

HYDRATED HALLOYSITE IN BLUE HILL SHALE

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ABSTRACT

Nodules of alunite and hydrated halloysite occur in the upper part of the Cretaceous Blue Hill shale at three localities in west-central Kansas. They have formed at the contact of septarian concretions with the shale and are associated with gypsum. The nodules are judged to have been formed by the action of sulfuric acid from pyrite on the potassium-bearing minerals of the Blue Hill shale, perhaps under special conditions of pH and Eh produced locally by the presence of septaria.

The minerals were studied and identified by x-ray diffraction, thermal data, chemical analysis, and electron and light microscopy.

INTRODUCTION

Scope of Report

Nodules containing hydrated halloysite and alunite were discovered during an investigation of a shale pit by the State Highway Commission of Kansas. It is the first halloysite reported from Kansas, and although it is not a commercial deposit, its occurrence is such as to warrant study.

The character and associations of the clay were observed in the field, and the minerals were studied in the laboratory by means of x-ray diffraction, differential thermal analysis, chemical analysis, and electron and light microscopy.

Location

The halloysite deposits described in this report occur mostly in the SW $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 23, T. 16 S., R. 21 W., and the SE $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 7, T. 17 S., R. 21 W., Ness County, Kansas. A few fragments of the clay were also found in the same type of geologic setting in the SW $\frac{1}{4}$ SW $\frac{1}{4}$ sec. 32, T. 14 S., R. 21 W., Trego County, Kansas.

Field Work

The halloysite nodules were first identified as such in the field during the spring of 1952. After that time a number of trips were made to the area by the writers for purposes of general reconnaissance and collection of samples.

It was not until late summer of 1953, however, that samples of the halloysite in hydrated form were collected. These samples were preserved

by wrapping them in wet cotton and aluminum foil as soon as they were removed from the ground. During this same period most of the field work to determine the occurrence and field relationships of the deposits was carried out.

Acknowledgments

Initial identification of the halloysite by x-ray diffraction was made by R. D. Dragsdorf, Kansas State College. The differential thermal curves in Figure 2 were made by Norman Plummer, and the chemical analyses were done in the laboratories of the State Geological Survey under the supervision of R. T. Runnels. Spectrographic analyses were made by John Schleicher.

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GENERAL GEOLOGY AND FIELD OCCURRENCE

The halloysite nodules occur in the upper part of the Blue Hill shale member of the Carlile shale of upper Cretaceous age. The Blue Hill shale member is a gray to bluish-black, noncalcareous silty clay shale with thin sandstone layers in the upper part. Zones of abundant calcareous septarian concretions of various sizes are also present in the upper half of the shale. The clay nodules occur around the periphery of these septaria at their contact with the shale.

The Blue Hill shale in this area is reported (Bass, 1926) to be 175 feet thick. No measurement of the entire thickness could be made in the area of occurrence of the clay nodules as there are no complete exposures.

The following section of approximately the upper one-half of the shale is the best one available at an occurrence of the clay nodules (SE $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 7, T. 17 S., R. 21 W., Ness County). This is a composite section in which part of the upper 5 feet of the Blue Hill shale was obtained by pitting, and the rest of the section was measured about 500 feet to the west.

<i>Bed</i>	<i>Thickness, feet</i>
Niobrara chalk	
Fort Hays limestone member	
Limestone, white, chalky; weathers to light yellowish-brown; contains one thin shale break.....	4.0
Carlile shale	
Blue Hill shale member	
Shale, gray to blue-gray; entire thickness limy with limy nodules in lower part	5.0
Sandstone, brown, medium-grained; cemented in streaks with lime. Sharks' teeth and numerous fossil fragments.....	0.5
Shale, gray to blue-gray, silty to clayey.....	3.5
Sandstone, tan to brown, fine-grained; cemented in part with pyrite; heavy limonite stains in zones surrounding the pyrite.....	0.05
Shale, gray to blue-gray, mottled, silty.....	1.0
Sandstone, light grayish-yellow, very fine-grained.....	0.2

<i>Bed</i>	<i>Thickness, feet</i>
Shale, blue-gray, clayey.....	4.5
Sandstone, light-yellow to tan, very fine-grained.....	0.05
Shale, gray to dark blue-gray, clayey to silty.....	3.7
Sandstone, tan to light-brown, very fine-grained.....	0.02
Shale, blue-gray, clayey to silty.....	1.3
Sandstone, light grayish-yellow, very fine-grained (nearly a siltstone).....	0.15
Shale, gray to blue-gray, clayey; contains a few small selenite crystals....	6.3
Sandstone, yellowish-tan to dark-tan, very fine-grained.....	0.25
Shale, blue-gray to gray, silty. Uppermost zone of septarian concretions found here which along with those occurring about 3 feet lower are hereafter referred to as <i>zone one</i> septaria (described later).....	5.6
Sandstone, tan to brown; contains brown streaks of limonite which seem to represent weathering of pyrite.....	0.2
Shale, blue-gray, clayey.....	2.2
Sandstone, yellowish-gray to tan; bends upward around lowermost of zone one septaria. Some associated alunite and halloysite.....	0.1
Shale, blue-gray, clayey.....	0.4
Sandstone, tan to light-gray, medium-grained; seems to bend downward around lowermost of zone one septaria.....	0.1
Shale, gray to blue-gray, nearly fissile. Some selenite crystals on surface..	4.7
Sandstone, tan, shaly, fine-grained. Centers of <i>zone two</i> septaria located in this sandstone. Abundant selenite crystals under septaria.....	0.35
Shale, light-gray, silty.....	1.5
Shale, tan, sandy.....	0.05
Shale, light-gray, clayey to silty.....	3.3
Shale, tan, sandy, very fine-grained.....	0.1
Shale, light-gray to blue-gray, clayey.....	2.7
Sandstone, tan, shaly, fine-grained.....	0.05
Shale, blue-gray, clayey.....	2.4
Shale, blue-gray to light-gray, silty.....	1.6
Sandstone, tan, fine-grained. Centers of <i>zone three</i> septaria located in this sandstone	0.1
Shale, light-gray to light blue-gray, clayey.....	1.2
Shale, light-gray slightly mottled with tan, clayey.....	4.9
Shale, dark bluish-gray, clayey. Selenite crystals becoming more abundant	7.8
Shale, dark bluish-gray, clayey. Abundant selenite crystals. <i>Zone four</i> septaria have their centers in this shale.....	3.5
Shale, dark blue-gray; clayey "paper" shale with abundant fine selenite crystals	11.3
Shale, dark blue-gray, clayey; contains <i>zone five</i> septaria.....	1.8
Shale, dark blue-gray, clayey; contains much gypsum.....	3.6
Total Blue Hill measured	86.07

The septarian concretions of *zone 1* are generally cream-yellow, flattened spheres which average about 2.0 feet by 1.5 feet in diameter. The body of the septarium is gray to dark gray showing faint radial structure that appears as pseudo-cone-in-cone on the weathered surface. The outer crystalline septa, which weather into prominent relief, join in the center to outline cavities lined with calcite crystals. Small fragments of weathered clay nodules are associated with some of the zone 1 concretions.

The *zone 2* septaria are brown on the surface and slightly larger than

those of zone 1, averaging about 2.5 feet by 1.5 feet. The interior is dark blue-gray and dense. The septa, although prominent, do not weather in as sharp relief as do those of zone 1. Zone 2 septaria are more abundant than those of zone 1.

The bedding of the shale and thin sandstones bends around some of the zone 2 septaria. Surrounding the harder ribbed part of the septaria is a soft, tan to brown, claystone layer 0.2 to 0.3 feet thick which shows a radial structure somewhat like that of cone-in-cone. Alunite nodules occur at the periphery of this layer at the contact with the shale and thin sandstones.

Zone 3 septaria have hard tan to red rims 0.5 feet thick, or more, which surround gray, dense interiors. The septaria of this zone are much larger than those of zones 1 and 2 and have dimensions as great as 10 feet by 15 feet by 4 feet. Although they are flattened spheres, the sphericity is less pronounced than that of the concretions of zones 1 and 2. Very thin gypsum rims and minor quantities of clay nodules occur around some of these septaria. A few septaria resembling those of zone 1 in size and color but with less perfect sphericity occur in this zone with associated alunite and halloysite.

Zone 4 septaria are similar in size and shape to those of zone 3 but lack the hard outer tan claystone rim. They are light gray in color and commonly have a thin gypsum coating. Thick dark-brown veins of calcite are prominent. Some clay is associated with these septaria in minor amounts.

The septaria of zone 5 are about the size and color of those of zone 1, but are more elongate. Ribs are present but not prominent. Gypsum rims are common, and alunite and halloysite are present in small amounts.

Some septaria of the Blue Hill shale contain hydrocarbons which give the brown calcite its color. Many septaria contain marcasite or pyrite, or limonite pseudomorphic after pyrite. This suggests the former presence of organic matter.

The clay nodules are associated with all five zones of septaria. Not all the septaria in any zone have halloysite or alunite associated with them, and the factors determining the presence or absence of these minerals are not known.

Gypsum is more common than either alunite or halloysite; some septaria have thick gypsum rims (Pl. 1A). Any halloysite or alunite associated with such septaria is found near the outer edge of the gypsum. Most of the halloysite and alunite occurs as small nodules (up to 2 inches in diameter) around the periphery of the septaria (Pl. 1B). One highly weathered septarium without gypsum shows a partial inner rim of halloysite and an outer rim of alunite.

In the nodules themselves alunite is more common than halloysite; many nodules consist of alunite alone. Many consist of a core of alunite surrounded by halloysite (Pl. 2A). Halloysite without associated alunite is rare (Pl. 2B).

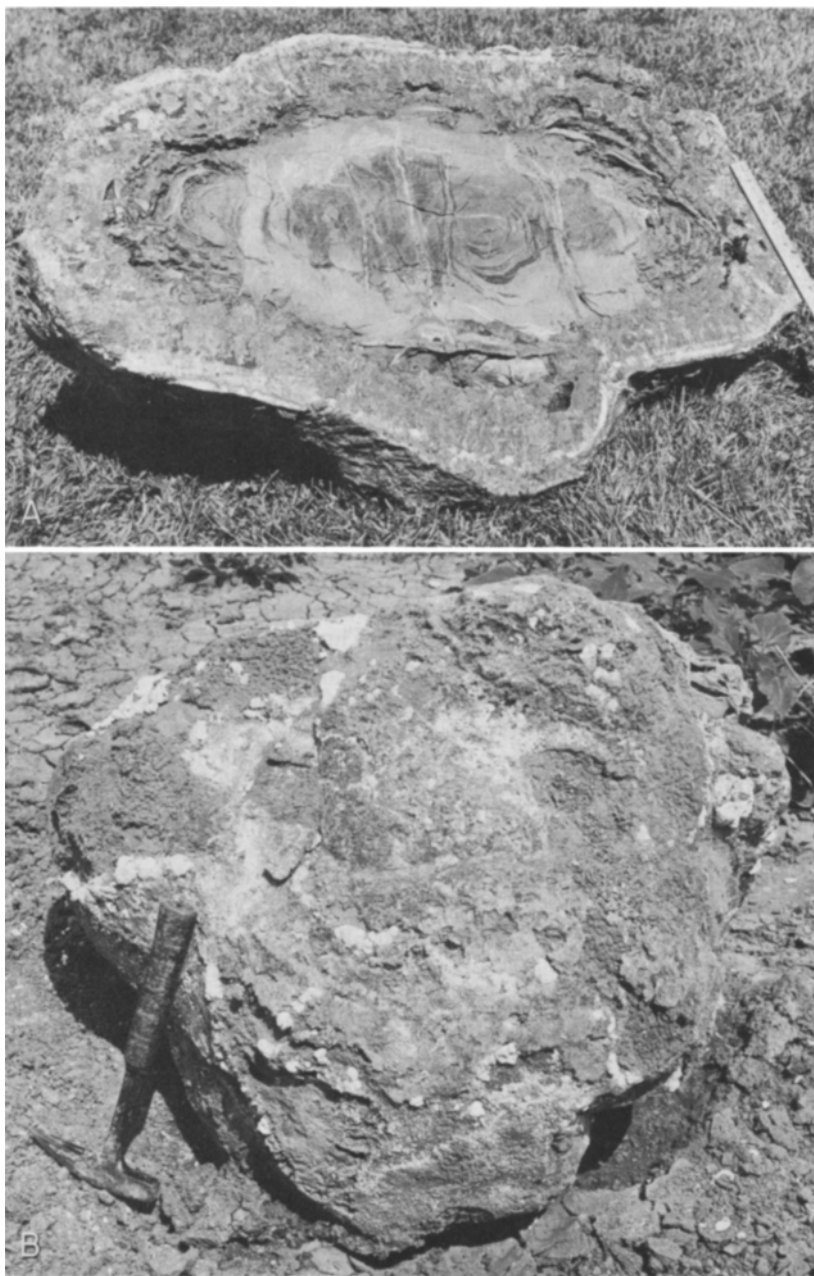


PLATE 1.—Septarian concretions from Blue Hill shale.

A. Slice through center of septarium showing hard calcite core, inner calcite-shale

zone, and four-inch rim of gypsum containing halloysite and alunite in outer part. Calcite veins cut core and calcite-shale zone.

B. Septarium with clusters of halloysite-alunite nodules at periphery.

LABORATORY DATA

X-ray Diffraction

Diffraction data were obtained with a G.E. diffractometer using nickel-filtered copper radiation and operated at a speed of $0.2^\circ 2\theta$ per minute. Standard methods of analysis were used (Brindley, 1951).

Minerals of the upper Blue Hill shale indicated by the diffraction patterns are, in rough order of abundance, montmorillonite, quartz, kaolinite, illite, feldspar, muscovite, and traces of chlorite and gypsum. The montmorillonite basal reflection (001), before treatment with glycerol, is about 15.3A; this suggests a Ca-saturated clay. No 14A reflections for chlorite are observed, and those peaks attributed to kaolinite are destroyed by heating at 600°C for 30 minutes. Traces of chlorite are suggested by a weak reflection at 4.7A. The chlorite, muscovite, gypsum, and most of the quartz and feldspar are concentrated in the fraction coarser than 0.6 microns.

The soft translucent hydrated halloysite shows reflections for that mineral only (Fig. 1A). After partial dehydration the mineral is more difficult to distinguish from alunite megascopically, and diffraction patterns from most halloysite nodules which have been partly dehydrated at the shale pit show alunite reflections as well as those from halloysite (Fig. 1B). Most specimens of seemingly pure alunite also give weak reflections for halloysite.

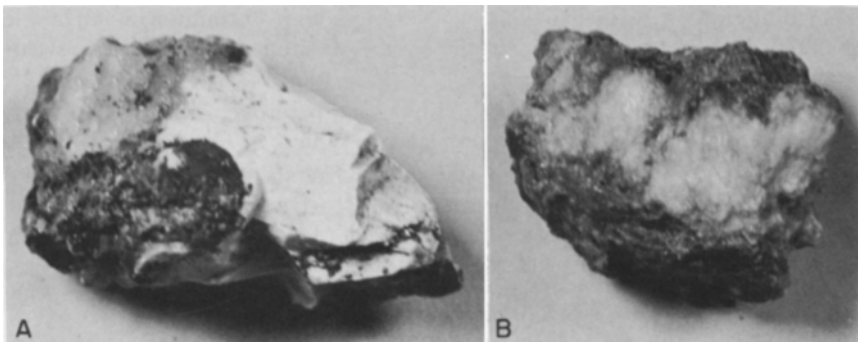


PLATE 2. — Halloysite-alunite nodules.

A. Part of a nodule having core of white alunite and outer portion of bluish-gray translucent hydrated halloysite. X 1.6.

B. Nodule containing only pink hydrated halloysite surrounded by shale. X 1.6

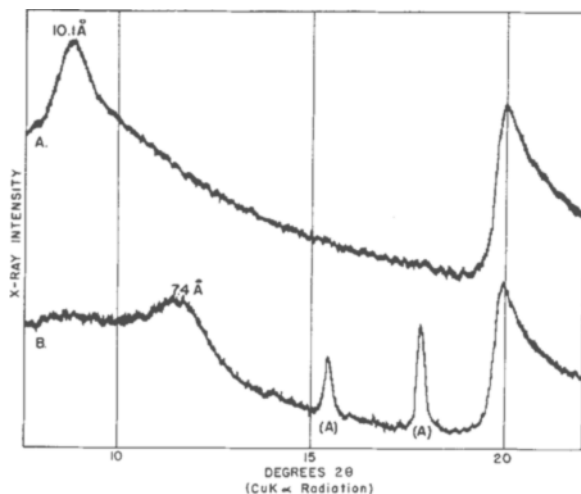


FIGURE 1.—X-ray diffractometer patterns of (A) hydrated halloysite, and (B) a mixture of alunite and halloysite which had been partly dehydrated at the exposure. The reflections for alunite are indicated by the letter *A*.

Some diffraction patterns from halloysite-alunite mixtures also show a faint suggestion of a low broad montmorillonite basal reflection at about 15Å.

Electron Microscopy

Samples of the pink hydrated halloysite (also used for chemical analysis) and of the minus 1 micron fraction of Blue Hill shale were examined in the electron microscope. The clay was deposited on collodion substrates from dilute water suspensions and shadowed with chromium at an angle of about 20 degrees. The preparations were examined in a Philips microscope (EM-100) operated at 40 kv.

The particles from the Blue Hill shale are heterogeneous in character, and many of them have a cottony appearance typical of Ca-montmorillonite.

Electron micrographs of the halloysite are shown in Plate 3. The particles in the halloysite preparation seem to consist almost entirely of halloysite tubes; few impurities are observed (Pl. 3A). Aggregates which show pronounced parallel orientation of the tubes are common (Pl. 3B).

Differential Thermal Analysis

Preliminary differential thermal analyses were made on most of the samples at a rate of 66° C per minute. Previous investigations had shown that this rate was adequate for rapid determination of clay minerals. It also permits several determinations to be made during one day using the same equipment.

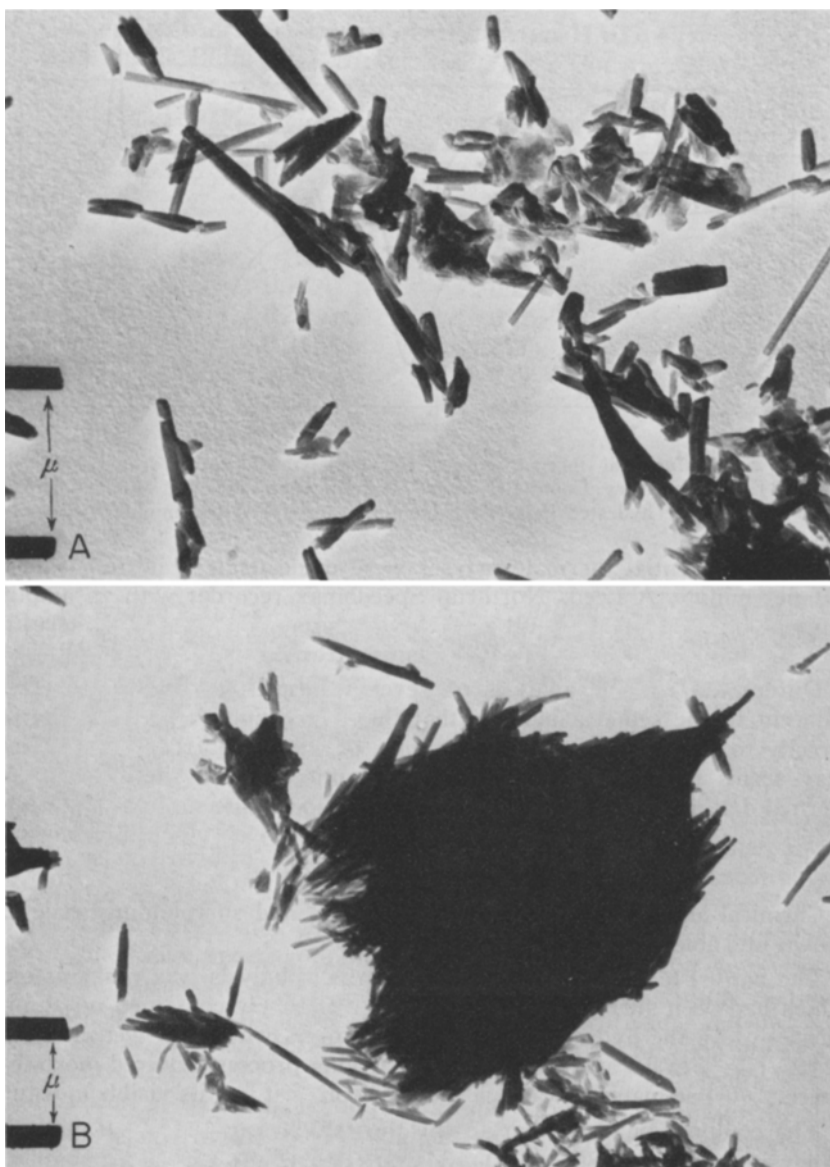


PLATE 3.—Electron micrographs of pink halloysite, shadowed with chromium from angle of 20 degrees.

A. Dispersed halloysite tubes. Magnification 20,000 X.

B. Aggregates of oriented tubes. Magnification 11,500 X.

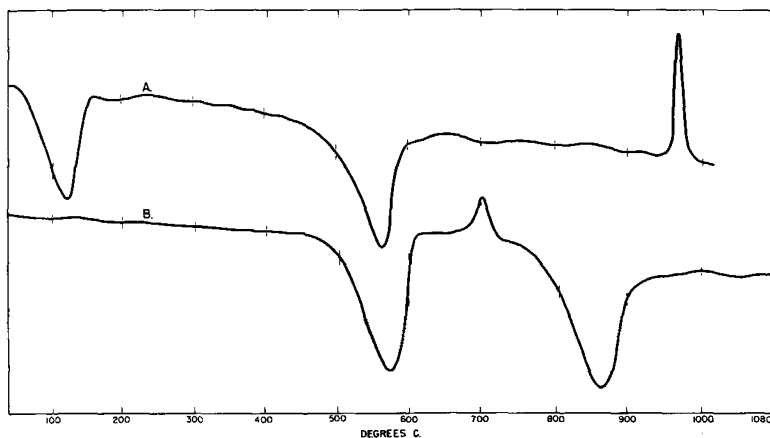


FIGURE 2.—Differential thermal curves for (A) translucent hydrated halloysite, and (B) alunite, Ness County, Kansas. Amplification for the alunite curve is twice that for the hydrated halloysite. Heating rate 10° C per minute.

Final differential thermal analyses were made using a heating rate of 10° per minute. A Leeds Northrup Speedomax recorder with an amplification of 4 and a pre-amplification of 20 was used for the halloysite (Fig. 2A), and a pre-amplification of 40 was used for the alunite (Fig. 2B).

Differential thermal analysis of several samples of shale from areas adjacent to the septaria indicate that the shale might have been altering directly to halloysite. Gradation in color of the shale from dark to light gray seems to be a function of the amount of halloysite present. No thermal data indicated an alteration of shale to alunite.

Chemical Composition

Chemical analyses of the halloysite, alunite, and surrounding shale are shown in Table 1.

The halloysite sample selected for chemical analysis was pink material which had been surrounded by shale and apparently contained no alunite. Originally in the hydrated form, it was ground while still wet, and then dried over silica gel at 5° to -5° C. The drying process required more than a week, and the material was analyzed as soon as it lost its visible moisture.

The composition is similar to the theoretical composition of hydrated halloysite (SiO_2 , 40.86; Al_2O_3 , 34.66; H_2O , 24.48 percent). If all the SiO_2 is assumed to be in halloysite, the material consists of 95.99 percent hydrated halloysite. Of the 4.01 percent impurities, 3.12 percent is adsorbed water. This value agrees with the quantity of adsorbed water at greater than 20 percent humidity as indicated by Brindley and Goodyear (1948, p. 409). The ratio $\text{SiO}_2:\text{Al}_2\text{O}_3$ is 194:100.

TABLE 1. — CHEMICAL ANALYSES OF HYDRATED HALLOYSITE, ALUNITE, AND UPPER BLUE HILL SHALE FROM NESS COUNTY, KANSAS

	Hydrated halloysite	Alunite	Upper Blue Hill shale
SiO ₂	39.22	0.90	63.31
Al ₂ O ₃	34.22	35.36 ³	18.61
Fe ₂ O ₃	0.10	0.21	4.29
TiO ₂	trace (<.0001)	—	1.09
CaO	0.18	0.22	0.40
MgO	0.29	0.26	1.72
MnO ₂	0.01	N.D.	N.D.
P ₂ O ₅	N.D.	0.37	0.07
SO ₃	none	35.45	0.07 ⁵
K ₂ O	0.09	10.19	3.62
Na ₂ O	0.10	0.42	0.25
H ₂ O at 105° C	13.00	0.13	—
H ₂ O at 140° C	0.62	0.03	—
Ignition loss	13.00 ¹	16.69 ⁴	6.40 ⁶
Total	100.83 ²	100.23	99.84

¹ At 1000° C.

² Ni, .0074 ± .0025; Cr, .0063 ± .0001; V, .0037 ± .0003; Ga, .0035 ± .0008; Mo, .0035 per cent, determined spectrographically.

³ Includes MnO₂, TiO₂, etc., if present.

⁴ At 500° C.

⁵ Sulfide sulfur (S) = 0.10. Calc. FeS₂ = 0.19.

⁶ At 1100° C.

An analysis of an alunite nodule which contained no visible porcellaneous halloysite indicates that the sample consists of 91.7 percent alunite, if all the SO₃ is assigned to this mineral. There may be slight substitution of Na₂O for K₂O.

Some nodules are coated with black material at their surfaces and along cracks. Qualitative spectrographic analysis of the black coating scraped from an alunite nodule indicates the presence of Mn, Ca, Sr, Al, Si, and Mg as major constituents, Fe and Co as minor constituents, and Cr, Ni, Ti, Na, Cu, V, Mo, Sn, B, and P as trace elements. The coating is primarily manganese oxide.

Comparison of the composition of a sample from the upper part of the Blue Hill shale with that of the nodules shows primarily a decrease in silica, magnesia, and iron oxide, and an increase in alumina to form the nodules. Sulfide sulfur in the shale suggests the presence of about 0.2 percent FeS₂.

Optical Data

The halloysite was examined under the petrographic microscope in thin section and as fragments in index liquids.

Index of refraction.—Optical determinations were made on the alunite-free pink hydrated halloysite and on some porcellaneous halloysite which had been partly dehydrated at the surface of the pit. Index determinations were made with Shillaber's liquids using monochromatic light.

The index of refraction of hydrated halloysite is difficult to determine: if the material is too wet the observed value is abnormally low. If, on the other hand, the clay is allowed to dry thoroughly, there is a possibility of partial dehydration. Indices were therefore determined on samples which had been dried in two different ways. One was ground wet and air-dried for 2 hours at 33° C and 50 percent relative humidity; the other was dried in a beaker over water at 25° to 29° C for 72 hours. The resulting values for n were identical: $1.522 \pm .003$.

The index of halloysite which had been partly dehydrated (by exposure to the atmosphere at the shale pit) is $1.534 \pm .003$. The index of some of the hydrated mineral which had been oven-dried at 100° C is $1.548 \pm .003$.

The 1.522 value for the hydrated halloysite is less than the reported index of 1.526 to 1.532 for hydrated halloysite (Grim, 1953, p. 279), but still does not approach the 1.490 figure computed by Alexander and others (1943) from Hendricks' (1938) structure.

Birefringence.—Index determinations were made on fragments which had been crushed to 0.3 mm diameter or finer. All fragments showed definite double refraction, thus indicating marked preferred orientation. Interference colors are as high as second order yellow in some of the larger fragments. Conservative estimates of thickness suggest that the birefringence is greater than .002. This may be in part a function of Wiener's (1912) "form birefringence." According to Grim (1953, p. 292) optical characteristics of oriented halloysite may be affected by this phenomenon, particularly if there is a large difference between the index of the liquid and that of the clay. However, the double refraction does not seem to vary with the index liquid used, and is still present in a matching liquid.

Some elongate fragments have nearly straight sides. These show essentially parallel extinction and most of them have positive elongation. A few fragments show somewhat radiating orientation, although the change in extinction covers only a few degrees.

The birefringence of some of the fragments nearly approaches that of kaolinite, and it is seemingly higher than that of aggregates oriented on glass slides. It is possible that the c -axes in laboratory-oriented aggregates are more likely to be normal to the plane of the microscope stage, particularly if the mineral is not hydrated or if it is allowed to dehydrate during drying. Thus the apparent birefringence of naturally occurring oriented aggregates may be higher.

Thin sections.—Eight thin sections showing mutual relationships between halloysite, alunite, and gypsum were examined. Low but distinct

birefringence is characteristic of nearly all the halloysite present, even where admixed with alunite. Large areas of halloysite having the same birefringence and showing the same direction of extinction indicate that the halloysite in those areas has marked preferred orientation. This bears out the evidence shown in the electron micrographs (Pl. 3B). The question of orientation in halloysite has been discussed at some length by Ross and Kerr (1934, p. 139), and also by Brindley, Robinson, and Goodyear (1948, p. 426-427) who suggested that orientation and porcellaneous character may be a function of pressure. The Ness County material has produced fair evidence of good orientation in one occurrence of porcellaneous halloysite; there is no indication that it was produced by compression.

Cracks or veins in the alunite filled with halloysite, but also containing small relict fragments of alunite, indicate that halloysite replaces alunite in some instances. This sequence is just the reverse of that noted by Ross and Kerr (1934, p. 143) in samples from Indiana and Belgium. There is no evidence in any of the Ness County slides for the sequence suggested by Ross and Kerr. However, the concretion with the inner rim of halloysite and outer rim of alunite indicates that the alunite may possibly replace halloysite.

Admixtures of alunite and halloysite are also common, and in such cases there is no evidence indicating that either replaced the other, but that they were probably deposited at the same time.

A thin section made from the nodule of pink halloysite shown in Plate 2B shows the contact between halloysite and shale to be gradational; halloysite seems to have formed at the expense of the shale. This relationship has already been indicated by differential thermal analysis. In many instances the alteration of shale to halloysite occurs at an alunite-shale contact, but the formation of alunite at the direct expense of shale has not been observed although it is considered possible. The halloysite may be a product of reaction between the alunite and constituents of the shale.

The alunite occurs as a fine-grained mosaic. In some thin sections it appears to be intergrown with gypsum. There seems to be either mutual replacement between alunite and gypsum or co-deposition of the two minerals.

ORIGIN

A detailed analysis of the problem of origin of the halloysite is beyond the scope of this report. The association of sulfate minerals with the halloysite, the presence of pyrite in the overlying sandstones as well as in the shale and in the septaria themselves, and the common limonite stain, suggest that the origin of the Ness County halloysite is similar to that of halloysite associated with alunite in other nonhydrothermal deposits.

Restriction of the mineral to the vicinity of calcareous concretions may be due to local reducing conditions caused by the organic matter present in the septaria. The concretions were probably nearly syngenetic; the

adjacent shale beds bend around them. The accumulation of calcite in the otherwise noncalcareous shale may be a function of the local concentration of the decaying organic matter, as suggested by Weeks (1953).

Circulating water in the overlying pyritiferous sandy zones may have oxidized the pyrite, and sulfuric acid may have leached some alumina from part of the Blue Hill shale. Possible sources for potassium ion are the illite and feldspar in the shale. The concretions supplied calcium ion for the formation of gypsum, and seem to have provided a favorable pH and oxidation potential for the growth of halloysite and alunite.

SUMMARY

In summary, the order of events in the origin of the halloysite is not clearly established, and nearly any sequence seems possible. However, the following time sequence is observed:

First, deposition of the sediments which make up the shale, with syngenetic development of the calcareous septarian concretions.

Second, reaction between the calcareous concretions and sulfate-bearing water (from pyrite) to form gypsum and/or alunite. The formation of gypsum seems to have been a continuous process and to have occurred before, during, and after the formation of alunite and halloysite.

Third, development of halloysite. There is clear evidence of replacement of alunite by halloysite. Halloysite also seems to form at the expense of shale at an alunite-shale contact and to be a product of reaction between alunite and constituents of the shale. The formation of alunite at the expense of shale has not yet been observed but is considered possible.

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