The composition of zircon in Variscan granites from Northern Portugal

Composición del circón de granitos variscos del Norte de Portugal

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ABSTRACT

A group of slightly peraluminous Variscan plutons in Northern Portugal were selected from the study of zircon composition. The selected plutons are: the Vila Pouca de Aguiar and the Lavadores-Madalena plutons with I-type affinities and the Vieira do Minho pluton, an I-S transitional type. Zircon occurs as euhedral to subhedral crystals and exhibit finely concentric oscillatory magmatic zoning mainly related to variations of Hf, Y, U and Th concentrations. Most zircon crystals show the dominant “xenotime” substitution. The zircon crystals have Zr/Hf ratio in the range of 21 to 52, with no significant differences between the different granites. These values are in the same range of other peraluminous granites and are in accordance with a crustal signature of zircon. Moreover, the range of Zr/Hf values in zircon crystals overlaps with that of crustal sources and consequently to the potential protoliths proposed in the genesis of the Vieira do Minho and the Vila Pouca de Aguiar plutons, namely meta-igneous crustal sources at different levels. Although zircon from the Lavadores-Madalena pluton has a compositional range similar to the other plutons, an origin by hybridisation has been proposed. However, similar zircon chemistry between this pluton and Vila Pouca de Aguiar and Vieira do Minho plutons could also suggest a similar crustal source.

Keywords: zircon composition; trace elements; Variscan granites

RESUMEN

Se han seleccionado tres plutones graníticos variscos en el norte de Portugal para el estudio de la composición del circón. Los plutones son: Vila Pouca de Aguiar y Lavadores-Madalena con afinidad de tipo-I y el plutón de Vieira do Minho de tipo transicional I-S. Los circones se presentan en cristales euhédricos a subhédricos y tienen zonas magmáticas, concéntricos oscilatorios finos ligados principalmente a variaciones de las concentraciones del Hf, Y, U y Th. La mayoría de los cristales de circón muestran la sustitución dominante “xenotima”. Los zircones tienen relaciones Zr/Hf que varían en el rango 21–52, sin diferencias significativas entre los diferentes granitos. Estos valores son idénticos a otros granitos peraluminícos y son consistentes con circones de origen cortical. Además, las relaciones Zr/Hf coinciden con las de protolitos corticales y, en consecuencia con los propuestos en la génesis de los plutones de Vila Pouca de Aguiar y Vieira de Minho, en particular rocas metálgicas. Aunque los circones del plutón Lavadores-Madalena tienen una composición similar a los otros plutones, fue propuesto un origen por hibridación. Sin embargo la similitud química de los circones de este plutón con los otros puede también sugerir un origen similar.

Palabras clave: composición de circón; elementos traza; granitos Variscos


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Introduction

Zircon is an invaluable tool in countless geological studies due to its wide distribution in a spectrum of rock types and particularly in granites. The importance of this accessory mineral lies in the combination of its tendency to incorporate trace elements, its chemical and physical durability and its remarkable resistance to high-temperature diffusive re-equilibration (Watson, 1996; Watson & Cherniak, 1997). Although the abundance of zircon is low, it may strongly affect the behaviour of many trace elements during the crystallization of magmas, and understanding its compositional variation is thus important for investigating the evolution of magmatic silicic systems (e.g. Hoskin et al. 2000; Belousova et al., 2002 and 2006; Claiborne et al., 2010).

Zirconium and Hf have a nearly identical geochemical behaviour, and therefore most of the crust maintains near-chondritic Zr/Hf ratios of ~35–40 (Hoskin & Schaltegger 2003). As zircon is the primary reservoir for both Zr and Hf and preferentially incorporates Zr, crystallization of zircon controls Zr/Hf, imprinting low Zr/Hf on coexisting melt. Thus, low Zr/Hf is a unique fingerprint of effective magmatic fractionation in the crust. Age and compositional zonation in zircons themselves provide a record of the thermal and compositional histories of magmatic systems. High Hf (low Zr/Hf) in zircon zones demonstrates growth from fractionated melt (Claiborne et al., 2006, 2010).

In addition to its dominant role in controlling zirconium and hafnium distribution during magma evolution, zircon may have a significant influence on the behaviour of rare earth elements (REE), Y, Th, U, Nb and Ta (Heaman et al., 1990; Bea, 1996; Belousova et al., 2002, 2006; Hoskin & Schaltegger, 2003).

Large ionic radii and high charges make these elements incompatible in many rock-forming silicate minerals and they generally become concentrated in the residual melts, where the eventual crystallisation of zircon is able to accommodate these elements. The abundance and ratios of these elements are potentially useful to distinguish zircons from different sources (Pupin, 2000; Belousova et al., 2002; Pérez-Soba et al., 2007).

In this paper, we study the composition of zircon from a group of late- to post-Variscan plutons in NW of Portugal which present variable typology (Martins et al., 2007, 2009 and 2013; Silva, 2010).

Geological and petrological features

The granitic plutons selected for this study are located the Central Iberian Zone and one of them on the western border of the same zone, NW Portugal, being the Vila Pouca de Aguiar pluton, the Vieira do Minho pluton and the Lavadores-Madalena pluton, respectively (Fig. 1). Their emplacement were controlled by tectonic regional structures during the late stages of the Variscan orogeny, mainly from 310 to 299 Ma (Martins et al., 2007, 2009, 2011, 2013). The Vila pouca de Aguiar pluton consists of two main biotite-bearing granitic rocks of monzonitic composition, the coarse-grained Vila Pouca de Aguiar granite (VPAG) as the dominant facies and the more leucocratic medium-grained Pedras Salgadas granite (PSG). These two granites are slightly peraluminous (0.99<A/CNK<1.11) and have an I-type affinity. The U-Pb zircon dating yields a consistent age of 299±3 Ma (Martins et al., 2009). The Vieira do Minho pluton is composed by the porphyrytic coarse-grained Vieira do Minho granite (VMG) and the medium-grained Moreira de Rei granite (MRG), both are biotite bearing granitic rocks of monzonitic-granodioritic composition (Almeida et al. 2002; Martins et al. 2013). They are peraluminous with A/CNK ranging from 1.04 to 1.24, and with a I-S transitional type affinity. The U-Pb isotopic analyses carried out on zircon and monazite from VMG indicate a crystallisation age of 310±2 Ma (Martins et al., 2013), and 308±4 Ma for MRG (Dias et al., 2002).

The Lavadores-Madalena pluton outcrops in a narrow band along the coast line, south of Porto river. The Lavadores granite (LG) is pinkish porphyritic, coarse-grained biotite granodiorite-monzogranite, with accessory amphibole. This granite presents abundant mafic microgranular enclaves with a wide range of compositions (Silva and Neiva, 1998; Silva, 2010). It has a gradual contact with the Madalena granite (MG), which show silimar characteristics. They are both weakly peraluminous (0.98<A/CNK<1.04) and have affinity with I-type granites. A U-Pb zircon age of 298±11 Ma was reported for the Lavadores granite (Martins et al., 2011).
The mineralogical data obtained on these granites are summarized in Table 1.

**Analytical methods**

Zircon was separated from <250 µm sieved fractions using standard heavy liquids and magnetic techniques, handpicked and mounted in epoxy resin. Imaging and chemical analyses were performed using a JEOL 8500 F electron microprobe at LNEG (Porto). Prior to quantitative analysis, the grains were imaged using a high-energy back-scattered electrons were recorded using a paired semiconductor detector, operating in compositional mode to obtain atomic number contrast (BSE). Most zircon analyses were carried out using a focused beam of 1 µm, a 20 nA beam current and with an acceleration voltage of 20 kv. A ZAF correction program was used.

The detection limits were 244 ppm for Si, 240 ppm for Fe, 224 ppm for Al, 243 ppm for P, 421 ppm for Hf, 1042 ppm for La, 111ppm for Ca, 663 ppm for
Pr, 836 ppm for Ce, 479 ppm for Zr, 667 ppm for Nd, 222 ppm for Ti, 786 ppm for Gd, 514 ppm for Th, 156 ppm for U and 421 ppm for Y.

Zircon Chemistry

Nearly 150 chemical analyses of zircon were carried out in the studied plutons. Representative results are shown in Table 2. The zircon crystals are euhedral to subhedral and exhibit finely concentric oscillatory zoning, typical of primary zircon growth (e.g., Smith et al., 1991; Hanchar & Miller, 1993). The zoning is characterized by anti-correlated BSE intensities. In general these crystals show a weakly zoned core surrounded by an outer oscillatory rim (Martins et al., 2014). Internal zoning is related to variations of Hf, Y, U and Th concentrations, so these elements can be main indicators of the degree of magmatic evolution. The compositional range of the elements analysed according to the studied plutons is presented in Figure 2. The compositional range is independent of their host granite, as described in other works (Pérez-Soba et al., 2007 and references therein). It can be seen that all granites present similar medians and low values in the oxides considered, although with different ranges especially in UO₂ and Y₂O₃ (Abreu, 2012).

Table 1.—Summary of magmatic mineralogy of the studied plutons

<table>
<thead>
<tr>
<th>Pluton</th>
<th>Texture</th>
<th>Major minerals</th>
<th>Accessory minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vieira do Minho</td>
<td>monzogranite</td>
<td>Qtz, Pl, Kfs, Bt</td>
<td>Ms, Zr, Mnz, Ap, Ilm, Crd, And</td>
</tr>
<tr>
<td>granodiorite</td>
<td>porphyritic, coarse-grained</td>
<td>Qtz, Pl, Kfs, Bt</td>
<td>Ms, Zr, Ap, Ilm, Aln, Thr</td>
</tr>
<tr>
<td>Vila Pouca de Aguiar</td>
<td>monzogranite</td>
<td>Qtz, Pl, Kfs, Bt</td>
<td>Zr, Ap, Aln, Ilm</td>
</tr>
<tr>
<td>granodiorite</td>
<td>porphyritic, medium-grained</td>
<td>Qtz, Pl, Kfs, Bt</td>
<td>Ms, Zr, Ap, Mnz, Xnt, Aln, Ilm</td>
</tr>
<tr>
<td>Lavadores-Madalena</td>
<td>monzogranite</td>
<td>Qtz, Pl, Kfs, Bt</td>
<td>Hbl, Zr, Ap, Mnz, Aln, Mt</td>
</tr>
<tr>
<td>granodiorite</td>
<td>porphyritic, medium-grained</td>
<td>Qtz, Pl, Kfs, Bt</td>
<td>Zr, Ap, Mnz, Ilm, Mt</td>
</tr>
</tbody>
</table>

The Vieira do Minho Pluton

The Vieira do Minho granite (VMG) presents HfO₂ values ranging from 1.21 to 2.17 wt%, Y₂O₃ from 0 to 3.2 wt%, ThO₂ from 0 to 0.17 wt%. As regards the Moreira de Rei granite (MRG) the HfO₂ values are between 0.18 to 2.55 wt%, Y₂O₃ values from 0 to 0.57 wt% and the contents of ThO₂ range from 0 and 0.13 wt%. The UO₂ contents in both granites are low and very similar, showing values from 0 to 0.07 wt%. In both granites zoning shows a compositional trend of increasing HfO₂, Y₂O₃ and UO₂ from core to rim.

The Vila Pouca de Aguiar Pluton

The compositional ranges in the Vila Pouca de Aguiar granite (VPAG) zircon are (in wt%): 1.29–2.07 HfO₂, 0–0.07 UO₂, 0–0.09 ThO₂ and 0–0.1 Y₂O₃, whereas the Pedras Salgadas granite (PSG) zircon displays a slightly lower range in HfO₂ (1.24–1.9 wt%) and higher range in UO₂ (0–0.41 wt%), ThO₂ (0–1.28 wt%) and Y₂O₃ (0–4.22 wt%) (Fig. 2). In both granites the zircon zoning exhibits a compositional trend of decreasing ThO₂ and Y₂O₃ and increasing UO₂ from core to rim.

The Lavadores-Madalena Pluton

The Madalena granite (MG) has the largest compositional range of HfO₂ (1.29 to 2.92 wt%) and UO₂ (0–1.8 wt%) compared to the Lavadores granite (LG) (HfO₂: 2.04 to 1.04 wt% and UO₂: 0–1.2 wt%). In both granites the Y₂O₃ and ThO₂ contents are low and similar, being the highest value 0.5 wt% and 0.3 wt%, respectively. In general, it is observed in zircon of these granites a positive correlation of, U, Th and Y, which increases from core to rim. The HfO₂ contents from zircons of the Madalena granite increase from core to the rims. As we found in the Vila Pouca de Aguiar pluton, the HfO₂ contents of zircon from the Lavadores-granite are also distributed in an almost uniform way both in the core and in the rims in most of the analysed zircons.
Table 2.—Representative electron microprobe analyses of zircon in Variscan granites from Northern Portugal

<table>
<thead>
<tr>
<th>Plutons</th>
<th>Vila Pouca de Aguiar</th>
<th>Vieira do Minho</th>
<th>Lavadores Madalena</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Z1</td>
<td>Z1</td>
<td>Z2</td>
</tr>
<tr>
<td></td>
<td>Core</td>
<td>Rim</td>
<td>Core</td>
</tr>
<tr>
<td>SiO₂</td>
<td>34.75</td>
<td>34.57</td>
<td>34.60</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>61.56</td>
<td>61.42</td>
<td>63.36</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.03</td>
<td>0.06</td>
<td>–</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.18</td>
<td>0.15</td>
<td>0.06</td>
</tr>
<tr>
<td>UO₂</td>
<td>0.20</td>
<td>0.15</td>
<td>0.06</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>0.29</td>
<td>0.08</td>
<td>–</td>
</tr>
<tr>
<td>HfO₂</td>
<td>1.45</td>
<td>1.68</td>
<td>1.62</td>
</tr>
<tr>
<td>ThO₂</td>
<td>0.07</td>
<td>0.01</td>
<td>–</td>
</tr>
<tr>
<td>La₂O₃</td>
<td>–</td>
<td>0.05</td>
<td>0.03</td>
</tr>
<tr>
<td>Pr₂O₃</td>
<td>–</td>
<td>0.3</td>
<td>–</td>
</tr>
<tr>
<td>Ce₂O₃</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Nd₂O₃</td>
<td>0.02</td>
<td>–</td>
<td>0.08</td>
</tr>
<tr>
<td>Gd₂O₃</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>TiO₂</td>
<td>–</td>
<td>–</td>
<td>0.04</td>
</tr>
<tr>
<td>CaO</td>
<td>–</td>
<td>0.05</td>
<td>–</td>
</tr>
<tr>
<td>FeO</td>
<td>0.04</td>
<td>0.07</td>
<td>–</td>
</tr>
<tr>
<td>Total</td>
<td>98.60</td>
<td>98.34</td>
<td>99.85</td>
</tr>
</tbody>
</table>

Horizontal line indicates contents below detection limit.
Discussion and conclusions

The zircon compositional zoning observed in the studied granites is similar and common to other peraluminous granites, namely monzogranites and granodiorites from the Spanish Central System (Pérez-Soba et al., 2007).

All zircon studied are large euhedral crystals and exhibit finely concentric oscillatory zoning in BSE images. These crystals commonly show an unzoned inner part and outer oscillatory bands. Its composition is close to that of pure zircon, with increasing Hf, Y, U and Th contents from core to rim in granites from the Vieira do Minho Pluton and in the Lavadores granite, whereas in the Madalena granite and in the Vila Pouca de Aguiar pluton, zircons show a different trend with a decrease of Th, U, Y from core to rim and Hf shows an almost uniform distribution both in the core and in the rims in most of the analysed zircons. The decrease of Th-U-Y contents could suggest cocrystallization with other accessory phases rich in Y (xenotime), or rich in U and Th.

Fig. 2.—Compositional comparison between zircon of the studied granites. Bar shows the complete range of zircon composition (vertical line), including the median (short horizontal line).
The composition of zircon in Variscan granites from Northern Portugal


Zr can be replaced by others tetravalent cations (Hf, Th, U) by single isovalent replacement or by coupled substitutions where divalent (Ca, Fe, Mg, Mn) and trivalent (REE, Y, Fe) cations may be incorporated (Hosking & Schaltegger, 2003). In the studied zircons, many elements behave coherently because they participate in a coupled substitution in the zircon crystal structure. Phosphorus concentrations show a positive correlation with Y content, reflecting the dominant “xenotime” substitution: \((\text{REE, Y})^{3+} + \text{P}^{5+} = \text{Zr}^{4+} + \text{Si}^{4+}\) (e.g. Speer, 1980).

Uranium and Th substitute directly for Zr, however they both show a positive correlation with Y as well as with P. This widely reflects the trace element composition of the parental rocks, where the incompatible element concentrations tend to be higher since these rocks are fractionated granites.

The incorporation of Hf in the structure of zircon seems to be strongly dependent on temperature rather than the melt chemistry (Clairborne et al., 2006; Watson et al., 2006). On the other hand, the Th/U ratio has shown to be sensitive to temperature variations (e.g. Gagnevin et al., 2010, and references therein). Nevertheless, in all the studied plutons, \(\text{UO}_2\) and \(\text{ThO}_2\) in zircon show no correlation with \(\text{HfO}_2\) and Th/U ratio (Fig. 3). However, in both granites of the Vieira do Minho Pluton and in the Madalena granite, the increasing Hf from core to rim in most of zircon grains suggests magma differentiation during crystal fractionation (Benisek & Finger, 1993; Hoskin & Schaltegger, 2003). Accordingly, in the Vila Pouca de Aguiar pluton and in the Lavadores granite, the homogeneous Hf concentrations from core to rim may suggest that zircon crystallization occurred in a short period before large fractionation of the magma which reflects the constant Zr/Hf ratio of the melt during zircon formation.

Because hafnium is nearly identical in size and charge to zirconium, the two behave nearly identically. Zircon, therefore, is essentially a zircon–hafnion solid solution, with most natural zircons containing between 1 and 2 wt% \(\text{HfO}_2\) (Hoskin & Schaltegger, 2003; Belousova et al., 2002; Bea et al., 2006; Clairborne et al., 2006 and references therein) and is the major reservoir for the crust’s Hf. As zircon is the primary reservoir for the crust’s Hf, growth of zircon controls the Hf composition of any melt. As zircon grows, both the Zr and Hf concentrations in the magma will decrease. However, this growth preferentially incorporates Zr over Hf and therefore leads to a decrease in the Zr/Hf ratio of the remaining melt. This process leads to increasing Hf concentration in growing zircon crystals, so the the Zr/Hf ratio has been used as an index of magmatic differentiation (Černy et al., 1985). Nevertheless Pérez-Soba et al. (2007), suggest that Zr/Hf ratio can be used with caution as an index of magmatic fractionation, because Zr in zircon is also replaced by other elements and Hf may increase or decrease in a zoned single crystal of the same rock, which is observed in most of the zircons analysed.

The Zr/Hf ratio of the studied granites, ranges from 21 to 52, without significant differences between the tree plutons (mean Zr/Hf: VPAG=41, PSG=40; VMG=36, MRG=37; LG=39; MG=37) (Fig. 4). These values are in the same range observed in other peraluminous granites and are in accordance with a crustal signature of zircon, as suggested by several authors (e.g. Pupin, 2000; Pérez-Soba et al., 2007). The range of Zr/Hf values in zircon crystals of the studied granite plutons overlaps with that of crustal sources and consequently to the potential protoliths proposed in the genesis of the Vieira do Minho and the Vila Pouca de Aguiar plutons (Martins et al., 2009).
Although zircon from the Lavadores-Madalena pluton has a compositional range similar to the other plutons, Silva (1995) has proposed an origin by hybridisation, between basic and felsic magmas, based on isotopic data. However, the similarity in zircon chemistry and also isotopic data between this pluton and Vila Pouca de Aguiar and Vieira do Minho plutons could also suggest an origin by metagneous crustal sources.

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