X CONGRESSO IBÉRICO DE GEOQUÍMICA

Tungsten-bearing molybdenite from Borralha

Molibdenite tungstífera da Borralha

Silva, T. P.[1*]; Figueiredo, M. O.[1,2]; Veiga, J. P.[2]; de Oliveira, D.[1]; Batista, M. J.[1]; Noronha, F.[3]

[1] LNEG – Laboratório Nacional de Energia e Geologia, I.P., Unidade de Recursos Minerais e Geofísica, Estrada da Portela, Apartado 7586, 2610-999 Amadora, Portugal, * teresa.pena@lneg.pt

[2] CENIMAT/I3N – Centro de Investigação em Materiais, Departamento de Ciência dos Materiais, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

[3] FCUP – Faculdade de Ciências da Universidade do Porto, Departamento de Geociências, Ambiente e Ordenamento do Territorio, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal

Abstract

The Borralha mine is located in northern Portugal where two main mineralization stages are known: the first, the cristalization of W oxides, namely wolframite [(Fe,Mn)WO_4] and scheelite ($CaWO_4$), followed by the formation of Fe-Cu-Zn-Mo-Pb-Bi sulphides in the second. In that region, molybdenite (MoS_2) appears frequently as aggregates in quartz veins, being isostructural with tungstenite (WS_2), a mineral that seldom occurs in Nature. The results obtained through an X-ray absorption spectroscopy (XANES) study with synchrotron radiation, for W-molybdenite from various provenances, combined with geochemical data, are described and discussed. A solid-solution between molybdenite and tungstenite resulting from the strong structural similarities between the two minerals (where tungsten is incorporated as a trace constituent in the molybdenite structure by substitution of molybdenum), seems to be the situation of tungsten-bearing molybdenite from Borralha, considering the output of the present study.

Keywords: Molybdenite, tungstenite, Borralha mine, XANES, tungsten.

Resumo

As minas da Borralha situam-se no norte de Portugal e encontram-se descritos dois estágios de mineralização principais para a sua formação: no primeiro, deu-se a cristalização dos óxidos de W, ou seja, wolframite [(Fe,Mn)WO_4] e scheelite ($CaWO_4$), seguido da formação de sulfuretos Fe-Cu-Zn-Mo-Pb-Bi no segundo estágio. Nesta região, a molibdenite (MoS_2) aparece frequentemente em agregados nos filões de quartzo, sendo isoestrutural com a tungstenite (WS_2), um mineral que raramente ocorre na natureza. Os resultados obtidos através de um estudo de espectroscopia de absorção de raios X (XANES) com radiação de sincrotrão, para molibdenite tungstífera de várias proveniências, combinados com dados geoquímicos, são descritos e discutidos. Tendo em conta o resultado do presente trabalho, uma solução sólida entre a molibdenite e a tungstenite resultante das semelhanças estruturais entre os dois minerais (onde o tungsténio é incorporado como elemento traço na estrutura da molibdenite substituindo o molibdénio) parece ser a situação da molibdenite tungstífera da Borralha.

Palavras-chave: Molibdenite, tungstenite, minas da Borralha, XANES, tungsténio.

Introduction

The Borralha mine is located in Montalegre (Northern Portugal) and is a past producer of tungsten concentrate (wolframite – $(Fe,Mn)WO_4$ – and lesser amounts of scheelite – $CaWO_4$). It was the second largest tungsten mine in Portugal (after Panasqueira) until its closure in 1985 as a result of the decline in metal price. The deposit is composed of several sets of quartz veins (vertical and subhorizontal) and two well-developed breccia pipes (Noronha, 1983). Two main mineralization stages seem to have occurred: 1: the cristalization of W oxides and 2: the formation of Fe-Cu-Zn-Mo-Pb-Bi sulphides.

Molybdenite (MoS_2), whose crystal structure is based on the stacking of [S-Mo-S] layers with Mo^{4+} cations in prismatic coordination between two superimposed closest-packed layers of S^{2-} anions, appears frequently as aggregates in quartz veins. The occurrence of such layers gives rise to polytypism: the common natural molybdenite polytype is hexagonal and currently labelled 2H, but a natural rhombohedral polytype (3R) was reported for the first time fifty years ago (Traill, 1963).

In a previous study (Silva *et al.*, 2013) the replacement of Mo by Re ions in molybdenites was analyzed through X-ray absorption spectroscopy (XANES) using synchrotron radiation. Actually, information on the local symmetry, coordination, and valence of the metal could be attained through the study of L_3-edge.

The results obtained in similar experiments for W-molybdenite from Borralha, combined with a geochemical study, are described and discussed as an attempt to improve the optimization of mineral resources.

Materials and Methods

Museum specimens (from the Museu de Jazigos Minerais Portugueses at LNEG and from Noronha's personal collection) of molybdenite samples collected at Borralha, Carris and Venturinha mine, were irradiated in Grenoble, France at the European Synchrotron Radiation Facility (ESRF), with the instrumental set up of beamline BM 25-A. The XANES study was performed at W L_3-edge by irradiating MoS_2 samples, along with reference minerals (wolframite from Panasqueira and scheelite from Santa Comba Dão) and a model compound, synthetic WS_2 (from Sigma-Aldrich) all previously characterized by X-ray diffraction (XRD) in the laboratory. Re metal was used for energy calibration; powdered samples were placed between two Kapton foils to collect the absorption spectra.

Using the instrumental facilities available at the beamline, the phase constitution of irradiated materials from Borralha (placed inside a capillary tube that was rotated during the exposure to synchrotron radiation), was achieved by high-resolution powder diffraction (HRPD).

The chemical constitution of studied materials at the irradiated points was obtained by X-ray fluorescence spectrometry and the energy dispersive spectra (EDXRF) were fitted using the *PyMCA* software (Solé *et al.*, 2007).

Results and Discussion

W L_3-edge XANES spectra obtained for Borralha molybdenite samples and for tungstenite are reproduced in Fig. 1, displaying identical layouts (white-line at 10209 eV). This similarity conforms to the idea that W^{4+} replaces Mo^{4+} ions in molybdenite assuming a prismatic coordination. Both WS_2 and MoS_2 minerals are isostructural, but the first one (tungstenite) occurs very seldom in Nature; in fact, the capability of W^{6+} to form tungstates dominates in natural compounds compared to that of W^{4+} in forming the sulphide (WS_2). This is the case of tungsten in molybdenite samples from Carris and Venturinha (Fig. 2) whose spectra details and energy of the white-line conforms to W-O rather than to W-S bonding. In wolframite, the splitting of the

white-line reflects the distortion of the W^{6+} octahedra in the crystal structure (Yamazoe *et al.*, 2008) while in scheelite W^{6+} ions have tetrahedral coordination and the white-line instead of split is only broadened (Kuzmin & Purans, 2001).

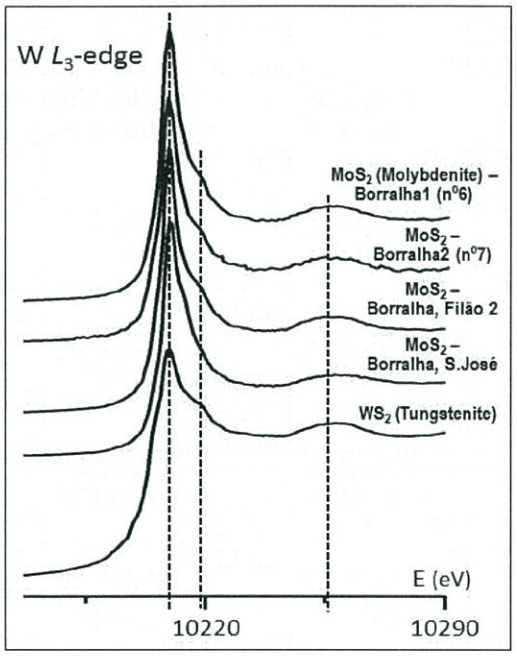

Fig. 1 – W L_3-edge XANES spectra collected from Borralha molybdenite samples and from tungstenite (model compound).

According to the collected HRPD patterns from the Borralha samples, molybdenite is the only dominant phase and polytype 2H was identified in samples with references *nº6* and *Filão 2*, while a mixture of polytypes 2H plus 3R was assigned in MoS_2 samples *nº7* and *S.José* (Silva *et al.*, 2014).

The high bismuth and lead contents are apparent from the collected EDS-XRF spectra (Fig. 3), where the W peak is assigned with a line for a quick visualisation. The chemical constitution is similar for all samples with the exception of molybdenite sample *nº7*, which presents higher Fe, Cu, Zn, Se and Pb contents.

The comparison between chemical concentrations of some significant elements (Table 1) shows a clear difference amongst Borralha (Bo) and Carris/Venturinha MoS_2 samples.

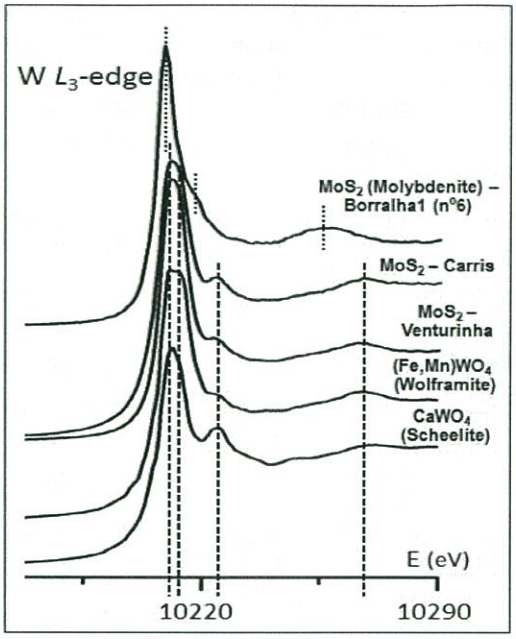

Fig. 2 – W L_3-edge XANES spectrum collected from Borralha molybdenite compared with XANES spectra of tungsten in MoS_2 from Carris and Venturinha mine and with tungstates as reference minerals.

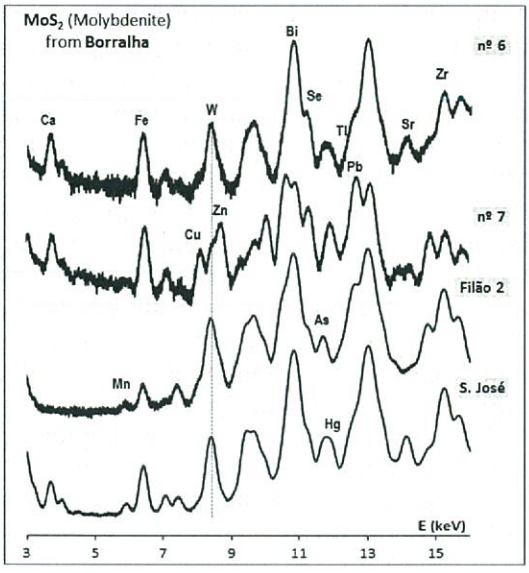

Fig. 3 – Energy dispersive X-ray fluorescence (EDS-XRF) spectra obtained for MoS_2 from Borralha, irradiated to collect the W L_3-edge XANES spectra. Only the diagnose peak of each element is assigned.

Tungsten content is higher (about 5x) in the last ones. Actually, Borralha and Carris constitute similar mineralized zones (Noronha, 1984), but distinct in terms of a

higher percentage of scheelite and absence of cassiterite in the Borralha deposit, while the main minerals found in the Venturinha region (Viseu) were feldspars and quartz (Correia Neves, 1962).

Table 1 – Concentrations (mg/kg or ppm) of some significant elements in studied molybdenite samples (analyses from ACTLABS)

	As	W	Pb	Bi
Bo (nº6)	24.1	1420	276	>10000
Bo (nº7)	21.7	2100	>5000	>10000
Bo (Filão2)	28.1	1940	3040	>10000
Bo (S.José)	47	877	14.2	9550
Carris	1660	10000	1020	1660
Venturinha	3840	9360	1790	3250

Final Comments

The present results obtained for the tungsten-bearing molybdenite from Borralha point to a solid-solution between molybdenite and tungstenite. Such unusual occurrence, reported in the Kola Peninsula (Barkov *et al.*, 2000) and also in Serra de Arga, Northern Portugal (Dias *et al.*, 2010), results from the strong structural similarities between the two minerals, where W is incorporated as a trace constituent in MoS_2 structure by Mo diadochic replacement. The layered nature of these minerals enhances the possibility of intercalation of organometallic species and cations (Benavente *et al.*, 2002), making them potentially useful for new technological applications, thus improving the optimization of mineral resources by the reuse of dump material from previous exploration activities.

Acknowledgements

Work developed within the project MinReMol (Ref. EXPL/AAG-REC/0978/2012, COMPETE: FCOMP-01-0124-FEDER-027516) financed by FEDER Funds through "Programa Operacional Factores de Competitividade (COMPETE)" and by National Funds through FCT (Fundação para a Ciência e a Tecnologia). EU financial support to perform the experiments (EV-13 and ES-128) at the ESRF is acknowledged. Authors affiliated to CENIMAT/I3N acknowledge FEDER funds through the COMPETE 2020 Programme and National Funds throught FCT - Portuguese Foundation for Science and Technology under the project UID/CTM/50025/2013.

References

Barkov, A.Y., Martin, R.F., Poirier, G., 2000. Zoned tungstenoan molybdenite from a fenitized megaxenolith in the Khibina alkaline complex, Kola peninsula, Russia. *The Can. Miner.*, 38, 1377-1385.

Benavente, E., Santa Ana, M., Mendizábal, F., González, G., 2002. Intercalation chemistry of molybdenum disulfide. *Coord. Chem. Rev.*, 224, 87–109.

Correia Neves, J.M., 1962. Pegmatito da região da Venturinha (Penalva do Castelo, Viseu). Memórias e Notícias do Museu e Lab. Mineral. e Geol. da Univ. Coimbra, 54, 1-135.

Dias, P.A., Leal Gomes, C., Guimarães, F., 2010. W-molybdenite in Silurian meta-volcanic rocks of Northern Portugal. *Acta Miner.-Petrogr. Abstract Series*. 6, 546.

Kuzmin, A., Purans, J., 2001. Local atomic and electronic structure of tungsten ions in AWO4 crystals of scheelite and wolframite types. *Radiation Measurements*, 33, 583–586.

Noronha, F.M.P., 1983. Estudo metalogénico da área tungstífera da Borralha. Unpublished PhD thesis, Sciences Faculty, Oporto Univ., 413 pp.

Noronha, F.M.P., 1984. Mineralizações espacial e genéticamente associadas ao maciço granítico da Serra do Gerês. Um exemplo de zonalidade. *Cuad. Lab. Xeol. Laxe*, 7, 87-99.

Silva, T.P., Figueiredo, M.O., de Oliveira, D., Veiga, J.P., Batista, M.J., 2013. Molybdenite as a Rhenium Carrier: First Results of a Spectroscopic Approach Using Synchrotron Radiation. *J. Minerals and Materials Character and Engineering*, 1, 207-211.

Silva, T.P., Figueiredo, M.O., Santos, R., Oliveira, D., Veiga, J.P., Batista, M.J., 2014. Valorização de recursos minerais: contribuição do projecto MinReMol para uma recuperação sustentável do rénio a partir de resíduos mineiros. *Com. Geol.*, 101, 855-858.

Solé, V.A., Papillon, E., Cotte, M., Walter, Ph. Susini, J., 2007. A multiplatform code for the analysis of energy-dispersive X-ray fluorescence spectra. *Spectrochim. Acta*, 62, 63-68.

Traill, R.J., 1963. A rhombohedral polytype of molybdenite. *The Can. Miner.*, 7, 524-526.

Yamazoe, S., Hitomi, Y., Shishido, T., Tanaka, T. 2008. XAFS Study of Tungsten L_1- and L_3-Edges: Structural Analysis of WO_3 Species Loaded on TiO_2 as a Catalyst for Photo-oxidation of NH_3. *J. Phys. Chem. C*, 112, 6869-6879.