U–Pb and Re–Os dating of wolframite and molybdenite: Constraints on mineralization and cooling history (⁴⁰Ar/³⁹Ar)for the magmatic– hydrothermal system at Borralha, Northern Portugal

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The Borralha area reflects a long-lived and multiphase magmatism (ca. 316 to 300 Ma), characterized by three types of granite emplacement during two different extensional events (E1 and E2) and one contractional event (C3) within the Variscan orogeny. The W-(Cu) mineralization styles correspond to veinlets and quartz veins, and disseminations in the Santa Helena breccia pipe. Molybdenite coexists with an Fe-bearing wolframite–quartz assemblage only in the Venise breccia pipe.

The geochemistry and geochronology of wolframite and molybdenite samples were studied by electron probe microanalysis, in-situ U–Pb laser ablation-inductively coupled plasma mass spectrometry and Re–Os thermal ionization mass spectrometry. Wolframite samples correspond to a ferberite composition with a hübnerite/ferberite ratio of <29%. High amounts of Nb and low amounts of REEs and conversely low amounts of Nb and Ta and high amounts of REEs characterize the samples studied. The REEs normalized spectra of the wolframite samples record a mixed signature. Large and positive Eu/Eu* and Er/Er* anomalies were identified, whereas negative Ce/Ce* and Nd/Nd* anomalies were observed in two samples. The wolframite yields a U–Pb age of 315.2 \pm 4.7 Ma (2s), representing the first episode of W deposition for the Iberian Massif.

Low Re concentrations (<1 ppm) were found in the molybdenite samples. Besides Re and W, chalcophile and siderophile elements were detected in the molybdenite structure. Molybdenite Re–Os dating yields absolute ages from 305.1 to 303.8 \pm 2.2 Ma (2s), corresponding to E2 biotite granite (Peneda–Gerês; I-type; <305 Ma) emplacement at the start of the E2 extensional stage.

Constraints between the timing of W- and Mo-deposition and a protracted cooling history are confirmed by ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ mica dating. The ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ ages (2s) obtained for micas from Mo-(277.3 ± 1.2 and 287 ± 2 Ma; Venise breccia pipe) and W-(Cu)-orebodies (286.8 ± 1.2 and 279.0 ± 4 Ma; Santa Helena breccia

pipe) track the cooling history of the magmatic–hydrothermal system at Borralha after E2 granite emplacement in the region associated with late-Variscan deformation. The ⁴⁰Ar/³⁹Ar ages provide evidence for a prolonged and multi-stage alteration–mineralization process lasting more than 12 Ma.