

## HYDROBASALUMINITE FROM SHOALS, INDIANA

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### ABSTRACT

Hydrobasaluminite is found as irregular patches and lenses in allophane and halloysite at the Mississippian-Pennsylvanian unconformity near Shoals, southwestern Indiana. The clay mineral deposits are underlain by the Glen Dean Limestone of late Mississippian age, and are overlain by quartz pebble conglomerate of the Mansfield Formation of early Pennsylvanian age. The hydrobasaluminite appears to have formed by alteration of allophane which replaces the Glen Dean Limestone, or by direct replacement of the limestone.

X-ray investigation shows that the Shoals hydrobasaluminite is identical to that reported from England, France, Kansas, and other places. The Shoals hydrobasaluminite dehydrates to basaluminite at room temperature (26°C), dehydrates further to metabasaluminite at about 100°C, and decomposes to amorphous material at about 200°C. Poorly crystalline  $\text{Al}_2\text{O}_3$  forms between 940° and 1000°C. Electron micrographs indicate that the hydrobasaluminite (converted to metabasaluminite during microscopy) consists of plates up to 5  $\mu\text{m}$  in diameter and about 0.05  $\mu\text{m}$  thick, some with rhombic shapes. Chemical analyses suggest the formulas  $\text{Al}_4\text{SO}_4(\text{OH})_{10} \cdot 12\text{H}_2\text{O}$  for hydrobasaluminite,  $\text{Al}_4\text{SO}_4(\text{OH})_{10} \cdot 5\text{H}_2\text{O}$  for basaluminite, and  $\text{Al}_4\text{SO}_4(\text{OH})_{10} \cdot \text{H}_2\text{O}$  for metabasaluminite.

### INTRODUCTION

Two new aluminum sulfate minerals, hydrobasaluminite, given as  $\text{Al}_4\text{SO}_4(\text{OH})_{10} \cdot 36\text{H}_2\text{O}$ , and basaluminite, given as  $\text{Al}_4\text{SO}_4(\text{OH})_{10} \cdot 5\text{H}_2\text{O}$ , were first reported in 1948 from Irchester, Northamptonshire, England (Bannister and Hollingworth, 1948). A subsequent article by the same writers (Hollingworth and Bannister, 1950) described the new minerals more fully and indicated that, in addition to the original locality, the minerals also had been identified in existing mineral collections at the British Museum. Basaluminite was identified in museum collections from Brighton, England; Épernay, France; and Irchester, England. Hydrobasaluminite was identified in the interior of basaluminite fragments from the Brighton locality. Since the original discoveries, hydrobasaluminite or basaluminite have been reported from Tennessee and Kentucky (Milton, 1955), Indiana (Sunderman, 1963), Russia (Fominykh, 1965), Kansas (Tien, 1968), and Utah (Fronde, 1968).

In the spring of 1963 hydrobasaluminite was discovered near Shoals, Indiana, during the progress of an investigation of the minerals found at the Mississippian-Pennsylvanian unconformity in that area (Sunderman, 1963). The hydrobasaluminite was found in an abandoned halloysite prospect tunnel, called the Johnson-Chenoweth prospect, located in the

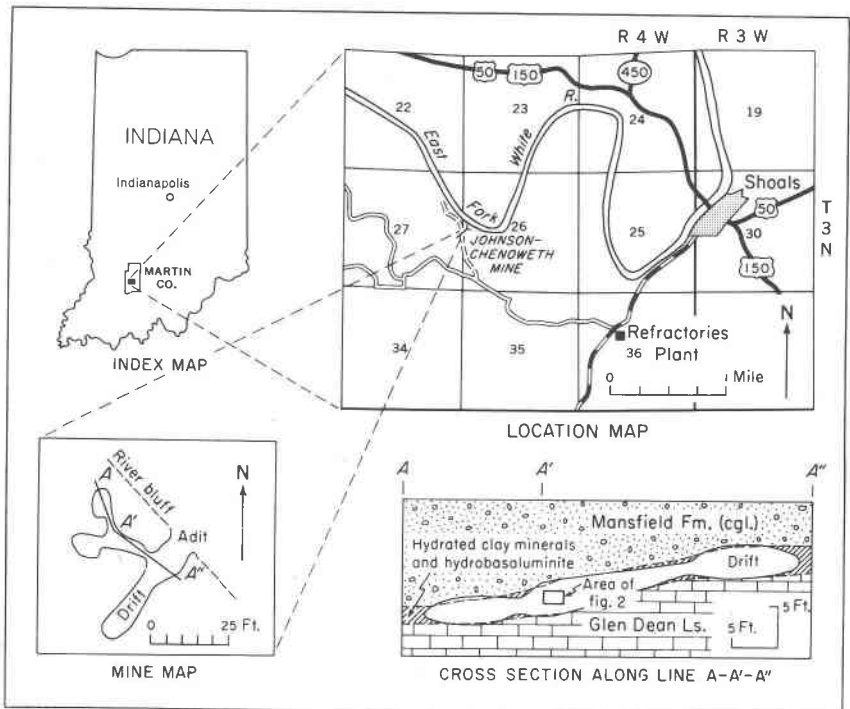


FIG. 1. Maps and section of hydrobasaluminite occurrence, Shoals, Indiana.

SW $\frac{1}{4}$ NW $\frac{1}{4}$  sec. 26, T. 3 N., R. 4 W., about 2 miles west of Shoals (Fig. 1). The opening to the tunnel is in the south bluff of the valley of the East Fork of the White River, about 40 feet above river level. The hydrobasaluminite occurs in an inclined shaft extending to the west-northwest from the main drift of the prospect. (See Fig. 1.)

#### GEOLOGIC ENVIRONMENT

Relatively pure lenses of hydrobasaluminite are interlayered with allophane in the walls of the shaft. Gibbsite and halloysite are present in the same bed with the hydrobasaluminite—gibbsite a few inches below the hydrobasaluminite, and halloysite in the walls of the upper drift. The entire zone of hydrated minerals is sandwiched between oolitic and fragmental limestone beds of the Glen Dean Limestone of late Mississippian age, and quartz pebble conglomerate of the Mansfield Formation of early Pennsylvanian age. (See Figs. 1 and 2.)

#### MINERALOGY

*Physical properties.* Hydrobasaluminite from Shoals occurs in three dis-

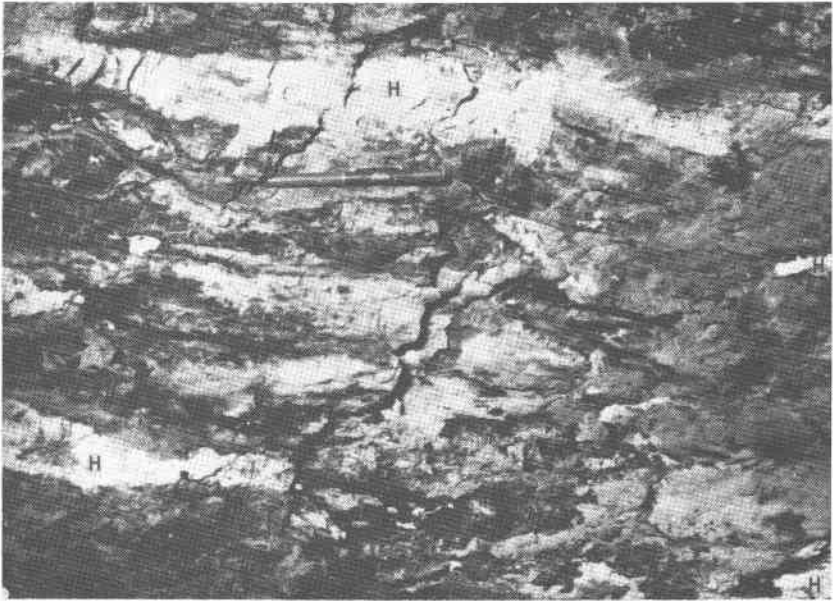


FIG. 2. Lenses of hydrobasaluminite (H) interlayered with allophane, Shoals, Indiana.

tinct habits: white, brittle and powdery; pale yellow, dense and earthy; and pale yellow to white, opaline to porcelaneous. The latter two habits are strikingly similar to the habits of the associated halloysite. The hydrobasaluminite appears colorless to pale yellow in reflected light; basaluminite has a similar appearance but the yellow tint is most pronounced along desiccation cracks. Both minerals appear to consist of a mosaic of small crystals ranging up to 5 microns in maximum dimension.

Specific gravity was determined by the pycnometer method, using boiled distilled water as the liquid. Special precautions were necessary for the determination of the specific gravity of the hydrobasaluminite. Porcelaneous material was stored in an airtight plastic bag until ready for use, then ground and weighed as rapidly as possible. Repeated determinations gave a mean value of 1.86 for hydrobasaluminite. Basaluminite was prepared by drying in air at room temperature for up to 36 days. A constant specific gravity value of 2.08 was obtained after about 12 days drying. This compares with a value of 2.12 reported by Hollingworth and Bannister (1950), and a value of 2.10 reported by Tien (1968).

Special precautions also were necessary for determination of the index of refraction of hydrobasaluminite. Small fragments of porcelaneous material were stored under water until ready for use, dried briefly, then crushed under index oils to preserve the water of hydration. Hydro-

TABLE 1. CHEMICAL ANALYSES OF HYDROBASALUMINITE, BASALUMINITE, AND METABASALUMINITE, SHOALS, INDIANA

Specimen #1						
	Hydrobasaluminite		Basaluminite		Metabasaluminite	
	Percent	Molecular Ratios	Percent	Molecular Ratios	Percent	Molecular Ratios
SiO <sub>2</sub>	0.30		0.37		0.44	
Al <sub>2</sub> O <sub>3</sub>	35.20	2.039	44.08	2.041	52.08	2.040
Fe <sub>2</sub> O <sub>3</sub>	0.058		0.071		0.084	
P <sub>2</sub> O <sub>5</sub>	0.017		0.021		0.025	
SO <sub>3</sub>	13.36	1.000	16.72	1.000	19.76	1.000
H <sub>2</sub> O	50.77	16.825	38.58	10.196	27.42	6.108
Total	99.705		99.842		99.809	
Specimen #2						
	Hydrobasaluminite		Basaluminite		Metabasaluminite	
	Percent	Molecular Ratios	Percent	Molecular Ratios	Percent	Molecular Ratios
SiO <sub>2</sub>	2.38		2.90		3.44	
Al <sub>2</sub> O <sub>3</sub>	35.89	2.034	43.77	1.998	51.84	2.050
Fe <sub>2</sub> O <sub>3</sub>	0.62		0.78		0.92	
P <sub>2</sub> O <sub>5</sub>	0.61		0.75		0.91	
SO <sub>3</sub>	12.30	1.000	15.27	1.000	17.75	1.000
H <sub>2</sub> O	48.06	16.852	36.27	10.050	25.32	5.866
Total	99.86		99.74		100.18	

Specimen #1, white porcelaneous hydrobasaluminite.

Specimen #2, pale yellow earthy hydrobasaluminite.

Analyst, Maynard E. Coller.

basaluminite and basaluminite were found to be weakly birefringent. An approximate range of refractive index values was determined for hydrobasaluminite as 1.466 to 1.477, and for basaluminite as 1.512 to 1.517. The values for basaluminite compare with published mean refractive index values for this mineral of 1.519 (Hollingworth and Bannister, 1950),  $1.520 \pm 0.002$  (Fominykh, 1965; Tien, 1968), and 1.525 (Fron del, 1968).

*Chemical analyses.* Hydrobasaluminite exists at a constant 56°F in a moist atmosphere in the Johnson-Chenoweth prospect shaft. Samples

were collected in airtight plastic bags and stored in a freezer. Chemical analyses (Table 1) were made on both the white porcelaneous and pale yellow earthy forms of hydrobasaluminite, on hydrobasaluminite that stood at 26°C for 24 hours (basaluminite), and on hydrobasaluminite heated to 160°C (metabasaluminite).

The SiO<sub>2</sub> in the analyses were assigned to allophane, and proportional amounts of Al<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>O were subtracted from the basic aluminum sulfates. The molecular ratios in Table 1 were calculated after these corrections were made. Results of these calculations give hydrobasaluminite as Al<sub>4</sub>SO<sub>4</sub>(OH)<sub>10</sub>·12H<sub>2</sub>O, basaluminite as Al<sub>4</sub>SO<sub>4</sub>(OH)<sub>10</sub>·5H<sub>2</sub>O, and metabasaluminite as Al<sub>4</sub>SO<sub>4</sub>(OH)<sub>10</sub>·H<sub>2</sub>O. Corresponding compositions listed by Hollingworth and Bannister (1950) are Al<sub>4</sub>SO<sub>4</sub>(OH)<sub>10</sub>·36H<sub>2</sub>O, Al<sub>4</sub>SO<sub>4</sub>(OH)<sub>10</sub>·5H<sub>2</sub>O, and Al<sub>4</sub>SO<sub>4</sub>(OH)<sub>10</sub>.

*X-ray diffraction data.* X-ray powder diffraction data were obtained for the Shoals hydrobasaluminite and its states of lower hydration by the diffractometer technique using filtered copper radiation. Because of the ease with which water is lost from hydrobasaluminite at room temperature, the X-ray pattern was obtained in two ways: in a closed camera with a water-saturated atmosphere, and from overlapping traces using a fresh sample every 10°2θ. The X-ray patterns of basaluminite were obtained from hydrobasaluminite that stood at 26°C for 24 hours and from a sample heated to 160°C. Data for the d-spacings and intensities of these compounds correspond well with similar data from Hollingworth and Bannister (1950), and from Tien (1968).

An oscillating X-ray pattern over the 12.6 Å hydrobasaluminite peak and the 9.35 Å basaluminite peak at room temperature is shown in Fig. 3. In this run the hydrobasaluminite peak steadily decreased in intensity and practically disappeared in about 20 minutes, with the concomitant appearance of and steady increase in intensity of the basaluminite peak.

An oscillating-heating X-ray diffraction run (Fig. 4A) again shows dehydration of hydrobasaluminite to basaluminite at room temperature in about 20 minutes. At about 85°C the intensity of the basaluminite 9.35 Å peak increased, then began to decrease at about 100°C, indicating dehydration to metabasaluminite (Fig. 4B). The metabasaluminite was stable to about 200°C, at which temperature it decomposed to amorphous material (Fig. 4C). Poorly crystalline Al<sub>2</sub>O<sub>3</sub> formed in the range 940–1000°C. These values compare well with those given by Tien (1968).

*Differential thermal analysis.* Differential thermal analyses of two different hydrobasaluminite samples from Shoals showed endothermic peaks at 150, 200, 350, and 940°C; and at 130, 145, 355, and 950°C. These values also agree with those given by Fominykh (1965) and Tien (1968).

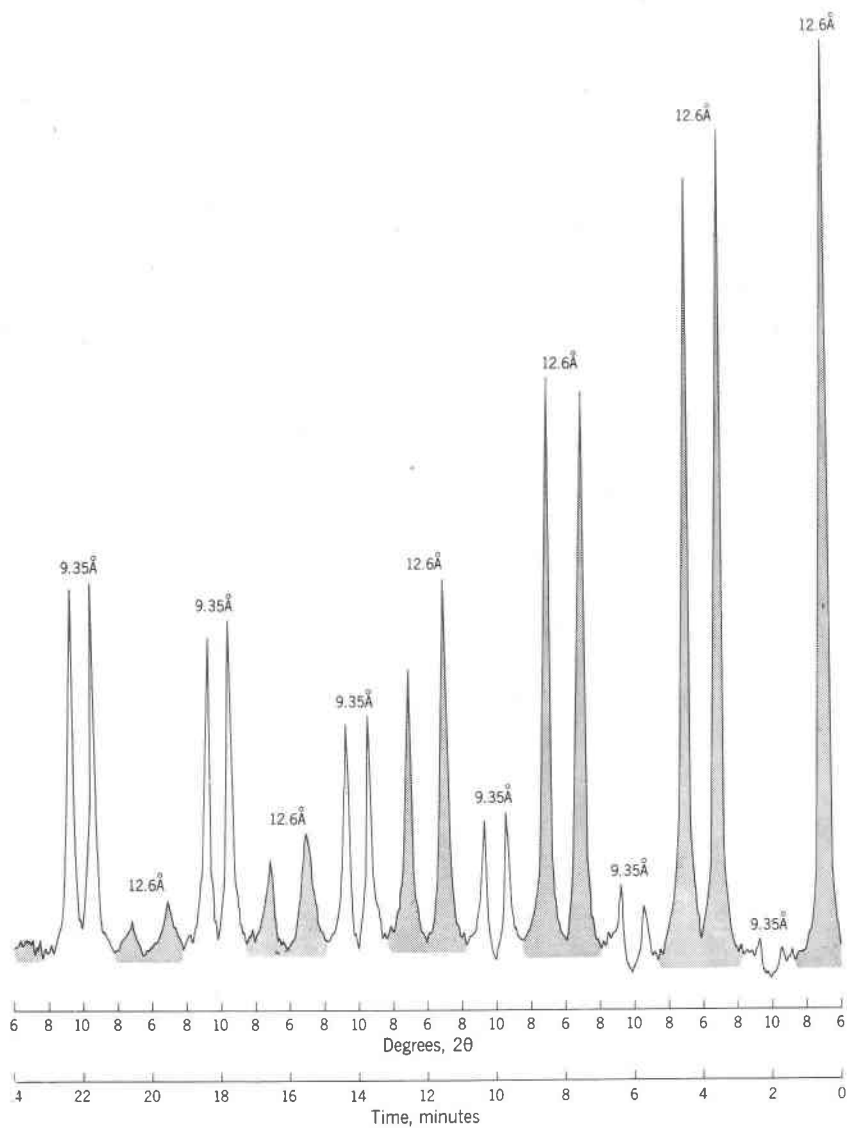


FIG. 3. Oscillating X-ray pattern over 12.6Å hydrobasaluminite peak, showing conversion to basaluminite (9.35Å) at room temperature.

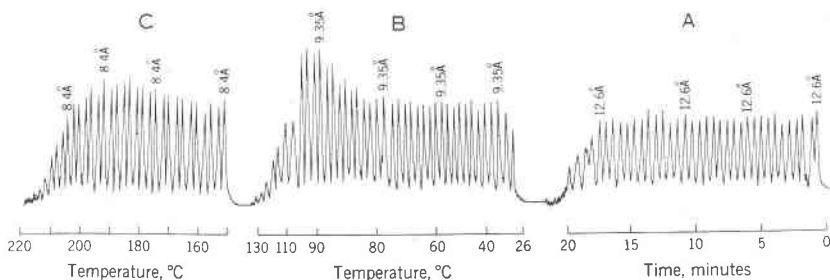


FIG. 4. Oscillating-heating X-ray pattern of hydrobasaluminite.

*Electron microscopy.* An electron micrograph of hydrobasaluminite (Fig. 5A) reveals that the material has a thin platy habit and that many crystallites exhibit rhombic shapes. Some well-developed crystallites show angles near  $120^\circ$ . Most crystallites are  $1\text{--}2\ \mu\text{m}$  in maximum dimensions, but they range up to 5 microns in width. Thicknesses as low as  $30\ \text{\AA}$  were measured by means of a variation of Bradley's (1959) platinum-carbon shadowing technique, in which Pt-C pellets instead of Pt-C rods are used. Most crystallites appear to be about  $0.05\ \mu\text{m}$  thick. Great magnification (Fig. 5B) shows a rough irregular filamentous surface.

An electron microscope diffraction pattern transmitted perpendicular to the plates gave an orthogonal pattern, but it could not be related to hydrobasaluminite or to basaluminite. An electron diffraction powder pattern was obtained showing 16 rings that correspond well with metabasaluminite, however, and the conditions of electron diffraction appear to have been sufficient to have dehydrated the specimen to metabasaluminite. The vacuum was on the order of  $10^{-4}$  mm; the temperature of the irradiated specimen is difficult to estimate, but  $100^\circ\text{C}$  is a reasonable estimate, and  $+200^\circ\text{C}$  is not impossible.

#### ORIGIN

The mineral assemblages of the Shoals, Indiana and the Irchester-England deposits are strikingly similar. Both deposits contain hydrobasaluminite and basaluminite, halloysite and allophane, and gibbsite and hydrated iron and manganese oxides. The Irchester deposit also contains gypsum and aragonite.

The formation of the hydrated minerals at Irchester is attributed to infilling and precipitation along joint fissures beneath a 60-foot clay bed. Periglacial freezing of the surface material during Pleistocene time, with consequent trapping of groundwater in a local structural basin, is called upon to concentrate all of the ions necessary to produce the hydrated minerals. The oolitic limestone has been weathered along joints in some

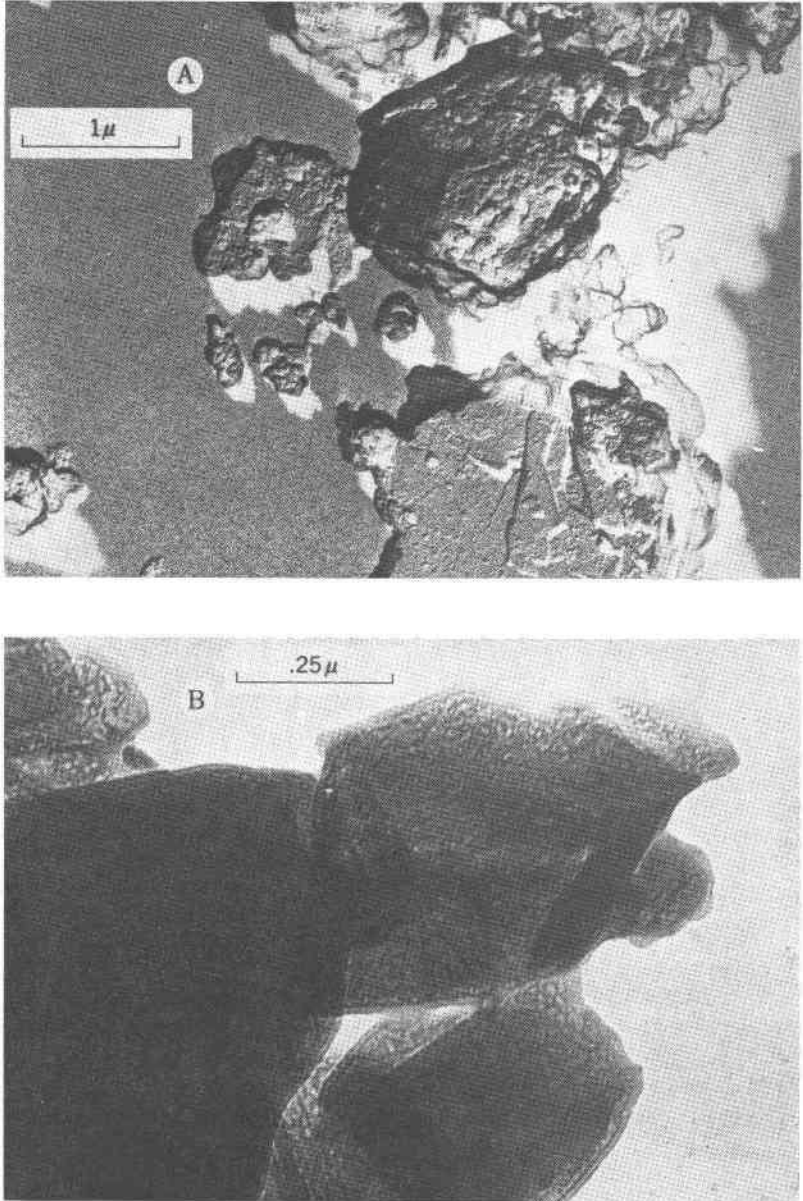


FIG. 5. Electron micrograph of hydrobasaluminite:  
A.  $\times 40,000$ ; B.  $\times 160,000$ .



places so that only cores of fresh carbonate remain between joints. The possibility of ancient weathering on a pre-clay Jurassic erosion surface is mentioned by Hollingworth and Bannister (1950) as a mode of origin for deposits, but it is dismissed by them as without supporting evidence.

Milton and others (1955) reported the formation of basaluminite in sub-Chattanooga residuum in Tennessee and Kentucky and attributed the origin to the action of  $H_2SO_4$  (derived from oxidized pyrite) on the shale. Fominykh (1965) found basaluminite as a fine-scaled aggregate associated with kaolinite, concentrated in voids in quartzite. Tien (1968) found hydrobasaluminite in the Cabaniss Formation (middle Pennsylvanian) in southeastern Kansas, associated with gypsum and iron oxides above a coal bed, and found basaluminite as debris on dry slopes. Tien related the formation of hydrobasaluminite ". . . to weathering, local structure, topography, and mineral composition of associated rocks."

Bassett and Goodwin (1949) studied the system  $Al_2O_3-SO_3-H_2O$  under various equilibrium conditions and obtained a wide range of hydrated aluminum sulfates. Most of the equilibrium mixtures were prepared by the addition of  $H_2SO_4$  to amalgamated aluminum. They concluded that the only well-defined basic aluminum sulfate minerals are aluminite, basaluminite, and hydrobasaluminite. Frondel (1968), however, has reported the new mineral meta-aluminite,  $Al_2SO_4(OH)_4 \cdot 5H_2O$  from Emery County, Utah, in association with basaluminite. According to Frondel, the basic aluminum sulfate minerals probably were formed by the alteration of clay minerals in sandstone by acid sulfate solutions derived from the oxidation of pyrite.

The origin of the hydrobasaluminite found near Shoals, Indiana, is related to the origin of an extensive but discontinuous clay mineral zone at the Mississippian-Pennsylvanian unconformity in this area. This zone contains a variety of clay minerals, as well as beds of iron oxides. The clay mineral beds are of two types: a plastic, reddish-brown, iron-rich clay material consisting dominantly of illite and kaolinite; and clay lenses consisting dominantly of clear, white, blue, or tan halloysite and allophane in various proportions. The illite-kaolinite clay material has been interpreted as a residual or colluvial soil which developed on Mississippian rocks in pre-Mansfield time (Sunderman, 1963). This clay rests on different rock formations of latest Mississippian age at various localities in the Shoals area, which suggests that the soil developed after post-Mississippian uplift and exposure, and that the residual clay is very early Pennsylvanian in age.

The time of origin of most of the halloysite-allophane beds is thought to be one cycle removed from that of the illite-kaolinite residual clays. Much of the halloysite and allophane in the upper part of the Johnson-

Chenoweth prospect and at other places in the general Shoals area is interbedded with quartz pebble conglomerate of the basal part of the Mansfield Formation. The halloysite and allophane are believed to have been derived initially from the residual clays, reworked by early Mansfield streams, incorporated into the Mansfield Formation in a plastic state, then altered to halloysite and allophane after deposition (Sunderman, 1963). It is possible that the hydrobasaluminite at Shoals has formed in this way also, by alteration of reworked residual clay, but another origin is favored.

Some of the halloysite and allophane, and minor amounts of gibbsite, have formed by replacement of limestone in the Johnson-Chenoweth prospect and elsewhere in the Shoals area. Some allophane completely replaces limestone in the Johnson-Chenoweth prospect, as indicated by the presence of replaced crinoid fragments and oolites identical to those in the underlying Glen Dean Limestone (Sunderman, 1963). No replaced structures have been observed in the hydrobasaluminite, but it is interbedded with allophane of known replacement origin (Fig. 2). Therefore it is likely that the hydrobasaluminite has formed by replacement of the limestone also, or that it has replaced the pseudomorphic allophane.

The time of formation of the hydrobasaluminite is perhaps questionable, but it is probably post-Mansfield. No known source of sulfate was available to form the hydrobasaluminite during the soil-forming process in early Pennsylvanian pre-Mansfield time, although the limestone replacement conceivably could have taken place then. It is considered more likely that the hydrobasaluminite and allophane formed by replacement of small masses of saprolitic limestone after deposition of the Mansfield Formation. Associated residual clays could have furnished alumina and silica for the hydrobasaluminite and allophane, and the quartz pebble conglomerate of the Mansfield, which contains some pyrite, probably furnished sulfate and additional silica for the replacement minerals.

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