

The crystal structure of vauquelinite and the relationships to fornacite

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Vauquelinit $\text{Pb}_2\text{CuCrO}_4\text{PO}_4\text{OH}$ hat die Gitterkonstanten $a = 13,754$, $b = 5,806$, $c = 9,563 \text{ \AA}$, $\beta = 94^\circ 34'$. Raumgruppe ist $P2_1/n$. Die Struktur wurde nach der Methode „trial and error“, von den im $\text{Pb}_2\text{CuCrO}_4\text{AsO}_4\text{OH}$ gefundenen Atomlagen ausgehend, bestimmt. Die Verfeinerung nach der Ausgleichsmethode ergab $R = 0,089$. Die Atomanordnung im Vauquelinit ist sehr ähnlich der des Fornacits; geringe Unterschiede bestehen nur in der Umgebung der Pb-Ionen und in der Anordnung der Symmetrieelemente (Fornacit hat die Raumgruppe $P2_1/c$).

Abstract

Vauquelinite, $\text{Pb}_2\text{Cu}[\text{CrO}_4\text{PO}_4\text{OH}]$, is monoclinic, with $a = 13.754$, $b = 5.806$, $c = 9.563 \text{ \AA}$, $\beta = 94^\circ 34'$, space group $P2_1/n$. The crystal analysis of the mineral was determined by the trial-and-error method starting from the atomic positions found in fornacite. The refinement carried out by the least-squares method gave a final discrepancy index R of 0.089.

The atomic packing in vauquelinite is very similar to that in fornacite. Some differences occur in coordination around lead ions and in the arrangement of symmetry elements in the two minerals.

Introduction

The mineral vauquelinite is a basic lead and copper chromophosphate belonging to the monoclinic system with space group $C_{2h}^5-P2_1/n$ (BERRY, 1949). GUILLEMIN and PROUVOST (1951) assigned the formula $\text{Pb}_2\text{Cu}[\text{CrO}_4\text{PO}_4\text{OH}]$ to the mineral. From diffractometric data and chemical analogies between vauquelinite and fornacite, a basic lead and copper chromoarsenate, these authors suggested the two minerals belong to an isomorphous series. BARIAND and HERPIN (1962) determined the unit cell of fornacite and related its lattice parameters to those of vauquelinite. The crystal analysis of fornacite was carried out (COCCO, FANFANI and ZANAZZI, 1967). In order to explain better the relations between the two minerals, the present investigation was undertaken.

Crystal data

Crystals of vauquelinite from Beresov were used for the present work. The lattice parameters previously reported (BERRY, 1949) were refined by least-squares computations employing data from a powder diffractogram. The unit-cell constants are as follows:

$$\begin{aligned} a &= 13.754 \pm .005 \text{ \AA} \\ b &= 5.806 \pm .006 \text{ \AA} \\ c &= 9.563 \pm .003 \text{ \AA} \\ \beta &= 94^\circ 34' \pm 2'. \end{aligned}$$

The space group is $P2_1/n$, $Z = 4$ and $D_x = 6.16 \text{ g cm}^{-3}$. The observed value D is 6.16 g cm^{-3} (GUILLEMIN and PROUVOST, 1951). The linear absorption coefficient μ is 1021 cm^{-1} for $\text{CuK}\alpha$ radiation.

A spherical specimen with radius 0.11 mm was prepared for the intensity-data collection. X-ray diffraction effects $h0l$, $h1l$, $h2l$, and $h3l$ were recorded by an integrating Weissenberg apparatus on multiple films using Ni-filtered $\text{CuK}\alpha$ radiation. A total of 1067 independent reflections were observed and they were measured with the help of a microdensitometer. Empirical correction for α_1 — α_2 doublet resolution was applied. Then Lorentz-polarization and absorption corrections were carried out. The transmission factors at different θ for a value $\mu R = 11.3$ were obtained by graphical interpolation from the values of EVANS and EKSTEIN (1952).

Crystal-structure determination

There are evident similarities between fornacite and vauquelinite. The lattice parameters of vauquelinite are very close to those of fornacite when one chooses as a and c axes of the unit-cell the $[101]$ and $[10\bar{1}]$ directions. The values of the parameters of vauquelinite according the new orientation are here compared with those of fornacite:

$$\begin{array}{ll} \text{vauquelinite} & a = 16.110 \text{ \AA}, b = 5.806 \text{ \AA}, c = 17.366 \text{ \AA}, \beta = 110^\circ 28' \\ \text{fornacite} & a = 8.101 \text{ \AA}, b = 5.893 \text{ \AA}, c = 17.547 \text{ \AA}, \beta = 110^\circ 00'. \end{array}$$

The two minerals show the same prominent pseudocell, corresponding to the cell of fornacite with c halved. Furthermore, assuming the same orientation for the two cells, the intensities of correspondent spots are similar. Figure 1 shows a part of the $h3l$ layer of the weighted reciprocal lattice for vauquelinite and fornacite.

From these considerations it follows that the two structures are closely related. Therefore we were led to propose a trial arrangement

for the heavy atoms in vauquelinite derived from the arrangement found in fornacite. The agreement between calculated and observed structure factors was satisfactory. A first refinement of the locations of these atoms was carried out with a Fourier synthesis. Then it was possible to locate oxygen atoms from difference-Fourier syntheses and stereochemical considerations.

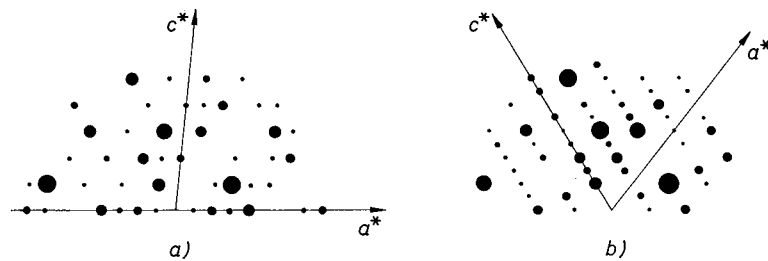


Fig. 1. A part of the $h3l$ layer of the reciprocal lattice of (a) vauquelinite, and (b) fornacite. The size of spots is set approximately proportional to the F_o^2

The refinement of the structure was performed with the least-squares method. The weighing scheme suggested by CRUICKSHANK *et al.* (1961) was employed and the unobserved reflections were not included in the calculations. After four cycles of isotropic refinement, each followed by a proper rescaling of $|F_o|$'s, the discrepancy index $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ for 523 observed reflections fell to the final

Table 1. Fractional atomic coordinates with standard deviations and isotropic temperature factors

Atom	x	y	z	B
Pb(1)	.7363 ± .0002	.2256 ± .0013	.4954 ± .0002	2.99 Å ²
Pb(2)	.0535 1	.7686 12	.1666 2	2.22
Cu(1)	.0000 —	.0000 —	.5000 —	2.96
Cu(2)	.0000 —	.5000 —	.5000 —	1.33
Cr	.8620 6	.2625 47	.1811 8	1.69
P	.1584 9	.2737 59	.3207 13	1.83
O(1)	.1203 37	.0478 128	.3806 53	3.13
O(2)	.1104 37	.4780 117	.3868 54	3.25
O(3)	.1192 29	.2589 179	.1679 43	2.53
O(4)	.2683 31	.2951 136	.3470 45	2.50
O(5)	.8910 36	.0281 124	.1013 53	2.53
O(6)	.9103 36	.4836 124	.0964 54	1.98
O(7)	.9113 28	.2360 192	.3381 40	1.91
O(8)	.7470 30	.2735 145	.1838 44	2.32
OH	.9529 28	.7837 181	.3841 42	2.21

Table 2. (Continued)

h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c
16 3 0	20.5	-15.4	1 3 - 3	282.5	308.4	5 3 5	74.9	71.8	10 3 - 7		0.8
0 3 1		63.0	2 3 3		-33.0	5 3 - 5		84.0	11 3 7		29.4
1 3 1		10.6	2 3 - 3		-34.4	6 3 5		-65.0	11 3 - 7	44.4	-54.0
1 3 - 1	245.4	238.0	3 3 3		9.0	6 3 - 5		-5.0	12 3 - 7		50.8
2 3 1	50.6	-63.8	3 3 - 3	51.7	-41.8	7 3 5	171.0	-187.8	13 3 - 7	29.3	28.6
2 3 - 1	125.4	-129.8	4 3 3		-78.8	7 3 - 5		-18.8	0 3 8		97.2
3 3 1	350.8	-367.0	4 3 - 3		112.0	8 3 5		49.8	1 3 8		32.6
3 3 - 1	64.8	-65.6	5 3 3		231.2	8 3 - 5		75.6	1 3 - 8	39.0	-24.8
4 3 1	56.7	110.2	5 3 - 3		228.1	9 3 5		59.4	2 3 8		2.8
4 3 - 1		15.4	6 3 3		56.3	9 3 - 5		110.8	2 3 - 8	90.7	99.4
5 3 1	63.7	53.0	6 3 - 3		-60.0	10 3 5		5.0	3 3 8		22.2
5 3 - 1	70.6	64.4	7 3 3		14.8	10 3 - 5		-3.0	3 3 - 8		-14.2
6 3 1		-5.0	7 3 - 3		27.0	11 3 5		47.1	4 3 8		-12.0
6 3 - 1	91.2	-85.4	8 3 3		-8.2	11 3 - 5		49.8	4 3 - 8	66.8	72.4
7 3 1		-30.8	8 3 - 3		1.6	12 3 5		43.4	5 3 8	30.1	39.0
7 3 - 1	326.9	-350.2	9 3 3	129.7	118.8	12 3 - 5		13.0	5 3 - 8		-30.6
8 3 1	90.8	85.2	9 3 - 3	155.1	141.8	13 3 5	23.2	22.8	6 3 8	81.4	101.6
8 3 - 1	67.1	69.8	10 3 3		-52.8	13 3 - 5	103.4	100.6	6 3 - 8		16.2
9 3 1	129.3	128.8	10 3 - 3		-72.0	14 3 5	21.6	-21.4	7 3 8		-28.6
9 3 - 1	51.7	-49.4	11 3 3	101.9	-105.0	0 3 6		-12.0	7 3 - 8		-50.6
10 3 1		4.6	11 3 - 3	149.0	-145.8	1 3 6		-19.4	8 3 8	32.0	40.2
10 3 - 1		-11.8	12 3 3		47.9	1 3 - 6		-47.2	8 3 - 8	69.8	-79.0
11 3 1	48.6	58.6	12 3 - 3		43.6	2 3 6	63.3	-68.2	9 3 8		9.8
11 3 - 1	70.2	-64.4	13 3 3		56.3	2 3 - 6	83.4	-88.8	9 3 - 8		0.8
12 3 1		0.6	13 3 - 3		60.2	3 3 6	55.2	-60.4	10 3 8	71.8	92.8
12 3 - 1		49.8	14 3 3		-0.4	3 3 - 6		-48.2	10 3 - 8	22.8	-25.0
13 3 1	115.0	116.0	14 3 - 3		-6.2	4 3 6	168.3	-176.8	11 3 8		-8.2
13 3 - 1	42.4	36.8	15 3 3	45.2	-51.4	4 3 - 6	146.6	-146.0	12 3 8	68.3	-82.6
14 3 1	30.1	-36.4	15 3 - 3	68.3	-63.2	5 3 6		10.8	0 3 9		72.0
14 3 - 1	30.1	21.0	0 3 4	94.9	99.4	5 3 - 6		16.0	1 3 9	73.3	94.4
15 3 1		5.4	1 3 4		-0.6	6 3 6		-36.6	1 3 - 9	110.4	129.8
15 3 - 1		19.4	1 3 - 4		76.4	6 3 - 6	61.7	-54.6	2 3 9		0.2
16 3 1		-6.8	2 3 4	186.8	204.6	7 3 6		2.4	2 3 - 9		-4.6
16 3 - 1		20.2	2 3 - 4	50.2	-51.8	7 3 - 6		17.2	3 3 9	30.9	37.4
0 3 2	135.8	-139.2	3 3 4		-49.0	8 3 6	65.6	-73.0	3 3 - 9		-14.8
1 3 2		-79.8	3 3 - 4		53.8	8 3 - 6	86.1	-90.6	4 3 9		34.4
1 3 - 2	80.3	-33.4	4 3 4	63.3	62.6	9 3 6		43.2	4 3 - 9		46.6
2 3 2		-6.4	4 3 - 4		-15.2	9 3 - 6		39.4	5 3 9	67.1	91.2
2 3 - 2	202.6	213.8	5 3 4	54.0	-13.8	10 3 6	51.7	52.0	5 3 - 9	96.5	112.2
3 3 2	50.9	44.4	5 3 - 4		47.8	10 3 - 6	46.7	49.0	6 3 9		-17.0
3 3 - 2		-32.6	6 3 4	74.9	70.0	11 3 6		-11.6	6 3 - 9		-35.0
4 3 2		-25.0	6 3 - 4	138.9	144.4	11 3 - 6		2.6	7 3 9		-4.4
4 3 - 2	109.2	107.2	7 3 4	102.6	-92.4	12 3 6		11.4	7 3 - 9	27.0	20.8
5 3 2	74.9	74.2	7 3 - 4		-37.6	12 3 - 6		27.0	8 3 9		-5.8
5 3 - 2		-25.6	8 3 4	174.0	-173.8	13 3 6		27.0	8 3 - 9		5.0
6 3 2	184.8	183.4	8 3 - 4	92.2	96.8	13 3 - 6	25.9	24.6	9 3 9	52.1	60.0
6 3 - 2	59.0	52.8	9 3 4		-4.2	14 3 6	88.8	95.2	0 3 10	37.8	43.6
7 3 2		-36.6	9 3 - 4		15.0	0 3 7		28.4	1 3 10		0.4
7 3 - 2	93.6	-103.6	10 3 4		-15.8	1 3 7		32.2	1 3 - 10		17.8
8 3 2	79.9	44.4	10 3 - 4	132.0	129.2	1 3 - 7	105.0	122.2	2 3 10	81.8	83.2
8 3 - 2	191.0	-180.8	11 3 4		-20.0	2 3 7		-25.0	2 3 - 10	35.9	-35.4
9 3 2	62.1	40.8	11 3 - 4		-74.8	2 3 - 7		-70.0	3 3 10		-33.2
9 3 - 2		-14.0	12 3 4	100.3	-103.2	3 3 7	176.7	-209.4	3 3 - 10		16.2
10 3 2	153.6	148.2	12 3 - 4	68.7	-65.6	3 3 - 7		-29.4	4 3 10	27.0	26.0
10 3 - 2		-11.4	13 3 4		35.2	4 3 7		70.2	4 3 - 10		15.2
11 3 2		-74.8	13 3 - 4		-3.8	4 3 - 7		-0.2	5 3 10		-1.6
11 3 - 2		-26.2	14 3 4		3.0	5 3 7		-6.0	5 3 - 10		11.2
12 3 2	93.4	-84.8	14 3 - 4	24.3	21.6	5 3 - 7		35.4	6 3 10	27.8	41.8
12 3 - 2	119.6	-120.4	0 3 5		38.0	6 3 7		16.4	6 3 - 10	66.4	71.0
13 3 2		-15.6	1 3 5	126.2	138.0	6 3 - 7		-58.6	7 3 10		-2.6
13 3 - 2		43.0	1 3 - 5	52.9	-42.0	7 3 7		4.2	8 3 10	49.4	34.8
14 3 2		11.4	2 3 5	106.6	-99.8	7 3 - 7	199.5	-204.6	0 3 11		14.6
14 3 - 2		-2.6	2 3 - 5		-54.6	8 3 7		42.6	1 3 11	24.3	43.2
15 3 2		-3.2	3 3 5	71.0	-81.8	8 3 - 7		35.2	1 3 - 11	32.8	-27.6
16 3 2	37.8	-38.2	3 3 - 5	284.8	-295.4	9 3 7	69.8	85.0	2 3 11		-15.0
0 3 3	132.8	140.4	4 3 5		11.0	9 3 - 7		-17.0	3 3 11	80.3	-102.0
1 3 3	215.7	229.0	4 3 - 5	106.8	98.0	10 3 7		6.4			

value 0.089. The R index without the contributions of the oxygen atoms was 0.15.

The atomic coordinates with their standard deviations and the isotropic thermal parameters are given in Table 1. The observed and calculated structure factors are compared in Table 2. The scattering-factor values by CROMER and WEBER (1965) for the Pb^{+2} ion, and by International Tables (1962) for Cu^{+2} , Cr, P and O^{-1} , were used for the calculations. Contribution of the real component of the anomalous dispersion to the scattering factors of the heavy atoms was taken into account: correction was applied with the values $\Delta f'$ determined for $CuK\alpha$ radiation by CROMER (1965). All the calculations were performed with an IBM 1620 computer.

Discussion of the structure

Bond lengths and angles, as well as their standard deviations (CRUICKSHANK and ROBERTSON, 1953; DARLOW, 1961) are listed in Table 3 and 4. The atomic array of vauquelinite projected along b axis is shown in Fig. 2.

The arrangement of oxygen atoms around phosphorus and chromium is tetrahedral. The mean P—O and Cr—O distances are 1.52 and 1.62 Å respectively, in agreement with those found in literature.

The Cu^{+2} ions are in special position at inversion centers. They have six nearest oxygen atoms forming distorted tetragonal bipyramids. Two of the six oxygen atoms belong to hydroxyl groups. The distances in the planar squares range from 1.76 to 2.10 Å.

Pb(1) has nine nearest oxygen neighbours, the Pb—O bond lengths varying from 2.40 to 3.17 Å. Two larger distances occur with values 3.36 and 3.38 Å. Pb(2) binds ten near oxygen atoms with distances in the range 2.47 to 3.09 Å.

Table 3. Bond lengths and their standard deviations

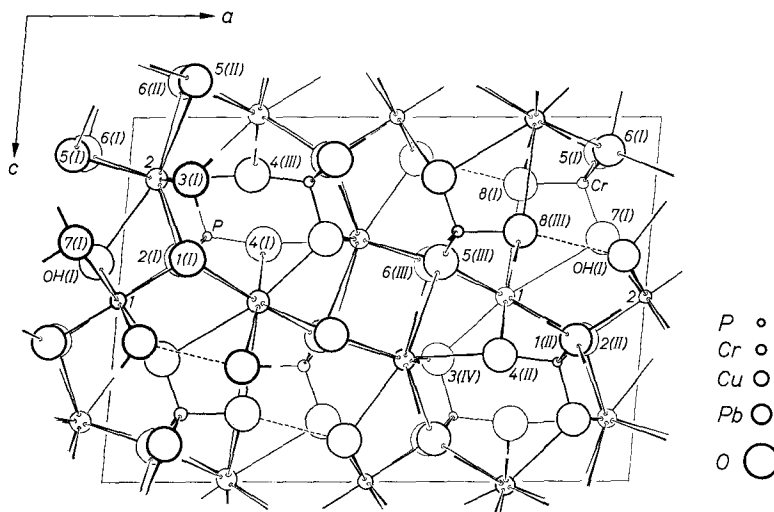
(I: x, y, z ; II: $\bar{x}, \bar{y}, \bar{z}$; III: $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; IV: $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; the label indicates atoms of adjacent cells)

Pb(1,I)—O(1',II)	2.73 Å ± .06 Å	Cu(1,I)—O(1,I)	2.10 Å ± .05 Å
O(2,II)	2.88 .06	OH('I)	1.76 .08
O(3,IV)	2.40 .04	O(7',I)	2.34 .07
O(4,II)	3.17 .07		
O(5,III)	2.60 .06	Cu(2,I)—O(2,I)	1.94 Å ± .05 Å
O(6',III)	2.56 .06	OH('I)	2.06 .09
O(7,I)	2.94 .04	O(7',I)	2.44 .08
O(8,I)	3.01 .04		
O(8',III)	3.15 .07	Cr(1,I)—O(5,I)	1.63 Å ± .07 Å
		O(6,I)	1.68 .07
O(4',II)	3.38 .07	O(7,I)	1.60 .04
O(4,IV)	3.36 .04	O(8,I)	1.59 .04
Pb(2,I)—O(1',I)	2.71 Å ± .06 Å		
O(2,I)	2.76 .06	P(1,I)—O(1,I)	1.54 Å ± .07 Å
O(3,I)	3.09 .10	O(2,I)	1.52 .07
O(3',I)	2.99 .10	O(3,I)	1.51 .04
O(4,III)	2.47 .04	O(4,I)	1.52 .04
O(5',I)	2.73 .06		
O(5',II)	2.97 .05	OH(I)—O(8,III)	2.77 Å ± .06 Å
O(6',I)	2.62 .06		
O(6',II)	2.99 .05		
OH('I)	2.59 .04		

Table 4. Bond angles and their standard deviations in $\text{CuO}_4(\text{OH})_2$, PO_4 and CrO_4 coordination polyhedra

$\text{O}(1,\text{I})-\text{P}(\text{I})-\text{O}(2,\text{I})$	$110^\circ \pm 3^\circ$
$-\text{O}(3,\text{I})$	$102^\circ \quad 4^\circ$
$-\text{O}(4,\text{I})$	$112^\circ \quad 4^\circ$
$\text{O}(2,\text{I})-\text{P}(\text{I})-\text{O}(3,\text{I})$	$108^\circ \quad 4^\circ$
$-\text{O}(4,\text{I})$	$109^\circ \quad 4^\circ$
$\text{O}(3,\text{I})-\text{P}(\text{I})-\text{O}(4,\text{I})$	$116^\circ \quad 2^\circ$
$\text{O}(5,\text{I})-\text{Cr}(\text{I})-\text{O}(6,\text{I})$	$107^\circ \pm 3^\circ$
$-\text{O}(7,\text{I})$	$105^\circ \quad 4^\circ$
$-\text{O}(8,\text{I})$	$109^\circ \quad 3^\circ$
$\text{O}(6,\text{I})-\text{Cr}(\text{I})-\text{O}(7,\text{I})$	$112^\circ \quad 4^\circ$
$-\text{O}(8,\text{I})$	$114^\circ \quad 3^\circ$
$\text{O}(7,\text{I})-\text{Cr}(\text{I})-\text{O}(8,\text{I})$	$110^\circ \quad 2^\circ$
$\text{O}(1,\text{I})-\text{Cu}(1,\text{I})-\text{OH}(\text{I}')$	$91^\circ \pm 2^\circ$
$-\text{O}(7,\text{I}')$	$87^\circ \quad 2^\circ$
$\text{OH}(\text{I}')-\text{Cu}(1,\text{I})-\text{O}(7,\text{I}')$	$82^\circ \quad 3^\circ$
$\text{O}(2,\text{I})-\text{Cu}(2,\text{I})-\text{OH}(\text{I}')$	$89^\circ \pm 2^\circ$
$-\text{O}(7,\text{I}')$	$89^\circ \quad 2^\circ$
$\text{OH}(\text{I}')-\text{Cu}(2,\text{I})-\text{O}(7,\text{I}')$	$92^\circ \quad 3^\circ$

The presence of hydrogen bond $\text{OH}(\text{I})-\text{O}(8,\text{III})$, 2.77 Å long, was deduced from the interatomic distances between the OH group and the neighbouring oxygen atoms.

Fig. 2. The structure of vauquelinite projected along the b axis

The vauquelinite structure consists of chains of linked polyhedra of oxygen atoms and hydroxyls about Cu extending parallel to the b axis. The individual polyhedra are joined together by an edge. These chains are linked to phosphate and chromate tetrahedra and to lead polyhedra in a compact three-dimensional array which explains the lack of cleavage in the mineral.

Relationships between vauquelinite and fornacite

As expected from the close relations between fornacite and vauquelinite structures, the packing of the atoms is essentially identical in the two minerals. In Table 5 the atomic coordinates of vauquelinite

Table 5. *Comparison of atomic parameters in vauquelinite and fornacite*
The atomic coordinates of vauquelinite are referred to the cell having the same b , $2a' = [101]$ and $c' = [10\bar{1}]$

Atom		Vauquelinite	Fornacite	Atom		Vauquelinite	Fornacite
Pb(1)	x	.232	.219	O(3)	x	.287	.290
	y	.226	.220		y	.259	.209
	z	.380	.376		z	.024	.015
Pb(2)	x	.220	.223	O(4)	x	.614	.638
	y	.769	.773		y	.295	.315
	z	.057	.059		z	.040	.048
Cu(1)	x	.500	.514	O(5)	x	.993	.994
	y	.000	.008		y	.028	.032
	z	.250	.251		z	.105	.102
Cu(2)	x	.500	.486	O(6)	x	.007	.004
	y	.500	.508		y	.484	.473
	z	.250	.249		z	.096	.094
P,As	x	.479	.487	O(7)	x	.250	.250
	y	.274	.260		y	.236	.248
	z	.081	.081		z	.213	.214
Cr	x	.043	.050	O(8)	x	.931	.927
	y	.263	.260		y	.274	.289
	z	.159	.159		z	.219	.218
O(1)	x	.501	.541	OH	x	.338	.344
	y	.048	.028		y	.784	.761
	z	.132	.138		z	.215	.219
O(2)	x	.498	.472				
	y	.478	.478				
	z	.140	.132				

referred to the unit cell with $2a' = [101]$ and $c' = [10\bar{1}]$ are compared with those found in fornacite.

Because of the particular locations of Pb(1), Pb(2), Cr, P, O(3), O(4), O(7), O(8) and OH at y about $1/4$ and $3/4$, and of Cu(1), Cu(2), O(1), O(2), O(5) and O(6), lying two by two at the same x and z coordinates and at y approximately 0 and $1/2$, the two structures simulate the presence of mirror planes at $y = 1/4$ and $3/4$. In such a way it is possible to explain the presence of a pseudocell with the same orientation as in fornacite but with c halved and with space group

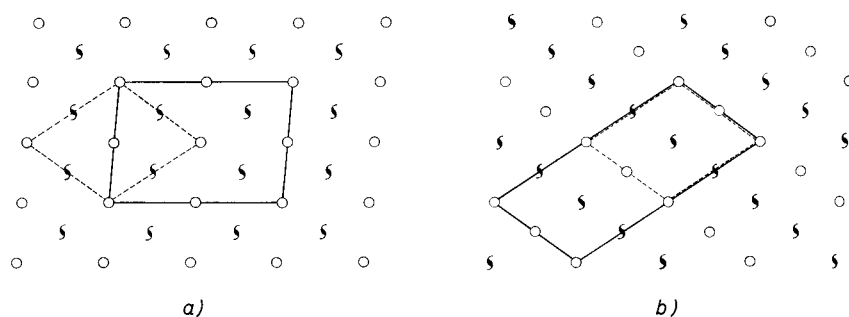


Fig. 3. The different arrangement of symmetry elements in vauquelinite (a) and in fornacite (b). The pseudocells are marked by dashed line

$P2_1/m$. Recently the new formula $Pb_2Cu[SO_4PO_4OH]$ was assigned to the mineral tsumebite (BIDEAUX, NICHOLS and WILLIAMS, 1966) which crystallizes in the space group $P2_1/m$ with the following lattice parameters: $a = 8.70 \text{ \AA}$, $b = 5.80 \text{ \AA}$, $c = 7.85 \text{ \AA}$ and $\beta = 111^\circ 30'$. Similarities in the chemical formula and comparison of the lattice parameters and space group of tsumebite with the pseudocell found in fornacite and vauquelinite, suggest that the structure of this mineral can be taken as a model from which the structures of vauquelinite and fornacite derive if we suppose that the replacement of SO_4 with CrO_4 groups cause the disappearance of the mirror planes with a general rearrangement of atoms in the space group $P2_1/n$. A private communication of M. C. NICHOLS on the crystal structure of tsumebite confirms our supposition.

Some differences occur in the coordination of oxygen atoms around the lead ions in fornacite and vauquelinite. In fornacite both distinct lead ions in the unit cell show coordination number $9 + 1$, while in vauquelinite the number is $9 + 2$ for Pb(1) and 10 for Pb(2).

The Cu^{+2} ions in vauquelinite are at inversion centers, while in fornacite they are located near to the screw axis. It is remarkable

in fact that, though fornacite and vauquelinite belong to the same space group C_{2h}^5 , the symmetry elements in the cells are arranged in a different way, as shown in Fig. 3.

In conclusion the two structures are closely related, and according GUILLEMIN and PROUVOST (1951) the minerals could form an isomorphous series. However the chemical analyses in literature show only a small miscibility.

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