

The crystal structure of alleghanyite, $\text{Mn}_5[(\text{OH})_2](\text{SiO}_4)_2$

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Auszug

Die Kristallstruktur des Alleghanyits, $\text{Mn}_5[(\text{OH})_2](\text{SiO}_4)_2$, von Bald Knob, North Carolina, wurde mit Hilfe dreidimensionaler Diffraktometer-Daten (equi-inclination) bestimmt, wobei die Isotypie zum Chondrodit berücksichtigt wurde. Die Gitterkonstanten sind: $a = 8,2747$, $b = 4,8503$, $c = 10,7198 \text{ \AA}$, $\beta = 108,64^\circ$; $Z = 2$, Raumgruppe $P2_1/c$. Atomparameter und anisotrope Temperaturfaktoren wurden nach der Methode der kleinsten Quadraten bis zu $R = 0,075$ verfeinert.

Das SiO_4 -Tetraeder ist wenig verzerrt mit fast gleichen Si–O-Abständen. Mittlerer Si–O-Abstand $1,627 \text{ \AA}$ und O–O-Abstand $2,652 \text{ \AA}$. Die Mn-Atome besetzen oktaedrische Positionen in einer wenig verzerrten hexagonalen Kugelpackung von O-Atomen. Alle Mn-Oktaeder sind stark verzerrt und gehören drei Typen an: das Mn(1)-Oktaeder enthält eine OH-Gruppe, das Mn(2)-Oktaeder zwei OH-Gruppen, und das Mn(3)-Oktaeder keine OH-Gruppe. Die mittleren Mn–O-Abstände in den drei Typen von Oktaedern sind: $2,221$, $2,199 \text{ \AA}$ bzw. $2,215 \text{ \AA}$. Die entsprechenden O–O-Abstände sind: $3,122$, $3,090$ und $3,117 \text{ \AA}$.

Die Mn-Oktaeder haben mit Nachbar-Oktaedern zwei, drei oder vier Kanten und mit SiO_4 -Tetraedern eine oder zwei Kanten gemeinsam. Sie bilden Zickzack-Ketten, welche in Schichten parallel (010) liegen und mit der Periode von fünf Oktaedern entlang der a -Achse verlaufen. Nachbarketten einer Schicht werden durch ähnliche Ketten von Oktaederlücken getrennt. Die Ketten werden durch isolierte SiO_4 -Tetraeder verbunden. Aufeinander folgende Schichten sind um $b/2$ voneinander entfernt und um $c/2$ gegeneinander verschoben.

Abstract

The crystal structure of alleghanyite, $\text{Mn}_5[(\text{OH})_2](\text{SiO}_4)_2$, from Bald Knob, North Carolina, has been determined using three-dimensional equi-inclination diffractometer data and taking into consideration its isotypism to chondrodite. The cell constants are: $a = 8.2747$, $b = 4.8503$, $c = 10.7198 \text{ \AA}$, $\beta = 108.64^\circ$; $Z = 2$, space group $P2_1/c$. Atomic parameters and anisotropic temperature factors were refined by least squares to $R = 0.075$.

The SiO_4 tetrahedron is slightly distorted with almost equal Si–O distances, averaging 1.627 \AA , and mean O–O distance 2.652 \AA . The Mn atoms occupy

octahedral sites in a slightly distorted hexagonal close-packed array of O atoms. All the Mn octahedra are highly distorted. They are of three types: the Mn(1) octahedron includes one OH group, the Mn(2) octahedron two OH groups, whereas no OH group belongs to the Mn(3) octahedron. The average Mn—O distances in the three types of octahedra are: 2.221, 2.199 and 2.215 Å respectively. The corresponding O—O distances are: 3.122, 3.090 and 3.117 Å.

The Mn octahedra share two, three or four edges with adjacent octahedra and one or two edges with SiO₄ tetrahedra. Serrated zigzag octahedral chains are formed, lying on layers parallel to (010). The octahedra in the chains repeat themselves periodically along the *a* axis, with a repeat period of five octahedra. Adjacent chains are separated by similar chains of octahedral voids. Linkage is effected by isolated SiO₄ tetrahedra. Neighboring octahedral layers, with a height difference of *b*/2, are displaced by *c*/2.

Introduction

Alleghanyite, Mn₅[(OH)₂|(SiO₄)₂], is a bright pink to red-brown mineral, first discovered in a manganese-bearing vein at Bald Knob, Alleghany County, North Carolina, U.S.A., in association with manganese-bearing calcite, tephroite, galaxite, rhodonite, spessartite and some other minerals (ROSS and KERR, 1932). It was named after Alleghany County.

Chemical analyses carried out by SHANNON and GONYER (ROSS and KERR, 1932) failed to detect the presence of water and led to the incorrect formula 5 MnO · 2 SiO₂. ROSS and KERR (1932) examined alleghanyite optically and took powder diagrams, but they were unable to make a satisfactory morphological study because the mineral usually appears in the form of rounded grains which, under the microscope, almost invariably show lamellar twinning. Based upon an incorrect chemical formula, which is remotely reminiscent of tephroite, 2MnO · SiO₂, and observing some similarities in the powder patterns of the two minerals, they came to the conclusion that alleghanyite was related to tephroite and that it, too, was orthorhombic.

A careful morphological and chemical examination by ROGERS (1935), however, proved alleghanyite to be monoclinic with the formula 2Mn₂SiO₄ · Mn(OH, F)₂. ROGERS pointed out the close similarity of this formula to that of chondrodite, 2Mg₂SiO₄ · Mg(OH, F)₂, although the fluorine content of alleghanyite is very low compared to that of chondrodite (cf. RANKAMA, 1938; SAHAMA, 1953, and JONES *et al.*, 1969), and he finally came to the conclusion that the two minerals are isotypic. His chosen orientation of the crystallographic axes of alleghanyite gives the angle β a value of nearly 90°.

CAMPBELL SMITH, BANNISTER and HEY (1944) reported a new occurrence of alleghanyite with clove-brown color in the Benallt manganese mine at Rhiw, Wales, in association with banalsite and tephroite. Chemical analyses yielded a formula similar to that of ROGERS, but the TiO_2 content amounted to 4.8%, almost 30 times as much as in the Bald Knob material, and no fluorine could be detected. The final formula for the Rhiw alleghanyite is $2\text{Mn}_2(\text{Si}, \text{Ti})\text{O}_4 \cdot (\text{Mn}, \text{Ti})(\text{O}, \text{OH})_2$. As the cell constants, determined from Laue photographs, were comparable with those of chondrodite, CAMPBELL SMITH *et al.* (1944) came to the same conclusion as ROGERS that the two substances should be isotypic.

The investigation of the crystal structure of alleghanyite was undertaken because of a long-time interest in the behaviour of Mn in nesosilicates and especially in the Mn members of the olivine and humite groups. It was also thought that, since the isotypism to chondrodite was very probable, an exact determination of the structure of alleghanyite would give more reliable data also for chondrodite, the structure of which is, so far, only approximately known (TAYLOR and WEST, 1928).

Experimental

A small prism of alleghanyite, $0.36 \times 0.14 \times 0.12$ mm in size and elongated parallel to the b axis, was obtained from the badly twinned material of Bald Knob. The usual orientation for monoclinic crystals (b axis unique), adopted by STRUNZ (1966) for alleghanyite and by SAHAMA (1953) and also by DEER, HOWIE and ZUSSMAN (1962) for chondrodite, was preferred to that of CAMPBELL SMITH *et al.* (1944), who followed the orientation of TAYLOR and WEST (1928) for chondrodite.

From systematic absences on zero- and higher-level Weissenberg photographs about the b axis and on the complementary precession photographs, the space group was found to be $P2_1/c$. Cell parameters were obtained by measuring high-order reflections on zero- and higher-level Weissenberg photographs and refining by least squares. They are given in Table 1, together with those obtained by LEE (1955) for the alleghanyite of Bald Knob and those of CAMPBELL SMITH *et al.* (1944) for the alleghanyite of Rhiw, Wales. The corresponding data for a chondrodite (JONES *et al.*, 1969) are included for comparison.

The rather large differences in the values of c and β are remarkable. Actually, on first examining the zero-level Weissenberg

Table 1. *Unit-cell data for alleghanyite*
 Standard errors, given in parentheses, refer to last digit)

	Alleghanyite Bald Knob (RENTZEPERIS)	Alleghanyite Bald Knob (LEE)*	Alleghanyite Rhiw, Wales (CAMPBELL SMITH <i>et al.</i>)*	Chondrodite N° 2 (JONES <i>et al.</i>)*
<i>a</i>	8.2747 (8) Å	8.24 Å	8.3 Å	7.8404 (2)
<i>b</i>	4.8503 (5)	4.94	4.86	4.7284 (3)
<i>c</i>	10.7198 (10)	10.55	10.46	10.2539 (3)
β	108.64° (1)	109.13°	109.17° (15)	109.059° (2)
Γ	407.675 Å ³	405.73 Å ³	398.63 Å ³	359.295 Å ³
<i>Z</i>	2	2	2	2

$\rho_{\text{meas}} = 4.020 \text{ g} \cdot \text{cm}^{-3}$ (ROSS and KERR, 1932).

$\rho_{\text{calc}} = 4.013 \text{ g} \cdot \text{cm}^{-3}$.

Space group: $P2_1/c$.

* Reoriented.

film, two central lines were chosen, which gave the following constants:

$$a = 8.297 \text{ \AA}, \quad \beta = 109.12^\circ, \quad c = 10.743 \text{ \AA}.$$

The values of *a* and β almost coincide with those given by CAMPBELL SMITH *et al.* (1944), but *c* again differs considerably. However, when the higher-level photographs were taken into account, the chosen 0 0 *l* line necessitated that both indices *h* and *l* of the zero-level reflection be even. Consequently, a new 0 0 *l* line was chosen, which easily allowed indexing of all the observed reflections with space group $P2_1/c$. As can be seen from Table 1 the actual value of β differs from the above value 109.12° by about half a degree. It is quite possible that former investigators were misled by the fact that this latter value almost coincides with that of chondrodite.

The new values of the cell parameters give a normalized unit-cell volume $V' = V/5 = 81.535 \text{ \AA}^3$, which brings alleghanyite almost on the line of best fit in the diagram V' vs. *Average radius of octahedral cation* in the paper of RIBBE, GIBBS and JONES (1968).

Three-dimensional intensity data were collected with a manually operated single-crystal equi-inclination diffractometer, equipped with a proportional counter connected to a pulse-height analyser. Using $\text{CuK}\alpha$ (Ni filter) radiation, 746 nonequivalent reflections, belonging to six levels about *b*, were measured. Integrated intensities were

Table 2. Observed and calculated structure factors for alleghanyite

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 $	h k l	$ F_o $	$ F_c $					
0 0	2	10.2	9.2	10 0	-4	17.0	19.5	4 1	2	11.5	12.5	0 2	6	44.9	49.9				
4	77.7	75.4		-2	30.0	32.9		3	59.3	59.6		7	1.9	0.4					
6	95.1	99.4	0 1	1	38.9	35.9	4	22.5	22.5	8	22.0	21.9		-6	17.1	20.2			
8	47.5	45.3		2	37.1	28.9		5	4.2	2.0		9	16.0	16.9		-5	19.8	25.1	
10	12.0	10.5		3	105.5	93.3		6	6.5	6.7		10	15.1	17.4		-4	35.5	37.9	
12	19.4	16.6		4	4.6	4.5		7	8.1	8.2		11	3.6	4.4		-2	17.1	18.5	
10 -12	17.2	17.0		5	54.5	55.8		8	7.7	7.4	1 2	-12	16.6	13.2		-2	22.8	22.0	
-10	48.5	47.4		6	14.8	16.4		9	4.0	2.5		-11	5.4	3.9		-1	22.1	20.4	
-8	21.5	22.8		7	4.6	4.3	5 1 -12	5	3.6	4.2		-10	26.4	25.6		0	70.3	64.5	
-6	29.0	29.3		8	14.1	14.1		-11	15.7	15.1		-9	3.8	3.2		1	32.8	30.6	
-4	77.3	82.5		9	76.7	70.4		-10	8.3	6.8		-8	42.9	41.3		3	35.4	32.6	
-2	33.5	44.5		10	29.5	8.0		-9	68.9	65.7		-7	8.6	10.1		3	9.0	2.2	
0	21.7	14.8		11	5.0	4.3		-8	19.5	17.4		-6	5.7	2.2		4	28.3	25.9	
2	38.7	25.1		12	3.0	1.5		-7	33.1	33.6		-5	5.7	5.1		5	16.7	16.1	
4	22.2	22.1		1 1 -12	3.3	2.1		-6	6.6	7.8		-4	125.2	139.1		6	41.6	39.3	
6	141.1	150.1		-11	15.8	15.2		-5	22.6	28.8		-3	12.9	15.1		7	1.4	3.0	
8	12.2	14.4		-10	5.5	2.8		-4	12.6	16.3		-2	1.8	2.3	6 2 -11	1	4.3	1.4	
10	37.8	34.3		-9	13.9	13.8		-3	81.8	88.4		-1	23.5	25.7		-10	10.5	10.8	
12	38.5	37.8		-8	14.4	15.1		-2	6.0	5.0		0	6.4	5.7		-9	1.7	2.2	
2 0	34.8	33.8		-7	11.8	13.0		-1	16.5	16.6		1	37.9	32.5		-8	39.1	39.5	
-10	34.6	32.4		-6	14.4	15.5		0	2.0	0.5		2	36.8	33.6		-7	10.1	10.3	
-8	38.7	37.9		-5	20.1	21.1		1	6.6	5.4		3	15.7	15.3		-6	37.6	37.1	
-6	10.9	9.9		-4	65.1	68.8		2	12.8	13.3		4	18.1	18.0		-5	1.9	2.3	
-4	70.9	61.4		-3	120.2	128.8		3	34.3	31.2		5	15.6	16.3		-4	62.0	63.1	
-2	26.7	15.8		-2	15.7	18.2		4	4.2	4.4		6	41.7	45.2		-3	6.8	6.8	
0	31.6	21.1		-1	24.3	24.9		5	18.5	19.5		7	27.8	30.0		-2	21.5	20.5	
2	110.4	113.0		0	25.1	21.1		6	14.9	16.6		8	5.4	5.2		-1	13.1	11.7	
4	8.7	1.0		0	116.9	99.5		7	19.5	18.6		9	4.7	2.6		0	9.9	9.0	
6	52.8	56.3		2	9.2	8.6		8	1.1	1.2		10	30.2	30.3		1	17.5	16.1	
8	15.1	13.3		3	113.1	101.0		6 1 -12	2.7	3.5		11	8.7	11.5		2	32.1	30.7	
10	26.2	23.5		4	4.7	2.0		-11	1.4	1.2		2 2 -12	14.4	16.7		3	12.7	11.6	
-12	24.2	22.2		5	79.8	82.7		-10	1.7	1.3			8.5	8.5		4	5.8	5.8	
-10	25.7	25.0		6	4.0	4.0		-9	13.9	13.0		-10	28.1	28.6		5	1.4	2.1	
-8	6.1	4.6		7	25.6	27.2		-8	11.3	12.3		-9	8.4	8.3		6	24.7	23.7	
-6	96.8	91.1		8	18.0	19.8		-7	15.6	17.5		-8	35.5	46.4		7 2 -10	30.7	31.5	
-4	59.0	64.4		9	21.5	21.0		-6	15.1	16.0		-7	18.8	12.7		-9	8.1	7.3	
-2	100.8	103.3		10	1.1	1.3		-5	25.3	30.3		-6	1.9	2.0		-8	23.3	24.7	
0	70.4	57.9		11	11.5	8.7		-4	17.3	19.8		-5	7.7	8.4		-7	8.3	9.5	
2	9.2	10.3		2 1 -12	3.8	2.6		-3	50.6	55.5		-4	46.4	50.4		-6	9.4	8.6	
4	87.5	92.6		-11	12.3	12.8		-2	7.6	7.5		-3	3.4	3.7		-5	6.8	7.3	
6	11.2	13.0		-10	10.3	10.5		-1	25.2	24.6		-2	31.4	30.5		-4	24.3	26.0	
8	25.4	25.8		-9	17.1	16.3		0	21.2	20.9		-1	19.7	19.4		-3	16.2	15.0	
10	13.4	13.1		-8	14.2	14.1		1	23.4	21.1		0	15.4	16.1		-2	12.2	14.2	
4 0	-12	25.2	26.0		-7	118.3	116.9		2	3.9	3.4		1	6.1	6.7		-1	15.6	14.7
-10	51.9	49.8		-6	10.0	8.6		3	67.9	67.0		2	158.8	156.9		0	35.1	30.5	
-8	30.4	27.6		-5	41.2	38.6		4	1.9	1.8		3	6.3	7.9		1	6.1	5.2	
-6	144.6	146.5		-4	1.9	0.8		5	19.8	18.5		4	11.0	8.7		2	50.8	44.3	
-4	23.1	25.6		-3	107.7	117.2		6	4.3	4.3		5	16.8	17.2		3	4.4	3.6	
-2	2.0	0.3		-2	29.9	29.0		7	19.0	19.3		6	22.5	25.0		4	11.3	10.0	
0	19.2	17.9		-1	113.8	110.2		7 1 -11	9.2	8.7		7	6.6	6.7		5	5.0	6.5	
2	55.0	56.4		0	26.6	20.8		-10	1.5	0.9		8	46.8	53.0		8 2 -9	5.0	5.5	
4	43.4	46.9		1	121.4	117.8		-9	7.1	5.9		9	10.1	10.6		-8	7.5	2.8	
6	10.4	11.5		2	68.8	58.8		-8	3.7	2.8		10	18.4	17.9		-7	4.4	3.8	
8	5.5	4.3		3	5.2	5.0		-7	63.0	65.2		3 2 -12	2.4	0.9		-6	7.7	8.1	
5 0	-12	19.0	20.6		4	18.1	18.8		-6	3.9	1.2		-11	4.2	3.3		-5	11.5	12.9
-10	6.8	4.9		5	8.8	9.6		-5	8.9	9.4		-10	35.5	34.6		-4	31.2	42.7	
-8	41.4	39.3		6	15.1	16.7		-4	4.1	4.9		-9	10.4	10.1		-3	8.8	9.0	
-6	53.2	53.3		7	5.9	5.1		-3	39.4	40.6		-8	7.0	7.0		-2	42.1	39.3	
-4	65.6	66.6		8	4.8	3.8		-2	8.3	9.3		-7	6.4	5.9		-1	6.3	6.0	
-2	65.2	66.1		9	24.4	25.0		-1	68.3	65.1		-6	31.8	32.3		0	31.1	26.4	
0	185.4	181.3		10	4.8	4.2		0	12.8	11.7		-5	24.7	23.4		1	12.0	11.3	
2	47.1	46.5		11	26.0	24.8		1	39.5	36.0		-4	57.7	59.4		2	14.6	13.4	
4	16.7	17.6		1 1 -13	1.0	0.2		2	4.6	2.0		-3	11.0	11.9		3	4.7	3.0	
6	62.6	63.3		-12	2.9	6.1		3	12.4	11.3		-2	147.7	152.9		9 2 -7	7.6	8.4	
8	16.0	15.4		-11	41.4	40.0		4	1.4	1.3		-1	8.8	8.5		-6	19.4	17.2	
6 0	-12	15.1	17.0		10	6.3	3.9		5	3.6	4.3		0	49.3	45.3		-5	9.2	8.0
-10	11.8	13.3		-9	8.1	8.9		8 1 -10	3.2	0.1		1	16.8	15.8		-4	14.5	14.7	
-8	8.5	4.3		-8	8.3	4.7		-9	10.1	9.8		2	5.4	5.6		-3	2.8	1.7	
-6	31.1	34.3		-7	7.5	6.1		-8	11.9	3.9		3	11.9	15.1		-2	4.0	3.0	
-4	40.3	43.8		-6	2.3	1.6		-7	1.7	3.0		4	36.4	37.0		-1	9.2	8.8	
-2	8.9	6.7		-5	34.9	33.6		-6	4.9	6.2		5	10.3	13.2		0	11.1	11.2	
0	16.7	15.2		-4	2.2	1.3		-5	24.4	25.2		6	10.4	10.8		1	43.9	45.0	
2	19.3	21.6		-3	24.4	27.4		-4	11.3	7.9		7	2.9	3.5		2	15.5	15.4	
4	26.5	28.0		-2	65.6	62.5		-3	7.8	6.3		8	24.5	25.6		3	41.7	43.4	
6	47.2	45.6		-1	103.4	105.8		-2	5.6	6.2		9	3.0	5.8		4	25.7	26.5	
7 0	-12	27.3	28.6		0	11.1	9.3		-1	35.3	33.2		4 2 -12	15.3	15.8		5	21.7	23.6
-10	40.9	38.6		1	44.2	41.4		0	6.2	7.5		-11	11.0	12.3		6	16.1	17.8	
-8	20.9	18.8		2	66.0	59.2		1	3.9	2.9		-10	38.6	36.0		7	20.1	22.2	
-6	19.6	22.8		3	80.5	81.5		2	7.9	8.2		-9	8.6	8.9		8	13.9	14.4	
-4	15.1	17.7		4	6.0	6.1		3	18.7	19.3		-8	33.6	28.1		9	43.0	46.2	
-2	24.5	24.9		5	61.4	66.7		-7	28.8	26.4		-7	28.8	26.4		10	4.0	3.2	
0	31.1	31.7		6	1.9	2.2		9 1 -9	11.9	11.8		-6	40.6	43.4		1 3 -10	23.7	20.9	
2	37.2	35.0		7	62.2	62.2		-8	4.0	2.5		-5	19.6	21.5		2	1.4	1.6	
4	11.4	10.7		8	1.6	0.9		-7	5.1	5.1		-4	18.4	14.2		-8	1.5	0.5	
6	8.1	9.4		9	28.0	28.0		-6	3.3	2.5		-3	4.9	3.9		-7	15.4	13.7	
8 0	-10	11.4	12.4		10	7.6	7.2		-5	23.4	22.7		-2	2.0	1.6		-6	17.5	18.0
-8	8.0	7.6		4															

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 $	h k l	$ F_o $	$ F_c $
1 3 9	4.5	2.2	4 3 -1	34.8	34.4	7 3 2	25.5	22.8	3 4 -9	18.0	15.5	6 4 2	12.3	11.3
10	8.2	9.5	0	20.9	20.2	5	6.3	7.4	-8	21.2	17.9	7 4 -5	12.2	12.0
2 3 -11	4.1	3.8	1	58.6	55.9	8 3 -7	1.1	0.7	-7	3.8	1.5	-4	5.6	5.6
-10	5.7	6.0	2	23.0	22.5	-6	14.4	13.6	-6	37.5	34.4	-7	4.5	4.4
-9	12.8	13.8	3	41.5	39.7	-5	18.9	17.7	-5	17.4	16.7	-2	3.8	2.8
-8	43.4	40.0	4	18.9	17.7	-4	10.4	10.8	-4	11.2	11.8	-1	1.0	0.6
-7	77.7	72.2	5	4.6	4.8	-3	6.3	6.2	-3	6.6	6.7	0 5 1	17.7	17.6
-6	22.7	21.6	6	12.8	12.1	-2	16.9	16.0	-2	57.9	56.0	2	3.7	5.0
-5	8.7	7.8	7	8.7	8.8	-1	14.9	14.7	-1	27.5	26.2	3	7.4	8.6
-4	38.1	38.3	5 3 -10	6.0	5.7	0	10.3	9.3	0	9.9	8.0	4	3.5	5.1
-3	55.3	63.0	-9	46.8	45.2	0 4 1	15.8	16.9	1	17.8	17.2	5	22.9	22.7
-2	28.1	27.6	-8	12.8	13.4	2	2.6	2.4	2	9.7	11.6	1 5 -6	9.1	7.7
-1	52.8	53.7	-7	1.6	0.7	3	17.7	19.8	3	5.9	6.3	-5	15.2	14.7
0	15.0	16.2	-6	9.6	9.2	4	14.2	14.5	4	30.4	32.1	-4	10.7	10.5
1	56.7	57.4	-5	16.2	22.2	5	21.5	23.7	5	11.1	11.9	-3	38.7	40.0
2	65.7	63.2	-4	26.4	29.9	6	28.1	29.0	6	7.1	8.9	-2	9.9	11.3
3	10.3	10.6	-3	51.6	54.0	7	1.2	2.2	4 4 -9	5.2	5.4	-1	20.0	21.1
4	1.6	0.9	-2	21.9	21.9	8	8.9	10.6	-8	22.9	20.8	0	2.4	3.2
5	19.7	21.3	-1	26.8	34.8	-9	4.2	1.0	-7	7.9	7.2	1	34.8	33.5
6	11.7	13.0	0	1.7	1.7	-8	26.3	23.0	-5	46.2	43.4	2	8.5	9.2
7	10.8	12.8	1	17.9	17.0	-7	6.2	6.9	-5	11.8	11.5	3	15.6	15.6
8	6.2	3.1	2	11.4	11.1	-6	16.8	18.0	-4	8.2	8.7	4	1.0	1.5
9	11.3	11.5	3	15.7	14.6	-5	16.7	18.6	-3	23.9	23.8	5	37.4	39.0
3 3 -11	35.2	31.0	4	10.3	9.9	-4	48.7	51.4	-2	16.3	16.6	2 5 -6	7.7	7.6
-10	6.0	5.3	5	9.7	2.8	-3	6.3	6.3	-1	14.3	12.6	0	8.7	8.9
-9	5.1	2.6	6	14.6	15.7	-2	6.0	6.1	0	1.5	1.4	-4	12.9	12.7
-8	1.6	1.1	6 3 -10	14.3	13.8	-1	5.7	6.6	1	6.8	5.5	-3	9.8	8.6
-7	14.4	13.8	-9	1.2	0.5	0	1.9	2.2	2	10.4	8.7	-2	17.6	17.1
-6	21.2	20.4	-8	5.3	2.5	1	3.6	2.5	3	13.3	11.2	-1	30.3	30.2
-5	27.6	28.5	-7	16.7	17.0	2	16.5	17.0	2	16.5	17.0	0	8.7	8.9
-4	7.6	9.8	-6	7.5	8.9	3	21.8	23.1	5	10.4	11.1	1	10.3	11.0
-3	4.6	4.2	-5	12.8	13.7	4	5.5	7.2	5 4 -8	9.4	8.1	2	3.0	1.7
-2	58.8	56.7	-4	25.0	25.5	5	6.5	8.2	-7	1.3	2.1	3	18.1	17.1
-1	34.3	34.9	-3	35.7	34.8	6	42.6	45.0	-6	14.7	14.1	4	2.5	4.7
0	28.9	21.4	-2	15.9	15.0	7	12.7	12.1	-5	12.3	12.9	5 5 -6	32.0	34.4
1	12.6	12.0	-1	5.0	5.6	8	2.6	5.0	-4	14.3	14.9	-4	3.2	3.0
2	13.4	13.5	0	8.9	7.6	2 4 -9	3.3	0.5	-3	13.1	13.1	-3	22.0	21.0
3	44.7	45.7	1	30.2	27.3	-8	22.9	20.6	-2	30.8	28.0	-2	3.0	2.2
4	38.5	39.3	2	15.0	14.2	-7	8.2	10.0	-1	12.1	11.5	-1	10.3	8.7
5	35.6	38.4	3	46.9	42.8	-6	12.7	12.1	0	51.2	55.7	0	11.3	10.7
6	6.3	5.1	4	19.5	18.4	-5	18.3	18.3	1	20.2	17.0	1	16.4	16.9
7	40.1	41.0	5	19.6	18.8	-4	18.5	19.1	2	17.0	15.8	2	10.5	11.3
8	26.3	26.7	7 3 -9	4.6	3.6	-3	3.0	2.2	3	9.6	8.6	3	4.7	4.7
4 3 -11	4.5	5.2	-8	21.2	20.0	-2	9.6	9.0	4	2.8	1.8	4 5 -5	39.6	37.2
-10	19.6	16.6	-7	40.8	39.9	-1	9.1	9.1	-7	3.8	2.3	-4	1.9	1.9
-9	6.1	3.7	-6	15.6	15.3	0	12.3	12.9	-6	25.5	24.1	-3	2.6	2.4
-8	5.5	6.1	-5	14.9	17.4	1	20.7	21.2	-5	7.0	6.9	-2	8.0	7.2
-7	5.3	5.3	-4	13.9	15.2	2	56.1	58.1	-4	31.9	30.9	-1	30.9	31.8
-6	1.9	1.1	-3	21.5	21.3	3	2.9	0.0	-3	5.2	2.8	0	10.8	10.6
-5	61.9	62.4	-2	21.2	19.2	4	11.7	13.6	-2	18.5	17.4	1	38.5	37.3
-4	13.2	13.6	-1	48.3	42.6	4	10.9	12.4	-1	2.5	0.9			
-3	5.8	5.6	0	1.5	0.7	6	20.8	22.5	0	5.9	3.6			
-2	5.2	4.6	1	16.1	13.0	7	8.3	8.1	1	2.5	2.7			

converted to $|F|$ values in the usual way. For accidentally zero reflections the HAMILTON (1955) correction was applied.

As alleghanyite highly absorbs the radiation used ($\mu = 681.28 \text{ cm}^{-1}$) an approximate absorption correction was applied assuming a cylindrical crystal with $r = 0.065 \text{ mm}$, the mean of the lateral dimensions of the crystal used. It is of interest to note that no significant change in the final positional atom parameters or the R value resulted by assuming various cylinder radii in the range between $r = 0.060$ and 0.075 mm . The isotropic temperature factors varied by about 8%.

All subsequent computations were carried out on the C D C 3300 computer at the Nuclear Research Center „Democritus“ in Athens. The crystallographic programs incorporated in the *Program System for x-ray Crystallography* of the Chemistry Departments of the Universities of Washington and Maryland (STEWART and HIGH, 1965), were used throughout. The system includes also a slightly modified

version of the least-squares refinement program ORFLS by BUSING *et al.* (1962), which was exclusively used for least-squares refinement. The weighting scheme in the program is similar to that suggested by HUGHES (1941).

Determination of the structure and refinement

Alleghanyite has long been considered isotypic with chondrodite, so the first step was to make a structure-factor calculation with the positional parameters for chondrodite given by TAYLOR and WEST (1928). The metal ions are divided into three groups: Mn(1) and Mn(2), occupying the general position $4e: \pm(x, y, z; x, \frac{1}{2} + y, \frac{1}{2} - z)$, and Mn(3) occupying the special position $2d: \frac{1}{2} \frac{1}{2} 0; \frac{1}{2} 0 \frac{1}{2}$. All the other atoms are in the general position $4e$: there are one Si group, four O groups and one OH group, which is designated O(5).

Half-ionized state for all the atoms was assumed and probable isotropic temperature factors, known from other silicates, were assigned to them. Atomic-form factors, and also anomalous-dispersion corrections for the Mn atoms, were obtained from the *International tables*, vol. III. A separate scale factor was used for each level. The initial structure-factor calculation, including all measured reflections, gave $R = 0.41$.

No fluorine contribution was taken into account because, on the one hand, ROSS and KERR (1932) and CAMPBELL SMITH *et al.* (1944) do not report its presence in their analyses of alleghanyite and, on the other hand, the amount reported by ROGERS (1935) does not exceed 5% of the total OH + F content.

Refinement with isotropic temperature factors proceeded smoothly down to $R = 0.083$. At this stage anisotropic temperature coefficients

Table 3. *Atomic parameters and equivalent isotropic temperature factors for alleghanyite with their standard deviations*

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
Mn(1)	0.3110	0.0002	0.0087	0.0004	0.1719	0.0002	2.29 Å ²	0.05 Å ²
Mn(2)	0.0772	0.0002	0.0137	0.0004	0.3812	0.0002	2.48	0.05
Mn(3)	$\frac{1}{2}$		0		$\frac{1}{2}$		2.34	0.05
Si	0.2976	0.0004	0.5773	0.0006	0.3569	0.0003	2.02	0.06
O(1)	0.2945	0.0008	0.7123	0.0016	0.4952	0.0007	2.26	0.13
O(2)	0.1347	0.0009	0.7185	0.0016	0.2469	0.0007	2.21	0.13
O(3)	0.4632	0.0008	0.7143	0.0016	0.3303	0.0007	2.10	0.13
O(4)	0.2976	0.0008	0.2430	0.0016	0.3537	0.0007	1.94	0.13
O(5)	0.0973	0.0010	0.2530	0.0017	0.0566	0.0007	2.54	0.14

Table 4. *Anisotropic temperature coefficients β_{ij} for alleghanyite with their standard deviations*(Temperature factor = $\exp[-h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}]$)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mn(1)	0.00857	0.02593	0.00550	-0.00036	0.00171	0.00001
σ	0.00026	0.00080	0.00016	0.00034	0.00017	0.00027
Mn(2)	0.00962	0.02564	0.00626	-0.00075	0.00205	0.00002
σ	0.00027	0.00082	0.00017	0.00036	0.00018	0.00028
Mn(3)	0.00898	0.02417	0.00598	0.00058	0.00120	0.00003
σ	0.00037	0.00110	0.00023	0.00049	0.00024	0.00038
Si	0.00772	0.02074	0.00503	-0.00073	0.00124	-0.00031
σ	0.00041	0.00120	0.00025	0.00059	0.00026	0.00046
O(1)	0.00734	0.02732	0.00589	0.00005	0.00141	0.00019
σ	0.00105	0.00346	0.00068	0.00160	0.00068	0.00129
O(2)	0.00824	0.02203	0.00556	0.00159	0.00063	-0.00083
σ	0.00109	0.00329	0.00067	0.00155	0.00069	0.00122
O(3)	0.00815	0.02296	0.00504	0.00156	0.00093	-0.00005
σ	0.00106	0.00327	0.00064	0.00157	0.00068	0.00120
O(4)	0.00674	0.02590	0.00489	0.00030	0.00109	0.00140
σ	0.00101	0.00337	0.00063	0.00152	0.00065	0.00117
O(5)	0.01276	0.02942	0.00540	0.00570	0.00261	0.00273
σ	0.00130	0.00364	0.00070	0.00181	0.00079	0.00132

Table 5. *Anisotropic temperature coefficients B_{ij} for alleghanyite* $(B_{ij} = 4\beta_{ij}/\bar{a}_i^* \cdot \bar{a}_j^*)$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn(1)	2.11	2.44	2.27	0	0.01	0
Mn(2)	2.37	2.41	2.58	0	0.02	0
Mn(3)	2.21	2.27	2.47	0	0.03	0
Si	1.90	1.95	2.08	0	-0.31	0
O(1)	1.80	2.57	2.43	0	0.19	0
O(2)	2.03	2.07	2.29	0	-0.83	0
O(3)	2.00	2.16	2.08	0	-0.05	0
O(4)	1.66	2.44	2.02	0	1.40	0
O(5)	3.14	2.77	2.23	0	2.72	0

were introduced and in four further cycles the refinement of the atomic parameters practically converged with $R = 0.075$.

Careful examination of the Fourier and difference Fourier maps in the neighborhood of the hydroxyl group, O(5), indicated possible positions of the H atom, but none could be considered as unambiguously locating it. Attempts to have the H position refined resulted

in an unacceptable O(5)—H distance. A probable H position is discussed at the end of this paper. No H contribution was considered in the final cycle.

Table 2 gives the $|F_o|$ and $|F_c|$ values obtained from the final parameters listed in Tables 3, 4 and 5. The interatomic distances and angles are given in Tables 6 and 7. The coordination of the O atoms with the corresponding distances and angles is shown in Table 8.

Description of the structure and discussion

The structure of alleghanyite, $Mn_5[(OH)_2(SiO_4)_2]$, determined in this investigation, is, if details are not taken into account, essentially similar to that of chondrodite, described by TAYLOR and WEST (1928). Basically, it can be visualized as a slightly distorted hexagonal close-packed array of O ions, with Mn and Si occupying octahedral and tetrahedral sites respectively. Owing to its very small amount in alleghanyite, F was not considered any further; it cannot play

Table 6. *Interatomic distances in alleghanyite*

SiO ₄ tetrahedron			
Si—O(1)	1.628 Å	O(4)—O(1)	2.740 Å
O(2)	1.631	O(2)	2.732
O(3)	1.628	O(3)	2.718
O(4)	1.622	O(3)—O(1)	2.579
		O(2)	2.576
Average Si—O	1.627 ± 0.008	O(1)—O(2)	2.567
		Average O—O	2.652 ± 0.011
Mn(1) O ₆ octahedron			
Mn(1)—O'(1)	2.143 Å	O'(1)—O(2)	3.379 Å
O(2)	2.346	O(3)	3.431
O(3)	2.267	O'(3)	3.066
O'(3)	2.125	O(5)	2.979
O(4)	2.289	O(2)—O(3)	2.576
O(5)	2.159	O(4)	2.935
		O(5)	3.252
Average Mn(1)—O	2.221 ± 0.008	O'(3)—O(3)	3.144
		O(4)	3.213
		O(5)	3.451
		O(4)—O(3)	2.956
		O(5)	3.085
		Average O—O	3.122 ± 0.011

Table 6. (*Continued*)

Mn(2)O ₆ octahedron			
Mn(2)-O(1)	2.337 Å	O(1)-O(2)	2.567 Å
O(2)	2.189	O(4)	2.992
O'(2)	2.099	O'(5)	3.242
O(4)	2.235	O''(5)	3.116
O'(5)	2.155	O(2)-O'(2)	3.309
O''(5)	2.178	O(4)	2.935
Average Mn(2)-O	2.199 ± 0.008	O''(5)	3.277
		O'(2)-O(4)	3.392
		O'(5)	3.209
		O''(5)	2.991
		O'(5)-O(4)	3.128
		O''(5)	2.926
		Average O-O	3.090 ± 0.011
Mn(3)O ₆ octahedron			
Mn(3)-O(1) [2]	2.187 Å	O(1)-O(3) [2]	2.579 Å
O(3) [2]	2.229	O'(3) [2]	3.585
O(4) [2]	2.230	O(4) [2]	2.992
Average Mn(3)-O	2.215 ± 0.008	O'(4) [2]	3.250
		O(4)-O(3) [2]	2.956
		O'(3) [2]	3.339
		Average O-O	3.117 ± 0.011

here the important role it plays in the structures of the Mg members of the humite group.

As can be seen from Table 3, the unit cell may be considered as made up of two closest-packed O layers, parallel to (010) at heights $y \simeq 0.25$ and 0.75 , linked together by layers of Mn and Si at heights $y \simeq 0$ and 0.50 .

The structure can better be described in terms of the coordination polyhedra around the cations. Figure 1 is a projection of the structure parallel to b .

As described in detail further down, there are three different types of distorted MnO₆ octahedra, one around each of the three different Mn atoms, i.e. Mn(1), Mn(2) and Mn(3). These octahedra share two, three or four edges with adjacent octahedra and one or two edges with isolated SiO₄ tetrahedra. Since, as mentioned above, the Mn and Si ions form layers parallel to (010) at heights $y \simeq 0$ and 0.50 , the

Table 7. Bond angles in alleghanyite

SiO ₄ tetrahedron		Mn(1)O ₆ octahedron	
O(4)–Si–O(1)	114.93°	O'(1)–Mn(1)–O(2)	97.57°
		O(3)	102.13
		O'(3)	91.87
O(3)–Si–O(1)	104.74	O(5)	87.67
		O(2)–Mn(1)–O(3)	67.87
O(1)–Si–O(2)	103.89	O(4)	78.58
		O(5)	92.30
Average	109.28 ± 0.40	O'(3)–Mn(1)–O(3)	91.38
		O(4)	93.35
		O(5)	107.34
		O(4)–Mn(1)–O(3)	80.89
		O(5)	87.78
		Average	89.89 ± 0.30
Mn(2)O ₆ octahedron		Mn(3)O ₆ octahedron	
O(1)–Mn(2)–O(2)	69.01°	O(1)–Mn(3)–O(3) [2]	71.45°
		O'(3) [2]	108.55
		O(4) [2]	85.26
		O'(4) [2]	94.74
O(2)–Mn(2)–O'(2)	101.00	O(4)–Mn(3)–O(3) [2]	83.04
		O'(3) [2]	96.96
		Average	90.00
O'(2)–Mn(2)–O(4)	102.98		
O'(5)–Mn(2)–O(4)	90.86		
Average	89.75 ± 0.30		

coordination polyhedra around the cations also form layers parallel to (010). Figure 2 shows schematically one such layer at $y \approx 0$.

As in the case of the olivines (BIRLE *et al.*, 1968) and norbergite (GIBBS and RIBBE, 1969), the structure can now be neatly described as follows: Within an octahedral layer, serrated zigzag octahedral chains repeat themselves periodically along the a axis. These chains alternate with similar chains of octahedral voids, also repeating themselves periodically along the a axis, but which are displaced by $c/2$. Adjacent zigzag chains are linked together by isolated SiO₄ tetrahedra.

There are five octahedra in the two branches of the repeat period of a zigzag chain. The cations of the three octahedra in the first

Table 8. *Coordination of the O atoms with the corresponding distances and angles**

Distances		Angles	
O(1)			
O(1)—Mn'(1)	2.143 Å	Mn'(1)—O(1)—Mn(2)	126.59°
Mn(2)	2.337	Mn(3)	117.97
Mn(3)	2.187	Si	126.07
Si	1.628	Mn(2)—O(1)—Mn(3)	94.35
		Si	90.51
		Mn(3)—O(1)—Si	92.28
		Average	107.96
O(2)			
O(2)—Mn(1)	2.346 Å	Mn'(2)—O(2)—Mn(1)	122.73°
Mn(2)	2.189	Mn(2)	115.36
Mn'(2)	2.099	Si	126.80
Si	1.631	Mn(1)—O(2)—Mn(2)	97.04
		Si	92.22
		Mn(2)—O(2)—Si	95.84
		Average	108.33
O(3)			
O(3)—Mn(1)	2.125 Å	Mn(1)—O(3)—Mn''(1)	124.55°
Mn''(1)	2.267	Mn(3)	114.19
Mn(3)	2.229	Si	127.07
Si	1.628	Mn''(1)—O(3)—Mn(3)	96.77
		Si	95.23
		Mn(3)—O(3)—Si	90.78
		Average	108.10
O(4)			
O(4)—Mn(1)	2.289 Å	Si —O(4)—Mn(1)	120.99°
Mn(2)	2.235	Mn(2)	119.28
Mn(3)	2.230	Mn(3)	121.24
Si	1.622	Mn(3)—O(4)—Mn(1)	96.10
		Mn(2)	96.05
		Mn(1)—O(4)—Mn(2)	97.40
		Average	108.51
O(5)			
O(5)—Mn(1)	2.159 Å	Mn(1)—O(5)—Mn'(2)	130.19°
Mn'(2)	2.178	Mn''(2)	127.49
Mn''(2)	2.155	Mn'(2)—O(5)—Mn''(2)	95.05

* Standard errors are given in Tables 6 and 7.

branch, Mn(1), Mn(3) and Mn'(1), lie very nearly on a plane parallel to $(\bar{3}05)$, whereas Mn'(1) and the other two cations of the second branch, Mn'(2) and Mn(2), lie approximately on a plane parallel to (101) . The number of the octahedra in the repeat period of the chains is different in the various members of the humite group and in olivine (RIBBE *et al.*, 1968).

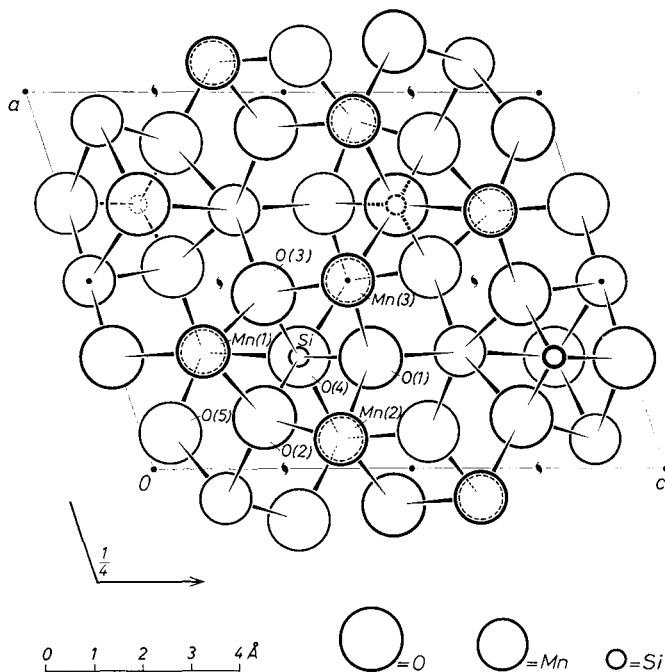


Fig. 1. Projection of the structure parallel to b . Atoms with greater y are indicated with heavier circles. In case of atoms differing by one b translation, the lower atom is shown as a dashed circle

Neighboring octahedral layers, at a distance $b/2$, are displaced by $c/2$. In this way, the structure, viewed along the b axis, shows octahedral chains normal to b , lying above similar chains of octahedral voids.

According to ROGERS (1935) alleghanyite shows imperfect cleavage parallel to* (100) , which is also the commonest plane of twinning. Both could be explained by the facts that the most vulnerable positions in the structure, the hydroxyl groups, lie on planes parallel to (100) , and also that the SiO_4 tetrahedra form layers parallel to this plane.

* Indices refer to the setting in this paper.

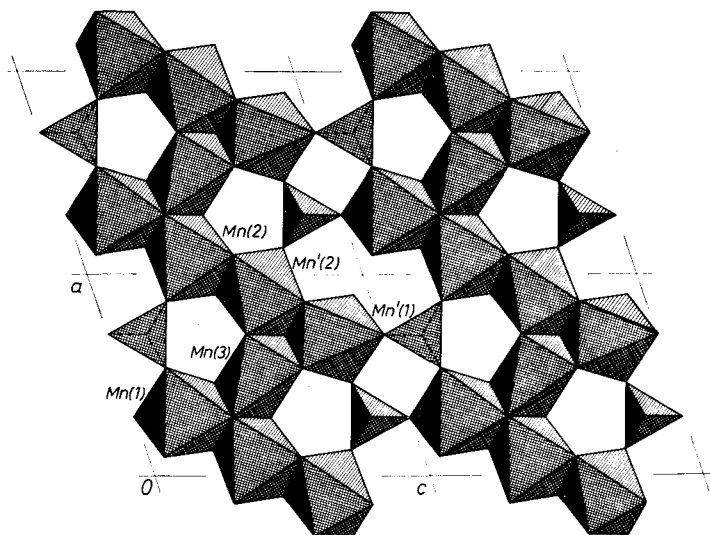


Fig. 2. A layer normal to b formed by chains of edge-sharing Mn octahedra linked together by SiO_4 tetrahedra. The cations are at $y \approx 0$. Four unit cells are shown. The five octahedra in the repeat period along the a axis are labeled

In Fig. 3 are shown the coordination polyhedra around the cations, with the corresponding interatomic distances. Their main characteristics are as follows:

SiO₄ tetrahedron. The SiO_4 tetrahedron is slightly distorted with almost equal Si—O distances. Their average value, 1.627 Å, is shorter than the value 1.635 Å predicted by GIBBS and BROWN (1968) for the bond length between Si and a four-coordinated oxygen. The three tetrahedron edges shared with Mn octahedra are almost the same length, averaging 2.574 Å. Likewise, the three unshared edges are close to one another with an average value 2.730 Å. The O—Si—O angles are also divided into two groups of almost equal values: the three angles opposite the shared edges average 104.35°, while those opposite the unshared edges, formed between O(4) and the other O atoms, have a mean value 114.20°. Actually, the SiO_4 tetrahedron is a trigonal pyramid with O(4) at its apex and with its base parallel to (010). It is of interest to note that all the average distances are very near those given for norbergite by GIBBS and RIBBE (1969).

All the Mn octahedra are highly distorted. The excellent account on the distortion of the Mg octahedra in olivine, given by BIRLE *et al.* (1968), would need only a slight modification in the case of alleghanyite.

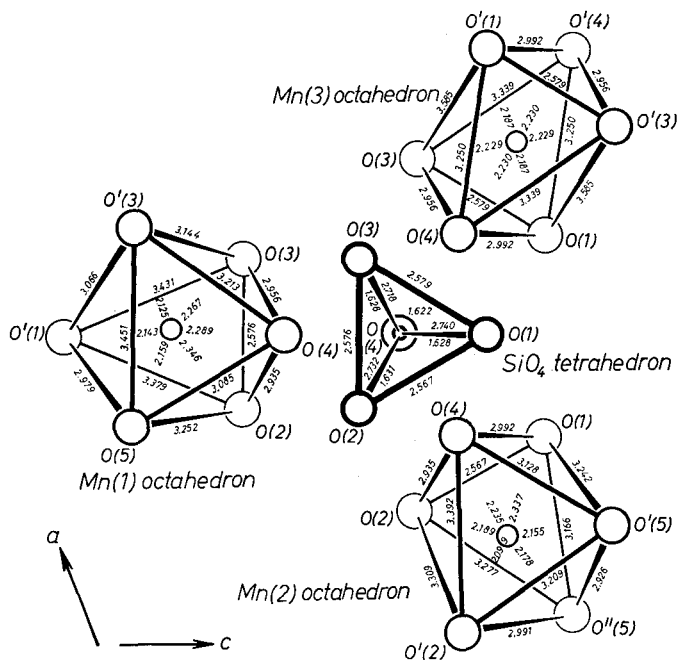


Fig. 3. Coordination polyhedra around the cations, shown separated from one another. The orientation of the polyhedra is for the cations in the asymmetric unit (see Figure 1). Differences in height are indicated by heavier circles

In general, the shared edges appear shortened, whereas the bond distances to O atoms at the ends of shared edges are lengthened. As each octahedron shares one edge with a SiO₄ tetrahedron, this edge is much smaller than the others.

Mn(1) octahedron. Mn(1) is surrounded by five O atoms and one OH group. Three Mn(1)—O distances are shorter and three longer than the average distance 2.221 Å. This distance coincides with the average Mn—O distance in hodgkinsonite (RENTZEPERIS, 1963) and is close to the values found in other silicate structures. The average Mn—O distances in the two other Mn octahedra are also near this value.

Two edges of an octahedral face, namely O(2)—O(4) and O(4)—O(3), are shared with one Mn(2) octahedron and one Mn(3) octahedron, whereas the third edge of the face, O(2)—O(3), is shared with a SiO₄ tetrahedron. In accordance with what has already been said, these are the shortest edges and the corresponding bond lengths, Mn(1)—O(2), Mn(1)—O(4) and Mn(1)—O(3), are the longest. The average O—O distance is 3.122 Å, close again to that in hodgkinsonite and in other

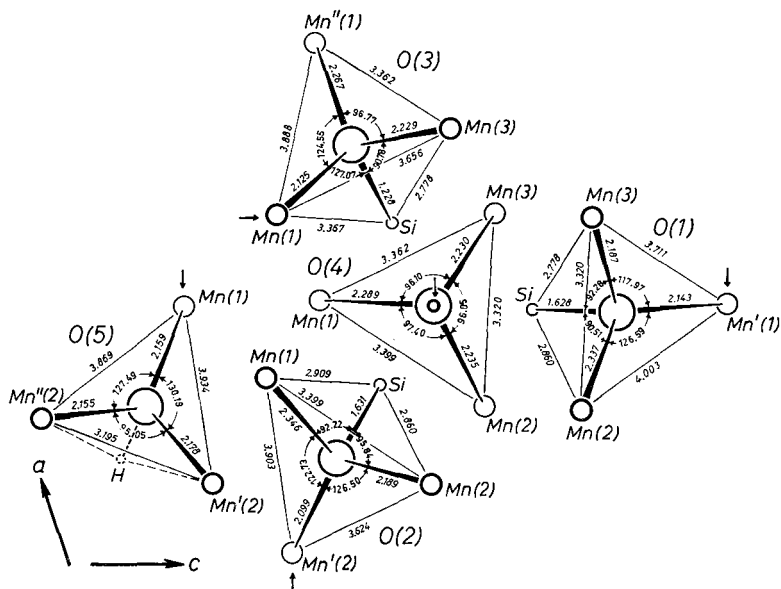


Fig. 4. Coordination pyramids around the O atoms, shown detached from one another. The orientation is for the O atoms in the asymmetric unit (see Figure 1). Heavier circles denote greater height. Apical cations are indicated with an arrow. In O(5) a possible H position is shown by the small dashed circle

Mn silicates. The average O—Mn(1)—O angle is 89.90° but some angles differ considerably from this value.

Mn(2) octahedron. Mn(2) is bonded to four O atoms and two OH groups. It shares the two edges of a face, O(2)—O(4) and O(1)—O(4), with one Mn(1) octahedron and one Mn(3) octahedron respectively. The third edge, O(1)—O(2), is shared with a SiO₄ tetrahedron. A fourth edge, O'(5)—O''(5), connecting two OH groups, is shared with another Mn(2) octahedron. The average Mn(2)—O and O—O distances, 2.199 Å and 3.090 Å respectively, are slightly shorter than in the Mn(1) octahedron. The average O—Mn(2)—O angle is 89.75° . Here again the shared edges are the shortest, and the shortest Mn—O bond distance corresponds to O'(2), the only O atom not shared with other octahedra.

Mn(3) octahedron. This octahedron differs from the other two in that it possesses a center of symmetry, since Mn(3) lies on a center, and in that it contains no OH group. It shares the six edges of two opposite faces with two Mn(1) octahedra, two Mn(2) octahedra and two SiO₄ tetrahedra. Four bond lengths are almost equal, 2.230 Å, whereas the other two are shorter. The average Mn(3)—O and O—O distances,

2.215 Å and 3.117 Å respectively, almost coincide with those of the Mn(1) octahedron. Again the unshared edges are the longest.

Figure 4 shows the coordination of the O atoms in alleghanyite. The four O atoms forming SiO₄ tetrahedra, are tetrahedrally surrounded by three Mn atoms and one Si atom, whereas O(5) is bonded to three Mn atoms and one H atom. O(1) and O(4) are bonded to one Mn(1), one Mn(2) and one Mn(3); O(2) and O(5) to one Mn(1) and two Mn(2); and O(3) to two Mn(1) and one Mn(3). Notwithstanding their different surroundings, the angles around O(1), O(2), O(3) and O(4) are essentially the same. They fall into two groups: three large angles, averaging 120.5°–123.5°, and three small angles, averaging 92.4° to 96.5°. The three larger angles are formed at O by one cation and the three others. This cation forms, as it were, the apex of a trigonal pyramid around the O atoms. The apical cation for O(1) is Mn(1), for O(2) is Mn(2), for O(3) is Mn(1), whereas for O(4) is Si. In the first three pyramids, the bond distance to the Mn atom at the apex is the shortest of the three Mn—O distances. Of course, in the O(4) pyramid the distance to Si is the shortest.

Considering the two large and almost equal angles formed at O(5) by Mn(1) and the two Mn(2) atoms and also the small angle at O(5) between the two Mn(2) atoms, one is led to suppose that the apical atom in the O(5) pyramid is actually Mn(1), with the H atom forming with it at O(5) a large angle of over 120°. For an O(5)—H bond length 0.97 Å the most probable H position would be: $x = -0.007$, $y = 0.169$, $z = 0.001$. In Fig. 1 this position is just over the symmetry center at the origin.

Structure-factor calculation, including the H atom, gave the same *R* value as before. However, attempts to refine this position by least squares resulted in unacceptable O(5)—H distance.

The angles of the O pyramids given in Table 8 are very close to those found for norbergite by GIBBS and RIBBE (1969). Their strain analysis for norbergite could easily be applied to alleghanyite with only slight modifications.

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