MINERALOGICAL NOTES

THE CRYSTALLOGRAPHY OF COLUSITE

PHILIP N. DANGEL AND B. J. WUENSCH, *Ceramics Division,*
Department of Metallurgy and Materials Science,
Massachusetts Institute of Technology, Cambridge,
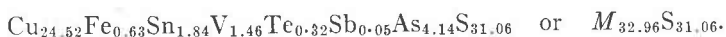*Massachusetts 02139.*

ABSTRACT

Colusite, a Cu, V, Sn, As sulfide, is isometric, space group $P\bar{4}3m$, with $a = 10.629 \pm .003$ Å. The structure is a superstructure based upon a sphalerite-like arrangement of atoms, but is not related to structures of the tetrahedrite family in spite of a similar supercell geometry. Four different sets of idealized atomic positions are permitted by the subcell-supercell relationship. Only one array is compatible with the chemical information presently available.

Colusite is a sphalerite-related sulfide of Cu, Sn, V, and As which occurs at Butte, Montana. The mineral has a distinctive bronze color. Its morphology is unusual in that the tetrahexahedron {210} and the tetrahedron are both prominent forms. The mineral, first fully described by Landon and Mogilnor (1933), corresponds to the "bronze enargite" mentioned by Murdoch (1917) and tentatively assigned to the tetrahedrite group by Schneiderhöhn and Ramdohr (1931). Concurrent with Landon and Mogilnor's description, Zachariasen (1933) proposed that colusite had the sphalerite structure, but with approximately one-quarter of the sulfur atoms statistically absent. Both reports were subsequently shown to be only partially correct. Nelson (1939) and Berman and Gonyer (1939) independently demonstrated that the original chemical analysis was in error. Berman and Gonyer further found that colusite actually possessed a superstructure based on the sphalerite structure and had a lattice constant double that reported by Zachariasen. A powder diffraction study by Murdoch (1953) confirmed the larger cell.

Many references assign space group $I\bar{4}3m$ to colusite. This has no doubt arisen because the similar dimensions of the tetrahedrite and colusite supercells suggested that colusite might be a member of the tetrahedrite group (Berman and Gonyer, 1939). The space group of colusite had in fact not been determined. The powder pattern reported by Murdoch (1953) contains many reflections which violate the pattern

of systematic absences required by a body-centered lattice. The space group of colusite therefore cannot be the same as that of tetrahedrite. The stoichiometries of the phases further suggest that their structures may be quite distinct. Members of the tetrahedrite group have compositions $Cu_{12}(Sb,As)_4S_{13}$ (Wuensch, 1964; Wuensch et al., 1966). The composition of colusite, while still uncertain, has a metal:sulfur ratio which is closer to unity. The results of Berman and Goyner (1939) provide cell contents for colusite of

$$Cu_{24.52}Fe_{0.63}Sn_{1.84}V_{1.46}Te_{0.32}Sb_{0.05}As_{4.14}S_{31.06} \quad \text{or} \quad M_{32.96}S_{31.06}.$$

A recent microprobe analysis of colusite by Springer (1969) provides a composition

$$Cu_{25.04}(V_{0.57}, Sn_{0.43})_{3.25}(Sb_{0.08}, As_{0.92})_{4.00}S_{31.68},$$
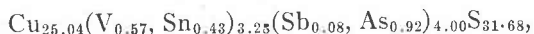
assuming a total of 64 atoms per cell. Tellurium present in earlier analyses was shown by Springer to be due to probable contamination by a tellurian tetrahedrite. The As:Sb and V:Sn ratios were found to be variable, and this may account for the marked zoning in colusite observed by Nelson (1939).

The crystallography of colusite was examined in the present work in order to establish its relationship to the tetrahedrite family. Our interest was in part stimulated by an observation of Parthé (1964). The valence electron concentration of colusite does not permit formation of a tetrahedral structure. Alternatively, the compositions previously reported may be incorrect.

The crystals used in the present work were obtained from the same specimen (Harvard Catalogue No. 92255) studied by Berman and Gonyer. A qualitative microprobe analysis of the material indicated the presence of Cu, As, V, Sn and S as major components, plus a small amount of Fe. These were the only elements detectable. Some material was found to consist of a two-phase mixture of colusite and smaller amounts of a Sn-free phase. These mixtures produced diffraction patterns resembling those which might be obtained from a single crystal with lineage structure. Intergrowths of tetrahedrite and colusite with textures resembling those observed in the present work were described by Landon and Mogilnor (1933). Accordingly, we suspect that the second phase was tetrahedrite rationally intergrown with colusite.

Very small (ca. 0.02 mm) fragments of colusite were selected for X-ray examination in order to minimize the possibility of tetrahedrite inclusions. Precession and Weissenberg photographs showed that colusite is

isometric with diffraction symmetry $m3m$. No systematic absences of reflections were observed.[1] The diffraction symbol for colusite is therefore $m3mP \cdots$, which permits $P\bar{4}3m$, $P43$, and $Pm3m$ as possible space groups. The morphology of colusite has marked $\bar{4}3m$ symmetry, and this permits designation of $P\bar{4}3m$ as the correct space group. An attempt was made to obtain a precise lattice constant from a back-reflection Weissenberg film. Only a few sphalerite substructure reflections were observable in the back-reflection region. Not enough data were obtained to permit a least squares extrapolation. The value of a reported in Table 1 is an average of the results obtained from six high index $hk0$ reflections, and agrees with values obtained by previous workers.

The superstructure intensities present in diffraction patterns obtained from colusite are not only weaker, but bear no relation to corresponding intensities in patterns obtained from tetrahedrite and tennantite. This, along with different space groups and stoichiometries, implies that colusite and tetrahedrite are different sphalerite derivative structures. The weakness of all superstructure intensities in colusite further suggests that most, if not all, atoms in the structure are located close to the positions of an ideal sphalerite-like array. The subcell-supercell relationship permits only a limited number of possibilities for such a structure. In deriving a superstructure with space group $P\bar{4}3m$, a number of the symmetry operations present in the sphalerite structure must be suppressed. The point symmetries $\bar{4}3m$ which are retained must coincide with those present in the $P\bar{4}3m$ supercell. The ideal sphalerite subcell has $\bar{4}3m$ symmetry at four independent locations: 000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, and $\frac{3}{4}\frac{3}{4}\frac{3}{4}$. Placement of each of the four points in coincidence with the $\bar{4}3m$ symmetry center in the supercell leads to only four possible sets of idealized coordinates for the structure of colusite. Two results are tabulated in Table 2.

TABLE 1. LATTICE CONSTANT OF COLUSITE
(λCuK$\alpha_1 = 1.54051$ Å)

Zachariasen (1933)[a]	$1/2 \times 10.629 \pm .002$ Å
Berman and Gonyer (1939)[a]	$10.62 \pm .01$
Murdoch (1953)[a]	10.629
present work	$10.629 \pm .003$

[a] Reported value multiplied by 1.00202 to convert from kX units to Å.

[1] The absence of an n-glide (which would require space group $P\bar{4}3n$) was established only with difficulty since most superstructure intensities were very weak. However, Weissenberg photographs revealed the definite presence of 333 and 993 reflections and extremely weak but probable 773 and 555 reflections.

The remaining two possibilities are obtained upon interchanging metal and sulfur positions for each of the two models listed. If Cu, (V,Sn) and (As,Sb) are ordered, as suggested by Springer, the stoichiometry $Cu_{25}(V,Sn)_3(As,Sb)_4S_{32}$ can be accommodated only by the equipoint multiplicities provided by model 1. To resolve this question, a complete crystal structure determination of colusite is in progress.

TABLE 2. SETTINGS OF A SPHALERITE-LIKE ARRAY OF ATOMS PERMITTED IN SPACE GROUP $P\bar{4}3m$ (TWO ADDITIONAL MODELS ARE OBTAINED UPON INTERCHANGING THE DESIGNATIONS M AND S)

	M	S
Model 1	1 a $\bar{4}3m$ 0 0 0 1 b $\bar{4}3m$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ 3 c $\bar{4}2m$ 0 $\frac{1}{2}$ $\frac{1}{2}$ 3 d $\bar{4}2m$ $\frac{1}{2}$ 0 0 12 i m xxz $x \approx \frac{1}{4}$ $z \approx 0$ 12 i m xxz $x \approx \frac{1}{4}$ $z \approx \frac{1}{2}$	4 e $3m$ xxx $x \approx \frac{1}{8}$ 4 e $3m$ xxx $x \approx \frac{5}{8}$ 12 i m xxz $x \approx \frac{3}{8}$ $z \approx \frac{1}{8}$ 12 i m xxz $x \approx \frac{1}{8}$ $z \approx \frac{5}{8}$
Model 2	4 e $3m$ xxx $x \approx \frac{1}{4}$ 4 e $3m$ xxx $x \approx \frac{3}{4}$ 6 f mm $x00$ $x \approx \frac{1}{4}$ 6 g mm $x\frac{1}{2}\frac{1}{2}$ $x \approx \frac{1}{4}$ 12 h 2 $x\frac{1}{2}0$ $x \approx \frac{1}{4}$	4 e $3m$ xxx $x \approx \frac{3}{8}$ 4 e $3m$ xxx $x \approx \frac{7}{8}$ 12 i m xxz $x \approx \frac{1}{8}$ $z \approx \frac{3}{8}$ 12 i m xxz $x \approx \frac{5}{8}$ $z \approx \frac{7}{8}$

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RELATIONSHIP BETWEEN PRESSURE SHADOWS AND SHEAR FRACTURE ORIENTATION

H. ROBERT BURGER, BARBARA E. PERRY, AND BRIAN WHITE,
*Department of Geology, Smith College,
Northampton, Massachusetts 01060.*

ABSTRACT

Quartz pressure shadows surrounding authigenic pyrite grains in a shale from the Porsanger Dolomite Formation, West Finnmark, Norway, are associated with contemporaneous shear and extension fractures. Maximum compressive stress (σ_1) orientations based on pressure shadow geometry agree with σ_1 orientations derived from fracture sets.

Numerous shale samples from a unit within the Porsanger Dolomite Formation near West Finnmark, Norway, contain abundant pyrite grains wholly or partially surrounded by growths of feather quartz. These structures represent what has classically been known as "pressure shadows" and commonly are thought to illustrate pressure-solution phenomena. Detailed and comprehensive studies of pressure shadow relationships and genesis are few, but the works of Mügge (1930) and Pabst (1931) do present thorough analyses; the reader is referred to these works for a general introduction to the subject.

The significant aspect of the pressure shadows found in the Norway samples is their occurrence with sets of shear and extension fractures (Fig. 1). The consistent angular relationship among the fractures which agrees with that derived experimentally (Fig. 2), observation of the correct sense of movement on fractures believed to be shear fractures, and lack of any observed movement on fractures ascribed as extensional in origin supports the belief that the fractures in these samples form sets from which the direction of the maximum compressive stress (σ_1) can be