

## Trolleite, $\text{Al}_4(\text{OH})_3[\text{PO}_4]_3$ : A Very Dense Structure with Octahedral Face-Sharing Dimers

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### Abstract

Trolleite,  $4\text{Al}_4(\text{OH})_3[\text{PO}_4]_3$ ,  $a$  18.894(5) Å,  $b$  7.161(1) Å,  $c$  7.162(2) Å,  $\beta$  99.99(2)°, space group  $I2/c$ , is a valid species. For 2010 independent reflections,  $R(hkl)$  converged to 0.036. Estimated standard errors in distances are Me-O  $\pm$  0.002 Å and O-O'  $\pm$  0.003 Å. Its crystal structure consists of Al-O octahedral face-sharing dimers which link by corner-sharing hydroxyl groups to form an infinite double-chain which runs parallel to the [001] direction. The  $[\text{PO}_4]$  tetrahedra bridge these chains to produce a very dense three-dimensional structure.

The structure is topologically related to that of lazulite,  $\text{MgAl}_2(\text{OH})_2[\text{PO}_4]_2$ . This is particularly evident if the orientations of the  $[\text{PO}_4]$  tetrahedra are noted: the lazulite tetrahedra and the oxygen packing can be approximately superimposed upon those of trolleite.

Severe distortions occur on account of the face-sharing and result from the cumulative effects of cation-cation repulsion and deviations of the anions from local electrostatic neutrality by the coordinating cations. The octahedra are distorted into elongate trigonal antiprisms with the Al-O distances toward the shared face longer (1.94-2.09 Å) than those to the opposing free face (1.79-1.96 Å). Average polyhedral distances are Al(1)-O 1.915, Al(2)-O 1.905, P(1)-O 1.528, and P(2)-O 1.528 Å. Difference synthesis provided locations of the hydrogen atoms. The proposed hydrogen bonding scheme involves bifurcated hydrogen bonds from the octahedral groups to phosphate oxygens.

### Introduction

The peculiar mineral trolleite has recently been characterized by Sclar, Carrison, and Schwartz (1965), who proposed the formula  $\text{Al}_{5.33}(\text{OH})_4[\text{PO}_4]_4$ . According to these authors, it is an unusually hard substance, about 8.5 on Mohs scale. Originally named by Blomstrand (1869) from a small iron ore deposit at Westanå near Kristianstad in Skåne, Sweden, it occurred with a host of unusual phosphate minerals such as attacolite, cirrolite, augelite, lazulite, and berlinite. What remains of the old mine dump was visited by the senior author in 1968; the phosphates occur rarely as lenticular masses and blebs associated with quartz, pyrophyllite, rutile, etc. A similar paragenesis has been recently noted from the White Mountains, Mono County, California, where trolleite has been found (C. B. Sclar, private communication). Specimens of the California material are appearing in mineral dealer's catalogues, but a detailed characterization—including single crystal study—is evidently lacking. Most systems and compendia of mineralogy place the mineral in a dubious position or group it with lazulite as a variety of that mineral. Sclar *et al* (1965) propose

a structural kinship with lazulite  $\text{MgAl}_2(\text{OH})_2[\text{PO}_4]_2$ .

Our continued interest in the systematics of Al-O clustering, phosphate crystal chemistry, and dense structures in general prompted a detailed investigation on trolleite, and this study not only reveals the unique status of the mineral but also provides evidence for Al-O octahedral face-sharing dimers.

### Experimental

A specimen of trolleite from California was kindly donated by Mr. A. L. McGuinness. It consists of a compact and dense mass of small pale green trolleite grains, blue-black prisms of scorzalite, white cleavage surfaces of augelite and minor amounts of an unidentified granular pale orange phase. A portion of the sample was crushed and trolleite grains were hand-picked. From these, a small crystal fragment was examined by rotation, Weissenberg, and precession photography. Some grains were ground with silicon standard ( $a = 5.4301$  Å), and a chart diffractogram was prepared. These data were indexed on the basis of the strong intensity single crystal data and are listed in Table 1. The crystal cell parameters in Table 2 were derived by least-

squares refinement from twelve high angle reflections on a PICKER automated diffractometer. These results and the density calculation for  $\text{Al}_4(\text{OH})_3[\text{PO}_4]_3$  agree well with the original analysis, specific gravity determination, and description of the material by Blomstrand (1869), and with the results of Sclar *et al* (1965). Although we have not examined a type specimen, we are confident that the Californian and Swedish trolleites are in fact the same mineral and conclude that trolleite is a valid species, distinct from the lazulite group of minerals. The powder data in Table 1 match those published by Sclar *et al* (1965).

It immediately became apparent that the structure analysis would prove a difficult problem since about 80 percent of the reflections were relatively weak. This explains the rather simple powder pattern despite a cell of considerable complexity.

The crystal originally selected was a small chip about 60 microns in average dimension. From this crystal, the structure was eventually solved but the data were of such poor quality that a search for a superior crystal was undertaken. Over 20 crystal fragments were examined by film techniques until a superior roughly equant crystal of 0.2 mm size was found. Detailed restudy was undertaken on the superior crystal. Two-thousand and eighteen independent reflections to  $\sin \theta/\lambda = 0.80$  were collected on a PAILRED automated diffractometer of the 0- to 10-layers with *b* as rotation axis. We utilized  $\text{MoK}\alpha$  radiation, graphite monochromator, scan speed of  $1.0^\circ/\text{minute}$ , with half-angle scans of  $1.6^\circ$ , widening to  $3.9^\circ$  at the high levels. Strong reflections

TABLE 1. Trolleite. Powder Data\*

I/I <sub>0</sub>	d(obs)	d(calc)	hkl
35	6.667	6.683	110
20	5.016	5.025	011
25	4.649	4.652	400
10	4.197	4.209	211
10	3.502	3.506	202
40	3.336	3.342	220
100	3.208	3.203	112
90	3.095	3.101	600
50	3.075	3.079	402
45	2.519	2.523	521
10	2.221	2.226	231
35	1.983	1.986	910
		1.986	132
15	1.798	1.803	802
		1.800	323
15	1.607	1.610	822
10	1.598	1.601	224
30 brd	1.547	1.553	242
		1.551	12,0,0
20	1.537	1.540	804
10	1.396	1.399	134
10	1.392	1.393	415

\*  $\text{Cu}/\text{Ni}$  radiation, chart diffractogram,  $1/2^\circ 2\theta/\text{minute}$  scan, Si standard.

TABLE 2. Trolleite. Crystal Cell Parameters

	Trolleite	Lazulite*
$a(\text{\AA})$	18.894(5)	7.16
$b(\text{\AA})$	7.161(1)	7.26
$c(\text{\AA})$	7.162(2)	7.24
$V(\text{\AA}^3)$	954.3	323.7
$Z$	99.99(2)	120.67 <sup>o</sup>
space group	I2/c	P2 <sub>1</sub> /c
formula	$\text{Al}_4(\text{OH})_3[\text{PO}_4]_3$	$\text{MgAl}_2(\text{OH})_2[\text{PO}_4]_2$
$Z$	4	2
specific gravity	3.09†	3.12
density (calc.), $\text{gm cm}^{-3}$	3.08	3.14
volume/oxygen atom, $\text{\AA}^3$	15.9	16.2
hardness	8.5†	5½ - 6

† Sclar *et al.* (1965).

\* Lindberg and Christ (1959).

with a wide scan range (and the very low angle reflections) were obtained manually. All but eight reflections were accepted for the ensuing study. These rejected reflections were of very low angle and eventually revealed differences resulting from our scattering curve for  $P^\circ$  and the scattering profile of  $P$  in the crystal.

### Solution and Refinement

The data were processed by conventional computational methods to obtain  $|F(\text{obs})|$  from which a Patterson synthesis,  $P(uvw)$ , was prepared. On account of many overlapping *y*-coordinates of the atomic species situated at  $y \sim 0, 1/4$ , solution proved difficult but successive  $\beta$ - and  $\gamma'$ -syntheses (Ramachandran and Srinivasan, 1970) led to the resolution of all cations and anions (except hydrogen) on the final Fourier synthesis.

Likewise, refinement of the structure proved rather slow and tedious. Full-matrix least-squares atomic coordinate and anisotropic thermal vibration parameter refinement led to the results in Table 3. Unobserved reflections with  $I < 2\sigma(I)$  were set as  $\sigma(I)$ . Reflections were weighted based on counting statistics, long term intensity fluctuations, and the effect of  $0.1^\circ$  mis-setting of the  $\mu$ -angle for our diffractometer.

TABLE 3. Final Refinement of Trolleite

$R(hkl) = \frac{\sum  F(\text{obs})  -  F(\text{calc}) }{\sum  F(\text{obs}) }$			
Relative $ F(\text{obs}) $	Number of reflections		R(hkl)
Above	0.0	2010	0.036
"	4.2	1784	0.31
"	12.6	1364	0.24
"	25.2	873	0.21

For the refinement, we employed a local version (IBM 360 computer) of the familiar ORFLS program of Busing, Martin, and Levy (1962); and the scattering curves of Cromer and Mann (1968) for  $\text{Al}^{2+}$ ,  $\text{P}^{\circ}$  and  $\text{O}^{1-}$ . Table 4 provides the atomic coordinate and isotropic thermal vibration parameters, and Table 5 lists the structure factor data. Tables 6a and 6b provide the anisotropic thermal vibration parameters and the orientations of these ellipsoids respectively.

## Description of the Structure

### Topology and Geometry

Trolleite is a most fascinating structure since its underlying principle is a face-sharing dimer of aluminum-oxygen octahedra. The dimer has composition  $[\text{Al}_2(\text{O}_P)_6(\text{OH})_3]$ , where  $\text{O}_P$  is the phosphate oxygen, but further polymerizes to equivalent dimers by corner-sharing hydroxyl groups to form an infinite double-chain with composition  $[\text{Al}_4(\text{O}_P)_{12}(\text{OH})_3]$ . Thus, all oxygen atoms in the unit cell can be associated with the octahedral fraction of the structure. The octahedral double-chains run parallel to  $[001]$  and are linked to equivalent chains (related by the  $I$ -centering) by the  $\text{PO}_4$  tetrahedra in general positions. The result is a very dense three-dimensional framework of octahedra and tetrahedra. The unusual hardness is attributed to a rather uniform distribution of strong Al-O-P-O bonds.

The trolleite structure is topologically and geometrically related to the lazulite arrangement, confirming the proposal of Sclar *et al* (1965). Figure 1 reveals the octahedral double-chain in trolleite; the stippled octahedra in this chain coincide nearly

exactly with the loci of the stippled octahedra of the lazulite structure in Figure 2. The structure data of lazulite were obtained from Lindberg and Christ (1959). To derive the octahedral dimers from the lazulite structure, the  $\text{MgAl}$  octahedral pair is replaced by  $\text{AlAl}$ .

The relationship between the two structures can be better visualized on the basis of the packing of the  $[\text{PO}_4]$  tetrahedra. Figure 3 shows the disposition of the tetrahedra in trolleite projected down the  $b$ -axis. At  $b/2$  from each tetrahedral center is an  $(\text{OH})^-$  group. The tetrahedra are oriented on a checkerboard such that their pseudo- $\bar{4}$  axes are parallel to  $b$ . If the tetrahedra in lazulite are projected down the lazulite  $b$ -axis (Fig. 4a), all tetrahedra coincide in the two structures. An identical arrangement of tetrahedra occurs in the structure of lipscombite (Fig. 4b). These tetrahedra were plotted from the results of Katz and Lipscomb (1951). The difference between the lazulite and lipscombite structures evidently involves the degree of ordering of the octahedral cations: in lipscombite these are disordered leading to partly occupied chains of face-sharing octahedra (see Moore, 1970, for the relationship of lazulite and lipscombite to the large family of "5.1 Å fiber structures"). The density of  $(\text{OH})^-$  groups and  $[\text{PO}_4]$  tetrahedra are identical in the trolleite and lazulite structures. Thus we can write a general crystal-chemical relationship between the two structures, *viz*:



and conclude that on the basis of 30 oxygen atoms, lazulite contains nine occupied octahedra and trolleite contains eight. Hence, although the oxygen packing efficiency of trolleite is greater than that of lazulite ( $15.9 \text{ \AA}^3/\text{O}^{2-}$  vs  $16.2 \text{ \AA}^3/\text{O}^{2-}$ ), the latter species is denser ( $3.08$  vs  $3.14 \text{ gm cm}^{-3}$ ). Trolleite, in effect, is an ordered derivative structure of lazulite. Although the oxygen packings are topologically identical, the octahedral sites occupied are distinguishable. Since the isotropic temperature factors are 0.38 and  $0.43 \text{ \AA}^{-2}$  for Al(1) and Al(2) respectively, we conclude that these sites in trolleite are fully occupied.

### Analysis of Polyhedral Distortions and Distances

The existence of a shared octahedral face for each of the two non-equivalent octahedra in trolleite results in severe polyhedral distortion. We examine

TABLE 4. Trolleite. Atomic Coordinates and Equivalent Isotropic Thermal Vibration Parameters\*

	x	y	z	B ( $\text{\AA}^2$ )
Al(1)	0.16778 (3)	-.00654 (8)	0.32059 (8)	0.38 (1)
Al(2)	.07570 (3)	.27118 (8)	.41714 (8)	.43 (1)
P(1)	.00000	.88269 (9)	.25000	.35 (1)
P(2)	.16844 (2)	.36728 (7)	.08109 (6)	.36 (1)
O(1)	.06458 (8)	.01173 (21)	.32611 (21)	.60 (2)
O(2)	.02064 (8)	.76272 (22)	.09579 (22)	.74 (2)
O(3)	.23738 (8)	.46488 (22)	.16861 (21)	.73 (2)
O(4)	.11114 (8)	.50844 (21)	.00803 (22)	.73 (2)
O(5)	.14191 (8)	.24551 (20)	.23708 (21)	.56 (2)
O(6)	.18216 (8)	.23516 (21)	-.07554 (22)	.75 (2)
OH(1)	.0000	.36428 (28)	.2500	.62 (3)
OH(2)	.16141 (8)	.87900 (20)	.06966 (20)	.53 (2)
H(1)	.000	.484	.250	
H(2)	.190	.809	.072	

\* Estimated standard errors refer to the last digit. The hydrogen atom positions were located on the difference synthesis.

TABLE 5. Trolleite. Observed and Calculated Structure Factors

Table with 24 columns (H, K, L, F3, FC, H, K, L, F3, FC, H, K, L, F3, FC, H, K, L, F3, FC, H, K, L, F3, FC, H, K, L, F3, FC) and multiple rows of numerical data representing structure factors.

TABLE 5, Continued

Table with multiple columns labeled H, K, L, FO, FC and rows of numerical data. The table is organized into several groups, each starting with a header row. The data consists of integers, some positive and some negative, representing values for each parameter combination.

TABLE 6a. Trolleite. Atomic Anisotropic Thermal Vibration Parameters ( $\times 10^4$ )\*

Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Al(1)	2.8(1)	13.4(8)	22.3(8)	-0.3(2)	0.5(2)	-2.4(5)
Al(2)	3.4(1)	16.7(8)	22.7(8)	-0.6(2)	0.7(2)	-1.0(5)
P(1)	2.4(1)	12.8(9)	22.1(9)	0.0	0.0(3)	0.0
P(2)	2.8(1)	12.2(7)	21.3(8)	-0.0(2)	-0.0(2)	1.3(4)
O(1)	3.1(3)	22.2(1.6)	42.6(1.9)	-1.6(5)	-1.4(5)	-11.1(1.3)
O(2)	6.1(3)	40.6(1.9)	39.6(2.0)	2.6(6)	7.1(6)	19.2(1.4)
O(3)	2.9(3)	41.1(1.8)	45.3(2.0)	-3.3(5)	0.1(5)	-8.4(1.5)
O(4)	4.7(3)	22.1(1.7)	51.0(2.0)	-3.0(5)	-0.8(5)	-14.3(1.4)
O(5)	5.0(3)	20.7(1.6)	29.7(1.8)	1.8(5)	4.7(5)	9.0(1.2)
O(6)	8.8(3)	22.2(1.7)	32.2(1.9)	-2.3(5)	6.3(6)	-11.7(1.3)
OH(1)	4.0(4)	21.7(2.5)	38.4(2.8)	0.0	-3.8(9)	0.0
OH(2)	3.6(3)	25.0(2.0)	25.0(1.9)	-1.2(5)	-1.9(6)	0.1(1.2)

\* Coefficients in  $\exp[-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$ .

the consequent distortions in considerable detail because trolleite is an extreme example of anisotropic polyhedral distortion for ionic structures containing  $Al^{3+}$ . The analysis of the distortions in trolleite shall include comparisons with similar shared faces in lazulite and corundum. For trolleite, the estimated standard errors in atomic distances are Me-O  $\pm$  0.002 Å and O-O'  $\pm$  0.003 Å. The structure of lazulite was approximately refined by Lindberg and Christ (1959). They did not state errors and, as the structure was refined on the basis of two two-dimensional projections, uncertainties in error estimates arise. We feel, however, that the effects of distortions are so great that the errors would have to be severe (above Al-O  $\pm$  0.1 Å) to eliminate their results from consideration. Consistencies in their P-O distances suggest that uncertainties in their study are not serious, probably not over  $\pm$  0.06 Å in Al-O distances. Corundum,  $\alpha$ - $Al_2O_3$ , has been refined by Newnham and DeHaan (1962) and their estimated standard errors are  $\pm$  0.02 Å in Al-O distances.

For comparison among structures, we utilize congruently oriented Schlegel diagrams (*cf* Moore, 1970) showing Al-O and O-O' distances as well as the O-Al-O' angles. The following statements are essential in comparing distortions among these structures.

1. *The topology of the neighborhood about the polyhedron.* Al(1) and Al(2) in trolleite and Al in lazulite are the same; each polyhedron has one shared face, all other shared topological elements being corners. Corundum differs in having three additional shared edges.
2. *The nature of the cations across the shared*

faces. For trolleite and corundum, these are Al-Al cations. In lazulite, they are Mg-Al. Distortion of the Al-O polyhedra should be more severe for the former two structures.

### 3. *The deviations of the anions from electrostatic*

TABLE 6b. Trolleite. Parameters for the Vibration Ellipsoids\*

	i	$\mu_i (\times 10^2)$	$\theta_{ia}$	$\theta_{ib}$	$\theta_{ic}$
Al(1)	1	7.8	122°	100°	25°
	2	5.7	82	18	75
	3	7.0	146	74	109
Al(2)	1	8.1	147	85	47
	2	6.4	75	21	78
	3	7.4	119	69	135
P(1)	1	7.8	121	90	21
	2	5.8	90	0	90
	3	6.3	149	90	111
P(2)	1	7.9	131	83	32
	2	5.6	88	170	81
	3	6.6	138	97	120
O(1)	1	11.3	110	109	21
	2	5.6	54	48	68
	3	8.1	137	47	84
O(2)	1	12.8	67	50	53
	2	6.9	110	124	37
	3	8.1	148	58	81
O(3)	1	11.5	92	128	39
	2	6.4	29	69	79
	3	10.2	60	134	127
O(4)	1	12.3	110	107	20
	2	5.6	66	35	69
	3	9.7	148	60	90
O(5)	1	10.3	50	66	57
	2	6.2	94	145	55
	3	8.1	40	114	128
O(6)	1	12.6	26	101	76
	2	6.1	94	36	53
	3	9.4	64	55	140
OH(1)	1	11.6	131	90	30
	2	6.9	40	90	59
	3	7.5	90	180	90
OH(2)	1	9.7	139	75	43
	2	6.5	49	76	52
	3	8.0	87	19	109

\*  $\mu_i$  = r.m.s. amplitude of  $i$ -th principal axis. The  $\theta$  values are the angles between the  $i$ -th axis and the crystal axes  $\underline{a}$ ,  $\underline{b}$  and  $\underline{c}$ .

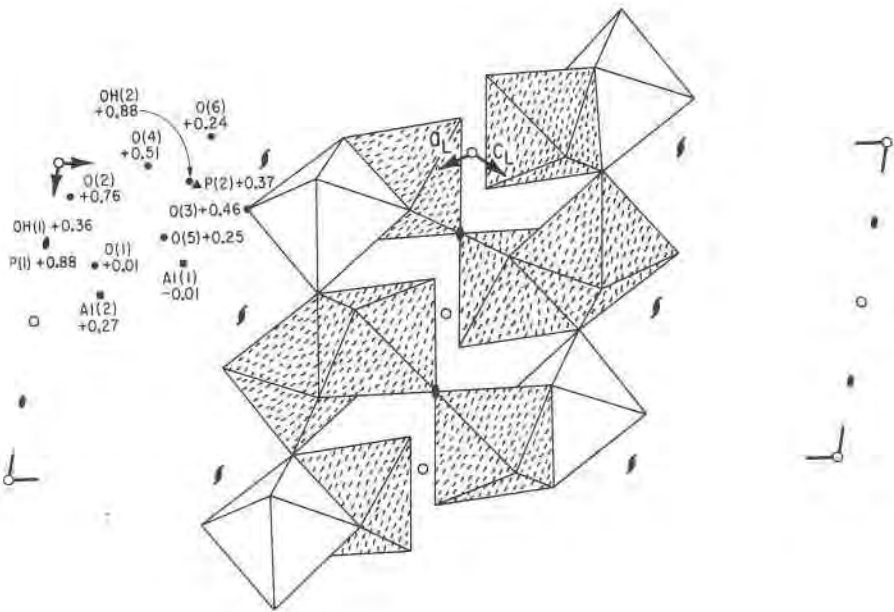


FIG. 1. Octahedral double chain in the trolleite structure. The cell is outlined and inversions, rotations, and 2-fold screws are placed appropriately. Labelled atom positions correspond to Table 4. Heights are given as fractional coordinates  $y$ . The cell  $a_L$  and  $c_L$  refer to the origin for lazulite. Octahedra which are identical in position to those in lazulite are stippled.

*neutrality when compared on a congruent basis.* Calculating the deviation from neutrality on the basis of the bond strengths, the oxygen environment about Al(1) in trolleite and Al in lazulite are similar, with Al(2) in trolleite significantly different and Al in corundum very different.

Geometrically, the Al-O octahedra can be broken into three regions: the shared face, the opposite un-

shared face (the back face), and the remaining six linking edges. Starting with an undistorted isolated neutral dimeric species with local electrostatic neutrality of anions about cations, repulsion across the shared face would result in a foreshortening of the edges on the shared face, a lengthening of the Al-O distances toward that face, and O-Al-O' angles toward that face which are considerably less than  $90^\circ$ . The opposite face in turn will reveal lengthened edges, shorter Al-O distances, and O-Al-O' angles greater than  $90^\circ$ .

In Figure 5, we present the interatomic distances and deviations from local electrostatic neutrality (with OH<sup>-</sup> treated as a single negative ion) for the Al-O octahedra in trolleite, lazulite, and corundum. Table 7 presents a tabulation of the O-Al-O' angles,

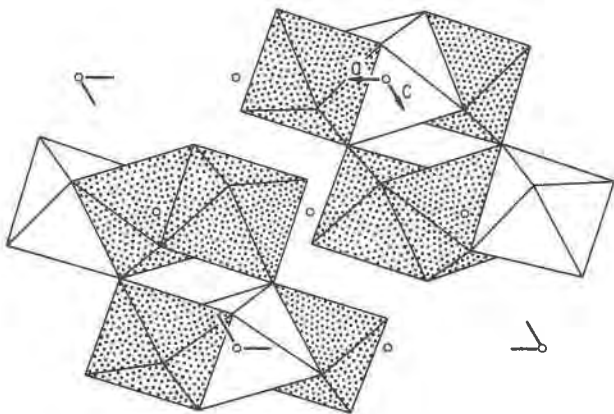


FIG. 2. Octahedra in lazulite which correspond to the octahedra in trolleite of Figure 1. Similar octahedra are stippled. Inversion centers are shown and the lazulite cell is outlined.

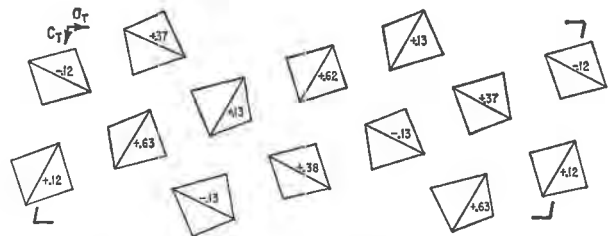


FIG. 3. Orientation of the tetrahedra in the trolleite cell. Heights are given as fractional coordinates in  $y$ .

listed according to the three geometrically distinct regions. For trolleite, in all instances but one, the Al-O distances toward the shared face are lengthened and those opposite are shortened. The exception is the bond to the severely oversaturated OH(2) anion on the back face of Al(1). In addition, the O-Al-O' angles toward the shared face are less than  $90^\circ$ , ranging between  $73^\circ$  and  $79^\circ$ . We note another important feature among the structures. In corundum, the anions are all formally neutral. In trolleite and lazulite they are over-saturated (severely in the former) about the shared face and two of the three anions on the back face are undersaturated. This results in a "double-distortion," first by cation-cation repulsion and second by additional lengthening of the Al-O bond due to oversaturation or shortening due to undersaturation. This results in long Al-O distances to the shared face (1.94 to 2.09 Å) in trolleite and very short Al-O distances to the opposite face (ranging from 1.79 to 1.96 Å). The mean O-Al-O' angles to the back face deviate only moderately from  $90^\circ$ , ranging from  $88^\circ$  to  $97^\circ$ . In corundum, the differences between the two faces are  $79.5^\circ$  and  $101.0^\circ$  for the shared and back faces respectively. These distortions affect edges linking shared and back faces (herein called the antiprismatic edges) in trolleite and lazulite: the corresponding O-Al-O' angles are all greater than  $90^\circ$ . The result is an elongate trigonal antiprism whose direction of elongation is parallel to the cation-cation axis.

The severe oversaturation of OH(2), since it is bonded to three  $\text{Al}^{3+}$  cations, makes the trolleite

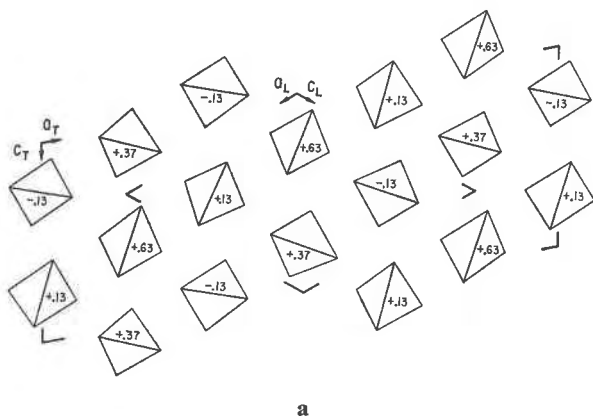


FIG. 4a. Orientation of the tetrahedra in lazulite. The cell  $a_L$  and  $c_L$  refers to lazulite,  $a_T$  and  $c_T$  to trolleite. Heights are given as fractional coordinates in  $y$ .

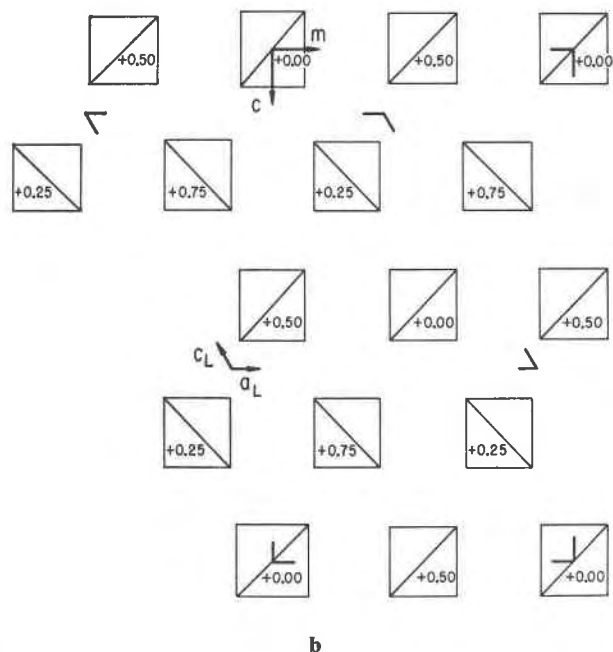


FIG. 4b. Orientation of tetrahedra in lipscombite. The lipscombite cell is outlined by  $c$  and  $m(=[110])$  with  $a_L$  and  $c_L$  referring to lazulite. Exact correspondence to Figure 4a occurs if  $+0.13$  is everywhere added to the heights.

structure rather queer and creates more asymmetrical distortions. This deviation of  $+0.50$  for an  $(\text{OH})^-$  group, disregarding the hydrogen bond, is unusually high for a mineral structure but it is known to occur in the basic ferric phosphate mineral leucophosphite (Moore, 1972a) and the basic ferric arsenate mineral pharmacosiderite (Buerger, Dollase, and Garayococha-Wittke, 1967); both structures show long  $\text{Fe}^{3+}$ - $(\text{OH})^-$  distance averages (2.16 and 2.08 Å, respectively). The Al-OH(2) average is 2.03 Å, about 0.1 Å greater than the Al-OH grand average of 1.93 Å (Moore, 1972b).

### Hydrogen Bonds and Location of the Hydrogen Atoms

Hydrogen bond formation in trolleite and in lazulite is severely limited by the spatial restrictions of these rather dense structures. Since the  $(\text{OH})^-$  anions are displaced  $b/2$  away from the tetrahedral centers which are located above and below the locus of the  $(\text{OH})^-$  anions (Fig. 1), it is not possible to geometrically predict whether the hydrogen atoms point up or down. Thus, we can conceive the hydrogen atoms pointing toward the O(1)-O(1)'' or



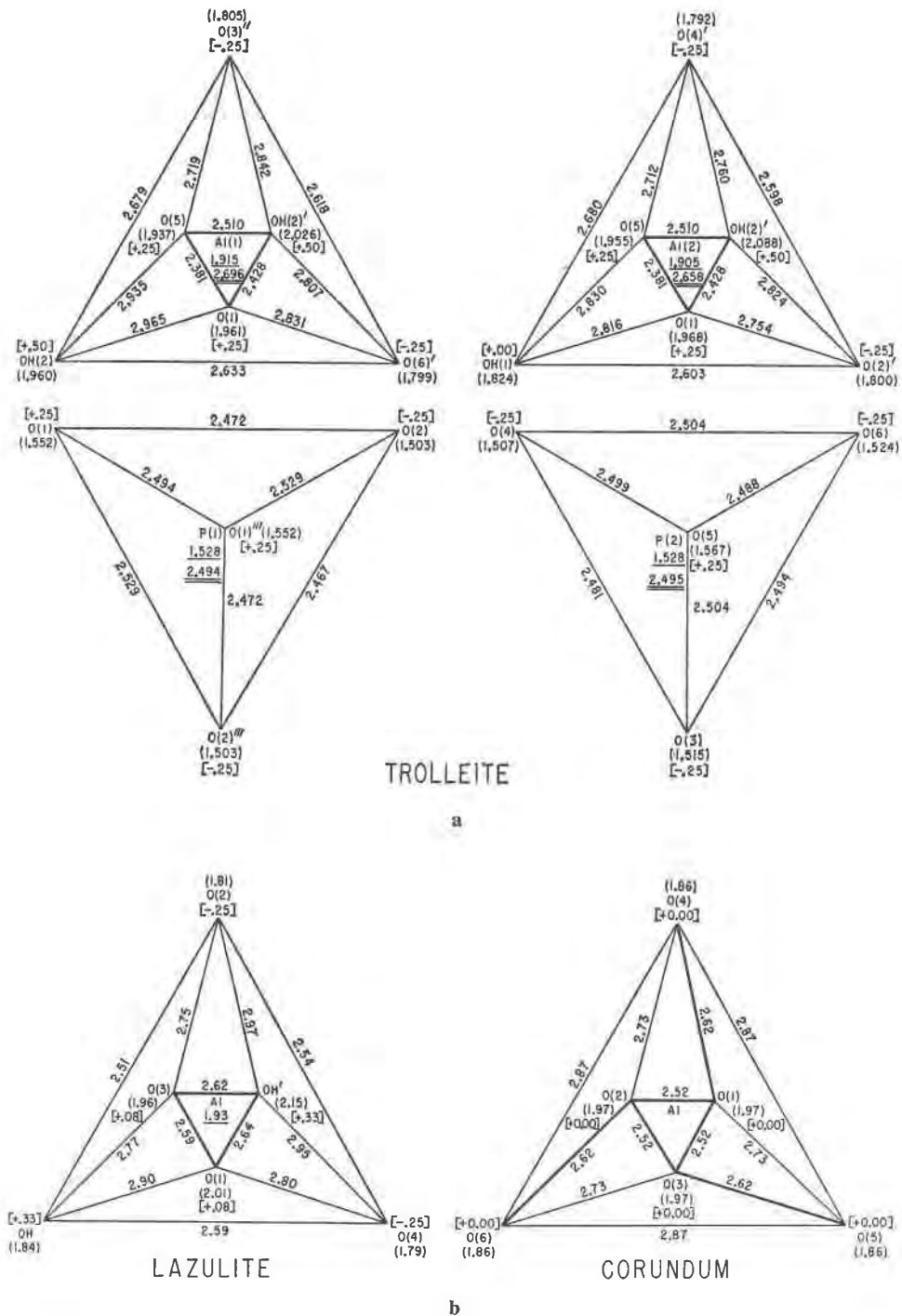


FIG. 5. Schlegel diagrams of (a) the Al(1), Al(2), P(1), and P(2) octahedra and tetrahedra in trolleite; (b) of Al in lazulite and Al in corundum. For trolleite, atoms are labelled according to Table 4, with superscript ' =  $x, -y, 1/2 + z$ ; " =  $1/2 - x, 1/2 - y, 1/2 - z$ ; "' =  $-x, y, 1/2 - z$ . For lazulite and corundum, atoms are labelled according to the references (see text). Shared edges are drawn bold. Me-O distances are included parenthetically, local electrostatic deviations (based on  $\text{OH}^- = \text{X}^-$ ) are in brackets. Me-O averages are underlined once and O-O' averages underlined twice.

TABLE 7. Trolleite and Related Structures: O-Me-O' Angles

TROLLEITE, Al(1)		TROLLEITE, Al(2)		IAZULITE		CORUNDUM					
Shared face		Shared face		Shared face		Shared face					
O(5)	-Al(1)-O(1) <sup>i</sup>	75.3 <sup>o</sup>	O(5)	-Al(2)-O(1)	74.7	O(3)	-Al-O(1) <sup>i</sup>	81.2	O(2)	-Al-O(3)	79.5
O(5)	- " -OH(2) <sup>i</sup>	78.6	O(5)	- " -OH(2) <sup>i</sup>	76.7	O(3)	- " -OH <sup>i</sup>	79.1	O(2)	- "O(1)	79.5
O(1)	- " -OH(2) <sup>i</sup>	75.0	O(1)	- " -OH(2) <sup>i</sup>	73.5	O(1)	- " -OH <sup>i</sup>	78.5	O(3)	- "O(1)	79.5
average		76.3	average		75.0	average		79.6	average		79.5
Back face		Back face		Back face		Back face					
OH(2)	- " -O(3) <sup>ii</sup>	90.6	OH(1)	- " -O(4) <sup>i</sup>	96.7	OH	- "O(2)	86.9	O(6)	- "O(4)	101.0
OH(2)	- " -O(6) <sup>i</sup>	88.8	OH(1)	- " -O(2) <sup>i</sup>	91.8	OH	- "O(4)	91.0	O(6)	- "O(5)	101.0
O(6) <sup>i</sup>	- " -O(3) <sup>ii</sup>	93.2	O(2) <sup>i</sup>	- " -O(4) <sup>i</sup>	94.9	O(2)	- "O(4)	89.7	O(4)	- "O(5)	101.0
average		90.9	average		94.5	average		89.2	average		101.0
Antiprismatic edges		Antiprismatic edges		Antiprismatic edges		Antiprismatic edges					
O(5)	- " -OH(2)	97.7	O(5)	- " -OH(1)	96.9	O(3)	- " -OH	93.5	O(2)	- "O(6)	86.3 (shared edge)
OH(2)	- " -O(1)	98.3	OH(1)	- " -O(1)	95.8	OH	- "O(1)	97.3	O(6)	- "O(3)	90.9
O(1)	- " -O(6) <sup>i</sup>	97.6	O(1)	- " -O(2) <sup>i</sup>	93.8	O(1)	- "O(4) <sup>i</sup>	94.4	O(3)	- "O(5)	86.3 ( " " )
O(6) <sup>i</sup>	- " -OH(2) <sup>i</sup>	94.2	O(2) <sup>i</sup>	- " -OH(2) <sup>i</sup>	92.9	O(4) <sup>i</sup>	- " -OH <sup>i</sup>	96.5	O(5)	- "O(1)	90.9
OH(2) <sup>i</sup>	- " -O(3) <sup>ii</sup>	95.6	OH(2) <sup>i</sup>	- " -O(4) <sup>i</sup>	93.3	OH <sup>i</sup>	- "O(2)	96.8	O(1)	- "O(4)	86.3 ( " " )
O(3) <sup>ii</sup>	- " -O(5)	93.1	O(4) <sup>i</sup>	- " -O(5)	94.6	O(2)	- "O(3)	93.6	O(4)	- "O(2)	90.9
average		96.1	average		94.6	average		95.4	average		88.6
Grand average		89.9	Grand average		89.7	Grand average		89.9	Grand average		89.4
TROLLEITE, P(1)		TROLLEITE, P(2)									
O(1)	-P(1)-O(2) <sup>iii</sup>	111.8 <sup>o</sup>	O(4)	-P(2)-O(3)	110.4						
O(1)	- " -O(1) <sup>iii</sup>	106.9	O(4)	- " -O(5)	108.8						
O(1)	- " -O(2)	108.1	O(4)	- " -O(6)	111.4						
O(2) <sup>iii</sup>	- " -O(2)	110.3	O(3)	- " -O(6)	110.3						
O(1) <sup>iii</sup>	- " -O(2)	111.8	O(5)	- " -O(6)	107.2						
O(1) <sup>iii</sup>	- " -O(2)	108.1	O(5)	- " -O(3)	108.7						
average		109.5	average		109.5						

O(2)-O(2)''' edges for OH(1) and toward the O(3)-O(4) or the O(5)-O(6) edges for OH(2).

Fortunately, the quality of the data permitted unambiguous location of the hydrogen atom positions on a three-dimensional difference Fourier map. The coordinates are H(1) 0, 0.484, 1/4 and H(2) 0.190, 0.809, 0.072. Thus, H(1) points toward the O(2)-O(2)''' edge and H(2) points toward the O(3)-

O(4) edge. Calculated distances are O-H(1) 0.86 Å and O-H(2) 0.74 Å. The H(1)...O(2) distance is 2.34 Å and H(2)...O(3) and H(2)...O(4) are 2.67 and 2.61 Å, respectively.

We propose a bifurcated hydrogen bonding model where H(1), on the 2-fold rotor, provides bonds to O(2) and O(2)''' simultaneously; and H(2) provides bonds to O(3) and O(4) simultaneously. These proposed bonds are in consonance with the electrostatic balance of cations about anions in Table 8; O(2), O(3), and O(4) are all formally undersaturated with respect to nearest neighbor cations. For these cations, we elected the O-H...O bond strength  $\xi = +1/6$  proposed by Baur (1970), and, accordingly, distributed half this bond strength to each of the three undersaturated anions.

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TABLE 8. Electrostatic Valence Balances of Cations about Anions in Trolleite\*

Anion	Coordinating cations	$\Delta$	Deviation
O(1)	P(1)+Al(1)+Al(2)	+0.25	all +
O(2)	P(1)+Al(2)+1/2H(1)	-0.17	all -
O(3)	P(2)+Al(1)+1/2H(2)	-0.17	all -
O(4)	P(2)+Al(2)+1/2H(2)	-0.17	all -
O(5)	P(2)+Al(1)+Al(2)	+0.25	all +
O(6)	P(2)+Al(1)	-0.25	Al(1)-; P(2) $\pm$
OH(1)	2Al(2)-H(1)	-0.17	all -
OH(2)	2Al(1)+Al(2)-H(2)	+0.33	all +

\*  $\Delta$  is the deviation from local electrostatic neutrality. Under "Deviation" are Me-O bonds longer (+) or shorter (-) than polyhedral averages.

## References

- BAUR, W. H. (1970) Bond length variation and distorted coordination polyhedra in inorganic crystals. *Trans. Am. Crystallogr. Assoc.* **6**, 129–155.
- BLOMSTRAND, C. W. (1869) Über neue schwedische Mineralien. *Neues Jahrb. Mineral. Geol. Palaeontol.* **1869**, 481–482.
- BUERGER, M. J., W. A. DOLLASE, AND J. GARAYOCOCHEA-WITTKE (1967) The structure and composition of the mineral pharmacosiderite. *Z. Kristallogr.* **125**, 92.
- BUSING, W. R., K. O. MARTIN, AND H. A. LEVY (1962) ORFLS, a Fortran crystallographic least-squares program. *U.S. Natl. Tech. Inform. Serv.* ORNL-TM-305.
- CROMER, D. T., AND J. B. MANN (1968) X-ray scattering factors computed from numerical Hartree-Fock wavefunctions. *Acta Crystallogr.* **A24**, 321–324.
- EVANS, H. T., Jr. (1972) Heteropoly and isopoly complexes of the transition elements of groups 5 and 6. *Perspectives in Structural Chemistry*, vol. 4, John Wiley and Sons, 2–59.
- KATZ, L., AND W. N. LIPSCOMB (1951) The crystal structure of iron lazulite; a synthetic mineral related to lazulite. *Acta Crystallogr.* **4**, 345–348.
- LINDBERG, M. L., AND C. L. CHRIST (1959) Crystal structures of the isostructural minerals lazulite, scorzalite, and barbosalite. *Acta Crystallogr.* **12**, 695–697.
- MOORE, P. B. (1970) Crystal chemistry of the basic iron phosphates. *Am. Mineral.* **55**, 135–169.
- (1972a) Octahedral tetramer in the crystal structure of leucophosphate. *Am. Mineral.* **57**, 397–410.
- (1972b) Aluminum-13A. *Handbook of Geochemistry* II-3, Ed. K. H. Wedepohl, Springer-Verlag, New York.
- NEWHAM, R. E., AND Y. M. DEHAAN (1962) Refinement of the  $\alpha$ - $\text{Al}_2\text{O}_3$ ,  $\text{Ti}_2\text{O}_3$ ,  $\text{V}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  structures. *Z. Kristallogr.* **117**, 235–237.
- RAMACHANDRAN, G. N., AND R. SRINIVASAN (1970). *Fourier Methods in Crystallography*. Wiley-Interscience, New York, p. 96–119.
- SCLAR, C. B., L. C. CARRISON, AND C. M. SCHWARTZ (1965) Synthesis and properties of trolleite (aluminian lazulite?), a high pressure mineral from the Westanå iron deposit, Kristianstad, Sweden (abstract). *Amer. Mineral.* **50**, 1965.

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