American Mineralogist, Volume 79, pages 750–762, 1994

New occurrences and refined crystal chemistry of colusite, with comparisons to arsenosulvanite

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ABSTRACT

Structural refinements of Sn-rich and Sn-poor colusite from the Lorano marble quarry, Italy, revealed that the crystals are isometric and belong to space group $P\bar{4}3n$. For Sn-rich colusite, CuS_4 and $(As,Sn)S_4$ tetrahedra are connected through corner sharing in a sphalerite structure with the composition $Cu_{26}Sn_2As_4S_{32}$, and two V atoms are stuffed into interstitial sites in a sulvanite-like arrangement. For Sn-poor colusite, CuS_4 and AsS_4 tetrahedra are connected in a similar arrangement through corner sharing in a sphalerite-like structure with the composition $Cu_{24}As_6S_{32}$, with the two V atoms located in the same arrangement as in Sn-rich colusite. The number of valence electrons contributed by metal atoms is 64 for Sn-rich and Sn-poor colusite, whereby the substitution of two Sn atoms with two As atoms is balanced by two vacancies in one of the Cu sites. Based on structural and compositional considerations, a general formula for colusite is $Cu_{24+x}V_2(As,Sb)_{6-x}(Sn,Ge)_xS_{32}$, where $x = 0–2$.

Selected-area electron diffraction (SAED) patterns and high-resolution transmission electron microscopy (HRTEM) imaging of Sn-poor colusite with a composition of $Cu_{24.3}V_{2.0}(As_{5.7}Sb_{0.6}Fe_{0.1})S_{32}$ from the epithermal Gies gold-silver telluride deposit, Montana, revealed that it is composed of domains of ordered and disordered cations. The ordered domain has space group $P\bar{4}3n$ and $a = 1.068$ nm and consists of Sn-poor colusite. The disordered domain, with similar composition, has space group $F\bar{4}3m$ and $a = 0.534$ nm. Simulated images based on proposed structural models produced an acceptable match to observed HRTEM images. One-dimensional modulations, with a wavelength of 3.57 nm, are possibly responsible for the optical anisotropism and possibly for the anomalously low Vickers hardness.

Another isometric sulfosalt, arsenosulvanite $[Cu_3(As,V,Sb,Fe,Ge)S_4]$, with X-ray and optical properties similar to colusite, has been introduced in the mineralogical literature. The results of the present study and a review of the literature on the chemical composition, X-ray crystallography, and crystal chemistry of colusite and arsenosulvanite strongly suggest the same identity for the two species.

INTRODUCTION

Colusite is an isometric copper vanadium sulfosalt that forms in porphyry copper (e.g., Terziev, 1966; Springer, 1969; Kachalovskaya et al., 1975; Criddle and Stanley, 1993), copper vein (Gazizova and Yarenskaya, 1966), porphyry molybdenum copper (Strashimirov, 1982), volcanogenic massive sulfide (Bideaux, 1960; Matsukuma and Yui, 1979), and gold vein deposits (Kessler et al., 1981; Tourigny et al., 1993), as well as in marble (Orlandi

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0003–004X/94/0708–0750$02.00

TABLE 1. Chemical analyses of colusite

	1*	2*	3*	4	5	6	7	8	9	10	11	12	13	14	15
Cu	48.0	46.9	47.99	50.8	49.5	50.1	49.5	50.41	47.98	49.40	48.5	47.4	49.3	50.4	49.5
V	nd	nd	2.28	3.2	3.0	3.3	3.1	3.52	2.95	3.18	2.7	2.2	2.7	3.6	3.05
Fe	nd	nd	1.09	nd	nd	nd	nd	0.58	1.10	0.35	nd	1.8	nd	nd	1.5
Ge	nd	nd	nd	nd	nd	0.63	1.1	2.85	0.14	4.52	6.2	nd	nd	nd	nd
Sn	6.9	5.8	6.71	7.3	5.31	0.26	6.6	3.17	8.42	nd	nd	7.6	5.9	1.3	4.65
As	6.8	8.4	9.54	8.6	8.6	13.6	8.8	8.12	3.61	8.64	10.0	7.5	12.1	10.7	11.05
Sb	2.6	0.64	0.19	1.1	1.1	1.4	0.92	nd	6.59	0.34	nd	1.4	nd	nd	nd
S	27.5	29.2	30.65	30.1	31.6	31.2	30.2	29.69	29.77	33.13	32.3	31.2	28.2	31.9	30.55
Total	94.8	95.8	99.71	100.0	99.1	100.49	100.22	98.69	101.06	101.24	99.7	99.3	98.2	97.9	100.30
Unit-cell content recalculated on the basis of 32 S atoms															
Cu	28.182	25.933	25.281	27.250	25.292	25.927	26.464	27.414	26.022	24.075	24.2	24.530	28.227	25.510	26.161
V	nd	nd	1.498	2.141	1.912	2.130	2.067	2.388	1.996	1.193	1.7	1.420	1.928	2.273	2.011
Fe	nd	nd	0.653	nd	nd	nd	nd	0.359	0.679	0.194	nd	1.060	nd	nd	0.902
Ge	nd	nd	nd	nd	nd	0.286	0.515	1.358	0.067	1.931	2.7	nd	nd	nd	nd
Sn	2.170	1.718	1.894	2.098	1.454	0.072	1.891	0.924	2.447	nd	nd	2.107	1.810	0.353	1.317
As	3.386	3.939	4.262	3.727	3.727	5.969	3.990	3.745	1.661	3.571	4.2	3.292	5.876	4.593	4.953
Sb	0.797	0.185	0.052	nd	0.293	0.378	0.257	nd	1.661	0.087	nd	0.373	nd	nd	nd
S	32.000	32.000	32.000	32.000	32.000	32.000	32.000	32.000	32.000	32.000	32.000	32.000	32.000	32.000	32.000

Note: column numbers are defined as follows: 1. Leonard mine, Butte, Montana (Landon and Mogilnor, 1933), also contains 3.0 wt% Te; 2. Mountain View mine, Butte, Montana (Landon and Mogilnor, 1933), also contains 0.4 wt% Te and 0.9 wt% Zn; 3. Butte, Montana (Berman and Gonyer, 1939), also contains 1.26 wt% Te; 4. Butte, Montana (Lévy, 1967); 5. Butte, Montana (Springer, 1969); 6. and 7. Lorano, Italy (Orlandi et al., 1981); 8. Gay deposit, Russia (Pshenichnyy et al., 1974), also contains 0.35 wt% Zn; 9. Kayragach deposit, Uzbekistan (Spiridonov et al., 1984), also contains 0.07 wt% Zn and 0.40 wt% Mo; 10. San Fernando deposit, Cuba (Krapiva et al., 1986), also contains 0.04 wt% Ni, 0.33 wt% Zn, and 0.12 wt% Bi; 11. An unnamed Cu deposit, Kazakhstan (Mitryaeva et al., 1968); 12. Chizeuil, France (Delfour et al., 1984), also contains 0.3 wt% Mo; 13. and 14. Bor deposit, Serbia (Kachalovskaya et al., 1975); 15. Medet deposit, Bulgaria (Strashimirov, 1982).

* Te derived from an intergrowth with tellurian tennantite.

et al., 1981). It usually occurs in minor or trace amounts and coexists with a wide variety of sulfides (e.g., pyrite, bornite, sphalerite, chalcopyrite, and galena), sulfosalts (e.g., enargite, sulvanite, mawsonite, luzonite, tetrahedrite, and tennantite), and tellurides (e.g., hessite). As a result of similar X-ray and optical properties and chemical compositions, colusite may be confused easily with another isometric copper sulfosalt, arsenosulvanite [$Cu_3(As,V,Sb,Fe,Ge)S_4$]. In this paper, we review the literature on the chemical compositions and crystal chemistry of colusite and arsenosulvanite to evaluate whether they can be unambiguously distinguished as two mineral species. We present compositional, HRTEM, and SAED studies of Sn-free colusite from the Gies gold-silver telluride deposit, Montana, in addition to new compositional data for colusite from marbles in the Carrara area (Lorano and Calagio), Italy, and single-crystal structural refinements of Sn-poor and Sn-rich colusite from Lorano.

CHEMISTRY AND STRUCTURE OF COLUSITE

Colusite was first noted as a probable new mineral by Murdoch (1916) and was termed bronze enargite. However, the first published account of colusite was by Landon and Mogilnor (1933), who presented partial analyses of samples from the Leonard and Mountain View mines from the Butte district, Montana (Table 1, analyses 1 and 2, obtained by the Geological Department of the Anaconda Copper Mining Company), and a new complete analysis obtained by S. T. Gross, which gave results markedly different from the preceding ones. Subsequent studies by Berman and Gonyer (1939; Table 1, analysis 3) and Nelson (1939) confirmed the first partial analyses but not that obtained by Gross. Nelson (1939) suggested that Gross's analysis was not representative of colusite and should not be considered further. Berman and Gonyer (1939) first indicated that V is an essential component of colusite and proposed the formula $Cu_{24}(As,Sn,V,Fe,Te)_8S_{32}$. However, Lévy (1967), through electron microprobe studies, explained the presence of Te in colusite from Butte as being due to impurities of a white associated mineral that has a composition corresponding to tellurian tennantite. Lévy's (1967) new and complete analysis (Table 1, analysis 4) was confirmed by Springer (1969; Table 1, analysis 5).

After its discovery at Butte, colusite was reported from several other localities, primarily copper sulfide deposits. Table 1 shows the chemical compositions of colusite from various localities; Cu, V, As, and S are essential components, whereas Sn, Sb, Fe, and Ge are often present in significant quantities.

The first X-ray diffraction study of colusite was by Zachariasen (1933), who proposed a face-centered unit cell (a = 0.5314 nm) and a sphalerite-type structure. In a comprehensive account of the troubled history of X-ray crystallographic studies of colusite, Dangel and Wuensch (1970) pointed out that Berman and Gonyer (1939) found that colusite had a lattice constant twice that reported by Zachariasen (1933). They also indicated that Murdoch (1953) confirmed the larger cell, and that "many references assign space group $I\bar{4}3m$ to colusite." Their single-crystal study corroborated the cell parameter of 1.0629 nm for colusite and proposed that it belongs to the space group $P\bar{4}3m$.

More recently, Orlandi et al. (1981), on the basis of

Table 2. Experimental data for crystals of colusite from Lorano

Mineral	Sn-poor colusite (crystal 1)	Sn-rich colusite (crystal 2)
Space group	$P\bar{4}3n$	$P\bar{4}3n$
a (nm)	1.0538(1)	1.0621(1)
Unique reflections	576	590
R_{int}	0.047	0.051
Reflections with $F_o > 4\sigma(F_o)$	467	434
R	0.059	0.055
$R_w\{w = 1/[\sigma(F_o)]^2\}$	0.048	0.043

systematic absences observed on precession and Weissenberg photographs obtained from crystals of colusite from the Lorano marble quarry, indicated $P\bar{4}3n$ as the correct space group. Wuensch (personal communication in Orlandi et al., 1981) independently determined that the weak reflections 333, 993, 773, and 555 (violating the $P\bar{4}3n$ symmetry) recognized by Dangel and Wuensch (1970) were spurious and that the correct space group is $P\bar{4}3n$. Orlandi et al. (1981) determined cell edges of a = 1.0538 and 1.0621 nm for Sn-poor and Sn-rich colusite from Lorano, respectively.

The various choices of space group assigned to colusite are understandable considering the peculiar diffraction pattern characterized by classes of reflections with strongly differing intensities. Short exposure times could result in a full class of reflections being lost, with consequent mistakes in the choice of the unit-cell parameter (0.530 nm, instead of 1.060 nm) and lattice centering.

Orlandi et al. (1981) also reviewed the literature on colusite and, primarily on the basis of compositional data and preliminary structural data, proposed that its unit cell consists of 66 atoms rather than the 64 atoms that were assumed previously. They suggested that the ideal chemical formula for colusite is $Cu_{26}V_2(As,Sn)_6S_{32}$, implying fixed atom ratios for Cu:V:S of 26:2:32. Despite the studies of Orlandi et al. (1981), the number of Cu atoms in colusite from worldwide localities listed in Table 1 (assuming 32 S atoms) ranges from 22.471 to 28.227 and does not agree well with their proposed fixed value of 26 Cu atoms. The Te-bearing colusite samples from Butte (Table 1, analyses 1, 2, and 3) were excluded from this range. If samples of colusite from Bor (Table 1, analysis 13 only) that contain anomalously low amounts of S are also omitted, the range of Cu atoms in colusite is 24.075–27.414. Most compositions of colusite contain between 24 and 26 Cu atoms (Table 1).

The crystal chemistry of colusite is revised and reassessed here on the basis of structural studies carried out on the two crystals from the Lorano quarry that were originally studied by Orlandi et al. (1981). The two crystals have different chemical compositions: crystal 1 is Sn-poor colusite, and crystal 2 is Sn-rich colusite. The latter has a composition more typical of colusite found elsewhere (Table 1).

The intensity data were collected with a Philips PW 1100 single-crystal automatic diffractometer at the following conditions: operating voltage and current of 48 kV and 28 mA (T = 298 K), Mo$K\alpha$ radiation (λ = 0.71069 Å), a graphite crystal monochromator, a scan range (ω) of 2–30°, and a mode of ω–2θ. The absorption correction is derived from North et al. (1968). Unit-cell parameters, reliability (R) factors, and other experimental data are included in Table 2. The structure determination was first carried out for crystal 2 (Sn-rich colusite), assuming a sphalerite-like topology and distributing the metal atoms according to the $P\bar{4}3n$ space group. However, the refinement failed because the R value did not fall below 0.20. For our subsequent attempt, we assumed that V atoms were located in the structure in the same way as they are in sulvanite (Cu_3VS_4), where the VS_4 tetrahedra share their six edges with CuS_4 tetrahedra, as found by Pauling and Hultgren (1933) and discussed by Pauling (1965). A reliable model was obtained using this assumption, with CuS_4 and $(As,Sn)S_4$ tetrahedra connected through corner sharing in a sphalerite-like scaffolding with the composition $Cu_{26}Sn_2As_4S_{32}$ and two V atoms in interstitial sites at 0,0,0, and ½,½,½ in a sulvanite-like arrangement.

Table 3. Atomic positional coordinates, multiplicity factors, and anisotropic displacement parameters in Sn-rich colusite (crystal 2) from Lorano

Atom	*x*	*y*	*z*	*K*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
V	0.0	0.0	0.0	0.083	0.0096	0.0096	0.0096	0.0	0.0	0.0
	0.0	0.0	0.0	0.0	0.0011	0.0011	0.0011	0.0	0.0	0.0
Cu1	0.2570	0.0	0.0	0.5	0.0124	0.0152	0.0257	0.0050	0.0	0.0
	0.0001	0.0	0.0	0.0	0.0007	0.0010	0.0012	0.0015	0.0	0.0
Cu2	0.2495	0.2495	0.2495	0.333	0.0264	0.0264	0.0264	0.0012	0.0012	0.0012
	0.0002	0.0002	0.0002	0.0	0.0004	0.0004	0.0004	0.0005	0.0005	0.0005
Cu3	0.25	0.0	0.5	0.25	0.0112	0.0285	0.0285	0.0	0.0	0.0
	0.0	0.0	0.0	0.0	0.0019	0.0012	0.0012	0.0	0.0	0.0
0.64As + 0.36Sn	0.25	0.5	0.0	0.25	0.0173	0.0066	0.0066	0.0	0.0	0.0
	0.0	0.0	0.0	0.0	0.0013	0.0006	0.0006	0.0	0.0	0.0
S1	0.1192	0.1192	0.1192	0.333	0.0186	0.0186	0.0186	−0.0015	−0.0015	−0.0015
	0.0002	0.0002	0.0002	0.0	0.0014	0.0014	0.0014	0.0014	0.0014	0.0014
S2	0.3704	0.3734	0.1220	1.0	0.0140	0.0061	0.0207	−0.0004	0.0001	−0.0020
	0.0002	0.0002	0.0002	0.0	0.0018	0.0015	0.0016	0.0013	0.0015	0.0012

Note: standard deviations are given in the second row for each atom.

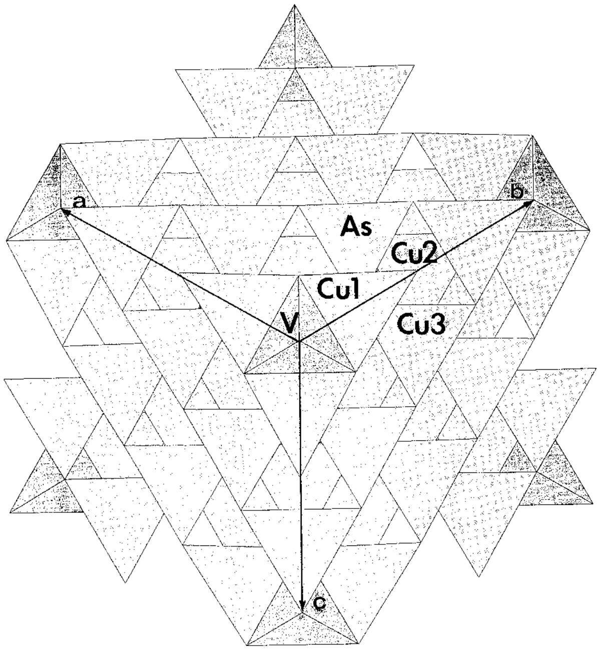

Fig. 1. The crystal structure of colusite as seen along [111]. The figure was generated using the program Atoms (Dowty, 1990).

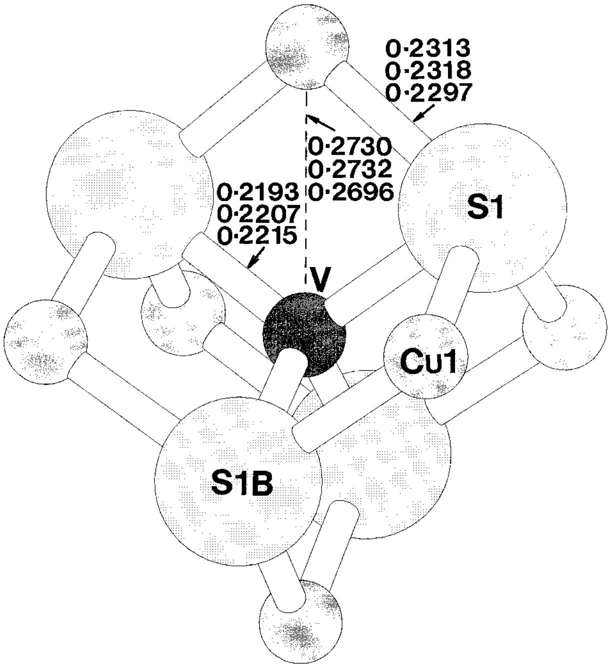

Fig. 2. The structural arrangement around the VS_4 tetrahedron, with indicated bond distances (nm) for V-S, Cu-S, and V-Cu in Sn-rich colusite (top), Sn-poor colusite (middle), and sulvanite (bottom). The figure was generated using the program Atoms (Dowty, 1990).

By refining this model, the R value dropped to 0.055 for 434 reflections with $F_o > 4\sigma(F_o)$ (reflections $\bar{2}22$, 222, and 440 were rejected as apparently affected by extinction), with $R_w = 0.043$. In the last least-squares cycles, the occupancy factors of As and Sn in site 6c at ¼,½,0 were introduced among the refinement parameters. The atomic parameters for the refined model are presented in Table 3. The resulting formula is $Cu_{26}V_2As_4Sn_2S_{32}$. The structure is represented in Figure 1 as seen along [111], whereas Figure 2 presents the peculiar sulvanite-like arrangement around the VS_4 tetrahedron.

A similar refinement was carried out with data collected from crystal 1 (Sn-poor colusite), placing As in site 6c, at ¼,½,0. The refinement converged to $R = 0.085$ for 467 reflections with $F_o > 4\sigma(F_o)$ (reflections $\bar{2}22$, 222, and 440 were rejected as apparently affected by extinction). A difference in R values of 0.055 for the Sn-rich variety, compared with 0.085 for the Sn-poor variety, is difficult to rationalize, considering that the low R value (0.055) was obtained for the Sn-rich variety, which should possess the higher structural disorder, with Sn and As distributed in the same site. Furthermore, relatively high displacement parameter values were obtained for Cu2 in the Sn-poor colusite.

We refined the site-occupancy factor (K) for Cu2 in Sn-poor colusite and obtained a value of K(Cu2) = 0.25 instead of the theoretical value of ⅓, corresponding to full occupancy of the site. Since K(Cu1) = ½ and K(Cu3) = ¼, the Cu content in the unit cell of the Sn-poor colusite is 24 instead of 26. As a check, we also refined K(Cu1) and K(Cu3) in the Sn-poor colusite and K(Cu1), K(Cu2), and K(Cu3) in the Sn-rich colusite; however, all these values remained essentially the same as the theoretical values.

The final R value for Sn-poor colusite, with 24 Cu atoms in the unit cell, is $R = 0.059$ ($R_w = 0.048$), which compares satisfactorily with the R value of Sn-rich colusite (0.055). The atomic parameters for Sn-poor colusite are given in Table 4.

The ideal crystal-chemical formulae for the two varieties of colusite from Lorano are $Cu_{24}V_2As_6S_{32}$ and $Cu_{26}V_2Sn_2As_4S_{32}$. The total number of valence electrons (ve) contributed by metal atoms is 64 for both formulae; the substitution of the two Sn atoms (4 ve) for two As atoms (5 ve) is balanced by two vacancies in the Cu2 site.

The chemical data presented by Orlandi et al. (1981) do not indicate a content of 24 Cu atoms for Sn-poor colusite (Table 1, analysis 6). It is possible that errors were made in the determination of the chemical contents because of unsuitable standards. Therefore, as an independent chemical check was necessary, three new colusite specimens, two from Lorano and one from Calagio (also in the Carrara area), were analyzed by electron microprobe. The results are given in Table 5, together with analyses of colusite from the Gies gold-silver telluride deposit, Montana. Analyses were obtained at the University of Modena (specimens from Lorano and Calagio) and at Iowa State University (specimens from Gies), uti-

TABLE 4. Atomic positional coordinates, multiplicity factors, and anisotropic displacement parameters in Sn-poor colusite (crystal 1) from Lorano

Atom	*x*	*y*	*z*	*K*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
V	0.0	0.0	0.0	0.083	0.0079	0.0079	0.0079	0.0	0.0	0.0
	0.0	0.0	0.0	0.0	0.0009	0.0009	0.0009	0.0	0.0	0.0
Cu1	0.2592	0.0	0.0	0.5	0.0136	0.0228	0.0191	−0.0047	0.0	0.0
	0.0001	0.0	0.0	0.0	0.0006	0.0009	0.0009	0.0011	0.0	0.0
Cu2	0.2513	0.2513	0.2513	0.245	0.0194	0.0194	0.0194	0.0012	0.0012	0.0012
	0.0002	0.0002	0.001	0.001	0.0006	0.0006	0.0006	0.0005	0.0005	0.0005
Cu3	0.25	0.0	0.5	0.25	0.0262	0.0269	0.0269	0.0	0.0	0.0
	0.0	0.0	0.0	0.0	0.0019	0.0010	0.0010	0.0	0.0	0.0
As	0.25	0.5	0.0	0.25	0.0064	0.0077	0.0077	0.0	0.0	0.0
	0.0	0.0	0.0	0.0	0.0010	0.0006	0.0006	0.0	0.0	0.0
S1	0.1209	0.1209	0.1209	0.333	0.0088	0.0088	0.0088	−0.0004	−0.0004	−0.0004
	0.0002	0.0002	0.0002	0.0	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008
S2	0.3655	0.3742	0.1208	1.0	0.0286	0.0090	0.0144	−0.0008	−0.0065	0.0065
	0.0002	0.0002	0.0002	0.0	0.0017	0.0015	0.0012	0.0009	0.0011	0.0011

Note: standard deviations are given in the second row for each atom.

lizing ARL-SEMQ electron microprobes operating at 15 kV and a specimen current 0.20 μA. Chalcopyrite (Cu and S), synthetic stibnite (Sb), synthetic orpiment (As), cassiterite (Sn), and metals (V and Ge) were used for standards at the University of Modena. The data were reduced using the program Magic 4 (Colby, 1968). Synthetic V_2O_5 (V), synthetic As_2Te_3 (Te), Sn metal (Sn), synthetic chalcocite (Cu and S), synthetic stibnite (Sb), synthetic orpiment (As), synthetic pyrrhotite (Fe), and synthetic sphalerite (Zn) were used as standards at Iowa State University. ZAF corrections employed the PRSURP program (Donovan et al., 1992).

The two samples from Lorano contain approximately 0.05 Sn atoms, with 24 Cu atoms in the unit cell, indicating the ideal crystal formula $Cu_{24}V_2As_6S_{32}$. The Sn content was higher in the sample from Calagio, with correspondingly higher Cu content (Table 5).

The geometrical features of the various tetrahedra in Sn-poor and Sn-rich colusite are compared in Table 6. No significant differences were observed for corresponding tetrahedra apart from those containing $(As,Sn)S_4$, which exhibit significantly longer metal-S distances in the Sn-rich variety. All tetrahedra are regular with S-metal-S angles differing only slightly from the ideal tetrahedral value of 109.47°, except S1-Cu-S1 has the lowest value in both varieties. It corresponds to the S1···S1 edge, which is significantly shortened, since it is shared between VS_4 and CuS_4 tetrahedra (Fig. 2). The peculiar arrangement of V atoms stuffed into tetrahedral interstices is shown in Figure 2, where bond distances V-S1, Cu1-S1, and V-Cu1 in the two varieties of colusite from Lorano are given along with those for sulvanite, in which the same structural arrangement occurs.

The results of the structural studies suggest a general formula for colusite of $Cu_{24+x}V_2(As,Sb)_{6-x}(Sn,Ge)_xS_{32}$, with $x = 0–2$. This formula cannot be tested with the analyt-

TABLE 5. Analytical data on colusite samples from localities in the Carrara area, Italy, and the Gies deposit, Montana

	Lorano 1 (five analyses)	Lorano 2 (five analyses)	Calagio (four analyses)	Gies* (21 analyses)
	Weight percent			
Cu	48.72	48.46	49.11	48.89
V	3.18	3.08	3.19	3.20
Sn	0.24	0.20	1.09	0.05
Ge	0.14	0.14	0.00	0.01
As	13.88	13.56	12.82	13.41
Sb	1.22	1.52	1.86	2.36
S	32.41	32.51	32.08	32.44
Total	99.79	99.47	100.15	100.36
	Unit-cell content recalculated on the basis of 32 S atoms			
Cu	24.27	24.07	24.72	24.33
V	1.98	1.91	2.00	1.99
Sn	0.06	0.05	0.29	0.01
Ge	0.06	0.06	0.00	0.01
As	5.87	5.71	5.47	5.66
Sb	0.32	0.39	0.49	0.61
S	32.00	32.00	32.00	32.00

* The sample also contains 0.11 wt% Fe.

TABLE 6. Bond distances (nm) and angles (°), with standard deviations in parentheses, in the various tetrahedra for both varieties of colusite

Atoms	Sn-poor colusite	Sn-rich colusite
V-S1 (× 6)	0.2207(2)	0.2193(2)
S1-V-S1^a (× 6)	109.47(8)	109.47(8)
Cu1-S1 (× 2)	0.2318(2)	0.2313(2)
Cu1-S2^b (× 2)	0.2316(2)	0.2314(2)
S1-Cu1-S1^a	102.06(7)	101.47(8)
S2^b-Cu1-S2^c	113.82(7)	112.52(8)
S1-Cu1-S2^b (× 2)	108.76(7)	110.12(7)
S1-Cu1-S2^c (× 2)	111.41(7)	111.04(7)
Cu2-S1	0.2380(3)	0.2397(3)
Cu2-S2 (× 3)	0.2240(3)	0.2284(3)
S1-Cu2-S2 (× 3)	106.83(11)	108.36(11)
S2-Cu2-S2^d (× 3)	111.98(12)	110.56(12)
Cu3-S2^d (× 4)	0.2311(2)	0.2300(2)
S2^d-Cu3-S2^e (× 4)	108.70(7)	108.94(8)
S2^d-Cu3-S2^f (× 2)	111.02(7)	110.53(8)
(As,Sn)-S2 (× 4)	0.2204(2)	0.2263(2)
S2-(As,Sn)-S2^g (× 4)	107.75(8)	108.62(8)
S2-(As,Sn)-S2^h (× 2)	112.97(8)	111.19(8)

Note: symmetry codes for atoms in equivalent positions are as follows: a = $x, -y, -z$; b = $\frac{1}{2} - z, -\frac{1}{2} + y, \frac{1}{2} - x$; c = $\frac{1}{2} - z, \frac{1}{2} - y, -\frac{1}{2} + x$; d = y, z, x; e = $\frac{1}{2} - y, -\frac{1}{2} + x$; $\frac{1}{2} - z$; f = $y, -z, 1 - x$; g = $\frac{1}{2} - x, \frac{1}{2} + z, \frac{1}{2} - y$; h = $x, 1 - y, -z$.

TABLE 7. Compositional and structural data for some sulfides and sulfosalts with an interstitial metal atom in a tetrahedral site

Mineral	Composition	Space group	Cell edges (nm)			Interstitial metal atom	*M/S**	Reference
			a	*b*	*c*			
Colusite	$Cu_{24+x}V_2(As,Sb)_{6-x}(Sn,Ge)_xS_{32}$	$P\bar{4}3n$	1.0621–1.0538			V	1/16	Orlandi et al. (1981); this study
Nekrasovite	$Cu_{18}(Cu,Fe,Zn)_8(V,Fe)_2(Sn,As,Sb)_6S_{32}$	$P\bar{4}3n$	1.073			V,Fe	1/16	Kovalenker et al. (1984)
Sb-dominant member	$Cu_{26}V_2(Sb,Sn,As)_6S_{32}$	$P\bar{4}3n$	1.0705			V	1/16	Mandarino (1992)
Ge-dominant member	$Cu_{26}V_2(Ge,As)_6S_{32}$	$P\bar{4}3n$	1.0568			V	1/16	Mandarino (1992)
Germanite	$Cu_{26}Fe_4Ge_4S_{32}$	$P\bar{4}2n$	1.0586			Cu	1/16	Tettenhorst and Corbató (1984)
Renierite	$Cu_{20}(Zn_{2-x}Cu_x)(Ge_{4-x}As_x)Fe_8S_{32}$	$P\bar{4}2c$	1.0622–1.060		1.0551–1.045	Fe	1/16	Bernstein (1986); Bernstein et al. (1989)
Vinciennite**	$Cu_{22}Fe_8Sn_2As_2S_{32}$	—	1.0697		1.0697	—	1/16	Cesbron et al. (1985); this study
Talnakite	$Cu_{18}Fe_{16}S_{16}$	$I\bar{4}3m$	1.0593			Fe	1/16	Hall and Gabe (1972)
Stannoidite	$Cu_{16}(Fe,Zn)_6Sn_4S_{24}$	$I222$	1.0767	0.5411	1.6118	Cu	1/12	Kudoh and Takéuchi (1976)
Mooihoekite	$Cu_9Fe_9S_{16}$	$P\bar{4}2m$	1.0585		0.5383	Fe	1/8	Hall and Rowland (1973)
Mawsonite	$Cu_6Fe_2SnS_8$	$P\bar{4}m2$	0.7603		0.5358	Fe	1/8	Szymanski (1976)
Haycockite	$Cu_4Fe_5S_8$	$P2_12_12_1$	1.0705	1.0734	3.1630	Fe	1/8	Rowland and Hall (1975)
Sulvanite	Cu_3VS_4	$P\bar{4}3m$	0.5391			V	1/4	Pauling and Hultgren (1933); Trojer (1966)

* *M/S* = number of interstitial metal atoms per number of S atoms.

** The structure has not been resolved; a tetragonal lattice has been found (Cesbron et al., 1985). A new formula is proposed by the present study.

ical data presented in Table 1. Some analyses were carried out on impure material; however, further problems arose when pure, or almost pure, material was used because the recalculation of the atomic contents (carried out on the basis of 32 S atoms in the unit cell) may result in relatively large errors in the number of Cu atoms if poor determinations of S are obtained. Some of the recalculated Cu contents even appear unreliable on structural grounds, having more than 26 Cu atoms. An unequivocal test of this proposed formula must await a careful reexamination of compositions ranging from Sn-poor to Sn-rich varieties of colusite through electron microprobe studies of specimens from the various localities, or of additional samples, carried out in the same laboratory.

The structural analysis and chemical compositions (Table 1) indicate that colusite is characterized by V atoms predominantly in site 2a at 0,0,0 and As atoms predominantly in site 6c at ½,½,0. When other metals are dominant in the 6c site, new mineral species in the colusite group may be defined. All four possible species have been reported. Apart from colusite sensu stricto (As dominant), nekrasovite (the Sn-dominant analogue) has been defined by Kovalenker et al. (1984), and the Sb-dominant and the Ge-dominant members were approved as new

TABLE 8. Chemical analyses of arsenosulvanite

	1	2	3	4	5	6	7
Cu	48.84	46.55	48.8	50.6	50.35	46.2	49.4
V	4.16	5.20	3.7	3.4	3.7	3.1	3.2
Fe	nd	nd	nd	nd	nd	3.4	nd
Ge	nd	nd	nd	0.62	nd	nd	nd
Sn	nd	nd	nd	nd	nd	1.0	nd
As	12.80	11.67	12.4	13.2	13.35	10.2	12.3
Sb	nd	nd	nd	nd	nd	3.9	nd
S	33.14	31.66	31.7	32.22	32.55	31.8	33.9
Total	98.94	95.18	99.96	100.04	99.95	99.6	97.8
Unit-cell content calculated on the basis of 32 S atoms							
Cu	23.795	23.791	24.856	25.343	24.976	23.458	24.252
V	2.528	3.380	2.351	2.124	2.289	1.963	1.959
Fe	nd	nd	nd	nd	nd	1.964	nd
Ge	nd	nd	nd	0.266	nd	nd	nd
Sn	nd	nd	nd	nd	nd	0.272	nd
As	5.289	5.048	5.357	5.616	5.616	4.392	5.122
Sb	nd	nd	nd	nd	nd	1.034	nd
S	32.000	32.000	32.000	32.000	32.000	32.000	32.000

Note: column head numbers are defined as follows: 1. and 2. Mongolia, Kafan deposit (Mikheev, 1941); 3. Bor deposit, Serbia (Kachalovskaya et al., 1975); 4. Bor deposit, Serbia (Cvetković and Karanović, 1993); 5. South Yakutia, Russia (Novikov et al., 1974); 6. Hayakawa deposit, Japan (Ishiyama et al., 1990); 7. Osarizawa deposit, Japan (Taguchi and Kizawa, 1973). The abbreviation nd = not determined.

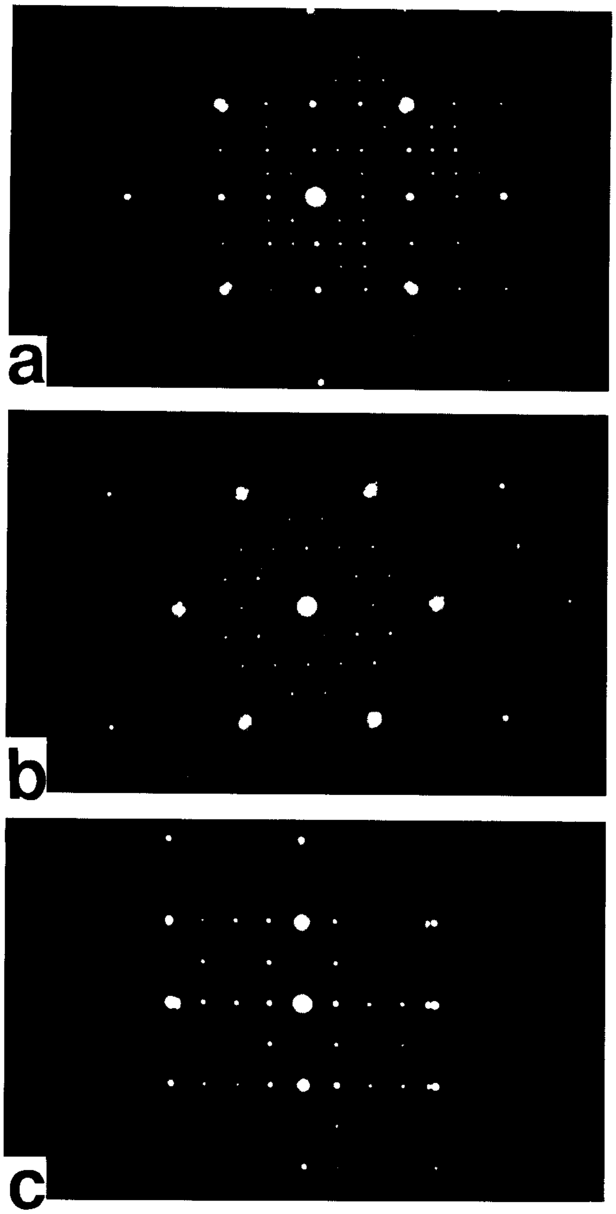

Fig. 3. SAED patterns of Sn-free colusite along (**a**) [100], (**b**) [111], and (**c**) [211].

minerals by the Commission on New Minerals and Mineral Names of the International Mineralogical Association (Mandarino, 1992).

Two other sulfosalts, germanite ($Cu_{26}Fe_4Ge_4S_{32}$) and renierite [$Cu_{20}(Zn_{2-x}Cu_x)(Ge_{4-x}As_x)Fe_8S_{32}$ where $x = 0$–2], are isostructural with colusite, and their structures were determined on the basis of the preliminary structural results presented by Orlandi et al. (1981). Germanite, like colusite, is cubic and has the same space group $P\bar{4}3n$ and $a = 1.0586$ nm. The structural difference between colusite and germanite is that Cu atoms in the interstitial tetrahedral site 2a occur at 0,0,0 in germanite (Tettenhorst and Corbató, 1984). In renierite, the ordering of the metal atoms in a colusite-type structure results in a reduction of symmetry from cubic to tetragonal, with space group $P\bar{4}2c$ and cell parameters $a = 1.0623$ and $c = 1.0551$ nm (Bernstein et al., 1989). The crystal chemistry and various occurrences of renierite were discussed by Bernstein (1986), and the chemical variability was explained by him as resulting from continuous solid solution between the end-members $Cu_{20}Zn_2Ge_4Fe_8S_{32}$ and $Cu_{22}Ge_2As_2Fe_8S_{32}$, through the coupled substitution of $Zn^{2+} + Ge^{5+} = Cu^+ + As^{5+}$. The end-member $Cu_{22}Ge_2As_2Fe_8S_{32}$ was simply referred to as arsenian renierite by Bernstein (1986). It is likely that the mineral described by Matsukuma and Yui (1979) as Ge- and Sn-bearing colusite is actually arsenian renierite.

Vinciennite, first found by Cesbron et al. (1985) in the pyrite deposits of Chizeuil, Saône-et-Loire (France), and Huaron (Peru), and subsequently by Jambor and Owens (1987) in the Maggie porphyry Cu deposit, British Columbia, appears to be the stannian counterpart of arsenian renierite. This suggests the formula $Cu_{22}Sn_2As_2Fe_8S_{32}$ for vinciennite, rather than $Cu_{20}Sn_2As_2Fe_8S_{32}$, as proposed by Cesbron et al. (1985). This new formulation gives a better agreement with the analytical data of Cesbron et al. (1985). The agreement becomes perfect with the data presented by Jambor and Owens (1987) for the specimens from British Columbia. Moreover, the heterovalency of Fe, claimed by these authors to reconcile the theoretical and actual compositions, is no longer necessary.

The mineral species described above are characterized by the ratio $M/S = 1/16$, where M = number of interstitial atoms and S = number of S atoms. The same M/S ratio is found also in talnakite (Hall and Gabe, 1972), for space group $I\bar{4}3m$ with $a = 1.0593$ nm, that is isostructural with colusite. The structural arrangement of stuffing a metal atom into a tetrahedral interstice is not confined to the minerals of the colusite, germanite, or renierite group because metal atoms are located in this position for a variety of sulfides, including sulvanite (Pauling and Hultgren, 1933; Trojer, 1966), mooihoekite (Hall and Rowland, 1973), talnakite (Hall and Gabe, 1972), mawsonite (Szymanski, 1976), stannoidite (Kudoh and Takéuchi, 1976), and haycockite (Rowland and Hall, 1975). Compositional and structural data for these minerals are summarized in Table 7.

CHEMISTRY AND STRUCTURE OF ARSENOSULVANITE

Arsenosulvanite is a rare copper, arsenic, vanadium sulfosalt that was identified by Betekhtin (1941) and Mikheev (1941) in quartz-calcite veins cutting bituminous limestone in Mongolia. Betekhtin suggested a formula of $Cu_3(As,V)S_4$ (Table 8, analyses 1 and 2), whereas X-ray data of Mikheev suggested that it has a cubic cell with $a = 0.5257$ nm, a $P\bar{4}3m$ space group, and a sphalerite-type structure. Arsenosulvanite was subsequently described from the Bor porphyry copper deposit, Serbia (Sclar and Drovenik, 1960; Kachalovskaya et al., 1975; Cvetković and Karanović, 1993), the Kafan Cu deposit,

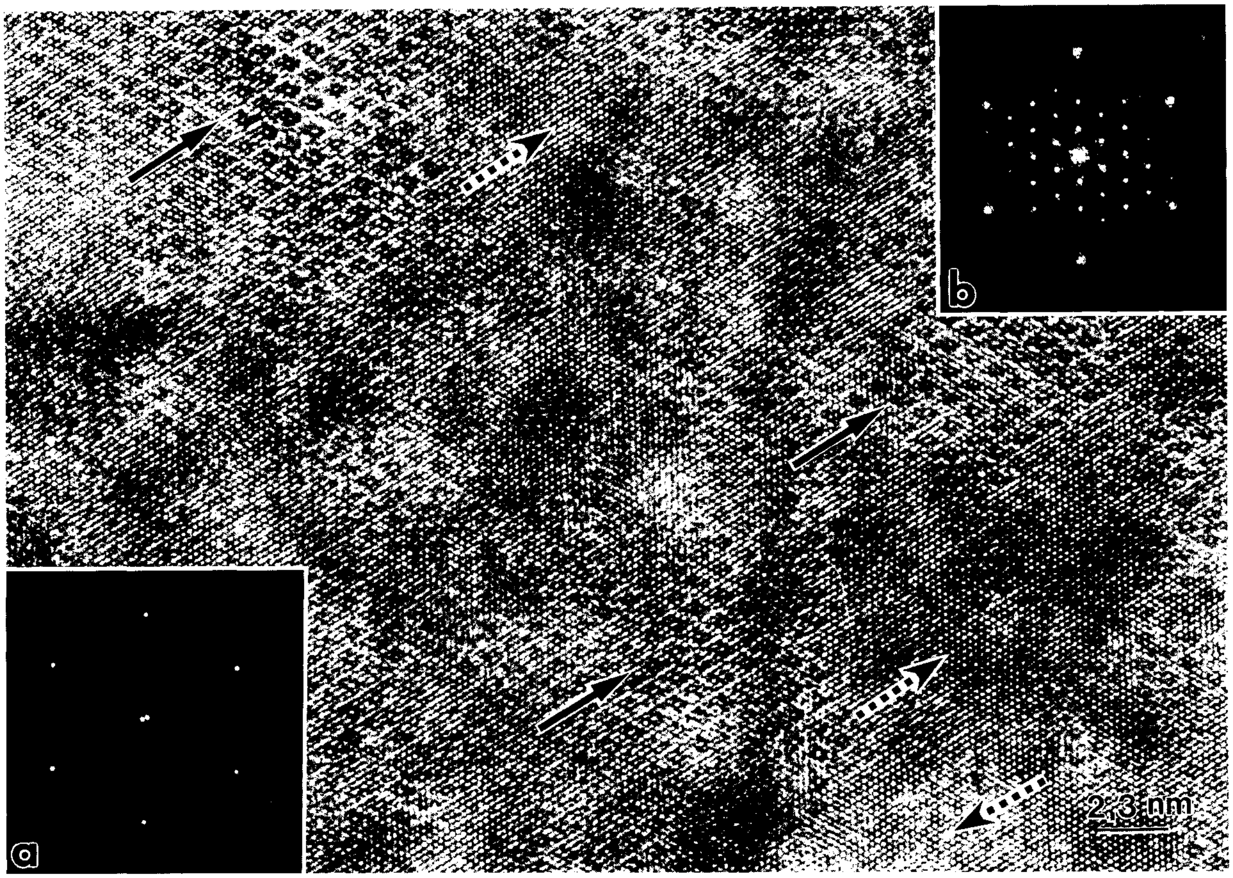

Fig. 4. The [111] HRTEM image of Sn-free colusite, showing domains corresponding to two sublattice reflections (cf. Fig. 3). (**a**) An optical diffraction pattern of an ordered domain (solid arrows); (**b**) an optical diffraction pattern from a disordered domain (dashed arrows). The three dashed arrows point to disordered regions that appear to have reversed contrast, which is presumably the result of a difference in thickness.

Armenia (Afanas'yeva et al., 1972), the Lebdynov Au deposit in South Yakutia (Novikov et al., 1974; Khoroshilova et al., 1984), the Osarizawa Cu deposit, Japan (Taguchi and Kizawa, 1973), and the Hayakawa Cu-Pb-Zn deposit, Japan (Ishiyama et al., 1990). Despite the descriptions of arsenosulvanite from these localities, there is still confusion concerning its chemistry and structure, as well as its relationship with colusite. For example, the available compositional data (Table 8) show striking similarities with those given in Table 5 for Sn-free colusite from Lorano and Calagio (Italy) and Gies (Montana), with a common ideal chemical formula $Cu_{24}V_2As_6S_{32}$.

The similarities between arsenosulvanite and colusite are strengthened when one considers that the large variety of proposals for space groups, cell dimensions, and structures for arsenosulvanite closely follows that already presented for colusite. Cell dimensions of 0.5257 (space group $P\bar{4}3m$) and 0.5260 nm were given by Mikheev (1941) for arsenosulvanite from Mongolia and Osarizawa, respectively. However, a doubled parameter was found by Khoroshilova et al. (1984) (a = 1.0527 nm, $I\bar{4}3m$) for arsenosulvanite from South Yakutia, as well as by Kachalovskaya et al. (1975) (a = 1.052 nm, $P\bar{4}3m$) and Cvetković and Karanović (1993) (a = 1.0552 nm, $P\bar{4}3m$) for arsenosulvanite from Bor.

There is considerable evidence to suggest the space group $P\bar{4}3n$ and a colusite-like structure for arsenosulvanite. The X-ray powder diffraction pattern obtained by Cvetković and Karanović (1993) is representative of arsenosulvanite from Bor. (The powder pattern of Kachalovskaya et al., 1975, has weak reflections, 0.313, 0.243, 0.1906, and 0.1627 nm, which do not appear in the powder pattern of Cvetković and Karanović; these reflections correspond to strong reflections of sulvanite, which is commonly mixed with arsenosulvanite at Bor.) The powder pattern of Cvetković and Karanović (1993) matches that of colusite 1 (Sn-free colusite) presented by Orlandi et al. (1981), and no reflection violates the n-glide rule (hhl present only for $l = 2n$). Moreover, we recalculated the intensities assuming a colusite-type structure and found good agreement with the visually estimated intensities. In contrast, the intensities calculated on the basis of the sphalerite-type structure proposed by Cvetković and Karanović (1993) show marked discrepancies with

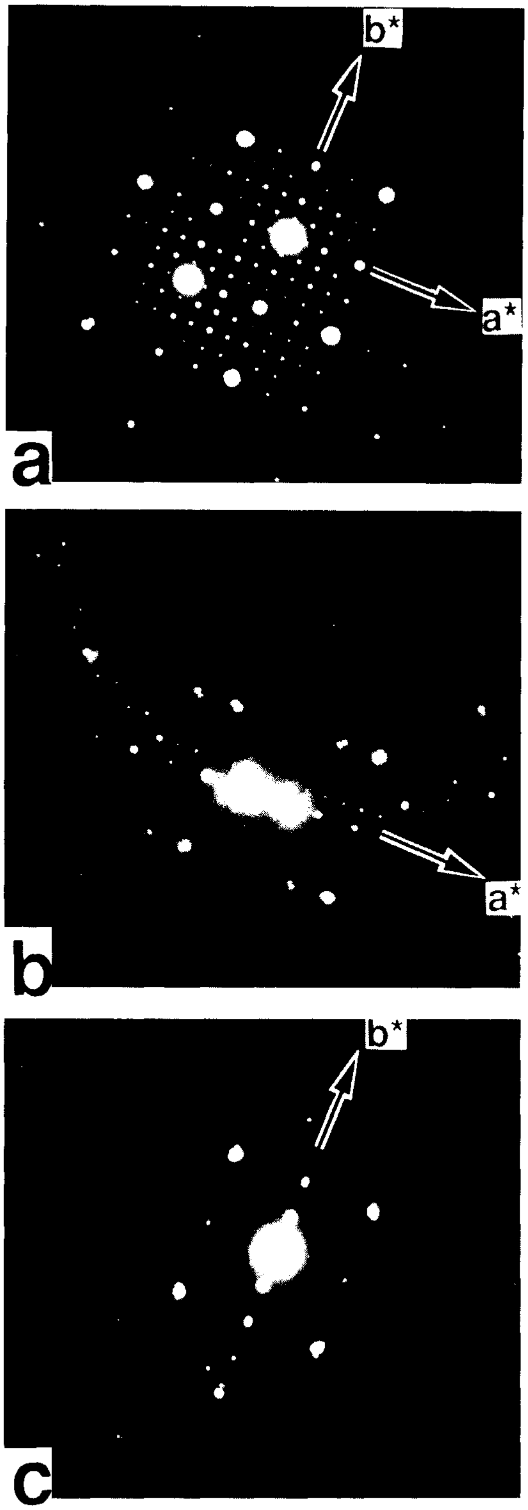

Fig. 5. (**a**) A [100] SAED pattern of Sn-free colusite. (**b**) A [100] SAED pattern of Sn-free colusite tilted around the **a*** axis, and (**c**) tilted around the **b*** axis.

estimated intensities. For example, reflections 210, 200, and 420 should be unobserved, yet these peaks are evident.

The evidence for a colusite-type structure for arsenosulvanite is supported by the results of the structural study of Khoroshilova et al. (1984). Their refinement, carried out in space group $I\bar{4}3m$ (a = 1.0527 nm), utilized reflections collected with an automatic diffractometer from a single crystal of arsenosulvanite from South Yakutia and assumed atoms are stuffed into tetrahedral interstices, as in colusite-type structures. Khoroshilova et al. refined the structure to $R = 0.071$ and obtained the crystal formula $Cu_{24}V_2As_6S_{32}$. The relatively low R value indicates that the solution is close to correct, notwithstanding the following problems: (1) As atoms occupy the tetrahedral interstices at 0,0,0; this appears unusual for As (no other example is known); (2) the occupancy factor is 1.2 (higher than the theoretical 1.0) for As at 0,0,0; and (3) As-S and (As,V)-S distances are 0.230 nm, considerably larger than the value of 0.220 nm for Sn-poor colusite. In our opinion, these inconsistencies derive from the assumption of I centering assumed, when weak reflections with $h + k + l = 2n + 1$ are disregarded. If data had been collected assuming space group $P\bar{4}3n$ and a structural model of colusite had been used for the corresponding refinement, a lower R value would be obtained and the inconsistencies would be removed.

Optical studies of colusite and most examples of arsenosulvanite suggest isotropic behavior in polarized light, which is consistent with colusite and arsenosulvanite having isometric symmetry. Exceptions include samples of arsenosulvanite from the Lebdynov (Novikov et al., 1974) and Bor deposits (Kachalovskaya et al., 1975; Cvetković and Karanović, 1993), which exhibit distinct anisotropy.

CHARACTERISTICS OF COLUSITE FROM THE GIES DEPOSIT

The epithermal Gies deposit consists of gold-silver telluride veins that occur along the contact between Late Cretaceous to Paleocene alkaline intrusive rocks (quartz monzonite, syenite, and tinguaite porphyries) and sedimentary rocks (shale, sandstone, conglomerate, limestone, and dolomite) of Middle Cambrian to Late Paleocene age in the Judith Mountains, Montana. Thirty-eight minerals occur over four stages of mineralization. Colusite occurs in stage III, which is dominated by quartz, gold-silver tellurides, and roscoelite. Fluid inclusion studies by Zhang and Spry (1991, 1994) suggest that stage III mineralization formed between 185 and 237 °C (average = 220 °C) from a fluid containing between 6.6 and 7.9 equivalent wt% NaCl. Colusite had previously been reported from the Judith Mountains by Forrest (1971), who identified it in the small Collar Gulch silver deposit, 4 km southwest of the Gies deposit. Unfortunately, no compositional or optical data were given.

Anhedral colusite up to 1.5 mm in size is intergrown with chalcopyrite, tetrahedrite, pyrite, hessite, enargite, and chalcocite. It is intimately associated with tetrahe-

Fig. 6. A [211] HRTEM image of Sn-free colusite, showing a modulation in the [110] direction. The wavelength of the modulation is 3.57 nm.

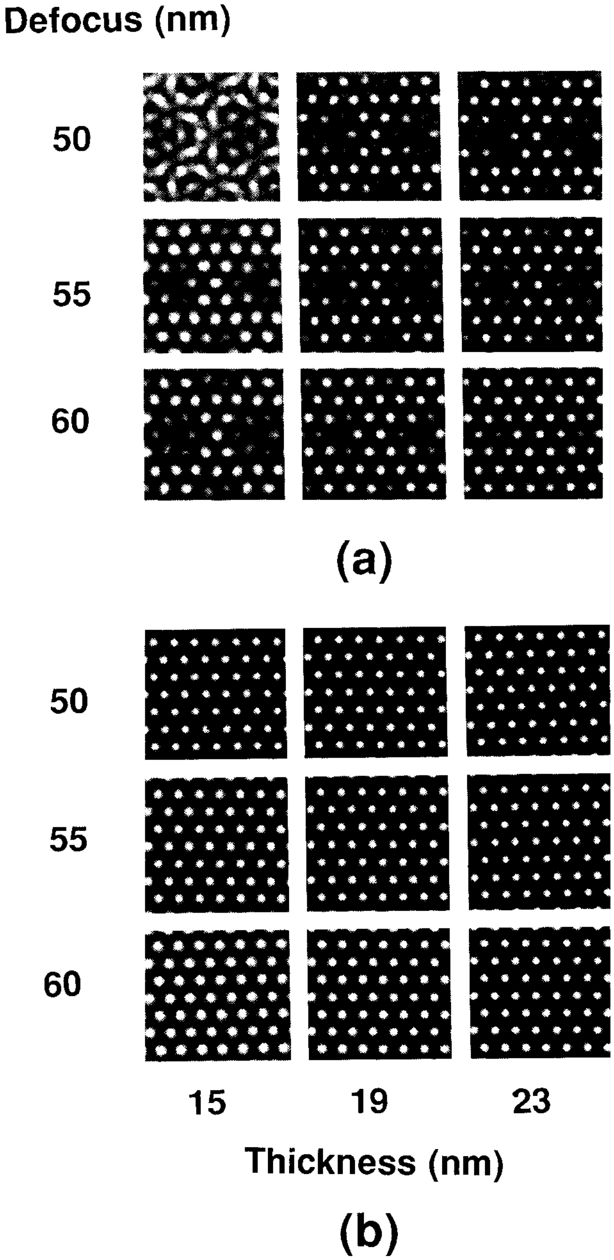

Fig. 7. Simulated HRTEM images at different values of defocus and thickness for the (**a**) ordered and (**b**) disordered structures.

drite, chalcopyrite, or pyrite. In reflected light, colusite exhibits weak pleochroism (cream yellow to pale brownish yellow) and anomalous, moderate to strong anisotropy (dark blue to dark brown). These optical properties are unusual because previous publications suggested that colusite shows isotropic behavior. Some grains of colusite from the Gies deposit appear to display twin lamellae. Reflectance measurements in air at a wavelength of 546 nm are 31–33%, comparable to those for colusite from Lorano (Orlandi et al., 1981), Gay (Pshenichnyy et al., 1974), Medet (Strashimirov, 1982), and Kounrad (Gazizova and Yarenskaya, 1966). The range of microindentation hardness (Vickers hardness) is 183–207 kg/mm^2, which is considerably lower than values reported for colusite from Lorano (342–350 kg/mm^2), Kayragach (260–320 kg/mm^2), and Gay (258–357 kg/mm^2) (Pshenichnyy et al., 1974; Orlandi et al., 1981; Spiridonov et al., 1984). Colusite from the Gies deposit is Sn-poor (up to 0.2 wt%) and contains 12.1–14.9 wt% As, 0.5–4.3 wt% Sb, and 3.1–3.3 wt% V, and it compositionally resembles colusite from the Lorano marble quarry (Table 5).

Sample and TEM experimental details

Sample 89-G5 from the Gies deposit was polished to a thickness of 0.03 mm and then thinned using a Gatan 600B ion mill. A cooling stage was used to minimize damage during milling. HRTEM experiments were conducted with JEOL 2000F and 4000EX transmission electron microscopes using an accelerating potential of 400 kV for high-resolution imaging.

HRTEM and SAED observations

SAED patterns obtained along the [100], [111], and [211] axes of sample 89-G5 show a set of weak superstructure reflections in addition to strong sublattice reflections (Fig. 3). The corresponding HRTEM images indicate two types of domains (Fig. 4). Optical diffraction patterns of these domains (insets in Fig. 4) indicate that only one of the domains displays the superstructure reflections. Therefore, the two sets of reflections are caused by structural differences. Upon visual inspection, the energy-dispersive spectra show no obvious compositional differences. The crystal system indicated by the superstructure reflections is isometric, with systematic absences *hhl* with $l = 2n + 1$, as observed by tilting the specimen around the **a*** and **b*** axes (Fig. 5), which is consistent with space group $P\bar{4}3n$ or $Pm3n$. The lattice parameter determined from electron diffraction is $a =$

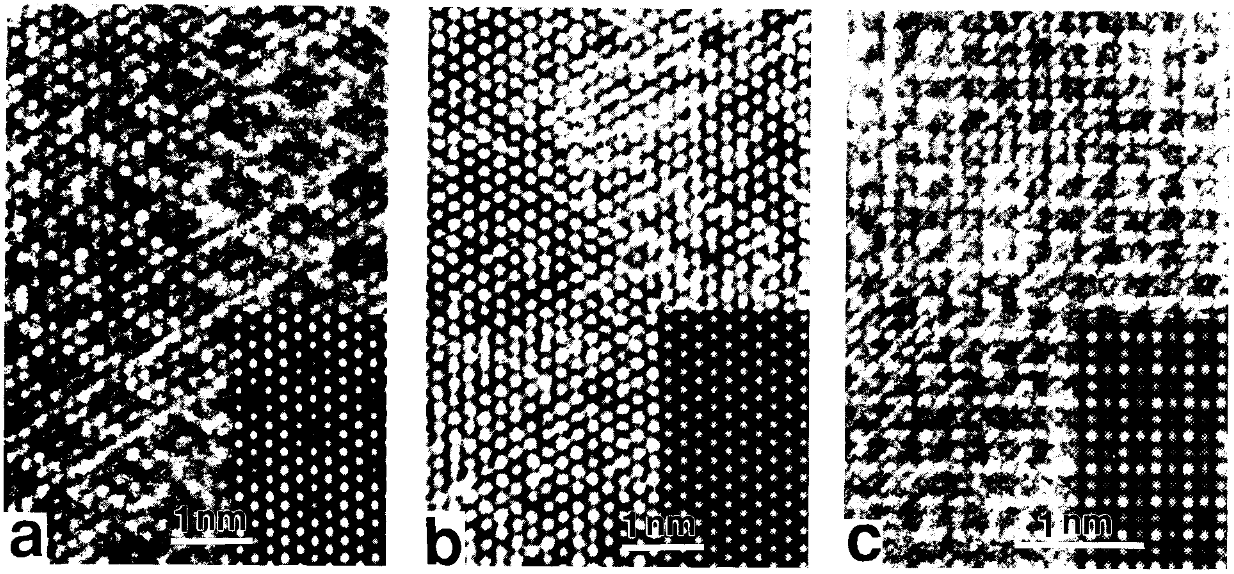

Fig. 8. Comparison between the observed and simulated HRTEM images. (**a**) A [111] HRTEM image of Sn-free colusite, together with an image simulated at a thickness of 35 nm and a defocus of 20 nm (inset). (**b**) A [111] HRTEM image of a disordered domain, simulated at a thickness of 20 nm and a defocus of 60 nm. (**c**) A [100] HRTEM image of Sn-free colusite, simulated at a thickness of 21 nm and a defocus of 20 nm.

1.068 nm. These observations are consistent with those obtained by Orlandi et al. (1981: a = 1.053 nm for Sn-poor colusite). From the systematic absences of the main reflections, hkl with $h + k = 2n + 1$, $h + l = 2n + 1$, and $k + l = 2n + 1$, it follows that the space group of the disordered domain is $F\bar{4}32$, $F\bar{4}3m$, or $Fm3m$, with a = 0.534 nm. No known mineral corresponds to the composition, lattice parameter, and possible space groups of the domain indicated by the main reflections.

One-dimensional structure modulations along [110], with a wavelength of 3.57 nm, occur in [211] HRTEM images (Fig. 6). The cause of the modulation is uncertain. Equally uncertain is the cause for the anisotropism of colusite in sample 89-G5. Although speculative, the modulation might be responsible for its anisotropism (see Janner and Janssen, 1977).

DISCUSSION

HRTEM images for Sn-poor colusite from the Gies deposit show that ordered and disordered domains are coherently intergrown. The space group $P\bar{4}3n$ is appropriate for the superstructure (colusite) domains, whereas $F\bar{4}3m$ seems consistent with the disordered domains.

The EMS program of Stadelmann (1987) was used for image simulations and showed ordered and disordered structures at different values of focus and specimen thickness (Fig. 7). Although both ordered and disordered domains have the same distribution of bright spots for HRTEM images observed along [111] (Fig. 5), they show different contrast details. The contrast of the ordered domains varies strongly as a function of specimen thickness, whereas changes for the disordered domain are more subtle. Simulated images clearly display contrast differences between the two types of domain (Figs. 7, 8a, and 8b). The consistency between the observed and simulated HRTEM images supports the supposition that two types of domain occur in colusite from the Gies deposit (Fig. 8a and 8b). Both ordered and disordered structural models are idealized to be free of modulations.

The structures derived from the single-crystal X-ray diffraction studies are consistent with the structure derived from HRTEM and SAED studies for the ordered domain of the Gies colusite. A sphalerite-like arrangement, with a random distribution of Cu, As, V, Sb, and Fe on the Zn sites of the sphalerite structure, was assumed by us as a model for the disordered domains (face-centered cubic cell, a = 0.534 nm). However, V in sulfides and sulfosalts shows a strong preference for the arrangement presented in Figure 2, as in sulvanite (Cu_3VS_4) and also around the V site in all members of the colusite group.

Experimental studies on the system Cu_3VS_4-Cu_3AsS_4 (sulvanite-enargite) by Riedel and Paterno (1976) identified an intermediate compound, with a Cu_3VS_4:Cu_3AsS_4 molar ratio of 1:3. The compound, $Cu_{12}VAs_3S_{16}$, displayed a diffraction pattern similar to that of Sn-free colusite (and arsenosulvanite). The powder pattern lines are consistent with a cubic cell (a = 1.0528 nm) and space group $P\bar{4}3n$. Furthermore, the intensities of the powder pattern lines agree with those calculated from the coordinates in Table 2 for our Sn-poor colusite. The infrared spectra presented by Riedel and Paterno (1976) for $Cu_{12}VAs_3S_{16}$, sulvanite, and enargite support that V is incorporated in $Cu_{12}VAs_3S_{16}$ in the way that it is in sulvanite. This supports our inference that the intermediate compound is Sn-free colusite.

For different molar ratios of Cu_3VS_4 and Cu_3AsS_4, two phases were obtained by Riedel and Paterno (1976), one corresponding to colusite and the other corresponding to sulvanite or enargite, depending on whether Cu_3VS_4 or Cu_3AsS_4 exceeded the amount necessary to form $Cu_{12}VAs_3S_{12}$. In our view, the results of Riedel and Paterno's study not only point to the same structure for $Cu_{12}VAs_3S_{12}$ as for the ordered domain in sample 89-G5 from the Gies deposit but also indicate, as stressed by the authors, that no solid solution exists between the end-members. Solid solution is prevented by the tendency of the V atoms to occupy interstitial positions. Therefore, it seems probable that V is also located in interstitial sites of the disordered domain observed in sample 89-G5. Whereas V atoms are regularly distributed on sites at 0,0,0 (and equivalent sites at ½,½,½) in the ordered domain of sample 89-G5, V atoms are randomly distributed over all interstitial sites in the disordered domain, with a coordinated distribution of As and Cu over the normal tetrahedral positions so as to avoid adjacent VS_4 and AsS_4 tetrahedra. With such a random distribution of V atoms, a structure with a cubic unit cell of $a = 0.534$ nm and space group $F\bar{4}3m$ is obtained. The results of Riedel and Paterno's (1976) study are also pertinent to understanding the presence of ordered and disordered domains in sample 89-G5. Although a speculative suggestion, it is likely that the disordered domain is the stable form at high temperature. As temperature decreases, interstitial V atoms distribute in a regular manner according to the ordered colusite structure ($P\bar{4}3n$, $a = 1.06$ nm).

ACKNOWLEDGMENTS

We thank Don Eisenhour and Matthew Kramer for helpful discussions and the Blue Range Mining Company for access to the Gies deposit. Richard Hagni assisted with reflectance and hardness measurements, and Taras Bryndzia kindly translated some of the references. The manuscript was improved by the reviews of Eugene Foord and Jeffrey Post. Joe Mandarino is thanked for providing useful references on the discreditation of lazarevićite. Luciano Ungaretti assisted with the collection of X-ray diffraction data for the structural analyses, and Giovanna Vezzalini performed the new microprobe analyses of specimens of colusite from Lorano and Calagio. HRTEM studies were performed at the Center for High Resolution Electron Microscopy at Arizona State University (ASU). The ASU facility is supported by the National Science Foundation (NSF) and ASU. This study was supported by NSF grant EAR-9219376 (to P.R.B.), by the Iowa State Mining and Mineral Resources Research Institute program administered by the U.S. Bureau of Mines under allotment grants G1194119, G1104119, and G1114119 (to P.G.S. and X.Z.), and by the Graduate College at Iowa State University (to X.Z.).

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Manuscript received May 24, 1993
Manuscript accepted February 18, 1994