between orogenic granites, anatexis and metamorphic grade in orogenic context.

Geological Setting

The studied granite is mapped on the Geological Map of Portugal scale 1/50.000 (9C-Porto) (Carrington da Costa and Teixeira, 1957) and it has been classified as an alkaline two-mica granite. The Pedregal granite is a NW-SE elongated small granite body (ca. 3 km²) that is exposed to the north margin of the Douro river (Fig. 1). This pluton is intruded in staurolitic micaschists that belong to a metapelitic sequence of Edicarian-Cambrian age known as the "Complexo Xisto-Grauváquico" (CXG). The Pedregal granite body, with a SHRIMP U-Pb zircon age of 311 ± 5 Ma (Ferreira et al., 2014) is spatially associated with other synorogenic granites: Porto granite, a medium-grained alkaline two-mica granite with a zircon/monazite age of 318±14 Ma (Martins et al., 2001, Gondomar granite, a coarse-grained alkaline tourmaline-rich granite) and Fânzeres granite, a foliated garnet-rich granite with a Rb-Sr age of 320 Ma (Pinto, 1987) (Fig. 1). The country rocks are also represented by gneissmigmatite rocks. Locally, the contact is marked by igneous breccias with clasts of gneiss-migmatite and the Pedregal granite as matrix.

The Pedregal granite is a fine to medium-grained two mica granite, with small biotitic nodules (1 to 2 cm) that present an internal foliation whose direction ranges between NE-SW and E-W. This trend is opposite to regional NW-SE metamorphic structure and to the elongation of the pluton. It is a homogeneous rock, with an isogranular texture and locally the xenoliths have a preferential orientation.



Fig. 1.—Geological sketch map of the studied area, based on the 1/50 000 geological map of Porto (Carrington da Costa & Teixeira, 1957 modified).

Analytical methods

The petrography analysis was done through the observation of seven samples of the Pedregal granite using a transmission microscope. Some samples were analyzed by SEM (Scanning Electron Microscope), specifically the EDS (X-ray microanalysis) method, for identification and qualitative analysis of accessory and opaque minerals. These methodologies were carried out in the laboratories of the "Departamento de Geociências, Ambiente e Ordenamento do Território" (DGAOT) and "Centro de Materiais da Universidade do Porto" (CEMUP).

The whole-rock geochemistry analyses for lithogeochemistry purposes were done in the Activation Lab in Ontario, Canada, to obtain the major and trace element composition. These analyses were performed in five samples of the Pedregal granite (same samples of the petrographic study). The lithogeochemistry analyses required a lithium metaborato/ tetraborate fusion with subsequent ICP (Inductively Coupled Plasma) and ICP-MS (Inductively Coupled Plasma-Mass Spectrometer) (FUS-ICP-MS). Fused sample is diluted and analyzed by Perkin Elmer Sciex ELAN 6000, 6100 or 9000 ICP/MS. Three blanks and five controls (three before sample group and two after) are analyzed per group of samples. Duplicates are fused and analyzed every 15 samples. Instrument is recalibrated every 40 samples (http:// www.actlabs.com/).

Petrography

The Pedregal granite has a holocristallyne and heterogranular fine to medium-grained texture. The mineral assemblage consists of quartz + plagioclase + K-feldspar + biotite + muscovite + zircon + apatite + monazite + rutile \pm sillimanite \pm allanite \pm Zn-rich hercynite.

The biotite crystals are elongated and corroded. The biotite-quartz and biotite-plagioclase intergranular boundaries (Fig. 2A) point to a textural disequilibrium suggesting that biotite could be a residual phase. The subhedral biotite crystals are



Fig. 2.—Photomicrographs: A–elongated and corroded crystal of biotite surrounded by quartz and plagioclase (N//); B.–quartz with sillimanite inclusions (N//); C–muscovite with zircon pleocroic halos and quartz inclusions (NX); D–euhedral muscovite with anomalous birefringence (NX).

often chloritized and contain small zircon and rutile needle-like inclusions. Small grains of no-altered biotite are included in subhedral muscovite. The elongated biotite crystals show preferential alignment and homogeneous distribution. In the small nodules the biotite is subhedral and less corroded than the elongated crystals. These nodules present compositional banding marked by biotite and secondary muscovite.

The quartz is subhedral to anhedral and when included in others minerals (muscovite and plagioclase) assumes a globular shape. Frequently, the quartz crystals show inclusions of sillimanite and rutile needles (Fig. 2B).

The albite-oligoclase plagioclase is more abundant than K-feldspar, although the later presents crystals with great dimensions (ca. $600 \ \mu m$). The plagioclase crystals are subhedral and frequently altered.

The muscovite has a secondary character, distinguishing two types: a subhedral muscovite showing irregular borders and quartz droplet inclusions (Fig. 2C) and an euhedral muscovite, with anomalous birefringence (Fig. 2D). The zircon, sillimanite and hercynite are included in both types of muscovite.

Whole-Rock Geochemistry

The Pedregal granite is peraluminous (A/CNK parameter ranges from 1.18 to 1.62 and ASI ranges from 1.23 to 1.71), with a magnesian and alkali to alkali-calcic signature.

The major elements composition of the Pedregal granite shows relative low values of SiO₂ (65–69 wt.%) and high concentrations of Al₂O₃ (15.71–16.68 wt.%) and K₂O (5.21–5.96 wt.%) (Fig. 3). This granite has also high values of minor elements like TiO₂ and P₂O₅. The granite shows high contents in Zr (388–435 ppm), La (91.6–130 ppm), Ce (243–320 ppm) and Th (72.3–137 ppm) (Table 1). The Harker diagrams show the values of the Pedregal granite compared to the country rocks (staurolite schist and greywacke), and the adjacent Porto



Fig. 3.—Harker diagrams comparing the compositions of the Pedregal granite, Porto two-mica granite and staurolitic schist and greywacke.

two-mica granite. The contents of TiO_2 , P_2O_5 , Zr and Th for Pedregal granite are higher than other plotted rocks. On the other hand, the content of alkalis is similar for the Pedregal granite and other plotted rocks.

The REE exhibit an almost flat pattern from La to Pr, but it doesn't continue towards Sm without significant fractionation of LREE $(La/Sm)_N = 2.59-4.43)$ (Fig. 4). The heavy rare earth elements (HREE) show a pattern slightly more fractionated $(Gd/Yb)_N = 5.74-8.89)$. The Eu negative anomaly $(Eu/Eu^* = 0.20-0.40)$ is pronounced (Fig. 4). The low HREE content is opposed by the high Zr concentrations (Fig. 5A), which suggests different mineralogical controls. On the other hand the high LREE and also Th content could be controlled by the presence of monazite (Bea, 1996) (Fig. 5B).

The trace element contents of the Pedregal granite has been compared with the average composition of materials similar to the country rocks (SGC): NIBAS (Neoproterozoic Iberian Average Shale) (Ugidos *et al.*, 2010). In the spider diagram the Pedregal granite shows a positive anomaly for Zr, LREE, Hf, Th and U and a negative anomaly in Y, Yb, Lu Ta (Fig. 6A).

The moderate SiO_2 values (65–69 wt.%), high ASI parameter (1.23 to 1.71), high contents of LREE, Zr, and Th, and the contrasts with more differentiated granites such as the Porto two-mica granite (Fig. 6B) put in evidence a peraluminous granite (Pedregal granite) without significant magmatic differentiation.

Discussion and Conclusions

Field, petrographical and chemical data of the Pedregal granite allow to emphasize the following features: (i) the intrusive character of Pedregal granite in the border of a synorogenic variscan granite-migmatite complex; (ii) the lithology of the host rocks consisting of staurolite-micaschist and banded gneiss-migmatite rocks; (iii) the peculiar structural/textural aspects of the granite, namely the abundance of small biotitic nodules

Table 1.—Whole rock major and minor (%) and trace (ppm) elements composition of Pedregal granite

	P1	P2	P3	P6	P7
SiO ₂	65.28	68.57	69.18	65.3	66.38
Al_2O_3	15.71	16.12	15.98	16.68	16.46
$Fe_2O_3(T)$	3.68	2.93	2.5	2.59	2.28
MnO	0.036	0.019	0.012	0.018	0.014
MgO	1	0.81	0.73	0.8	0.71
CaO	1.58	0.7	0.52	0.65	0.33
Na ₂ O	2.89	2.21	2.01	2.5	2.03
K ₂ O	5.21	5.96	5.69	5.63	5.72
TiO ₂	0.886	0.747	0.688	0.701	0.676
P ₂ O ₅	0.43	0.5	0.52	0.55	0.42
LOI	1.74	2.3	2.55	2.79	3.3
Total	98.44	100.9	100.4	98.21	98.33
A/CNK	1.18	1.42	1.53	1.46	1.62
Ва	1005	677	533	527	527
Sr	228	113	71	94	84
Υ	14	12	11	12	9
Zr	435	416	388	398	389
Zn	50	160	120	140	110
Rb	266	344	333	405	385
Nb	9	6	5	5	5
Cs	5.5	4.9	4.4	63.8	6.1
La	114	130	101	91.6	98.9
Ce	246	320	264	243	260
Pr	30.7	41.5	37.6	35.3	37.1
Nd	110	156	146	142	148
Sm	16.2	22.2	22.2	22.3	22.1
Eu	1.39	1.03	0.89	0.89	0.95
Gd	7.1	7.6	7.2	8.7	7.7
Tb	0.7	0.6	0.6	0.7	0.6
Dy	3.4	3	2.6	2.9	2.5
Но	0.5	0.4	0.4	0.4	0.4
Er	1.4	1.1	1	1.1	0.9
Tm	0.18	0.14	0.14	0.15	0.12
Yb	1	0.8	0.8	0.8	0.7
Lu	0.15	0.1	0.12	0.13	0.1
Hf	10.8	10.5	10.3	10	9.7
Та	0.6	0.4	0.3	0.4	0.3
Pb	57	47	56	39	32
Bi	<0.4	<0.4	<0.4	<0.4	<0.4
Th	72.3	133	137	130	135
U	8.8	13.4	12	9.9	12.8

and the corroded biotite crystals point to a textural reequilibrium in solid state; (iv) the geochemical composition, in particular the high peraluminous



Fig. 4.—REE chondrite-normalised patterns for Pedregal granite, Porto two-mica granite and country rocks (staurolitic schist and greywacke) (Evensen *et al.*, 1978).

and low fractionated signature and the high content of Zr, Th, Ti and LREE.

The emphasized features suggest an origin by crustal partial melting with emplacement without magmatic differentiation.

Furthermore, according to Sylvester (1998) and Dong *et al.* (2013), the CaO/Na₂O and Al₂O₃/TiO₂ ratios give information about the nature of the magmatic source and the temperatures of partial melting in a strongly peraluminous system. In a granitic system, the CaO/Na₂O ratio of strongly peraluminous granites derived from plagioclase-poor and clay-rich sources are lower (<0.3) than that of plagioclase-rich and clay-poor sources (>0.3). The high Al₂O₃/TiO₂ ratios (>100) of strongly peraluminous granites point to cooler (<875 °C) granite melts and low Al₂O₃/TiO₂ ratios (<100) to hotter (>875 °C) ones. Although this information is qualitative, it is in agreement with Zr saturation temperatures (Watson & Harrison, 1983) higher than 890 °C for the Pedregal granite.

In the Pedregal granite, the CaO/Na₂O versus Al_2O_3/TiO_2 and Rb/Ba versus Rb/Sr diagram point to a mixture of pelitic and psammitic sources, and formation of granitic melts at high temperatures (Fig. 7).

Although some of the geochemical peculiarities of the Pedregal granite could be explained by secondary processes (mainly muscovitization), the presence of dispersed corroded biotite and concentrated in banded nodules, point to a diatexite rock.



Fig. 5.—Variation diagrams for the Pedregal granite, Porto two-mica granite and country rocks (staurolitic schist and greywacke): A – Yb *versus* Zr; B – La *versus* Th.

The intrusive character and the presence of metasedimentary xenoliths imply some vertical migration.

The slightly high content of $Fe_2O_3 + MgO$, and the high content of Zr, Th, Ti and LREE, could be explained by previous partial melting and segregation of a peritectic garnet-rich melt. This garnet was observed in field in the associated gneiss-migmatite rocks (Fig. 1), which may correspond to a first segregated melt. Therefore the source of the Pedregal rock was a residual biotite-rich pelitic/psammitic rock depleted by this first episode of melting. The high content of LREE,





Fig. 6.—A – Multi-element variation diagram for the Pedregal granite, normalized to NIBAS (Ugidos *et al.*, 2010); B – Ta *versus* SiO_2 for the Pedregal granite and Porto two-mica granite (data from two-mica granite by Almeida, 2001).

Fig. 7.—CaO/Na₂O versus Al_2O_3/TiO_2 and Rb/Ba versus Rb/Sr diagrams for the Pedregal granite (Dong *et al.*, 2013 after Sylvester, 1998).

Th and U could be explained by the presence of monazite, and the high values of Zr and Ti by the abundance of rutile. The biotite and these associated accessories phases as source minerals may justify the geochemical features of the Pedregal granite.

Taking into account all the above considerations the Pedregal granite may be considered as a secondary diatexite, resulting from a second phase of crustal partial melting in prograde conditions, after the segregation of a first melt with peritectic garnet.

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