

Structural similarities of some secondary lead minerals

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Summary. Some structural analogies found in tsumebite, vauquelinite, fornacite, and brackebuschite make it possible to place these secondary lead minerals in the same series with general formula $\text{Pb}_2\text{MeII}(Z)(\text{XO}_4)(\text{YO}_4)$, where MeII is a bivalent cation as Cu^{2+} or Mn^{2+} , Z is the hydroxyl group or the water molecule, X is S, Cr, or V, and Y is P, As, or V. Some crystallochemical considerations are developed in order to explain how the replacement of these elements affects the crystal structure in these substances.

RECENT studies undertaken in this Institute on the crystal structure of fornacite and vauquelinite show that close similarities exist between these and two other lead minerals: tsumebite and brackebuschite. The results allow us to place these minerals in the same series, according to their structural relationships, and, though their structures are quite complicated, to develop some crystallochemical considerations concerning the effects that replacements of ions of differing sizes may cause in these structural frameworks.

The structure of brackebuschite, $\text{Pb}_2\text{Mn}(\text{VO}_4)_2\text{H}_2\text{O}$, was determined in 1955 (Donaldson and Barnes). The unit-cell parameters are $a = 7.68 \text{ \AA}$, $b = 6.15 \text{ \AA}$, $c = 8.88 \text{ \AA}$, $\beta = 111^\circ 50'$ and the space group is $P2_1/m = C_{2h}^2$.

In 1966 Nichols determined the structure of tsumebite, $\text{Pb}_2\text{Cu}[\text{PO}_4\text{SO}_4\text{OH}]$, which has the space group $P2_1/m = C_{2h}^2$ and parameters $a = 8.70 \text{ \AA}$, $b = 5.80 \text{ \AA}$, $c = 7.85 \text{ \AA}$, $\beta = 111^\circ 30'$. Bideaux, Nichols, and Williams (1966) described a new mineral, analogous to tsumebite, with formula $\text{Pb}_2\text{Cu}[\text{AsO}_4\text{SO}_4\text{OH}]$, the same space group as tsumebite and parameters $a = 8.85 \text{ \AA}$, $b = 5.92 \text{ \AA}$, $c = 7.84 \text{ \AA}$, $\beta = 112^\circ 36'$. Cocco, Fanfani, and Zanazzi (1967) determined the crystal structure of fornacite, $\text{Pb}_2\text{Cu}[\text{AsO}_4\text{CrO}_4\text{OH}]$. Its parameters are $a = 8.10 \text{ \AA}$, $b = 5.90 \text{ \AA}$, $c = 17.55 \text{ \AA}$, $\beta = 110^\circ 00'$ with space group $P2_1/c = C_{2h}^5$.

Finally in 1967 Fanfani and Zanazzi carried out the structure of vauquelinite, $\text{Pb}_2\text{Cu}[\text{PO}_4\text{CrO}_4\text{OH}]$; its space group is $P2_1/n = C_{2h}^5$ and

its lattice constants are $a = 13.75 \text{ \AA}$, $b = 5.81 \text{ \AA}$, $c = 9.56 \text{ \AA}$, $\beta = 94^\circ 33'$.

Notwithstanding the differences in space groups and the apparent diversity in the parameters, the cells of these minerals show remarkable analogies both in symmetry and in dimensions, if suitable orientations are chosen. In order to display the similarities of cell parameters, the crystallographic constants of the five minerals are set out together with their space groups in table I.

TABLE I. Chemical formulae, parameters and space groups of the five minerals*

		a	b	c	β	
Tsumebite	$\text{Pb}_2\text{Cu}[\text{PO}_4\text{SO}_4\text{OH}]$	7.85 \AA	5.80 \AA	8.70 \AA	$111^\circ 30'$	$P2_1/m$
'As-tsumebite'	$\text{Pb}_2\text{Cu}[\text{AsO}_4\text{SO}_4\text{OH}]$	7.84	5.92	8.85	$112^\circ 36'$	$P2_1/m$
Vauquelinite	$\text{Pb}_2\text{Cu}[\text{PO}_4\text{CrO}_4\text{OH}]$	2×8.06	5.81	2×8.68	$110^\circ 28'$	$P2_1/n$
Fornacite	$\text{Pb}_2\text{Cu}[\text{AsO}_4\text{CrO}_4\text{OH}]$	8.10	5.89	2×8.77	$110^\circ 00'$	$P2_1/c$
Brackebuschite	$\text{Pb}_2\text{Mn}(\text{VO}_4)_2\text{H}_2\text{O}$	7.68	6.15	8.88	$111^\circ 50'$	$P2_1/m$

* With the name 'As-tsumebite' we indicate the analogue of tsumebite where arsenic takes the place of phosphorus. In tsumebite and 'As-tsumebite' the parameters a and c are inverted in respect of those assumed by Nichols. The parameters of vauquelinite are those when the directions $[101]$ and $[10\bar{1}]$ are chosen as a and c axes respectively.

A short outline of the crystal structure of tsumebite, which will be chosen as reference member in this series, will better explain the structural relationships occurring between the five minerals. The crystal structure of tsumebite is shown in fig. 1. All the heavy atoms occupy special positions in the space group C_{2h}^{2h} : Cu^{2+} ions are at inversion centres; the two lead ions, phosphorus, and sulphur of the asymmetric unit lie on planes at $y = \frac{1}{4}$ and $\frac{3}{4}$. Phosphorus and sulphur show the usual tetrahedral coordination, with two oxygen atoms necessarily on the mirror plane and two oxygen atoms one above and one below the same plane. Each Cu^{2+} ion joins two hydroxyls at distances of 1.88 \AA , two oxygen atoms of the phosphoric anion at 2.03 \AA and two oxygen atoms of an SO_4 tetrahedron at a larger distance of 2.37 \AA . The two independent lead ions coordinate eight and ten oxygen atoms respectively, with bond lengths in a range from 2.43 \AA to 3.11 \AA , forming very irregular polyhedra.

In the other minerals the atomic array is very similar to that one of tsumebite. In table II the atomic coordinates of vauquelinite, fornacite, and brackebuschite are compared with those found in tsumebite, after a convenient orientation of the cell and a shift of the origin. Table II confirms the structural analogies and therefore it is justifiable to

collect these lead minerals into a series with the general formula $Pb_2Me^{\text{II}}(Z)(XO_4)(YO_4)$, where Me^{II} is a divalent cation, such as Cu^{2+} or Mn^{2+} , Z is the hydroxyl group or the water molecule, X is S, Cr, or V, and Y is P, As, or V.

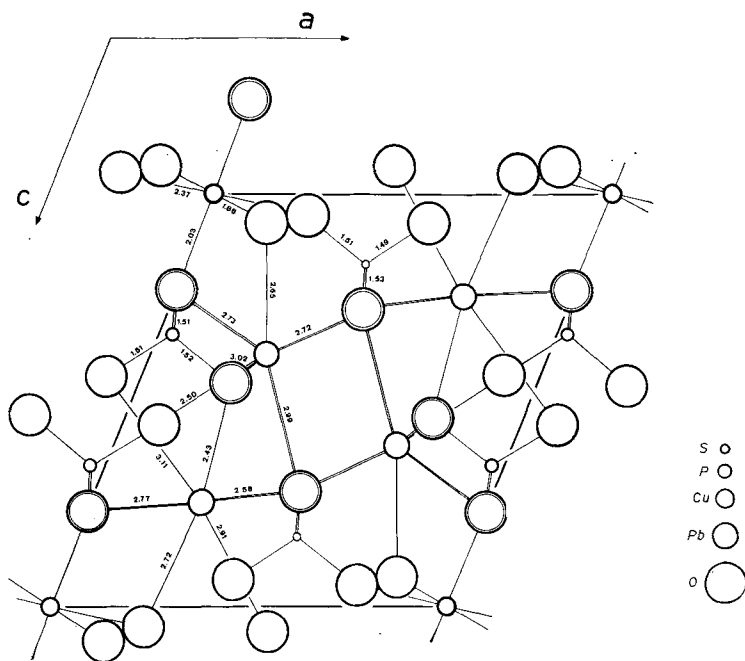


FIG. 1. The crystal structure of tsumebite projected along the b axis.

It is now interesting to see how the substitution of P by As or V and of S by Cr or V affects the crystal structure.

The replacement of phosphorus in tsumebite by arsenic does not change the symmetry of the crystal structure but it causes an increase in b and c , without any change in a . Analogous behaviour occurs on passing from vauquelinite to fornacite. A structural interpretation of these experimental data can be found as follows: each PO_4 tetrahedron is connected to the chains of Cu coordination octahedra along the b axis through two oxygen atoms, forming the edge of the tetrahedron parallel to b , so that one of these oxygen atoms is tied by a Cu^{2+} ion and the

other one by another adjacent Cu^{2+} ion, as sketched in fig. 2. Therefore it is plain that any increment of the length of this edge is reflected in the length of b . Nevertheless the actual increase of the b parameter is less than would be expected if the positions of the oxygen atoms around Cu remained unaltered, because it would imply too large a distortion in the

TABLE II. Coordinates of heavy atoms in tsumebite, vauquelinite, fornacite, and brackebuschite. The unit cells of vauquelinite, fornacite, and brackebuschite are suitably oriented (see table I) and shifted for better comparison with tsumebite.

Coordinates cited as 0, $\frac{1}{4}$, $\frac{1}{2}$, or $\frac{3}{4}$ are in special positions.

<i>Atom</i>		<i>Tsumebite</i>	<i>Vauquelinite</i>	<i>Fornacite</i>	<i>Brackebuschite</i>
Pb_1	x	0.729	0.732	0.719	0.740
	y	$\frac{1}{4}$	0.226	0.220	$\frac{1}{4}$
	z	$\frac{1}{4}$	0.259	0.251	0.251
Pb_2	x	0.288	0.280	0.277	0.324
	y	$\frac{1}{4}$	0.231	0.227	$\frac{1}{4}$
	z	0.393	0.387	0.382	0.402
Me_1^{II}	x	0	0	0.014	0
	y	0	0	0.008	0
	z	0	0	0.003	0
Me_2^{II}	x	0	0	-0.014	0
	y	$\frac{1}{2}$	$\frac{1}{2}$	0.508	$\frac{1}{2}$
	z	0	0	-0.003	0
X	x	0.454	0.457	0.450	0.440
	y	$\frac{3}{4}$	0.737	0.740	$\frac{3}{4}$
	z	0.171	0.181	0.182	0.173
Y	x	0.032	0.021	0.013	0.041
	y	$\frac{3}{4}$	0.726	0.740	$\frac{3}{4}$
	z	0.340	0.338	0.337	0.329

Me^{II} is Mn^{2+} for brackebuschite and Cu^{2+} in the other minerals.

X is S in tsumebite, Cr in vauquelinite and fornacite, and V in brackebuschite.

Y is P in tsumebite and vauquelinite, As in fornacite, and V in brackebuschite.

Cu coordination pseudo-octahedron. In the change from the phosphorous to the arsenical member there must be a slight change in angles and distances in the planar coordination around Cu and the resulting increase in b is only 0.1 Å.

The different behaviour of the a and c parameters in the passage from the phosphorous to the arsenical member can be explained thus: the larger size of AsO_4 complexes does not affect in the same way the bonds between the Pb and Cu ions and the oxygen atoms of these complexes, the effect depending on the reciprocal orientation of As-O and Cu-O or Pb-O bonds. When, for certain bonds, the effect is large a proportionate

deformation of the coordination polyhedra around Pb and Cu in angles or in bond values cannot take place; only an increase of the cell parameters related to the orientation of these bonds can yield a deformation small enough to maintain the general features of the structure. This happens when the longer As-O bonds shorten Cu-O bonds

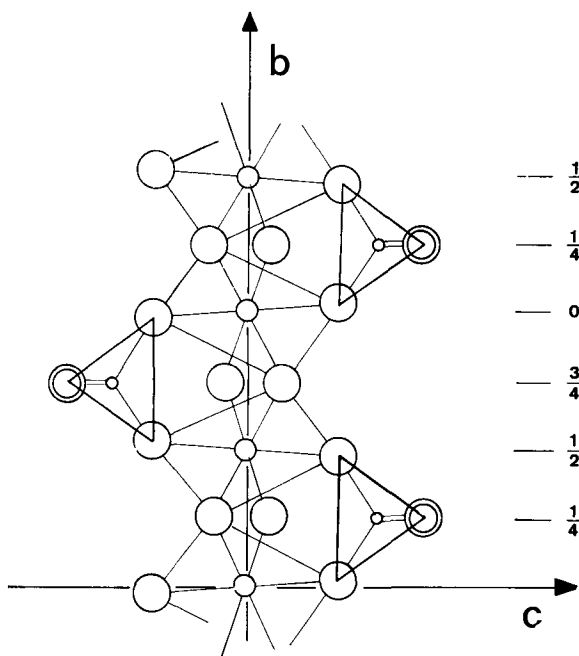


FIG. 2. A schematic view of the chain formed by Cu coordination polyhedra and PO_4 tetrahedra in the direction of the b axis. For key to the several atoms see fig. 1.

and cause an excessive distortion in the planar coordination around Cu. Because of the direction of these Cu-O bonds parallel to the c axis, as shown in fig. 2, a significant increase of this parameter occurs. The lead coordination polyhedra are generally more deformable than the Cu polyhedra, the range of Pb-O distances and O-Pb-O angles being very large; it follows that an increase in the parameters can happen only if very short Pb-O bonds, unable to be further shortened, occur in a direction approximately parallel to these parameters. In tsumebite and in vauquelinite the only bond near to a critical value is Pb(1)-O(3), with a distance of 2.43 Å and 2.40 Å respectively in the two minerals and a

direction approximately parallel to the c axis; this again is in accord with the increase of c . In the a direction, on the contrary, the observed Pb–O_P distances are quite regular and so the a parameter does not change.

The replacement sulphur–chromium requires more notable structural modifications than the replacement phosphorus–arsenic. In fact, as is shown in table I, in the passage from tsumebite to vauquelinite besides the increase of the a parameter there is a change in the space group. Since the difference in size of CrO₄ and SO₄ tetrahedra is much greater than that between AsO₄ and PO₄ tetrahedra, strict maintenance of the structure is impossible. A general rearrangement of the atomic array takes place: Pb ions move slightly along the b axis from $y = \frac{1}{4}$ and $\frac{3}{4}$ together with chromium and phosphorus atoms, whose coordination tetrahedra rotate through a small angle along an axis almost parallel to c , while Cu ions remain in special positions at inversion centres but with a very distorted coordination around them. In vauquelinite, referring to the symmetry elements of the space group $P2_1/m$ to which tsumebite belongs, the mirror planes and alternate inversion centres and screw axes disappear as shown in fig. 3. The resulting space group is $P2_1/n$ though the atomic arrangement shows the presence of a pseudocell with dimensions and symmetry corresponding to those of the unit cell of tsumebite.

The modification of the parameters in consequence of the larger size of CrO₄ tetrahedra can again be related to the lengths and directions of the bonds that Cu and Pb form with the oxygen atoms of the tetrahedron around the chromium. The direction of the Cu–O_{Cr} bonds parallel to a requires the lengthening of this parameter. A similar effect arises from the rotation of the chromium tetrahedron, which would cause an excessive shortening of the bonds Pb–O_{Cr} approximately arranged in the a direction. By contrast, the c parameter does not change because of the greater lengths and consequently greater possibility of variation of Pb–O_{Cr} bonds in its direction. The almost unchanged value of the b parameter is explained when we note that the removal of lead, chromium, and phosphorus ions from $y = \frac{1}{4}$ and $\frac{3}{4}$, consequent on the lack of mirror planes, allows a more compact arrangement along this direction in vauquelinite.

The atomic array in fornacite, which represents in this series the member containing chromium and arsenic, may once more be interpreted by referring to tsumebite, taking into account however that the replacement As–P affects a structural pattern already distorted by the

replacement Cr-S. Since the larger size of the AsO_4 tetrahedron mostly affects the coordination around the copper ion, as happens from tsumebite to its arsenic analogue, we are led to think that the planar coordination around Cu, very irregular in vauquelinite, needs a rearrangement for the new replacement. It happens therefore that Cu ions leave inversion centres and rearrange themselves around screw axes. There

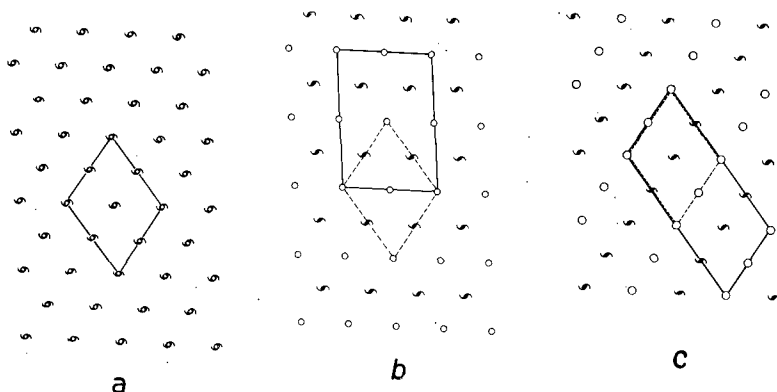


FIG. 3. The array of the symmetry elements (a) in tsumebite, (b) in vauquelinite, and (c) in fornacite.

follows a slight structural modification along As-Cu-As directions, which explains how in fornacite and in vauquelinite, though the space group in both is C_{2h}^6 , the symmetry elements are differently arrayed in these directions, as is shown in fig. 3. Though at first sight improbable, it can easily be shown that the transposition of centres and screw axes does not require any remarkable structural changes, if we consider that in both minerals the same pseudocells, corresponding to the cell of tsumebite, are present, and that therefore in both structures all the symmetry elements of the space group $P2_1/m = C_{2h}^2$ must coexist partially as true and partially as pseudo-elements. The remarkable result in the rearrangement is the regular planar coordination around Cu, very similar in bond lengths and angles to that occurring in tsumebite; however the displacement of copper ions from the special positions at inversion centres causes the pseudocell corresponding to tsumebite to be less well defined in fornacite than in vauquelinite.

Brackebuschite can be considered as a particular member in this series; it differs considerably in its cell parameters, a being much shorter and b much longer than in the other minerals, and in its chemical com-

position, as manganese takes the place of copper and vanadium of sulphur and phosphorus in tsumebite; the hydroxyl group is evidently replaced by a water molecule. The structure of brackebuschite is clearly related to that of the minerals already described but it is not well enough known to allow any particular consideration; there is doubt, too, about its space-group, which may be $P2_1/m$ or the non-centrosymmetrical $P2_1 = C_2^2$. In this connexion it seems unlikely that this mineral belongs to the space-group $P2_1/m$ because the larger size of VO_4 tetrahedra leads us to expect a considerable distortion of the atomic array of tsumebite and consequently a lower symmetry.

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