THE STRUCTURAL SCHEME OF ATTAPULGITE*

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The name attapulgite was applied in 1935 by J. De Lapparent[1] to a clay mineral which he encountered in fuller's earths from Attapulgus, Georgia, and Mormoiron, France. Objections have been raised, and these objections were recently reviewed by De Lapparent,[2] that the material involved does not justify the application of a mineral name. However, no attempt has been made to study the crystal structure. De Lapparent himself has suggested for classification purposes that attapulgite is a layer silicate related to the micas, but some obvious inconsistencies with the x-ray powder diffraction patterns of the mineral have suggested the desirability of attempting a better explanation. The material used in this investigation was obtained from the Attapulgus Clay Co., Attapulgus, Ga. The raw clay was dispersed and freed of large crystalline impurities by sedimentation. Centrifuge fractions were then obtained, of which particularly the fraction between .1 and .05μ appeared homo-

TABLE 1. CHEMICAL ANALYSES OF ATTAPULGITE

	A	B
SiO_2	53.64	55.03
TiO_2	0.60	n.d.
Al_2O_3	8.76	10.24
Fe_2O_3	3.36	3.53
FeO	0.23	n.d.
MnO	0.03	n.d.
MgO	9.05	10.49
CaO	2.02	—
Na_2O	0.83	n.d.
K_2O	0.75	0.47
P_2O_5	0.79	n.d.
H_2O+	10.89	10.13
H_2O-	9.12	9.73
Exchange capacity (me/100 gr.)	n.d.	21
Optical data		$\gamma = 1.540$
		$\gamma - \alpha = .032$
		$(-)$; 2 V small

A. Analysis given by De Lapparent (op. cit.)
B. Analysis of clay fraction used for this study.
n.d. = not determined.

[1] An essential constituent of fuller's earth. *Compt. rend.* **201**, 481–483 (1935).
[2] Defense of attapulgite: *Bull. soc. fr. de Min.* **61**, 253–83 (1938).

geneous and showed no extraneous lines in its diffraction diagram. Flake-shaped aggregates of this material were employed in obtaining the subsequent data. The chemical analyses and optical data given in Table 1, and the powder diffraction diagram in Fig. 1 leave no doubt of the identity of this material with that originally described by De Lapparent.

"Fibre diagrams" of the above flaky aggregates immediately distinguish attapulgite from the common clay minerals with prominent basal cleavage. For the small values of sin θ the distribution of visually estimated diffracted intensity in a given ring tends to vary inversely with the angular displacement from the horizontal direction (zero layer line). Such a distribution results from the restriction of one axis (later chosen as c) of the individual crystallites to the plane of the flake. For the clays with basal cleavage, similarly prepared flakes consist of aggregates of particles each of whose basal planes lies in the plane of the flake.[3]

A series of diffraction patterns made with radiation incident at various inclinations to such flakes served to provide optimum conditions for the observation of interferences of the type $hk0$, and permitted the identification of about 15 such interferences. A few poorly defined arcs on residual first and second layer lines indicate a periodicity of about 5.2Å, along the third, or c, axis. Figure 1 includes three of the "fibre diagrams" at increasing angles of incidence. Figure 2 is a plot of observed values of sin θ up to .5 for the interferences which showed arcs across the equatorial layer line.

Too few interferences appear to attempt a complete solution of the structure, but many silicate structures are available from which reasonable analogies may be drawn. Figure 3 is a projection onto 001 of an idealized monoclinic structural scheme consistent with the diffraction data. The composition of this ideal cell is $(OH_2)_4(OH)_2Mg_5Si_8O_{20} \cdot 4H_2O$, in good agreement with the chemical analyses if trivalent cations are considered equivalent to 1.5 Mg^{++}. The dimensions of this section are $a_0 \sin \alpha = 12.9$Å, and $b_0 = 18$Å. There are two molecules in the unit cell and the space group is probably $C_{2h}^3 - C^2/m$. The silicate chains running parallel to c along $00z$ and $\frac{1}{2}\frac{1}{2}z$ are similar to amphibole chains. Oxygens at the corners of the chains link each to four neighbors. Chains of water molecules, also running parallel to c fill the interstices between amphibole chains, and this water represents that which is lost below 100°C. without material effect upon the diffraction patterns. An equal amount of water appears, coordinated about Mg, representing that less easily removed, and four OH groups per cell represent the water not driven off below 500 or 600°C.

    [3] Clark, G. L., Grim, R. E., and Bradley, W. F., Notes on the identification of minerals in clays by x-ray diffraction: *Zeits. Krist.* **96**, 322–324 (1937).
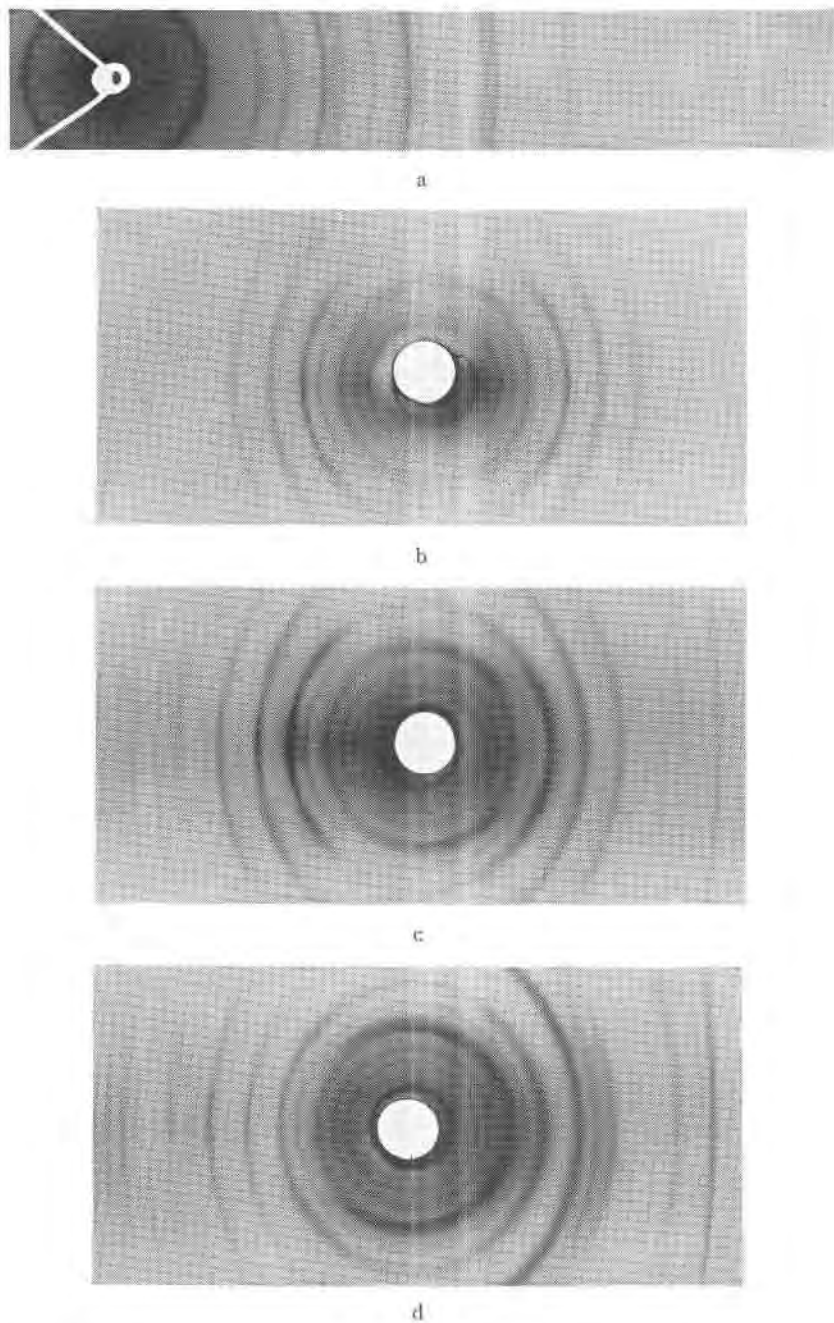
Fig. 1. Diffraction patterns of attapulgite. (a) powder, (b), (c) and (d) flakes inclined to beam at angles of 0, 15°, 35°. All patterns registered with Fe Kα radiation. Camera radius for (a) = 6.3 cm.; for (b), (c), and (d) = 2.8 cm.
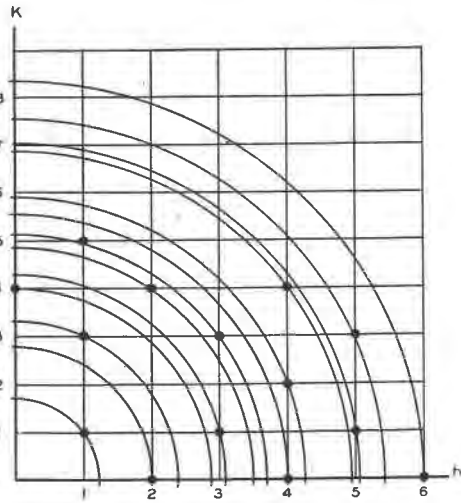
Fig. 2. Observed values of sin θ for the prismatic interferences of attapulgite plotted as radii of circles, indicating the corresponding indices.
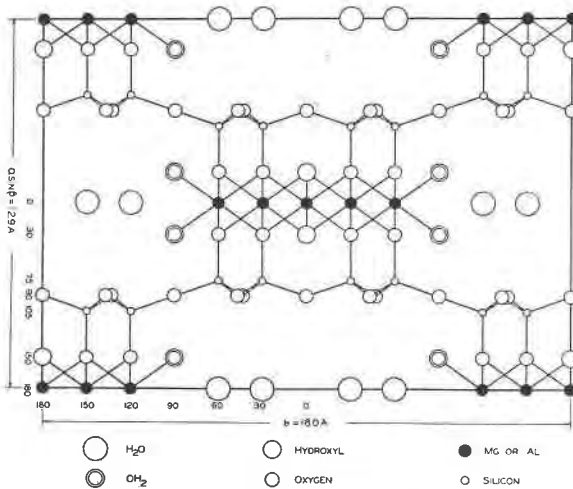

Fig. 3. Idealized proposed structure for attapulgite projected onto 001.

TABLE 2. ATOMIC COORDINATES IN ATTAPULGITE

	x	y	probable set of equivalent positions
4 OH	30	0	i
8 O_I	30	30	j
8 O_{II}	30	60	j
8 OH_2	30	90	j
4 O_{III}	90	0	i
4 O_{IV}	90	90	f
8 O_V	90	45	j
8 O_{VI}	90	45	j
4 H_2O_I	0	120	h
4 H_2O_{II}	0	150	g
2 Mg_I	0	0	a
4 Mg_{II}	0	30	h
4 Mg_{III}	0	60	g
8 Si_I	75	30	j
8 Si_{II}	75	60	j

TABLE 3. COMPARISON OF CALCULATED WITH OBSERVED INTENSITIES IN THE $hk0$ ZONE

Indices	d_{hkl} calc.	d_{hkl} obs.	F²X Lorenz Factor ÷ 1000	Visually* Estimated Intensities
110	10.48	10.50	330	ss
200	6.45	6.44	17	ms
130	5.44	5.42	12	m
220	5.24	—	1	—
040	4.50	4.49	66	s
310	4.18	4.18	13	w
240	3.69	3.69	18	m
330	3.49 }	3.50	12 }	w
150	3.47 }		2 }	
400	3.23	3.23	120	ss
420	3.04	3.03	3	ww
350	2.76	—	2	—
440	2.62	2.61	43	s
510	2.56	2.55	8	w
530	2.38	2.38	5	w
080	2.25	—	1	—
600	2.15	2.15	15	m
550	2.10	—	1	—
480	1.845	—	1	—
390	1.815	1.82	3	ww
660	1.75	—	1	—
800	1.615	1.62	3	ww
680	1.555	1.56	17	w
0120	1.50	1.50	40	m

* ss = very strong, s = strong, ms = medium strong, m = medium, w = weak, ww = very weak — = not observed.

In Table 2 are listed ideal x and y coordinates for the cross section, and in Table 3 various calculated $hk0$ intensities are compared with those visually estimated on the films. In view of the meagre data available, and the uncertainties in the exact manner of isomorphous replacement, no attempt has been made to adjust coordinates for distortion of coordination polyhedra due to sharing. The excellent qualitative agreement noted seems sufficient to establish the gross features of the structure, and can probably even be said to lend some credence to such features as the distribution and status of the three sorts of water involved. A secondary tendency of the b-axes to lie near the plane of the flakes more often than perpendicular to them modifies the observed relative intensities somewhat, but can hardly invalidate the agreement shown.

Easy cleavage parallel to 110 is apparent from Fig. 3 and accounts for both the fibrous occurrence and the secondary orientation tendency mentioned above. The failure of the mineral to build longer chains, like tremolite or chrysotile, is probably related to the more variable chemical composition. The distribution of Al ions among the five available octahedral positions in a chain can be accommodated either by vacancies in the octahedral positions or by some replacement of Si by Al. Either process, however, should weaken the chains. It would appear doubtful if an Al end member could exist.

In several instances, optical examinations have led to the designation of attapulgite as montmorillonite. It is interesting to observe that a section through the above structure parallel to 010 presents the same sequence of layers of atoms as does a section of the montmorillonite structure parallel to c when one layer of water molecules is present.[4] Optical data are commonly obtained from oriented flakes similar to those used in these x-ray diffraction studies, and the respective orientations of attapulgite and montmorillonite flakes result in a similar disposition within the flakes of the directional properties of the crystallites which govern the optical characteristics. Optical data alone, therefore, can not be critical for distinction between the two minerals.

The inorganic base exchange capacity, which amounts to less than one ion per unit cell, probably involves exchange of ions associated with the water chains. The clay as examined in this study was ammonia saturated.

Note. Since the preparation of this manuscript it has come to the author's attention that in *Nature*, **142**, 114–115 (1938), G. Nagelschmidt has suggested the likelihood of just such a structural scheme as the above for attapulgite as well as for some other related minerals.

[4] Bradley, W. F., Grim, R. E., and Clark, G. L., A study of the behavior of montmorillonite upon wetting: *Zeits. Krist.*, **97**, 216–222 (1937).

Hendricks, S. B., and Jefferson, M. E., Structures of kaolin and talc-pyrophyllite hydrates and their bearing on water sorption of the clays: *Am. Mineral.* **23**, 863–875 (1938).