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COLUSITE: A NEW OCCURRENCE AND CRYSTAL CHEMISTRY

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ABSTRACT

A new occurrence of colusite in vugs of the marble quarried at Lorano, near Carrara, Apuan Alps, Italy, is reported. The tetrahedral bronze-brown crystals are cubic, space group $P\bar{4}3n$. Two different crystals of colusite were studied by X-ray-diffraction and electron-microprobe methods. The first crystal, with cell edge $a = 10.538(6)$ Å, has a composition corresponding to $Cu_{26}V_2As_6S_{32}$, whereas the second crystal, with $a = 10.621(6)$ Å, has the composition $Cu_{26}V_2As_4Sn_2S_{32}$. Published analytical data have been recalculated on a basis of 66 atoms *per* unit cell. Reflectance, measured at 470, 546, 589 and 650 nm, varies between 26.7 and 32% in air and between 13.3 and 17.9% in oil. VHN_{100} is in the range 342-350.

Keywords: colusite, sulfosalt, Carrara, Italy, marble.

SOMMAIRE

Nous décrivons un nouvel exemple de colusite, formée dans les cavités du marbre de la carrière de Lorano (région de Carrare, alpes Apouennes, Italie). Les cristaux, tétraédriques et bronze-brun, sont cubiques, groupe spatial $P\bar{4}3n$. Deux cristaux ont été étudiés par diffraction X et par microsonde électronique. Le premier, qui possède une maille d'arête $a = 10.538(6)$ Å, a la composition $Cu_{26}V_2As_6S_{32}$; le second, qui donne $a = 10.621(6)$ Å, répond à la composition $Cu_{26}V_2As_4Sn_2S_{32}$. Pour les colusites analysées antérieurement, les formules ont été recalculées pour 66 atomes par maille. La réflectance de la colusite, mesurée à 470, 546, 589 et 650 nm, varie entre 26.7 à 32% dans l'air et entre 13.3 à 17.9% dans l'huile; sa dureté VHN_{100} est de 342 à 350.

(Traduit par la Rédaction)

Mots-clés: colusite, sulfosel, Carrare, Italie, marbre.

INTRODUCTION

We are presently studying the minerals that occur in the marble formation of the Apuan Alps. To date, forty-seven mineral species have been observed inside vugs in the marble. The minerals are all well crystallized; many species, such as famatinite, sulvanite, zinckenite, boulangerite, seligmannite, wurtzite, sphalerite, tetrahedrite, covellite, enargite, jordanite, geocronite and colusite, belong to the sulfosalt and sulfide groups (Orlandi *et al.* 1980).

Colusite was found in the Lorano quarry, in the Carrara area, where carbonate rocks (Hettangian marbles) are found forming part of the metamorphic Tuscan Series. Colusite is a rare sulfide of copper, vanadium, arsenic and tin, first described from Butte, Montana by Landon & Mogilnor (1933). Nelson (1939) reportedly observed this mineral, associated with enargite, in a sample from Red Mountain, Colorado. However, he did not describe any of the properties of the mineral from this locality. Among the various authors who described and studied colusite from Butte, Berman & Gonyer (1939) presented correct chemical data indicating that vanadium is an essential component. Dangel & Wuensch (1970) reviewed the whole literature and, on the basis of new X-ray-diffraction data, indicated colusite to be isometric, with space group $P\bar{4}3m$, a 10.62$_9$ Å, and characterized by a sphalerite-like arrangement of atoms.

Further occurrences of colusite were reported from Chizeuil, Saône-et-Loire (Picot *et al.* 1963), from the Kounrad copper deposit (Gazizova & Yarenskaya 1966), from the copper deposit of Chelopech, Bulgaria (Terziev 1966) and from the Gay copper–zinc deposit in the southern Urals (Pshenichnyi *et al.* 1974).

This paper presents new data on colusite, describes its occurrence and gives chemical and crystallographic data for two varieties. On the basis of these data and structural results, the

crystal chemistry of colusite is revised and assessed.

Occurrence and Properties

Numerous quarries of the well-known marble can be found in the surroundings of Carrara. Colusite was found only in the Lorano quarry, which is five kilometres from the town.

Colusite occurs as small (1 mm^3) crystals that show a characteristic habit (Fig. 1); the most frequent form is the tetrahedron, often associated with the tristetrahedron {211} and rarely with the cube. The snow-white matrix of the marble makes a considerable contrast for the epitactic overgrowths of the mineral on sphalerite or on wurtzite individuals; this feature makes these specimens particularly beautiful.

The colusite crystals are bronze-brown with metallic lustre. No definite cleavage was observed. The specific gravity was not measured because of the very small quantity of material. All the physical and chemical studies were made on two small crystals found in vugs in two different blocks of marble; both have a tetrahedral habit and are much smaller than the crystal represented in Figure 1. Crystal 1 was found associated with quartz, albite, fluorite and dolomite, whereas crystal 2 was found associated with quartz, dolomite and sulvanite.

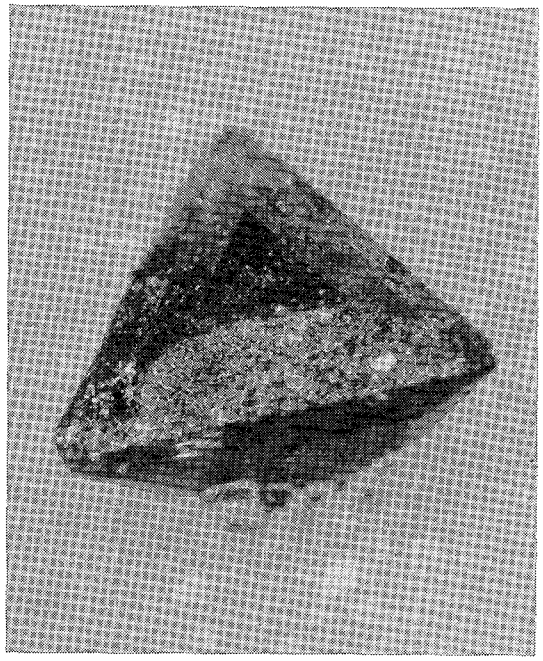

Fig. 1. Colusite crystal from Lorano quarry. The edge of the tetrahedron is nearly 1 mm long.

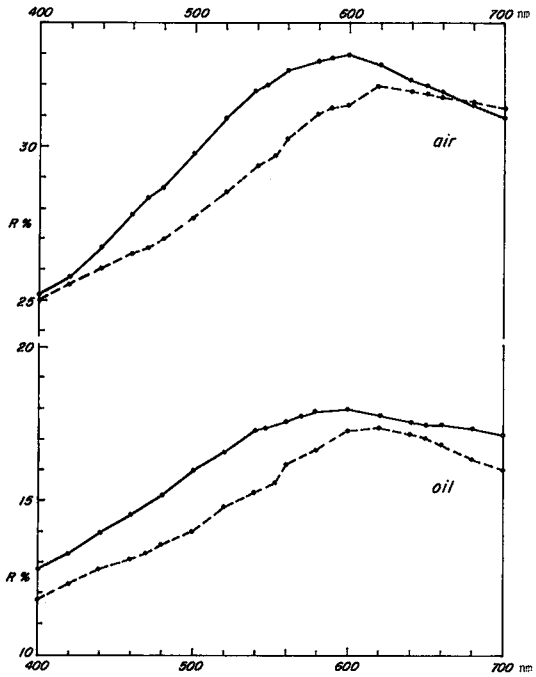

Fig. 2. Reflectances at various wavelengths. Continuous and dashed lines refer to crystals 1 and 2, respectively.

In reflected light, colusite appears cream colored in polished sections. Internal reflections, zonal structures or heterogeneities were not observed. Reflectance was measured using tungsten–titanium carbide No. 144 (Zeiss) as a standard (Fig. 2). Values at the four standard wavelengths are listed in Table 1. The range of micro-indentation hardness was found to be 342–350 kg/mm^2 for a 100-g load.

The cell parameters of the two crystals of colusite were obtained by Weissenberg and precession photographs, with Cu $K\alpha$ radiation; they were refined by least-squares methods on the basis of the X-ray powder-diffraction data,

TABLE 1. REFLECTANCE MEASUREMENTS IN AIR AND IN OIL

	(1)		(2)	
λ, nm	R(air)	R(oil)	R(air)	R(oil)
470	28.2%	14.9%	26.7%	13.3%
546	32.0	17.4	29.7	15.6
589	32.9	17.9	31.3	17.0
650	32.0	17.5	31.7	17.1

1) Crystal No. 1: cell dimension a=10.532Å
2) Crystal No. 2: cell dimension a=10.606Å

TABLE 2. X-RAY POWDER-DIFFRACTION DATA

1				2				3		
d_{obs}	d_{calc}	I_{est}	hkl	d_{obs}	d_{calc}	I_{est}	hkl	d_{obs}	I/I_1	hkl
-	-	-	-	-	-	-	-	6.15	5	111
5.25	5.27	w	200	5.32	5.30	w	200	5.34	5	002
4.70	4.71	vw	210	4.72	4.74	w	210	4.77	5	012
4.30	4.30	w	211	4.30	4.33	w	211	4.35	10	112
3.32	3.33	vw	310	3.37	3.35	w	310	-	-	-
3.04	3.04	s	222	3.06	3.06	s	222	3.07	100	222
2.82	2.81	w	321	2.84	2.83	w	321	2.86	5	123
2.63	2.63	w	400	2.65	2.65	w	400	2.65	20	004
2.48	2.48	w	330	-	-	-	-	2.51	5	033,114
2.351	2.355	w	420	2.38	2.37	vw	420	2.38	5	024
2.245	2.245	w	332	2.255	2.261	vw	332	2.26	5	233
2.065	2.066	w	431	2.083	2.080	vw	431	2.08	5	015,134
1.952	1.956	vvw	432	1.977	1.970	vw	432	1.973	5	025,234
1.860	1.862	s	440	1.876	1.875	s	440	1.881	60	044
1.806	1.806	vvw	433	-	-	-	-	-	-	-
1.755	1.755	w	442	-	-	-	-	-	-	-
1.709	1.709	vw	532	-	-	-	-	-	-	-
1.586	1.588	ms	622	1.601	1.599	ms	622	1.600	40	226
1.554	1.553	vw	631	-	-	-	-	1.575	5	136
1.520	1.520	w	444	-	-	-	-	1.540	5	444
1.462	1.461	vvw	640	-	-	-	-	-	-	-
1.434	1.433	vw	552	-	-	-	-	-	-	-
1.338	1.338	vw	651	-	-	-	-	-	-	-
1.317	1.317	m	800	1.325	1.326	w	800	1.324	20	008
1.209	1.208	m	662	1.215	1.217	m	662	1.222	30	266
1.178	1.178	m	840	1.184	1.816	w	840	1.183	10	048
1.074	1.075	m	844	1.081	1.083	ms	844	1.085	30	448
1.012	1.013	m	10.2.2	1.020	1.021	m	10.2.2	1.024	20	666
0.931	0.931	m	880	0.938	0.937	m	880	0.940	10	088
-	-	-	-	-	-	-	-	0.898	20	2.6.10
-	-	-	-	-	-	-	-	0.841	10	0.4.12
-	-	-	-	-	-	-	-	0.811	5	6.6.10

1) Colusite No. 1 from Lorano quarry (a=10.532 Å)
2) Colusite No. 2 from Lorano quarry (a=10.606 Å)
3) Colusite from Butte, JCPDS card No. 9-10. The reflection at 6.15 Å was not observed in colusite from Lorano. It is absent also in X-ray powder pattern reported by Lévy (1967) for colusite from Butte. The assigned indices 111 are not compatible with space group $P\bar{4}3n$.

collected using the Gandolfi camera, with Cu $K\alpha$ radiation. Table 2 compares the X-ray powder patterns for the two crystals of colusite from Lorano with that of colusite from Butte (PDF 9–10). The cell parameters are a 10.532(7), 10.606(7) Å for crystals 1 and 2, respectively. the systematic absences (hhl absent for $l=2n+1$), determined by means of Weissenberg and precession photographs, indicated $Pm3n$ or $P\bar{4}3n$ space groups. However, only $P\bar{4}3n$ is consistent with the $\bar{4}3m$ point group indicated by a morphological study of the crystals; therefore, this space group is assumed to be the correct one for the mineral. Dangel & Wuensch (1970) proposed the space group $P\bar{4}3m$ for colusite from Butte, mainly on the basis of some very weak hhl ($l=2n+1$) reflections, such as 333, 993, 773 and 555, observed in its diffraction pattern. Such reflections have not been observed at all in the diffraction pattern of colusite from Lorano, even with Weissenberg and precession photographs obtained from very small fragments of the mineral during extremely long exposures. B.J. Wuensch (pers. comm. 1980) independently determined that the extra reflections can be considered spurious and also concluded that the correct space group is $P\bar{4}3n$. Single-crystal diffractometer data were collected on crystals 1 and 2 to solve their crystal structures. These data confirmed the choice of space group $P\bar{4}3n$ and gave unit-cell parameters a 10.538(6) Å and 10.621(6) Å for crystals 1 and 2, respectively.

The microprobe analytical data obtained for the two crystals of colusite previously studied by X-ray methods are given in Table 3. The analysis was done with an ARL–SEMQ electron microprobe at 15 kV and 0.20 μA specimen current. The following standards were used: galena for sulfur, chalcopyrite for copper, synthetic sulfides of antimony and arsenic for these elements, and metals for vanadium, tin and germanium. The data were computed on-line using the program Magic 4 (Colby 1968).

TABLE 3. CHEMICAL DATA, COLUSITES FROM LORANO

	Wt.%(1)	Wt.%(2)
V	3.3	3.1
Cu	50.1	49.5
S	31.2	30.2
Sb	1.4	0.92
Sn	0.26	6.6
Ge	0.63	1.1
As	13.6	8.8
Total	100.49	100.22

(1) Crystal No. 1: cell dimension a=10.532Å
(2) Crystal No. 2: cell dimension a=10.606Å

Crystal Chemistry of Colusite

The crystal structure of colusite was solved by one of us and will be fully described and discussed elsewhere (S. Merlino, in prep.). We are concerned here only with the main features of the structure, as they provide a sound basis on which the crystal chemistry of colusite may be assessed.

The structure of colusite can be easily described as derivative from that of sphalerite by substitution and insertion. The $[CuS_4]$ and $[(As, Sn)S_4]$ tetrahedra are connected in three dimensions by corner-sharing in a sphalerite-like structure. Two vanadium atoms are stuffed in tetrahedral sites at 0, 0, 0 and ½, ½, ½. The $[VS_4]$ tetrahedron shares six edges with the $[CuS_4]$ tetrahedra, as in the crystal structure of sulvanite (Pauling 1965, Trojer 1966). The structures of the colusites found at Lorano quarry were refined to reliability values of 0.070 and 0.054 for crystals 1 and 2 (the Sn-rich variety), respectively. The crystal–chemical formulae obtained as a result of the refinements are $Cu_{26}V_2As_6S_{32}$ and $Cu_{26}V_2As_4Sn_2S_{32}$ (crystals 1 and 2, respectively).

We note that, in contrast to the generally accepted assumption of 64 atoms in the unit cell, with a metal:sulfur ratio equal to one, the structural study indicates a unit-cell content of 66 atoms, with 26 copper atoms and a total of 34 metal atoms.

We recalculated the unit-cell contents of colusites from various sources on the basis of 66 atoms in the unit cell, as indicated by the structural results (Table 4). An ideal crystal–chemical formula for colusite is $Cu_{26}V_2(As,Sn)_6S_{32}$. The data reported in Table 4 indicate that iron may enter either the V site, as shown by

TABLE 4. UNIT-CELL CONTENTS FOR COLUSITE FROM VARIOUS SOURCES

	1	2	3	4	5	6	7
Cu	25.63	26.01	25.30	26.24	25.96	26.61	26.48
V	2.11	2.03	1.50	2.06	1.74	2.16	2.31
Fe	-	-	0.65	1.12	-	0.82	0.30
Zn	-	-	-	-	-	0.29	0.19
Ge	0.28	0.50	-	-	-	1.27	1.31
Sn	0.07	1.85	1.89	2.02	2.48	0.95	0.89
As	5.90	3.92	4.27	3.76	2.96	3.09	3.62
Sb	0.38	0.25	0.05	-	0.48	-	-
Te	-	-	0.33	-	-	-	-
S	31.63	31.44	32.01	30.80	32.38	30.80	30.91

1,2 - Sn-poor and Sn-rich colusite from Carrara (this study)
3 - Colusite from Butte (Berman & Gonyer 1939)
4 - Colusite from Butte (Lévy 1967)
5 - Colusite from Chizeuil (Lévy 1967)
6,7 - Colusite from Gay (Pshenichnyi et al.1974)

colusite from Butte (no. 3, Table 4), or the (As, Sn) site, as shown by colusite from Gay (nos. 6 and 7, Table 4). Germanium may also substitute for (As,Sn), as in colusite from Gay.

Murdoch (1953) claimed colusite and germanite to be isostructural. If this claim can be proved, colusite from Gay will represent an intermediate member, together with the vanadium arsenic germanate studied by Mitryaeva *et al.* (1968), compositionally between colusite and germanite, as suggested by Pshenichnyi *et al.* (1974). However, the whole problem of the relationship of structure and crystal chemistry among colusite, germanite and renierite deserves a close re-examination and will be discussed elsewhere.

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