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Short communication

The H/F ratio as an indicator of contrasted wolframite deposition mechanisms

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ABSTRACT

Understanding wolframite deposition mechanisms is a key to develop reliable exploration guides for W. In quartz veins from the Variscan belt of Europe and elsewhere, wolframites have a wide range of compositions, from hübnerite- ($MnWO_4$) to ferberite-rich ($FeWO_4$). Deposition style, source of Mn and Fe, distance from the heat/fluid source and temperature have been proposed to govern the wolframite H/F (hübnerite/ferberite ratio) defined as 100 at. Mn/(Fe + Mn). The Argemela mineralized district, located near the world-class Panasqueira W mine in Portugal, exposes a quartz-wolframite vein system in close spatial and genetic association with a rare-metal granite. Wolframite is absent as a magmatic phase, but W-rich whole-rock chemical data suggest that the granite magma is the source of W. Wolframite occurs as large homogeneous hübnerites (H/F = 64–75%) coexisting with montebrasite, K-feldspar and cassiterite in the latest generation of intragranitic veins corresponding to magmatic fluids exsolved from the granite. Locally, early hübnerites evolve to late more Fe-rich compositions (H/F = 45–55%). In a country rock vein, an early generation of Fe-rich hübnerites (H/F = 50–63%) is followed by late ferberites (H/F = 6–23%). Most Argemela wolframites have H/F ratios higher than at Panasqueira and other Variscan quartz-vein deposits which dominantly host ferberites. In greisens or pegmatitic veins, wolframites generally have intermediate H/F ratios. In those deposits, fluid-rock interactions, either involving country rocks (quartz-veins) or granite (greisens) control W deposition. In contrast, at Argemela, wolframite from intragranitic veins was deposited from a magmatic fluid. Differentiation of highly evolved peraluminous crustal magmas led to high Mn/Fe in the fluid which promoted the deposition of hübnerite. Therefore, the H/F ratio can be used to distinguish between contrasted deposition environments in perigranitic W ore-forming systems. Hübnerite is a simple mineralogical indicator for a strong magmatic control on W deposition.

1. Introduction

W is a critical metal, essential for many industrial applications. As for other metals and commodities, exploration for W now focuses on sub-surface to deep contexts in complex geological settings (e.g., Poitrenaud, 2018, www.almonty.com, www.wolfminerals.com.au). Targeting of mineralized systems requires the integration of geological, geophysical and geochemical data sets and their interpretation in the light of an ore deposition model (McCuaig et al., 2010; McCuaig and Hronsky, 2014). With the development of analytical tools, mineralogical compositions of both gangue and ore minerals are increasingly used to footprint the presence of proximal orebodies (Belousova et al., 2002; Codeço et al., 2017; Harlaux et al., 2018; Neiva, 2008).

W mineral deposits include quartz veins, stockworks, greisens, skarns and breccia pipes spatially associated with granitic bodies, and are thought to result from magmatic and hydrothermal processes, combined (Bobos et al., 2018; Harlaux et al., 2015; Kelly and Rye, 1979; Ramboz et al., 1985; Smith et al., 1996). Although the main parameters controlling the transport of W have been identified (Che et al., 2013; Heinrich, 1990; Wood and Samson, 2000), there is as yet no comprehensive model for W deposition.

Quartz veins such as found in Southeast China and in the Variscan belt of Europe form an important class of W deposits. W, in the form of the dominant ore mineral wolframite ([Fe,Mn]WO4), is generally associated with other metals such as Sn, Cu, Ag. The group of quartz-wolframite deposits is diverse. It includes intragranitic (e.g., Smith et al., 1996) and country rock (e.g., Kelly and Rye, 1979) veins with a wide range of geometries, widths and extensions (e.g., Giuliani, 1985). Quartz and wolframite can be accompanied by various gangue (e.g., tourmaline, Codeço et al., 2017) and ore (e.g., cassiterite, Noronha

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Table 1
Representative electron microprobe analyses of wolframite from the Argemela Mineralized District.

Major elements (wt%)	E WI		Mean (19)	σ	L WI		Mean (9)	σ	E WII		Mean (32)	σ	L W II		Mean (25)	σ
	min	max			min	max			min	max			min	max		
MnO	15.40	12.21	14.58	0.92	5.75	1.40	3.37	1.59	18.15	15.59	17.27	0.69	13.26	10.82	12.18	0.93
FeO	8.98	12.24	9.88	0.97	19.08	23.41	21.32	1.50	6.19	8.82	7.17	0.67	10.95	13.53	12.37	0.94
Nb_2O_5	0.59	0.22	0.36	0.15	0.36	0.60	0.40	0.19	0.74	0.49	0.46	0.22	0.74	1.05	0.68	0.25
SnO_2	0.08	0.01	0.04	0.03	0.00	0.00	0.02	0.02	0.00	0.07	0.05	0.07	0.13	0.15	0.10	0.06
Ta_2O_5	0.11	0.00	0.06	0.06	0.04	0.09	0.04	0.05	0.00	0.10	0.16	0.25	0.36	0.22	0.18	0.19
WO_3	76.65	76.97	76.95	0.34	76.67	76.81	76.88	0.43	75.62	75.62	76.55	0.63	75.99	75.12	76.05	0.52
Total	101.96	101.81	102.00	0.32	102.04	102.52	102.24	0.39	100.71	100.79	101.68	0.42	101.50	100.96	101.65	0.41
Number of cations based on 4 oxygens																
Mn	0.643	0.513	0.610	0.038	0.241	0.058	0.141	0.067	0.767	0.660	0.724	0.028	0.557	0.456	0.511	0.038
Fe	0.370	0.507	0.408	0.040	0.789	0.964	0.881	0.062	0.258	0.368	0.297	0.028	0.454	0.563	0.513	0.040
Nb	0.013	0.005	0.008	0.003	0.008	0.013	0.009	0.004	0.017	0.011	0.010	0.005	0.017	0.024	0.015	0.006
Sn	0.002	0.000	0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.001	0.003	0.003	0.002	0.001
Ta	0.001	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.000	0.001	0.002	0.003	0.005	0.003	0.002	0.003
W	0.980	0.989	0.986	0.003	0.983	0.980	0.985	0.004	0.978	0.979	0.982	0.006	0.977	0.969	0.976	0.006
Total	2.013	2.014	2.014	0.002	2.021	2.017	2.016	0.004	2.020	2.021	2.016	0.004	2.012	2.019	2.019	0.004
H/F	63.5	50.3	59.9	3.9	23.4	5.7	13.8	6.4	74.8	64.2	70.9	2.8	55.1	44.8	49.9	3.8

E: Early and L: Late. WI: wolframite in country rock vein; WII: wolframite in intragranitic vein. For each wolframite type, min and max are compositions that give the minimum and maximum H/F ratios respectively. The H/F ratio is calculated as 100 at. Mn/(Fe + Mn).

et al., 1992) minerals. Wolframites have compositions ranging from hübnerite ($MnWO_4$) to ferberite ($FeWO_4$, e.g., Harlaux et al., 2018; Lecumberri-Sanchez et al., 2017). Factors of controls of wolframite composition are the subject of an intense debate. The deposition style, source of Mn and Fe, distance from the heat/fluid source and temperature have been proposed to govern the wolframite H/F (i.e., hübnerite/ferberite) ratio, hereafter calculated as 100 at. Mn/(Fe + Mn). Hosking and Polkinghorne (1954) pointed out that wolframites in Cornish pegmatites are relatively Mn-rich while wolframites from quartz veins have high Fe contents. Greisens generally have wolframites with intermediate Fe/Mn (e.g., Breiter et al., 2017; Hosking and Polkinghorne, 1954). Several studies have suggested that Mn-rich wolframites precipitate at higher temperatures than Fe-rich wolframites (e.g., Oelsner, 1944, Leutwein, 1952, Taylor and Hosking, 1970). However, attempts to use the H/F ratio as a geothermometer (Moore and Howie, 1978) have failed as temperature is not the only factor controlling wolframite composition (Amossé, 1978).

Recent studies in the Central Iberian Zone (which includes the world class Panasqueira W deposit) have identified a quartz-wolframite vein system (Michaud et al., 2018) spatially and genetically associated with a Rare-Metal Granite (RMG), the Argemela granite (Charoy and Noronha, 1996). Field, structural, mineralogical and geochemical evidence suggest that the intragranitic wolframite-bearing veins are the expression of magmatic fluids exsolved from the granite at the magmatic-hydrothermal transition. Below, the main characteristics of the Argemela veins are summarized and compared with other W vein systems. Focus is placed on wolframite compositions, essentially Mn-rich at Argemela and Fe-rich in the neighboring Panasqueira and most other Variscan country rock vein systems. This first-order compositional contrast between wolframites suggests major differences in W deposition mechanisms. It is proposed that the H/F ratio can be used as an exploration tool to help distinguishing between contrasted types of W deposition environments.

2. Analytical techniques

Samples from the Argemela W veins were collected and thin as well as polished sections prepared. Preliminary petrographic and textural observations were conducted with a petrographic microscope. Backscattered electron (BSE) images and EDS element mapping were obtained using a Merlin compact ZEISS Microscope equipped with a Bruker EDS detector and working under an acceleration voltage of 15 kV. Wolframites were analyzed by electron microprobe at ISTO, Orléans (France). Punctual analyses, traverses and elements distribution maps for major and minor elements were obtained with a CAMECA SX Five microprobe operated under an acceleration voltage and a beam current of 20 kV and 40nA respectively. Standards included SnO_2 (Sn*Lα*), Fe_2O_3 (Fe*Kα*), $MnTiO_3$ (Mn*Kα* and Ti*Kα*) and pure Nb (Nb*Lα*), Ta (Ta*Lα*) and W (W*Lα*) metals.

3. The Argemela W vein system

The Variscan Argemela Mineralized District (AMD) occurs within the Central Iberian Zone (CIZ, Central Portugal) and is divided in two subsystems at < 0.5 km from each other but evolving separately. The first (the Argemela tin mine, ATM) consists of a vein swarm emplaced in low grade metamorphic rocks from the Neoproterozoic Schist and Greywacke Complex (SGC, Meireles et al., 2013). Veins can be up to 2 m wide, are anastomosed and contain Sn and Li mineralization in the form of cassiterite and montebrasite. No W concentration has been recognized. The second (the Argemela Hill Top, AHT) comprises a RMG with disseminated Li, Sn, Nb, Ta mineralization in the form of magmatic montebrasite, cassiterite and columbo-tantalite. The granitic intrusion is associated with a network of intragranitic veins, and a few quartz veins occur in country rocks near the granite contact. Although wolframite is absent as a magmatic phase, W enrichment is marked by granite whole-rock concentrations ranging up to ~20 ppm W (Charoy and Noronha, 1996). Three generations of intragranitic veins occur within the granite. Field evidence (confinement of veins inside the granite), structural (granite and veins are emplaced in the same structural context), mineralogical (veins lack hydrothermal alteration aureoles and the earliest have a “pegmatitic” texture and a granitic mineral assemblage) and stable isotope data indicate that the intragranitic veins are the expression of fluids exsolved from the granite at the magmatic-hydrothermal transition (Michaud et al., 2018). Wolframite occurs in variable amounts in the third and latest generation of intragranitic veins which are numerous but of restricted size, never exceeding a 10 cm width. It is mostly associated with quartz, K-feldspar and montebrasite, with quartz and montebrasite only in some other veins, and cassiterite is occasionally present. Wolframites form mostly large homogeneous crystals with hübnerite compositions (early WII, H/F between 64 and 75%, Table 1 and Fig. 1). On the eastern border, the granite is affected by a dextral shear zone and the intragranitic veins host wolframites with a patchy texture made of early hübnerites

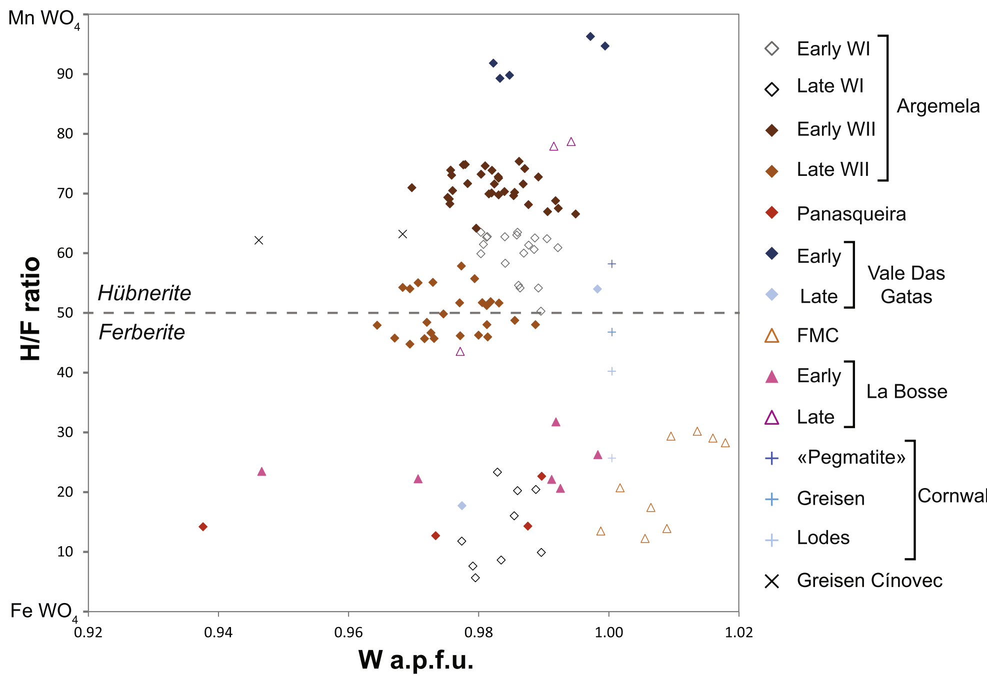

Fig. 1. H/F ratio vs atomic W concentration for wolframites from representative Variscan deposits. Argemela data are from this study (Table 1). For other deposits see references in Table 2.

evolving to more Fe-rich compositions (late WII, H/F from 45 to 55%, Table 1, Fig. 1, e.g. Baumann, 1964). This late wolframite ore deposition stage is followed by sulfides (arsenopyrite) and other phases (vivianite); cassiterite is transformed into stannite.

Wolframite is also present in one country rock vein crosscut by the granite. It appears as large crystals and in variable amounts associated with milky geodic quartz typical of hydrothermal veins in the AMD. In contrast to intragranitic veins, K-feldspar is absent. Wolframite crystals can be homogeneous but most show textural evidence for recrystallization (Fig. 2). Early wolframites are Fe-rich hübnerites (early WI, H/F from 50 to 63%, Table 1 and Fig. 1). The second generation crystallizes in fractures or near the margins of early wolframites and is a ferberite with high Fe contents (late WI, H/F = 6–23%, Table 1, Figs. 1 and 2). This late stage is followed by the deposition of iron oxides.

4. Comparison with other wolframite vein systems

Wolframite occurs as the dominant ore mineral in several types of Variscan W deposits and is characterized by highly variable compositions, from hübnerite to ferberite. The Panasqueira W world class mine, located at only 13 km west from Argemela, provides an excellent comparison point with the AMD. The deposit consists of > 1000 nearly horizontal veins emplaced in SGC metamorphic rocks on top of a granite cupola (Neiva, 2008; Foxford et al., 2000). The hydrothermal veins, which can exceed 1 m widths, host wolframite, quartz, muscovite, tourmaline, topaz, arsenopyrite and early cassiterite (Kelly and Rye, 1979, Polya et al., 2000). Wolframites form large chemically homogeneous crystals with H/F ratios generally < 23% (e.g. ferberite), in strong contrast with most AMD wolframites (Table 2 and Fig. 1). Same as at Panasqueira, in the French Massif Central (FMC), most Variscan W deposits show wolframites with ferberite compositions (Harlaux et al., 2018 and references therein, Table 2 and Fig. 1). For example, the stockwork of La Bosse (north FMC) consists in a network of interconnected subhorizontal quartz veins emplaced in metamorphic rocks; wolframite has H/F ratios between 21 and 32% (Aubert, 1969; Aïssa et al., 1987, Table 2 and Fig. 1). Other representative examples of ferberite-bearing vein-type W deposits in the FMC include Enguialès, Leucamp and St-Goussaud (e.g., Harlaux et al., 2018 and references therein).

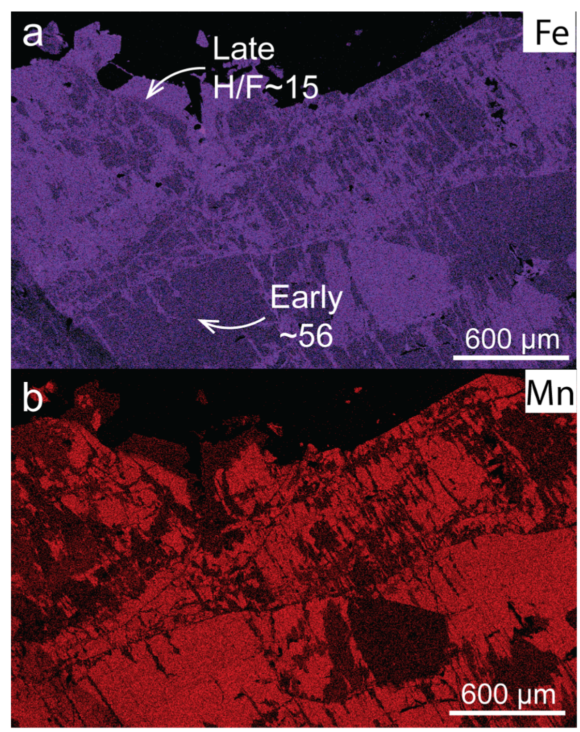

Fig. 2. Patchy texture of Argemela WI (schist-hosted vein) illustrating evolution of the H/F ratio between early and late crystallization stages. EDS map of (a) Fe and (b) Mn.

Both the Panasqueira and the FMC deposits are representative of perigranitic hydrothermal systems developed in metamorphic country rocks. In the case of Panasqueira, ferberite deposition is controlled by fluid-rock interactions involving SGC country rocks (Lecumberri-Sanchez et al., 2017) and, so, there is a significant non-magmatic contribution to the ore-forming system (e.g., Polya et al., 2000).

Other Variscan W deposits show a closer spatial association with

Table 2
Compositional data for wolframites from representative Variscan deposits.

Name	Metallogenic province	Deposit type	Deposition stage	H/F	Mean	σ	W a.p.f.u.	References
Vale Das Gatas	Variscan - Portugal	Intragranitic and country rocks veins	Early	96.2	92.30 (5)	3.05	1.00	Neiva (2008)
				89.2			0.98	
			Late	54.0	35.86 (2)	25.62	1.00	
				17.7			0.98	
Panasqueira	Variscan - Portugal	Country rocks veins		22.7	16.00 (4)	4.51	0.99	Neiva (2008)
				12.7			0.97	
Enguialès-Leucamp	Variscan - FMC	Country rocks veins		30.2	22.37 (10)	7.53	1.00	Harlaux et al. (2018)
				12.3			1.02	
St Goussaud	Variscan - FMC	Intragranitic and country rocks veins		24.7	22.74 (5)	1.66	1.01	Harlaux et al. (2018)
				20.4			1.00	
La Bosse	Variscan - FMC	Country rocks veins	Early	31.8	24.43 (6)	4.06	0.99	Aïssa et al. (1987)
				20.7			0.99	
			Late	78.7	64.20 (4)	17.10	0.98	
				43.6			0.99	
Le Mazet	Variscan - FMC	Country rocks vein		78.8	–	–	–	Aubert (1969)
Gilbert	Variscan - FMC	Country rocks vein		88.2	–	–	–	Aubert (1969)
Cornish wolframites	Variscan - Cornwall	"Pegmatitic veins"		58.2	52.5 (2)	8.06	1.00*	Hosking and Polkinghorne (1954)
				46.8			1.00*	
		Greisen		46.8	43.52 (2)	4.63	1.00*	
				40.3			1.00*	
		Lodes		40.3	32.97 (2)	10.29	1.00*	
				25.7			1.00*	
Cligga Head	Variscan - Cornwall	Intragranitic veins		35–40^{+}	–	–	–	Unpublished
Cínovec	Variscan - Bohemian Massif	disseminated in greisen		63.6	57.70 (6)	7.45	0.90	Breiter et al. (2017)
		quartz veins and greisen		45.8			0.82	

Maximum and minimum H/F values are shown for each type. + data obtained from EDS. *fixed to 1 (no data available).

granitic rocks. This is the case of Cligga Head (Cornwall, UK) where wolframite is deposited together with cassiterite, arsenopyrite and other sulfides in a dense network of intragranitic veins (Charoy, 1979). Wolframite is ferberite-rich (H/F = 35–40%, Table 2, Charoy, 1979; Michaud, unpublished) and, although the mineralizing fluids have been interpreted as magmatic (Smith et al., 1996), W deposition at Cligga Head is associated with hydrothermal alteration around the veins indicating fluid-granite equilibration at subsolidus temperatures (300–400 °C, Charoy, 1979). At Cínovec (Bohemia, DE and CZ), wolframite occurs disseminated both in greisens and in quartz veins within the host RMG. H/F ratios are intermediate (between 45 and 63%, Table 2 and Fig. 1, Breiter et al., 2017) consistent with the presence of sub-equal concentrations of Fe and Mn in fluid inclusions (Korges et al., 2018). Sn-W deposition is associated either with greisenisation of the granite (i.e., with fluid-rock reaction at subsolidus temperatures) or with boiling of the magmatic fluid (Korges et al., 2018). Last, deposits from Cornwall (UK) demonstrate a systematic increase of H/F ratios from pegmatites and early feldspathic veins (H/F = 47–58), greisens (H/F = 40–47) to quartz lodes (H/F = 26–40, Table 2 and Fig. 1, Hosking and Polkinghorne, 1954). In the South Crofty Mine, the "pegmatitic vein swarms", mainly composed of quartz, feldspar and other accessory minerals, contain wolframites of intermediate compositions (H/F = 37–60, Taylor and Hosking, 1970).

In some deposits, several wolframite crystallization stages can be identified, indicating distinct deposition mechanisms. For example, the La Bosse stockwork contains a late generation of hübneritic wolframite (H/F = 44–79%, Table 2 and Fig. 1) developed in minor amounts on early ferberites (H/F = 21–32%, see above) and attributed to the influence of the late Beauvoir RMG (Aïssa et al., 1987). Isolated hübnerite-bearing veins occur north of the La Bosse deposit (e.g., Le Mazet and Gilbert veins, Table 2) and they have been interpreted as footprints of another Beauvoir-type RMG at depth (Aubert, 1969). In the Portuguese CIZ, the Vale Das Gatas deposit consists of quartz veins cutting the contact between SGC country rocks and a muscovite > biotite granite (Neiva, 2008). The veins are characterized by at least two ore deposition stages, the first involving cassiterite and wolframite and the second only wolframite. Wolframites are mostly hübnerites (H/F = 89–96%) except rims that range from Fe-rich hübnerite to ferberite (H/F = 18–54%, Table 2 and Fig. 1).

5. Wolframite deposition mechanism

None of the wolframite deposition mechanisms mentioned above is directly applicable to the AMD since none explains the precipitation of hübnerite directly from a magmatic fluid. At Argemela, the W-bearing intragranitic veins show no hydrothermal interaction aureole at their margins. The earliest veins exhibit "pegmatitic" textures and crystallize a granitic mineral assemblage (Michaud et al., 2018). Quartz in the granite and veins both have high δO^{18} (respectively 13.7–14.5 and 14.5–15.9‰). Therefore, the intragranitic veins formed from fluids exsolved from the crystallizing granite and fluid-granite equilibration was originally established at relatively elevated temperatures. Using solidus temperatures for RMG (Pichavant et al., 1987a) and oxygen isotope thermometry on quartz and muscovite from the granite, magmatic fluids were originally at equilibrium with the granite at temperatures of 500–550 °C. Their subsequent evolution within the intragranitic veins most probably followed a fluid-buffered instead of a rock-buffered path (e.g., Heinrich, 1990). There is no evidence for postmagmatic hydrothermal interaction processes such as greisenisation around the veins. Quartz from the relatively late wolframite-bearing veins have the same stable isotope signature (δO^{18}: 15.5–15.9‰; δD: −25 to −31‰) than quartz from the early veins (δO^{18}: 14.5–15‰; δD: −21 to −35‰). Furthermore, the surrounding Beira schists are W-depleted and cannot be the source of W (Charoy and Noronha, 1996). Although the intragranitic vein system was not closed to external non-magmatic contributions (as suggested by the mineralogical data summarized above), wolframite deposition in the Argemela intragranitic veins resulted from cooling of the igneous fluid in isolation from the enclosing rock, in contrast with mechanisms proposed for W deposition in other contexts (e.g., Lecumberri-Sanchez et al., 2017).

Wolframite deposition necessitates a source of Fe and Mn, in addition to W. Amossé (1978) demonstrated that the composition of the deposited wolframite depends essentially on two factors, temperature and aMn/aFe of the ore fluid. The Mn/Fe ratio is always higher (and so the H/F ratio higher) in the deposited wolframite than in the equilibrium fluid. Because lowering temperature slightly increases Mn/Fe in wolframite, Amossé (1978) emphasized the importance of the Mn/Fe ratio of the mineralizing fluid as the main factor controlling wolframite composition. At Argemela, the Mn/Fe of the ore fluid is defined by fluid/melt partitioning for Mn and Fe. Both elements partition similarly between melt and fluid as shown by their nearly identical ratios in coexisting silicate melt and fluid inclusions from Ehrenfriedersdorf (Zajacz et al., 2008). Thus, the Mn/Fe of the magmatic fluid that deposited hübnerite at Argemela was essentially that of the crystallizing granitic melt. Although this Mn/Fe ratio is unknown, Variscan RMG (e.g., Beauvoir, Raimbault et al., 1995) and pegmatites (Chèdeville, Raimbault, 1998), and equivalent volcanic products (Macusani, Pichavant et al., 1987b), demonstrate a general increase of Mn/Fe during magmatic differentiation. The whole-rock data for the Argemela granite show such an increase (Charoy and Noronha, 1996), also marked in the enrichment of disseminated columbo-tantalites in $MnTa_2O_6$ (Michaud et al., 2018, see also Raimbault, 1998; Linnen and Cuney, 2005). Therefore, the magmatic evolution of the Argemela RMG led to the exsolution of relatively high Mn/Fe igneous fluids. We suggest that the deposition of hübnerite in perigranitic magmatic-hydrothermal systems is the signature of metals and fluids originating from highly evolved peraluminous crustal magmas similar to the Argemela granite.

W is known to be transported in hydrothermal fluids as an oxyanion, ${WO_4}^{2-}$, complexed with Na+, K+, or H+ (Wood and Samson, 2000; Heinrich, 1990). Substitution of Na for Li does not change wolframite solubilities in granitic melts (all the other parameters being equal, Linnen, 1998) and, so, Li is a W complexing agent with an efficiency comparable to Na. Thus, destabilization of Li-W complexes as a result of precipitation of a Li-bearing phase will cause wolframite deposition. Montebrasite ($LiAlPO_4$ (OH, F)) is a systematic phase in the Argemela intragranitic veins where it is accompanied by K-feldspar (whose crystallization removes K from the fluid). Muscovite never occurs as a mineral in the veins suggesting that the pH of the fluid was never strongly acid. Compositions of montebrasites (Michaud et al., 2018) in K-feldspar-bearing veins show no variations in F content (Loh and Wise, 1976) and so deposition was probably not driven by a drastic increase of the fluid pH. However, montebrasites from montebrasite-wolframite veins can have F contents nearly twice as elevated as montebrasites in K-feldspar-bearing veins, which indicates a significant pH decrease (thus counteracting wolframite precipitation). Therefore, a decrease in temperature is probably the main factor controlling wolframite deposition (Heinrich, 1990).

One element specific of the Argemela magmatic-hydrothermal system is phosphorus. The Argemela granite, with whole-rock concentrations of up to ~ 2 wt% P2O5 (Charoy and Noronha, 1996), is a good example of a peraluminous high phosphorus (PHP) rare-metal granite (Linnen and Cuney, 2005). Montebrasite crystallizes as a magmatic phase in the Argemela granite and is also a key phase in intragranitic veins (Charoy and Noronha, 1996). Phosphorus increases wolframite solubility in peraluminous granitic melts (Che et al., 2013). Its influence is however indirect, through the formation of AlPO4 species which increases the availability of Na, K and Li to complex with W. Therefore, removal of such species by phosphate crystallization will cause wolframite deposition. The overall mechanism of wolframite precipitation in the Argemela intragranitic vein system is summarized with the following reaction:

$$\underset{fluid}{LiNaWO_4} + \underset{fluid}{(Mn, Fe)^{2+}} + \underset{fluid}{AlPO_4} + \underset{fluid}{H_2O} = \underset{montebrasite}{LiAlPO_4OH} + \underset{wolframite}{(Mn, Fe)WO_4} + \underset{fluid}{Na^+} + \underset{fluid}{H^+} \quad (1)$$

An equivalent reaction can be written for the fluorine Li phosphate end-member (amblygonite). Eq. (1) is probably driven to the right by a decrease in temperature, i.e., by cooling of the intragranitic vein fluids.

6. Discussion and implications for exploration

The model proposed for Argemela emphasizes the differences with other W deposition environments, and has direct implications for exploration. The model applies to hübnerite deposition from a magmatic fluid. Wolframite composition reflects enrichment in Mn relative to Fe in the crystallizing granite which is the source of both W and fluids. Wolframite deposition calls upon a specific chemical environment (presence of both Li and P) in a magmatic-hydrothermal system that evolves under fluid-buffered conditions. Li, together with F and P, is systematically enriched in Variscan granitoïds from the CIZ (Roda-Robles et al., 2018 and references therein). Such anomalies reflect the specific chemistry (Al-, P-, F- and Li-rich, Ca-poor) of the metasedimentary rock sources of granitic magmas (Roda-Robles et al., 2018). The Li- and P-rich geochemical signature exhibited by the Argemela granite is a reflection of such specific crustal sources. Therefore, the W deposition mechanism proposed at Argemela also probably applies to other similar W occurrences in the CIZ.

The model for the AMD differs from others where a magmatic source for W is assumed but fluid interactions with country rocks are considered necessary for W deposition (Lecumberri-Sanchez et al., 2017). One first-order difference between the two types of models is that, in the former case, veins are intragranitic (Argemela) and, in the latter, within country rocks (Panasqueira). Therefore, each corresponds to a specific type of W deposition environment, as reflected by the composition of wolframite, hübnerite in the former and ferberite in the latter (Fig. 3). In the case of intragranitic vein systems, a magmatic origin for the ore fluid has been generally proposed (e.g., Korges et al., 2018; Smith et al., 1996). However, one major difference between Argemela and these systems (Cligga Head and Cínovec respectively) is the temperature and mechanism of fluid-rock equilibration. At Argemela, the composition of the ore fluid is defined by fluid/melt equilibrium at near-solidus temperatures; the magmatic fluid evolves along a fluid-buffered path. At Cligga Head and Cínovec, the fluid is buffered by fluid-rock interaction at subsolidus temperatures (greisenisation). Therefore, Argemela can be viewed as a high temperature variant of the Cligga Head and Cínovec cases. Preservation of the high temperature intragranitic vein system at Argemela was probably favored by the small volume of the granite intrusion which prevented the development of a large long-lived hydrothermal system involving adjacent country rocks and fluids.

Our results suggest that the H/F ratio can be used as an indicator of contrasted W deposition environments in perigranitic ore-forming systems (Fig. 3). Hübnerite crystallization is associated with the following key features for exploration: (1) source of W resides in nearby igneous rocks, (2) highly evolved granitic magmas are present, (3) ore fluids have a magmatic origin and (4) a “high temperature” magmatic-hydrothermal stage is preserved. Overall, hübnerite can be viewed as a relatively simple indicator of a strong magmatic control on W deposition. The fact that, in W deposits, ferberite compositions are generally more common than hübnerite could be the consequence of early hübnerite recrystallizing to lower H/F ratios as observed for example in Fig. 2. Although, at Argemela hübnerite deposition is the consequence of a high Mn/Fe in the ore fluid, hübnerite crystallization progressively depletes the fluid in Mn (Amossé, 1978) and, therefore, precipitation of wolframites with progressively lower H/F ratios is expected (Fig. 3). However, large variations of the H/F ratio within a given deposit (for example at La Bosse, Vale Das Gatas, Argemela, Fig. 3) are the mark of a

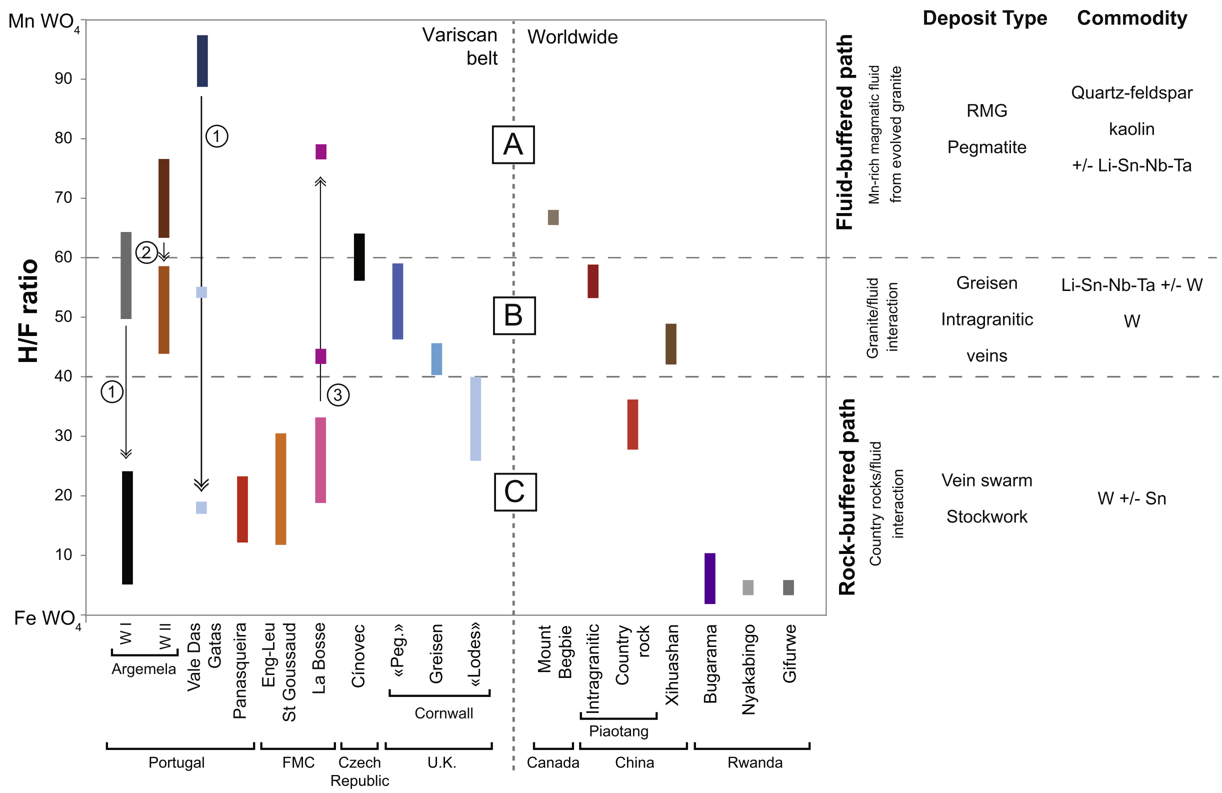

Fig. 3. Environments and mechanisms of W deposition as revealed by the H/F ratio for several representative Variscan deposits and extension to worldwide deposits. Source of data in Table 2 for Variscan deposits and see Zhang et al. (2018), Dixon et al. (2014) and Goldmann et al. (2013) for worldwide deposits. Three main H/F domains corresponding to different wolframite deposition mechanisms are identified: (A) for H/F ratio > 60, wolframite precipitates from a Mn-rich magmatic fluid evolving under a fluid-buffered path (Heinrich, 1990); (B) for H/F ratio between 40 and 60, wolframite precipitates from a fluid buffered by granite/fluid interactions (Smith et al., 1996); (C) for H/F ratio < 40, wolframite precipitates from a fluid carrying a significant non magmatic signature derived from country rocks (Lecumberri-Sanchez et al., 2017). Three main mechanisms controlling variations of the H/F ratio in a single deposit are illustrated: (1) step decrease of the H/F ratio resulting from addition of Fe through fluid-rock interactions (Lecumberri-Sanchez et al., 2017); (2) Progressive decrease of the H/F ratio due to Mn removal during hübnerite crystallization (Amossé, 1978) and (3) step increase of the H/F ratio due to influx of Mn-rich magmatic fluid. Deposit type and commodity associated with the three domains are detailed. Eng-Leu: Enguialès-Leucamp; FMC: French Massif Central; "peg": pegmatitic veins (Hosking and Polkinghorne, 1954).

complex multi-phase deposition history involving ore fluids with contrasted Fe/Mn and different, superimposed, wolframite deposition environments. Wolframite can recrystallize to lower H/F ratios (WI in the Argemela country rock vein, Fig. 3) when the magmatic-hydrothermal system becomes open to fluids derived from Fe-, S-rich metamorphic country rocks (Lecumberri-Sanchez et al., 2017). Alternatively, overprinting of early low H/F ratios in country rock veins by magmatic fluids derived from a crystallizing RMG can be also observed in the FMC (La Bosse, Fig. 3).

Hübnerite is a tracer of proximal highly evolved igneous bodies such as RMG and/or pegmatite with potential for commodities such as quartz and feldspar, kaolin and disseminated Li-Sn-Nb-Ta ores (e.g., Aubert, 1969; Fig. 3), in addition to W. Wolframite with intermediate H/F ratios is characteristic of medium temperature rock-buffered hydrothermal systems with a strong magmatic signature, both for the fluids and the metals (Fig. 3, Smith et al., 1996; Korges et al., 2018). These compositions are typical of greisen-type (both vein and massive) deposits where mostly Li-Sn-Nb-Ta are economically interesting and of intragranitic vein type deposits that follow a rock-buffered path. Lastly, H/F ratios < 40 and down to 0 indicate W deposition environments where a significant non-magmatic contribution to the ore fluid and W deposition is necessary (Fig. 3, Lecumberri-Sanchez et al., 2017). Ferberites showing a low H/F ratio are tracers of W-bearing veins/stockwork deposits of great economic importance.

The comparison can be extended to deposits worldwide (Fig. 3). Fractionated Li-bearing pegmatites from Mount Begbie (Bristish Columbia; Dixon et al., 2014) exhibit scarce hübnerites with a high H/F ratio, similar to Argemela (Fig. 3). Intragranitic veins of the Piaotang and Xihuashan W-deposits (Zhang et al., 2018) are characterized by an alteration halo at vein margins which indicates a rock-buffered path (i.e., granite-fluid interaction). These vein systems behave similarly to Cligga Head and both show comparable intermediate H/F ratios. In comparison, Piaotang country rock veins show a lower H/F ratio (Zhang et al., 2018), most probably a consequence of interaction with these rocks. The Bugarama, Nyakabingo and Gifurwe vein-type deposits from the "tungsten belt" of Rwanda are all hosted in country rocks and wolframite shows very low H/F ratio (Goldmann et al., 2013), comparable to the Panasqueira compositions. Thus, the H/F ratio appears as a reliable exploration tool worldwide despite differences in ages and geodynamic contexts between deposits.

7. Conclusions

Intragranitic veins in the Argemela Mineralized District remarkably illustrate the case of wolframite precipitation directly from relatively "high temperature" magmatic fluids. High H/F ratios wolframites (hübnerites) are characteristic of this specific W deposition environment which contrasts with other mechanisms that lead to intermediate to low H/F ratios. It is proposed that the H/F ratio can be used as an indicator of wolframite deposition style for Variscan deposits (and beyond) and thus as a relevant exploration tool. Lastly, it should be emphasized that the genesis of Variscan W deposits does not only result from locally favorable country rocks, as for Panasqueira (e.g., Lecumberri-Sanchez et al., 2017). Chemically specific source rocks and granite magma types are also necessary.

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