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## **Insights into the magmatic-hydrothermal evolution at the Panasqueira W-Cu-Sn deposit, Portugal from chemical and B-isotopic studies of tourmaline and white mica: a review**

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Tourmaline and white mica are common gangue minerals in hydrothermal ore deposits. These minerals are the most abundant alteration phases throughout the Panasqueira W-Sn-Cu deposit and, therefore, the prime indicators for the composition and source of the mineralizing fuids. The deposit consists of sub-horizontal ore-bearing quartz veins hosted by metasedimentary rocks above a late-Variscan granite and its greisen cupola (e.g., Kelly & Rye, 1979).

This contribution summarizes the results of three studies that combine in-situ analyses of major elements by EPMA, trace elements by laser ablation ICP-MS, and boron isotopes by SIMS in tourmaline and white mica at the Panasqueira deposit (Codeço *et al*., 2017, 2019, 2021). The SIMS results were also used to test the application of B-isotope exchange between muscovite and tourmaline as a geothermometer (Codeço *et al*., 2019). In addition, the bulk chemical changes caused by the hydrothermal alteration are addressed, based on analyses of altered and unaltered host rocks, granite, and greisen from drill core samples presented by Codeço *et al*. (2021).

Whole-rock data from altered host rocks show enrichments in W, Sn, Cu, Zn, As, F, Li, Rb, and Cs relative to the unaltered metasediments. Most of these elements are also enriched in the greisen relative to the unaltered granite. The observed variations in whole-rock composition with distance to ore veins reflect the alteration intensity and different modal abundances of tourmaline and mica (Codeço *et al*., 2021).

Tourmaline has intermediate schorl-dravite compositions and is chemically zoned, with increases in Fe/ Mg and F from core to rim, while Ca and Al contents decrease (Codeço *et al*., 2017). White mica comprises muscovite, phengite, and celadonite components and has systematic variations in Fe/Mg according to the setting within the deposit (greisen, vein selvage, alteration zone,

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late mineralized fault), indicating an evolution with time (Codeço *et al*., 2019). In contrast, tourmaline compositions are similar throughout the deposit (but greisen is tourmaline-free). This is ascribed to a stronger dependence of tourmaline on host-rock compositions, while white mica is the better recorder of the changing fuid composition (Codeço *et al*., 2021). The in-situ trace-element data show that Rb, Cs, Ba, Li, Nb, Ta, W, and Sn are preferentially partitioned into white mica over tourmaline while  $Zn$ ,  $\overline{V}$ , and  $\overline{S}r$  show the opposite trend (Fig. 1) (Codeço *et al*., 2021).



Fig.1 - Trace-element partitioning between tourmaline and white mica expressed as apparent D values. The squares show the median values for each element, and the shadowed feld corresponds to the full range of values. Adapted from Codeço *et al*. (2021).

The B-isotope composition  $(\delta^{11}B)$  of coexisting tourmaline and white mica pairs are shown in Figure 2, along with the derived isotope exchange temperatures. Boron isotopic compositions of tourmaline in direct contact with mica have median values of -9‰ (Fig. 2). There is no isotopic zoning but a slight variation with distance from the ore veins. White mica has a more variable composition. The median  $\delta^{11}B$  values of mica from greisen and vein selvages overlap (-17 to -18‰), whereas late-stage muscovite has lower values (down to -23‰). The B-isotope

composition of tourmaline-mica pairs from vein selvages provides an estimate for the temperature of vein formation (450  $\pm$ 50°C). The temperature estimate for a latemineralized fault zone is about 260°C (Fig. 2). The higher temperatures agree well with Ti-in-quartz thermometry from wall-rock alteration zones (503  $\pm$  24 $^{\circ}$ C) and arsenopyrite geothermometry  $(438 \pm 44^{\circ}C)$  from vein selvages (Fig. 2). The lower temperature of late mineralization

overlaps with the range of fuid inclusion homogenization temperatures in vein quartz (360 to 230 °C).

In summary, the B-isotope data from both minerals are consistent with a magmatic source of fuids during the stages of mineralization represented by mica and tourmaline samples, which supports the concept of multiple injections of magmatic-hydrothermal fuids (Codeço *et al*., 2017, 2019).



Fig. 2 - Temperature and  $\delta^{11}B_{\text{fluid}}$  estimates calculated from Panasqueira mica-tourmaline pairs using the fractionation factors of Wunder *et al.*, 2005 (mica-fluid) and Meyer *et al.*, 2008 (tourmaline-fluid). Solid lines are isotherms, and dashed lines are isopleths of  $\delta^{11}B_{\text{fluid}}$ composition. The median  $\delta^{11}B$  values of tourmaline-mica pairs are indicated by circles, with the red and green symbols representing vein selvages and late fault zone, respectively. The black lines correspond to the 25<sup>th</sup> to 75<sup>th</sup> percentile range. Independent temperature estimates are shown in gray bars at the bottom of the plot: 'Fluid inclusions from Kelly & Rye (1979), Bussink (1984), Jaques & Pascal (2017), and Lecumberri-Sanchez *et al.* (2017); <sup>2</sup>Arsenopyrite geothermometry (Apy-geoth) from Jaques & Pascal (2017); <sup>3</sup>Ti-in-quartz (TitaniQ) geothermometry from Codeço *et al*. (2017). Adapted from Codeço *et al*. (2019).

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