

Titanite as a tracking accessory mineral of Na-Li-Fe-rich metasomatism (La Pedriza granite massif, Iberian Variscan belt)

Pérez-Soba, C.^{1,*}, Villaseca, C.^{1,2}

¹ *Departamento de Petrología y Geoquímica, Facultad de Ciencias Geológicas, Universidad Complutense de Madrid, Madrid, Spain*

² *Instituto de Geociencias (UCM-CSIC, Madrid, Spain)*

* *E-Mail: pesoa@ucm.es*

In the surroundings of the La Pedriza leucogranite pluton (Spanish Central System, Central Iberian Zone) discrete lenticular bodies of albitite (5 to 100m long) outcrop replacing peraluminous granitic wall rocks. The La Pedriza pluton is a highly fractionated Variscan I-type leucogranite. The albitite paragenesis consists of H₂O-poor or anhydrous minerals: albite, quartz, Li-Na-rich amphibole (ferri-ferropedrizite to sodio-ferripedrizite), Na-Fe-rich pyroxene (aegirine to ferrosylite), Li-Fe-rich micas (taneolite to siderophyllite), titanite, grossular-andradite, magnetite, fluorite, apatite and rutile. Only K-feldspar, apatite and zircon of the parental granite are variably preserved. These albitized granites have been interpreted as resulting from Li-F-Fe-rich alkaline fluid expelled from the nearby I-type leucogranite. The albitization conditions has been estimated previously (Pérez-Soba et al. 2015) yielding temperatures of 500-630 °C and pressures about 0.2 GPa. High oxygen fugacity is deduced according to the mineral paragenesis. In situ LA-ICP-MS U-Pb titanite dating (306 ± 12 Ma) is in the range of the regional granite emplacement (305 ± 6 Ma).

Three textural domains within the albitized granite can be identified: 1) *relic granite framework* that shows pervasive albitization of plagioclase, resulting in dirty cores with abundant growth of anhedral Ca-bearing minerals (fluorite, apatite, garnet and/or titanite), and clean rims (frequently displaying chess texture) with acicular amphibole and titanite 2) *interstitial granoblastic aggregates* of quartz or albite with amphibole, pyroxene and titanite; 3) *interstitial aggregates of mafic minerals* (pyroxene, amphibole, titanite, magnetite, micas), occasionally as inclusions within andradite and/or titanite poikiloblasts (up to 1.5 mm size). Therefore, titanite is the main accessory mineral in the three domains. The wide range of isomorphic substitutions (especially the rare-earth elements -REE- and high-field-strength elements) and sensitivity to oxygen and water fugacity make titanite a good indicator of compositional changes and conditions during magmatic and metamorphic processes. We attempt to use the titanite formation to infer evolution paths of this alkaline metasomatic process.

Three titanite generations according to their location within the albitite textural domains can be distinguished: type 1 (dirty and clean: T1d, T1c), type 2 (T2) and type 3 (T3). T1 titanite crystals are usually anhedral and small (<90 µm in length); T2 are subhedral to euhedral and usually larger (<280 µm in length) and occasionally it is replacing ilmenite; and T3 are variable in shape and size (with interstitial crystals smaller than poikiloblastic ones). Most crystals are free of inclusions (occasional rutile), with the exception of the T3 poikiloblastic titanite. Backscattered electron images (BSE), coupled with microprobe analyses (about 100 spots in a total of 71 grains), show complex chemical zoning in most of the titanite generations, with predominant patchy and sector patterns, frequently combined with sectors of fine scale oscillatory zoning, which usually defines an outer rim. Occasionally, a whole crystal exhibits oscillatory or concentric

zoning. In the largest T2 crystals is possible to observe dissolution-reprecipitation textures.

Titanite shows similar compositional ranges and trends regardless of its zoning type or occurrence within any albitite body. The compositional ranges of significant non-structural cations are (in wt%): $(\text{Fe}_2\text{O}_3)_{\text{total}}=0.38-7.79$, $\text{Al}_2\text{O}_3=0.02-6.39$ (mostly <0.84), $\text{Y}_2\text{O}_3<4.07$, $\text{MnO}<3.38$, $\text{Na}_2\text{O}<1.93$ (average of 0.32), $\text{Nb}_2\text{O}_5<0.75$, $\text{Ta}_2\text{O}_5<0.26$, $\text{SnO}_2<3.63$, $\text{ZrO}_2 (<1.05)$ and $\text{F}<1.35$, and (in ppm) $\text{REE}=3700-22000$, $\text{U}=46-1270$, $\text{Th}=24-176$. The high Fe_2O_3 and Na_2O contents are the most outstanding data in comparison with hydrothermal or metamorphic titanite. Significant high Y, Zr (Hf), Nb (Ta), Sn and U contents are remarkable also for igneous (including granite pegmatite) titanite (e.g., Reguir et al., 1999). A limited number of trace element compositions of T3 titanite crystals (LA-ICP-MS analyses) show variable flat REE-chondrite normalized patterns (e.g., $(\text{La}/\text{Sm})_{\text{N}}=0.22-4.43$; $(\text{La}/\text{Yb})_{\text{N}}=4.6-0.6$; $(\text{Eu}/\text{Eu}^*)_{\text{N}}=0.42-0.09$), with a significant and systematic Ho-Lu concave pattern, opposite to REE patterns from associated amphibole and pyroxene. In BSE images the brighter sectors are systematically higher in Fe^{3+} (and Al) and lower in Ti contents than the darker ones, whereas Ca, Mn, REE, Y, Na, and Nb do not show consistent correlations with brightness.

Titanite analyses show that Si tetrahedral site is not always completely full, suggesting that part of Ti may be substituting for Si. In the octahedral site, mainly Fe^{3+} substitutes for $^{\text{VI}}\text{Ti}$ along 1:1 vector, whereas in the seven-fold coordinate Ca site, $(\text{REE} + \text{Y})^{3+}$ content defines good correlation for Ca along the 1:1 substituting vector. The positive correlation between these two groups of trivalent cations suggest a charge balance substitution mechanism as: $\text{Ca}^{2+} + \text{Ti}^{4+} = (\text{REE}, \text{Y})^{3+} + (\text{Fe}, \text{Al})^{3+}$. Importantly, $(\text{Y} + \text{HREE})$ also substitutes for Ca according $2\text{Ca}^{2+} = 2(\text{Y} + \text{HREE})^{3+} + \text{Na}^+$. The Na-rich fluid may explain the favourable coupled incorporation of Y+HREE into titanite and, therefore, its tendency to flat REE patterns. The variety of cations that enter in the Ca-site may explain the lack of systematic correlation between brightness and Ca contents. Cation variations in sector or oscillatory zoning are not reliable of large scale compositional evolution as depend on preferential incorporations along specific crystal faces (sector zoning) or crystal/fluid local disequilibrium along different diffusion of specific cations (Paterson and Stephens, 1992). Origin of patchy zoning is not clear, so large-scale concentric zoning would be the best record of the fluid evolution (McLeod 2007). If we consider only compositional changes of the otherwise scarce concentric zoned crystals, we found that no systematic variations in the fluid are defined.

The similar compositional range of the titanite types from the albitite bodies suggest a high ratio hot fluid/rock along the replacement channels, yielding a broad similar “co-crystallizing” paragenesis and preventing significant equilibrium between the granite minerals and the alkaline fluid. These conditions imply a compositionally and physically stable reactive flow pattern.

References:

- McLeod GW (2007) Titanite zoning and magma mixing. Ph D, University of Glasgow, 233 pp <http://theses.gla.ac.uk/914/1/2007mcleodphd.pdf>. Accessed 15 May 2017
- Paterson BA, Stephens WE (1992) Kinetically induced compositional zoning in titanite – Implications for accessory-phase melt partitioning of trace-elements. *Contrib Mineral Petr* 109:373–385
- Pérez-Soba C, Villaseca C, Chicharro, E (2015) Na-Li-F-metasomatism related to a highly fractionated peraluminous I-type granite (La Pedriza, Spain, Iberian Variscan belt). Book of abstracts, 8th Hutton Symposium on granite and related rocks, 40 (PT.016)
- Reguir, E.P., Chakhmouradian, A.R., Evdokimov, M.D. (1999) The mineralogy of a unique baratovite- and misserite-bearing quartz-albite-aegirine rock from the Dara-i-Pioz complex, northern Tajikistan. *Can Mineral* 37:1369-1384