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## **Geoquímica de rocha total dos pórfiros graníticos de Vila Pouca de Aguiar (norte de Portugal), integrada com análise petrográfica e microanálise de raios-X**

### ***Whole-rock geochemistry of the Vila Pouca de Aguiar granitic porphyries (northern Portugal), integrated with petrographic and SEM-EDS analysis***

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**Resumo:** Em Vila Pouca de Aguiar existem dois pórfiros de composição granítica/riolítica os quais intruem o granito biotítico, pós-tectónico de VPA. Ambos apresentam orientação aproximada N-S, sendo designados pórfiros de Loivos e de Póvoa de Agrações.

Os pórfiros de VPA exibem textura porfírica com matriz microcristalina. A sua paragéneses mineral é composta por quartzo + feldspato potássico + plagioclase + moscovite (sericite) + biotite + máficos + apatite ± clorite ± zircão ± monazite ± alanite ± opacos. No entanto, com recurso a SEM-EDS, foi possível identificar minerais raros de provável origem hidrotermal, nomeadamente fosfatos de Fe, Al e Mn (childrenite + scorzalite??), e fosfatos de Na, Mn e Fe (gayite??).

A análise geoquímica de rocha total revelou teores mais elevados em SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3t</sub>, MgO, K<sub>2</sub>O, e TiO<sub>2</sub> em Loivos, e teores mais altos em Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, e MnO em Póvoa de Agrações. Ambos apresentam um cariz peraluminoso altamente félsico, uma composição típica de um contexto pós-orogénico, e enriquecimento em Be, Rb, Sn, Cs, Nb, Ta e W. Os espetros de ETR são paralelos, com um perfil de fracionamento geral fraco e com forte anomalia negativa em Eu. Os diagramas multielementares evidenciam também perfis paralelos, anomalias positivas em elementos HFS, e anomalias negativas em LILE.

**Palavras-chave:** pórfiros graníticos, Vila Pouca de Aguiar, geoquímica de rocha total, alteração hidrotermal

**Abstract:** In Vila Pouca de Aguiar there are two porphyries of granitic/rhyolitic composition that intrude the biotite-rich, post-tectonic, VPA granite. Both are N-S trending, being designated Loivos and Póvoa de Agrações porphyries.

The VPA porphyries exhibit porphyritic texture and microcrystalline groundmass. Their characteristic mineral assemblage is composed of quartz + K-feldspar + plagioclase + muscovite (sericite) + biotite + mafic minerals + apatite ± chlorite ± zircon ± monazite ± allanite ± opaque minerals. However, through SEM-EDS, some rare minerals of probable hydrothermal origin have been identified, namely Fe, Al and Mn phosphates (childrenite + scorzalite??), and Na, Mn and Fe phosphates (gayite??).

Whole-rock geochemistry analysis revealed higher SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3t</sub>, MgO, K<sub>2</sub>O, and TiO<sub>2</sub> contents in Loivos, and higher Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, and MnO contents in Póvoa de Agrações. Both porphyries present a highly felsic peraluminous nature, a chemistry typical of a post-orogenic setting, and enrichment in Be, Rb, Sn, Cs, Nb, Ta and W. REE spectra are parallel, with general weak fractionation, and pronounced negative Eu anomalies. Multielemental diagrams are also parallel, showing positive anomalies in HFS elements, and negative anomalies in LILE.

**Keywords:** granitic porphyries, Vila Pouca de Aguiar, whole-rock geochemistry, hydrothermal alteration

## 1. Introduction

Porphyries are igneous, subvolcanic, felsic rocks which display porphyritic texture. Although the presence of these lithologies throughout the Central Iberian Zone (CIZ) has been described in both Portugal (e.g. Sant'Ovaia et al., 2011) and Spain (e.g. Corretgé & Suárez, 1994), very few studies about them have been conducted. In the Portuguese sector of the CIZ, porphyries occur either as vein-like structures or masses.

In the present study, we report whole-rock geochemistry data regarding the two vein-like granitic/rhyolitic porphyries which outcrop in the Vila Pouca de Aguiar region and their correlation with petrographic and SEM-EDS observations.

## 2. Geological Setting

The Vila Pouca de Aguiar region (northern Portugal, located at approximately 117 km NE of Porto) is situated in the transition between the CIZ and the Galiza Trás-os-Montes zone (GTMZ), the first being composed of autochthonous formations, and the second represented by allochthonous and parautochthonous formations of the Variscan belt (Ribeiro et al., 2006). According to the Geological Map of Portugal 6-D, scale 1:50 000, there are two porphyries of granitic/rhyolitic composition, which intrude the post-tectonic, biotite-rich, medium to coarse grained, Vila Pouca de Aguiar (VPA) phaneritic porphyritic granite ( $299 \pm 3$  Ma; Martins et al., 2009). Both veins are N-S trending, named as Loivos and Póvoa de Agrações porphyries (at west and at east, respectively) (Fig. 1). The Loivos porphyry extends for more than 7 km, while Póvoa de Agrações has an extension of nearly 6.5 km. Through field observation it was possible to confirm that the Loivos porphyry only intersects the VPA granite, presenting in certain outcrops a spacially associated microgranitic facies. However, the Póvoa de Agrações porphyry not only intrudes the previously mentioned granite, but also quartzphyllites which compose the Santa Maria de Émeres Unit (Lower to Upper Silurian; Sant'Ovaia et al., 2011), presenting occasionally a very fine grained, compact, and banded lithology in close association.

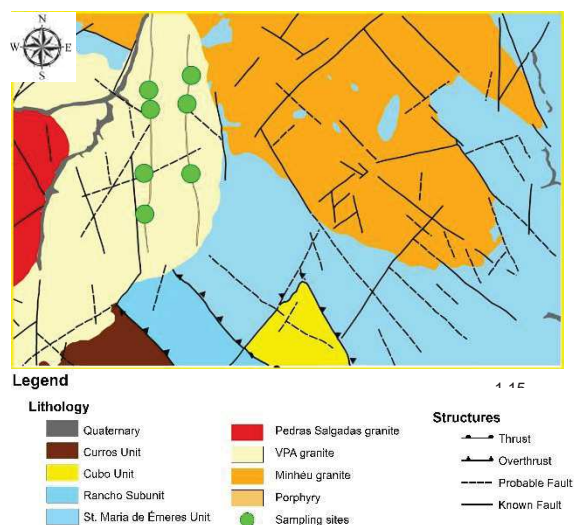


Fig. 1 – Simplified geological map of the Loivos region (Geological Map of Portugal 6-D, scale 1:50000, Vila Pouca de Aguiar).

## 3. Petrography

Under optical microscopy, the granitic/rhyolitic nature of the porphyries was verified: both present a mineral assemblage of quartz + K-feldspar (orthoclase or adularia) + plagioclase ( $An_0 - An_8$ ) + muscovite (sericite) + biotite + mafic minerals (unidentified) + apatite  $\pm$  chlorite  $\pm$  zircon  $\pm$  monazite  $\pm$  allanite  $\pm$  opaque minerals.

Both porphyries are porphyritic, however the groundmass in Póvoa de Agrações is more microcrystalline. Other textural aspects singular to these rocks include: “drop-like” textures in quartz groundmass; groundmass grains aligned around quartz and K-feldspar microphenocrysts and phenocrysts; corrosion gulfs; granophyric texture; rapakivi and antirapakivi; glomeroporphyritic texture; kinks and cleavage bending in mica grains; and symplectitic texture.

## 4. SEM-EDS analysis

Scattering electron microscopy and energy dispersive X-ray spectroscopy were performed in the IMICROS laboratory, CEMUP, Porto.

EDS analysis on opaque minerals revealed an ilmenite [ $FeTiO_3$ ] and brookite or anatase [ $TiO_2$ ] composition, both presenting high grades (weight %, in semiquantitative analysis) in Nb and Ta.

In the Póvoa de Agrações porphyry some minute amounts of cassiterite [ $SnO_2$ ] and

columbite-tantalite  $[(\text{Mn,Fe})(\text{Ta,Nb})_2\text{O}_6]$  were detected. This facies is also the only one presenting rare Fe-Mn-Al/Na phosphate minerals (childrenite + scorzalite + gayite??), which are typical of hydrothermally altered granitic rocks (Petřík et al., 2011).

### 5. Whole-rock geochemistry

A total of 10 samples, 4 from the Loivos porphyry, 4 from Póvoa de Agrações, and 2 of the banded lithology, were analysed through ICP-MS after dissolution with lithium metaborate/tetraborate at Actlabs, Ontario, Canada.

#### 5.1 Major and minor elements

By comparing both porphyries it was verified that Loivos is richer in  $\text{SiO}_2$  (72.83-74.15%),  $\text{Fe}_2\text{O}_3$  (1.01-1.10%),  $\text{MgO}$  (0.15-0.17%),  $\text{K}_2\text{O}$  (4.49-4.72%), and  $\text{TiO}_2$  (0.097-0.102%), while Póvoa de Agrações has the highest  $\text{Al}_2\text{O}_3$  (14.98-15.83%),  $\text{Na}_2\text{O}$  (3.77-4.64%),  $\text{P}_2\text{O}_5$  (0.28-0.76%), and  $\text{MnO}$  (0.047-0.062%) contents. The results for major and minor elements do not reveal any evolutionary trend between both porphyries.

Based on the classification proposed by Frost et al. (2001), all analysed samples are ferroan, alkali-calcic, peraluminous (ASI between 1.3 and 1.6), and highly felsic (Villaseca et al., 1998).

According to the geotectonic classification of Batchelor & Bowden (1985), the three facies fall in the transition between the syn-collision and post-orogenic/anorogenic fields (Fig. 2).

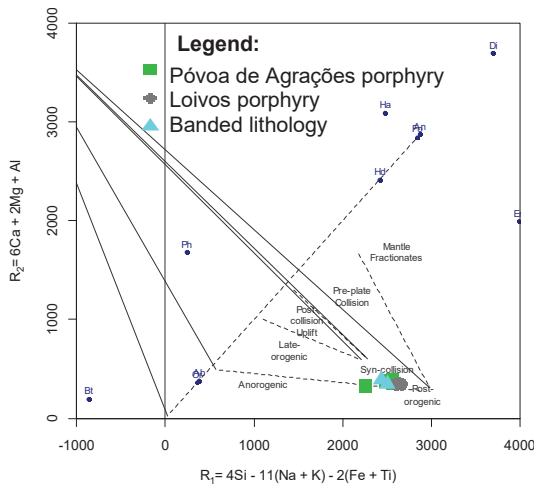


Fig. 2 – Projection of the analysed samples in the Batchelor & Bowden (1985) diagram.

#### 5.2 Trace elements

The VPA porphyries reveal high contents in rare metal, incompatible elements such as Be, Rb, Sn, Cs, Nb, Ta and W. Despite the small distance between veins (about 1 km), this enrichment is clearly more pronounced in Póvoa de Agrações (Be: 20-49 ppm; Rb: 856-1000 ppm; Sn: 151-214 ppm; Cs: 84.1-271 ppm; Nb: 35-53 ppm; Ta: 28-35.5 ppm; W: 6-16 ppm). The banded lithology presents a similar trace element composition to this porphyry. Just as indicated before, there is no discernible evolutionary trend marked by the trace elements.

Both porphyries and the banded lithology are depleted in REE ( $\Sigma\text{REE} = 20.33\text{-}45.27$  ppm) when compared to the VPA granite ( $\Sigma\text{REE} = 114.74\text{-}190.68$  ppm; Martins et al., 2009). The REE spectra reveal a general weak fractionation ( $3.93 < (\text{La}/\text{Yb})_N < 5.91$ ), a stronger HREE fractionation ( $1.27 < (\text{Gd}/\text{Yb})_N < 2.06$ ) than in LREE ( $1.83 < (\text{La}/\text{Sm})_N < 2.63$ ), and pronounced negative anomalies in Eu ( $0.15 < (\text{Eu}/\text{Eu}^*)_N < 0.25$ ). The banded lithology is the poorest in REE, while the Loivos facies is the richest. All REE diagrams show parallel patterns (Fig. 3).

By comparing the composition of both porphyries to the Bulk Continental Crust standard of Taylor & McLennan (1995), and the Primitive Mantle composition determined by McDonough & Sun (1995), the resulting multielemental diagrams display clear positive anomalies in HFS elements (Nb, Ta, U), Cs, P and Pb, and clear negative anomalies in LIL elements (Ba, Sr). These diagrams also reveal parallel patterns for the porphyries and the banded lithology.

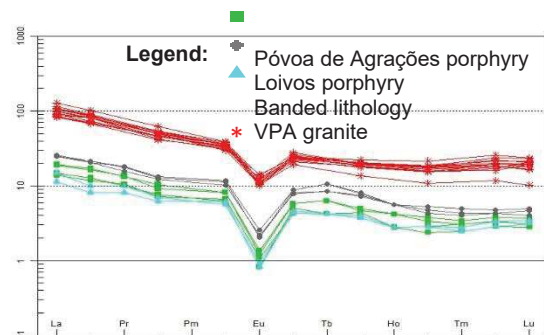


Fig. 3 – REE spectra of the analysed samples. Normalization according to Boynton (1984).

## 6. Final remarks

Spatial proximity, geometry, petrography, REE spectra and multielemental diagrams might imply an eventual genetic link between both porphyries. By comparing the data of the present study to the analytical results published in Martins et al. (2009), the main achieved conclusion is that both porphyries did not derive from the same source which originated the VPA, post-tectonic granite. Field observations, petrography and the geochemical results indicate that the banded lithology is the Póvoa de Agrações porphyry without any phenocrysts.

Textural elements such as rapakivi and antirapakivi (Stimac & Wark, 1992), the general weak fractionation in REE spectra, and the clear positive anomaly in Pb may suggest that the melt from which the porphyries crystallized resulted from mixing of different magmas.

Both porphyries have suffered hydrothermal alteration, as evidenced by their low Nb/Ta and K/Rb values (Ballouard et al., 2016), and petrographic characteristics such as rubefaction, muscovitization, sericitization and the occurrence of rare phosphates. In Póvoa de Agrações this alteration is clearly more developed.

The Vila Pouca de Aguiar porphyries have high contents in rare metal, incompatible elements (Be, Rb, Sn, Cs, Nb, Ta and W), with the majority of them fractionated in Fe-Ti oxides such as ilmenite and brookite/anatase, or cassiterite and columbite-tantalite crystals. Despite the narrow proximity between veins, Póvoa de Agrações shows significantly higher contents of those elements. This difference could be related to the magmatic and post-magmatic events which affected the chemistry of these rocks.

We are aware that further results, namely more field work, other trace elements, SEM-EDS and isotopic data, may help to understand the differences between the two porphyries.

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