STUDIES OF TYPE PAVONITE MATERIAL

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ABSTRACT

New compositional data of type pavonite from the Porvenir mine, Cerro Bonete, Sur Lipez, Bolivia suggest a general formula $4[(Ag,Cu)(Bi,Pb)_3S_5]$. X-ray studies gave a 13.36, b 4.02, c 16.38Å, β 94°11', confirming the unit cell reported by Nuffield (1954). Reflectance values are 470nm, 40.9-46.5; 546nm, 39.3-45.0; 589nm, 38.5-44.1; 650nm, 38.2-44.1. The micro-indentation hardness is VHN_{50} 172 to 197 kg/mm^2, average 188.

RÉSUMÉ

De nouvelles données de composition de pavonite type de la mine Porvenir, Cerro Bonete, Sur Lipez, en Bolivie, suggèrent une formule générale $4[(Ag,Cu)(Bi,Pb)_3S_5]$. Des études aux rayons-x ont donné les résultats suivants: a 13.36, b 4.02, c 16.38Å, β 94°11', confirmant la cellule d'unité rapportée par Nuffield (1954). Les valeurs de réflexion sont de 470nm, 40.9-46.5; 546nm, 39.3-45.0; 589nm, 38.5-44.1; 650nm, 38.2-44.1. La micro-dureté Vickers est de VHN_{50} 172 à 197 kg/mm^2, une moyenne de 188.

INTRODUCTION

Pavonite was described originally from Cerro Bonete, Sur Lipez, Bolivia by Nuffield (1954), with x-ray crystallography, $C2/m$, $a = 13.35$, $b = 4.03$, $c = 16.34$Å and $\beta = 94.5°$. The original chemical analyses by Herzenberg (in Ahlfeld 1926) and analysis by Nuffield (1954) showed the presence of Bi, Ag, Pb, Cu, Fe and trace amounts of Zn and As. Due to the presence of aikinite and chalcopyrite in the analyzed material, the Pb, Cu, Fe and a portion of Bi were attributed to impurities, and the chemical formula thus derived was $AgBi_3S_5$ with $Z = 4$. The formula was further supported by the fact that synthetic $AgBi_3S_5$ gave the same x-ray powder diffraction pattern. Van Hook (1960) reported that this synthetic phase had the same unit cell as that of pavonite. Today, $AgBi_3S_5$ is generally accepted as the ideal formula.

No pavonite with the ideal formula has been reported in nature, whereas "pavonites" with substantial amounts of Cu and Pb have been reported (Karup-Møller 1972). The observed compositions depart significantly from the ideal formula. Pavonite with slightly different x-ray powder data, or with triclinic symmetry, was also reported by Karup-Møller. In addition, a synthetic phase $(Ag,Cu)_2Bi_4S_7$ having x-ray powder data and cell dimensions ($a = 13.32$, $b = 4.04$, $c = 16.24$Å, $\beta = 92°56'$, $C2/n$?-PDF 22-1327) similar to those of pavonite has been reported (Shadlun *et al.* 1969). In view of the uncertainty in the composition of pavonite and its similarity to other phases in the Cu-Ag-Pb-Bi-S system, a re-examination of the type material using the electron microprobe was considered essential to characterize the mineral.

For this study, Prof. E. W. Nuffield kindly provided a tiny specimen of type pavonite from the Porvenir mine, Cerro Bonete, Sur Lipez, Bolivia, which he had examined in his original study in 1954.

X-RAY DATA

Precession photographs, taken with MoKα radiation, show a space-group symmetry $C2/m$, and $a = 13.36$, $b = 4.02$, $c = 16.38$Å, $\beta = 94°11'$, which confirm the unit cell reported by Nuffield. The x-ray powder-diffraction data taken with a Gandolfi camera using CuKα radiation are also exactly the same as those given by Nuffield. The extra lines in the powder pattern, or the triclinic cell as reported from other localities (Karup-Møller 1972) were not found in the type material.

REFLECTANCE AND MICRO-INDENTATION HARDNESS

Details of the equipment and techniques used in determining the reflectance and micro-indentation hardness have been reported in previous studies (Thorpe & Harris 1973).

The reflectance measurement of type pavonite at the four standard wavelengths are as follows: 470nm, 40.9-46.5; 546nm, 39.3-45.0; 589nm, 38.5-44.1; 650nm, 38.2-44.1.

The micro-indentation hardness for six determinations varies from $VHN_{50} = 172$ to 197 kg/mm^2, with an average value of 188.

COMPOSITION

The composition of pavonite was determined using a Materials Analysis Company electron microprobe operated at 25 kilovolts. Synthetic $AgBiS_2$, PbS and CuS were used as standards and corrections were applied using Edition VII of the program by Rucklidge & Gasparrini (1969). Several areas were examined and found to be homogeneous within the error limits of the analysis. The analysis gave Cu 1.7±0.2, Ag 11.1±0.2, Pb 3.5±0.3, Bi 64.5±0.5, S 18.3 ±0.2, total 99.1 wt %. The composition indicates that significant amounts of Cu and Pb are present in the pavonite type specimen. Using a density of 6.8 g/cm^3 as determined by Nuffield on synthetic $AgBi_3S_5$ and $Z = 4$, the analysis is calculated to $(Cu_{0.24}Ag_{0.93})_{\Sigma 1.17}(Pb_{0.15}Bi_{2.80})_{\Sigma 2.95}S_{5.17}$, comparable with the ideal formula $AgBi_3S_5$. Crystal structure studies have confirmed that Ag and Cu can occupy the same structural site, as in tetrahedrite $Cu_{12}Sb_4S_{13}$ (Wuensch 1964), and that disorder of Pb and Bi are also not uncommon, as for example, in the structures of nuffieldite $Pb_2Cu(Pb,Bi)Bi_2S_7$ (Kohatsu & Wuensch 1973), heyrovskyite Pb_6-Bi_2S_9, lillianite $Pb_3Bi_2S_6$ (Takagi & Takeuchi 1972), and $(Pb,As,Bi)Cu_4Bi_5S_{11}$ (Kupcik & Makovicky 1968). Assuming that similar substitutions occur in pavonite, the new compositional data suggest a general formula $4[(Ag,Cu)(Bi,Pb)_3S_5]$.
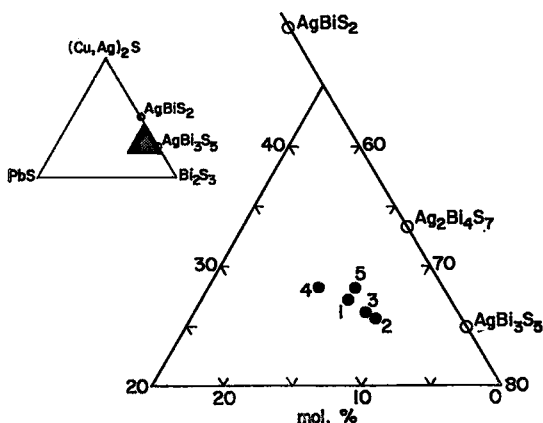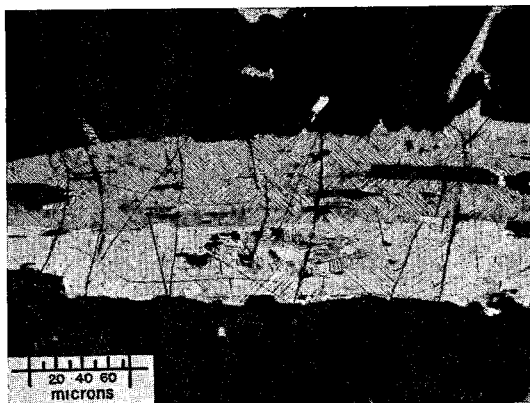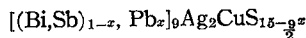

FIG. 2. "Pavonite" from Mike mine, San Juan County, Colorado. The mineral consists of aikinite (dark grey, strongly etched phase) and berryite (light grey, lighter etched phase). Etched with Cr_2O_3 (50%) + HCl conc. for 30 seconds.

The new formula also agrees well with the analyses given by Karup-Møller (1972). The compositions of pavonite show a range with $Cu/(Cu + Ag) = 0.21$-0.30, and $Pb/(Pb + Bi) = 0.04$-0.06. The relatively small amount of Pb substitution for Bi is probably limited by the significant difference in atomic radii (Pb^{2+} 1.20Å, Bi^{3+} 0.96Å) and the valence charges of Pb and Bi. Chen & Chang (1974) showed that $AgBi_3S_5$ and $CuBi_3S_5$ formed complete solid solution at 454°C. However, the apparent variation of composition, shown in Figure 1, may not be real but due to poor analyses.

Karup-Møller (1972) assumed that Ag and Cu occupy different structural locations, and proposed a formula

$$[(Bi,Sb)_{1-x}, Pb_x]_9Ag_2CuS_{15-\frac{9}{2}x}$$

with $x \leqslant 0.1$ for pavonite.† The equipoints for the space groups corresponding to the diffraction aspect $C^*/^*$ have orders of 8, 4, and 2. Karup-Møller's formula does not satisfy these requirements.

A specimen labelled as "pavonite" from Mike mine, San Juan County, Colorado, was also studied. Optically, the material resembles a twinned mineral with the larger areas showing very little variation in composition by microprobe analysis, suggesting a single phase. However, after etching with Cr_2O_3(50%) + HCl conc. for at least 30 seconds, these areas were

FIG. 1. Distribution of compositions of pavonite in the $(Cu,Ag)_2S$-PbS-Bi_2S_3 diagram. (1) this study; (2-5) Karup-Møller (1972).

† $[(Bi,Sb)_{1-x}, Pb_x]_9Ag_2CuS_{15-9\cdot\frac{1}{2}x}$ was given in Karup-Møller (1972), apparently due to typographical error.

found to consist of two phases, a heavily-etched aikinite and a more lightly-etched berryite (Fig. 2). The aikinite has the composition $Cu_{0.8}Pb_{0.8}Bi_{1.0}S_{2.7}$, and the berryite, $(Cu_{2.0}Ag_{1.3})Pb_{2.0}Bi_{4.8}S_{11.0}$. The compositions were determined on areas where the two phases had exsolved to coarser laths and this identification was confirmed by x-ray powder diffraction studies. The intergrown texture of these two phases, as shown in Figure 2, suggests the exsolution may have developed from the cooling of a high-temperature homogeneous phase.

The results of this study emphasize the importance of etching during the examination of all sulphosalts and that intergrowths of optically and chemically similar sulphosalts are probably more common than is supposed. Also, investigators should be cautioned that optical analysis alone is not sufficient to characterize a complex sulphosalt, but single-crystal studies are required.

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