

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

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

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

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15 **ABSTRACT**

16 Tungsten mineralization is typically associated with reduced granitic magmas of
17 crustal origin. While this type of magmatism is widespread, economic tungsten deposits
18 are highly localized with ~90% produced from only three countries worldwide.

19 Therefore, the occurrence of reduced magmatism, while necessary for tungsten
20 enrichment, seems to be insufficient to form such rare deposits. Here, we explore the
21 mechanisms that lead to wolframite precipitation and evaluate whether they may exert a
22 decisive control on tungsten global distribution. Tungsten differs from other rare metals

23 enriched in magmatic-hydrothermal ore deposits because it is transported as an anionic
24 species. Precipitation of the main tungstate minerals scheelite, CaWO_4 , and wolframite,
25 $(\text{Fe,Mn})\text{WO}_4$, thus depends on the availability of calcium, iron or manganese. We
26 demonstrate quantitatively that magmatic fluids at Panasqueira, Portugal, provide
27 tungsten in solution, whereas the host rock contributes the iron required to precipitate
28 wolframite. The combination of special source conditions with specific reactive host
29 rocks explains why major wolframite deposits are rare and confined to a few ore
30 provinces globally.

31 **INTRODUCTION**

32 Tungsten metal and tungsten alloys are characterized by toughness, corrosion
33 resistance, and high strength at extreme temperatures. These physical properties make
34 tungsten essential for many industrial applications and, in combination with its localized
35 distribution, a *critical* metal and a high trade risk commodity (Klimek et al., 2015).
36 Despite previous studies outlining possible precipitation mechanisms (Heinrich, 1990;
37 Wood and Samson, 2000), indispensable controls on tungsten mineralization that
38 determine local and global resource distribution have not yet been identified for any
39 major deposit. Economic tungsten deposits represent >1000-fold enrichment in W from
40 background crustal levels of ~1 ppm (Rudnick and Gao, 2003) to ore grades of 1000–
41 50'000 ppm. The few global provinces hosting world-class tungsten deposits share
42 common magmatic-hydrothermal features. Deposits are typically associated with specific
43 magma types formed by melting of sedimentary rocks that may have been enriched in W
44 via weathering (Romer and Kroner, 2014, 2016); magmatic fractionation in the resulting
45 reduced melts causes selective enrichment of tungsten in the residual silicate melt

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

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

61 **RESULTS**

62 To identify the primary controls on tungstate precipitation, fluid and rock
63 chemistry have been analyzed at different spatial scales at a world-class wolframite vein
64 deposit. Panasqueira (Portugal) is a giant tungsten deposit, one of the historic leading
65 tungsten producers in Europe and one of the geologically best-characterized and best-
66 preserved tungsten vein deposits in the world (Kelly and Rye, 1979; Thadeu, 1951).
67 Mineralization at Panasqueira consists of wolframite (dominantly FeWO_4) in sub-
68 horizontal cm- to m-scale quartz veins with lateral extents of hundreds of meters, hosted

69 in a vertically foliated biotite - chlorite schist (Foxford et al., 2000; Kelly and Rye, 1979).
70 The main oxide - silicate stage minerals in the veins include quartz + muscovite +
71 wolframite + arsenopyrite ± topaz. Ore veins cross-cut a hydrothermally altered granite
72 cupola and are asymmetrically disposed around it (Foxford et al., 1995).

73 Fluid inclusions associated with the main oxide - silicate stage in wolframite -
74 quartz veins at Panasqueira are CO₂-bearing water-rich liquids of uniform low salinity (5
75 - 8 wt% NaCl_{eq}). Laser-ablation inductively-coupled plasma mass spectrometry (LA-
76 ICPMS) using a high-sensitivity magnetic sector-field instrument (Wälle and Heinrich,
77 2014) was used to analyze W concentrations in the range of 1–70 ppm, together with
78 other elements including B, Fe, Mn (Fig. 1) Li, Cs and Rb (Appendix 2). While previous
79 studies have suggested that certain components such as He are mantle derived (Burnard
80 and Polyá, 2004), fluids are systematically enriched in incompatible elements such as Li,
81 Cs and Rb, which is consistent with these components being derived from an evolved
82 magma. Importantly, fluids related with wolframite precipitation at Panasqueira
83 consistently show Fe and Mn concentrations below detection limit throughout the
84 deposit, even though the detection limits are as low as 0.3 (Mn) and 2 ppm (Fe) in the
85 best analyses provided by the largest inclusions (Fig. 1). These results show that the fluid
86 carried significant and variable concentrations of W, but insufficient Fe and Mn to
87 precipitate a significant fraction of the tungsten in the fluid alone. Wolframite deposition
88 therefore requires an external source of Fe. Multiple vein-type tungsten deposits show
89 chemical evidence of extensive fluid-rock interaction in tungsten vein type deposits
90 (Chicharro et al., 2016; Hulsbosch et al., 2015). Therefore, we focused our attention to
91 the host rock surrounding the veins.

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

105 To test whether reaction of the vein fluid with the wall rocks could provide the
106 missing Fe for wolframite precipitation, we studied the chemical and mineralogical
107 variation of the host rock as a function of distance from the vein. Decimeter-scale
108 samples of host rock contiguous to the vein wall were collected in schist (see appendix 1
109 for detailed methods). The schists proximal to the veins are systematically depleted in
110 iron, and enriched in potassium, aluminum, boron, tungsten and tin (Fig. 2). Iron
111 depletion in the regions proximal to the vein approach 40 wt% relative to sample
112 background in the spotted schist, and ~5–10 wt% in the fine grain schist. Note that the
113 elements enriched in the fluid (e.g., B, K, As, W) correspond systematically to those
114 enriched in the host rock (see Fig. 1). By contrast, elements absent in the fluid that are

115 common in the vein mineralogy (e.g., Fe) are systematically depleted in the host rock.
116 The chemical alteration in the host rock correlates also with changes in mineralogy. The
117 schist proximal to the vein is systematically depleted in chlorite and biotite, and enriched
118 in tourmaline, muscovite and arsenopyrite with the typical alteration mineralogy at
119 Panasqueira consisting of proximal early tourmaline and distal muscovite rich haloes
120 (Neiva, 2008) formed previous to coeval with mineralization (Marignac, 1982). Bleached
121 margins consisting dominantly of muscovite overprint the early alteration (Foxford, 1992
122 and references therein). Mass balance calculation indicates that even for relatively narrow
123 alteration haloes within the mine, the iron depletion from the host rock would yield
124 enough Fe to account for the main oxide - silicate stage mineralization (cut-off grade of
125 10 kg/m^2) in quartz veins at Panasqueira (Appendix 1 and 3). The lack of detectable iron
126 in the fluid is also consistent with iron being immediately removed from the fluid by
127 mineral precipitation.

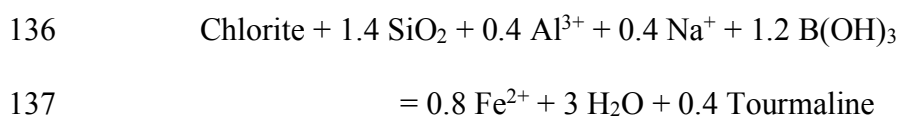
128 **DISCUSSION**

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

132 Muscovitization



135 Tourmalinization



161 temperature decrease. Sudden pulses of pressure change may have contributed to
162 wolframite precipitation, but cannot precipitate ferberite unless iron is added to the
163 system. The spatially and temporally random variation in W concentration, the
164 homogeneous major composition, and the constant salinity of the mineralizing fluid
165 suggests that tungstate precipitation is not due to fluid mixing or boiling. More likely, it
166 reflects limited iron availability from variably permeable and reactive host rocks, which
167 controlled the slow growth of large wolframite crystals in the open vein space.

168 **IMPLICATIONS FOR GLOBAL TUNGSTEN DISTRIBUTION**

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

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

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

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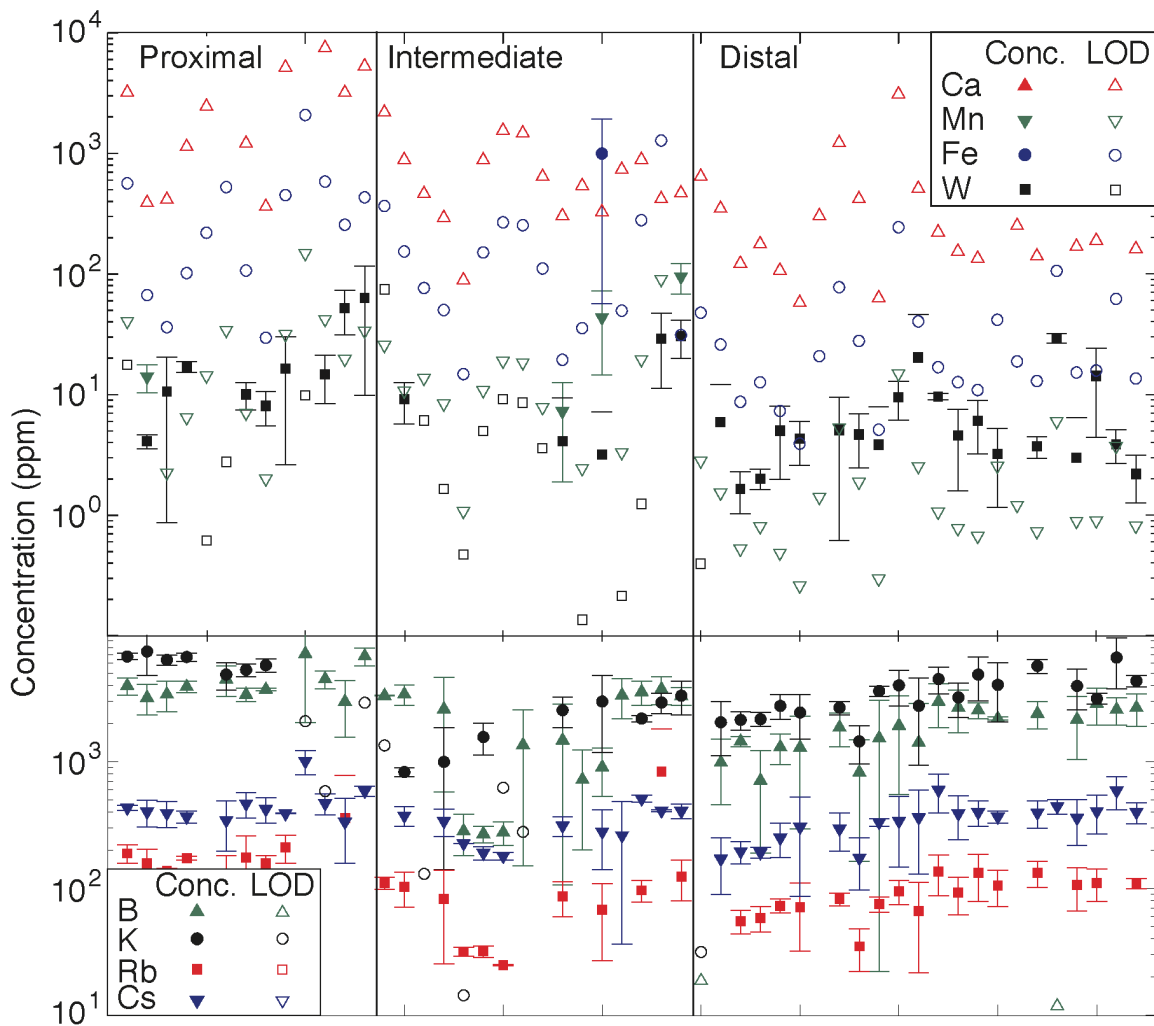
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β06

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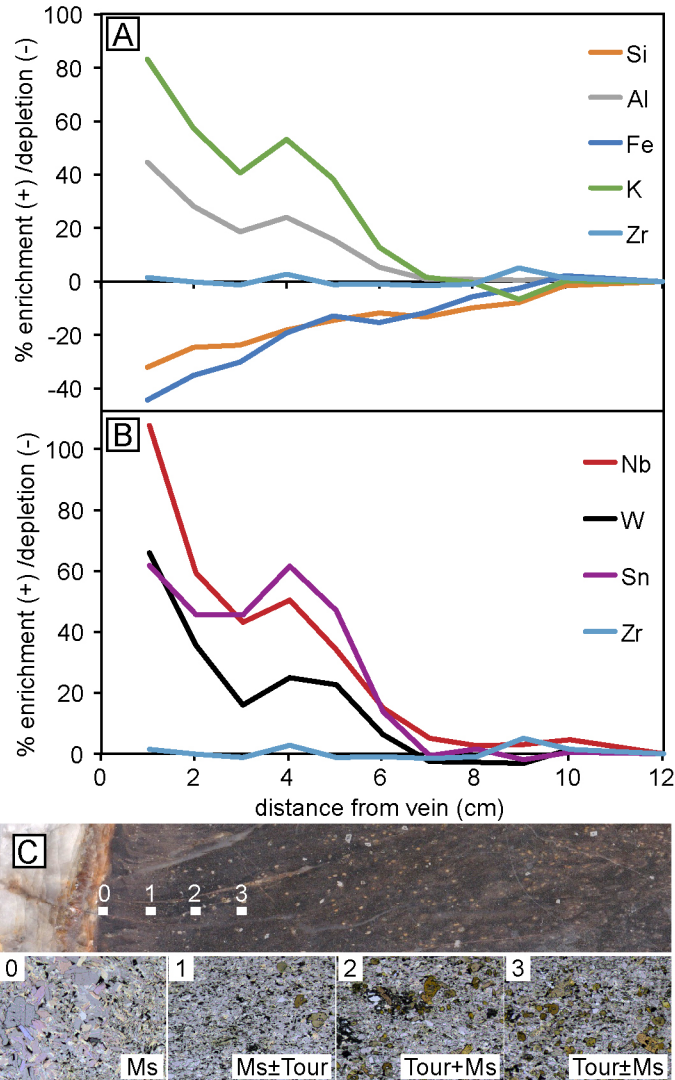
308 FIGURE CAPTIONS



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

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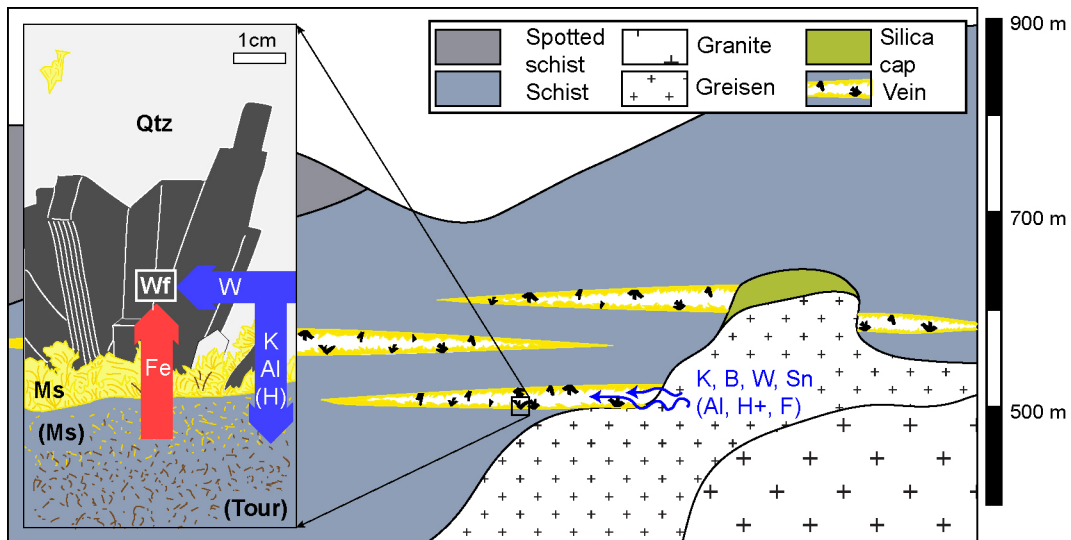
320 Figure 2. Mass percent element enrichment and depletion (A and B) and mineralogical
321 change (C) of semipelitic schist hosting the Panasqueira ore veins, as a function of
322 distance from the vein wall. Concentration changes are normalized to Zr (an immobile
323 element) using the most distal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

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

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337 ¹GSA Data Repository item 2017xxx, xxxxxxxx, is available online at

338 www.geosociety.org/datarepository/2017 or on request from editing@geosociety.org.

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