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Thermodynamic constraints of tungsten transport and wolframite precipitation in high-temperature hydrothermal fluids

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Granite-related tungsten-(tin) mineralization in Iberia occurs as endo- to peri-granitic porphyry-like, breccia pipes, quartz-vein, greisen, and calcic and magnesian skarns. More than the 80% of wolframite mineralization in Iberia is hosted by endo- to exo-granitic well-defined large quartz-muscovite veins and their greisenized selvages. Less common, but also economic, mineralization is associated with A-type quartz-feldspar veins, pegmatites and miarolitic cavities within zones of pervasive feldspar (potassic and sodic) metasomatic alteration in the apex of felsic intrusives (e.g., Las Sombras and Carris) or even as likely magmatic disseminations in evolved granitic cupolas (e.g., Fontao and Santa Comba). This early magmatic to early magmatic-hydrothermal mineralization is thought to be equivalent to that forming porphyry systems.

Related granitoids show extensive metasomatic hydrothermal alteration which commonly starts at high temperature during the magmatic-hydrothermal transition in the form of a feldspar-biotite potassic alteration followed by a later and pervasive, more acid and lower temperature hydrothermal alteration dominated by the quartz-muscovite assemblage.

Fluid inclusion, thermodynamic constraints and isotopic data show that this mineralization is formed at temperatures between ca. 250°C and 400 °C, fluid pressures between 200 and 1500 bar, and related with fluids with a pH at or slightly below the QFMASH equilibria and fO_2-fS_2 close to the PPM and NNO buffers. These fluids are systematically of low to intermediate density (<15 wt % NaCl eq., and abundant CO_2-CH_4). Within this work we present a novel thermodynamic model for tungsten transport in high temperature (up to 500°C) aqueous hydrothermal fluids and we evaluate the different mechanisms which potentially trigger the wolframite precipitation. Numerical calculations using CHNSOZ and SOLVEQ-XPT programs show that tungsten was dominantly transported as H_2WO_4 and HWO_4^- aqueous complexes and wolframite precipitation is driven by different mechanisms, dominantly boiling, fluid mixing and fluid-rock reaction.

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