HIGH TEMPERATURE PHASES IN SEPIOLITE, ATTAPULGITE AND SAPONITE

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ABSTRACT

The high temperature reactions of sepiolite, attapulgite and saponite were studied by continuous high temperature x-ray diffraction techniques.

The easy formation of enstatite from the fibrous minerals is explained by structural analogy. The reactions of the well crystallized specimens of sepiolite and attapulgite differ somewhat from those of their massive sedimentary varieties. The differences cannot be explained with the chemical and structural data, suggesting possible variations in some intimate details of the framework of these two varieties.

INTRODUCTION

The nature of the crystalline phases formed by firing the magnesian clay minerals has been described (2, 3, 7, 10, 12, 15, 16), but only for the well crystallized chlorites (3) have the precise conditions of formation of these phases as well as their structural relationships with the starting material been clearly determined.

The three minerals chosen for this investigation provide different structural arrangements of the same type of lattice in a series of Al-Mg hydrous silicates. Saponite and sepiolite have the same bulk composition but they differ in the mode of assemblage, i.e. layers or ribbons, of their structural units. Attapulgite has the same kind of framework as sepiolite, but a large proportion of magnesium has been replaced by aluminum or iron. It was thought that, by taking advantage of these features and by using a method of continuous high-temperature x-ray diffraction analysis, a new contribution to the problem would be possible.

Details of the procedure were described previously (8, 9). Differential thermal curves with a heating range extended to 1400° C. were also obtained.

SAMPLES INVESTIGATED

Sepiolite

Sepiolite may occur either in large fibrous crystals associated with hydrothermal deposits, or in cryptocrystalline masses of sedimentary origin. Specimens of both types were included in this investigation. Many samples, from various localities were examined and their purity checked by x-ray diffraction. Two apparently homogeneous specimens were retained for high temperature study: an excellent fibrous sepiolite from Ampandandrava (Madagascar) and a fine grained sedimentary one

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from Vallejas (Spain). The former contains some free cristobalite which could not be separated but did not affect the high temperature reactions (Fig. 1).

Attapulgite

Attapulgite also occurs in sedimentary as well as in probable hydrothermal deposits (mountain leather). A sample of mountain leather from the Aleutian Islands* appeared to be a very well crystallized and seemingly pure attapulgite (Fig. 1), but it was impossible to find a sedimentary attapulgite free of other clay minerals. For example, in the course of an extensive study of every clay horizon of the Hawthorne formation, in the Attapulgus, Georgia, area (more than 500 samples have been so far examined and determined), attapulgite was always found with variable amounts of other clay minerals: sepiolite, montmorillonite, illite, or kaolinite. The selected sample contained an estimated 5 to 10% montmorillonite which was removed by centrifugation (Fig. 1).

No chemical analysis of the mountain leather was available, but data published for specimens of similar origin suggest a relatively high aluminum content (Table 1). The Attapulgus sample is rich in magnesium and iron.

Saponite

The selected sample comes from the bentonite deposits of Ksabi (Morocco). It is apparently free of impurities, but its very poor diffrac-

TABLE 1. CHEMICAL DATA OF RAW SAMPLES (RECOMPUTED WITHOUT THE WATER)

	1	2	3	4	5	6
SiO_2	66.82	70.57	63.07	66.67	67.28	69.68
MgO	27.12	21.82	34.12	13.86	8.42	6.93
Al_2O_3	.76	2.79	1.02	10.72	18.05	17.17
Fe_2O_3	3.81	2.20	1.19	3.78	2.04	2.67
FeO	.89				.41	
CaO	.60	2.62	.01	1.92	3.80	3.55
TiO_2				.61		
Na_2O				.52		
K_2O			.60	.43		
P_2O_5				1.61		

1. Sepiolite from Ampandandrava (after Caillere) (5).
2. Sepiolite from Vallejas (after Vivaldi, Cano Ruiz) (11).
3. Saponite from Ksabi (after Millot) (13).
4. Attapulgite from Attapulgus (courtesy of Minerals and Chemical Corp. of America).
5. Palygorskite from Nijni-Novgorod (after Caillere) (5).
6. Palygorskite from Taodeni (after Caillere) (5).
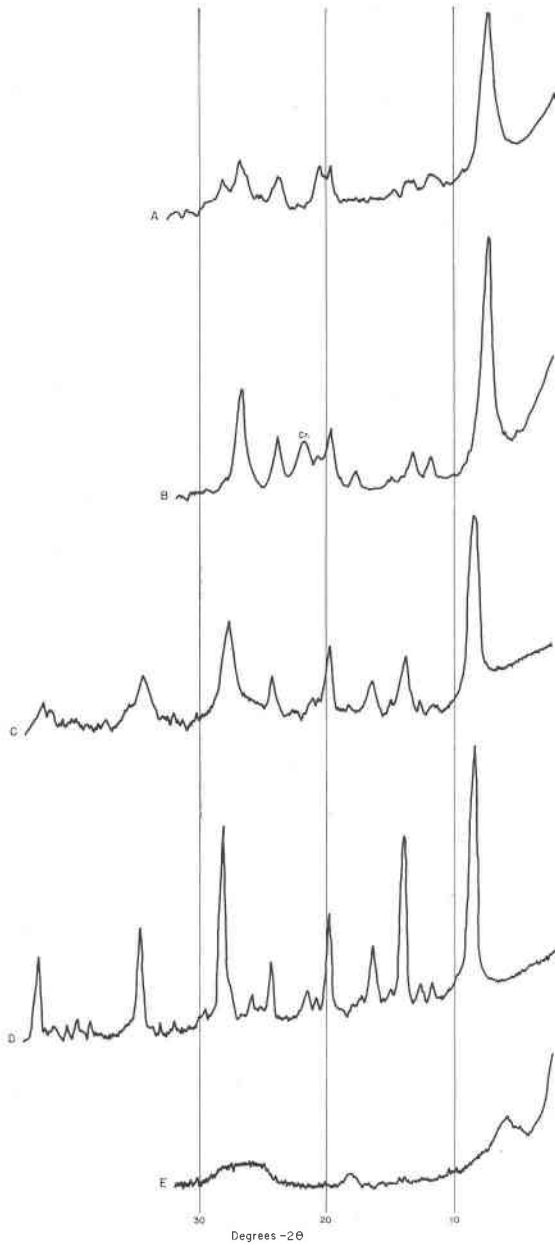
* Courtesy of Dr. W. F. Bradley.

FIG. 1. X-ray spectrometer traces: A. Sepiolite (Vallejas). B. Sepiolite (Ampandan-drava). C. Attapulgite (Georgia). D. Attapulgite (Aleutian Islands). E. Saponite (Ksabi). Unoriented aggregate. CuKα. 2°/1 minute.
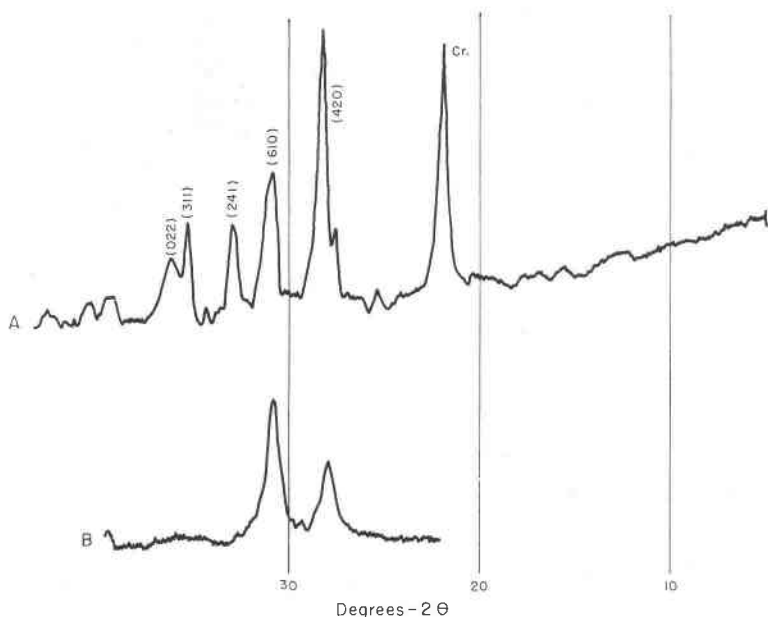
FIG. 2. X-ray spectrometer traces: A. Sepiolite (Vallejas) heated at 1400° C. B. Sepiolite (Ampandandrava) heated at 850° C. Enstatite lines are indexed. Cr: cristobalite.

tion diagram (Fig. 1) suggests many dislocations and lattice irregularities. It is believed to have the same composition as the specimen described by G. Millot from the same deposit (13) which has but little substitutions for magnesium (Table 1).

The influence of exchanged or adsorbed cations on the nature and the conditions of formation of high temperature phases in clay minerals was shown previously (9). Most of these cations can be eliminated by two 15 minute soakings in HCl N/10, followed by a filtration. Except when otherwise indicated, the specimens of this study received this treatment.

RESULTS

Sedimentary sepiolite

The diffraction pattern of the mineral disappears around 800° C. (Fig. 3-A). Simultaneously, two broad lines at 3.20 Å (27.8°, 2θ) and 2.90 Å (30.8°, 2θ) are recorded. These lines grow slowly between 1100° C. and 1350° C., and at that temperature they increase substantially and sharpen, while others appear, completing a pattern of enstatite (Fig. 2-A). Some β-cristobalite is formed at the same time (1350° C). When the firing is stopped, at 1500° C., the sample is sintered but not melted, and enstatite and β-cristobalite are still present. Below 1400° C. the two
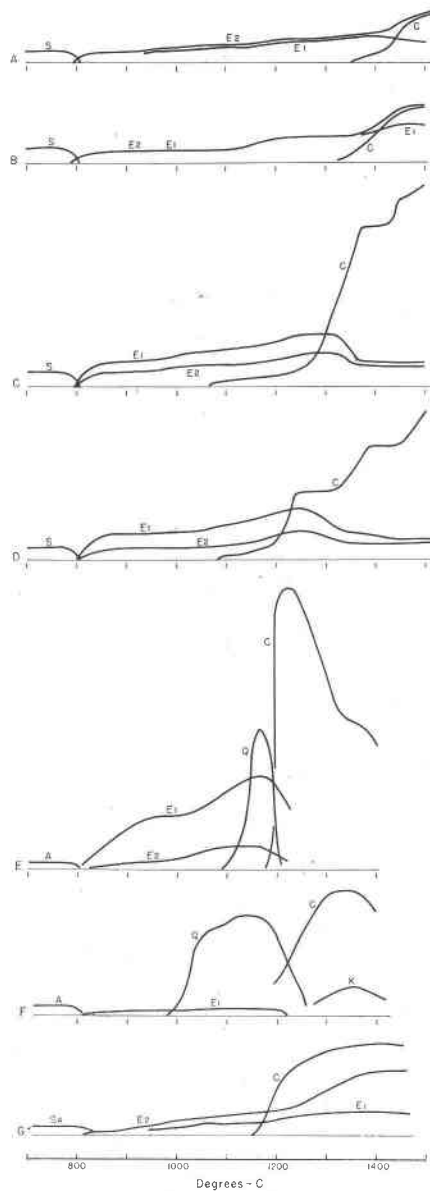
FIG. 3. Intensity of diffraction by high temperature phases in heated specimens of: A. Sepiolite (Vallejas). Treated with HCl. B. Sepiolite (Vallejas). No treatment. C. Sepiolite (Ampandandrava). Treated with HCl. D. Sepiolite (Ampandandrava). No treatment. E. Attapulgite (Georgia). Treated with HCl. F. Attapulgite (Aleutian Island). Treated with HCl. G. Saponite (Ksabi). Treated with HCl. E_1 and E_2: (610) and (420) of enstatite.

main reflections of enstatite (610) and (420) have approximately the same intensity; between 1400° C. and 1500° C. the pattern becomes normal and (420) is twice as intense as (610).

The differential thermal analysis curve shows an endothermic peak at 800° C. followed immediately by an exothermic reaction (Fig. 4-A). The endothermal figure can be related to the departure of water shown on the dehydration curves (10, 11, 12). The exothermal branch is very sudden and sharp, suggesting, according to Bradley and Grim (2), "the incorporation into new phases of large articulate units from reactant structures, without catastrophic rearrangements within the units." There is no other peak on the curve but, above 1200° C., the shrinkage of the sample due to sintering and, possibly, the slow crystallization of β-cristobalite, cause the curve to rise gradually.

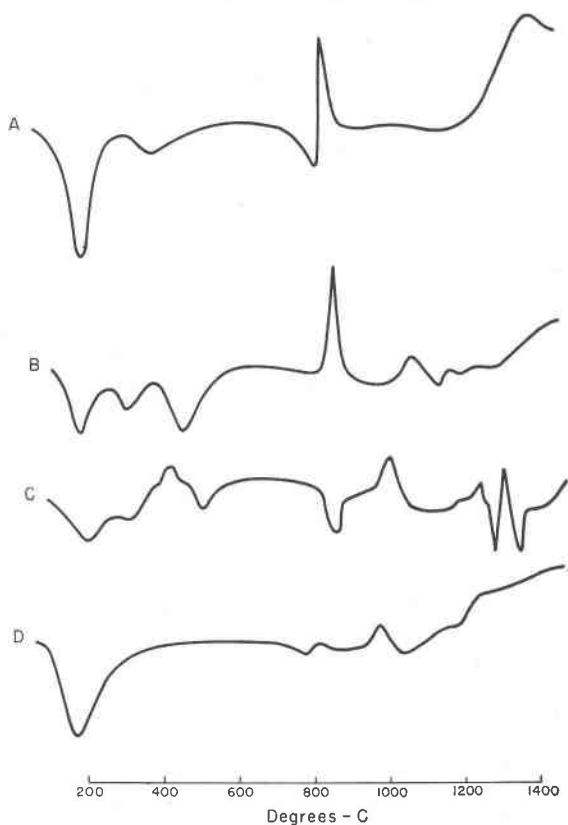Since there is no difference in the high temperature reactions before

Fig. 4. D.T.A. curves. Specimens treated with HCl. A. Sepiolite (Vallejas). B. Attapulgite (Georgia). C. Attapulgite (Aleutian Islands). D. Saponite (Ksabi).

and after HCl treatment, it can be concluded that exchangeable Mg and extraneous Ca cations have no appreciable influence on these reactions (Fig. 3-A, B).

Hydrothermal sepiolite

Enstatite begins to form at 800° C. (Fig. 3-C). Unlike the sedimentary sepiolite, the (610) reflection is more intense than (420). β-cristobalite appears at 1075° C., developing stepwise at 1300° C. and 1450° C. with corresponding decrease of enstatite. It is noteworthy that a sample heated at 1400° C. keeps the needle shape of its particles, as revealed by microscopic observation.

The removal of exchangeable or extraneous cations by HCl treatment does not notably affect the high temperature phases (Fig. 3-C,D).

The high temperature diagrams of the two sepiolite specimens (Fig. 3-A, C) show notable differences in the growing of enstatite, the temperature of initiation and the amount of β-cristobalite. These differences cannot be accounted for by the size of the crystals in the two specimens nor by the slight differences in bulk composition since the sepiolite which contains less silica grows more β-cristobalite and at a lower temperature. No explanation can be proposed at this time.

Sedimentary attapulgite

Like the sepiolite specimens, enstatite is formed when the clay structure is destroyed, at 800° C. (Fig. 3-E). The formation of β-quartz at 1100° C. seems to accentuate the enstatite reflections. Both minerals disappear at 1200° C. with the formation of β-cristobalite. The (420) reflection of enstatite is here 4 times smaller than (610), indicating the preferential growth of the crystals in the a direction.

The D.T.A. curve (Fig. 4-B) shows a single sharp exothermal peak at 800° C. marking the formation of enstatite. A second exothermal peak around 1100° C. can be correlated with the crystallization of β-quartz. The other features are faint and cannot be interpreted.

Various cations (NH_4, K, Cs, Al, Ba, Ni . . .) were fixed on the lattice by base exchange. They did not affect visibly the formation of enstatite, but they acted on the silica phases. The effects were similar to those observed with montmorillonites (9). The most notable was the absence of β-quartz and β-cristobalite in the specimens containing K or Cs.

Mountain leather

Enstatite is formed at the same temperature as for sepiolite but only in a small quantity (Fig. 3-F). It is not affected by the production of

β-quartz at 1100° C. At 1200° C. β-quartz inverts to β-cristobalite. Another magnesian phase, cordierite, appears at 1200° C. It must be noted here that, except for the formation of enstatite between 800° C. and 1200° C., this specimen behaves like a Mg-rich montmorillonite. Thus, a high temperature diagram like Fig. 3-F, including β-quartz, β-cristobalite and cordierite, is typical of a dioctahedral montmorillonite containing a considerable amount of Mg (4–5%) replacing Al (8, 9). Base exchange treatments were also made with various cations, but, unlike sedimentary attapulgite or montmorillonite, no appreciable change in the high temperature phases was recorded. Possibly this indicates only the difficulty of introducing significant amounts of cations inside the framework of this largely crystallized specimen.

At 1200° C. the material is well agglomerated and the needle shape of the starting product is no longer recognizable under the microscope.

Above 800° C., the D.T.A. curve differs completely from that of the Attapulgus sample (Fig. 4-C). Indeed, it is identical with a curve of Mg-rich dioctahedral montmorillonite (8, 9). The collapse of the structure seems to cause the endothermal peak at 805° C. and the crystallization of β-quartz correlates with the exothermic peak at 100° C.

Saponite

The reactions of saponite are very similar to those of the well crystallized sepiolite, but there is very little enstatite at the beginning and its growth is very slow (Fig. 3-G). The relative intensities of (420) and (610) are those of a normal pattern, indicating no preferential growing of the crystals. β-cristobalite appears in appreciable amount at 1200° C. and is accompanied by a substantial increase of enstatite. The reactions cannot be closely correlated with the thermal curves, probably because they are not sufficiently abrupt.

After heating at 1500° C. the specimen is not fused and the two phases are still present.

The high temperature diagrams of the specimens investigated show some significant differences between the well crystallized sepiolite and attapulgite and their sedimentary massive varieties. It has been noted for example that the former have many similarities with the layer minerals of the montmorillonite group. This is not expected from the composition nor the existing structural data. It is suggested that some intimate structural features may be responsible and that the distinction between the two varieties of sepiolite or attapulgite is more than an accidental difference in crystal size due to different growing environments. More studies are needed on this point.

REMARKS ON THE FORMATION OF ENSTATITE

The enstatite nucleation around 800° C. is a common feature of all specimens, which seems at first to indicate that the reaction is primarily due to the magnesium content, regardless of the structure of the starting material. However, it occurs more rapidly and with more intensity in most specimens of the fibrous type minerals, sepiolite and attapulgite, suggesting in turn a favorable effect of this kind of assemblage. This point seems to be supported by the examination of the different structures.

The various structures encountered in this study have been schematically represented in Figs. 5, 6, 7, 8 and 9. These stylized drawings are projections onto the *bc* plane for saponite, and *ab* for the others. It should
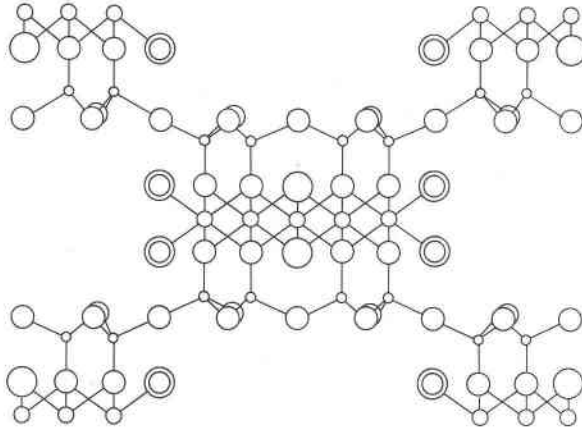

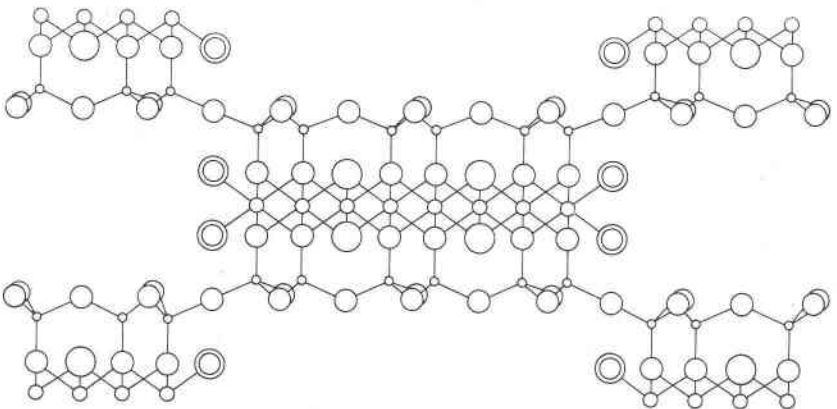FIG. 5. Idealized structure for attapulgite projected onto 001 (after Bradley).

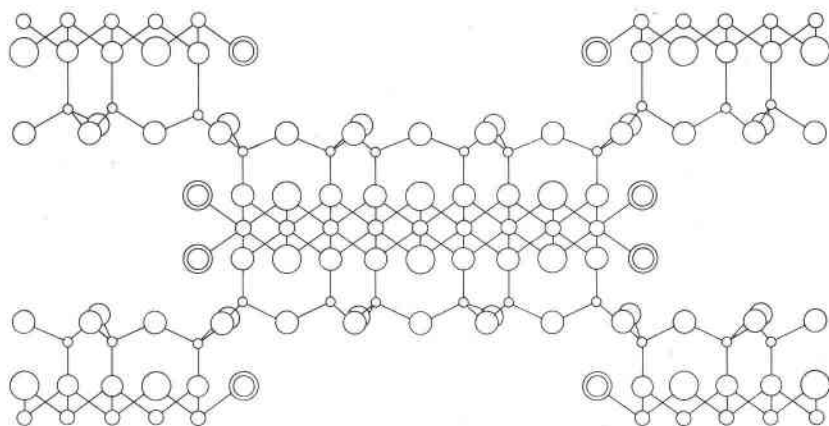FIG. 6. Idealized structure for sepiolite projected onto 001 (after Brauner-Preisinger).

Fig. 7. Idealized structure for sepiolite projected onto 001 (after Bradley).

be remembered that these planes are structurally identical, since the usage has been to call the 5.2 Å period of these silicates, *a* in the layer structures and *c* in the fibrous structures.

For the purpose of the discussion, the hexagonal net of tetrahedra making up the silica layers of all these minerals can be seen as groupings of silica chains $(Si_2 \cdot O_6)$ extending in a direction normal to the drawing. In fact, if we disregard isomorphous replacements, these structures are identically made of groups of "basic units" which are formed of two such silica chains linked by octahedral cations. The relative disposition of these units in the various structures is shown in Fig. 9.
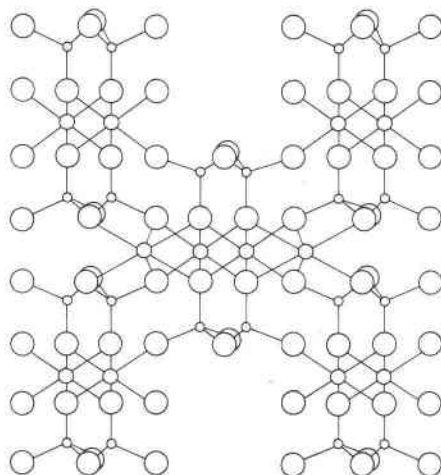

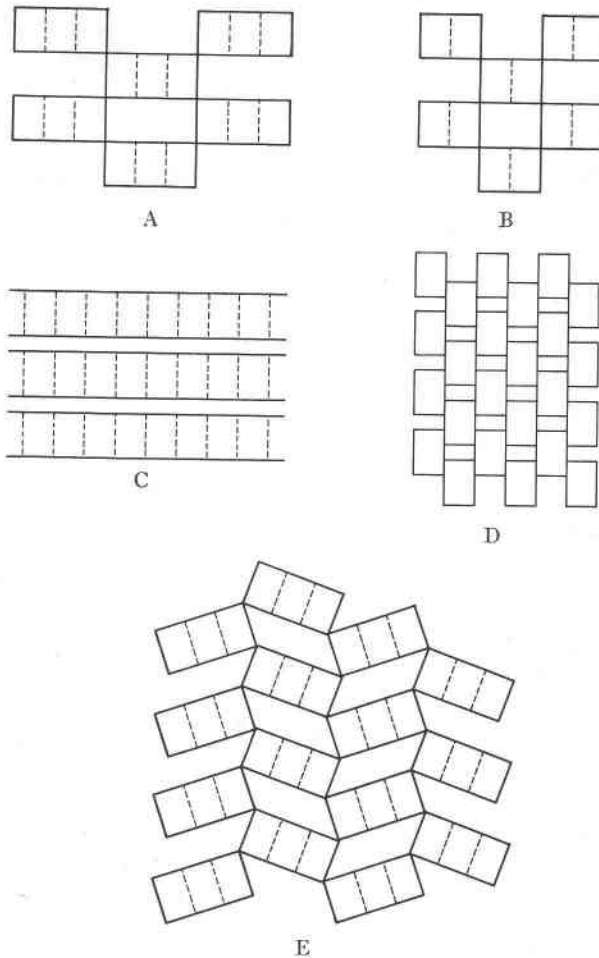Fig. 8. Idealized structure for enstatite projected onto 001.

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FIG. 9. Schematic structures for the investigated minerals showing the mode of associa-
tion of the "basic-chain-units" (dotted lines). A. Sepiolite projected onto 001 (Brauner-
Preisinger proposed structure). B. Attapulgite projected onto 001 (Bradley proposed
structure). C. Saponite projected onto 100. D. Enstatite projected onto 001. E. Dehydrated
sepiolite projected onto 001 (after Preisinger). The angle of tilting is arbitrary.

The close relationships between the enstatite structure and the
structures of sepiolite and attapulgite appear clearly. They explain the
ease of formation of the pyroxene from the latter minerals: the genera-
tion of enstatite can be achieved through the rearrangement of whole
"basic units" reacting edgewise and remaining parallel to their primitive
elongation, without any major disturbance within these units. Thus
enstatite nuclei will be generated upon breaking of the oxygen-ribbon-

edge bonds of the sepiolite assemblage and their linking to the Mg of the octahedral level (Fig. 6, 8 and 9). These nuclei extend mainly in the a and c directions, resulting in only two diffraction lines (610) and (420) with the predominance of (610). In another step, the 3 "basic units" making up a sepiolite ribbon will be separated and then complete the enstatite framework.

These views are based on one of the two alternative sepiolite structures (4, 14, 15) (Fig. 6). In the other one, where the ribbons are linked by double oxygen bonds (Fig. 7), the formation of enstatite as described does not appear immediately possible since it necessitates a more complete reorganization of the atoms. It is suggested that the differences in the production of enstatite in various sepiolite specimens might be due to the coexistence of both structures in a given specimen.

Preisinger (15) has shown that below 800° C. the ribbons of sepiolite take a tilted position as indicated in Fig. 9. The same thing has since been observed for attapulgite by W. F. Bradley and the author* who show that large exchangeable cations like potassium may prevent this tilting to a certain extent. However, in the experiments reported here the amount of tilting of the ribbons does not seem to affect the formation of enstatite.

In the case of attapulgite, the reaction could be theoritically seen in the same way, the variations in the production of enstatite indicating the existence of two alternative linkages of the ribbons (1, 14). However, the different composition of the octahedral layer may, in addition, cause some notable differences. In this mineral, chemical analyses indicate that, in general, only $\frac{1}{3}$ to $\frac{1}{2}$ of the octahedral cations are Mg. If the formation of enstatite necessitates Mg ions along the edges of the ribbons, it will vary with the proportion and with the position of this cation; but in every case it should be less intense than in a sepiolite specimen. On the contrary, high temperature diagrams indicate that, in some instances, enstatite forms more easily than from sepiolite (Fig. 3). It is suggested that the separation of the "basic units," which is necessary for the building of enstatite, is controlled by the disposition of the cations within the octahedral sheet. Unfortunately, nothing is known of the pattern versus composition of the octahedral level to predict the behavior of a specimen.

In saponite, the slowness of the enstatite crystallization may be attributed to the layer structure of the mineral. Some nuclei are first realized along the edge-contacts provided by latice irregularities and dislocations within the crystals. Although these are not negligible, the reaction remains limited to a relatively small number of positions. Upon

* Report in preparation.

increased heating, the "basic units" are progressively separated and they contribute to the gradual growing of the pyroxene structure.

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