Preliminary characterization of the Sn-Ta-Nb-Ti oxides in the quartz veins of the Pedroso de Acim granite cupola (Central Iberian Zone)

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INTRODUCTION

Cassiterite and wolframite represent the most common and economically relevant Sn and W minerals in quartz veins related to S-type granites. However, the presence of additional Sn-Ta-Nb-Ti oxides provides key genetic constraints on the magmatic-hydrothermal evolution of these deposits. This study focuses on a set of quartz-vein-hosted Sn-Ta-Nb-Ti oxides located in the Central Iberian Zone (CIZ) of the Variscan Iberian Massif, within the Schist-Greywacke Complex. They are adjacent to the hinge zone of a Paleozoic (Variscan) fold known as the Miravete-Cañaveral syncline and, more specifically, are hosted in a small stock known as the Pedroso de Acim granite cupola. This 3×1.5 km body consists of various facies of a fertile granite rich in tourmaline and muscovite (González Aguado, 1985); it falls within the category of medium-phosphorous, Nb-Ta poor rare-metal granites (López-Moro et al., 2024). The mineralized veins hosted within this cupola and its related apophyses are predominantly north-trending (NS to N20°E). This orientation differs from the N40°E strike of the regional Li-bearing pegmatites, which coincides with the direction of the Jurassic Alentejo-Plasencia tholeiitic dyke.

RESULTS

The Sn-Ta-Nb-Ti oxides occur in a set of cm-thick quartz veins hosted by a coarse-grained tourmaline-bearing porphyritic granite. These veins do not show muscovite-rich selvages. Mineralization mainly consists of cassiterite crystals that occur in both the cores and towards the margins of the quartz veins. Muscovite, K-feldspar, crandallite-group minerals, zircon, and Ti-Ta-Nb oxides occur as accessory phases.

Cassiterite occurs as brownish to reddish subhedral to euhedral crystals, mm to cm in size, that commonly show twinning and concentric zoning. Crystals are sometimes crosscut by a set of parallel fractures filled by quartz, oriented approximately N40ºE, and showing left-lateral displacement. Cassiterite hosts abundant irregular inclusions of Ti-Ta-Nb oxide minerals that are commonly aligned along growth planes. Locally, zircon and native Bi also fill voids and cracks. Cassiterite crystals display variable response under cathodoluminescence (CL) according to the concentrical zoning, while recrystallized domains are identified truncating these alternations, showing irregular contacts and sometimes confined in singular concentrical zones, in both cases showing higher response to CL. The Ti-Ta-Nb oxide inclusions do not show any response to CL and are frequently concentrated along the recrystallized brighter domains. Chemically, cassiterite varies between 90.7 and 99.0 wt.% SnO_2, with significant substitutions of Ta_2O_5 (up to 7.0, avg. 1.9 wt.%) and, to a lesser extent, TiO_2 (0.3-2.2, avg. 0.8 wt.%), Nb_2O_5 (0.1-2.0, avg. 0.6 wt.%), and FeO (up to 1.4, avg. 0.5 wt.%). Backscattered electron (BSE) images also reflect a fine rhythmic compositional zoning of Ta-rich bright bands, sometimes corresponding to recrystallized CL zones, where Ti-Ta-Nb oxide inclusions are generally found, and other darker bands with higher Ti and Nb contents. In all cases, cassiterite rims show higher Ta/Nb ratios compared to the inner zones of the crystals.

The Ti-Ta-Nb oxide minerals mainly consist of tantalian rutile and, to a lesser extent, wodginite group minerals (WGM). They occur as irregular inclusions, up to 200 μm in size, especially concentrated in the Ta-rich recrystallized domains observed in cassiterite under CL. Tantalian rutile is also found as tiny crystals rimming cassiterite, displaying irregular zoning in BSE, with darker areas enriched in TiO_2 (up to 49.4 wt. %) and brighter areas with a high content of Ta_2O_5 (up to 45.4 wt. %) and moderate contents of Nb_2O_5 (up to 15.6 wt. %), FeO (up to 11.1 wt. %) and SnO_2 (up to 10.7, avg. 3.2 wt. %). Occasionally, some oscillatory zoning is observed with a slight Ta enrichment towards the rims. WGM also occur as inclusions associated with tantalian rutile, exhibiting oscillatory zoning, although they are much less abundant and smaller in size (20-30 µm). WGM also form aggregates of subhedral crystals filling cracks in cassiterite alongside quartz. Their composition is rich in FeO and TiO_2 (up to 15.5 and 10.6 wt. %, respectively), thus they are mainly classified as ferrotitanowodginite. They also show significant contents of MnO (avg. 1.4 wt. %) and SnO_2 (avg. 4.3 wt. %), as well as minor contents of ZrO_2 (up to 0.7 wt. %).

DISCUSSION AND CONCLUSIONS

Textural and compositional observations indicate that there are at least three different hydrothermal stages in the mineralized quartz veins of the Pedroso de Acim granite cupola. Firstly, an early hydrothermal stage is represented by rhythmically zoned cassiterite crystals. Secondly, a subsequent hydrothermal activity promoted dissolution and recrystallization of early cassiterite, thus developing the Ta-rich brighter domains under CL, and the formation of tantalian rutile filling voids preferentially within these domains and rimming cassiterite crystals. Finally, a late stage is characterized by microfractures that crosscut both the early and recrystallized cassiterite as well as the tantalian rutile inclusions. These left-lateral microfractures are filled by quartz and locally contain ferrotitanowodginite, that also filled voids in cassiterite.

Oscillatory zoning in ferrotitanowodginite and tantalian rutile could be interpreted as a consequence of variable concentrations of Ti, Nb, Ta, Fe and Sn in the structure of these minerals. The incorporation of such variety of elements into tantalian rutile, ferrotitanowodginite and cassiterite corresponds to the ideal substitution trend $(Fe,Mn)^{2+} + 2(Nb,Ta)^{5+} \leftrightarrow 3(Ti,Sn)^{4+}$ (Černý and Ercit, 1985), which may be indicative of low oxygen fugacity during the crystallization of this mineral, whereas incorporation of Fe^{3+} in the structure of ferrotitanowodginite would be more typical of higher oxygen fugacity conditions. This zoning could result from different diffusion rates and fluctuations in the activity of the components involved, triggered by the mixing of the hydrothermal fluid with metamorphic and/or meteoric fluids enriched in Ti and Fe. The hydrothermal fluid would have been also enriched in Ta, Nb and Sn, probably due to dissolution of the host cassiterite. Alternatively, the muscovitization of biotite from the granitic host rock could have released Ti and Fe to the hydrothermal system.

Similar mineralogical associations and textural features have been described in other Sn mineralized quartz veins of the CIZ (e.g., Llorens and Moro, 2012; Timón Sánchez et al., 2018), although notably higher Ta contents are reported in the tantalian rutile of Pedroso de Acim, which suggest high HF activity during the hydrothermal stage. This would have promoted Ta and other High Field Strength Elements enrichment of the hydrothermal fluids. The fractures in cassiterite imply a late hydrothermal stage in a tectonic setting able to produce left-lateral displacements in N40°E-trending shear planes, such as those explaining the long-lived Alentejo-Plasencia fault system.

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