THE STRUCTURAL SCHEME OF SEPIOLITE*

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Abstract

An idealized structure for sepiolite is deduced from the zero layer *x*-ray diffraction effects from natural fibers. Linked hydrous $H_6Mg_8Si_{12}O_{30}(OH)_{10}+Aq$ chains are disposed in centered array in a cell of 13.4×27Å cross section.

Sepiolite is a hydrous magnesium silicate mineral, often referred to in textbooks by the approximate chemical formula of $3SiO_2 \cdot 2MgO \cdot xH_2O$. It is a fine grained material which may occur occasionally in the form of macroscopic fibers. Sepiolite can be classified as one of the clay minerals. A summary of the available *x*-ray diffraction data of sepiolite, together with the results of the physical, thermal and chemical investigations, have recently been reviewed in an authoritative manner by Caillere (1951).

The excellence of development of fibrous habit in several natural occurrences permits registration of *x*-ray fiber diagrams from which the probability of proper indexing of sufficient numbers of reflections, especially in the zero layer, seems high enough to justify a schematic analysis of the structure.

Fibers from Little Cottonwood, Utah, were used to obtain the *x*-ray diffraction data. The sample consisted of $1\frac{1}{2}$–2 cm. long, light gray colored fibers. Viewed at high magnification under the electron microscope the fibers appeared to have a lath or ribbon-like particle morphology. The fibrous habit of the Little Cottonwood sample is illustrated in Fig. 1. No certain diffraction maxima for any extraneous accessory minerals were observed on the *x*-ray patterns. Other sepiolite fibers, notably those from Ampandrandrava, Madagascar, are often associated with some opaline silica. The chemical analysis of the sample that was used for obtaining the diffraction data is listed in Table 1.

The *c* axis periodicity of about 5.3 Å has been recorded by Migeon (1936) and Longchambon (1937). The present analysis is limited to the establishment of an orthogonal net in the zero layer, which provides lat-

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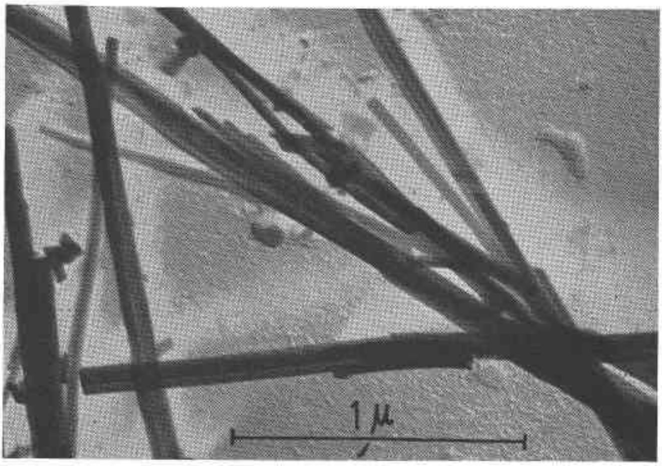

FIG. 1. Electron micrograph of the Little Cottonwood, Utah, sepiolite showing the fibrous and lath shaped morphology of sepiolite particles. Magnification 39,200×. Platinum shadowed.

tice parameters consistent with the dimensions of some reasonable model based on other known hydrous magnesium silicate crystal structures. Such a section has been found with $a_0 \sin\beta = 13.4$ and $b_0 = 27.0$ Å, for which all observed reflections are of the form $h+k=2n$. This net provides a b/c ratio of approximately $3\sqrt{3}$, consistent with the obvious pseudo-hexagonal character of the bc plane.

In these particulars the structure is analogous with an earlier schematic

TABLE 1. CHEMICAL ANALYSIS OF LITTLE COTTONWOOD SEPIOLITE

	Weight Per cent	Relative mol. populations	
SiO_2	52.97	12.00	
MgO	22.50	7.62	8.67
Al_2O_3	0.86	.23	
Fe_2O_3	0.70	.12	
Mn_2O_3	3.14	.55	
CuO	0.87	.15	
H_2O^+	9.90	7.50	
H_2O^-	8.80	6.64	
Total	99.74		

Additional spectrographically determined components: CaO: 0.14; K_2O: 0.17; BaO: 0.024; P_2O_5: 0.1; others: 0.01.

Idealized empirical formula: $12SiO_2$, 8–9 octahedral metal oxides, $14H_2O$.

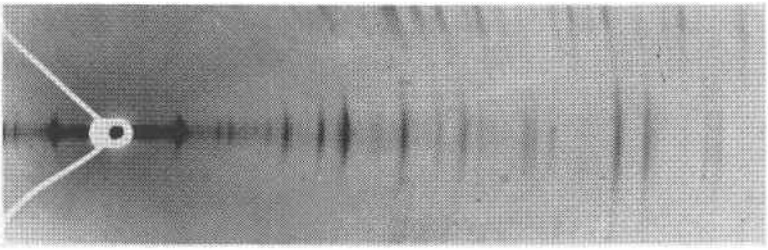

FIG. 2. The zero layer line of a sepiolite fiber x-ray diffraction diagram. Filtered Cu radiation. Camera radius = 6.35 cm.

analysis of the related mineral attapulgite, described by Bradley (1940). A projection of a model was therefore arranged, using centered amphibole-like chains of one and one half times the *b* dimension of chains found for attapulgite, and the zero layer diffraction effects were synthesized for the chemical components of a typical analysis distributed in accordance with the model. It is interesting to note one of the differences that exists between the attapulgite and sepiolite models. In the former one the chains are amphibole-type chains composed of two pyroxene-type chains. In the sepiolite model, however, the chains contain *three* instead of two pyroxene chain components; therefore, they are basically not amphibole-like in character but rather they represent a new silicate structure type.

Figure 2 is a reproduction of the zero layer diffraction effects of a Little Cottonwood sepiolite fiber. Figure 3 illustrates the proposed idealized structure with the angular plane coordinates indicated along the margins.

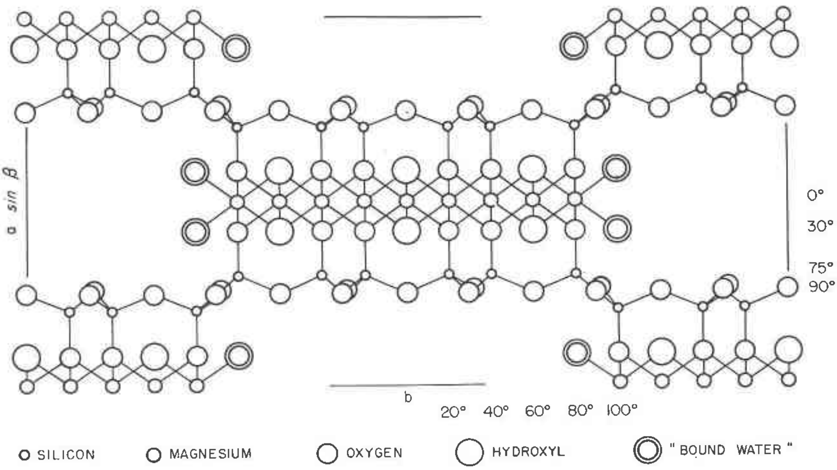

FIG. 3. Idealized proposed structure for sepiolite projected onto 001.

The ideal density is 2.2, comparing favorably with determined values ranging from 2.0 to 2.1. In Table 2 are assembled the calculated *F* factors for all possible reflections out to about 1.5 Å; a few additional entries for smaller periodicities are also included in order to match observed values below the 1.5 Å limit. In the table each entry on the left side of the columns is for the skeleton alone; a second entry at the right side of the columns includes the water allowance, and it refers to those small-angle reflections near a^* and b^* for which water contribution could be fairly estimated. For these *F* values octahedral ion occupants were taken as 8/9 Mg in view of the apparent octahedral deficiency which will be discussed later. The largest apparent departures between calculated and observed entries are concentrated systematically about the $b=6$, 12 and 18 levels, and are attributable to the arbitrary use of exact submultiples of the cell parameters as coordinates. In Table 3 the estimated observed, relative intensities are compared with the calculated intensities derived from Table 2; the calculated intensities include multiplicity, polarization and Lorentz corrections.

The general quality of the agreement is such that the gross features of the structure can be viewed with some confidence. The large number of coincident reflections, the large number of ions, mostly in general positions and the analytical uncertainties of actual chemical composition of any specific fiber seem to render pointless any attempts at further refinements.

Speculative aspects of the crystal chemistry can be outlined as follows: the scheme (per half cell) provides sites for twelve tetrahedral ions, nine octahedral ions, forty articulated oxygens and hydroxyls and room for about six molecules of low temperature water. Ideal occupation of tetrahedral sites by silicon and the octahedral ones by magnesium would lead to the formula $H_4Mg_9Si_{12}O_{30}(OH)_{10}\cdot 6H_2O$. It can be assumed that the four "extra" protons are associated with the edges of the brucite ribbons, indicated in Fig. 3 as OH_2 or "bound water." The chemical analyses indicate that fewer than nine octahedral sites are actually occupied, especially if allowance is made for aluminum ions in tetrahedral positions, for the uncertainty of the actual valence state of the minor constituents and for the possibility that the minor constituents may actually be accessory. Neutrality is maintained by the presence of sufficient additional protons and/or exchange ions to balance any residual charge deficiency. A practical rationalization of the formula is therefore written as $H_6Mg_8Si_{12}O_{30}(OH)_{10}\cdot 6H_2O$. This formula allows for water of four separate bonding energies; namely, (1) molecular water; (2) water bound on brucite ribbon edges; (3) hydroxyls analogous with those of various layer mineral structures; and (4) balancing protons

TABLE 2. CALCULATED *hk*0 STRUCTURE FACTORS PER $\frac{1}{4}$ CELL FOR THE IDEALIZED SEPIOLITE MODEL

b \ a	0	1	2	3	4	5	6	7	8	9	10	11	12
0			−43 −21		+95 +110		−75 −65		+24		+50		+36
1		+80 +65		− 2 −14		+31 +25		−34		+39		+20	
2	− 15		− 7		+ 6		+10		+ 4		− 3		− 5
3		−21 −14		− 2		−12		+ 5		−11		− 5	
4	+ 11		+ 6		− 5		− 8		− 3		+ 2		+ 4
5		+ 3 −11		+11		0		+12		0		+ 4	
6	− 61 −45		+42 +47		−30		+20		+ 2		− 8		+ 7
7		− 9 −15		+17		−36		+17		−18		+ 4	
8	+ 2		+ 1		− 1		− 2		− 1		0		+ 1
9		+ 4		− 9		+25		− 7		+13		− 1	
10	+ 2		+ 1		− 1		− 2		− 1		0		+ 1
11		− 8		+16		−32		+16		−17		+ 3	
12	+ 16		−26		+33		−34		+47		−41		+33
13		+ 2		+ 9		0		+ 9		0			
14	+ 7		+ 4		− 3		− 6						
15		−13		− 1		−10							
16	− 8		− 4		+ 3		+ 6						
17		+46		0		+27							
18	+104		+20		+20		+ 2						
19		+39											

TABLE 3. SUMMARY OF CALCULATED RELATIVE INTENSITIES FOR THE SEPIOLITE FIBER DIAGRAM IN THE ZERO LEVEL

Indices	*d* in Å	$nF^2\phi(\theta)\times 10^{-3}$	Estimated relative intensity in the fiber diagram
020	13.5	3.8	m
110	12.0	128.0	sss
130	7.5	3.7	m-w
040	6.7	.3	w
200		3.7	
220	6.0	.8	ww
150	5.0	1.5	w
240	4.75	.4	ww
060	4.50	11.2	m
310	4.40	2.1	w
330	4.00	.2	?
260	3.73	20.0	s
170	3.71	2.0	
350	3.45	1.0	w
080	3.35	.02	ss
400		48.0	
420	3.25	.3	?
440	3.00	.2	ww
370	2.93	2.0	w
190		.1	
460	2.69	5.6	s
510	2.68	3.9	
530	2.56	.8	w
2,10,0	2.50	.01	ww
390		.5	
550	2.40	.0	w
1,11,0	2.39	.4	
0,12,0	2.25	.6	m
600	2.24	10.0	
620	2.21	.5	m
570		6.2	
3,11,0	2.15	1.2	
2,12,0	2.13	3.1	w
640	2.12	.3	
1,13,0	2.05	.02	
660	2.00	1.7	ww
590		2.6	
710	1.91	4.5	w
3,13,0	1.88	.3	
730	1.87	.05	w
680		—	
4,12,0		4.2	
5,11,0	1.81	3.6	w
750	1.80	.5	

TABLE 3—(*continued*)

Indices	d in Å	$nF^2\phi(\theta)\times 10^{-3}$	Estimated relative intensity in the fiber diagram
1,15,0	1.78	.6	ww
6,10,0	1.73	.01	ww
770	1.71	1.0	ww
800	1.68	1.0	ww
840	1.63	.03	ww
790	1.61	.1	ww
6,12,0	1.58	3.5	s
1,17,0	1.57	6.3	
0,18,0	1.50	15.0	m-s
8,8,0		.0	
910	1.48	3.9	w
1,19,0	1.41	3.7	w
970	1.385	.8	
4,18,0	1.375	1.0	m
5,17,0	1.365	1.8	
8,12,0	1.345	5.3	m
10,0,0	1.34	3.0	
10,12,0	1.15	3.4	w
12,0,0	1.12	1.3	w
12,12,0	1.00	2.3	m

analogous with exchange ions. These categories are in the ratio of 6:4:3:1, and with some tolerance they can be regarded to be not in serious conflict with the results of the weight loss studies reported by Migeon and Caillere.

It is to be noted that oxygen ions at $\frac{1}{4}$, $\frac{1}{4}$, z, etc. positions which join chains in this structural scheme are double links as compared with the single link oxygen of the attapulgus. It is quite possible that both structures are actually alike, and that an improper choice of model was made in one case or the other. If the difference is real, however, it can be speculated that this is the factor which renders the sepiolite II modification, described by Longchambon, more stable than the comparable high temperature modification of attapulgite.

The entire structure could be either orthorombic or monoclinic. It seems more probable that it belongs to the space group $C\ 2/m$.

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