CALCAREOUS SHELLS REPLACED BY BEIDELLITE

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Our knowledge of the mineralogy of clays has been making rapid advances in recent years, but much remains to be determined about the mode of occurrence and genesis, especially as it seems evident that the same mineral may form in various ways. For that reason the formation of an unusually pure clay mineral of the montmorillonite group by replacement of calcareous shells will, no doubt, be of interest.

The replacement of molluscan shells by clay material was first observed (by L. W. S.) in a railroad cut one-half mile south by west of Pontotoc, Mississippi, in 1910, and subsequent visits were made to the locality in 1915, 1936 and 1938.

The shells occur in the coarse-grained, yellowish-brown basal sand of the Clayton formation of the Midway group of Eocene age, which immediately overlies the Owl Creek formation of Upper Cretaceous age. The occurrence, stratigraphic position, and age have been described in the Journal of Paleontology,[1] and this was accompanied by a note on the character of the clay material. The fossil shells are in a good state of preservation, but are very soft and easily damaged. The clay contains a large proportion of excess water, which quickly evaporates on exposure to the air, and the shells shrink and shrivel into thin flaky fragments. Even when packed in damp sand, and allowed to dry slowly for nearly a year, the final state of preservation is very poor. The shells have been reworked and redeposited from an underlying Cretaceous bed which is not exposed in the immediate vicinity, but which must have been nearby, for the shells show little evidence of wear by transportation. Therefore, this transportation must have occurred before their replacement by fragile clay material.

The Clayton sand in which the shells occur is made up mainly of angular to sub-rounded grains of quartz that average about 0.35 of a millimeter in diameter but are variable in size. They are thinly coated with an admixture of highly ferruginous clay and limonite. That is, calcareous shells while enclosed among sand grains coated with a small proportion of iron rich material, were replaced by an extremely pure clay mineral.

The shells are dull olive-gray when moist, and gray to brownish-gray when dry. The material is unusually translucent and resembles horn when dry. The original structure of the shells is very perfectly preserved

[1] Stephenson, L. W., Fossil mollusks preserved as clay replacements, near Pontotoc, Mississippi: *Jour. of Paleontology*, **13**, (no. 1), 96–99, pl. 16 (1939).

in the clay material. In one specimen the minute lamellae of the clay material average about 0.015 millimeter in width, but are sharply distinguishable by the different crystallographic orientation in adjoining areas. A material with a similar, but slightly coarser structure, is illustrated in the accompanying figure. No impurities of any kind were observable after obviously iron-stained material had been removed. The microscope reveals numerous areas where a uniform optical orientation of the clay material permits a determination of its optical properties. The mean index of refraction is about 1.53, which is a little high for minerals of the montmorillonite group, but is, no doubt, due to the iron content. The mineral is biaxial, negative, with a variable axial angle, and the birefringence is about 0.03.
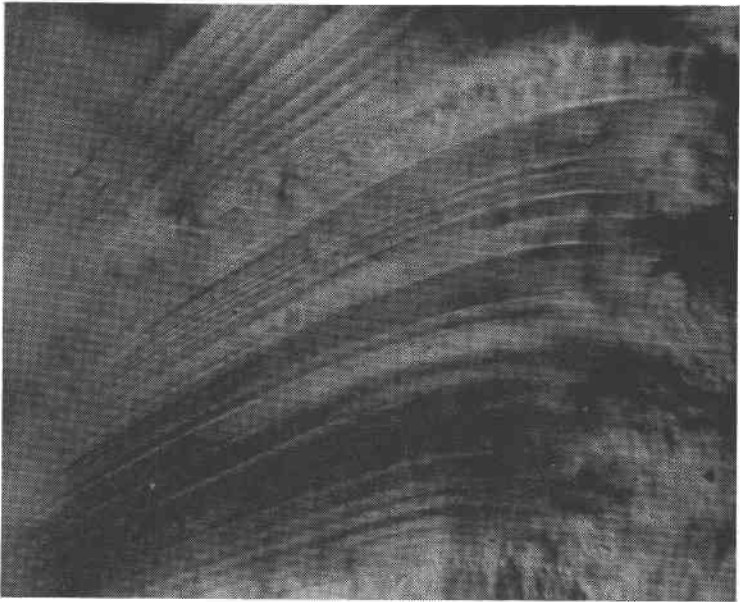

FIG. 1. Photomicrograph ($\times 260$) showing the fine structure of a fragment of a bivalve molluscan shell replaced by clay (beidellite). The photomicrograph was taken under crossed nicols, the structure being shown by a different optical orientation of the clay crystals in the different lamellae.

A sample was prepared for chemical analysis by scraping away the adhering sand grains and the iron stained portions. The results of a chemical analysis are given on opposite page.

CHEMICAL ANALYSIS OF PONTOTOC CLAY MINERAL

(J. G. Fairchild, analyst)

SiO_2	46.95
Al_2O_3	27.26
Fe_2O_3	2.26
FeO	0.32
MgO	1.39
CaO	None
Na_2O	0.20
K_2O	0.36
H_2O-	11.10
H_2O+	10.55
TiO_2	None
P_2O_5	0.03
MnO	0.01
	100.43

The chemical analysis shows that the mineral is the high aluminous beidellite member of the montmorillonite group.

The minerals of the montmorillonite group have a very complex composition which may be represented by several end members. Typical montmorillonite is represented by the following formula: $Al_2Si_4O_{10}(OH)_2$ or $Al_2O_3 \cdot 4SiO_2 \cdot H_2O + Aq$. It nearly always contains some proportion of the analogous nontronite molecule $Fe_2'''Si_4O_{10}(OH)_2$ or $Fe_2O_3 \cdot 4SiO_2 \cdot H_2O + Aq$. The magnesian end member is allied to the "bentonitic magnesian clay mineral" described by Foshag and Woodford,[2] $Mg_3Si_4O_{10}(OH)_2$ or $3MgO \cdot 4SiO_2 \cdot H_2O + Aq$, dimorphous with talc. In part, Al proxies Si in minerals of this group, but where this occurs a negative charge is induced, which must be neutralized by some other substitution. This is, no doubt, brought about in part by K, which forms a link between the sheets, giving the typical muscovite formula, $KAl_2AlSi_3O_{10}(OH)_2$ or $K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 2H_2O$.

The mica probably exists as an interstratification of muscovite and montmorillonite, giving a mixed-layer mineral as described by Gruner[3] for hydrobiotite.

A small part of the Na and perhaps even a little Ca may play the same role as K, but these elements have different ionic diameters and coordination numbers, and are very largely replaceable in the clays; and for the most part are probably not an essential part of the mineral.

[2] Foshag, W. F., and Woodford, A. O., Bentonitic magnesian clay mineral from California: *Am. Mineral.*, **21**, 238–244 (1936).

[3] Gruner, John W., The structure of vermiculites and their collapse by dehydration: *Am. Mineral.*, **19**, 557–575 (1934).

The K, and indeed all the bases other than the Mg, nearly all of which proxies Al and so plays a very different role, are commonly inadequate to balance this negative charge. This balancing is believed to be brought about by OH taking the place of one of the O ions for each Al ion that replaces Si.[4] The resulting formula then becomes $Al_2AlSi_3O_9(OH)_3$ or $3Al_2O_3 \cdot 6SiO_2 \cdot 3H_2O + Aq$.

Small amounts of ferrous iron, no doubt, play the same role as Mg. The Pontotoc clay would then be composed of the following molecules, together with their proportions, recalculated to 100 per cent:

$Al_2Si_4O_{10}(OH)_2$	Montmorillonite	30
$Al_2AlSi_3O_9(OH)_3$	Beidellite	53
$Fe_2Si_4O_{10}(OH)_2$	Nontronite	7
$Mg_3Si_4O_{10}(OH)_2$	Hector clay	6
$KAl_2AlSi_3O_{10}(OH)_2$	Muscovite	4

Dehydration tests of the Pontotoc clay were made by P. G. Nutting of the United States Geological Survey, and these show that it contains about 8 per cent of H_2O, which is lost above 430°C., where there is a sudden break in the dehydration curve. Normal montmorillonites (those which approximate a 1:4 silica:alumina ratio) contain 4 to 4.5 per cent of water under the same conditions. This greater percentage of high-temperature H_2O tends to confirm the conclusion that the high-alumina clays should be higher in essential water. In fact, 8 per cent is a little too high, as a pure beidellite $[Al_2AlSi_3O_9(OH)_3]$ should, according to the theory, contain about 7.5 per cent of H_2O.

The replacement of calcareous shells by clay material raises a question as to the chemistry of the process. It is evident that clay forming material must have been introduced into the shells from the outside and solutions of some kind are the only means for such replacement. Clay is a material that, no doubt, is commonly transported in colloidal solutions, which have small power of penetration, and are ineffective for the removal of replaced material. It, therefore, seems probable that the calcareous shells from near Pontotoc were replaced by solutions carrying the necessary elements for the formation of clay in true chemical solution. These solutions dissolved and removed the $CaCO_3$ of the shells and at the same time were introducing Al_2O_3, SiO_2, a little Fe_2O_3, MgO, and unimportant amounts of other elements. In these sands there is no evidence of thermal solutions, and the transfer seems to have been due solely to those acting at normal earth temperatures. The clay mineral contains no CaO, although a small percentage is normally present in minerals of this group. This is surprising, as it shows the complete removal of CaO from the calcium carbonate of the shells.

[4] Hendricks, Sterling B., Personal communication.

About 14 miles north of Pontotoc and $3\frac{1}{4}$ miles south of New Albany, there is a bed that contains abundant reworked Cretaceous shells and occupies the same position at the base of the Eocene. Here the shell bed is from 2 to 3 feet thick, and is a greenish-gray, sandy, coquina-like, friable limestone. The matrix between the shells contains abundant limonitic oolites, and a few spherical grains of calcite. The shells are for the most part calcium carbonate, but here and there the calcium carbonate has been partly replaced by clay material of the same type previously described.