Tungsten-bearing molybdenite from Borralha

Molibdenite tungstifera 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, 2610-599 Amadora, Portugal, *teresa.penaa@lneg.pt
2 CENIMAT/3N – 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 Território, 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 crystallization of W oxides, namely wolframite ([Fe,Mn]WO₄) and scheelite (CaWO₄), followed by the formation of Fe-Cu-Zn-Mo-Pb-Bi sulphides in the second. In that region, molybdenite (MoS₂) appears frequently as aggregates in quartz veins, being isocristal with tungstenite (WS₂), 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]WO₄) e scheelite (CaWO₄), seguido da formação de sulfetos Fe-Cu-Zn-Mo-Pb-Bi no segundo estágio. Nesta região, a molibdenita (MoS₂) aparece frequentemente em agregados nos filões de quartzo, sendo isocristal com a tungstenita (WS₂), 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 molibdenita tungstifera de várias proveniências, combinados com dados geoquímicos, são descritos e discutidos. Tendo em conta o resultado do presente trabalho, uma solução sólida entre a molibdenita e a tungstenita resultante das semelhanças estruturais entre os dois minerais (onde o tungstênio é incorporado como elemento traço na estrutura da molibdenita substituindo o molibdênio) parece ser a situação da molibdenita tungstifera da Borralha.

Palavras-chave: Molibdenita, tungstenite, minas da Borralha, XANES, tungstênio.
Introduction

The Borralha mine is located in Montalegre (Northern Portugal) and is a past producer of tungsten concentrate (wolframite – (Fe,Mn)WO₄ – and lesser amounts of scheelite – CaWO₄). 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 crystallization of W oxides and 2: the formation of Fe-Cu-Zn-Mo-Pb-Bi sulphides.

Molybdenite (MoS₂), whose crystal structure is based on the stacking of [S-Mo-S] layers with Mo⁴⁺ cations in prismatic coordination between two superimposed closest-packed layers of S²⁻ 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 L₃-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 L₃-edge by irradiating MoS₂ samples, along with reference minerals (wolframite from Panasqueira and scheelite from Santa Comba Dão) and a model compound, synthetic WS₂ (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 L₃-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 W⁴⁺ replaces Mo⁴⁺ ions in molybdenite assuming a prismatic coordination. Both WS₂ and MoS₂ minerals are isostructural, but the first one (tungstenite) occurs very seldom in Nature; in fact, the capability of W⁶⁺ to form tungstates dominates in natural compounds compared to that of W⁴⁺ in forming the sulphide (WS₂). 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\textsuperscript{6+} octahedra in the crystal structure (Yamazoe et al., 2008) while in scheelite W\textsuperscript{6+} ions have tetrahedral coordination and the white-line instead of split is only broadened (Kuzmin & Purans, 2001).

According to the collected HRPD patterns from the Borrinha samples, molybdenite is the only dominant phase and polytype 2H was identified in samples with references n\textsuperscript{66} and Filâo 2, while a mixture of polytypes 2H plus 3R was assigned in MoS\textsubscript{2} samples n\textsuperscript{77} 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 n\textsuperscript{77}, 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 Borrinha (Bo) and Carris/Venturinha MoS\textsubscript{2} samples.

Tungsten content is higher (about 5x) in the last ones. Actually, Borrinha 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)

<table>
<thead>
<tr>
<th></th>
<th>As</th>
<th>W</th>
<th>Pb</th>
<th>Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bo (r°8)</td>
<td>24.1</td>
<td>1420</td>
<td>276</td>
<td>&gt;10000</td>
</tr>
<tr>
<td>Bo (r°7)</td>
<td>21.7</td>
<td>2100</td>
<td>&gt;5000</td>
<td>&gt;10000</td>
</tr>
<tr>
<td>Bo (S-São)</td>
<td>28.1</td>
<td>1940</td>
<td>3040</td>
<td>&gt;10000</td>
</tr>
<tr>
<td>Bo (S-Jose)</td>
<td>47</td>
<td>877</td>
<td>14.2</td>
<td>9550</td>
</tr>
<tr>
<td>Carris</td>
<td>1660</td>
<td>10000</td>
<td>1020</td>
<td>1660</td>
</tr>
<tr>
<td>Venturinha</td>
<td>3840</td>
<td>9360</td>
<td>1790</td>
<td>3250</td>
</tr>
</tbody>
</table>

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 MoS₂ 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/ISN acknowledge FEDER funds through the COMPETE 2020 Programme and National Funds through FCT – Portuguese Foundation for Science and Technology under the project UID/CTM/50025/2013.

References


