

X-RAY STUDY OF THE STRUCTURE OF SEPIOLITE

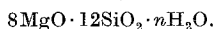
by

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ABSTRACT

Sepiolite is a valid mineral with the following chemical formula :

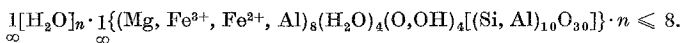


Its unit cell characteristics are :

$$a = 13.4\text{\AA} ; b = 26.8\text{\AA} ; c = 5.28\text{\AA} ; Z = 2 ; D_{2n}^5 - P \frac{2_1}{n} \frac{2}{c} \frac{2}{n}.$$

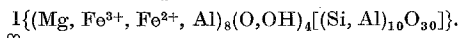
They were determined on the sepiolite from Ampandrandava (Madagascar). Its structure was determined by means of the "trial and error" method and the observed and calculated intensities rendered a good agreement.

The formula of the structure is :



The mineral contains zeolitic, crystal- and constitution-water. A good agreement was achieved between the chemical, thermal, and morphological qualities and the x-ray data. The mineral remains stable up to about 350°C and begins to change into an "anhydride" above this temperature.

The formula of the structure of sepiolite-"anhydride" is :



Its unit cell characteristics are :

$$a = 10.9\text{\AA} ; b = 23.3\text{\AA} ; c = 5.28\text{\AA} ; \alpha \approx 90^\circ ; Z = 2 ; C_{2n}^5 - P \frac{2_1}{n} 11.$$

The minerals xylotile, mountain wood and gunnbjarnite are isotypical with sepiolite.

The term, sepiolite, was introduced into the literature to designate a mineral with the composition of $2\text{MgO} \cdot 3\text{SiO}_2 \cdot n\text{H}_2\text{O}$.

The largest familiar occurrence, near Eskischir in Turkey, has been known for centuries and is utilized in industry. Besides this occurrence there are innumerable smaller sources all over the world. In recent times vast deposits of sepiolite are said to have been discovered in Amboschi (Tanganyika); they are held to be the most important deposits on earth.

Sepiolite is found in the form of fibers which are, however, commonly discernible only under the microscope, or under the electron microscope.

The most beautiful fibrous sepiolite is the one found at Ampandrandava, Madagascar, which was used for experiments by Migeon (1936), Longchambon (1937) and Caillère (1951). Brauner and Preisinger (1956) also used this material for their investigation.

The variety of sepiolite from Ampandrandava consists of yellowish fibers 2-3 cm long, in bundles. Under the microscope the mineral consists of bundles

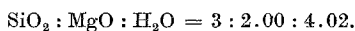
of fibers oriented in an exact parallel direction, of a slight yellow shade, and with parallel extinction. Pleochroism in the direction of the fiber is dark yellow, and normal to it lemon yellow, γ' in the direction of the fiber. The electron microscope shows that the thickness of the single fiber ranges in size over some hundreds of ångströms.

Because of the statistical distribution of the single fibers into bundles of fibers, as can be seen from rotation and Weissenberg photographs, no exact optical data can be given and, therefore, nothing can be said about the crystal system from optical data.

The chemical analysis of the sepiolite from Ampandrandava shows a proportion of $\text{SiO}_2 : \text{MgO} : \text{H}_2\text{O} = 3 : 2.00 : 4.02$ (Table 1). All other analyses of sepiolite found in the literature also show a proportion of $\text{SiO}_2 : \text{MgO}$ of approximately 3 : 2.

TABLE 1.—CHEMICAL ANALYSIS OF THE SEPIOLITE FROM AMPANDRANDAVA (CAILLÈRE, 1951)

	Weight (%)	Molquot. $\times 1000$
SiO_2	52.50	874.1
Al_2O_3	0.60	5.9
MgO	21.31	528.5
CaO	0.47	8.4
FeO	0.70	9.7
Fe_2O_3	2.99	18.7
H_2O	21.27	1180.6
Sum	99.84	



Minerals introduced under the names xylotile, mountain wood and gunnbjarnite also have a proportion of $\text{SiO}_2 : \text{MgO} = 3 : 2$ if one considers ferric ions as substituting for magnesium ions (Table 2). All these minerals proved to be isotypic with sepiolite and, because of their high ferric ion content, could be called ferrisepiolite.

The fluctuating water content shown by sepiolite analyses has led to many studies of its nature. The thermobalance and differential thermal analysis provide the best grounds for exact subdivision of the water content (Fig. 1). The water content of sepiolite depends on the humidity. Of the total water, about 60 percent is lost up to a temperature of 250°C. This process is reversible. Part of this water is zeolitic and part of it adsorbed (i.e. may be substituted by iodine, oil, mercury and alcohol). No essential change of the crystal lattice is caused by this loss of water. If sepiolite is heated above 350°C the crystal structure is eventually changed and about 25 percent more of the total water content is lost. This process is irreversible and is finished at $\leq 450^\circ\text{C}$. The mineral now still contains about 15 percent of the entire

TABLE 2.—CHEMICAL ANALYSES OF MOUNTAIN WOOD AND XYLOTILE FROM STERZING, TYROL (BRAUNER AND PREISINGER, 1956)

	Mountain Wood		Xylofile		
	Weight (%)	Molquot. × 1000	Weight (%)	Molquot. × 1000	
SiO ₂	49.58	825.5	50.50	840.8	} SiO ₂
Al ₂ O ₃	0.88	8.6	0.36	3.5	
Fe ₂ O ₃	17.20	107.7	16.46	103.1	
FeO	1.43	19.9	0.63	8.8	} MgO
CaO	0.72	12.8	0.42	7.5	
TiO ₂	Sp.	—	Sp.	—	
MgO	12.67	314.2	13.90	344.7	} H ₂ O
MnO	0.30	4.2	0.17	2.4	
H ₂ O up to 110°	7.12	983.0	8.38	1010.8	
H ₂ O over 110°	10.59	—	9.83	—	
	100.49	—	100.65	—	

SiO₂ : MgO : H₂O = 3 : 2.02 : 3.5 SiO₂ : MgO : H₂O = 3 : 2.01 : 3.75.

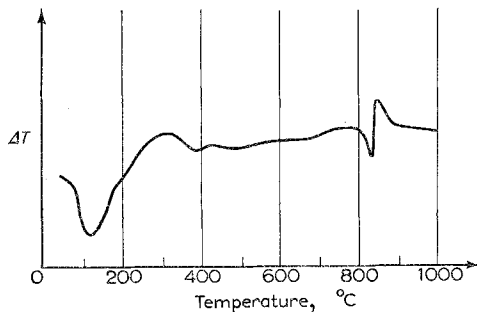
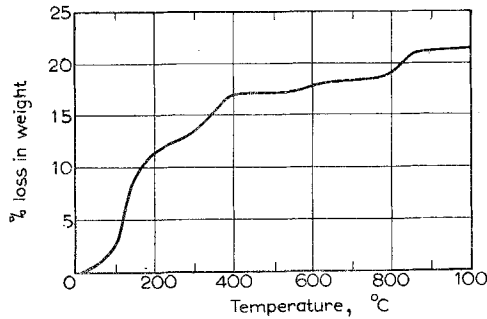


FIGURE 1.—Thermobalance and differential thermal curve of sepiolite from Ampandrandava.

water content which is driven off by heating above 700°C. By this process the lattice is completely destroyed.

The differential thermal curves of mountain wood and xylotile correspond to those of sepiolite.

From rotation photographs we obtained the same lattice constants as Nagy and Bradley (1955), which were

$$a = 13.4 \text{ \AA}, b = 26.8 \text{ \AA}, c = 5.28 \text{ \AA}.$$

As space group, however, we found

$$D_{2h}^6 - P \frac{2_1}{n} \frac{2}{c} \frac{2}{n},$$

and

$$Z = 2 \text{ for } 8 \text{ MgO} \cdot 12 \text{ S O}_2 \cdot 14 \text{ H}_2\text{O}.$$

Of the 16 H₂O resulting from the chemical analysis 2 H₂O were considered to be adsorptive water.

The density $\rho_r = 2.26$ and $\rho_{ex} = 2.08$ (by suspension). This difference in density values may be explained by the fact that the x-ray density referred to a single crystal; the macroscopic density, however, was determined on a bundle of fibers consisting of many single crystals and, consequently, of many cavities.

The space group D_{2h}^6 was determined by indexing the zero, first and second layer line round the fiber axis. Because of the statistical distribution of the single fibers rotation photographs with standing and rotating preparations showed the same intensity.

The structural scheme of Nagy and Bradley (1955) could not be made consistent with the space group determined by us.

We found the following structural build-up (Fig. 2): In the (100) plane there are layers of silicate with unshared corners of tetrahedra alternating after three chains. These layers of silicate are connected by magnesium ions, as in mica. Owing to the alternating tetrahedron corners a structure having large cavities results. Every Si is tetrahedrally surrounded by four oxygens, three at 1.56 Å and one at 1.66 Å. The Mg ions are surrounded octahedrally

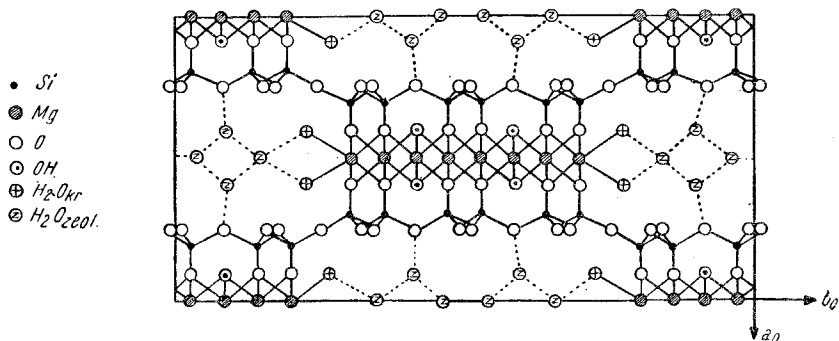
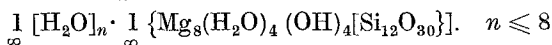


FIGURE 2.—Unit cell of sepiolite projected on the (001) plane.

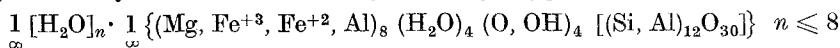
by oxygens and hydroxyl groups, the coordination of each Mg at the end of the complex involving 2 H₂O molecules. The distance Mg-O (OH) = 2.00 Å and 2.12 Å, Mg-H₂O = 2.25 Å. In the channel cavities there is zeolitic water. Between the single water molecules there is an interval of 2.72 up to 2.78 Å. As the number of bonds within the complex is greater than between the complexes the fibrous formation is understandable.

For this structural build-up the parameters were determined by means of the "trial and error" method. The intensities calculated from these parameters show good agreement with the ones observed (Brauner and Preisinger, 1956, fig. 13).

The described build-up corresponds to the following structure formula :



The rotation photographs of ferri-sepiolites (xylotile, mountain wood and gunnbjarnite) are identical with sepiolite. The formula is the same, except that magnesium is partly substituted by ferric iron. The charge is compensated by the substitution of hydroxyl by oxygen.



The lattice of sepiolite shows no essential change of the lattice constants when heating it up to 250°C in spite of a certain loss of water. Between 350 and 450°C there is a change of the lattice which can be seen from a change of intervals and of intensities. This change of the lattice is caused by the formation of sepiolite-"anhydride." The lattice constant in direction of the fiber axis remains unchanged.

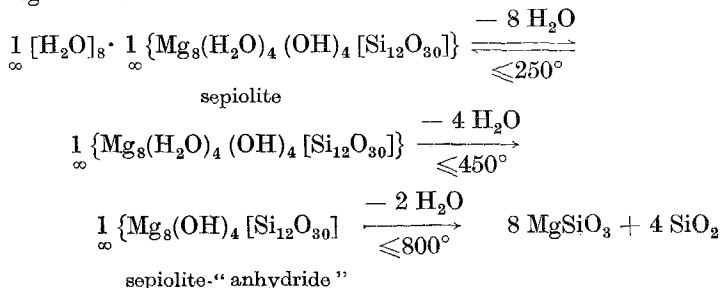
For this anhydride, the following lattice constants were obtained :

$$a = 10.9 \text{ \AA}, b = 23.3 \text{ \AA}, c = 5.28 \text{ \AA}, \alpha \approx 90^\circ, Z = 2 \text{ for } 8\text{MgO} \cdot 12\text{SiO}_2 \cdot 2\text{H}_2\text{O}.$$

Space group $C_{2h}^5 - P \frac{2}{n} 11$.

The idealized structure is shown in Fig. 3. The calculation of the exact parameters is in progress.

As the differential thermal analysis and thermobalance have shown, water is lost in different stages. First, the adsorbed and zeolitic water is lost, then the crystal water and, last, the constitution water. This loss of the water and the change of the structure are shown in Fig. 3 and may be expressed by the following formulas :



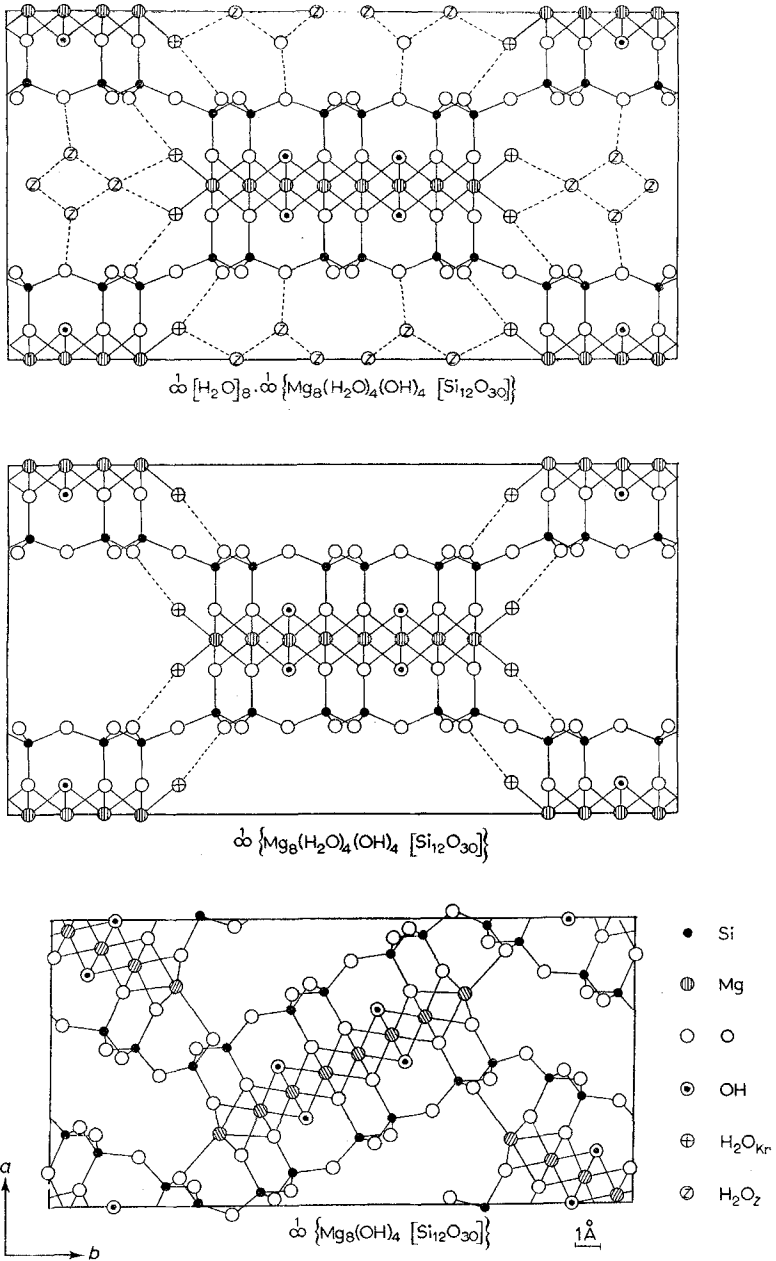


FIGURE 3.—Structure change, sepiolite-sepiolite-“anhydride.”
Unit cells projected on the (001) plane.

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