NEW DATA ON SEPIOLITE AND ATTAPULGITE[1]

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ABSTRACT

Hydrothermal studies have failed to yield synthetic attapulgite or sepiolites in the system $MgO-Al_2O_3-SiO_2-H_2O$. However, the natural minerals can be decomposed to yield montmorillonoids by mild hydrothermal treatment as low as 200°C and probably as low as 100°C. These data indicate that they are metastable and probably could not have formed at these temperatures.

Dry dehydration at 400° and 750°C gave no evidence for the presence of "zeolitic water" in these minerals and failed to establish the existence of "anhydride" phases. The field study of relationships in one sepiolite locality suggests the importance of structural control in the formation of these minerals.

INTRODUCTION

Recently several workers have investigated various subsystems and joins within the system $MgO-Al_2O_3-SiO_2-H_2O$ at elevated temperatures and pressures (Yoder, 1952; Roy and Roy, 1955; Mumpton and Roy, 1956). Although the stability regions for most of the natural minerals that fall in this system have been determined, there still remain several minerals that have not been synthesized,[2] or that can not be assigned definite stability limits. Owing to the difficulty or in many cases to the inability, of synthesizing such minerals as nacrite, dickite, anthophyllite, attapulgite,[3] and sepiolite, questions regarding the origin —whether stable or metastable—of these minerals are often raised and left unanswered.

This paper presents new data accumulated on the attempted syntheses, the stability relations, and the reactions of attapulgite and sepiolite under both dry and hydrothermal conditions. From these data suggestions regarding the origin of these phases can be correlated with those in the literature and with field observations.

Attapulgite and sepiolite are fibrous clay minerals easily confused with each other in hand specimen. Frequently field specimens of these minerals are described as mountain leather, mountain cork, and mountain wool, in obvious reference to their external appearance. However, sepiolite and attapulgite may readily be distinguished from each other as well as from other clay minerals by

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[2] Although Bowen and Tuttle (1949) claimed to have synthesized sepiolite, Professor Tuttle informs us that the evidence was scarcely sufficient for positive identification of this phase.

[3] The name palygorskite is essentially synonymous with attapulgite, and may have precedence.

powder x-ray diffraction patterns (Longchambon, 1937; Bradley, 1940). The general structure of attapulgite is well established (Bradley, 1940) ; it consists of a two-dimensional layer structure more closely related to the chainlike structures of the amphiboles than are other clay minerals. The structure of sepiolite has been suggested by Migeon (1936), Longchambon (1937), and Nagy and Bradley (1955), to be similar to that of attapulgite.

TABLE 1. — ANALYSES OF SEPIOLITES AND ATTAPULGITES

	1	2	3	4	5	6	7	8	9	10	11
SiO_2	54.83	49.30	52.50	55.34	55.25	51.17	46.67	53.96	54.71	54.04	55.03
Al_2O_3	0.28	1.95	0.60	1.81	9.67	13.73	9.84	8.56	13.48	9.83	10.24
Fe_2O_3	0.45		2.99	0.43	2.32	1.55	0.93	3.10	2.10	3.52	3.53
FeO	–	–	0.70	–	0.19	0.31	1.22	0.19	–	0.19	–
MgO	24.51	18.20	21.31	22.95	8.92	6.40	8.94	10.07	5.44	9.07	10.49
CaO	0.55	5.15	0.47	0.24	1.65	2.89	8.36	2.01	2.79	1.69	–
K_2O	0.03	–	–	–	0.10	–	–	0.03	–	0.08	0.47
Na_2O	0.35	–	–	–	0.76	–	–	0.39	–	0.57	–
H_2O^-	8.18	20.50	21.27	8.60	9.48	10.29	8.29	9.79	8.65	10.00	9.73
H_2O^+	10.74			10.20	10.03	13.24	15.84	11.51	12.63	10.93	10.13
CO_2	–	4.10	–	–	–	–	–	–	–	–	–
TiO_2	–	–	–	–	0.44	–	–	0.24	–	0.32	–
Total	99.92	99.20	99.84	99.57	99.81	99.58	100.09	99.85	99.80	100.24	99.62

1. Sepiolite, Yavapai County, Arizona (Kauffman, 1943).
2. Sepiolite, Salinelles (Gard), France (Migeon, 1936).
3. Sepiolite, Ampandandrava, Madagascar (Caillère, 1951).
4. Sepiolite, Durango, New Mexico (Shannon, 1929).
5. Attapulgite, Quincy, Florida (Kerr and others, 1949).
6. Palygorskite, Nizhni Novgorod, U.S.S.R. (Caillère, 1936).
7. Palygorskite, Siberia, U.S.S.R. (Caillère, 1936).
8. Attapulgite, Attapulgus, Georgia (Kerr and others, 1949).
9. Palygorskite, Taodeni, Sahara, Algeria (Caillère, 1936).
10. Attapulgite, Attapulgus, Georgia (Kerr and others, 1949).
11. Attapulgite, Attapulgus, Georgia (Bradley, 1940).

Several chemical analyses from the literature are listed in Table 1 and are included to show two important points. First, it is apparent from these analyses that sepiolites are hydrous magnesium silicates which contain small amounts of alumina, while attapulgites contain substantial quantities of alumina. In nature there does not seem to be any evidence for a continuous solid solution series between the two, although this might be expected from the postulated similarity of their structures. One cannot, however, arrive at any final conclusions from analyses of the mountain leather minerals because of (1) the relative paucity of analyses, and (2) the difficulty involved in obtaining pure samples free from admixed quartz, calcite, and other clay minerals. The second, and more important point to be made from the analyses is the fact that CaO is always reported in attapulgites and sepiolites. While this may be due to the frequently present lime-containing impurities such as calcite, montmorillonite, or amphi-

boles, it is more than possible that CaO is an essential constituent of these minerals themselves.

NATURAL OCCURRENCES

Sepiolite and attapulgite occur in soils, sedimentary "clay deposits," and alteration products of certain basic igneous rocks, and they are not uncommon as minor constituents of many sedimentary rocks. The literature, however, presents an ambiguous picture of the genesis of these minerals. Their presence is often reported, but detailed descriptions of their relation to accompanying minerals are frequently missing. Although both minerals are found in similar environments, the presence of both in the same deposit is not common.

Lapparent (1936) states that sepiolite is formed by the action of magnesium-rich solutions upon siliceous gels in the presence of lime. Longchambon (1935) attributes the origin of palygorskite to the alteration of pyroxenes and amphiboles, while Kerr (1937) suggests that the attapulgite from Georgia was formed by the alteration of montmorillonite minerals. Caillère and Hénin (1949) have said that certain sepiolites are secondary products resulting from the weathering of enclosing serpentine bodies. Sepiolite, resembling meta-colloidal asbestos, has been reported by Serdyuchenko (1949) to occur in silicified serpentinites accompanied by veinlets of quartz, opal, and calcite, replacing older carbonate host rock. Gerasimov, Grushko, and Chirvinsky (1949) state that palygorskite has been found as a fibrous vein mineral in cellular limestones and dolomites. Both fibrous and lamellar sepiolite were reported from solution cavities in a Madagascar limestone (LaCroix, 1940). In a recent paper, Heystek and Schmidt (1953) suggest that in the progressive weathering of a basalt, it alters first to montmorillonite and then to attapulgite. The amount of attapulgite in any one weathering zone of this basalt can be correlated roughly with the quantity of carbonate present.

From these reports a further question may be raised: if the sepiolite and attapulgite grains in certain sediments are not detrital, why should Mg^{2+}, SiO_4^{2-}, etc., have combined to form sepiolite (or attapulgite) rather than a montmorillonite or talc? This problem is accentuated by the inability to synthesize sepiolite or attapulgite.

EXPERIMENTAL

Although the authors (Mumpton and Roy, 1956) previously encountered neither sepiolite nor attapulgite in the montmorillonite-saponite portion of the system $MgO–Al_2O_3–SiO_2–H_2O$ (see Fig. 1), synthetic gel mixtures were specifically prepared with the approximate compositions of an average sepiolite and an average attapulgite (minus CaO). The oxide ratios in these two amorphous starting gels are:

Attapulgite gel, 69.0 SiO_2:9.2 Al_2O_3:21.8 MgO
Sepiolite gel, 59.6 SiO_2:2.3 Al_2O_3:38.1 MgO

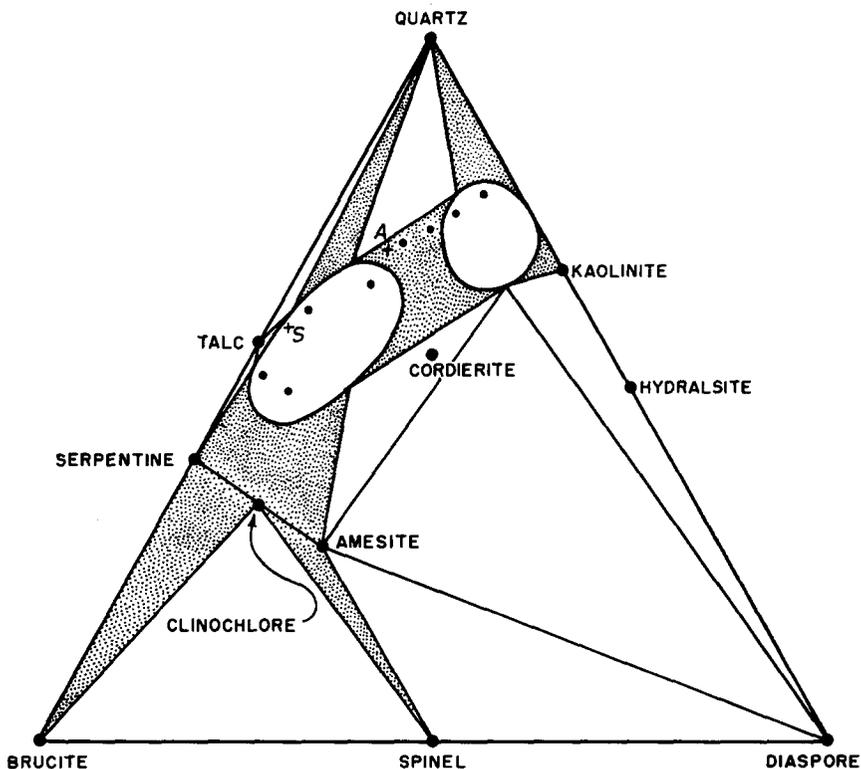FIGURE 1. — Compatibility tetrahedron for the system $MgO-Al_2O_3-SiO_2-H_2O$ (projected on the anhydrous base) at 300°C and 1000 atm., showing stable assemblage of phases. S and A represent the compositions of the sepiolite and attapulgite gels studied. Other solid dots represent compositions studied earlier. The white circular areas are single-phase montmorillonoid areas.

These gels were heated under high water pressure in "test tube" pressure vessels for periods varying from eight hours to three weeks. The details of the hydrothermal methods and equipment have been described by Roy and Osborn (1952), and Roy, Roy, and Osborn (1953).

In a series of about 100 runs these gels yielded only saponite and montmorillonite from about 200°C, under water pressures of from 10,000 to 25,000 psi in runs varying from a few hours to three weeks in duration. Above 350°C, talc, silica, and chlorite phases were found to be stable. These products correspond to those from other gels in this compositional region (Fig. 1). At 100°C and atmospheric pressure the authors previously have shown that gels of montmorillonite composition, on refluxing with water for more than six months, yield montmorillonite. The attapulgite and sepiolite gels were heated to about 300°C under 20,000 psi water pressure and quenched after only 8 and 24 hours in

TABLE 2. — ATTAPULGITE AND SEPIOLITE SPECIMENS

No.	Mineral	Locality
[1]H-43	Attapulgite	Attapulgus, Georgia
[1]H-46-1	Attapulgite	Quincy, Florida
K	Attapulgite	Korea
C	Sepiolite	Cornwall, Pennsylvania
S.L.U.	Sepiolite	Gouverneur, New York
[2]90719	Sepiolite	Jehoi, Mongolia
[2]50884	Attapulgite	Mt. Cook, Venezuela
[2]100400	Attapulgite	Metaline, Washington

[1] A.P.I. Reference Clay Collection.
[2] U.S. National Museum sample numbers.

hopes of metastably forming these minerals, but only montmorillonoid phases resulted.

Since all efforts to crystallize attapulgite and sepiolite from synthetic starting materials failed, one possible conclusion is that these minerals are not stable phases in this system in the presence of excess water. Of course, if lime is an essential constituent of these minerals, their equilibrium relations are thereby removed from the system $MgO–Al_2O_3–SiO_2–H_2O$. Further work on relevant portions of the quinary system $CaO–MgO–Al_2O_3–SiO_2–H_2O$ is contemplated.

Several natural specimens have also been studied under hydrothermal conditions in order to investigate further the stability relations of these minerals, and these are described in Table 2. The results indicated in Figure 2 show that even at temperatures as low as 200°C, under 20,000 psi water pressure, well-crystallized attapulgites and sepiolites break down into well-crystallized "expanding" saponite and montmorillonite structures. At temperatures higher than about 350°C, quartz, talc, and chlorite phases appear. On the other hand attapulgite (USNM 100400) and sepiolite (S.L.U.) remained unaltered after three months treatment in boiling water at atmospheric pressures. X-ray powder methods indicate that attapulgites and sepiolites remain apparently unaffected by hydrothermal treatment below 200°C for as long as three weeks, but electron micrographs show small but noticeable areas of fuzziness on the edges of the fibers which were not apparent in the untreated samples.

The results of dry, static heat[1] treatments for periods of 24 hours are indicated in Figure 3. Sepiolite and attapulgite remained almost unaffected up to about 400°C, where all but a few of the strongest diffraction peaks disappeared. The intensities of these remaining peaks were greatly diminished. At about

[1] After this paper was completed the work of Brauner and Preisinger (1956) came to our attention. It should be noted that the suggestion that reversibly removable zeolitic water is evolved only up to 250°C would explain both earlier references (loc. cit.) to "zeolitic" water and our inability to find any such water at 400°C. These authors have presented the most detailed crystal structure work on sepiolite as yet attempted. They have also indicated that sepiolite occurs in several serpentine deposits and have stressed the structural relationships between the parent serpentine minerals and the sepiolite derived therefrom.
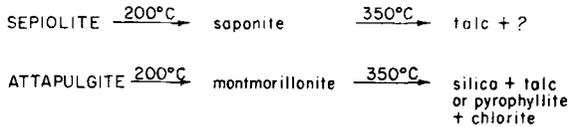
SEPIOLITE —200°C→ saponite —350°C→ talc + ?

ATTAPULGITE —200°C→ montmorillonite —350°C→ silica + talc or pyrophyllite + chlorite

FIGURE 2. — Results of hydrothermal treatments at 20,000 psi water pressure for periods from one to three weeks.

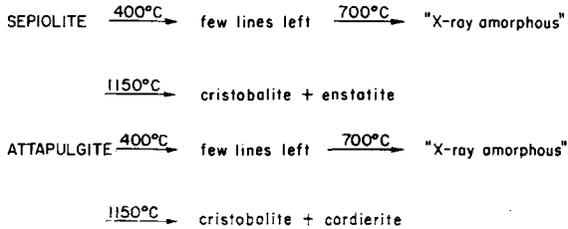SEPIOLITE —400°C→ few lines left —700°C→ "X-ray amorphous"

—1150°C→ cristobalite + enstatite

ATTAPULGITE —400°C→ few lines left —700°C→ "X-ray amorphous"

—1150°C→ cristobalite + cordierite

FIGURE 3. — Results of dry, static heating of sepiolite and attapulgite for 24-hour periods.

700° to 900°C the samples appeared almost x-ray amorphous except for the persistence of a calcite peak at ~ 3.02A. At 1150°C cristobalite and enstatite were formed from the sepiolite, and cristobalite and cordierite from the attapulgite. No trace of the "sepiolite II" or the "attapulgite II" of Migeon (1936) and Longchambon (1937) (supposedly formed above 400°C) was found.

OBSERVED FIELD RELATIONS OF A SEPIOLITE FROM BALMAT, NEW YORK

In August 1956, an opportunity presented itself for the examination of a sepiolite locality. With the kind permission of the Gouverneur Talc Company the occurrence of sepiolite in a talc-tremolite body at Balmat, St. Lawrence County, New York, was studied. The mineral occurs as spongy coatings on most of the fracture, cleavage, and joint surfaces as well as on many "bedding slips" between massive tremolite blocks in several drifts of the mine. When this water-soaked material is dried the characteristic leathery texture becomes apparent. There seems to be no relation between the concentration of talc and that of the sepiolite. Sepiolite appears to have been deposited from ground water and is obviously later than either the talc or the tremolite. A possible explanation is that tremolite has been attacked by ground water, breaking down into almost colloidal size particles which are transported by and redeposited from the ground water along joints, fractures, etc. These colloidal particles retain a structural memory inherited from the parent amphibole, tremolite. Low-temperature crystallization around these nuclei can reasonably lead to sepiolite. The presence of abundant lime at this locality was confirmed, but the question of its effect still remains to be solved. Sepiolite (S.L.U.) from this mine was readily converted to saponite at about 225°C under hydrothermal conditions.

SUMMARY AND CONCLUSIONS

From an analysis of the experimental data obtained from both natural samples and synthetic gel mixtures, sepiolite and attapulgite appear to be metastable phases with respect to saponite and montmorillonite, at least in the system $MgO-Al_2O_3-SiO_2-H_2O$. Under hydrothermal treatment natural samples and gel mixtures yield expanding montmorillonoids above 200°C, with no indication of the formation of sepiolite or attapulgite below. At lower temperatures (100°C) montmorillonite can be synthesized, while natural sepiolite and attapulgite are not rapidly destroyed. Thus, it can be demonstrated unequivocally that above 200°C montmorillonite and saponite are more stable than sepiolite or attapulgite; this is most probably true even at 100°C. Furthermore, it is unlikely that these stability relations will be reversed between 100°C and room temperature. The possibility remains to be investigated, however, that the presence of CaO may alter the stability relations, although it is to be noted that the natural samples, containing any CaO the structure "needs," were converted to montmorillonites by hydrothermal treatment.

Where they are associated with weathered pyroxenes and amphiboles, attapulgite and sepiolite are therefore quite likely to have been formed by the ground-water alteration of these chain structure minerals at low temperatures. The reason for the formation of a mountain leather mineral rather than montmorillonite or talc may be ascribed to structural control from the parent amphibole or pyroxene. The origin of either sepiolite or attapulgite in sediments and soils is still in doubt, although the role of structural control (and the presence of lime) must be an important factor. It would appear to be highly unlikely that a montmorillonoid would be converted to attapulgite or sepiolite.

ACKNOWLEDGMENTS

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