

Silver mineralization at the Vale das Gatas tungsten mine, Portugal

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Abstract

The Vale das Gatas tungsten mine is situated at the contact between Hercynian granite and Cambrian-Precambrian crystalline schists a few kilometers north of the village of Sabrosa, near Vila Real, in northern Portugal. Wolframite has been the principal product of the mine although several other metals of economic interest are known to occur there. The silver content of the ores was attributed by earlier workers to the presence of tetrahedrite and schapbachite, whilst this work shows matildite, pavonite, acanthite, and argyrodite to be present, together with Ag-bearing galena. The textures and compositions of these phases are described with preliminary results of fluid inclusion studies.

KEYWORDS: silver, tungsten, Portugal, Vale das Gatas, matildite, pavonite, galena.

Introduction

THE Vale das Gatas ore bodies are part of a complex suite of sheeted quartz veins, locally mineralized with wolframite, sulphides and subordinate cassiterite, and aplite-pegmatites containing cassiterite. This mineralization occurs in an area immediately to the north of the village of Sabrosa in the district of Vila Real de Trás-os-Montes in northern Portugal (Fig. 1). The mineralized veins cut Cambrian-Precambrian crystalline schists and Hercynian granite (300 ± 10 Ma: Priem *et al.*, 1970) which intrudes the schists. The schists form part of the Beira Complex known as 'Complexo Xisto-grauváquico Anté-ordovícico' (Ribeiro, 1974; Teixeira, 1979) and consist of flysch slates and greywackes with interbedded quartzites, limestones, calc-silicate rocks and conglomerates. The granites are considered by some authors (e.g. see Neiva, 1982) to be the result of two phases of intrusion whilst others (e.g. Merino, 1981) suggest they resulted from a single intrusive episode which produced several petrographically distinct facies.

The granites occupy the centre of an antiform with a NW-SE axis running from Mondim de Basto through Vila Real to Moncorvo. The antiform is flanked to the NE and SW by the Complexo Xisto-grauváquico Anté-ordovícico formation.

The village of Sabrosa lies near an embayment in the southern contact. Near the village the granite is a medium to coarse-grained, porphyritic two-mica granite which shows conspicuous foliation and contains megacrysts of perthitic microcline following late-stage potassic feldspathization. To the north, the granite is fine to medium-grained, contains two micas and shows less distinct foliation. The regional metamorphism of the schists is to chlorite grade but the thermal metamorphism of the intrusion has produced a biotite hornfels zone up to 3 km from the contact and, in a narrow zone (100 to 300 m wide) adjacent to the contact, has also produced andalusite. The granite is cut by NE-SW faults which parallel the regional fault pattern and carry barren quartz veins, 10 m or more in thickness. The wolframite-bearing quartz veins appear principally in the coarse, porphyritic,

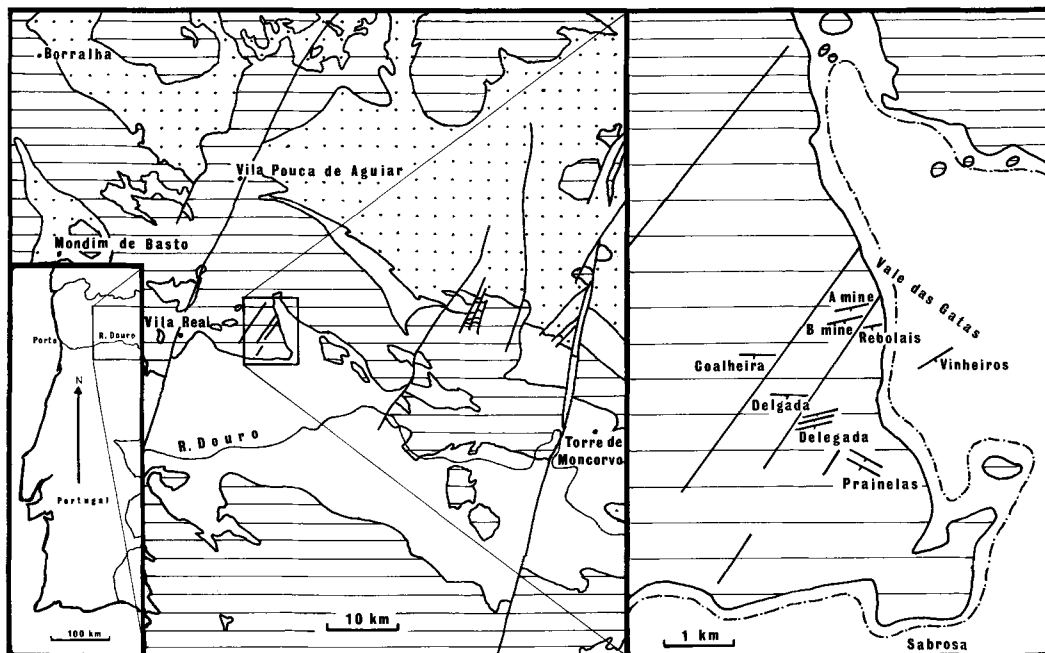


FIG. 1. Locality map of the Vale das Gatas tungsten mine, with geology after Brink (1960) and Teixeira (1972).

two-mica granite and occasionally extend a few kilometers into the schists. The NE-SW faulting and irregular development of the veins has led to selective mining of the deposit. General aspects of the mineralization are discussed by Thadeu (1973) and the mineralization in the Vila Real-Vila Pouca de Aguiar region has been described by Brink (1960), Westerveld (1956), Merino (1981) and Pereira and Cruz (1980).

The Vale das Gatas mine extracts ore from separate sections of a single vein, part of which has been removed by faulting. The sections of the mine in the granite are known as A mine and B mine. At Rebolais, a shaft intersects the vein where it crosses the contact between granite and schists, whilst at Vinheiros, an adit into the hillside at a lower level follows the continuation of the vein into the schists. Wolframite, cassiterite and scheelite have been the only minerals of economic interest to be produced at the mine although chalcopyrite and other common sulphides and sulphosalts occur in the quartz veins. The paragenesis was described by Brink (1960). The Companhia Mineraria do Norte de Portugal found a mineral separation problem in the ore dressing plant. Although silver occurs at economic concentrations in several of the mineral products of the plant, improved beneficiation is required to obtain it as a separate product and

enhance the value of the tin and tungsten output. The presence of silver was known to the earlier workers and attributed by them to tetrahedrite and schapbachite. This work describes a continuing investigation (Gaspar and Bowles, in press) to determine the mineralogy of the silver in the ores with the intention not only of improving the beneficiation of the ore currently being mined but also of reworking the sulphides dam which comprise some 400 tons of sulphides containing 1200 to 1500 g/t Ag, 0.3% Bi, 0.04% Cd and 12.9% As.

Structure of the mineralized veins

Recent work (Ribeiro, 1974; Ribeiro and Ramos, 1979; Pereira and Cruz, 1980; Merino, 1981) describes two fault lineaments. One of these is a thrust fault with a sinistral shear component dipping 40° SW which is mineralized in the Vale das Gatas veins A, B, Rebolais and Vinheiros. The veins are considered (Ribeiro, 1974) to have opened initially as tension gashes (Riedal type faults), providing a plane of weakness along which later shearing and thrusting forces could be accommodated. Only those faults which show the later movement producing conjugate tension faults are mineralized. Further sinistral shearing is sometimes superimposed on the earlier structures with a second

episode of mineralization. Examination of the ores (Merino, 1981) shows two textural styles of mineralization. The earlier style is composed of irregular shapes with rounded sulphides, and a 'pine cone' texture to the wolframite. The later style is laminated. The regional, normal, dextral faults which dip 50 to 70° WNW cut both the schists and the granite batholith and they offset the mineralized veins at Vale das Gatas into four blocks corresponding to the A, B, Rebolais and Vinheiros sections.

Paragenesis

The ore minerals which have been identified during this work on samples from Rebolais and Vinheiros are listed below in the order in which they were formed.

Cassiterite occurs as idiomorphic crystals which are replaced or enclosed by wolframite. Cassiterite is also enclosed in gangue minerals, especially in the alpite pegmatites in the granite.

Wolframite occurs as lath-shaped crystals showing the optical properties of the hübnerite ($MnWO_4$) end-member although a few coarse-grained crystals with short prismatic forms, visible zonation and optical properties indicative of ferberite ($FeWO_4$) are also seen. Microprobe examination has confirmed the optical identifications. The wolframite usually shows a reaction rim against gangue and sulphide minerals and the rim composition is close to hübnerite even when the rim encloses a ferberite crystal. Sulphides are sometimes developed along hübnerite cleavage planes.

Scheelite sometimes replaces wolframite (especially hübnerite) extensively. Sulphides are seen as fine strings along scheelite cleavage planes.

Arsenopyrite and *pyrite* are the most abundant sulphides and the first to crystallise. The arsenopyrite often shows idiomorphic outlines and the pyrite occurs in several forms including poikiloblastic textures and apparently as inclusions in globular masses of the other sulphides. Pyrite also occurs with galena in cross-cutting veinlets in arsenopyrite where it has a distinct anisotropism. These examples contain minor amounts of lead and arsenic. Some pyrite forms pseudomorphs after pyrrhotine.

Chalcopyrite, *sphalerite* and *galena* occur together and are usually intergrown. Sphalerite almost invariably contains inclusions and exsolutions of chalcopyrite, stannite and pyrrhotine. Chalcopyrite frequently contains inclusions of sphalerite, stannite, pyrrhotine and galena. The sphalerite inclusions are often oriented and sometimes form 'sphalerite stars' and the chalcopyrite

often shows the double concave lamellae of the transformation structure.

Galena generally crystallizes after chalcopyrite and sphalerite and tends to replace them. It occurs in two forms: as silver- and bismuth-rich solitary crystals with very well developed cleavages and as more massive crystals containing a little less silver and bismuth but either filled with inclusions and exsolutions of silver and bismuth sulphides and native bismuth or chalcopyrite or intergrown with similar phases. Galena of this type is also seen as veinlets cutting arsenopyrite. Grains of galena vary from about 20 to 250 μm in size.

Stannite is intergrown with chalcopyrite and occurs as exsolutions in sphalerite. It often replaces cassiterite.

Pyrrhotine has nearly always decomposed to form pyrite or fibrous crystals of marcasite and is generally preserved only by pseudomorphs. It also occurs as exsolution lamellae in sphalerite.

Marcasite is a product of the decomposition of pyrrhotine.

Matildite, $AgBiS_2$, and *pavonite*, $AgBi_3S_5$, usually occur as independent grains attached to Ag-rich galena and as oriented inclusions in galena. Matildite is usually 10 to 70 μm in size whilst pavonite shows a wide range of size distributions, from elongate grains 10 μm wide and about 70 μm in length to small grains 5 μm across. The matildite is presumably the phase described by Brink (1960) as schapbachite.

'*Neyite*', $Pb_7(Cu,Ag)_2Bi_6S_{17}$. A mineral with a composition approximating to neyite occurs as small isolated grains about 10 μm across and as bladed inclusions within galena.

Argyrodite, Ag_8GeS_6 , is abundant in some specimens but not widely distributed. It is intergrown with other Ag-bearing minerals and replaces matildite, acanthite, Ag-rich galena and chalcopyrite. Minor amounts of Fe and Pb occur as impurities in the argyrodite which occurs as grains from 5 to 40 μm across.

Proustite, Ag_3AsS_3 , occurs rarely as discrete grains associated with other Ag-bearing phases.

Tetrahedrite, $Cu_{10}(Zn,Fe)_2Sb_4S_{13}$ is rare and occurs as inclusions in galena or intergrown with stannite and chalcopyrite or with galena and bismuth. The Ag content is minimal.

Pearceite, $Ag_{16}As_2S_{11}$, is seen occasionally as discrete grains associated with other Ag-rich phases.

Acanthite, Ag_2S , occurs intergrown with Ag-Bi sulphides and as secondary veins cutting galena. The grain size is usually around 20 μm .

'*Geffroyite*', $(Ag,Cu,Fe)_9(Se,S)_8$. One example of a mineral containing major elements indicative of geffroyite has been seen associated with galena.

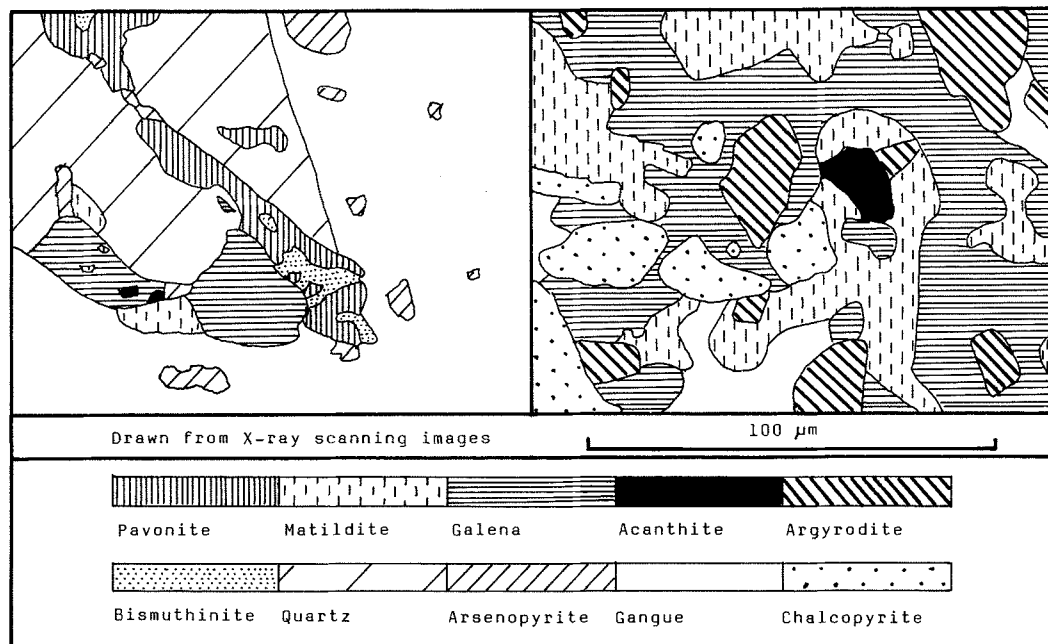


FIG. 2. Relationships of the principal Ag-bearing minerals. Chalcopyrite is cut and replaced by galena (1% Ag and 2–3% Bi), matildite and pavonite. These are replaced in turn by argyrodite and acanthite.

Bismuth occurs quite frequently associated with galena and sphalerite and intergrown with and replaced by cosalite.

Bismuthinite occurs as inclusions with the form of deformation lamellae in pyrite.

Magnetite and *hematite* occur in pyrite, probably as an alteration product with subsequent alteration of magnetite to hematite.

Covellite, *digenite*, *chalcocite* and *anglesite* occur as secondary alteration products.

'*Limonite*' forms by supergene alteration.

Typical relationships of the main silver-bearing phases are illustrated in Fig. 2.

Composition of the main Ag-bearing phases

The economically significant Ag-bearing phases were studied using a Cambridge Instruments Microscan 5 electron microprobe and the standards and methods described by Bowles (1975).

Galena. The galena contains up to 2.8% Ag. As a general rule, individual grains of galena contain the highest Ag levels (1.8 to 2.8%) whilst galena associated with other Ag-bearing minerals, some of which appear to exsolve from galena, contains lower levels (~1% Ag). Table 1 shows a range of compositions of galena of both types. Significantly,

bismuth is also present and, together with Ag, replaces Pb in the galena. The molecular proportions of bismuth and silver are approximately the same since equal amounts of Ag^+ and Bi^{3+} are required to replace Pb^{2+} in order to maintain the charge balance.

Table 1. Electron microprobe analyses of Ag- and Bi-rich galena

	1	2	3	4	5
Ag	1.03	1.07	1.79	2.32	2.83
Bi	2.70	3.32	4.41	4.43	5.24
Pb	83.37	82.76	80.51	79.50	77.47
S	13.48	13.54	13.37	13.41	13.50
Total	100.58	100.69	100.08	99.66	99.04
Number of ions per unit cell					
Ag	0.023	0.023	0.039	0.051	0.062
Bi	0.031	0.037	0.050	0.050	0.059
Pb	0.952	0.946	0.922	0.909	0.884
S	0.995	0.993	0.989	0.990	0.995
Ag+Bi+Pb	1.006	1.006	1.011	1.010	0.005

Galena has a larger grain size than the other silver-bearing phases and, since it forms a significant proportion of the sulphides, holds much of the recoverable silver in the mine.

Matildite, *pavonite* and '*neyite*'. Analyses of these

Table 2. Electron microprobe analyses of matildite, pavonite and neyite.

	1	2	3	4	5	6	7
Ag	24.64	28.32	12.20	12.05	8.56	8.31	6.23
Bi	53.23	54.85	65.23	70.04	39.10	39.13	36.19
Pb	5.75	-	4.95	-	37.11	36.95	41.86
S	17.20	16.83	18.46	17.91	15.70	15.64	15.73
Total	100.82	100.00	100.84	100.00	100.47	100.03	100.00
Molecular proportions							
Ag	0.872	1	0.993	1	2.715	2.650	2
Bi	0.973	1	2.741	3	6.402	6.440	6
Pb	0.106	-	0.210	-	6.129	6.134	7
S	2.049	2	5.056	5	16.754	16.776	17

1. Matildite from Vale das Gatas
2. Stoichiometric matildite
3. Pavonite from Vale das Gatas
4. Stoichiometric pavonite
- 5,6. Neyite from Vale das Gatas
7. Stoichiometric neyite with (Cu,Ag) represented by Ag only

phases are shown in Table 2. Both matildite and pavonite contain additional Pb which in matildite appears to substitute for Ag, whilst in pavonite the Pb appears to substitute for Bi. In both cases, if the charge balance is to be maintained, the actual substitution must be more complicated than this. Locally, particularly in the pavonite, Bi is present in sufficient concentrations to give rise to inclusions of native bismuth and bismuthinite. A third Ag-rich phase has a composition close to neyite. It has a little too much Ag and Bi and not enough Pb to correspond exactly to the ideal formula of neyite, but the chemistry and optical properties of this phase are close to those of neyite.

Fluid inclusion studies

Preliminary study of the fluid inclusions in samples of wolframite-bearing quartz shows inclusions represented entirely by simple, two-phase liquid/vapour systems which homogenize into the liquid phase. The inclusions rarely exceed 20 μm in diameter and their distribution within the quartz suggests entrapment along micro-fractures during crystal growth (i.e. pseudosecondary inclusions). The least deformed material gives a well defined mean homogenisation temperature of 225 ± 6 °C and salinity measurements suggest the inclusions contain about 6 wt.% NaCl equivalents. The quartz which shows significant intracrystalline deformation, possibly due to later movement along the veins, gives lower, less well defined temperatures (194 ± 21 °C). Without independent pressure estimates the temperatures cannot be corrected for lithostatic pressures and should therefore be regarded as minima. The absence of visible liquid CO_2 in all specimens implies less than 5 wt.% CO_2 in the fluid phase. Furthermore, vapour-rich inclusions are absent, suggesting that the fluids were not boiling during this stage of mineral deposition.

Conclusions

Studies of the structure and tectonism of the Vale das Gatas area, together with fabric studies of the veins, indicate that the mineralization was formed by late-stage fluids associated with the cooling of the Hercynian granite. The first episode of metalliferous mineralization is coarse-grained and contains the major proportion of the tungsten and sulphide mineralization. Preliminary fluid inclusion data suggest that quartz associated with the formation of the wolframite crystallized at temperatures in excess of 225 °C. This is 25 to 125 °C lower than pressure uncorrected homogenisation temperatures for tungsten mineralization at the Borralha mine 50 km northwest of Vale das Gatas (Noronha, 1974) and Panasqueira (Bussink, 1984). Bulk salinities fall within the range 2–10 wt.% NaCl equivalents noted for many other quartz-wolframite deposits (Bussink, 1984; Ball *et al.*, 1985; Kelly and Rye, 1979; Bril, 1982). The second episode of laminar textured mineralization occupies reactivated veins and gives generally lower temperatures around 194 °C. Sulphides, including the Ag-bearing sulphides, appear to be associated with both episodes of metalliferous mineralization.

Experimental studies of the Ag–Bi–Pb–S system indicate solid solution between PbS and AgBiS_2 at temperatures in excess of 215 ± 15 °C (Van Hook, 1960; Craig, 1967; Hoda and Chang, 1975). At lower temperatures, the matildite exsolves to produce lamellae or irregular inclusions within the galena or separate grains external to the galena. As a generalisation, it appears most likely that the examples of sulphide mineralization containing galena with exsolutions of Ag-bearing minerals were associated originally with the first episode of mineralization, even if they have since been modified by secondary vein movement, subsequent mineralization or low-temperature alteration. The

second episode of mineralization occurred at temperatures below those at which solid solution of galena and matildite forms, and the examples of galena associated with separate grains of Ag-bearing phases are thought to be mainly products of the second episode of mineralization. The paragenetic sequence of wolframite followed by As-Cu-Zn-Bi-Sb sulphides is typical of many quartz-wolframite deposits, including Panasqueira, and is attributed to deposition during a decrease in fluid temperatures accompanied by a progressive increase in sulphur fugacity (Bussink, 1984; Fortey *et al.*, 1984).

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