Characterization of the W ores at the Santa Comba mine, NW Spain.

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INTRODUCTION

The NW of the Iberian Peninsula is characterized for hosting W-Sn deposits related to peraluminous variscan granites. One of them is the Santa Comba mine, located 45 km to the northwest of Santiago de Compostela, Spain. The mine is set in a poly-intrusive epizonal complex which fits the Endogranite-Stockscheider-Exogranite model (Nesen, 1979). This deposit features two types of mineralization containing cassiterite (SnO₂), wolframite (FeMnWO₃), and scheelite (CaWO₄): a low tonnage high-grade mineralization concentrated in the quartz vein system that crosscuts the whole complex, and high tonnage low-grade disseminated mineralization hosted in the youngest intrusion (endogranite). The disseminated mineralization is related to zones of pervasive high-temperature hydrothermal alteration and stockwork-like systems, sometimes sharing features with porphyry-like deposits. A unique feature of this deposit is that the disseminated ore is enriched in wolframite but from a certain depth becomes enriched in scheelite. In this study, we applied microprobe analysis (EPMA), Raman spectroscopy, and a textural study through the petrographic microscope to identify and examine the characteristics of each ore.

GEOLOGY OF SANTA COMBA

The intrusive complex of Santa Comba is a syn-kinematic granitoid complex where all of the intrusions show a penetrative N-S trending magmatic foliation. This intrusion like most variscan granitoids dates from around 330-285 My ago (Gutiérrez-Alonso et al., 2011). The complex is made up of 3 concentric intrusions and a quartz vein system. The outer intrusions are two barren two-mica porphyritic granites (exogranites), differentiated by the more prominent mica. The outermost granite has a high biotite concentration, whereas in the inner unit muscovite is the more prominent mica. The youngest unit of the complex is a leucocratic equigranular granite (endogranite) which contains the mineralization. Although all lithologies show some degree of hydrothermal alteration, this unit shows intense albitic and potassic alteration overprinted by a later phyllic alteration. It also includes large but scarce pods of greisen alteration of uncertain chronology. Apart from the absence of biotite, the most distinctive feature of the endogranite is the presence of a "stockscheider" that shapes its contact with the exogranite. Nesen (1979) described this pegmatitic texture as consisting primarily of large, up to 10 cm long, perthitic alkaline feldspar crystals that grow inwards to the youngest intrusion. Cuenin (1982) also differentiated between common endogranite (muscovite-rich) and tourmaline-rich endogranite. The latest structure that cuts through the whole complex is an N-S trending swam of quartz veins with coarse-grained wolframite accompanied by cassiterite with small muscovite selvages.

RESULTS AND DISCUSSION

Scheelite and wolframite are the main tungsten ores in Santa Comba, each ore has two paragenesis depending on whether they are disseminated throughout the endogranite or located in veins. The disseminated wolframite, wf I, (Fig. 1a) is observed as large-sized slightly deformed crystals that seem to show association with the tourmaline-rich facies. The disseminated scheelite, sch I, (Fig. 1a) is considered an early-stage phase that forms small euhedral crystals showing signs of deformation such as undulant extinction and fractures, and hosts at least two generations of fluid inclusions. On the other hand, the wolframite found in veins, wf II, (Fig. 1a) has a highly variable grain size and often appears in veins with cassiterite and sulfides or as rims surrounding sch I crystals. The scheelite found in veins

sch II (Fig. 1a) is the youngest tungsten ore. This late-stage phase forms large anhedral crystals in contact with quartz and white mica and does not show signs of deformation.

Sch II is the most common scheelite, it often appears replacing wolframite along crystal edges and cracks or in veins with sulfides (mainly arsenopyrite). Sch I and wf I are only found as disseminated ore in the endogranite, while sch II and wf II can be found widespread throughout the whole complex but more commonly concentrated in veins. In previous studies, it was assumed that scheelite only occurred as a late-stage replacement for wolframite. However, the relationship between sch I and wf II indicates otherwise.

Raman spectroscopy was used to clearly differentiate the tungsten ores which are hard to identify under the petrographic microscope (Fig. 1b), especially when they are small size like the sch I crystals. Compositional differences obtained by EPMA between sch I and sch II are subtle but sch II appears to be more enriched in Fe and Mn (Table 1) which makes sense since it is often replacing wolframite. In wolframite there is a clear compositional difference, being the disseminated wolframite (wf I) Fe-rich, has a H/F (Hubnerite/Ferberite) ratio of ca. 52, while the wolframite found in veins and replacing scheelite (wf II) has a higher Mn concentration, H/F= 63. This can be interpreted as related to an increase in the Mn/Fe ratio of the fluid during the later stages of the magmatic-hydrothermal evolution which would agree with the observations of Borrajo et al. (2022).

There is still much to learn about these types of deposits. The identification of the different tungsten ore types and their paragenesis conducted in this study may provide insight into the precipitation mechanisms responsible for the mineralization in future studies.



Fig 1. (a) Photographs of two different wolframite-scheelite grains through a reflected light microscope. (b) Raman spectra of wolframite (red) and scheelite (blue).

Element	FeO	MnO	CaO	NiO	Nb ₂ O ₅	MoO ₃	Ta ₂ O ₅	WO ₃	SnO ₂	Total
Wfl	13.34	11.77	0.02	0.00	0.77	0.07	0.16	72.89	0.02	99.03
Wf II	8.29	16.13	0.15	0.00	0.02	0.03	0.00	74.01	0.02	98.64
Sch I	0.02	0.00	21.09	0.00	0.02	0.00	0.00	77.98	0.00	99.11
Sch II	0.17	0.15	21.27	0.02	0.00	0.05	0.05	78.09	0.00	99.79

Table 1. Table of EPMA mean compositions of each tungsten ore.

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