

The Crystal Structure of Serpierite

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Serpierite, $\text{Ca}(\text{Cu}, \text{Zn})_4(\text{OH})_6(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$, crystallizes in the monoclinic system, space group $C2/c$, with $a = 22.186$, $b = 6.250$, $c = 21.853$ Å, $\beta = 113.36^\circ$ and $Z = 8$.

The analysis of the crystal structure was carried out by the interpretation of the Patterson function and by three-dimensional Fourier syntheses and refined by the least-squares method to a final R index of 0.10. In the crystal structure there are calcium ions in sevenfold coordination, copper ions in both distorted octahedra and 4+2 coordination and slightly distorted SO_4 tetrahedra. All bond distances are within the limits given in the literature. The most interesting feature of the structure is the presence of a new type of complex sheet of Cu coordination polyhedra, parallel to (100). A structural interpretation of twinning in serpierite is given.

Introduction

The rare mineral serpierite is a hydrated basic copper calcium sulphate, found at Laurion (Greece) by Bertrand (1881). It was first described by Des Cloizeaux (1881) who gave the optics and the morphology of the crystals and assigned them to the rhombic system. Later Frenzel (1894) reported the chemical analysis from which the formula computed for the mineral is $(\text{Ca}, \text{Cu}, \text{Zn})_4(\text{OH})_6(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$. Faraone, Sabelli & Zanazzi (1967), in a mineralogical study on serpierite and devillite preliminary to this structural work, found that the mineral serpierite belongs to the monoclinic system; they determined the cell parameters and the space group and carried out a new investigation on the physical, morphological and chemical properties. The analysis of the mineral reported by these authors leads to the formula $\text{Ca}(\text{Cu}_{0.66}\text{Zn}_{0.34})_4(\text{OH})_6 \cdot (\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$.

The crystal analysis of the mineral devillite, which presents structural features very similar to those of serpierite, is now in progress in this laboratory.

Experimental

For the structural study of serpierite, a sample from the Laurion mine (Greece) was used. The crystals are thin sky-blue plates elongated [010], the only well developed form being the {100} pinacoid. The unit-cell parameters are:

$$a = 22.186 + 0.002, \quad b = 6.250 + 0.002, \quad c = 21.853 + 0.002 \text{ Å}, \quad \beta = 113.36^\circ + 0.01^\circ$$

as determined in a previous paper (Faraone, Sabelli & Zanazzi, 1967) by the application of the least-squares method to the 2θ data obtained from Weissenberg photographs calibrated with Ag powder diffraction effects. From the systematic absences two space groups

were possible: Cc and $C2/c$. From morphological considerations the space group $C2/c$ was chosen for further investigation and it was subsequently found to be correct. The observed density, measured by flotation in a mixture of methylene iodide and carbon tetrachloride, is 3.07 g.cm^{-3} ; the calculated density for eight units $\text{Ca}(\text{Cu}_{0.66}\text{Zn}_{0.34})_4(\text{OH})_6(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ is 3.08 g.cm^{-3} .

The intensity data were obtained with Ni-filtered Cu $K\alpha$ radiation by the multiple-film technique from zero to fourth layer equi-inclination Weissenberg photographs along the b axis. The crystal used was a thin fragment with dimensions $0.40 \times 0.13 \times 0.02$ mm. The appearance of the photographs was not very good: the reflexions with $k+l=2n+1$ are diffuse and the diffusion of the intensity takes place along the a^* reciprocal axis, thereby suggesting that the crystal shows multiple twinning. All the crystals tested for intensity collection were affected by this feature. These reflexions used in the first stages of the structure determination, were excluded from the last cycles of refinement.

A total of 2296 independent reflexions were collected; of these, 1336 were not observed. Intensities were measured with a microdensitometer. For the diffuse spots, the maximum of intensity in correspondence of the reciprocal lattice points was measured. Different layers were put on the same relative scale taking into account their exposure times. Empirical corrections for $\alpha_1 - \alpha_2$ doublet resolution were applied. The F_{hkl}^2 's were obtained by applying the Lorentz-polarization factor with the use of a program written for the IBM 1620 computer (Albano, Bellon & Pompa, 1963). Absorption correction was neglected.

Structure determination and refinement

From the first examination of Weissenberg photographs of serpierite, we remarked that the strongest spots have $l=8n$ on the $h0l$ and $h4l$ layers and $l=8n+4$

on the $h2l$, showing the presence of a well marked A -centered pseudocell with the same orientation as the true cell, and with $a' = \frac{1}{2}a$, $b' = \frac{1}{2}b$ and $c' = \frac{1}{4}c$. The three-dimensional Patterson function was computed; according to the above written pseudosymmetry, the most striking features of the maps were the highest peaks aligned in the c direction at $w = 0, \frac{1}{8}, \frac{1}{4}, \frac{3}{8}$ etc. on planes at $u = 0$ and $\frac{1}{2}$; the coordinate v of these peaks was alternately $0, \frac{1}{2}$ and $\frac{1}{4}, \frac{3}{4}$. We assigned these peaks to Cu–Cu vectors and located these atoms on planes parallel to (100) at $z = 0, \frac{1}{8}, \frac{1}{4}, \frac{3}{8}$ etc. and at y alternatively $0, \frac{1}{2}$ and $\frac{1}{4}, \frac{3}{4}$. The exact localization of these copper planes in the cell was at this stage impossible because there were three possibilities: the first with a Cu ion in special position on the inversion centre at the origin, the second with a Cu on the centre at $x = \frac{1}{4}$, $y = \frac{1}{4}$ and $z = 0$, the third with a Cu in general position at $x = z = 0$ and $y = \frac{1}{4}$. The further interpretation of the Patterson maps allowed us to recognize as Cu–O vectors some peaks at distances of approximately 2 Å from the highest ones, typical of octahedral copper coordination. These peaks, though weaker than those assigned to Cu–Cu vectors, were relevant, suggesting a similar orientation for all the coordination copper polyhedra. Furthermore it was possible to assign other weaker peaks to Cu–Ca vectors. In order to resolve the above ambiguities, all the possible sets of coordinates were tried and we were able to choose the most satisfactory arrangement by comparing observed and computed structure factors. The third hypothesis was found to be right, and the R index, computed with the contribution of the copper ions, the calcium and eight oxygen atoms, was 0.45 for all the observed reflexions.

A three-dimensional Fourier synthesis, computed with the phase signs given by these atoms, revealed the locations of the two sulphur atoms of the asymmetric unit. By successive electron density maps, the remaining oxygen atoms were found. A further and more detailed Fourier synthesis was then computed to improve the coordinates of all atoms previously placed. At this stage the reliability index $R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$ was 0.22.

The structure was refined by the method of least squares, with a program written by Albano, Bellon, Pompa & Scatturin (1963) for the IBM 1620 computer using the block-diagonal approximation and individual thermal parameters. The weighing scheme suggested by Cruickshank (1961), $w = 1/(a + F_o + cF_o^2)$ with $a = 2F_{\min}$ and $c = 2/F_{\max}$, was employed for the structure factors and the unobserved reflexions were not included in the calculations. Each cycle was followed by a proper rescaling of F_o 's. After three cycles, when the R index was 0.15, it was decided to leave out of the refinement the diffuse reflexions with $k + l = 2n + 1$, which are systematically underestimated, as well as the reflexions 200, 400 and 600 showing extinction. After three more cycles with the help of sharp reflexions only, the refinement was ended.

The atomic coordinates and isotropic thermal parameters are listed in Table 1. The final R value for the 730 reflexions with $k + l = 2n$ included in the last cycles of refinement is 0.099, and observed and calculated structure factors are listed in Table 2. In Table 3 are reported the F_{obs} 's and F_{calc} 's for the 227 reflexions with $k + l = 2n + 1$, calculated with the last atomic coordinates and roughly rescaled by comparing $\sum |F_{\text{obs}}|$ and $\sum |F_{\text{calc}}|$. Assuming the value 1 the scale factor for F_{obs} 's of the sharp reflexions, the scale factor for F_{obs} 's of diffuse reflexions is from 1.56 for $h1l$, to 1.23 for $h4l$ layers. The R index calculated for all reflexions, after rescaling of diffuse spots, is 0.11. For the calculations, the scattering factor values from the self-consistent model as listed in *International Tables for X-ray Crystallography* (1962) for Cu^{2+} , Ca, S, and O were used. No correction was applied to the Cu^{2+} scattering curve for the Zn content of the mineral. In view of the poor quality of the data, no attempt has been made to locate the hydrogen atoms in the structure or to introduce anisotropic temperature factors in the refinement.

Discussion of the structure

The projection of the structure of serpierite on (010) is shown in Fig. 1. The lists of bond lengths and bond angles are included in Tables 4 and 5.

In the asymmetric unit there are three copper ions in general positions and two more in special positions on the twofold axis. These five ions are all surrounded

Table 1. Fractional atomic coordinates and isotropic thermal parameters

The standard deviations ($\times 10^4$) of x , y and z respectively are: 2, 12, 2 for the Ca ion; 1, 8, 1 for the Cu ions; 3, 13, 3 for the S atoms; and 8, 40, 8 for the O atoms.

	x	y	z	B
Ca	0.2423	0.9153	0.1479	1.40 Å ²
Cu(1)	0.0010	0.2572	0.0029	1.72
Cu(2)	0.9957	0.0042	0.1241	1.97
Cu(3)	0.9966	0.5064	0.1240	1.92
Cu(4)	0.0000	0.7561	0.2500	1.70
Cu(5)	0.0000	0.2577	0.2500	2.05
S(1)	0.1503	0.1958	0.2269	1.29
S(2)	0.3526	0.3027	0.0102	1.48
O(1)	0.3292	0.6310	0.2020	1.84
O(2)	0.1624	0.0110	0.1895	2.60
O(3)	0.0811	0.2515	0.1975	2.87
O(4)	0.1936	0.3708	0.2303	2.73
O(5)	0.4237	0.2728	0.0402	2.01
O(6)	0.1627	0.0508	0.0518	2.46
O(7)	0.1808	0.3942	0.0080	3.85
O(8)	0.3338	0.4190	0.0593	2.95
O(9)	0.1836	0.5968	0.1197	1.81
O(10)	0.2984	0.8222	0.0762	3.41
O(11)	0.3087	0.2242	0.1578	3.58
O(12)	0.0405	-0.0034	0.0646	1.19
O(13)	0.0424	0.5158	0.0633	0.95
O(14)	0.0418	0.7663	0.1780	1.61
O(15)	0.4512	0.7723	0.0735	1.74
O(16)	0.4555	0.5220	0.1892	1.37
O(17)	0.4543	-0.0062	0.1890	1.39

by six oxygen atoms, but they exhibit two types of coordination. Cu(2), Cu(3) and Cu(5) have the usual 4+2 configuration with four oxygen atoms as nearest neighbours in an approximately square arrangement

at an average distance of 1.96 Å and two oxygen atoms at an average distance of 2.48 Å to complete a tetragonal bipyramid. These values are in agreement with the generally accepted ones. The other two non-equiva-

Table 2. Observed and calculated structure factors for reflexions with $k+1=2n$

Unobserved reflections are neglected; their calculated intensity is less than the minimum locally observed one.

H	K	L	F ₀	F _c	H	K	L	F ₀	F _c	H	K	L	F ₀	F _c	H	K	L	F ₀	F _c	H	K	L	F ₀	F _c	H	K	L	F ₀	F _c	H	K	L	F ₀	F _c
0	0	4	146.1	137.8	14	0	-20	121.1	-108.8	7	1	-15	45.5	42.2	6	2	6	76.7	-83.2	1	3	-13	83.0	85.8	0	4	4	57.2	33.2					
0	0	6	134.9	115.0	16	0	-22	94.5	107.4	9	1	-17	107.9	-96.4	6	2	-6	44.2	-36.4	1	3	-13	54.8	45.2	0	4	4	296.5	251.2					
0	0	8	419.4	462.6	18	0	-24	241.3	223.6	9	1	-21	95.8	-94.2	8	2	-8	94.6	-86.0	1	3	-13	44.8	-40.6	10	4	4	433.4	398.0					
0	0	14	146.1	130.4	26	0	-26	49.7	-52.0	9	1	-23	62.3	47.2	8	2	-8	244.0	-216.8	1	3	-17	98.0	-83.2	16	4	4	19.9	17.8					
0	0	16	496.7	480.0	0	0	0	299.0	340.6	9	1	-1	73.9	68.6	10	2	0	50.3	58.0	1	3	-19	59.9	56.6	16	4	4	16.4	14.4					
0	0	18	62.6	44.2	0	0	-2	111.9	-83.4	9	1	-1	62.3	-53.2	12	2	-8	248.8	-272.8	2	4	-23	41.0	33.2	2	4	4	601.9	714.6					
0	0	24	95.4	85.6	0	0	-4	143.9	-138.8	9	1	-3	73.7	-68.4	12	2	-12	93.4	-84.8	3	5	-23	24.2	-22.4	6	4	4	20.2	18.0					
0	0	30	388.5	668.6	0	0	-6	226.9	-208.0	9	1	-5	90.6	89.4	10	2	-16	69.1	-62.8	3	5	-23	155.4	145.4	6	4	4	35.0	30.6					
0	0	36	61.6	34.4	0	0	-8	73.7	-74.0	9	1	-7	124.4	-70.6	10	2	-20	209.7	-203.2	3	5	-23	45.9	-46.8	12	4	4	76.9	62.6					
0	0	42	183.9	165.6	0	0	-10	189.3	188.2	9	1	-9	128.1	-124.6	10	2	-24	245.6	-226.0	3	5	-23	35.4	-34.4	12	4	4	355.4	309.2					
0	0	48	80.7	-89.0	0	0	-12	295.6	353.6	13	1	-13	81.9	-96.2	10	2	-28	163.8	-159.0	3	5	-23	54.7	39.6	10	4	4	48.9	-52.2					
0	0	54	136.4	-126.8	0	0	-14	124.4	-124.6	13	1	-17	124.4	-70.6	10	2	-32	266.8	-330.6	3	5	-23	64.6	-61.8	14	4	4	38.7	36.8					
0	0	60	183.9	165.6	0	0	-16	45.5	54.8	13	1	-19	49.8	8.4	10	2	-36	518.4	-574.4	3	5	-23	79.2	-75.6	16	4	4	355.4	309.2					
0	0	66	488.1	512.6	0	0	-18	230.3	240.4	13	1	-21	75.6	64.6	10	2	-40	106.4	97.4	3	5	-23	9.2	88.0	16	4	4	92.4	316.0					
0	0	72	239.8	279.4	0	0	-20	98.5	-91.4	11	1	-23	86.5	71.2	12	2	-44	163.8	-159.0	3	5	-23	51.8	51.2	4	4	4	453.3	461.0					
0	0	78	136.4	-126.8	0	0	-22	195.7	196.2	11	1	-25	53.3	60.0	12	2	-48	266.8	-330.6	3	5	-23	64.6	61.8	10	4	4	16.3	14.4					
0	0	84	488.1	512.6	0	0	-24	246.6	262.6	11	1	-27	83.0	91.2	12	2	-52	506.0	-451.8	3	5	-23	128.4	-116.0	10	4	4	33.7	23.0					
0	0	90	136.4	-126.8	0	0	-26	84.2	-83.0	11	1	-29	100.4	97.4	12	2	-56	89.0	-111.2	3	5	-23	52.2	49.2	10	4	4	96.5	-80.0					
0	0	96	488.1	512.6	0	0	-28	81.6	89.4	11	1	-31	52.5	79.2	12	2	-60	232.3	-208.0	3	5	-23	81.7	-75.6	10	4	4	302.7	297.0					
0	0	102	136.4	-126.8	0	0	-30	314.5	330.6	11	1	-33	79.0	76.8	12	2	-64	518.4	-574.4	3	5	-23	79.6	89.4	10	4	4	468.7	386.4					
0	0	108	488.1	512.6	0	0	-32	73.8	65.2	11	1	-35	122.4	-133.8	12	2	-68	85.6	-81.4	3	5	-23	43.1	-33.0	10	4	4	50.5	45.2					
0	0	114	136.4	-126.8	0	0	-34	81.6	89.4	11	1	-37	49.3	60.0	12	2	-72	92.5	92.2	3	5	-23	62.3	49.2	12	4	4	12.5	11.8					
0	0	120	488.1	512.6	0	0	-36	425.4	497.4	11	1	-39	87.1	84.4	12	2	-76	331.8	-390.8	3	5	-23	89.0	92.2	12	4	4	16.4	14.4					
0	0	126	136.4	-126.8	0	0	-38	73.0	78.4	11	1	-41	77.3	69.6	12	2	-80	331.8	-407.0	3	5	-23	64.2	68.2	12	4	4	16.4	14.4					
0	0	132	488.1	512.6	0	0	-40	136.4	137.8	11	1	-43	118.4	-114.6	12	2	-84	105.7	-127.8	3	5	-23	44.0	34.2	12	4	4	39.4	32.6					
0	0	138	136.4	-126.8	0	0	-42	90.2	97.2	11	1	-45	88.3	79.2	12	2	-88	129.1	131.0	3	5	-23	83.9	72.2	12	4	4	39.4	32.6					
0	0	144	488.1	512.6	0	0	-44	232.9	-239.0	11	1	-47	65.6	50.0	12	2	-92	118.4	-107.6	3	5	-23	118.4	9.2	12	4	4	35.3	30.6					
0	0	150	136.4	-126.8	0	0	-46	46.4	38.0	11	1	-49	130.6	110.4	12	2	-96	129.1	131.0	3	5	-23	99.7	-98.4	12	4	4	35.3	30.6					
0	0	156	488.1	512.6	0	0	-48	466.7	497.4	11	1	-51	77.3	69.6	12	2	-100	169.7	-168.4	3	5	-23	107.0	-98.2	12	4	4	49.3	32.6					
0	0	162	136.4	-126.8	0	0	-50	678.1	683.0	11	1	-53	103.3	94.4	12	2	-104	169.7	-168.4	3	5	-23	81.7	-85.4	12	4	4	83.3	-99.6					
0	0	168	488.1	512.6	0	0	-52	376.4	-345.0	11	1	-55	155.3	-149.2	12	2	-108	98.7	81.8	3	5	-23	107.0	-98.2	12	4	4	49.3	32.6					
0	0	174	136.4	-126.8	0	0	-54	44.6	38.0	11	1	-57	172.4	-166.0	12	2	-112	169.7	-168.4	3	5	-23	117.0	-114.6	12	4	4	110.4	103.4					
0	0	180	488.1	512.6	0	0	-56	466.7	497.4	11	1	-59	103.3	94.4	12	2	-116	169.7	-168.4	3	5	-23	81.7	-85.4	12	4	4	83.3	-99.6					
0	0	186	136.4	-126.8	0	0	-58	224.3	247.6	11	1	-61	155.3	-149.2	12	2	-120	98.7	81.8	3	5	-23	107.0	-98.2	12	4	4	49.3	32.6					
0	0	192	488.1	512.6	0	0	-60	538.8	496.6	11	1	-63	172.4	-166.0	12	2	-124	169.7	-168.4	3	5	-23	117.0	-114.6	12	4	4	110.4	103.4					
0	0	198	136.4	-126.8	0	0	-62	193.9	-198.4	11	1	-65	140.9	146.4	12	2	-128	169.7	-168.4	3	5	-23	81.7	-85.4	12	4	4	83.3	-99.6					
0	0	204	488.1	512.6	0	0	-64	678.1	683.0	11	1	-67	58.3	60.4	12	2	-132	98.7	81.8	3	5	-23	107.0	-98.2	12	4	4	49.3	32.6					
0	0	210	136.4	-126.8	0	0	-66	81.6	-70.0	11	1	-69	146.6	-139.4	12	2	-136	169.7	-168.4	3	5	-23	117.0	-114.6	12	4	4	110.4	103.4					
0	0	216	488.1	512.6	0	0	-68	213.5	189.2	11	1	-71	82.6	-40.6	12	2	-140	98.7	81.8	3	5	-23	81.7	-85.4	12	4	4	83.3	-99.6					
0	0	222	136.4	-126.8	0	0	-70	54.9	-38.6	11	1	-73	171.6	67.2	12	2	-144	163.8	-184.0	3	5	-23	67.2	-59.6	12	4	4	33.2	34.6					
0	0	228	488.1	512.6	0	0	-72	194.2	199.4	11	1	-75	146.6	-139.4	12	2	-148	163.8	-184.0	3	5	-23	117.0	-114.6	12	4	4	110.4	103.4					
0	0	234	136.4	-126.8	0	0	-74	81.6	62.0	11	1	-77	117.4	-105.6	12	2	-152	117.4	-105.6	3	5	-23	91.6	98.0	12	4	4	35.3	30.6					
0	0	240	488.1	512.6	0	0	-76	282.9	-239.0	11	1	-79	124.4	-124.6	12	2	-156	134.7	-107.0	3	5	-23	56.9	54.6	12	4	4	6.1	5.4					
0	0	246	136.4	-126.8	0	0	-78	98.7	110.6	11	1	-81	124.4	-124.6	12	2	-160	134.7	-107.0	3	5	-23	104.8	39.8	12	4	4	281.0	266.6					
0	0	252	488.1	512.6	0	0	-80	369.6	356.4	11	1	-83	150.1	-149.4	12	2	-164	244.8	-277.6	3	5	-23	59.2	56.6	12	4	4	91.5	85.2					
0	0	258	136.4	-126.8	0	0	-82	63.5	-59.4	11	1	-85	50.3	-56.8	12	2	-168	336.3	-348.4	3	5	-23	68.5	76.6	12	4	4	58.5	41.6					
0	0	264	488.1	512.6	0	0	-84	104.7	-94.8	11	1	-87	133.3	130.8	12	2	-172	336.3	-348.4	3	5	-23	51.4	-49.2	12	4	4	70.7	64.4					
0	0	270	136.4	-126.8	0	0	-86	473.5	493.0	11	1	-89	103.3	94.4	12	2	-176	336.3	-348.4	3	5	-23	64.6	-68.2	12	4	4	16.4	14.4					
0	0	276	488.1	512.6	0	0	-88	84.2	82.2	11	1	-91	103.3	94.4	12	2	-180	75.3	-68.2	3	5	-23	91.2	104.4	12	4	4	16.4	14.4					
0	0	282	136.4	-126.8	0	0	-90	117.7	113.0	11	1	-93	144.4	-139.4	12	2	-184	75.3	-68.2	3	5													

are lower than those found for Cu(2), Cu(3) and Cu(5).

The calcium ion binds seven oxygen atoms arranged at the corners of a polyhedron similar to an octahedron

having one face centered, the Ca-O bond lengths ranging from 2.30 to 2.54 Å.

Both the SO₄ groups in the structure have the usual tetrahedral coordination slightly distorted; O-S-O

Table 4. Bond lengths

(I)	x, y, z		(IX)	$1+x, y, z$	
(II)	$-x, -y, -z$		(X)	$1+x, 1+y, z$	
(III)	$-x, y, \frac{1}{2}-z$		(XI)	$\frac{1}{2}+x, -\frac{1}{2}+y, z$	
(IV)	$\frac{1}{2}+x, \frac{1}{2}+y, z$		(XII)	$-\frac{1}{2}+x, -\frac{1}{2}+y, z$	
(V)	$\frac{1}{2}-x, \frac{1}{2}-y, -z$		(XIII)	$-\frac{1}{2}+x, \frac{1}{2}+y, z$	
(VI)	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$		(XIV)	$\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$	
(VII)	$x, 1+y, z$		(XV)	$\frac{1}{2}-x, \frac{3}{2}-y, -z$	
(VIII)	$-x, 1-y, -z$		(XVI)	$\frac{1}{2}-x, \frac{1}{2}+y, z$	
Cu(1)(I)—O(6)(VII)	2.30 Å	Cu(1)(I)—O(12)(I)	2.07 Å		
—O(10)(I)	2.43	—O(12)(II)	2.11		
—O(11)(VII)	2.39	—O(13)(I)	2.06		
—O(1)(I)	2.54	—O(13)(VIII)	1.98		
—O(4)(VI)	2.49	—O(5)(V)	2.23		
—O(2)(VII)	2.37	—O(15)(XII)	2.23		
—O(9)(I)	2.32				
Cu(2)(VII)—O(12)(X)	1.93	Cu(3)(I)—O(13)(IX)	1.97		
—O(3)(X)	2.48	—O(3)(IX)	2.50		
—O(14)(IX)	1.92	—O(14)(IX)	2.02		
—O(16)(IV)	1.96	—O(17)(IV)	1.99		
—O(5)(IV)	2.38	—O(5)(IV)	2.53		
—O(15)(IV)	2.03	—O(15)(XI)	1.87		
Cu(4)(I)—O(14)(I)	2.12	Cu(5)(I)—O(3)(I)	2.49		
—O(16)(VI)	2.11	—O(16)(XIV)	1.97		
—O(17)(VI)	2.10	—O(17)(VI)	1.98		
S(1)(I)—O(1)(XIV)	1.49	S(2)(I)—O(5)(I)	1.46		
—O(2)(I)	1.50	—O(6)(V)	1.56		
—O(3)(I)	1.45	—O(7)(V)	1.41		
—O(4)(I)	1.44	—O(8)(I)	1.49		

Estimated standard deviations for Ca-O, Cu-O and S-O bond lengths are ≤ 0.02 Å.

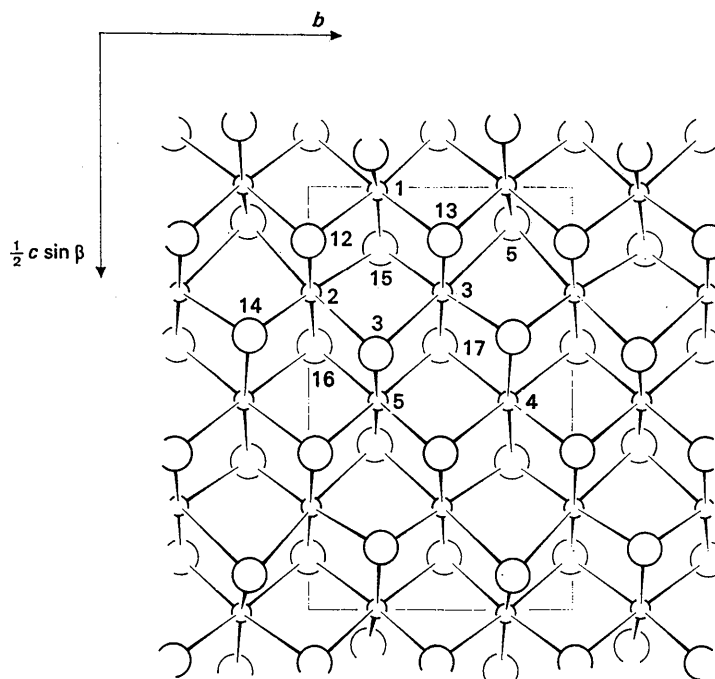


Fig. 2. A single copper-oxygen sheet in serpierite. Projection along [100].

angles are in the range 107–114°; the average S–O distances are 1.47 and 1.48 Å respectively for S(1) and S(2).

The distinction between oxygen atoms, hydroxyl groups and water molecules was made on the basis of Pauling's electrostatic valence rule. The oxygen atoms listed in Table 1 from O(12) to O(17) belong to hydroxyl groups, and those from O(9) to O(11) to water molecules. In Table 6 are listed the O–O distances attributable to hydrogen bonds. They range from 2.69 to 3.00 Å. Two further distances of 3.33 Å and 3.35 Å occur between O(15)(I) and O(8)(I) and between

O(7)(I) and O(11)(I) respectively. These large distances can be considered as very feeble H-bonds.

Table 6. *Hydrogen bond distances*

O(9) (I)–O(7)(I)	2.73 Å
O(9) (I)–O(4)(I)	2.73
O(10)(I)–O(7)(XV)	2.72
O(10)(I)–O(8)(I)	2.71
O(11)(I)–O(8)(I)	2.72
O(11)(I)–O(1)(I)	2.69
O(13)(I)–O(9)(I)	2.92
O(12)(I)–O(6)(I)	2.85
O(14)(I)–O(2)(VII)	3.00
O(16)(I)–O(1)(I)	3.00

Table 5. *Bond angles*

O(6)(VII)–Ca(I)——O(10)(I)	84.5°	O(12)(I)–Cu(1)(I) —O(12)(II)	79.6°
—O(11)(VII)	90.4	—O(13)(I)	103.5
—O(1)(I)	147.9	—O(13)(VIII)	173.9
—O(4)(VI)	157.4	—O(5)(V)	90.8
—O(2)(VII)	80.6	—O(15)(XII)	77.3
—O(9)(I)	85.8	O(12)(II)–	175.9
O(10)(I)–	78.2	—O(13)(I)	94.4
—O(11)(VII)	69.2	—O(13)(VIII)	80.4
—O(1)(I)	116.3	—O(15)(XII)	108.5
—O(4)(VI)	164.2	O(13)(I)–	82.5
—O(2)(VII)	90.0	—O(5)(V)	96.8
—O(9)(I)	101.3	—O(15)(XII)	75.0
O(11)(VII)–	85.6	O(13)(VIII)–	88.9
—O(1)(I)	106.9	—O(15)(XII)	104.1
—O(4)(VI)	168.0	O(5)(V)–	163.3
—O(2)(VII)	54.4		
—O(9)(I)	122.9	O(13)(IX)–Cu(3)(I)–O(3)(IX)	89.8°
O(4)(VI)–	76.5	—O(14)(IX)	95.8
—O(2)(VII)	79.3	—O(17)(IV)	177.3
—O(9)(I)	102.2	—O(5)(IV)	81.1
O(2)(VII)–	83.8	—O(15)(XI)	85.8
		—O(14)(IX)	93.7
O(12)(X)–Cu(2)(VII)–O(3)(X)	89.2°	—O(17)(IV)	87.8
—O(14)(IX)	95.9	—O(5)(IV)	170.7
—O(16)(IV)	176.0	—O(15)(XI)	88.4
—O(5)(IV)	80.4	—O(17)(IV)	83.1
—O(15)(IV)	85.6	—O(5)(IV)	85.4
O(3)(X)–	90.1	—O(15)(XI)	177.4
—O(14)(IX)	86.9	O(17)(IV)–	101.3
—O(16)(IV)	169.5	—O(15)(XI)	95.4
—O(5)(IV)	85.4	O(5)(IV)–	92.7
—O(15)(IV)	83.3		
O(14)(IX)–	91.9		
—O(5)(IV)	175.2		
—O(15)(IV)	103.5		
O(16)(IV)–	94.9		
—O(15)(IV)	92.8		
O(5)(IV)–			
		O(3)(I)–Cu(5)(I)——O(16)(XIV)	92.2°
O(14)(I)–Cu(4)(I)——O(16)(VI)	102.1°	—O(17)(VI)	92.9
—O(17)(VI)	104.5	—O(3)(III)	178.2
—O(14)(III)	176.6	—O(16)(XII)	86.4
—O(16)(XIII)	75.1	—O(17)(XIII)	88.4
—O(17)(XVI)	78.2	O(16)(XIV)–	96.8
O(16)(VI)–	103.1	—O(17)(VI)	83.0
—O(16)(XIII)	76.2	—O(16)(XII)	179.3
—O(17)(XVI)	179.1	—O(17)(XIII)	83.5
O(17)(VI)–	77.5	O(17)(VI)–	
		O(5)(I)–S(2)(I)——O(6)(V)	106.8°
O(1)(XIV)–S(1)(I)——O(2)(I)	108.2°	—O(7)(V)	111.6
—O(3)(I)	111.0	—O(8)(I)	107.5
—O(4)(I)	103.4	O(6)(V)–	111.0
O(2)(I)–	109.3	—O(7)(V)	108.3
—O(3)(I)	110.7	—O(8)(I)	111.3
—O(4)(I)	114.1	O(7)(V)–	
O(3)(I)–		—O(8)(I)	

Estimated standard deviations for O–Ca–O and O–Cu–O angles are $\leq 0.8^\circ$; for O–S–O angles are $\leq 1^\circ$.

The configuration shown by the cation–oxygen complexes is the following:

Cu(1)	links 1 O	and 5 OH
Cu(2)	2 O	and 4 OH
Cu(3)	2 O	and 4 OH
Cu(4)	6 OH	
Cu(5)	2 O	and 4 OH
Ca	4 O	and 3 H ₂ O

The calcium coordination polyhedra are not linked to each other and share one edge and two corners with three SO₄ groups. In particular the S(1) tetrahedron shares the O(1)–O(4) edge and the O(2) corner with two Ca polyhedra respectively; the S(2) tetrahedron shares the O(6) corner with a Ca polyhedron, the O(7) and O(8) corners are unshared with cation polyhedra and are hydrogen bonded to other oxygen atoms. Both SO₄ groups are linked to Cu coordination polyhedra through a corner, namely O(3) for S(1) and O(5) for S(2).

Each copper coordination octahedron shares six edges with six surrounding copper octahedra to form a close packed sheet parallel to (100), as shown in Fig. 2. The minimum Cu–Cu distance between adjacent ions is 3.03 Å, the maximum one is 3.16 Å. This layer of copper and oxygen atoms can be regarded as a variation of the C6 type hypothetical Cu(OH)₂ structure, where one quarter of the OH groups are replaced by O atoms of SO₄ groups. The result is the sheet ${}_{\infty}^2[\text{Cu}_2(\text{OH})_3\text{O}]^-$. Some complex sheets of copper coordination polyhedra had been found in basic copper minerals, but the type found in serpierite is quite new. In brochantite (Cocco & Mazzi, 1959) there are two kinds of chain, one formed by octahedra sharing one edge, and the other by octahedra sharing one corner. These chains are linked to each other by corners to form the sheet ${}_{\infty}^2[\text{Cu}_2(\text{OH})_3\text{O}_2]^{-3}$. In pseudomalachite (Ghose, 1963) two types of chain are joined alternately to form the sheet ${}_{\infty}^2[\text{Cu}_5(\text{OH})_4\text{O}_8]^{-10}$. In both these kinds of sheet some of the oxygen atoms are bound by three Cu ions and some by two Cu ions. In

the type of sheet found in serpierite all the oxygen atoms are bound by three Cu ions in a very compact arrangement. A configuration somewhat similar to this one was found in hydrozincite (Ghose, 1964); in this structure there are sheets of Zn coordination octahedra, but one quarter of the octahedral positions are not occupied by Zn ions, the resulting sheet being ${}_{\infty}^2[\text{Zn}_3(\text{OH})_6\text{O}_2]^{-4}$.

The layer structure found in serpierite accounts for the good {100} cleavage and for the optical negative character of the mineral.

Twinning

As mentioned above, a feature of the Weissenberg photographs of serpierite is the presence of some diffuse diffraction effects. This diffusion affects the reflexions with $k+l$ odd (or $h+l$ odd, for the symmetry of the space group) and it was attributed to twinning.

Because of their particular coordinates in the structure, the copper ions and the oxygen atoms of the copper coordination polyhedra give their contribution almost entirely to the reflexions with $k+l$ even, which are quite sharp. This fact led us to the conclusion that the copper–oxygen sheets do not change their stacking periodicity in the whole crystal. The lack of periodicity which occurs at the boundary of the twin individuals has to be attributed to the sulphur and calcium coordination polyhedra, in such a way as to affect the $k+l$ odd reflexions only. This condition occurs when the y coordinate of an atom in the A individual corresponds to the $\frac{1}{2}-y$ coordinate for the same atom in the B individual. This is the same as considering the origin of the B individual to be shifted $\frac{1}{2}b$ and $\frac{1}{2}c$ (or $\frac{1}{2}a$ and $\frac{1}{2}c$) from the origin of the A individual. In fact, the trigonometric parts of the F_c formulae in the $C2/c$ space group are:

$$8 \cos 2\pi(hx + lz) \cos 2\pi ky \quad \text{for } l=2n$$

and

$$-8 \sin 2\pi(hx + lz) \sin 2\pi ky \quad \text{for } l=2n+1.$$

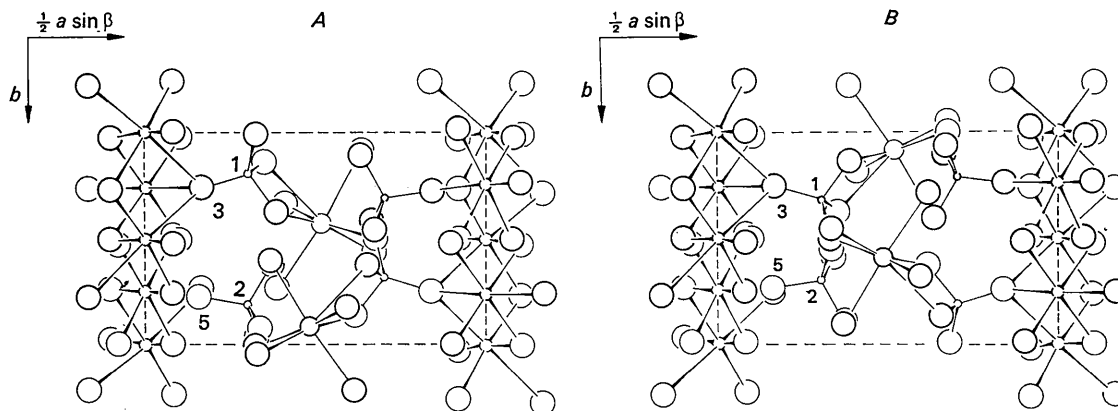
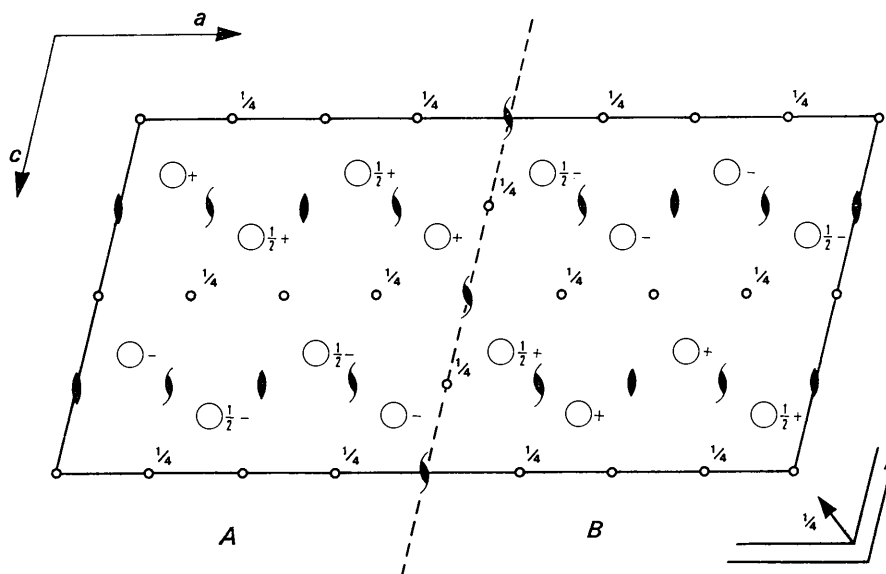


Fig. 3. The projection, along [001], of the same part of the structure of two individuals of the twin.



g. 4. The arrangement of representative points in a serpierite twin. The boundary, with the twin symmetry operations, is outlined by a dashed line.

From these expressions, taking into account that the x and z coordinates do not vary, for the y contribution only we have:

$$\left. \begin{aligned} \cos 2\pi ky &= \cos 2\pi k(\frac{1}{2} - y) \\ \sin 2\pi ky &= \sin 2\pi k(\frac{1}{2} - y) \end{aligned} \right\} \text{ if } k+l=2n$$

$$\left. \begin{aligned} \cos 2\pi ky &= -\cos 2\pi k(\frac{1}{2} - y) \\ \sin 2\pi ky &= -\sin 2\pi k(\frac{1}{2} - y) \end{aligned} \right\} \text{ if } k+l=2n+1$$

The change of the sign for the reflexions with $k+l$ odd shows the lack of periodicity between twinned individuals. Since the diffuse reflexions are smeared out along the a^* reciprocal axis, the discontinuity occurs in this direction, namely through copper-oxygen layers, broadening the reciprocal lattice points. The A and B individual structures projected along $[001]$ are shown in Fig. 3.

Fig. 4 illustrates two adjacent cells at the boundary of the twin. At the boundary there is the formation of twofold screw axes parallel to $[010]$ and inversion centres at $\frac{1}{4}$ and $\frac{3}{4}b$. These twin symmetry operations, however, are not independent, because each one may be the product of another by the axial glide present in the space group. The two-dimensional discontinuity at the twin boundary is bridged by copper-oxygen sheets, which are shared by both crystals. According to the twinning theory of Holser (1958), these sheets form the slice of the structure which contains the requisite symmetry for the twinning. In fact, it can be pointed out that the twin symmetry operations, namely the screw axes and the inversion centres, pre-exist in the copper-oxygen layers.

This kind of twinning is not considered in Friedel's (1926) classification, because the symmetry of the lattice is not greater than that of the crystal. Indeed the additional symmetry elements of the twin do not affect the symmetry of the lattice, being of the same kind as those still present in the structure, even if in positions not stated by the space group. In other words, a twin of this kind cannot be distinguished from a single crystal from the morphological point of view.

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