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Silver minerals of Panasqueira, Portugal: a new occurrence of Te-bearing canfieldite

THE tin-tungsten deposit of Panasqueira, Beira Baixa, Central Portugal, is Europe's largest producer of tungsten ore. The deposit consists of mineralized, sub-horizontal quartz veins with an average thickness of about 30 cm, which occur in a complex association of metamorphosed schists, phyllites, and greywackes. The mineralization is related to a granite batholith of Hercynian age, which is represented by a greisenized cupola exposed in the mine (Thadeu, 1951; Kelly and Rye, 1979). The most important mining areas nowadays are Barroca Grande, Panasqueira Deep, and Rebordões. Older areas are Rio, Corga Seca, Vale da Ermida, and Alvoroso (fig. 1).

High-quality concentrates of wolframite, cassiterite, and chalcopyrite are produced with 75.5% WO_3, 72% Sn and 22% Cu respectively. Production in 1984 amounted to 2085 tons wolframite, 158 tons cassiterite and 1427 tons chalcopyrite concentrate. The chalcopyrite concentrate contains varying amounts of silver. Gaines and Thadeu (1971) cite a 1970 figure of 868 g silver per ton concentrate. The source of this silver is uncertain. d'Orey (1967) reported native silver, freibergite, pyrargyrite, and stephanite associated with galena in samples from Vale da Ermida. More recent extensive studies of samples from other parts of the deposit do not confirm these observations, nor do they mention other silver-bearing minerals (Kelly and Rye, 1979; Bussink, 1984).

In this paper the occurrence of the silver minerals matildite, pavonite, canfieldite is reported, as well as rare Te-bearing canfieldite and argentiferous stannite. About thirty polished sections were studied

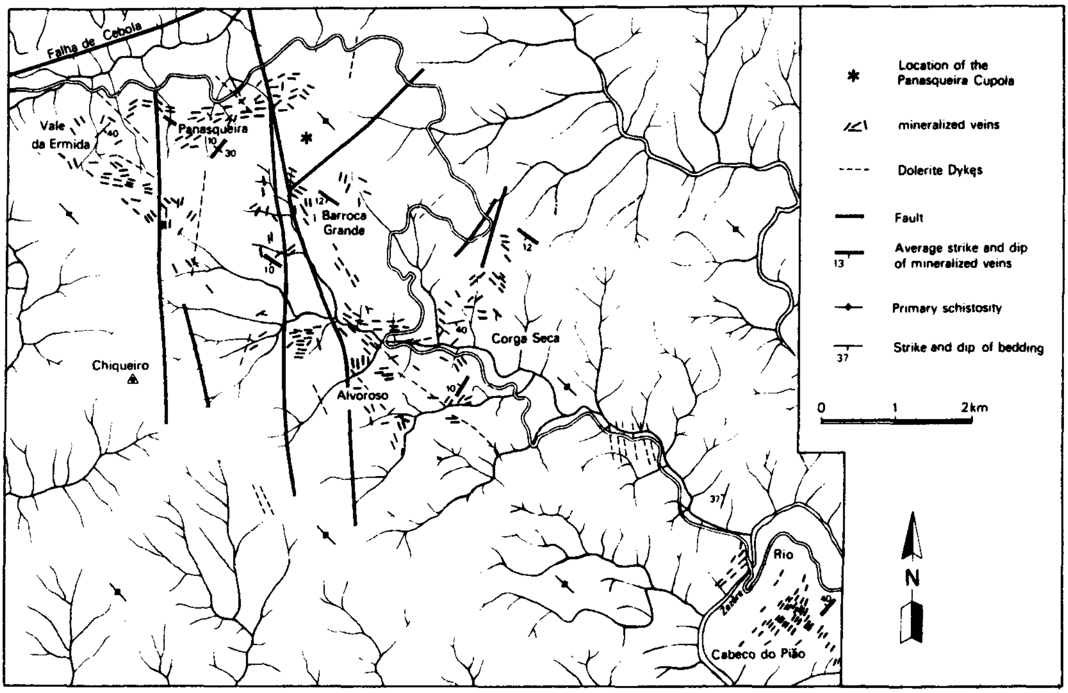

FIG. 1. The Panasqueira mining district (modified after Kelly and Rye, 1979, and Bussink, 1984).

optically, and a number of them were subsequently analyzed by electron microprobe (Table I). The samples were taken from several localities on level 2 at Barroca Grande as it was developed in April 1983.

Pavonite (< 30 μm) is present in only one sample, in which it is intergrown with bismuthinite in a matrix of chalcopyrite. Karup-Møller and Makovicky (1979) found that natural pavonite usually contains several weight percent Pb and Cu, which substitute for Ag and Bi. Panasqueira pavonite, however, contains very little Pb and Cu, as shown by the analyses in Table I.

Matildite occurs in very small amounts in most of the samples, mainly as small, anhedral grains (< 50 μm) and veinlets (< 220 μm × 20 μm) in arsenopyrite and chalcopyrite. Inclusions and intergrowths of matildite in native bismuth are common. Matildite may also be intergrown with bismuthinite and stannite; sometimes it forms rims around the former. Matildite is difficult to recognize where it is intergrown with bismuthinite: X-ray images of what looks, in reflected light, to be an aggregate of bismuthinite, may often reveal the presence of silver throughout the aggregate, mainly as intimately intergrown matildite. Sometimes matildite is present as single grains, which closely resemble galena, both in colour and reflectance. In one sample matildite is present as a network of exsolution lamellae in a groundmass of galena. This texture probably results from greatly reduced mutual solubility between matildite and galena with the inversion of α matildite → β matildite at 197 °C (Craig, 1982).

Argentiferous stannite has been confirmed in one sample, where a first indication of the silver content

Table I. Electron-microprobe analyses of silver-bearing minerals from Panasqueira, Portugal

mineral species		Te	Zn	Fe	Sn	Ag	Cu	S	Total
Te-canfieldite		17.10	0.12	2.91	9.41	56.44	3.13*	10.74	99.85
		21.09	0.04	1.00	10.19	58.33	1.74	8.99	101.38
				Fe	Sn	Ag	Cu	S	Total
canfieldite				-	11.43	70.55	0.13	17.41	99.52
				1.23	11.59	68.30	0.57	16.86	98.55
			Zn	Fe	Sn	Ag	Cu	S	Total
argentiferous stannite			1.01	13.42	27.08	0.48	28.36	29.50	99.85
			3.71	12.43	27.72	0.10	28.22	28.79	100.97
			1.15	12.78	27.83	0.29	29.38	29.37	100.80
	Pb	Sb	Zn	Fe	Bi	Ag	Cu	S	Total
pavonite	0.28	-	-	0.69	67.73	11.66	0.03	17.87	98.26
	0.28	0.12	2.05**	0.69	67.95	11.64	-	18.02	100.75
				Sb	Bi	Ag	Cu	S	Total
matildite				0.07	54.16	28.10	0.07	16.94	99.34
				0.06	54.49	28.16	0.10	17.15	99.96
				0.03	54.14	28.55	0.29	16.94	99.95

* Cu content due to groundmass chalcopyrite

** Zn content due to the influence of a large grain of sphalerite, close to the small grain of pavonite that was analyzed

Instrument: Cambridge Instruments Microscan Mk.9

Accelerating voltage: 20 kV. Beam current: 50 μA

Standards: pure elements, $CuFeS_2$, SnS, ZnS, HgTe, PbS, Sb_2S_3

Radiations: Cu-Kα, Ag-Lα, Sn-Lα, Fe-Kα, Zn-Kα, Te-Lα, Sb-Lα, Pb-Lα, Bi-Lα, S-Kα

of the stannite was the rapid tarnishing of the surrounding chalcopyrite. Chen *et al.* (1980) found this phenomenon to occur when chalcopyrite is in contact with silver-bearing minerals. As this has been observed in several other samples, it seems likely that argentiferous stannite is also present in these. The stannite may contain up to 0.5 wt. % silver (Table I). Stannite from elsewhere in the deposit (level 1, Barroca Grande) contains no silver above the detection limit of 0.01 wt. % (Wimmers, 1983).

Canfieldite was identified in two samples as very small grains (< 30 μm). It occurs in pyrite and chalcopyrite, either as anhedral, single grains, or intergrown with stannite.

Te-bearing canfieldite is present in one sample, as somewhat elongated, anhedral grains (< 50 μm). These occur in a groundmass of chalcopyrite and most are intergrown with native bismuth, matildite, and minor galena. One grain, however, is intergrown with sphalerite showing stannite inclusions; another is in contact with a small pyrrhotine grain. A typical assemblage with Te-bearing canfieldite is shown in fig. 2. The simultaneous occurrence of both canfieldite and Te-bearing canfieldite has not previously been reported. Te-bearing canfieldite has a slightly bluish tint compared with more pinkish brown canfieldite. Although rather few samples and grains are present, the association of canfieldite with stannite and that of Te-bearing canfieldite with native bismuth and matildite suggests that the two minerals have different places in the paragenetic sequence. On grounds of textural evidence, native bismuth is presumed to be an early phase (see e.g. Kelly and Rye, 1979). Thus it seems likely that Te-bearing canfieldite was deposited somewhat earlier and at higher temperatures than canfieldite.

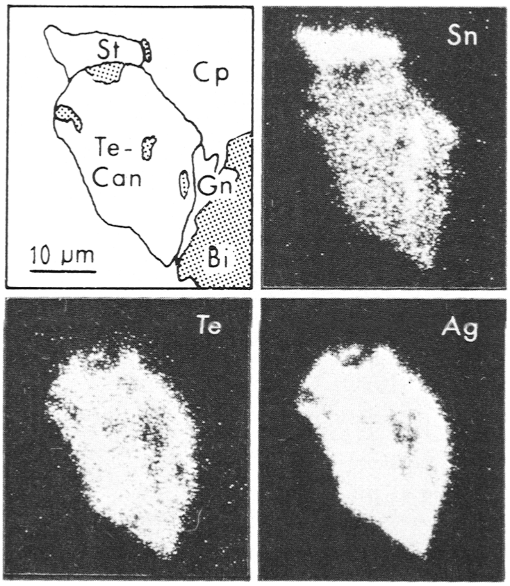

FIG. 2. Sketch and X-ray image for Sn-$L\alpha$, Te-$L\alpha$, Ag-$L\alpha$, showing the element distribution of a typical assemblage with Te-bearing canfieldite (Te-Can), stannite (St), galena (Gn), bismuth (Bi), and chalcopyrite (Cp). Specimen 4W4, Panasqueira.

The occurrences of Te-bearing canfieldite have been reviewed extensively by Soeda *et al.* (1984). According to them, Te-bearing canfieldites have been reported from three skarn deposits and two ore deposits, of which ore types are not given in the literature. This study reveals the presence of Te-bearing canfieldite in the Panasqueira deposit, which is of hydrothermal origin. Soeda *et al.* (1984) state that all Te-bearing canfieldites occur in similar mineral assemblages, particularly with pyrrhotine and/or native bismuth. The close association of the Panasqueira Te-bearing canfieldite with native bismuth and some pyrrhotine is thus in good accordance with their observations.

Soeda *et al.* (1984) suggest acid solutions, low oxidation and intermediate sulphidation states as formation conditions during the deposition of the mineral. Temperatures of formation for the association Te-bearing canfieldite, pyrrhotine, native bismuth, arsenopyrite, and stannite were estimated at 331–334 °C from fluid inclusions (Watanabe *et al.*, 1981) at Tsumo-mine. Estimates for temperatures of the main sulphide stage at Panasqueira are, however, somewhat lower, at around 275 °C (Bussink, 1984).

Discussion. The discovery of silver-bearing minerals in ores of the Panasqueira deposits throws a new light on the problem of the source of silver in the chalcopyrite concentrate. The suggestion of Bussink (1984) that silver is present in solid solution in chalcopyrite is proved to be wrong; electron microprobe analyses of chalcopyrite show that no Ag could be detected in amounts above the detection limit of 0.01 wt. %, compared to about 0.08 wt. % Ag in the chalcopyrite concentrate. On the other hand, silver minerals with a high silver content such as matildite may be responsible for a great part of the silver. Argentiferous stannite will also contribute to the total amount of silver present in the chalcopyrite concentrate, as stannite is a common minor constituent. The rare minerals canfieldite and pavonite play a subordinate role as contributors of silver. All these minerals mainly occur in chalcopyrite and they are extracted with the chalcopyrite concentrate. Minor silver, however, is lost in the sulphide tailings (Wimmers, 1983). This can be explained by the presence of some of the matildite in arsenopyrite, which goes into the tailings.

The occurrence of both canfieldite and Te-bearing canfieldite, as well as the fact that the silver minerals reported by d'Orey (1967) from Vale da Ermida were not confirmed to be present in the ores of level 2 at Barroca Grande, indicate that conditions during the sulphide stage of mineral formation were not uniform in the different parts of the deposit.

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Diamonds from nepheline mugearite? A discussion of 'Garnet websterites and associated ultramafic inclusions from a nepheline mugearite in the Walcha area, New South Wales, Australia'

STOLZ (1984) gives a thorough description of xenoliths in this dyke and discusses their likely origins and pressure-temperature (PT) equilibration regimes. He also comments on the megacrysts and host rock. This site is also being investigated by the present authors and has additional features to which Stolz's study can be related.

Diamond association. Most significantly, diamonds are present at this site. This association of diamonds with basaltic volcanism, in a region generally lacking 'classical' kimberlites, is an enigmatic feature of eastern Australia (Hollis *et al.*, 1983; Jacques *et al.*, 1984). Diamonds in the Copeton area, 150 km NNW of Walcha, occur in sub-basaltic gravels and are also recorded from a dolerite dyke (MacNevin, 1977). Copeton diamonds show unusual features (exceptional 'hardness', a new 'grospyte' mineral inclusion suite and an abnormal