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STRUCTURAL STUDY OF TOCHILINITE.
PART I. THE ISOMETRIC VARIETY

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A structure study is presented for the new mineral tochilinite $6(Fe_{0.9}S) \cdot 5[Mg_{0.71}Fe_{0.29} \cdot (OH)_2]$. The centered triclinic cell has $a = 5.37$ b = 15.65, c = 10.72 Å; $\alpha = \gamma = 90$, $\beta = 95°$; space group C1, Z = 2. The structure consists of layers of iron sulfide (mackinawite) type alternating with layers of brucite type along the c axis. The x and y coordinates were determined by electron diffraction from a microcrystal, while the z coordinates were deduced from x-ray evidence.

The new mineral tochilinite $6(Fe_{0.9}S) \cdot 5[Mg_{0.71}Fe_{0.29}(OH)_2]$ was described recently [1] and is the second after valleriite $2[Cu, Fe)S] \cdot 1.526[Mg, Al(OH)_2]$ [2] to show a hybrid structure,[1] in which sulfide layers alternate with brucite layers. Tochilinite occurs in nature as two varieties, the first forming isometric and rounded clumps and the second radially radiated and acicular clumps.

Here we present a structure study for the isometric variety. Single crystals were not available, so only powder x-ray photographs could be taken. These showed [1] texture lines from the basal planes, which gave $d_{001} = 10.68$ Å. All the powder-pattern lines were indexed to a centered Bravais C lattice having $a = 5.37$, b = 15.65, c = 10.72 Å; $\alpha = \gamma = 90$, $\beta = 95°$.

Chemical analysis by V. A. Moleva showed that the iron and sulfur are accompanied by magnesium and water, which with $d_{001} = 10.68$ Å (compare the 11.37 Å for valleriite) indicated that sulfide and brucite layers alternate along the c axis. An acicular specimen of the second variety gave ten reflections of $00l$ type with x rays (the powder pattern from an isometric specimen had only three $00l$ reflections). Figure 1 shows the final one-dimensional electron-density synthesis, which confirms that the structure is of hybrid type.

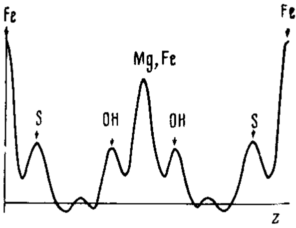

Fig. 1. One-dimensional electron-density projection on the z axis for tochilinite.

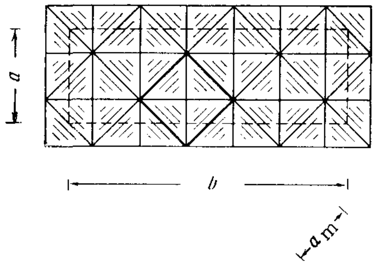

Fig. 2. Normal projection of the ideal structure of a sulfide layer in tochilinite. The dashed lines indicate the unit cell of tochilinite, while the heavy lines indicate that of mackinawite.

The cell size in the plane of a layer enables us to construct a model; b is about three times *a*. Mackinawite (tetragonal) is FeS with a layered

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[1] Evans and Alman [2] proposed this name for minerals in which brucite layers alternate with layers of a different chemical nature.

structure that has $a = 3.679$ Å in the layer plane [3] and is somewhat similar to tochilinite. This parameter is the shortest distance between S atoms which lie in the (001) planes in a square pattern. The diagonal of a unit mackinawite cell corresponds to the a parameter of tochilinite: $a_m\sqrt{2} = 5.16$ Å (Fig. 2).

A brucite layer is inscribed naturally in the tochilinite unit cell; the hexagonal cell of brucite has $a = 3.12$ Å, and $5a_{br} = 15.60$ Å if the b axis of tochilinite coincides with the a axis of brucite, and a for tochilinite is obtained by multiplying a_{br} by $\sqrt{3}$ (Fig. 3). The c sin β for tochilinite (10.68 Å) is less than the 11.37 Å for valleriite because a sulfide layer in mackinawite is 2.523 Å thick, which is 0.62 Å less than the value for valleriite. The monoclinic form of the unit cell of tochilinite indicates a systematic shear along the a axis for the superimposed layers. Figures 2 and 3 show that the overall symmetry of the structure is not higher than C1.

We used electron diffraction to obtain information on the intensities. The perfect cleavage forced us to use selected area diffraction. There are [4] considerable difficulties in using the intensities from selected area electron diffraction in structure analysis; important features are the crystal quality and thickness (which determine whether the interaction is kinematic or dynamic), the angles between the mosaic blocks, and the two-dimensional diffraction. Very little has been published [4, 5] on structure elucidation by selected area diffraction.

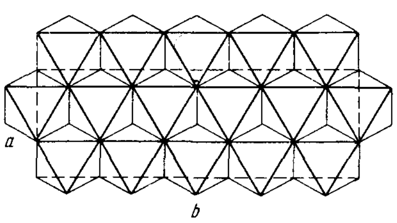

Fig. 3. Normal projection of a brucite layer. The dashed lines indicate the unit cell.

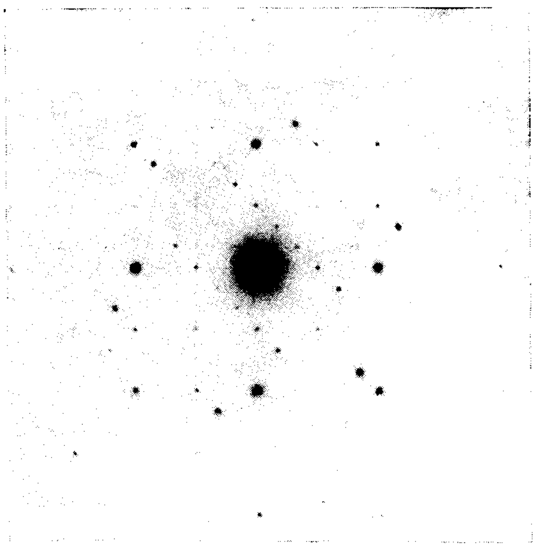

Fig. 4. Selected area diffraction pattern from tochilinite.

We examined numerous crystals in the electron microscope. Figure 4 shows a typical selected area diffraction pattern, which contains reflections of hk0 type, which form a rhombic pattern having Cmm symmetry (reflections with h + k = 2n are present). The values a sin $\beta = 5.35$, b = 15.65 Å agree with the x-ray evidence. The general features are: 1) constancy in the relative intensities; 2) virtual absence of evidence for secondary diffraction, which occurs mainly when there are reflections whose strength is comparable with that of the primary beam, the other reflections tending to become equalized in intensity; 3) presence of large crystals showing uniform blackening when viewed in transmission; 4) absence of extinction bands. All these features indicate kinematic interaction and fairly high quality in the crystals, i.e., no substantial angular spread in the mosaic blocks.

Some of the intensities were measured by microphotometer, while the others were estimated visually by comparison with the first or via plates with various exposures. In all we examined 49 independent reflections having a maximal sin ϑ/λ of 0.64, which corresponded to coverage of almost the entire surface of the plate. We averaged the intensities for symmetrically placed reflections. It was found that the observed and theoretical amplitudes agreed best if no corrections were applied for the angular spread of the mosaic blocks. We used [6] for the electron-scattering curves.

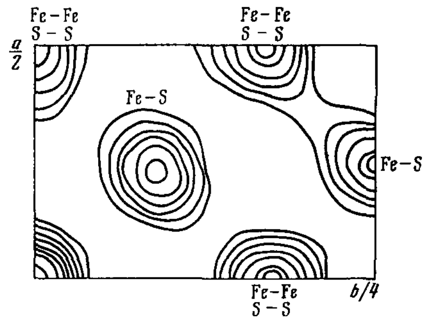

Fig. 5. Patterson projection along the c axis of tochilinite.

Figure 5 shows the Patterson projection along the c axis. The peak pattern corresponds to the model described above for the sulfide layer; the peaks at u = 0 and u = 0.5 are separated by b/6 along the v axis and correspond to Fe–Fe and S–S vectors. At u of 0.25 and 0.75 with v = n/12 the ends of the Fe–S vectors lie within a layer. All peaks were of approximately the same height. We obtained R as 42% by specifying ideal coordinates for all 16 independent atoms in planar group C1m. Successive potential projections with suitable shifts improved R if allowance was made for the low weight of one of the four crystallographically independent Fe atoms that is in a symmetry plane in the projection. One of the tetrahedra is not completely populated on account of an ordered distribution in the vacancies. We reduced R to 23% by least-squares refinement of the population coefficient μ for the incompletely filled tetrahedra (μ was reduced from 2 to 1.3, which corresponds to a filling probability of 0.65). Several successive potential projections and final least-squares refinement reduced R to 12.2%; Fig. 6 shows the corresponding projection of the potential. Table 1 gives the observed and theoretical intensities, while Table 2 gives the atomic coordinates. The x and y coordinates for 16 atoms are independent, while the others are obtained via the C1m symmetry operations (this is the symmetry of the projection along the c axis). The z coordinates were deduced from a one-dimensional Fourier synthesis (Fig. 1) for the isometric variety (the powder patterns for the two varieties are similar but not identical). Tables 3 and 4 give the interatomic distances for the sulfide and brucite parts. Figures 7 and 8 show the projections of the sulfide and brucite layers on the *a*b plane in the real structure.

TABLE 1. Observed and Theoretical hk0 Intensities

hkl	F_o^2	F_t^2	*hkl*	F_o^2	F_t^2
000	--	57140	370	12	13.4
200	60	87.3	080	—	4.9
400	400	399	190	16	23.3
600	20	23	390	8	9.3
110	20	28.1	590	4	1.4
310	8	32.6	0.10.0	400	410
510	10	10	2.10.0	12	17.5
020	12	12.5	4.10.0	10	2.2
220	8	13.8	1.11.0	11	2.4
420	4	4.	3.11.0	4	4.6
130	48	65.4	5.11.0	8	1.4
330	28	2	0.12.0	400	426
530	8	10.8	2.12.0	12	12
040	4	21.4	4.12.0	40	42
240	20	19.5	1.13.0	0.4	0.8
440	0.4	0.4	0.14.0	0.4	0.3
150	48	48.2	1.15.0	12	12.5
350	400	405	3.15.0	28	22.6
550	8	8.9	0.16.0	0.4	1.6
060	28	27.4	2.16.0	8	1.4
260	1600	1647	1.17.0	0.4	0.3
460	16	4.6	0.18.0	0	2.2
660	20	18.2	2.18.0	16	19.2
170	0.8	1.7	1.19.0	0.4	0.3

The sulfide layer shows considerable distortion of the ideal pattern, which consists of a set of tetrahedra lying on their edges and each sharing four edges with the nearest adjacent tetrahedra. The mean Fe–S distance for all tetrahedra is 2.32 Å (range 2.14-2.47 Å). The lengths of the unshared edges range from 3.68 to 3.84 Å with a mean of

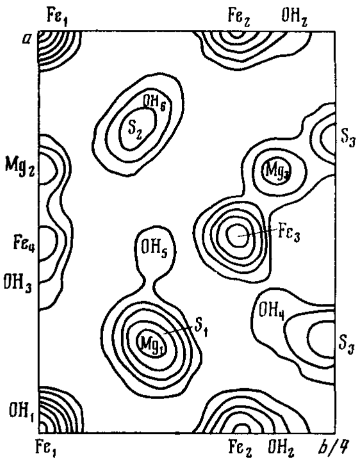

Fig. 6. Final potential projection along the c axis.

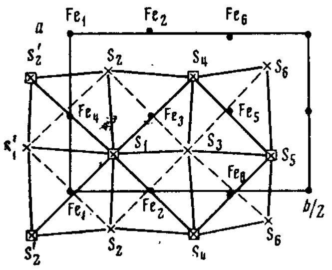

Fig. 7. Normal projection of a sulfide layer after refinement.

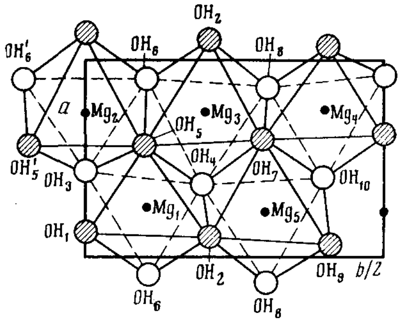

Fig. 8. Normal projection of a brucite layer after refinement.

3.74 Å, while the shared ones give 3.62-4.09 Å (mean 3.83 Å). Adjacent planes containing S atoms are separated by 2.76 Å. A sulfide layer in valleriite consists of tetrahedra set on their bases, all tetrahedra being filled with randomly distributed Cu and Fe [2]. Half of the tetrahedra have their tops pointing in one direction and the other half in the opposite direction. Each tetrahedron is surrounded by three neighbors. The mean length of the unshared edges in a sulfide layer in valleriite is 3.79 Å, while the shared edges give 3.81 Å (the first is greater than that in tochilinite, while the second is less). The mean Me–S distance of 2.33 Å is almost the same for the two structures. The sulfide layers differ substantially in thickness: 3.14 Å for valleriite, 2.76 Å for tochilinite. The hexagonal close-packed layers of S atoms in valleriite cannot come so close together as those in tochilinite because the S atoms within a plane in the latter are further apart. There is also a difference between the distances separating adjacent planes of S atoms and hydroxyl groups: 3.11 Å for valleriite but 2.92 Å for tochilinite.

The brucite layer in tochilinite is also distorted. The mean Mg–OH distance taken over all octahedra is 2.09 Å, ranging from 2.05 Å for Mg$_1$ to 2.11 Å for Mg$_3$. The OH–OH distances at the top and bottom ends of the octahedra range from 2.79 to 3.40 Å with a mean of 3.13 Å, while the side edges common to two octahedra are 2.51-2.89 Å (mean 2.76 Å). The top and bottom faces of the octahedra are 2.10 Å apart. The mean Mg-O distance is [6] 2.10 Å, while Fe^{2+}–O is 2.12 and Fe^{3+}–O is 2.01. The Mg–OH distances in the various octahedra indicate an ordered distribution of the Fe(III) over the various structural positions

TABLE 2. Atomic Coordinates for Tochilinite

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Fe$_1$	0	0	0	S$_4$	0.737	0.257	0,129
Fe$_2$	0.011$_7$	0.165$_6$	0	S$_5$	0.241	0.420	0.129
Fe$_3$	0.480$_1$	0.164$_7$	0	S$_6$	0.760	0.412	−0.129
Fe$_4$	0.486$_4$	0	0	OH$_1$	0.027	0	0.598
Fe$_5$	0.511$_7$	0.334$_4$	0	OH$_2$	0.008	0.208	0.598
Fe$_6$	0.980$_1$	0.335$_3$	0	OH$_3$	0.362	0	0.402
Mg$_1$	0.170$_1$	0.100$_1$	0.5	OH$_4$	0.299	0.196	0.402
Mg$_2$	0.661$_7$	0	0.5	OH$_5$	0.466	0.095	0.598
Mg$_3$	0.658	0.198$_5$	0.5	OH$_6$	0.838	0.102	0.402
Mg$_4$	0.670$_1$	0.399$_9$	0.5	OH$_7$.	0.508	0.292	0.598
Mg$_5$	0.158	0.301$_5$	0.5	OH$_8$	0.996	0.405	0.598
S$_1$	0.260	0.088	0.129	OH$_9$	0.799	0.304	0.402
S$_2$	0.741	0.080	−0.129	OH$_{10}$	0.338	0.398	0.402
S$_3$	0.237	0.243	−0.129				

TABLE 3. Interatomic Distances (Å) in the Sulfide Part of the Tochilinite Structure

Fe$_1$ tetrahedron

Fe$_1$ — S$_1$	2.33	S$_1$ — S$_2'$	3.83
Fe$_1$ — S$_2$	2.25	S$_2$ — S$_1'$	3.83
Fe$_1$ — S$_1'$	2.47	S$_1$ — S$_2$	3.76
Fe$_1$ — S$_2'$	2.40	S$_1'$ — S$_2'$	4.09
Mean	2.36	S$_1$ — S$_1'$	3.70
		S$_2$ — S$_2'$	3.73
		Mean	3.84

Fe$_2$ tetrahedron

Fe$_2$ — S$_1$	2.20	S$_2$ — S$_3$	3.69
Fe$_2$ — S$_3$	2.26	S$_1$ — S$_4$	3.86
Fe$_2$ — S$_2$	2.34	S$_1$ — S$_2$	3.76
Fe$_2$ — S$_4$	2.54	S$_3$ — S$_4$	4.02
Mean	2.33	S$_1$ — S$_3$	3.67
		S$_2$ — S$_4$	3.92
		Mean	3.82

Fe$_3$ tetrahedron

Fe$_3$ — S$_1$	2.24	S$_1$ — S$_4$	3.68
Fe$_3$ — S$_2$	2.44	S$_2$ — S$_3$	3.72
Fe$_3$ — S$_3$	2.21	S$_3$ — S$_4$	3.69
Fe$_3$ — S$_4$	2.36	S$_1$ — S$_2$	3.94
Mean	2.31	S$_1$ — S$_3$	3.67
		S$_2$ — S$_4$	3.92
		Mean	3.77

Fe$_4$ tetrahedron

Fe$_4$ — S$_1$	2.36	S$_1'$ — S$_2$ S$_2'$ — S$_1$	3.68$_5$
Fe$_4$ — S$_2$	2.38		
Fe$_4$ — S$_1'$	2.24	S$_1$ — S$_2$	3.94
Fe$_4$ — S$_2'$	2.24	S$_1'$ — S$_2'$	3.62
Mean	2.30$_5$	S$_1$ — S$_1'$	3.70
		S$_2$ — S$_2'$	3.73
		Mean	3.76

Fe$_5$ tetrahedron

Fe$_5$ — S$_3$	2.40	S$_3$ — S$_6$	3.86
Fe$_5$ — S$_4$	2.13	S$_4$ — S$_5$	3.67
Fe$_5$ — S$_6$	2.32	S$_4$ — S$_3$	3.69
Fe$_5$ — S$_5$	2.47	S$_5$ — S$_6$	4.09
Mean	2.34	S$_3$ — S$_5$	3.91
		S$_4$ — S$_6$	3.69
		Mean	3.82

Fe$_6$ tetrahedron

Fe$_6$ — S$_4$	2.33	S$_4$ — S$_5$	3.72
Fe$_6$ — S$_3$	2.47	S$_3$ — S$_6$	3.68
Fe$_6$ — S$_6$	2.31	S$_4$ — S$_3$	4.02
Fe$_6$ — S$_5$	2.14	S$_6$ — S$_5$	3.62
Mean	2.31	S$_3$ — S$_5$	3.91
		S$_4$ — S$_6$	3.69
		Mean	3.77

TABLE 4. Interatomic Distances (Å) in the Brucite Part of the Tochilinite Structure

		Mg_1 octahedron			
$Mg_1 - OH_3$	2.10	$OH_3 - OH_4$	3.09	$OH_3 - OH_5$	2.67
$Mg_1 - OH_4$	1.92	$OH_3 - OH_6$	3.23	$OH_5 - OH_4$	2.83
$Mg_1 - OH_6$	2.15	$OH_4 - OH_6$	2.88	$OH_4 - OH_2$	2.51
$Mg_1 - OH_1$	2.00	$OH_1 - OH_2$	3.26	$OH_2 - OH_6$	2.88
$Mg_1 - OH_2$	2.13	$OH_1 - OH_5$	2.79	$OH_6 - OH_1$	2.89
$Mg_1 - OH_5$	1.98	$OH_5 - OH_2$	3.03	$OH_1 - OH_3$	2.64
Mean	2.05		Mean	2.89	
		Mg_2 octahedron			
$Mg_2 - OH_3$	2.00	$OH_6 - OH_6'$	3.19	$OH_6 - OH_1$	2.89
$Mg_2 - OH_6$	2.07	$OH_6 - OH_3$	3.01	$OH_5 - OH_6$	2.77
$Mg_2 - OH_5$	2.06	$OH_5 - OH_5'$	2.97	$OH_3 - OH_5$	2.67
$Mg_2 - OH_1$	2.30	$OH_5 - OH_1$	3.36		
Mean	2.09		Mean	2.96	
		Mg_3 octahedron			
$Mg_3 - OH_6$	2.03	$OH_6 - OH_8$	3.17	$OH_6 - OH_2$	2.88
$Mg_3 - OH_8$	2.06	$OH_6 - OH_4$	3.25	$OH_4 - OH_7$	2.88_5
$Mg_3 - OH_4$	2.27	$OH_4 - OH_8$	3.17	$OH_2 - OH_8$	2.88_5
$Mg_3 - OH_2$	2.23	$OH_5 - OH_7$	3.09	$OH_7 - OH_8$	2.51
$Mg_3 - OH_5$	2.14	$OH_5 - OH_2$	3.40	$OH_5 - OH_4$	2.83
$Mg_3 - OH_7$	1.93	$OH_2 - OH_7$	2.99	$OH_5 - OH_6$	2.77
Mean	2.11		Mean	2.99	

in the brucite layer (ferric iron enters this layer to balance the negative charge of the vacant sulfide layer; see [1] for details of this in relation to the theoretical formula of tochilinite). The Fe(III) lies mainly in Mg_1 positions. A brucite layer in valleriite contains Al as well as Mg (we have in mind the particular specimen whose structure has been determined), with unshared edges 3.07 Å long and shared ones 2.69 Å.

The sulfide and brucite layers are disposed as follows in tochilinite. Figure 9 shows a somewhat idealized projection along the b axis. The observed β provides identical mutual disposition for adjacent layers of the different types of anion, and it would seem that this feature determines the mutual displacement of the layers along the *a* axis.

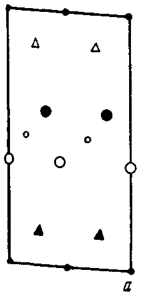

Fig. 9. Projection of the tochilinite structure along the b axis. The filled small circles are Fe, and the open small ones are Mg, while the large ones (filled and unfilled) are OH and the triangles are S.

The structure analysis [1] implies $6(Fe_{0.94})S \cdot 5[(Mg, Fe)(OH_2)]$ as the ideal formula of tochilinite. The results agreed with those from chemical analysis only after correction for the $Al(OH)_3$ (gibbsite) impurity revealed by selected area diffraction. The analysis gave $6(Fe_{0.9}S) \cdot 5[(Mg_{0.71}Fe_{0.29})(OH_2)]$, which is close to the theoretical composition.

We are indebted to A. D. Genkin for providing the specimen and to I. D. Borneman-Starynkevich for assistance in interpreting the chemical analysis.

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