Clays and Clay Minerals, 1973, Vol. 21, pp. 103–114. Pergamon Press. Printed in Great Britain

THE CRYSTAL STRUCTURE OF TALC

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(*Received* 28 *August* 1972)

Abstract—The crystal structure of a sample of talc from Harford County, Maryland, has been determined by least squares refinement from X-ray diffraction photographs. A triclinic cell with $a = 5{\cdot}293$, $b = 9{\cdot}179$, $c = 9{\cdot}496$ Å, $\alpha = 90{\cdot}57°$, $\beta = 98{\cdot}91°$, $\gamma = 90{\cdot}03$, space group $C\bar{1}$ is adopted. The layers of the structure have almost monoclinic symmetry but the nearly hexagonal rings of oxygen atoms on the surfaces of the layers, formed by the bases of the silica tetrahedra, are not held in register by interlayer ions as they are in micas but are partly displaced so that the stack of layers forms a triclinic crystal. The hexagons of surface oxygens are distorted by a 3·4° twist of the tetrahedra so that the b axis is 0·2 per cent shorter than in a structure with regular hexagons, and the twist brings the oxygen ions a little closer to the octahedral magnesium ions.

INTRODUCTION

THE CLAY fraction of soils commonly contains layer silicates, some of which have close counterparts in the well crystallised minerals in rocks and some of which have formed by alteration of minerals with an existing layer silicate structure. As part of our study of these minerals we have re-examined the structure of talc.

The structures of the layer silicates were outlined by Pauling (1930) and established by Gruner (1934) and Hendricks (1938), but more recent work (reviewed by Brown (1965) and by Bailey (1966)) showed that the structures are less regular and have additional general features. The tetrahedra of oxygen atoms are twisted from the ideal positions to allow a better fit between the tetrahedral and octahedral layers, and flattening of the oxygen octahedra parallel to the sheet allows a greater separation of the octahedral cations. Talc is the simplest of the layer silicate structures and should show these features without the complication of interlayer cations.

Hendricks took single crystal Weissenberg photographs of talc and pyrophyllite, but did not complete a structure determination for either. We have repeated his examination and published preliminary reports (Rayner and Brown, 1964, 1966). Like Hendricks', our structure of pyrophyllite is incomplete, as the photographs are strongly streaked because of disorder in the structure, but it was possible to refine a sub-cell of the structure. For talc, Hendricks proposed a monoclinic unit cell and space group $C2/c$ or Cc. We found a triclinic cell close to monoclinic in shape, but the intensities of the reflections quite clearly do not have monoclinic symmetry. When the photographs published by Hendricks (1940) were re-examined, one of them (Figs. 3a and d) was found to have the lower symmetry expected for a triclinic cell. It is possible that, because of twinning, parts of his sample appeared to be more symmetrical. Some of our photographs show evidence of a small twinned component. Ross, Smith and Ashton (1968) examined 14 talc crystals, 13 from Gouverneur, New York, and found them all triclinic.

OCCURRENCE AND CRYSTAL DESCRIPTION

Talc, ideally $Mg_3Si_4O_{10}(OH)_2$, is a hydrated magnesium silicate found as a soft crystalline, foliated or compact mineral of white, grey or pale green color and soapy feel. Its formation by hydrothermal alteration of basic rocks of thermal metamorphism of siliceous dolomites is summarised by Deer, Howie and Zussman (1962, p. 126). The specimen used for this analysis was a clear colorless cleavage flake from the same sample from Harford County, Maryland (U.S.N.M. No. 82519) used by Hendricks (1938) and kindly provided by him.

Optical description; colorless (slightly greenish-grey reflection from bent and split parts, brown stain near edge) optically negative with $2V_X$ ranging from 3–8° but commonly 6–7°, Dispersion of optic axes $r > v$. $X = 1{\cdot}538 \pm 0{\cdot}002$, Y and $Z = 1{\cdot}588 \pm 0{\cdot}002$.

The chemical composition is similar to the published composition of two other talcs of small aluminum content (Table 1), but other analysed samples contain more Al, up to 2–4% Al_2O_3 (Deer, Howie and Zussman, 1962). The composition is close to the ideal $Si_8Mg_6O_{20}(OH)_4$ but with nearly 2% of Mg replaced by Fe. The fluorine content, 0·06% is towards the lower end of the range found by Ross, Smith and Ashton (1968).

The loss in weight from 110 to about 950°C (Meker burner) agress well with the formula, but a

Table 1. Chemical composition of talc

	1			2		3		
Proportion	(%)	on basis of 22 O^{2-}		(%)	Proportion on basis Si + Mg = 14	(%)	Proportion on basis of 22O^{2-}	
SiO_2	63·22	8·043		62·68	7·916	62·61	7·99	8
Al_2O_3	not detected	0		0·06*	0·01	trace		
MgO	30·45	5·767	5·892	32·33	6·084	30·22	5·743	6·0
MnO	not detected	0		0·04*	0·004	0·01	0·007	
FeO	0·89	0·094		0·04*	0·004	2·46	0·261	
Fe_2O_3	0·33	0·031						
Na_2O	0·02	0·004		0·01*	0·003			
K_2O	0·05	0·008		0·001*	0·0002			
H_2O-	0·20	0·044		0·33	0·014			
Loss 110°–1000°C	4·78	4·052		5·27 (includes F)	4·035 + F	4·72	4·018	
F	0·06 ± 0·01	0·024		0·48	0·192			
Total (excluding H_2O^-)	99·80			100·76		100·02		
Correction for Fluoride replacing oxide	0·03			0·20				
	99·77			100·56				

1 Talc used in this structure determination. Harford County single crystal, analyst G. Pruden. CaO, Al_2O_3, P_2O_5, TiO_2 not detected. Another sample heated from room temperature to 1150°C Wt loss 5·9 ± 0·1 per cent, gain by anhydrous $Mg(ClO_4)_2$ 6·6 ± 0·2 per cent, analyst A. C. D. Newman.

2 Another talc known to be triclinic. Gouverneur talc district New York. (Ross, Smith and Ashton, 1968). *Spectrographic determination.

3 Talc low in Al_2O_3 reported by Deer, Howie and Zussman (1962), altered peridotite, Muruhatten, N. Sweden (Du Reitz, 1935).

separate experiment indicates that there is a further loss in weight and release of water on heating to 1150°C. This high temperature weight loss is also suggested by measurements for talc by Aleixandre and Alvarez Estrada (1952) reported by Mackenzie (1957). Deer, Howie and Zussman suggest that fine grained talcs may retain sorbed water above 110°C, but the appearance of the flakes as clear and apparently single crystals argues against a similar explanation for the behavior of our specimens. El-Attar, Jackson and Volk (1972) find that fluorine is lost completely from hectorite at 950°C in 6 hr, mainly as SiF_4, but if all F in talc is lost in this way it would not explain the whole of the weight loss to 1150°C.

Seeking evidence of sorbed water, infra-red absorption spectra with rather low dispersion in the 3000–4000 cm^{-1} region of two of the flakes of talc were taken on an Infracord spectrometer. There was only weak absorption and no clear peak at about 3450 cm^{-1} where an OH stretching vibration occurs in expanded layer silicates; this is attributed to interlayer water (Kodama and Oinuma, 1963). Sclar, Carrison and Schwartz (1965) find a peak of medium height at 3260 cm^{-1} in a Mg deficient talc with oxonium ions between the layers, and Farmer (1958) reports a broad weak band at 3413 cm^{-1} due to sorbed water in an oriented deposit of ground talc; these were not detected in the single crystal spectrum. The spectrum does show the expected peak, at about 3680 cm^{-1}, that in talcs is attributed to a structural OH surrounded by three Mg atoms (Farmer and Russell, 1964; Wilkins, 1967; Wilkins and Ito, 1967). However, at this resolution we did not detect the peak expected at about 3660 cm^{-1} for an OH surrounded by 2Mg + 1Fe. From the Fe content of the sample, this peak should have 1/15 the intensity of the 3680 cm^{-1} peak. When the talc flake was perpendicular to the infrared beam the 3680 cm^{-1} peak was six times weaker than when it was inclined at 30 or 60°. This change would be expected if most of the absorption due to stretching of OH bands in the structure occurred for vibrations perpendicular to the layers and would occur only if most of the OH bonds were oriented in this direction.

X-RAY MEASUREMENTS

The triclinic symmetry was established by X-ray single crystal oscillation and rotation photographs about all three 5·3 Å and all three 9·3 Å axes that lie in the plane of the sheets. None of these was a symmetry axis nor were they perpendicular to a symmetry axis. The rotation photographs for the three 5·3 Å axes were similar, but distinct, as are those for the three 9·3 Å axes, so the axes of a new crystal from the sample can be quickly identified.

The conventional choice of axes for a triclinic crystal are the edges of a primitive cell, but the talc structure can be compared more easily with other layer silicates if a *C* face-centered cell is chosen. Table 2 and Figure 1 show four possible choices of cell. The *C* cell is used in this paper. The axes of the *C* face-centered cell are related to the optical measurements so that approximately *a* is parallel to O.A.P. i.e. $a \approx Y, b \approx Z, c \approx X$.

Weissenberg photographs were taken for the

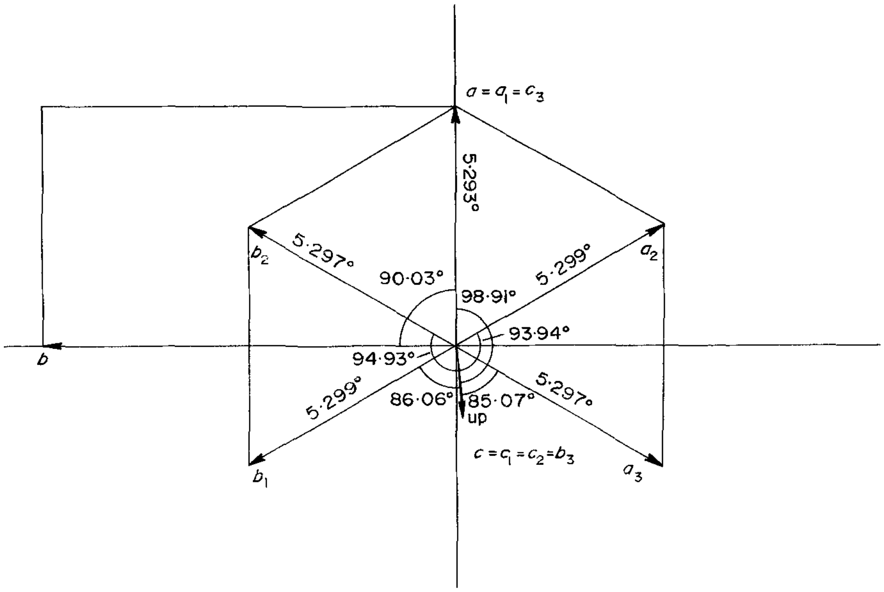

Fig. 1. Unit cells for talc. Axes without subscripts are for the *C* cell. Subscripts are for the three *P* cells (see Table 2).

Table 2. Unit cell and reciprocal cell dimensions for talc

	P_1	P_2	P_3	C
a	5·293(2) Å	5·299(2)	5·297(2)	5·293(2)
b	5·299(2)	5·297(2)	9·469(3)	9·179(3)
c	9·469(3)	9·469(3)	5·293(2)	9·469(3)
α	86·06(3)°	94·93(3)°	98·91(3)°	90·57(3)°
β	98·91(3)°	93·94(3)°	119·95(3)°	98·91(3)°
γ	119·99(3)°	120·06(3)°	85·07(3)°	90·03(3)°
a^*	0·2203(1) Å^{-1}	0·2199	0·2179	0·1912
b^*	0·2179(1)	0·2203	0·1069	0·1089
c^*	0·1069(0)	0·1069	0·2199	0·1069
α^*	89·42°	81·98°	82·55°	89·42°
β^*	81·98°	82·55°	60·42°	81·09°
γ^*	60·24°	59·34°	90·58°	89·88°

P_1 used in Rayner and Brown (1966)

P_2 Delaunay reduced cell; α, β and γ non-acute (Henry and Lonsdale, 1952).

P_3 Bravais reduced cell; $c < a < b$, α and β non-acute (Donnay, Donnay, Cox, Kennard and King, 1963; Kennard, Speakman and Donnay, 1967).

C *C* face-centred cell most nearly monoclinic in shape.

zero to fourth layers about the *b* axis and the zero, first and second layers about the *a* axis. The reflections were slightly split into up to four components, and over an angular range of up to 4° in the worst cases. Two batches of 3 films were exposed for each layer, and the intensities brought to a common scale by comparison of reflections common to several films, intensities were estimated visually with the aid of a calibrated scale using timed exposures of a single crystal reflection. Two crystals of about 0·2 mm × 0·2 mm × 0·03 mm were used for the two axes, and the intensities were corrected for Lorentz-polarisation by a program written in Extended Mercury Autocode. An attempt to put the structure factors for the two crystals on a common scale left systematic differences in the structure factors, and so at first the two sets were used separately in the structure determination and combined into a single set when these two sets had been shown to lead to consistent models for the structure.

TRIAL STRUCTURE

The layer spacing in the c^* direction is 9·4 Å, so the cell contains one 2 : 1 silicate layer. The layer is trioctahedral and the *b* axis length, 9·17 Å, suggests that the twist of the tetrahedra will be small (Radoslovich, 1962). An ideal layer with no twist can be fitted into the cell in six ways. A single layer has a perpendicular plane of symmetry that defines a unique direction in the plane of the layer (Brindley, Oughton and Robinson, 1950) and the orientation of the layer is completely defined if it is represented by a vector between any two atoms in this plane of symmetry. In Fig. 2 such a vector between the OH atom in the bottom half of the layer and the nearest OH atom in the top half is represented in stereographic projection for each of six distinct possible positions of the vector with respect to the crystal axes.

When the corresponding six possible structures are projected down the *a* axis, there are three different arrangements of the projected atoms, each representing two different three dimensional structures.

The one hundred 0kl structure factors corresponding to the *a* axis projections of these models were calculated from atomic coordinates estimated, in part using the methods of Donnay, Donnay and Takeda (1964), from an Mg–O distance of 2·10 Å, an unshared octahedral edge of $b/3$, and a Si–O bond length of 1·62 Å. The layer in these models has a center of symmetry at one of the Mg atoms and the trial structures all belong to the space group $C\bar{1}$. The *R* factors for comparison of these calculated 0kl structure factors with those observed are 38, 20 and 40 per cent suggesting that the second projected arrangement and hence one of the two corresponding three dimensional arrangements (2 or 2′ in Fig. 2) is correct. Structure factors for the 0kl, 1kl and 2kl reflections calculated for the arrangements represented by 2 and 2′ gave *R* factors of 22 and 59 per cent respectively. The *R* factors for structure 2 for each of the layer lines separately were 23, 19 and 23 per cent and so this structure was accepted for refinement.

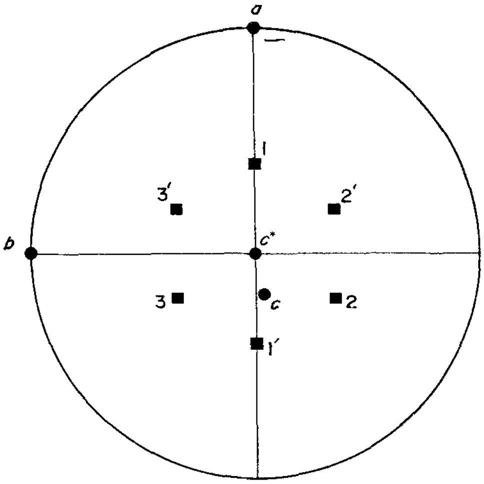

Fig. 2. The relationship of the six trial structures of talc to the crystal axes. The cell axes (●) and the six possible orientations of the layer represented by the shortest vector from lower to upper OH groups (■).

STRUCTURE REFINEMENT

The *a*-axis data were refined by least squares (using a program written in Extended Mercury Autocode for the Orion computer) to give the first of the three sets of coordinates in Table 3. The *R* factor for 384 *a*-axis non-zero reflections is 14·8 per cent for atoms with an isotropic temperature factor, and 14·2 per cent when all atoms are allowed to have anisotropic temperature factors. The *b* axis reflections give to the second set of coordinates in Table 3, with *R* factors of 17·3 per cent for isotropic and 15·7 per cent for anisotropic atoms. Different scale factors were refined for each of the *b* axis layer lines. The *R* factors were larger than expected for a structure of this size, and some of the error was due to the difficulty in making an estimate of the total intensity of a reflection when it was spread out and split into several parts. The splitting varied in a systematic way over the X-ray photographs as the angle between the beam and the flake varied. In an attempt to overcome this difficulty the *b* axis photographs were divided into seven regions, and separate scaling factors calculated. These factors showed that the estimated intensity did vary

Table 3. Atomic coordinates calculated by least squares from three sets of intensities

Atom	Data set	x	y	z	B (isotropic)
Si(1)	a	0·7476	0·0022	0·2922	0·99
	b	0·7473	0·0026	0·2908	2·34
	$a+b$	0·7472(6)	0·0027(4)	0·2910(3)	1·43(5)
Si(2)	a	0·7481	0·3368	0·2920	0·99
	b	0·7485	0·3342	0·2924	1·28
	$a+b$	0·7482(6)	0·3366(4)	0·2920(3)	1·46(8)
Mg(1)	a	0	0	0	0·96
	b				1·30
	$a+b$				1·33(8)
Mg(2)	a	0·0004	0·3326	0·0002	1·04
	b	0·0008	0·3324	0·0005	1·39
	$a+b$	0·0001(7)	0·3330(4)	0·0001(4)	1·38(7)
O(H)	a	0·215	0·168	0·114	1·44
	b	0·198	0·163	0·114	1·72
	$a+b$	0·1980(17)	0·1677(10)	0·1132(9)	1·50(12)
O(1)	a	0·711	0·001	0·119	1·53
	b	0·703	0·001	0·119	1·45
	$a+b$	0·7022(15)	0·0015(9)	0·1183(8)	1·50(12)
O(2)	a	0·716	0·337	0·122	1·57
	b	0·703	0·333	0·122	1·80
	$a+b$	0·7030(16)	0·3363(10)	0·1204(9)	1·80(13)
O(3)	a	0·738	0·170	0·344	1·40
	b	0·746	0·166	0·348	1·81
	$a+b$	0·7439(16)	0·1693(10)	0·3472(9)	2·07(14)
O(4)	a	0·520	0·428	0·345	1·59
	b	0·521	0·423	0·349	1·72
	$a+b$	0·5216(16)	0·4283(10)	0·3475(9)	2·13
O(5)	a	0·031	0·412	0·350	1·37
	b	0·019	0·419	0·350	2·11
	$a+b$	0·0202(16)	0·4122(10)	0·3487(9)	2·01(15)

*Set a: Intensities for crystal 1 rotated about a axis: Set b: Intensities for crystal 2 rotated about b axis: Set $a+b$: Scaled intensities from sets a and b.

significantly with the splitting of the spots, but the R factor was worse when the scaling factors were used to correct the intensity estimates, probably because the small number of regions gave too coarse a correction scale.

An improvement in the agreement between observed and calculated structure factors was obtained by scaling together the a and b axis intensity measurements after least squares refinements. The combined set of 669 structure factors gave $R = 14{\cdot}9$ per cent for isotropic and 13·5 per cent for anisotropic vibration of the atoms, and the derived coordinates form the third set in Table 3. In a further refinement a position $x = 0{\cdot}23 \pm 0{\cdot}04$, $y = 0{\cdot}20 \pm 0{\cdot}02$, $z = 0{\cdot}24 \pm 0{\cdot}02$ was found for hydrogen with a temperature factor $B = 3 \pm 5$. Including hydrogen did not significantly alter the parameters of the other atoms.

Layer symmetry

The layer fits into the cell so that the mirror plane in an ideal layer lies along the diagonal of the cell from 0, 0, 0 to 1, 1, 0 and perpendicular to the C face. This is the M arrangement of Brindley, Oughton and Robinson (1950). Other choices of the talc unit cell could give L or N arrangements, but would not be close to monoclinic in shape as this cell is. The center of symmetry implied by the $2/m$ symmetry of the ideal layer is retained in the $C\bar{1}$ symmetry of talc structure. The addition of a mirror plane to the center of symmetry generates a two fold axis, and vice versa and the small distortions from $2/m$ symmetry are conveniently measured as distances from the plane. The pseudo symmetry plane passes exactly through the Mg(1) atoms at the centers of symmetry and O(4) and OH are not significantly displaced (by $0{\cdot}004 \pm 0{\cdot}008$ and $0{\cdot}006 \pm 0{\cdot}008$ Å) from their images in the plane. Other atoms are significantly, but very little, displaced. The largest displacement is of O(2) from the mirror image of O(1) by $0{\cdot}025 \pm 0{\cdot}011$ Å; the most significant displacement is of Mg(2) from the image of the centrosymmetrically related Mg(2) atom, by $0{\cdot}018 \pm 0{\cdot}004$ Å.

INTERLAYER CONTACTS AND STACKING

The tetrahedral twist is only 3·4°, so that when the surface oxygen sheet is represented by lines between the centers of the oxygen atoms, it is only a little distorted from a quasi-regular tesselation of equilateral triangles and regular hexagons (Coxeter, 1948, p. 60). In micas, the distorted hexagons of adjacent layers lie over one another and form trigonally distorted hexagonal prisms round the interlayer cations. In paragonite, the sodium atom is small enough for the oxygen atoms of the two hexagons to be in van der Waals contact with one another (two O–O distances of 3·09 and four of 3·24 Å, Burnham, 1963). In talc, the adjacent layer surfaces are displaced so that the oxygen atoms can pack together and allow the layers to come closer together. Fig. 3 shows that there is a sequence of contacts O(3)–O(4)–O(4)–O(3)–O(3) zig-zagging between the sheets. The shortest distances are 3·093 Å between the O(3) and O(4) atoms if this contact distance were maintained, and if the hexagons were superposed without lateral displacement, as in mica, the layers would be 0·27 Å further apart.

The layers could be packed 0·1 Å closer together without any closer contact between oxygen atoms if O(3) were moved, as shown by the arrow in Fig. 3, to the center of the triangle formed by O(3), O(4) and O(5) in the adjacent layer. That this arrangement with closest approach to the layers is not found may be due to interaction of second nearest neighbors. In the structure we found the free space between the layers is concentrated around the centers of symmetry at $\frac{1}{4}, \frac{1}{4}, \frac{1}{2}$ and $\frac{3}{4}, \frac{3}{4}\ \frac{1}{2}$. However, the van der Waals contact radius is only about 0·8 Å so the space is unlikely to contain either the water or the small amounts of Na and K found in some analyses.

The contact distances between oxygen atoms of opposing layer surfaces are not all equal, but the packing of the layers causes little or no distortion of the surface, and the z coordinates of the surface oxygen atoms are not significantly different. The contact surfaces of the layers interpenetrate and so the layers cannot slide over one another without separation. Amelinckx and Delavignette (1961) showed by electron microscopy that talc sheets slide over one another by the movement of ribbons of dislocations in which three different slightly less stable arrangements of the contact surfaces are adopted locally, leaving most of the surface in a single relative position of close contact. The structure found here is similar to the stacking that, on the basis of a layer structure with untwisted tetrahedra, they thought most likely. The twist of the tetrahedra alters the arrangement of surface oxygen atoms from the regular hexagonal arrangement, but the positions of close approach at the ends of the partial Burgers' vectors are little altered by the tetrahedral twist.

In talc, if the hydroxyl oxygen lying below the center of the hexagon of oxygen atoms in each half layer is taken as a reference point, its displacement in the plane of the layers can be divided into two parts. Within the layer, the displacement from lower to upper half layer is nearly $(-1/6\,a - 1/6b)$, equivalent to about 1/3 of an a length axis, (the axis called a_3 by Brindley, Oughton and Robinson (1950)). Between layers, the displacement is rather less than this, $-0{\cdot}11a + 0{\cdot}16b$, so that the overall shift for one unit cell lies nearly along $-a$ and is about 1/4 a combined with a small displacement along $-b$.

This layer stacking in talc is one of the three possible stacking patterns found by a sub-cell refinement of the pyrophyllite structure (Rayner and Brown, 1965). Brindley and Wardle (1970) found triclinic samples of pyrophyllite with $a = 5{\cdot}173$, $b = 8{\cdot}960$, $c = 9{\cdot}360$Å, $\alpha = 91{\cdot}2°$, $\beta = 100{\cdot}4°$, $\gamma = 90{\cdot}0°$ similar to the C cell chosen for talc. The displacement between adjacent layers of this pyrophyllite is $-0{\cdot}3a - 0{\cdot}02b$ suggesting a similar stacking to that found for talc and this is confirmed by a structure refinement of the powder diffraction intensities (Wardle and Brindley, 1972).

BOND LENGTHS AND ANGLES

The standard deviations of the coordinates (Table 3) and bond lengths (Table 4) are obtained by least squares refinement and probably underestimate the errors, particularly when bond lengths are compared with those in different substances (Hamilton and Abrahams, 1970). Table 4 gives mean bond lengths and angles between chemically similar sets of atoms. The standard deviation of the means are calculated as though the bond lengths were independent, but in some cases this will

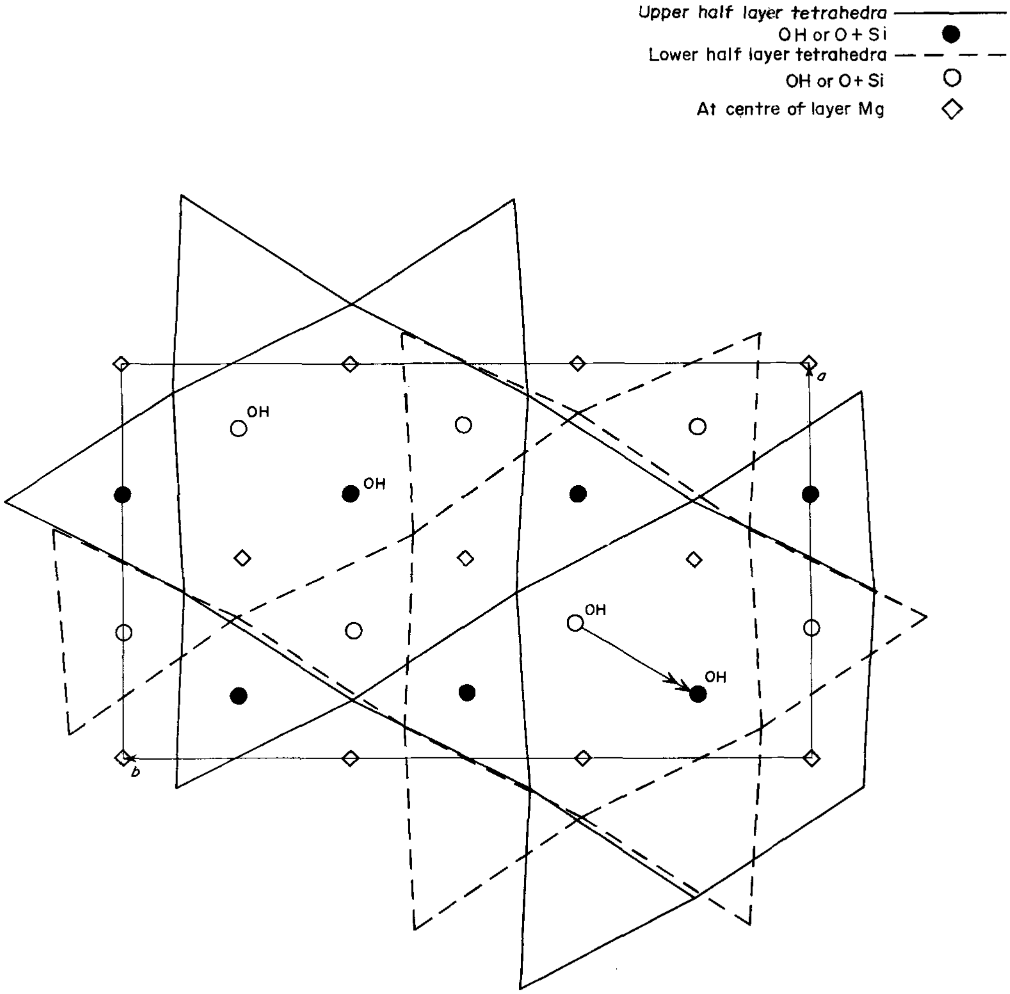

Fig. 3. Projection of a single layer of the talc structure perpendicular to the layer. The bases of the tetrahedra are outlined with continuous lines at the top of the layer ($z = 0{\cdot}35$) and with pecked lines at the bottom ($z = -0{\cdot}35$). Octahedral O and OH are shown as ● at $z = 0{\cdot}12$ and at ○ at $z = -0{\cdot}12$ and magnesium at the centre ($z = 0$) as △. The double headed arrow is the shortest OH–OH distance and this vector is used to show the orientation of the layers in Fig. 2.

overestimate the error in the mean bond lengths. For example, the means of angles for the tetrahedrally coordinated atoms are very close to the ideal tetrahedral angle 109·47° but this correspondence is a result of the tetrahedral geometry. If a regular tetrahedral arrangement is distorted, changing one of the angles by 1°, the mean angle alters by less than 0·01°*.

The two independent silicon–oxygen tetrahedra in the talc structure are regular and equal in size with Si–O bonds all 1·622 ± 0·003 Å. The standard deviations of the angles in the two tetrahedra calculated from the measured values are 0·48° and 0·54°, compared with a standard deviation of each measurement of 0·46° as estimated from the least squares calculation, and so there is no evidence of a significant distortion of the angles. Similarly the individual bond lengths within each tetrahedron show no significant difference from the mean, and the means for the two tetrahedra are not significantly different. No aluminum was detected in this sample. The tetrahedra thus probably contain silicon only, and the Si–O bond length 1·622 ± 0·003,

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*This situation can be used to detect errors; Takeuchi and Sadanaga (1965) find the mean tetrahedral angle in xanthophyllite to be 109·1°, but when the angles to O(3) are recalculated from the coordinates, the mean is 109·46°.

Table 4. Bond lengths (Å) and angles*

Tetrahedra

Surroundings of Si 1		of Si 2	
Si 1–O1 (apex)	1·625(7)	Si 2–O2 (apex)	1·617(9)
O3	1·621(8)	O3	1·627(8)
O4	1·624(8)	O4	1·618(9)
O5	1·625(9)	O5	1·615(8)
mean	1·624(4)	mean	1·619(4)

Si–O 1·621(3)

Angles			
O1–Si 1–O3	109·30°	O2–Si 2–O3	109·19°
O4	108·73°	O4	109·02°
O5	109·95°	O5	108·79°
mean O apex–Si 1–O	109·32°	mean O apex–Si 2–O	109·00°
O3–Si 1–O4	109·81°	O3–Si 2–O4	109·84°
O5	109·06°	O5	110·39°
O4–Si 1–O5	109·99°	O4–Si 2–O5	109·59°
mean O–Si 1–O non apex	109·62°	mean O–Si 2–O non apex	109·94°

mean O apex–Si–O 109·16°, O–Si–O non apex 109·78°
(mean O–Si–O 109·47°, see text)

Octahedra

Surroundings of Mg 1		of Mg 2	
Mg 1–OH (× 2)	2·054(8)	Mg 2–OH	2·058(9)
O1 (× 2)	2·065(8)	OH	2·060(8)
O2 (× 2)	2·087(8)	O1	2·084(8)
		O1	2·088(8)
mean Mg 1–(O, OH)	2·069(4)	O2	2·072(9)
		O2	2·096(8)
		mean Mg 2–(O, OH)	2·076(4)

mean Mg–OH 2·057(5), Mg–O 2·082(4)
mean Mg–(O, OH) 2·072(4)

Angles and Edges: Shared					
OH–Mg 1–O1	2·777(11)	84·77°	OH–Mg 2–OH	2·758(11)	84·08°
O2	2·805(10)	85·28°	O1	2·777(11)	84·10°
O1–Mg 1–O2	2·813(11)	85·28°	O2	2·805(10)	84·89°
			O1–Mg 2–O2	2·813(11)	85·18°
	2·789(6)	85·11°	O1	2·828(9)	85·36°
			O2–Mg 2–O2	2·842(12)	86·00°
				2·804(4)	84·94°

mean OH–Mg–OH 2·758(11), 84·08°, OH–Mg–O 2·791(8) 85·02°
O–Mg–O 2·828(6), 85·46°

mean shared 2·801(4), 85·02°

Unshared					
OH–Mg 1–O1	3·043(11)	95·23°	OH–Mg 2–O1	3·065(11)	95·45°
O2	3·046(12)	94·72°	O1	3·067(11)	95·34°
O1–Mg 1–O2	3·054(10)	94·72°	O2	3·054(10)	95·31°
			O2	3·075(11)	95·50°
	3·048(6)	94·89°	O1–Mg 2–O2	3·052(10)	94·40°
			O2	3·067(11)	94·41°
				3·063(4)	95·07°

mean unshared 3·055(3), 94·98°
Ratio mean shared/mean unshared = 0·917(1)

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*Calculated from final least squares co-ordinates for combined *a* and *b* axes data.

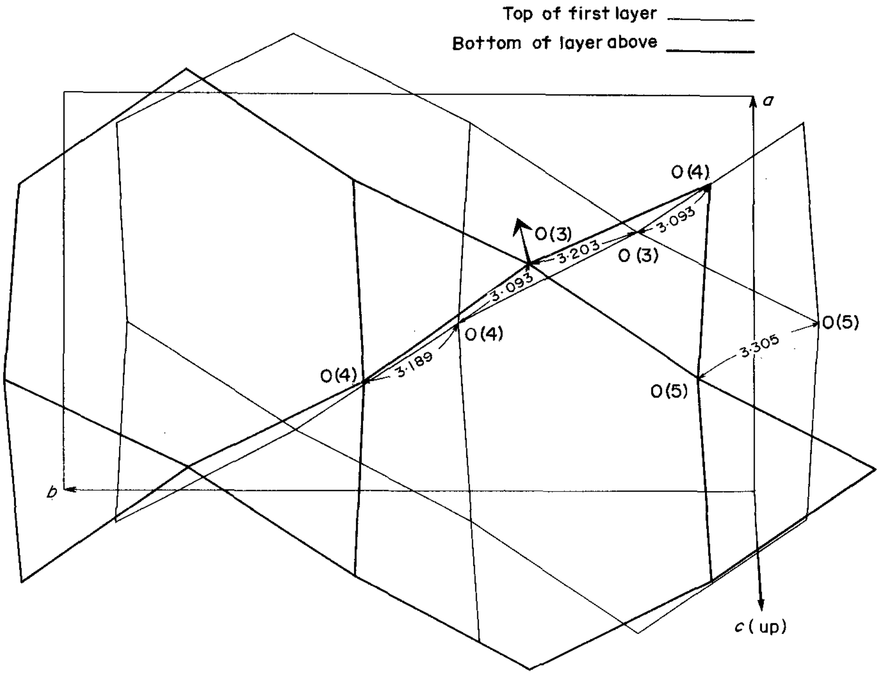

Fig. 4. Projection of parts of two talc layers in contact. The bases of the tetrahedra on the upper surface of the lower talc layer are represented by ——— and the lower surface of the upper talc layer by ——— The shorter O–O contact distances between the layers are given in Å. The arrow shows the displacement needed to bring the layers closest together (see text).

agrees well with estimates of 1·616–1·621 for tetrahedra containing only silicon (Smith and Bailey, 1963).

The tetrahedra in many other layer silicates are less regular. In xanthophyllite, for example, both the bond lengths and angles are significantly distorted (recalculated from Takeuchi and Sadanaga, 1965) and there are smaller but significant distortions in phlogopite (Rayner, unpublished). Drits (1969) attributed these distortions to a shortening of the basal edges relative to the lateral edges of the tetrahedra and a movement of the tetrahedral cation towards the base.

There are no significant differences in the bond lengths in the two types of octahedra, through they have different symmetry. Hydroxyl oxygens are at opposite corners of Mg(1) octahedra and at adjacent corners of Mg(2) (Table 4). The average bond length from Mg to all oxygen atoms (including OH) is 2·074 ± 0·004 Å but the bonds to hydroxyl oxygen are significantly shorter than to the oxygens bonded to silicon, 2·057 ± 0·005 Å against 2·082 ± 0·004 Å. This difference was also found in phlogopite (recalculated from Steinfink, 1962), ferriannite (Donnay, Morimoto, Takeda and Donnay, 1964). xanthophyllite and chromium chlorite (Brown and Bailey, 1963, but the distances are equal in vermiculite (Shirozu and Bailey, 1966). In brucite, $Mg(OH)_2$, all the Mg bonds are to hydroxyl and are 2·102 ± 0·003 Å long (Zigan and Rothbauer, 1967). In the brucite-like layer of chromium chlorite, the octahedral site occupied only by magnesium has a mean Mg (O, OH) of 2·068 ± 0·006 Å. This suggests that the influence of other layers in the structure is to compress the brucite layer from the dimensions it has when it crystallizes alone. The talc-like layer of the same chlorite has bonds to magnesium Mg – (O, OH) 2·078 ± 0·006, Mg – OH 2·064 ± 0·010 and Mg O 2·085 ± 0·007, which are indistinguishable from those we find for talc.

The ratio of the shared to unshared edges of octahedra in brucite, is 0·89. In talc this ratio is 0·92 and this larger value is typical of trioctahedral layer silicates (Table 2b of Bailey, 1966). The shared edges are about the same length in the silicates as in brucite, but the unshared edges (talc, 3·06 Å; Cr chlorite, 3·08 Å in the talc-like layer; vermiculite 3·09 Å) are shorter in the silicates than in brucite, for which it is 3·14 Å.

INTERACTION OF THE OCTAHEDRAL AND TETRAHEDRAL LAYERS

The tetrahedral and octahedral layers in a layer silicate must occupy the same area and repeat on the same net in the (001) plane if a regular crystal with flat layers is to be formed. The area occupied by tetrahedral layers depends on the angle of rotation of the tetrahedra. In micas the area can also be altered by shortening the basal O–O distances in the tetrahedra and increasing the O–O distances to the apical oxygen.

From a statistical analysis of the angles of twist in micas, McCauley and Newnham (1971) find that the strongest component in predicting the angle of twist is the ratio of tetrahedral to octahedral bond lengths estimated from the chemical composition and standard cation to oxygen bond lengths. A less important component is the field strength (valency/ionic radius) of the interlayer cation, which they suggest influences the angle by contracting the basal tetrahedral O–O distances. On this model the talc structure would have undistorted tetrahedra (as we have found) because there are no interlayer cations and adjustment of the tetrahedral layer area must be by twist only.

The octahedral layer area can be adjusted by shortening the shared octahedral O–O edges. This distortion from a layer of regular octahedra is found in micas and also in structures where the octahedral oxygen atoms are all attached to hydrogen rather than silicon as in $Mg(OH)_2$ (brucite), $Ca(OH)_2$ and $Al(OH)_3$ (gibbsite). That this arrangement of flattened layers is more stable because like charges within the layers are further apart is suggested by electrostatic energy calculations for crystals of $Ca(OH)_2$. Energies were calculated for structures with different ratios of shared (s) to unshared (u) octahedral edge lengths; the spacing of the layers was adjusted to keep the – OH groups in van der Waals contact. There is a minimum of electrostatic energy for the model $Ca^{2+}(O^{2-}H^{+})_2$ at $s/u = 0{\cdot}92$ and for a model with charges reduced to $Ca^{2+}(O^{1\frac{1}{2}-}H^{\frac{1}{2}+})_2$ at $s/u = 0{\cdot}87$, a ratio very close to the observed value of 0·86.

If the charges and other forces were well enough known then it would be possible to predict the s/u ratio of the octahedral layer in micas and the response of the layer to forces transmitted from the tetrahedral layer. McCauley and Newnham (1971) suggest that the changes in the angle of twist (α) are about half what they would be if all the adjustment was made by the tetrahedral layer. These authors also suggest that an equal adjustment is made by the octahedral layer. If their regression relationship, based on micas and on an Mg–O distance of 2·10 Å, is applied to talc, the predicted twist is 1·2° rather than the observed 3·4°.

The original prediction of Radoslovich (1962) suggests that the octahedral layer in talc would have a greater basal area than the tetrahedral layer and so the tetrahedra would have zero twist and would be distorted to increase the size of their bases. This prediction was based on a shorter Si–O distance, 1·60 Å, than was deduced later by Smith and Bailey (1963) from more accurately determined structures. Smith and Bailey's distance 1·616–1·621 Å would predict a zero to 2° twist but the change of cos α at α near zero is too small to make an accurate prediction. This value agrees with the measured small twist of 3·4° (esd 0·2°). This twist only reduces the size of the layer by 0·21 per cent of its linear dimensions, but shows that the layer is not being stretched by the octahedral layer.

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Résumé—La structure cristalline d'un échantillon de talc du Harford County, Maryland, a été déterminée par un raffinement par moindres carrés à partir de clichés photographiques de diffraction des rayons X. On a adopté une maille triclinique de groups $C\bar{1}$, avec $a = 5{,}293$ Å, $b = 9{,}179$ Å, $c = 9{,}496$ Å, $\alpha = 90{,}57°$, $\beta = 98{,}91°$ et $\gamma = 90{,}03°$.

Les couches de la structure ont presque une symétrie monoclinique, mais les anneaux d'atomes d'oxygène de surface, d'une forme voisine de l'hexagone, formés par les bases des tétraèdres de silice ne sont pas en correspondance exacte comme ils le sont dans les micas où se trouvent des ions interfeuillets; ils sont au contraire déplacés en partie, si bien que l'empilement des feuillets forme un cristal triclinique. Les hexagones des atomes d'oxygène de surface sont déformés à cause d'une rotation des tétraèdes de 3,4°; ainsi l'axe b est plus court de 0,2% de ce qu'il est dans une structure à hexagones réguliers, et la rotation des tétraèdres rapproche un petit peu les ions oxygène des ions magnésium octaédriques.

Kurzreferat—Die Kristallstruktur einer Talkprobe aus Harford County, Maryland, wurde aus Röntgenbeugungsaufnahmen unter Berechnung der kleinsten Abweichungsquadrate bestimmt. Es wurde eine trikline Zelle mit $a = 5{,}293$, $b = 9{,}179$, $c = 9{,}496$ Å, $\alpha = 90{,}57°$, $\beta = 98{,}91°$ und $\gamma = 90{,}03°$, Raumgruppe C1 angenommen. Die Schichten dieser Struktur haben fast monokline Symmetrie, doch werden die nahezu hexagonalen Ringe der Sauerstoffatome an den durch die Grundflächen der Si-Tetraeder gebildeten Schichtoberflächen nicht durch Zwischenschichtionen aufeinander ausgerichtet, wie dies bei den Glimmern der Fall ist. Sie sind vielmehr teilweise versetzt, so daß die Schichtfolge einen triklinen Kristall bildet. Die Sechsecke der Oberflächensauerstoffe sind durch eine 3,4°-Drehung der Tetraeder verzerrt, so daß die b-Achse um 0,2% kürzer ist als in einer Struktur mit regelmäßigen Sechsecken. Die Drehung bringt die Sauerstoffionen etwas näher an die oktaedrischen Magnesiumionen heran.

Резюме — Структура кристаллов талька определялась при помощи рентгенографии по образцу из харфордского округа, Мэриланд. Принята триклинная клетка с $a = 5{,}293$, $b = 9{,}179$, $c = 9{,}496$ Å, $\alpha = 90{,}57°$, $\beta = 98{,}91°$, $\gamma = 90{,}03$, промежуток группы $C1$. Слои структуры имеют почти что моноклинную симметрию, но на поверхности слоев имеются примерно шестигранные кольца атомов кислорода, которые не содержатся в равновесии в межслойных ионах как в слюде, а частично смещены, так что столбик слоя образует триклинный кристалл. Шестигранники поверхностных кислородов искажены скручиванием тетраэдры на 3,4°, таким образом ось b на 0,2% короче, чем структура с регулярными шестигранниками, а скручивание слегка приближает ионы кислорода к октаэдральным ионам магния.