Compositional variation in wolframites from the Barroca Grande mine, Portugal: evidence for fault-controlled ore formation

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Abstract

The major and trace element composition of over 40 wolframites from the Barroca Grande mine of the Panasqueira W–Sn–Cu quartz-vein hosted orebody have been determined by electron probe microanalysis.

The hübnerite content of wolframite is largely uniform (12 to 20 mol. %) throughout most of the mine, suggesting relative uniformity in composition of the main stage ore-forming fluids. However, wolframites show a striking pattern of enrichment in niobium adjacent to major sub-vertical fault zones. Typical wolframite Nb_2O_5 contents are below 1000 ppm, whilst values greater than 1000, 2000 and 4000 ppm are generally only found in wolframites less than 50, 30, and 10 metres respectively from major sub-vertical faults. This strongly suggests that some of these fault zones acted as major pathways for hydrothermal fluid migration during ore formation. The idea that the greisened cupola at Panasqueira was the sole major pathway for fluid movement is discounted.

KEYWORDS: wolframite, niobium, Barroca Grande mine, Panasqueira, Portugal.

Introduction

BARROCA GRANDE is the major mine currently working the Panasqueira orebody, a quartz-vein hosted W–Cu–Sn deposit associated with a post-orogenic Hercynian granite in north-eastern Portugal. The sub-horizontal vein network lies immediately above a greisened cupola of the granite. It has been proposed that the cupola acted as a major conduit for the flow of Hercynian ore-forming fluids (Clark, 1964; Kelly and Rye, 1979; Bussink, 1984); if this were the case, then a centrosymmetric pattern of mineralogical and mineral chemical variation might be expected around the cupola. Chemical analyses of wolframites provide an ideal way of testing this expectation since wolframites are distributed throughout the Barroca Grande mine and exhibit variations in both trace element and major element content. This paper reports the results of such a study and discusses the implications for the interpretation of major fluid flow pathways during ore formation.

Geology

Detailed accounts of the geology of the Panasqueira deposit may be found in Clark (1964), d'Orey (1967), Thadeu (1977), Kelly and Rye (1979), Bussink (1984) and Polya (1987).

The Panasqueira vein network is largely hosted by the pelitic Beira Schists, regionally metamorphosed to greenschist facies. A small part of the network also transects the upper margin of the underlying, pervasively greisened granite (Fig. 1).

The Panasqueira Granite has been described as a porphyritic two-mica granite (Clark, 1970*a*). It may be classified as an S-type granite, according to the terminology of Chappell and White (1974) on the basis of its peraluminous composition with normative corundum, abundant xenoliths and high initial $^{87}Sr/^{86}Sr$ ratios of around 0.713 (Kelly and Rye, 1979; Bussink, 1984). The granite also exhibits a number of features of ilmenite series granites (Ishihara, 1981); the association with Sn–W mineralization, less than 0.1 vol. % of the rock consists of magnetite and ilmenite, whole-rock Fe_2O_3/FeO is generally less than 0.5 (Bussink, 1984), whole rock $\delta^{18}O$ is probably high (Polya, 1987) and accessory phases include ilmenite and monazite.

Hydrothermal alteration of the granite is extensive. The cupola is altered to a quartz + muscovite + albite ± topaz assemblage with acces-

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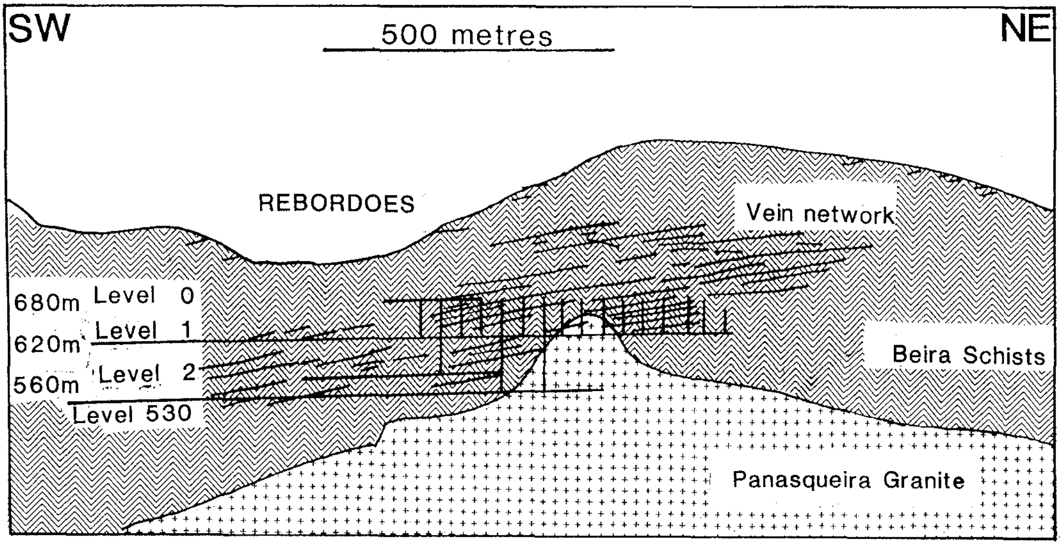

FIG. 1. Cross-section through the Panasqueira orebody (after Beralt Tin and Wolfram (Portugal) sections).

sory wolframite, cassiterite and sulphides. The alteration is mostly pervasive, but where the alteration is less extensive its distribution is fracture controlled.

The extent of the granite body is unknown, but drill hole data (Hebblethwaite and Antao, 1982) suggest that, in the immediate vicinity of the Barroca Grande mine, the upper granite surface forms an approximately one kilometre wide, NW-trending ridge, with at least one cupola. The extension of this ridge over a distance of at least 5 km is inferred from the surface distribution of contact metamorphosed schists (Polya, 1987).

The ore zone is asymmetrical in its disposition to the greisened cupola and the granite ridge, being developed to its greatest extent in a WSW direction on the southern flank of the ridge. Blattler (1985) proposes that this development is controlled by the steeply WSW dipping granite surface underneath. Another important control on the localization of the ore zone is that afforded by the preferred directions of structural weaknesses within the Beira Schists.

Previous studies

A number of major-element analyses of Panasqueira wolframite are reported by Thadeu (1951) and Dunn (1977) but the only substantial study is that of Saraiva (1971).

Saraiva (*op. cit.*) analysed over a hundred hand specimens of wolframite for Fe and Mn by wet chemical methods, and found hübnerite contents of 13 to 23 mol. %. Wolframite close (< 200 m) to the greisened cupola is relatively rich in manganese (17–20 mol. % hübnerite) compared to that in the rest of the deposit. Large variations in the compositions of single crystals were also noted (*ibid.*).

Saraiva (*op. cit.*) also carried out an X-ray diffraction (XRD) study. Numerous workers have determined near linear relationships between wolframite unit cell parameters and major-element composition (Sasaki, 1959; Sleight, 1972; Obermeyer *et al.*, 1973; Rafal'son and Sheinina, 1976*b*), however Saraiva (*op. cit.*) found a poor correlation between his wet chemical analyses and his XRD data. It is suggested in the present study that this is partly due to niobium substitution in the wolframite, since this increases the unit cell dimensions of wolframite (Rafal'son and Sheinina, 1976*a*; Polya, 1987). Significant errors may, therefore, result from the estimation of Mn/(Mn + Fe) in natural wolframites from XRD data. Significant errors may also result from the analysis of a heterogeneous bulk sample. Bulk analyses of Panasqueira wolframites are particularly susceptible to error because of the widespread occurrence of chalcopyrite in micrometre-scale fractures.

Microanalysis of wolframite by electron probe, therefore, provides a much more satisfactory way of determining Mn/(Mn + Fe) than previously used methods, and also enables trace element concentrations to be readily determined.

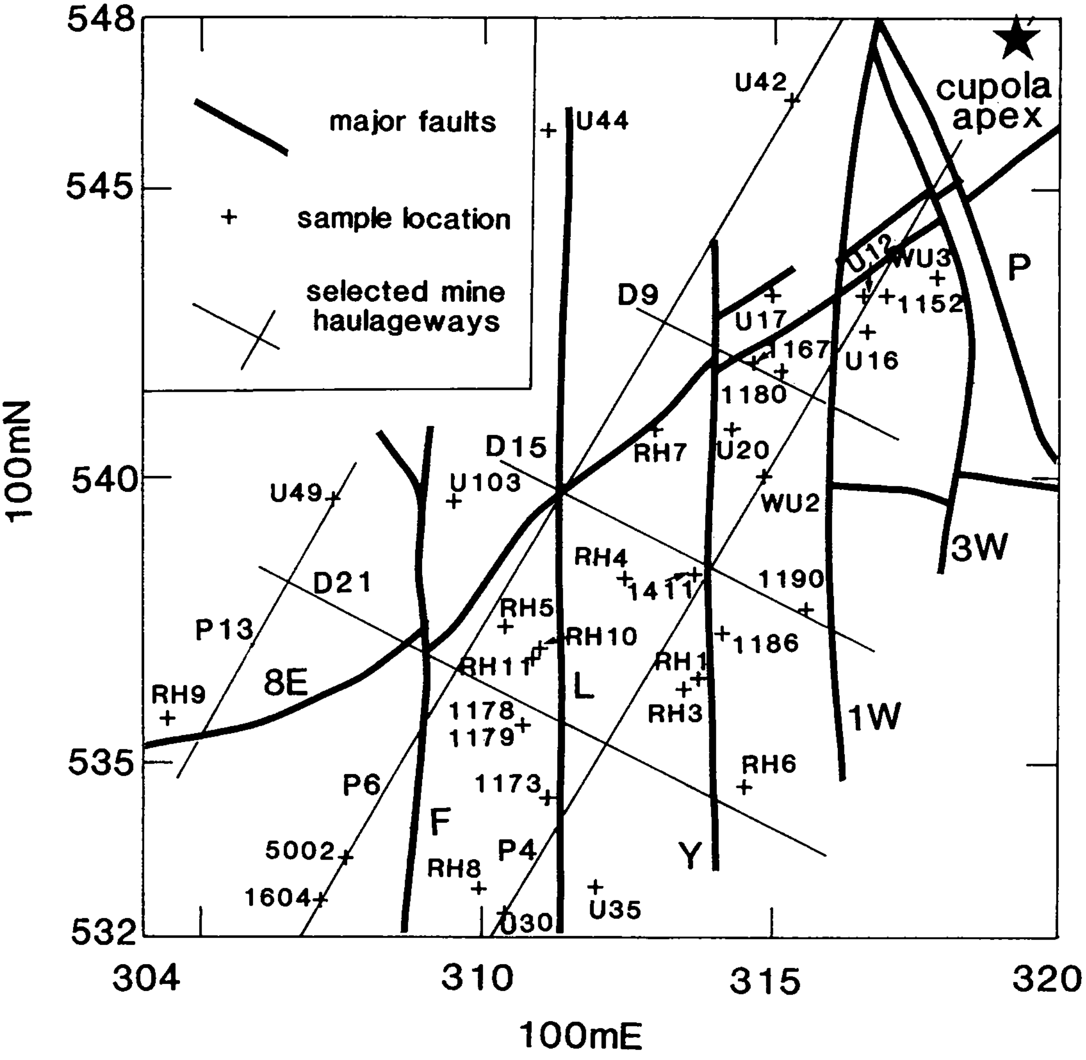

FIG. 2. Location of wolframite samples in the Barroca Grande mine. Projection onto mine level 2. Also shown are major faults, the apex of the greisened cupola and selected mine haulageways. Fault locations are simplified after Beralt Tin and Wolfram (Portugal) mapping. 8E—8 East fault; P—Principal fault; 3W—3 West fault; 1W—1 West fault; F—Vale de Freiras fault; L—Lameiras fault.

Sampling and analysis

Approximately 40 samples of wolframite were collected by the author and B.T.W.P. staff from a wide range of locations in the Barroca Grande mine. Samples were taken from four different levels, covering a vertical distance of 150 m and an area of about 10^6 m^2. The location of the samples with respect to the greisened cupola and major fault zones are illustrated in Fig. 2.

Samples were prepared as polished blocks and analysed by a Cameca Camebax automated electron probe microanalyser fitted with dual wavelength-dispersive spectrometers and a Link Systems energy dispersive spectrometer and software systems (Department of Geology, University of Manchester). An accelerating voltage of 15 kV was used on an 8 to 15 nA electron beam about 3–4 μm in diameter. Fe, Mn and W were determined by energy dispersive (ED) spectrometry. Nb was determined by wavelength dispersive (WD) spectrometry.

TABLE 1: Niobium and manganese contents of Barroca Grande wolframites

The columns labelled LOCATION describe the position of each sample with respect to mine levels and haulageways (panels,drives) and give the elevation relative to sea level (mRSL) as well as the horizontal coordinates (mE and mN) in the mine grid.

FAULT DISTANCE refers to the shortest distance, in metres, from the sample to the nearest major fault. Parentheses indicate some uncertainty in the reported datum.

COMPOSITION refers to the average determined wolframite compositions calculated from the specified NUMBER OF ANALYSES.

<DL indicates less than detection limits (about 300ppm Nb_2O_5).

SAMPLE LABEL	LOCATION DESCRIPTION	mRSL	mE mN	FAULT DISTANCE	COMPOSITION Nb_2O_5(ppm)	mol%$MnWO_4$	NUMBER OF ANALYSES
WU2	L530/P4/XS	530	31480/54000	80	800±300	15.7±0.6	20
WU3	L530/DW	530	31800/54360	(60)	900±400	11.8±4.1	5
1152	L2/P4/D5E	560	31700/54320	(60)	<DL	20.4±0.2	2
U12	L2/P4/D5W	560	31660/54320	10	1500±400	14.4±0.5	25
U16	L2/P4/D7E	560	31660/54260	5	1700±800	14.7±1.4	26
U17	L2/P4/D7W	560	31500/54310	10	2800±1400	17.3±0.8	8
1180	L2/P4/D9W	560	31520/54170	(30)	450±250	13.8±1.7	35
1167	L2/P4/D9W	560	31470/54200	10	4800±900	13.3±0.7	5
U20	L2/P4/D11W	560	31430/54080	40	1600±800	15.6±3.2	5
1190	L2/P4/D15E	560	31560/53770	30	6200±2400	14.4±3.1	31
1186	L2/P4/D19E	560	31420/53620	20	550±450	14.6±0.4	19
1178	L2/P4/D23W	560	31070/53560	80	300±400	13.2±0.5	19
1179	L2/P4/D23W	560	31070/53560	80	400±100	13.3±0.2	6
1179	L2/P4/D23W	560	31070/53560	80	500±400	13.6±0.3	5
U35	L2/P4/D27E	560	31200/53280	50	700±300	13.9±0.5	5
1173	L2/P4/D27W	560	31110/53440	30	1200±300	14.4±0.5	7
1173	L2/P4/D27W	560	31110/53440	30	500±200	13.7±0.4	5
1173	L2/P4/D27W	560	31110/53440	30	2300±800	14.9±0.3	10
1173	L2/P4/D27W	560	31110/53440	30	1800±1000	14.7±0.5	13
U30	L2/P4	560	31040/53240	100	400±300	13.4±0.5	6
RH1	L2/D19/R3	(580)	31380/53640	20	2600±800	13.9±0.3	25
RH3	L2/D19 Ramp	(580)	31350/53630	50	1300±400	13.2±0.2	7
RH4	L2/D19/R5	(580)	31250/53820	100	<DL	14.9±0.6	3
RH6	L2/D21/R2A	(580)	31470/53460	50	1000±400	19.5±3.9	10
RH7	L2/D13/R5	(580)	31300/54080	0	7400±600	14.2±0.5	10
RH7	L2/D13/R5	(580)	31300/54080	0	5700±1000	14.3±0.3	3
RH11	L2/D19/R5	(580)	31100/53690	50	500±200	14.5±0.3	3
1411	L1/P4/D23	620	31380/53830	20	<DL	14.5±0.3	5
U103	L1/P6/D17	620	30940/53960	40	600±400	13.6±0.4	5
5002	L1/P6/D29-31	620	30770/53330	120	400±400	14.3±4.0	27
1604	L1/P6/D31-33	620	30720/53260	140	<DL	14.8±0.4	7
RH5	L1/D19/R5	620	31050/53730	90	800±200	14.1±0.2	3
RH8	L1/D27/R3	620	31000/53280	120	<DL	14.3±0.4	10
RH8	L1/D27/R3	620	31000/53280	120	<DL	13.9±0.6	8
RH8	L1/D27/R3	620	31000/53280	120	<DL	16.1±3.3	3
RH9	L1/D29/R13	620	30450/53580	20	300±400	14.4±3.0	31
RH9	L1/D29/R13	620	30450/53580	20	1600±300	13.9±1.3	3
RH10	L1/D17/R9	620	31100/53690	60	<DL	14.8±0.5	3
U42	L0/P6/D1	680	31530/54650	120	700±300	18.2±0.6	7
U44	L0/P13/D3	680	31110/54600	20	500±300	17.7±0.2	5
U49	L0/P13/D19	680	30750/53970	(140)	<DL	13.9±0.2	5

ED spectra were collected over 200 to 6000 seconds and compared to tephroite (Mn), fayalite (Fe) and tungsten metal (W) standards. Although wolframite appears relatively insensitive to beam damage, with no significant change in analysed compositions over an 80 minute period, it was generally found more convenient to use shorter count times. The standard analytical errors (2σ) determined for 200 second count times were: $\pm 1.5\%$ (Fe) and $\pm 5\%$ (Mn). Individual determinations of Mn/(Mn + Fe) are considered to be precise to $\pm 1\%$ Mn/(Mn + Fe).

The response of the WD spectrometer and detector to niobium in wolframite, under the conditions specified, was found to be about 0.0011 counts/second/ppm Nb. Detection limits, using 360 seconds to collect counts on peak and on background, were calculated to be around 300 ppm Nb_2O_5 and the precision of individual analyses is similar.

A small number of wolframites were analysed for Ta, Mo and Sc. The concentration of all these elements was below detection limits (around 500 ppm).

Wolframite compositions

The average compositions of 41 Barroca Grande wolframites, determined from over 400 individual microanalyses, are presented in Table 1. Average major element compositions vary from 12 to 20 mol. % hübnerite, essentially the same range as that found by Saraiva (1971). Within single crystals, the hübnerite content generally varied by less than ± 2 mol. %. A substantial proportion of this variation can be attributed to the standard error of analysis. A number of samples, however, were considerably heterogeneous, with differences in composition of up to 20 mol. % hübnerite (RH9, individual analyses range from 7 to 27 mol. %

hübnerite). The hübnerite-rich areas of these samples were restricted to the cores or isolated inner patches of the crystals.

The average niobium content of the Barroca Grande wolframites varied from below detection limits up to 7400 ppm Nb_2O_5. Individual microanalyses as high as 12000 ppm Nb_2O_5 were determined (1190). Within single crystals, variations in Nb content were rarely greater than twice the standard (2σ) analytical error. In one sample (1190), however, individual microanalyses varied from 2500 to 12000 ppm Nb_2O_5.

No significant correlation could be found between hübnerite and Nb contents of the wolframites. This applies to both individual microanalyses and average sample compositions.

Form of niobium in wolframite

Transmission electron microscopy (TEM) of a Nb-rich wolframite (1190) revealed it to be a chemically homogeneous phase on a submicrometre scale (Dickinson and Polya, 1987). X-ray diffraction analyses showed the unit cell parameters of Nb-rich wolframite (1190) to be greater than those for Nb-poor wolframite (1411) of similar major element composition (Polya, 1987), confirming the presence of Nb in solid solution.

Niobium is probably incorporated into the wolframite lattice by means of a coupled substitution:

$$(\mathrm{Fe^{II}},\mathrm{W^{VI}}) \rightleftharpoons (\mathrm{Fe^{III}},\mathrm{Nb^{V}})$$

This is consistent with the small amounts of ferric iron in Panasqueira wolframite reported by Clark (1970*b*).

Mine scale variations in wolframite composition

Systematic variations in the hübnerite content of wolframite with distance from the apex of the Panasqueira cupola are reported by Kelly and Rye (1979; after Saraiva, 1971). No such variations have been found in the present study (Table 1, Fig. 2). Nor could a significant relationship between the Nb content of wolframites and proximity to the cupola be found. It is noted, however, that the samples analysed in this study were taken from distances of 400 to 2000 m from the cupola and that Saraiva (1971) found enrichment in hübnerite at distances less than 200 m. This suggests that any zonation is limited to within 200 m of the cupola. Enrichment of niobium in wolframite close to major faults, however, is noted for the first time in this study. Fig. 3 clearly shows an inverse relationship between Nb content of wolframite and distance from major faults. Average Nb contents of 1000 ppm Nb_2O_5 are only found in wolframites within 50 m of major faults; values above 2000 ppm Nb_2O_5 are only found within 30 m of major faults; and the highest Nb concentrations are found in a sample adjacent to the 8-East fault.

Discussion

The equilibrium between wolframite and a hydrothermal solution (neglecting trace ions) may be expressed by:

$$\mathrm{FeWO_4(wolf)} + \mathrm{Mn^{2+}(aq)} \rightleftharpoons \mathrm{MnWO_4(wolf)} + \mathrm{Fe^{2+}(aq)}$$

for which the equilibrium constant may be approximated by:

$$K_{\mathrm{wolf}}(T,P) = \frac{(X^{\mathrm{wolf}}_{\mathrm{MnWO_4}})(a^{\mathrm{aq}}_{\mathrm{Fe^{2+}}})}{(X^{\mathrm{wolf}}_{\mathrm{FeWO_4}})(a^{\mathrm{aq}}_{\mathrm{Mn^{2+}}})}$$

At temperatures and pressures below 400 °C and 1000 bars, the equilibrium constant K_{wolf} exhibits only a small temperature and pressure dependence (Polya, 1987). Thus:

$$\frac{(X^{\mathrm{wolf}}_{\mathrm{MnWO_4}})}{(1-X^{\mathrm{wolf}}_{\mathrm{MnWO_4}})} \approx K_{\mathrm{wolf}} \frac{(a^{\mathrm{aq}}_{\mathrm{Mn^{2+}}})}{(a^{\mathrm{aq}}_{\mathrm{Fe^{2+}}})}$$

It follows that the major element composition of hydrothermal wolframites is primarily a function of the chemistry (ΣFe,ΣMn,ΣCl,f_{O_2}) of the aqueous solution from which the wolframite is precipitated and that it is *not* critically dependent on the temperature and pressure of formation. This is

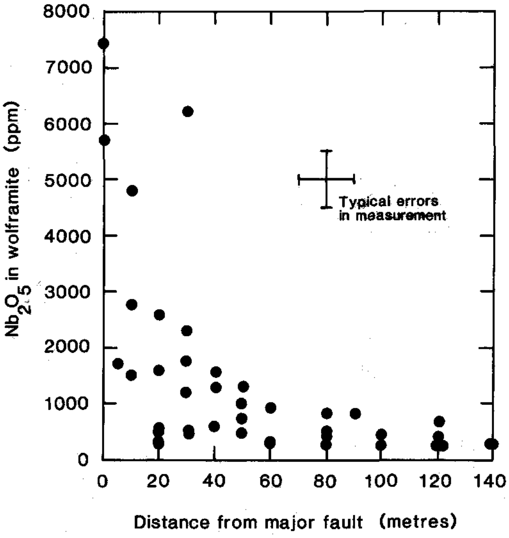

FIG. 3. Niobium content of Barroca Grande wolframites as a function of distance from major faults.

consistent with the discrediting of the use of the Mn/Fe ratio in wolframites as a geothermometer (Schrocke, 1960; Hsu, 1976; Amosse, 1978; Moore and Howie, 1978). It further implies that empirical relationships found between wolframite composition and temperature of formation (Taylor and Hosking, 1970; Singh and Varma, 1977) might well reflect systematic changes in fluid chemistry. The relationship between the regional variation in wolframite composition and the regional variation in source material (Groves and Baker, 1972) reflects the role of the source material in controlling hydrothermal solution chemistry. Nakashima *et al.* (1986) further demonstrate the importance of local wall-rock reactions in controlling hydrothermal wolframite compositions and this might well explain the enrichment of wolframite in the hübnerite component in the immediate vicinity of the greisened cupola at Panasqueira.

The two major source rocks at Panasqueira are the underlying granite and the Beira Schists. The granite contains around 0.5 wt. % MnO and 20 to 30 ppm Nb (Bussink, 1984). The Beira Schists typically contain less than 0.2 wt. % MnO and less than 15 ppm Nb (Polya, 1987). The relatively Mn-rich wolframites found by Saraiva (1971) adjacent to the greisened cupola may, therefore, reflect Mn-rich fluids flowing through a Mn-rich granitic source rock. The occurrence of Mn-rich pods within otherwise relatively homogeneous wolframites suggests that the Mn-rich wolframites represent an early stage of fluid movement and ore precipitation. The average bulk hübnerite contents of most of the (later) main stage wolframites analysed in this study are similar, suggesting that main-stage fluids were fairly uniform in composition with respect to Fe and Mn. Given this uniformity of composition, a mechanism is required to explain the preferential concentration of Nb near major fault zones.

One possibility considered was the leaching of wolframites by post-ore low-temperature fluids, whose flow was largely controlled by the major fault zones. This possibility, however, is discounted because there is no evidence for margin-related zonation of wolframite crystals with respect to Nb or the major elements.

It is considered more likely, therefore, that major fault zones, such as 8 East Fault, acted as pathways for the vertical flow of the main stage ore-forming fluids at Panasqueira. The study of Blattler (1985) indicates that several of the major faults were formed before ore formation and were active at around the same time as ore formation. Increases in fluid pressure ultimately led to the dilation of sub-horizontal fractures originating from these faults. Adjacent to the faults dilation would be rapid and accompanied by a rapid decrease in pressure, leading to wolframite precipitation (Polya, 1987). Nb was incorporated by co-precipitation with rapidly growing wolframite. Away from the faults, fracture dilation would have been slower and the solubility-controlling pressure decrease slower also. The model of the mechanism of Nb enrichment near the fault zones is rather speculative, mainly due to the lack of thermodynamic data on Nb in aqueous solutions, but the interpretation of the fluid pathway role of the faults does not critically rely on a detailed model being established.

It is interesting to note that Richardson and Pinckney (1984) also identified fracture zones as major fluid pathways in the Deardoff mine (Cave-in-Rock district). Their conclusions were based on fluid inclusion data and a similar study might be of some value at Barroca Grande.

Conclusions

The major element chemistry of wolframites in the Barroca Grande mine is uniform over distances of 2 km, reflecting the uniform chemical composition of the main-stage ore-forming fluids. However, considerable variations in the Nb content of wolframites exist. Nb-rich wolframites are only found within several tens of metres of major sub-vertical faults. This pattern of distribution is most readily explained by invoking major sub-vertical fault zones as major pathways for the movement of the main-stage ore-forming fluids. Although the greisened cupola may have been a focus for hydrothermal fluids, the movement of these fluids on a mine scale is more strongly influenced by the distribution of faults during ore formation. An implication of this study is that the mine-scale variation in ore mineral abundances and chemistry at Barroca Grande may be related to the proximity of certain major faults—this is worth further investigation.

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