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624767 - Formation of a giant tungsten deposit: Metal sources and fluid evolution at Panasqueira, Portugal (EC)

Fluid-rock interaction is decisive for the formation of tungsten deposits

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ABSTRACT

Tungsten mineralization is typically associated with reduced granitic magmas of crustal origin. While this type of magmatism is widespread, economic tungsten deposits are highly localized with ~90% produced from only three countries worldwide. Therefore, the occurrence of reduced magmatism, while necessary for tungsten enrichment, seems to be insufficient to form such rare deposits. Here, we explore the mechanisms that lead to wolframite precipitation and evaluate whether they may exert a decisive control on tungsten global distribution. Tungsten differs from other rare metals

enriched in magmatic-hydrothermal ore deposits because it is transported as an anionic species. Precipitation of the main tungstate minerals scheelite, $CaWO_4$, and wolframite, $(Fe,Mn)WO_4$, thus depends on the availability of calcium, iron or manganese. We demonstrate quantitatively that magmatic fluids at Panasqueira, Portugal, provide tungsten in solution, whereas the host rock contributes the iron required to precipitate wolframite. The combination of special source conditions with specific reactive host rocks explains why major wolframite deposits are rare and confined to a few ore provinces globally.

INTRODUCTION

Tungsten metal and tungsten alloys are characterized by toughness, corrosion resistance, and high strength at extreme temperatures. These physical properties make tungsten essential for many industrial applications and, in combination with its localized distribution, a *critical* metal and a high trade risk commodity (Klimek et al., 2015). Despite previous studies outlining possible precipitation mechanisms (Heinrich, 1990; Wood and Samson, 2000), indispensable controls on tungsten mineralization that determine local and global resource distribution have not yet been identified for any major deposit. Economic tungsten deposits represent >1000-fold enrichment in W from background crustal levels of ~1 ppm (Rudnick and Gao, 2003) to ore grades of 1000–50’000 ppm. The few global provinces hosting world-class tungsten deposits share common magmatic-hydrothermal features. Deposits are typically associated with specific magma types formed by melting of sedimentary rocks that may have been enriched in W via weathering (Romer and Kroner, 2014, 2016); magmatic fractionation in the resulting reduced melts causes selective enrichment of tungsten in the residual silicate melt

(Candela, 1992); saturation with alkali-rich magmatic volatiles results in tungsten transfer to a hydrothermal fluid phase, (Manning and Henderson, 1984; Zajacz et al., 2008); and finally precipitation of tungsten-rich minerals in sedimentary host rocks surrounding the granites concentrates W to economic ore grades up to several weight percent as the most significant enrichment step (Audétat et al., 2000).

The fundamental geochemical difference of tungsten compared to other rare metals enriched in magmatic-hydrothermal ore deposits (e.g., porphyry Cu-Au or Sn vein deposits) lies in the chemically 'hard' nature of metal – ligand interactions in aqueous solution (Pearson, 1963). Tungsten is transported as part of an oxy-anion, WO_4^{2-} that can be complexed with Na^+, K^+ or H^+ in hydrothermal fluids, in contrast to Cu^+, Sn^{2+} or Au^+ that are transported as metal ions complexed with anionic ligands such as Cl– or HS– (Wood and Samson, 2000). Because of this particular chemical property, the precipitation of the tungstate ore minerals requires that Fe, Mn or Ca are joined with W, but the geological processes how the two components meet, and hence the essential controls on tungsten ore deposition, are presently unknown.

RESULTS

To identify the primary controls on tungstate precipitation, fluid and rock chemistry have been analyzed at different spatial scales at a world-class wolframite vein deposit. Panasqueira (Portugal) is a giant tungsten deposit, one of the historic leading tungsten producers in Europe and one of the geologically best-characterized and best-preserved tungsten vein deposits in the world (Kelly and Rye, 1979; Thadeu, 1951). Mineralization at Panasqueira consists of wolframite (dominantly $FeWO_4$) in sub-horizontal cm- to m-scale quartz veins with lateral extents of hundreds of meters, hosted in a vertically foliated biotite - chlorite schist (Foxford et al., 2000; Kelly and Rye, 1979). The main oxide - silicate stage minerals in the veins include quartz + muscovite + wolframite + arsenopyrite ± topaz. Ore veins cross-cut a hydrothermally altered granite cupola and are asymmetrically disposed around it (Foxford et al., 1995).

Fluid inclusions associated with the main oxide - silicate stage in wolframite - quartz veins at Panasqueira are CO_2-bearing water-rich liquids of uniform low salinity (5 - 8 wt% $NaCl_{eq}$). Laser-ablation inductively-coupled plasma mass spectrometry (LA-ICPMS) using a high-sensitivity magnetic sector-field instrument (Wälle and Heinrich, 2014) was used to analyze W concentrations in the range of 1–70 ppm, together with other elements including B, Fe, Mn (Fig. 1) Li, Cs and Rb (Appendix 2). While previous studies have suggested that certain components such as He are mantle derived (Burnard and Polya, 2004), fluids are systematically enriched in incompatible elements such as Li, Cs and Rb, which is consistent with these components being derived from an evolved magma. Importantly, fluids related with wolframite precipitation at Panasqueira consistently show Fe and Mn concentrations below detection limit throughout the deposit, even though the detection limits are as low as 0.3 (Mn) and 2 ppm (Fe) in the best analyses provided by the largest inclusions (Fig. 1). These results show that the fluid carried significant and variable concentrations of W, but insufficient Fe and Mn to precipitate a significant fraction of the tungsten in the fluid alone. Wolframite deposition therefore requires an external source of Fe. Multiple vein-type tungsten deposits show chemical evidence of extensive fluid-rock interaction in tungsten vein type deposits (Chicharro et al., 2016; Hulsbosch et al., 2015). Therefore, we focused our attention to the host rock surrounding the veins.

The host rock at Panasqueira consists of vertically foliated biotite - chlorite schists of the Beira group, which contain up to 7 wt % iron oxide and up to 0.1 wt % manganese oxide (Polya, 1989). Trace metal enrichment of the schist occurs up to several kilometers away from the altered granite cupola (Polya, 1988). At the deposit scale, the highest tungsten grades are commonly associated with muscovite selvages growing into the veins and with muscovite haloes in the host rock. Alteration is more extensive (dm- to m-scale) in psammitic layers and spotted schists, compared to fine-grained schist and pelitic layers (Foxford et al., 2000; Polya, 1989). The oxygen and sulfur isotopic signature is purely magmatic previous to mineralization (Marignac, 1982, Polya et al., 2000), but the main mineralizing stage signature lies between the magmatic fluid and host rock signature (Kelly and Rye, 1979; Polya, 1989; Polya et al., 2000). Based on rock chemistry and the evidence of fluid-rock interaction (Foxford, 1992; Kelly and Rye, 1979), the Beira schist has the potential to contribute the cations required for tungstate precipitation.

To test whether reaction of the vein fluid with the wall rocks could provide the missing Fe for wolframite precipitation, we studied the chemical and mineralogical variation of the host rock as a function of distance from the vein. Decimeter-scale samples of host rock contiguous to the vein wall were collected in schist (see appendix 1 for detailed methods). The schists proximal to the veins are systematically depleted in iron, and enriched in potassium, aluminum, boron, tungsten and tin (Fig. 2). Iron depletion in the regions proximal to the vein approach 40 wt% relative to sample background in the spotted schist, and ~5–10 wt% in the fine grain schist. Note that the elements enriched in the fluid (e.g., B, K, As, W) correspond systematically to those enriched in the host rock (see Fig. 1). By contrast, elements absent in the fluid that are common in the vein mineralogy (e.g., Fe) are systematically depleted in the host rock. The chemical alteration in the host rock correlates also with changes in mineralogy. The schist proximal to the vein is systematically depleted in chlorite and biotite, and enriched in tourmaline, muscovite and arsenopyrite with the typical alteration mineralogy at Panasqueira consisting of proximal early tourmaline and distal muscovite rich haloes (Neiva, 2008) formed previous to coeval with mineralization (Marignac, 1982). Bleached margins consisting dominantly of muscovite overprint the early alteration (Foxford, 1992 and references therein). Mass balance calculation indicates that even for relatively narrow alteration haloes within the mine, the iron depletion from the host rock would yield enough Fe to account for the main oxide - silicate stage mineralization (cut-off grade of 10 kg/m^2) in quartz veins at Panasqueira (Appendix 1 and 3). The lack of detectable iron in the fluid is also consistent with iron being immediately removed from the fluid by mineral precipitation.

DISCUSSION

Reactions of the fluid with the wall rock involve removal of Fe from the rock to the fluid and addition of Al and B from the fluid to the rock. These chemical changes are manifested at the mineralogical scale as (Fig. 3):

Muscovitization

$$\text{Chlorite} + 2\,SiO_2 + Al^{3+} + K^+ = \text{Muscovite} + 2\,Fe^{2+} + H_2O$$

$$\text{Biotite} + 2\,Al^{3+} = \text{Muscovite} + 3\,Fe^{2+}$$

Tourmalinization

$$\text{Chlorite} + 1.4\,SiO_2 + 0.4\,Al^{3+} + 0.4\,Na^+ + 1.2\,B(OH)_3$$

$$= 0.8\,Fe^{2+} + 3\,H_2O + 0.4\,\text{Tourmaline}$$

$$\text{Biotite} + 1.4\ Al^{3+} + 0.4\ Na^{+} + 1.2\ B(OH)_3$$

$$= 0.4\ \text{Tourmaline} + 1.8\ Fe^{2+} + 0.6\ SiO_2 + 2\ H_2O + K^{+}$$

All these reactions liberate iron from the host rock into the fluid, and the dominant chlorite-consuming reactions sequester alkalis from the fluid into the host rock. Other muscovitization and tourmalinization reactions additionally lead to a pH increase in the fluid. Note that, according to these reactions, the degree of enrichment/depletion of different elements will depend on the chlorite/biotite content of the unaltered host rock, as well as on the lateral extent of muscovitization and tourmalinization away from the veins, which probably depends on rock permeability.

Precipitation of wolframite from an Fe-deficient ore fluid is driven by a threefold effect of fluid-rock interaction on ferberite solubility according to

$$Fe^{2+}(aq) + (Na,K)_2WO_4(aq) = FeWO_4\ (\text{wolframite}) + 2\ (Na,K)^{+}$$

$$Fe^{2+}(aq) + H_2WO_4(aq) = FeWO_4\ (\text{wolframite}) + 2\ H^{+}$$

Alkali depletion and pH neutralization in the fluid due to tourmalinization and muscovitization of the host rock *decrease* ferberite solubility. Iron enrichment in the fluid *increases* the ferrous-tungstate ion activity product. Simultaneous occurrence of these three processes thereby strongly promotes wolframite precipitation. The variability in the element concentrations in the fluid is independent of distance from the greisen cupola (especially for elements with low concentrations such as W, Fig. 1), and no systematic change in fluid concentrations as a function of temperature (Appendix 3) has been found during the tungsten mineralizing stage. These observations contrast, for example, with copper concentrations in fluids in porphyry systems (Landtwing et al., 2005), wherein a dramatic decrease in Cu concentration suggests chalcopyrite precipitation dominantly via temperature decrease. Sudden pulses of pressure change may have contributed to wolframite precipitation, but cannot precipitate ferberite unless iron is added to the system. The spatially and temporally random variation in W concentration, the homogeneous major composition, and the constant salinity of the mineralizing fluid suggests that tungstate precipitation is not due to fluid mixing or boiling. More likely, it reflects limited iron availability from variably permeable and reactive host rocks, which controlled the slow growth of large wolframite crystals in the open vein space.

IMPLICATIONS FOR GLOBAL TUNGSTEN DISTRIBUTION

Globally, different W deposits show a correlation of tungstate mineralogy (scheelite vs wolframite) with the nature of the wall rock (calcareous rocks vs iron-bearing schists and hornfels). The formation of scheelite deposits in skarns has previously been attributed to a local Ca source (really, here a reference is needed!), but this is the first study to demonstrate a host rock control on wolframite deposits. In particular, tungsten at Panasqueira occurs dominantly as ferberite ($FeWO_4$) with only minor hübnerite ($MnWO_4$; mole ratio of ~7:1 Fe:Mn). The predominance of iron tungstate over manganese tungstate further reflects the host rock composition: the Beira schist rocks are relatively iron rich but poor in manganese and calcium (Polya, 1989). Tungsten-vein deposits worldwide show common features with Panasqueira: they consist of wolframite-bearing veins associated with greisenized granites, but in contrast to tin greisens are most commonly not inside the granite but preferentially hosted in fine grained pelitic rocks (e.g., Audétat et al., 2000, fig. 2). Globally, 70%–85% of deposits are hosted in shales with various degree of contact metamorphism (Werner et al., 2014). Fractionated S-type granites commonly exsolve fluorine and/or boron rich fluids during late crystallization

(Pollard et al., 1987). Due to the low solubility of fluorite (CaF_2) and the strong partitioning of fluorine between fluid and ferromagnesian minerals, fluorine enrichment is typically limited to late-stage magmatic fluids that are relatively poor in calcium and iron (Barton, 1987). Scarcity of tourmaline in the granite despite the abundance of boron in the system, and abundant schorl in the schist as a result of alteration further point to low concentrations of iron in the magmatic fluid (Pivec et al., 1998). The consequence of the scarcity of Fe and Ca is that a fluorine- and/or boron-rich magmatic fluids characteristically derived from evolved granites, even if also rich in W, may be incapable of ferberite/scheelite mineralization without significant input from external host rock reactions. in tungsten vein deposits.

In summary, our study shows than not only scheelite deposits in Ca-rich rocks, but also giant ferberite vein deposits in silicate rocks owe their existence and extreme tungsten enrichment to reaction of fluids of magmatic origin with specific host rocks that provide the necessary cations to precipitate tungsten from its anionic complex in hydrothermal solutions.

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FIGURE CAPTIONS

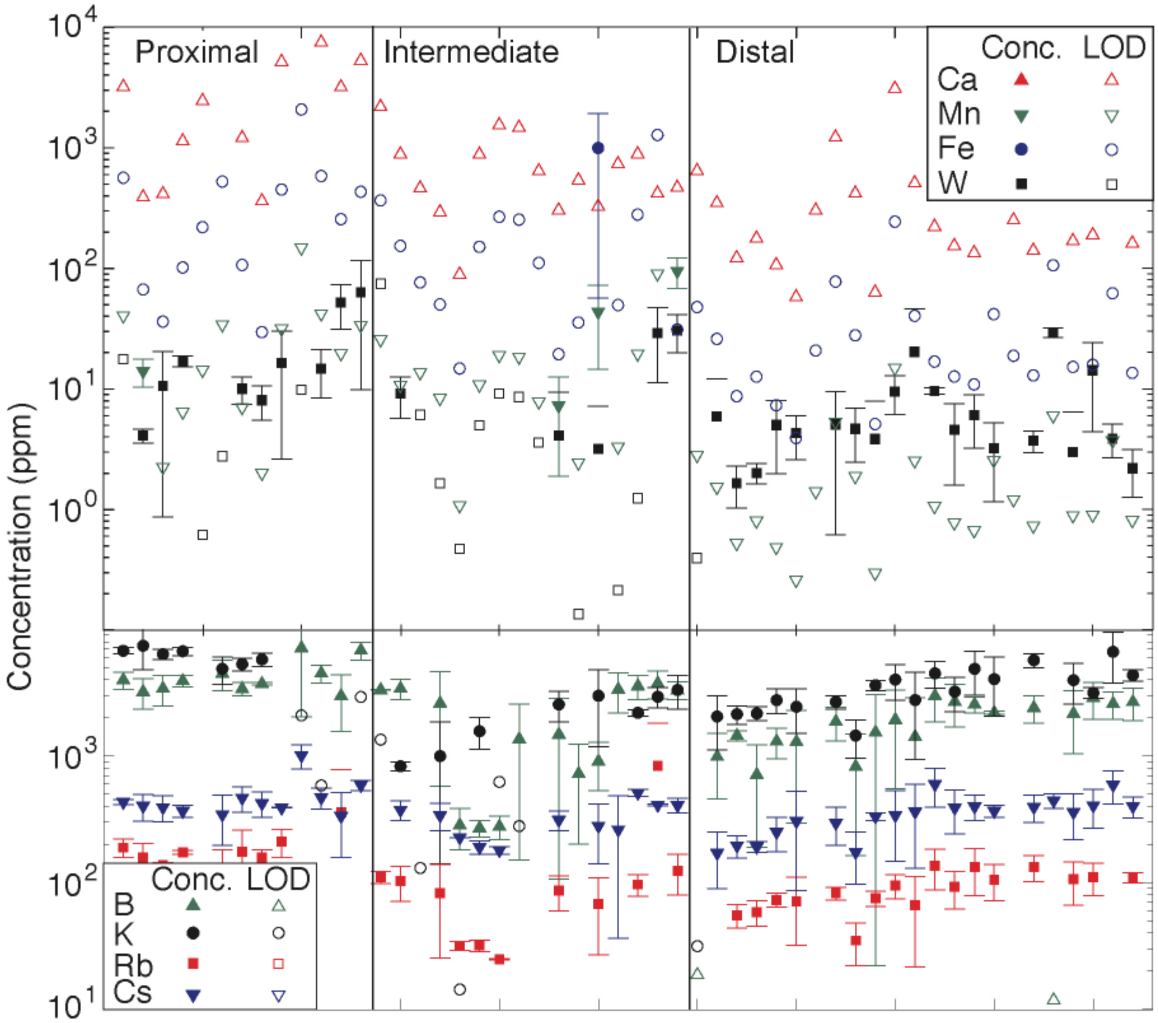

Figure 1. Average concentrations and standard deviations of assemblages of several individual fluid inclusion (arranged in the *x*-axis). Fluid inclusion assemblages where the concentration is below detection limit are indicated by open symbols. “Proximal” represents samples within <500 m from the greisen cupola at Panasqueira; “intermediate” represents 500–1000 m from the cupola; and “distal” represents >1000 m from the inferred magmatic source region.

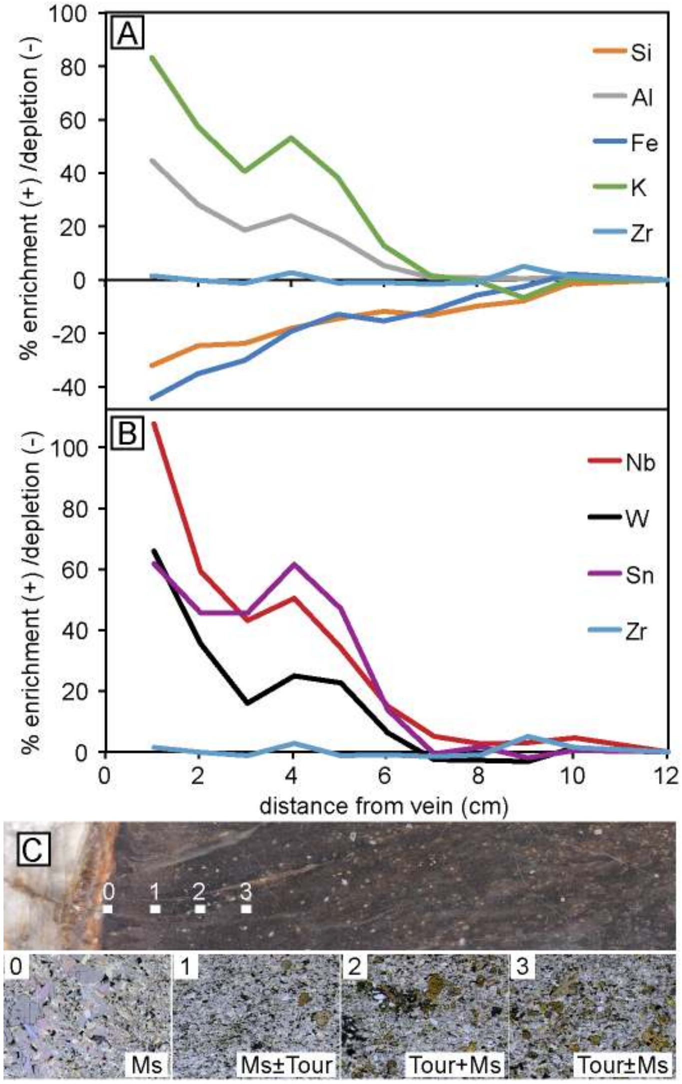

Figure 2. Mass percent element enrichment and depletion (A and B) and mineralogical change (C) of semipelitic schist hosting the Panasqueira ore veins, as a function of distance from the vein wall. Concentration changes are normalized to Zr (an immobile element) using the most distal sample as reference.

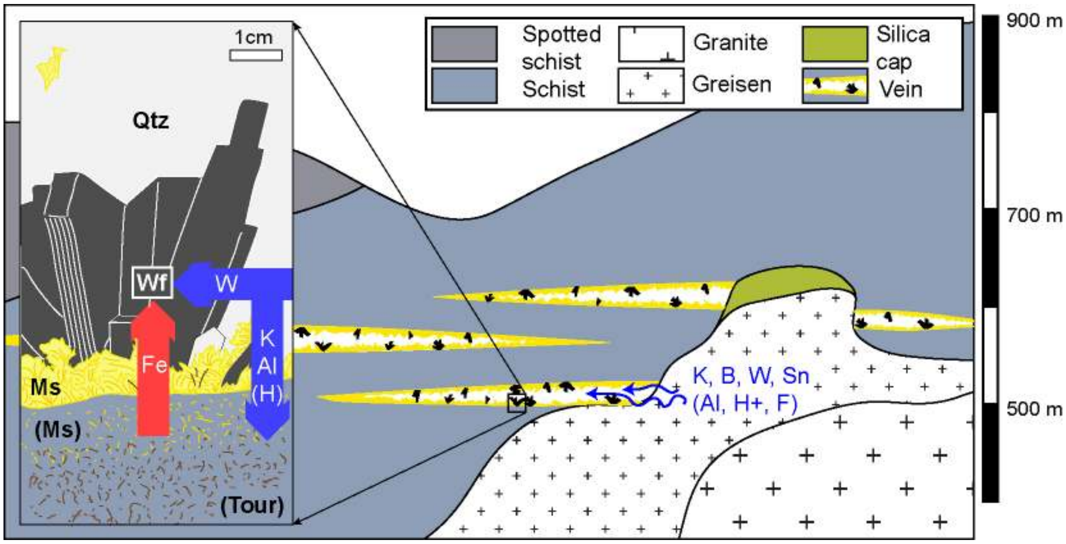

Figure 3. Schematic representation of the fluid – rock reaction process leading to wolframite ($FeWO_4$) mineralization at Panasqueira (Portugal), drafted on simplified cross section from Thadeu (1951). Wf = wolframite, Ms = muscovite, Tour = tourmaline, and Qtz = quartz.

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[1] GSA Data Repository item 2017xxx, xxxxxxxx, is available online at www.geosociety.org/datarepository/2017 or on request from editing@geosociety.org.