

AN OCCURRENCE OF FULLY-HYDRATED HALLOYSITE  
AT MUSWELLBROOK, N.S.W.

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ABSTRACT

An occurrence of halloysite( $4H_2O$ ) in commercial quantities, at Muswellbrook, N.S.W. is described. Intrusions of slag derived from the fusion of ferruginous sediments by the underground combustion of coal seams, have partly altered the associated strata to assemblages of tridymite, cristobalite and mullite. It is considered that the halloysite originated from the rehydration of metakaolinite formed by thermal metamorphism of well crystallized kaolinite.

OCCURRENCE AND MINERALOGY

A recent discovery of halloysite ( $4H_2O$ ) by the authors, on Portion 115, Parish Brougham, County Durham, six miles south of Muswellbrook, is of interest not only because the clay is available in commercial quantities, but also the occurrence affords an opportunity to study an unusual genesis for this comparatively rare mineral.

The deposit which forms part of the Permian Lower or Greta Coal Measures (Booker, 1953) outcrops over a thickness of 20 feet on the western side of a low conical-shaped hill known locally as "The Pimple" (Fig. 1). A laminated, dark-colored microbreccia composed essentially of well-crystallized kaolinite underlies the halloysite while the ten feet or so of overlying strata consists of siliceous shales characteristic of much of the Permian Coal Measures of N.S.W. The halloysite grades laterally into a rock similar to, but coarser-grained than, the underlying material. In thin section the microbreccia displays sub-angular, equidimensional clay-aggregates ranging up to 3 mm. in diameter, with a few scattered grains of quartz and finer chalcedony, while lenticules of organic matter impart the dark coloration. The kaolinite content varies from 75% to 90% and, in addition, a trace of partly-hydrated halloysite was detected in the majority of samples examined. Elsewhere in the area occasional quartz-enriched lenses may be observed occurring within the outcrops of the clay microbreccia.

The siliceous shales overlying the halloysite are considerably brecciated in places and the voids so created are infilled by two contrasting rock types, an earlier, fine-grained, contaminated "picrite basalt" and a later, highly-vesicular, dark colored slag.

In thin section, the "picrite basalt" is sub-ophitic to intergranular with strongly-zoned, equant anhedral diopside hedenbergite, up to 1 mm. in diameter, and slender plagioclase (anorthite?) laths ranging from 0.2 to 1 mm. Tridymite, cristobalite and brown glass comprise the groundmass.

On the other hand, the slag contains an abundance of cordierite mosaics, pleochroic from pale violet to colorless; fine, twinned, wedge-shaped crystals of tridymite; microlitic cristobalite; magnetite grains altering to hematite, and slender mullite needles often in the form of felted masses.

Generally the slag occurs marginal to the "picrite basalt" though inter-reaction and intimate admixture of the two are common. In such cases, the feldspar of the "basalt" frequently is altered to mullite though the pyroxene remains virtually unaffected. The low viscosity of the slag is evidenced by the high degree of penetration into the bedding planes of the shales whereas the more viscous "basalt" is restricted to the larger cavities.

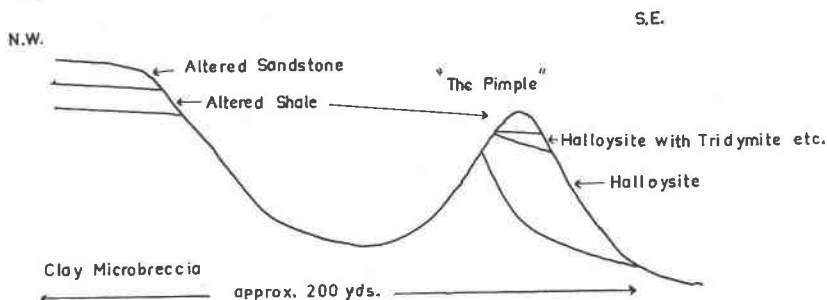


FIG. 1. Cross section of the halloysite deposit.

X-ray examination of the intruded shales revealed their almost entire alteration to an assemblage of tridymite, cristobalite and mullite. However, in thin section, a few silt-sized quartz grains were still apparent.

The bulk of the halloysite, on the other hand, consists of a dense, well-jointed, off-white clay with a texture similar to the clay-microbreccia. Examination by differential thermal, x-ray and chemical techniques (see Fig. 2 and Tables 1 and 2), indicated the presence of fully hydrated halloysite contaminated by a small quantity of relatively coarse quartz and a trace of kaolinite. However, electron micrographs failed to reveal any trace of the characteristic tube-like forms of halloysite.

Within a few feet of the base of the overlying shales, the halloysite assumes a platy structure which passes upward into an iron-stained zone. Though fully hydrated halloysite comprises much of both the platy and iron-stained clays, appreciable quantities of cristobalite and tridymite are also present. In addition, a few grains of quartz and possibly mullite were detected.

Approximately a hundred yards to the north of "The Pimple" the

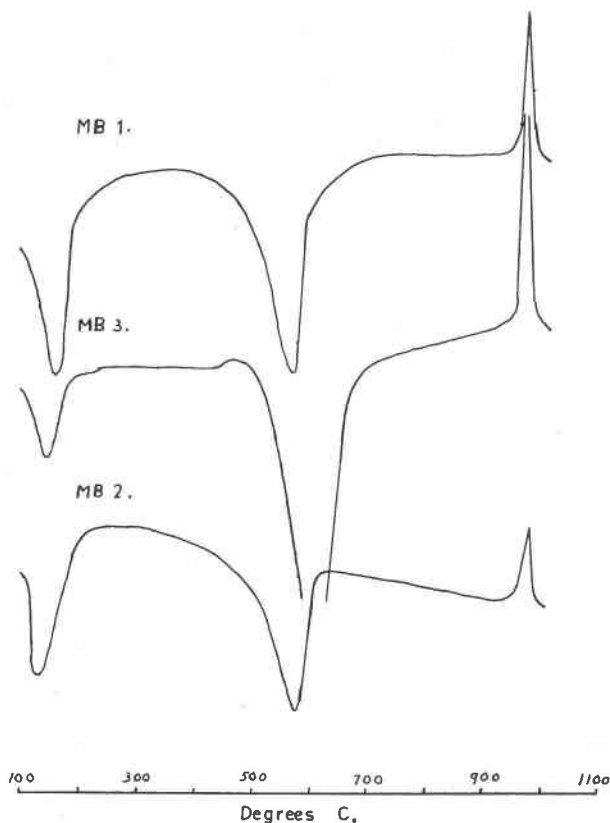


FIG. 2. DTA data. MB1—halloysite; MB2—platy halloysite near top of deposit; MB3—Clay-microbreccia.

same succession of strata outcrops on a flat-topped hill. Here, however, the brecciated shales are overlain by a few feet of sandstones which also have been metamorphosed to an assemblage of tridymite, cristobalite, mullite and interstitial glass though many of the larger quartz grains, generally rimmed with cristobalite, are still apparent in thin section.

On a ridge a few hundred yards south of "The Pimple," the succession is repeated, though with a greater thickness of the overlying sandstones, of which only the basal portion has been affected by metamorphism.

#### ORIGIN OF THE CLAY-MICROBRECCIA

The term "clay-microbreccia" is used in this paper to describe a type of sediment which, though relatively rare, has been recognized in many

TABLE 1. X-RAY DATA

MB1		MB1 (a)		MB2 (a)		MB3		MB4		MB5		MB6	
<i>d</i>	I	<i>d</i>	I	<i>d</i>	I	<i>d</i>	I	<i>d</i>	I	<i>d</i>	I	<i>d</i>	I
10.0	10	11.1	10	11.0	10	8-9	2 (b)					8.30	3
7.20	1	7.20	1			7.10	10	7.20	1	7.15	2		
		5.72	1					5.38	2	5.4	3		
4.84	1	4.84	1					4.80	1	4.80	3		
4.45	7	4.45	7			4.42	8						
				4.30	6			4.30	10	4.30	10	4.30	10
4.22	2	4.22	2										
						4.14	8						
				4.05	10			4.05	10	4.05	7	4.05	10
		3.75	4	3.81	3	3.84	2	3.81	7	3.81	7	3.81	6
3.52	2	3.52	2			3.56	10					3.66	1
								3.40	5	3.40	4	3.40	4
3.35	4	3.35	4	3.35	2	3.35	4	3.35	2	3.35	5		
												3.30	4
				3.14	1								
				2.98	1			2.98	3	2.98	4	3.00	6
				2.84	2			2.84	1	2.84	2		
				2.69	1			2.70	3	2.70	2	2.69	7
2.55	2	2.58	2	2.53	1	2.55	5	2.54	3	2.54	3	2.54	10
2.50	1	2.50	1	2.49	4	2.50	5	2.50	3	2.49	4		
						2.34	7						
				2.29	1	2.29	5	2.30	3	2.30	3	2.30	3
				2.20	1			2.21	4	2.20	3	2.20	3
				2.11	1			2.11	1	2.11	2	2.10	4
				2.09	1			2.08	1	2.08	2		

(a) Glycerol Treated.

(b) Broad and Diffuse.

MB1 Halloysite.

MB2 Platy halloysite near top of deposit.

MB3 Clay-microbreccia

MB4 Metamorphosed shales capping "The Pimple."

MB5 Metamorphosed sandstones overlying the shales.

MB6 Slag.

of the fresh-water deposits of N.S.W., including the Permian (both Lower and Upper Coal Measures), Triassic (Narrabeen Group) and Jurassic. Though only a few of these occurrences have been examined in detail (Loughnan, 1958), it would appear that the significant features are (a) a high kaolinite or metahalloysite content, (b) coarse subangular quartz rarely in excess of 10%, (c) a relatively high titania content, and (d) remnant volcanic textures in some of the clay aggregates. A rock with

these characteristics could have resulted from the extensive leaching of an intermediate or basic tuff, a parent material which under non-leaching conditions would have yielded bentonite. Significant in this respect are the occurrences of bentonite in both the Permian and Jurassic fresh-water sediments of N.S.W. (Loughnan and See, 1959). It is considered that the quartz represents contamination of the volcanic debris.

Closely related to the clay-microbreccias in occurrence and mineralogy are the chocolate shales of the Triassic and Jurassic of N.S.W. and probably these have had a somewhat similar origin.

TABLE 2. CHEMICAL DATA

	MB1	MB3	MB4	MB5	MB6	MB7	MB8
SiO <sub>2</sub>	42.3	50.1	65.7	80.7	58.4	64.7	62.6
Al <sub>2</sub> O <sub>3</sub>	30.4	31.8	23.4	13.2	14.4	11.9	11.5
Fe <sub>2</sub> O <sub>3</sub>	2.3	0.7	5.8	1.4	15.7	3.9	3.6
FeO	0.1	0.6	0.3	0.1	6.4	1.5	2.2
TiO <sub>2</sub>	1.7	2.1	1.4	0.5	—	0.6	0.5
CaO	0.0	0.1	0.2	1.4	0.5	8.6	10.7
MgO	0.1	0.1	0.1	0.3	1.7	2.4	3.6
Na <sub>2</sub> O	0.0	0.6	0.2	0.2	0.3	0.1	0.1
K <sub>2</sub> O	0.0	0.2	0.8	0.1	0.0	1.0	1.1
H <sub>2</sub> O <sup>+</sup>	11.5	12.0	2.1	0.7	0.3	2.1	1.9
H <sub>2</sub> O <sup>-</sup>	11.0	1.6	0.6	0.3	1.0	1.9	1.7
CO <sub>2</sub>	0.0	—	0.1	0.2	—	0.9	0.2
P <sub>2</sub> O <sub>5</sub>	0.5	—	0.1	0.2	—	0.9	0.2
MnO	0.0	—	0.0	0.0	—	0.1	0.1
	99.9	99.9	100.8	99.3	98.7	100.6	100.0

MB1—Halloysite, MB3—Clay-microbreccia, MB4—Shale, MB5—Sandstone, MB6—Slag, MB7 and MB8—"picrite basalt."

#### ORIGIN OF THE INTRUSIVE ROCKS

It was difficult to ascertain the relationship between the "picrite basalt" and the slag since in places each appears to have intruded the other. However, perhaps the most significant feature is that where the two are in contact, the "basalt" has been modified with much of its feldspar transformed to mullite whereas the slag is unaffected.

In the vicinity of the Savoy Trigonometrical Station, a few miles to the south of "The Pimple" and still within the Lower Coal Measures, Raggatt and Whitworth (1932) described analcite dolerite and syenite intrusions of sill-like character to which they assigned a Tertiary age. The analcite dolerite, which comprises the bulk of these extensive masses,

was correlated with the Older Basalts of N.S.W. and the syenite with the younger Alkaline Extrusives. Igneous rocks later than the Tertiary are unknown in the area.

In contrast to the above rock types, the "picrite basalt" (see chemical analyses, Table 2) is particularly calcic and notably deficient in the alkalis even after consideration is made for the high degree of silica contamination. Possibly the rock represents a particularly basic differentiate of the Tertiary intrusives or, alternatively, contamination by lime in addition to silica occurred, with a simultaneous release of alkalis to the country rock. In either case, the typical igneous texture of the rock indicates an essentially magmatic origin.

On the other hand, the slag closely resembles a furnace product and is dissimilar, in both composition and texture, to any igneous rock yet encountered. In a recent paper, Whitworth (1959) described similar slag-like intrusions from the Upper Coal Measures in the vicinity of Liddell, some ten miles or so in an east-south-east direction from "The Pimple," and reached the conclusion that the material represented highly-ferruginous sediments fused by burning coal seams *in situ*. Moreover, he considered that "the isolated outcrops of slag may be remnants (of a burnt-out seam) left by the erosion of a large area, or may represent 'chimneys' or fissures through which flames and hot gases escaped from an underlying fire and about which intense heating was localized."

The occurrence of slags from the burning of coal seams *in situ* had been recorded previously from the Lower Coal Measures at Cessnock (David, 1907) and Muswellbrook Open Cut (Booker, 1953).

Detailed examination revealed no trace of a coal seam in the strata between the clay-microbreccia and the uppermost sandstones in the vicinity of "The Pimple." However, it was ascertained from bores put down in the area during the immediate post-war years that a considerable amount of the coal underlying "The Pimple" is cindered.

From a consideration of these points it would appear that:

- (a) the slag was derived from the fusion of associated iron-rich sediments by burning of coal seams underground and has risen through vents and/or fissures to intrude the overlying sediments.
- (b) the vents or fissures were created by the earlier intrusions of "basalt" which brecciated and intruded the shales preferentially.
- (c) the shales and sandstones were intruded under low cover, as evidenced by the brecciation, and hence erosion in the area since the Late Tertiary has not been great.
- (d) the "basalt" intrusions pre-dated the injection of the slag though the time interval probably was small (in fact it is possible that the "basalt" magma actually fired the coal).
- (e) the metamorphic effects in the shales and sandstones were caused by the slag.

## ORIGIN OF THE HALLOYSITE

To account for the origin of the halloysite, two factors must be considered: the parent material and the mechanism of formation.

With respect to the former, there can be little doubt that the clay-microbreccia comprised the parent material for not only does a close similarity in chemical composition and micro-texture exist between the two, but every gradation both lateral and vertical may be observed in the field.

On the other hand, the mechanism by which the kaolinite was converted to a fully-hydrated halloysite is problematical. According to Bates (1952), the kaolinite-halloysite transition can be achieved only after the destruction of the initial kaolinite structure and a water saturated atmosphere is necessary for the genesis of fully-hydrated halloysite. Though halloysite ( $4\text{H}_2\text{O}$ ) readily loses water to form metahalloysite ( $2\text{H}_2\text{O}$ ), the process is irreversible, at least at atmospheric temperatures and pressures.

Roy and Osborn (1952 and 1954), working with pressures up to 30,000 psi, were unable to synthesize halloysite from the system  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ . However, from a study of the dehydration characteristics of this mineral, they concluded that the stability curve rises sharply with small increments of pressure to a temperature of  $175^\circ\text{C}$ . where the pressure is 5,000 psi. Beyond that temperature, irrespective of the pressure, halloysite is no longer stable.

As shown earlier, erosion in the vicinity of "The Pimple" since the Late Tertiary has been small, and hence the alteration of the clay-microbreccia to the halloysite was accomplished under low pressure, probably no more than 10 atmospheres. This would indicate a formation temperature for the halloysite of not much in excess of  $100^\circ\text{C}$ ., insufficient to cause the break-down of the parent kaolinite structure and permit the development of tridymite and cristobalite in the upper portion of the halloysite deposit.

In consequence, it is considered that there were two stages in the kaolinite-halloysite transition:

- (a) A period of thermal metamorphism during which a maximum temperature of  $850^\circ\text{-}900^\circ\text{C}$ . was reached in the upper part of the deposit, facilitating the quartz inversion to tridymite and cristobalite but insufficient to cause the destruction of the metakaolinite structure. The lower extent of the halloysite corresponded to the  $500^\circ\text{C}$ . isotherm, beyond which dehydroxylation did not occur.
- (b) A later, low-temperature period of hydrothermal activity, in which water, driven from the adjacent and underlying sediments as the burning section of the coal seam became more distant, permeated and reacted with the metakaolinite forming fully hydrated halloysite.

From the examination by infra-red absorption spectroscopy, of various metakaolins, preheated to 600°–850° C., Stubican found that those derived from well-crystallized kaolinite retained their initial atomic arrangement whereas poorly crystallized varieties readily rearranged to yield gamma-alumina in the gibbsite layers. Since it is doubtful that gamma-alumina or mullite, once formed, would recombine with silica and water to yield halloysite at a low temperature, it would follow that the development of the halloysite at "The Pimple" must have been considerably influenced by the high degree of crystallinity of the parent kaolinite. The failure of the tube-like form of halloysite to develop could be related to the retention of the initial kaolinite stacking of the layers.

Though the postulated origin appears the only one in accord with the data, it should be noted that Roy and Brindley (1956) studied the progressive rehydration of thermally decomposed members of the kaolin group, including kaolinite, disordered kaolinite, dickite, nacrite and halloysite, under varying conditions of time, temperature and water vapor pressure and were unable to synthesize halloysite from any of the products.

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#### REFERENCES

- BATES, T. F. (1952), Problems of clay and laterite genesis: *A.I.M.M.E.* (New York), 144–153.
- BOOKER, F. W. (1953), Ph.D. Thesis, Sydney University (unpublished).
- DAVID, T. W. E., SIR. (1907), The geology of the Hunter River Coal Measures, N.S.W.: *Mem. Geol. Surv. N.S.W.*, No. 4.
- LOUGHNAN, F. C. (1958), Ph.D. Thesis, University of N.S.W. (unpublished).
- LOUGHNAN, F. C. AND SEE, G. T. (1959), The bentonite and fuller's earth deposits of N.S.W., Pt. 1: *Aust. Inst. Min. Met.* No. 190, 85–104.
- RAGGATT, H. G. AND WHITWORTH, H. F. (1932), Igneous rocks of the Muswellbrook-Singleton Area: *Roy. Soc. N.S.W.*, **66**, 194–232.
- ROY, R. AND BRINDLEY, G. W. (1956), A study of the hydrothermal reconstitution of the kaolin minerals: *Clays and Clay Minerals*, *4th Nat. Conf.* 125–132.
- ROY, R. AND OSBORN, E. F. (1952), Problems of clay and laterite genesis: *A.I.M.M.E.* (New York) 76–80.
- ROY, R. AND OSBORN, E. F. (1954), The system  $Al_2O_3$ - $SiO_2$ - $H_2O$ : *Am. Mineral.*, **39**, 853–885.
- STUBICAN, V. (1959), Residual hydroxyl groups in the Metakaolin range: *Min. Mag.*, **32**, 38–52.
- WHITWORTH, H. F. (1959), Some fused sedimentary rocks in the Ravensworth District, N.S.W.: *Roy. Soc. N.S.W.* (in press).

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