SEPIOLITE AND RELATED COMPOUNDS: ITS STABILITY AND APPLICATION

by

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ABSTRACT

The unit-cell characteristics and structures of sepiolite, ferri-sepiolites (xylotile, mountain wood, gunnbjarnite), loughlinite and palygorskite (attapulgite) and their structural relationships are discussed. The chemical, morphological and thermal properties are explained by their structures. The unit-cell characteristics and structures of sepiolite "anhydride", loughlinite "anhydride" and palygorskite "anhydride" are given. Under low water vapor pressure the phase transformations sepiolite to sepiolite "anhydride" and palygorskite to palygorskite "anhydride" are reversible. It was not possible to synthesize sepiolite in the system $MgO–SiO_2–H_2O$ under confined pressure within a range of 80° to 300° C

The possibility of the application of sepiolite and related compounds in industry, specially in the automobile industry, is referred to.

There is much variety in the occurrences of sepiolite. Sepiolite occurs in the form of lumps (e.g. Eskischir, Turkey), sedimentary beds (e.g. Amboschi, Tanganyika), matted plates (so-called mountain leather), or fibers (e.g. Ampandrandava, Madagascar). All these forms are based on long single crystal fibers with thicknesses of only 100 Å to several hundred Å. The felting in one, two, or three dimensions of these extremely thin single crystal fibers leads to their aggregation into these various forms.

The structure of sepiolite was determined by Brauner and Preisinger (1956). The ideal formula of the structure is:

$$1 \, (H_2O)_n \cdot 1 \, \{Mg_8(H_2O)_4(OH)_4[Si_{12}O_{30}]\}; \quad n \leqslant 8.$$
$$\scriptstyle\infty \qquad\quad \infty$$
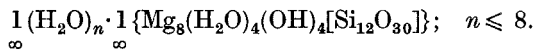
Its unit-cell characteristics are:

$$a = 13.4 \, \text{Å}; \quad b = 26.8 \, \text{Å}; \quad c = 5.28 \, \text{Å}; \quad Z = 2; \quad P\frac{2_1 \, 2 \, 2}{n \, c \, n} - D_{2h}^6.$$

The minerals known in the literature as xylotile, mountain wood and gunnbjarnite are isostructural with sepiolite (Brauner and Preisinger, 1956; Strunz, 1957). In all these minerals the Mg^{2+} ion is partly substituted by the Fe^{3+} ion,

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and the $(OH)^-$ group by the O^{2-} ion. The ideal formula of these ferri-sepiolites (xylotile, mountain wood and gunnbjarnite) is:

$$\underset{\infty}{1}(H_2O)_n \cdot \underset{\infty}{1}\{(Mg,Fe^{3+})_8(H_2O)_4(OH,O)_4[Si_{12}O_{30}]\}; \quad n \leqslant 8.$$
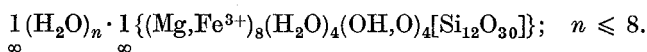
Very similar to the structure of sepiolite is the structure of the mineral loughlinite, in which some of the Mg ions are substituted by Na ions. The formula of the structure of loughlinite is:

$$\underset{\infty}{1}(H_2O)_n \underset{\infty}{1}\{Na_4Mg_6(H_2O)_4(OH)_4[Si_{12}O_{30}]\}; \quad n \leqslant 10.$$
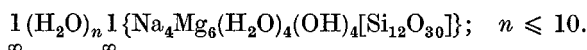
Its unit-cell characteristics are:

$$a = 14.66\,\text{Å}; \quad b = 26.71\,\text{Å}; \quad c = 5.26\,\text{Å}; \quad Z = 2; \quad P\frac{2_1\,2\,2}{n\;c\,n} - D_{2h}^6.$$

The difference between the two structures (Fig. 1) is only that the position of the Mg ion at the end of the complex is substituted by the two Na ions. One of these Na ions substitutes the Mg ion itself; the other is coordinated by 6 H_2O molecules. The calculation of the exact parameters is in progress. Fahey, Ross and Axelrod (1960) showed that loughlinite can be transformed into sepiolite by treating it with $MgCl_2$ solutions. When looking at these two structures (Fig. 1), one can readily understand the result of the experiment. The Na ions are deposited in the channels surrounded by water and thus are easily exchangeable.

A comparison of sepiolite (Brauner and Preisinger, 1956) and palygorskite (attapulgite; Bradley, 1940) shows a similar build-up (Fig. 2). In the (100) plane there are layers of silicate tetrahedra with unshared corners alternately pointed up or down. In palygorskite they alternate after two chains; in sepiolite they alternate after three chains. In palygorskite the six coordinated cations are Mg and Al, with a ratio of Mg : Al varying between 3 : 2 and 2 : 3 (Doelter, 1917).

The ideal formula for the structure of palygorskite is:

$$\underset{\infty}{1}(H_2O)_n \cdot \underset{\infty}{1}\{(Mg_{5-3x},Al_{2x})(H_2O)_4(OH)_2[Si_8O_{20}]\}; \quad n \leqslant 4.$$
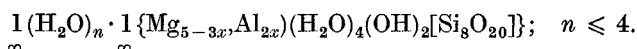
The unit-cell characteristics of palygorskite from Palygorskaja are:

$$a = 12.65\,\text{Å}; \quad b = 17.9\,\text{Å}; \quad c = 5.26\,\text{Å}; \quad Z = 2; \quad P\frac{2_1\,2\,2}{b\;m\,n} - D_{2h}^7.$$

A comparison of sepiolite with Mg-layer silicates, as talc, stevensite, saponite, vermiculite, etc., shows that all these possess layers of silicate with unshared corners of tetrahedra, but in all these latter minerals the direction of the tips does not alternate within the same sheet.

All these fibrous minerals, in which the layers of silicate tetrahedra alternate in orientation of unshared corners, contain three kinds of water molecules: zeolitic water, crystal water and constitution water (OH groups). The water

content of these minerals depends on the humidity. The zeolitic water lies in the channels and its loss is reversible. As shown by Preisinger (1959), no change in the unit-cell dimensions of sepiolite takes place up to 380° C. If sepiolite is
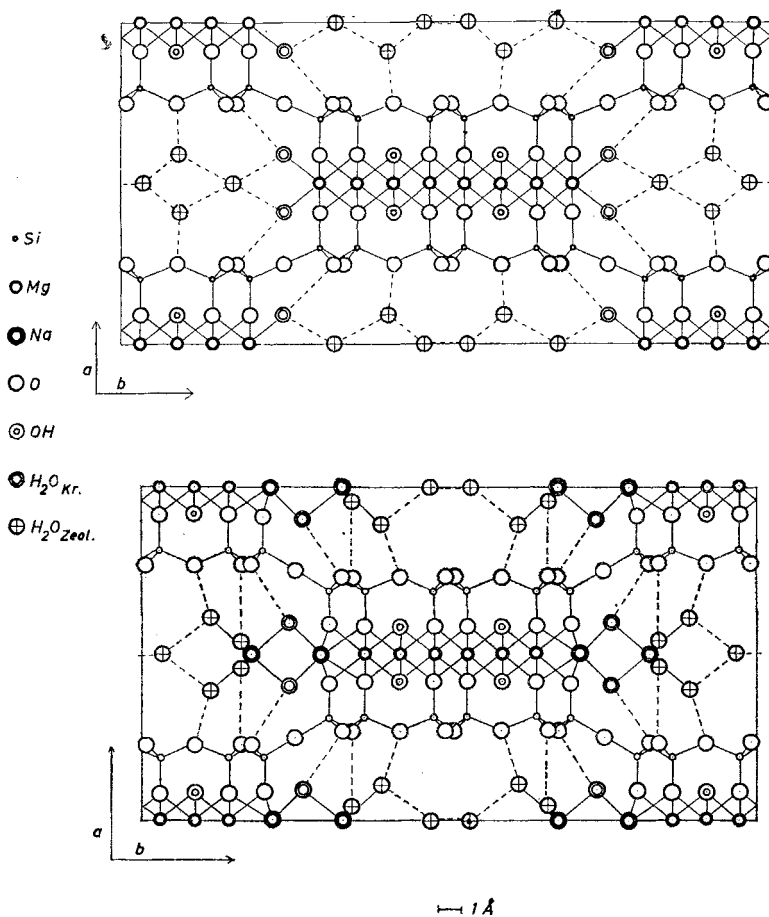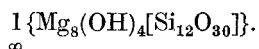

• Si
O Mg
● Na
O O
◎ OH
◐ H_2O Kr.
⊕ H_2O Zeol.

FIGURE 1.—Scheme of the structures of sepiolite and loughlinite projected on the (001) plane.

heated above 380° C, crystal water is lost and a phase transformation takes place (Fig. 3). This phase, sepiolite "anhydride", is stable up to 650° C.

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

$$\frac{1}{\infty}\{Mg_8(OH)_4[Si_{12}O_{30}]\}.$$

Its unit-cell characteristics are:

$$a = 10.9\,\text{Å};\ b = 23.3\,\text{Å};\ c = 5.26\,\text{Å};\ \alpha \sim 90°;\ Z = 2;\ P\frac{2_1}{n}11 - C_{2h}^5.$$

At the phase transformation of sepiolite into sepiolite "anhydride", the symmetry $2_{1/n}$, the c-direction (fiber axis) and c-dimension remain the same, but the layers of silicate become tilted.

- ∘ Si
- ⊙ Mg
- ◯ O
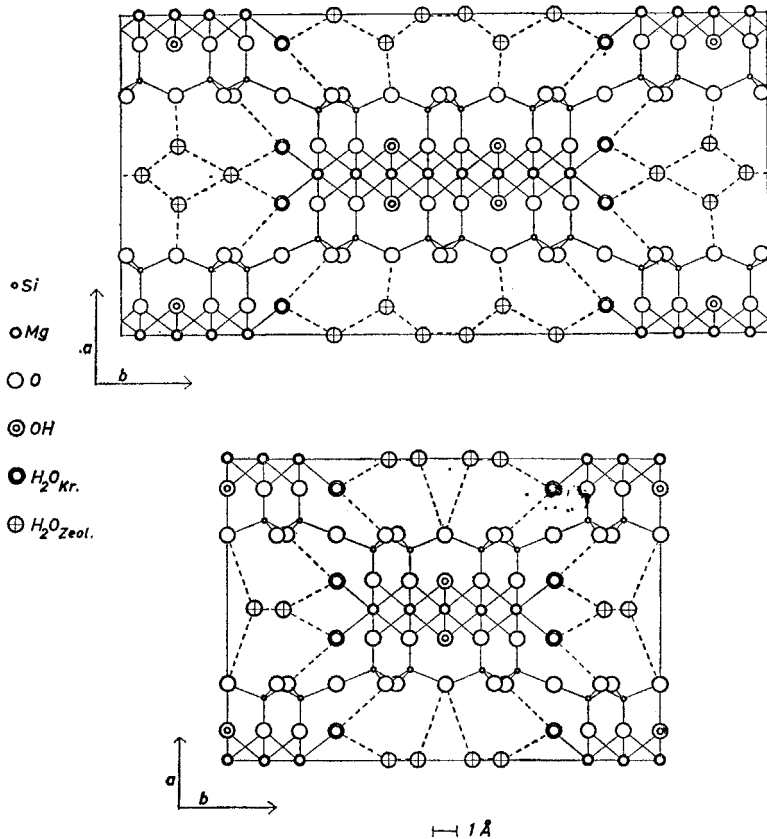- ⊚ OH
- ⬤ $H_2O_{Kr.}$
- ⊕ $H_2O_{Zeol.}$

FIGURE 2.—Scheme of the structures of sepiolite and palygorskite (after Bradley, 1940) projected on the (001) plane.

Very similar to the behavior of sepiolite is that of loughlinite. Loughlinite also changes into a loughlinite "anhydride" by loss of the zeolitic water and crystal water. The ideal formula of the structure of loughlinite "anhydride" is:

$$\overset{1}{\underset{\infty}{}}\{Na_4Mg_6(OH)_4[Si_{12}O_{30}]\}.$$
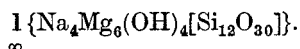
Its unit-cell characteristics are:

$$a = 11.4\,\text{Å};\ b = 24.1\,\text{Å};\ c = 5.26\,\text{Å};\ \alpha \sim 90°;\ Z = 2;\ P\frac{2_1}{n}11 - C^5_{2h}.$$

Calculation of the exact parameters of the structure and study of the thermal behavior are in progress.

If palygorskite is heated up to 350° C only the zeolitic water is lost and the dimensions of the unit cell are not changed. If it is heated above 350° C the crystal water is lost and the structure is changed into palygorskite "anhydride" (Fig. 4). The symmetry $2_{1/b}$, the c-direction (fiber axis) and c-dimen-
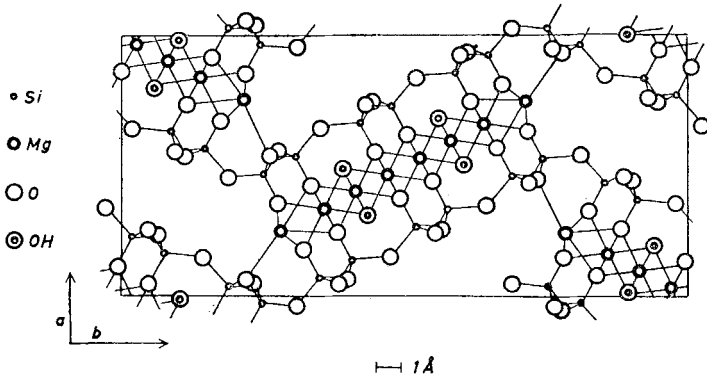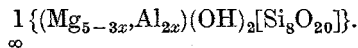

FIGURE 3.—Scheme of the structure of sepiolite "anhydride" projected on the (001) plane.

sion remain the same, but the layers of silicate become tilted. The ideal formula of the structure of palygorskite "anhydride" is:
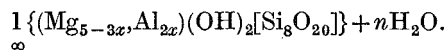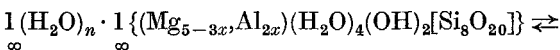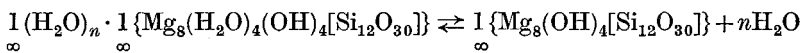
$$\underset{\infty}{1}\{(\mathrm{Mg}_{5-3x},\mathrm{Al}_{2x})(\mathrm{OH})_2[\mathrm{Si}_8\mathrm{O}_{20}]\}.$$

Its unit-cell characteristics are:

$$a = 10.7\,\text{Å};\ b = 15.3\,\text{Å};\ c = 5.26\,\text{Å};\ \alpha \sim 90°;\ Z = 2;\ P\frac{2_1}{b}11 - C^5_{2h}.$$

The palygorskite "anhydride" is stable up to 680° C.

Under low water vapor pressure the phase transformations sepiolite to sepiolite "anhydride" and palygorskite to palygorskite "anhydride" are reversible.

$$\underset{\infty}{1}(\mathrm{H}_2\mathrm{O})_n \cdot \underset{\infty}{1}\{\mathrm{Mg}_8(\mathrm{H}_2\mathrm{O})_4(\mathrm{OH})_4[\mathrm{Si}_{12}\mathrm{O}_{30}]\} \rightleftarrows \underset{\infty}{1}\{\mathrm{Mg}_8(\mathrm{OH})_4[\mathrm{Si}_{12}\mathrm{O}_{30}]\} + n\mathrm{H}_2\mathrm{O}$$

$$\underset{\infty}{1}(\mathrm{H}_2\mathrm{O})_n \cdot \underset{\infty}{1}\{(\mathrm{Mg}_{5-3x},\mathrm{Al}_{2x})(\mathrm{H}_2\mathrm{O})_4(\mathrm{OH})_2[\mathrm{Si}_8\mathrm{O}_{20}]\} \rightleftarrows$$

$$\underset{\infty}{1}\{(\mathrm{Mg}_{5-3x},\mathrm{Al}_{2x})(\mathrm{OH})_2[\mathrm{Si}_8\mathrm{O}_{20}]\} + n\mathrm{H}_2\mathrm{O}.$$

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If the sepiolite or palygorskite is heated above 650° C or 680° C, respectively, the constitution water (OH groups) is lost and clino-enstatite is formed.

The c-axis of the clino-enstatite has the same length and direction as the c-axis of sepiolite. The reaction takes place within the single fibers only. The diameters of these single fibers vary in the same range as the diameters of the single fibers of sepiolite; between 100 and 200Å. The unit-cell characteristics of clino-enstatite (formed by heating sepiolite) are:

$$a \cdot \sin \beta = 9.90 \, \text{Å}; \quad b = 9.19 \, \text{Å}; \quad c = 5.26 \, \text{Å}; \quad P\frac{2_1}{c} - C_{2h}^5.$$

According to Kulbicki (1959), cristobalite is formed if sepiolite is heated above 1200° C. This cristobalite does not show any orientation along the fiber axis.
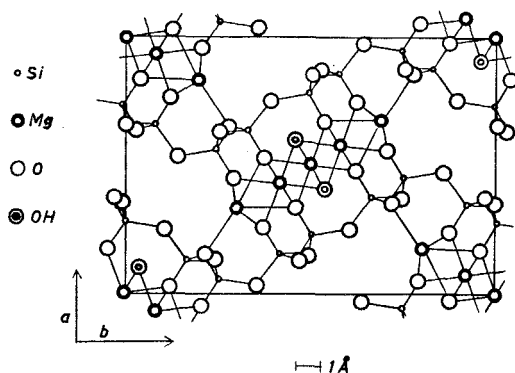

FIGURE 4.—Scheme of the structure of palygorskite "anhydride" projected on the (001) plane.

The range of stability of clino-enstatite formed by heating palygorskite is a function of the Mg:Al ratio. If the ratio is greater than 1, the stability extends up to 1000° C (Kulbicki, 1959). If the ratio is smaller than 1, the range of stability is very small. In the case of palygorskite from Palygorskaja with a Mg:Al ratio of 2:3, high-quartz is formed immediately when heated above 680° C. The unit-cell characteristics of this high-quartz are:

$$a = 10.2 \, \text{Å}; \quad c = 10.81 \, \text{Å}; \quad Z = 24.$$

The Si ions are partly substituted by the Al ions. The Mg ions lie in the channel of the Si(Al)–O framework.

We tried also to synthesize the sepiolite under hydrothermal conditions, but it was not possible to get sepiolite in the system MgO–SiO_2–H_2O under confined pressure within a range of 80° to 300° C.

Yang (1960) observed under hydrothermal conditions, at temperatures higher than 200° C, the formation of either chrysotile or talc depending on the $MgO:SiO_2$ ratio. In our observations with a $MgO:SiO_2$ ratio of 2:3 below 200° C

and various pressures of H_2O and CO_2, we found in all cases a product that could be identified as stevensite. Our own experiments on sepiolite synthesis are still in progress.

The properties of sepiolite that are important for industrial application are its large specific surface (*ca.* 150 m²/g) and the cavity channel in its structure. F. Engel (personal communication) had sepiolite tested for adsorption of exhaust gases and found that about 90 percent of the lead, bromine and sulfur compounds are retained. Only about 35 percent of the hydrocarbons are adsorbed. The experimental arrangement caused an energy loss, by choking, of only 5 percent.

A combination of adsorption and catalytic afterburning could increase the usefulness of sepiolite and related compounds and at the same time keep our cities free of the dangerous compounds of the exhaust gases.

ACKNOWLEDGMENT

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