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OCCURRENCE AND GENESIS OF HALLOYSITE, UPPER HUNTER VALLEY, NEW SOUTH WALES, AUSTRALIA

J. H. RATTIGAN,[1] *University of Newcastle, Australia.*

ABSTRACT

Halloysite, now dominantly metahalloysite or of mixed hydrated and dehydrated character, occurs in ash or collapse zones about naturally-fired coal seams and in associated thermally altered rocks and soils. No structural control for a kaolinite-halloysite transition is apparent in these occurrences as the bedrock or host rock may comprise a range of fired products of kaolinitic rocks including mullite-tridymite-cristabolite rocks, highly vitrified structureless material and buchites.

Halloysite also occurs in a more usual type of occurrence in pallid and mottled zones under a ferruginous capping of ancient lateritic soils and in recent soil profiles where the hydrated halloysite may fill shrinkage cracks in older, impure halloysite sheets.

A compositional control for halloysite occurrence is observed as most known occurrences are associated with highly aluminous rocks and minerals. Soils and permeable zones in bedrock are the loci of halloysite deposition and water saturated conditions appear to be the most dominant factor in halloysite formation from alumina-silica gels. Sulphate-bearing fluids may have been a factor in the formation of many of the deposits as there are many sources of sulphur and sulphates in bedrock and in the fumes, condensate and sinter from natural coal fires.

INTRODUCTION

Loughnan and Craig (1960) recorded the occurrence of fully hydrated halloysite from Muswellbrook, New South Wales. This occurrence was located over claystones of the Greta Coal Measures and from its proximity to baked and fused sediments the halloysite was considered to originate in two stages by thermal metamorphism of the well-crystallized kaolinite of the underlying section and subsequent rehydration of metakaolinite. A structural control was inferred for a kaolinite-halloysite transition.

Recently many halloysite occurrences have been found in the Upper Hunter Valley, New South Wales in the environs of the townships of Wingen and Murrurundi. Though always associated with a single rock unit, the Greta Coal Measures, the occurrences vary in habit and associations. These provide further data on conditions controlling the natural formation of halloysite, which mineral has never been synthesized.

Most halloysites reported on are dominantly of the metahalloysite type (Fig. 1, B) having been collected from exposed, dry occurrences. Some vein material, moist as collected, and some halloysite soil horizons did contain abundant fully hydrated (10 Å) halloysite on first collecting but were partially dehydrated during their transportation and storage and now are largely metahalloysite (Fig. 1, A and C).

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[1] Visiting, University of California, Riverside.

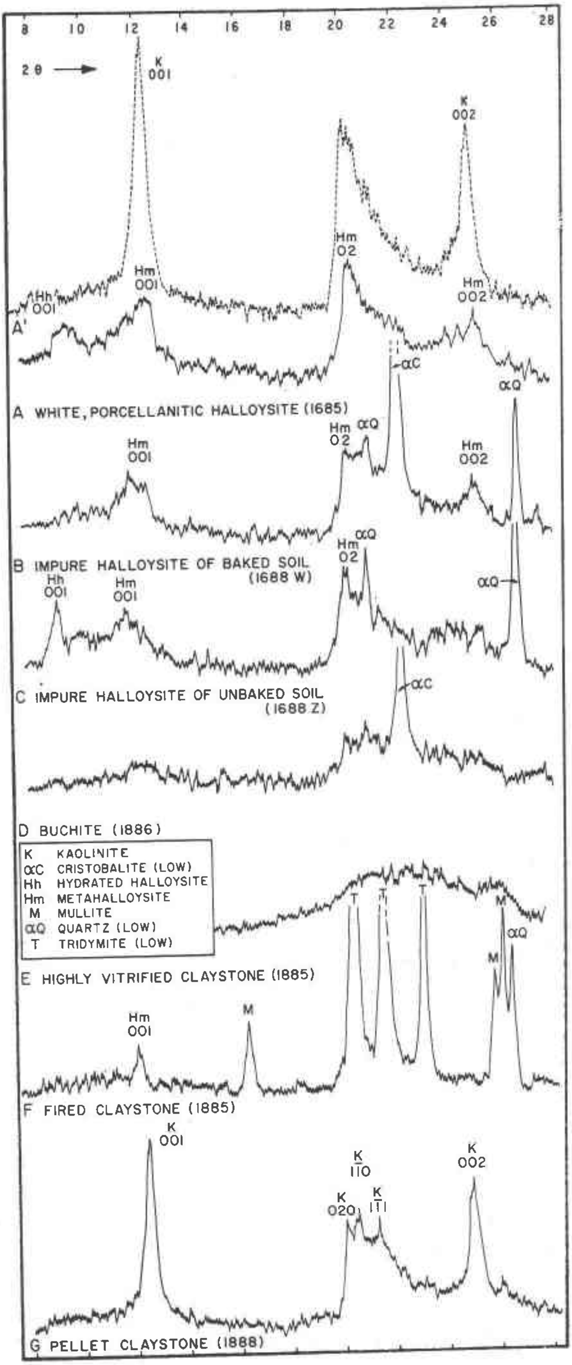

FIG. 1. X-ray diffraction diagrams of natural halloysites and their bed or host rocks. (CuKα, Ni filter, Norelso instrument). The broken trace A′ is for 1685 (A) heated to 300°C.

BEDROCK AND THE EFFECTS OF COAL FIRING

All occurrences are localized within or over rocks of the Permian unit known as the Greta Coal Measures which includes three types of sedimentation unit in the Upper Hunter district.

(1) Claystones, consisting of claystone fragments ranging from lutite to rudite sizings, but all dominantly composed of a somewhat disordered form of kaolinite (Fig. 1, G). The rocks can be described as shales (of the pellet tonstein type), clay-pellet conglomerate and claystone-pebble conglomerate. A considerable proportion of organic hydrocarbons and sulphides occur in some of these claystones.

(2) Arenites, or conglomeratic arenites, consisting of quartz and lithic grains, and pebbles in a kaolinitic matrix.

(3) Coal seams, with bands of pellet claystone between coal plies. The coal has abundant sulphide associated, chiefly as pyrite. One main coal seam has burnt by natural combustion over wide areas since prehistoric times and is still burning at the locality known as Burning Mountain, Wingen.

The phenomena associated with the coal firing on these sediments will be described in detail elsewhere. A summary of thermal and dynamic effects associated with burning is, however, given here as background to the current study. Zones of rock and soil, over coal burning at shallow depths (Fig. 2, A), are irregularly fissured and the intake of air through these fissures may introduce a blast-furnace effect to the natural combustion of coal and its gases. The zones are baked to red-white and white heat in domains immediately adjoining the fissures. In older, exposed fired zones, kaolinitic sandstones have been fused to irregular masses of vesicular buchite (Fig. 1, D; Fig. 2d, e) and the more refractory claystones (Fig. 1, G) have been converted to mullite-cristobalite-tridymite rocks (Fig. 1, F) or to a vitreous, structureless product (Fig. 1, E) heated to beyond the softening point. The temperatures reached are believed from laboratory firing and fusion tests on unfired material from the district, to range to more than 1700°C. Heated, hydrous fumes emanating from fissured ground give a sinter which is chiefly of β-quartz and haematite with abundant sulphur encrustations. Condensate from the fumes is highly acid, and strongly sulphatic.

The zone once occupied by coal is occupied after burning by a structureless ash formed chiefly of fired products of the abundant kaolinite of sedimentary bands formerly interleaved with the coal plies. Into this has fallen the super-incumbent strata now fired to mullite-tridymite-cristobalite or buchite. These rocks may be disrupted to a chaotic, collapse-breccia or retain their coherence by gentle subsidence between widespaced, normal faults.

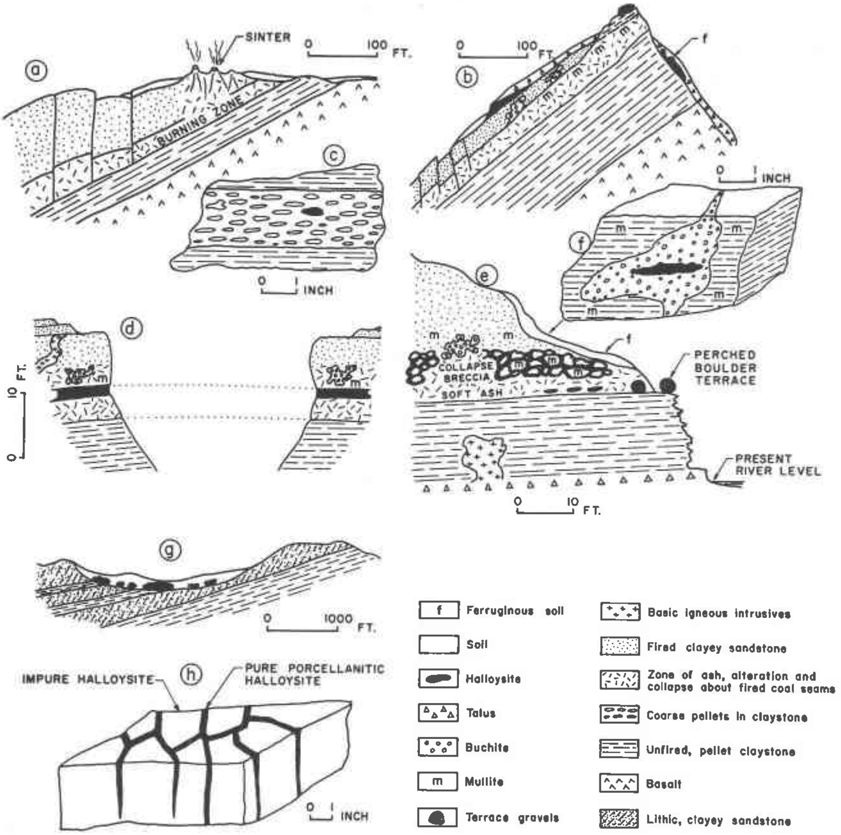

FIG. 2. Sketches illustrating the mode of field occurrence of halloysite. The scale of outcrop or specimens is of the order shown but there has been some distortion to illustrate the location of halloysite.

The collapse zones were presumably permeable, and subject to late thermal activity through the action of gases from the progressing, burning coal face as buchite selvedges and buchite intrusions characterize the interclast zones about the large, collapsed, mullite blocks. The zones were also subject to post-firing, groundwater permeation.

TYPES OF HALLOYSITE OCCURRENCE

The occurrences may be grouped broadly into three categories:

(1) Those associated with burning or burnt coal seams

(2) Those associated with Cainozoic weathering processes, or other supergene processes in the domains of groundwater circulation but not directly associated with burning coal

(3) Those occurring in clastic fragments of bedrock.

Deposits associated with burnt coal seams. Halloysite is found in several loci about fired coal seams. It occurs:

(a) as a replacement of the aluminous components of fired, fossil soils (Fig. 1, B) that once overlay the coal seams but are now massive buff sheets of halloysite rock, from 3″–15″ thick, exposed or concealed beneath recent talus deposits. This halloysite rock is chiefly metahalloysite associated with α-cristobalite and quartz. Sintered haematite outcrop and float overlie the deposits and may represent a fired, ferruginous zone of a lateritic soil in which the horizon now altered to a halloysite rock was a mottled or pallid zone.

(b) in ash zones of burnt seams, or in altered shales immediately beneath a burnt seam in association with α-cristobalite and low tridymite. Some occurrences at the Pimple, the locality described by Loughnan and Craig (1960), appear to be of this type (Fig. 2, d) though the main deposit at this locality had been stripped at the time the writer's study was undertaken.

(c) in collapse breccia zones where hydrated and metahalloysite occur as the outer exfoliation shells to spheroidally weathering blocks of mullite rock or vitrified claystone, and as material replacing interclast gouge and filling interclast openings.

(d) replacing refractory "inclusions" or relicts in a vesicular buchite host (Fig. 2, f).

Deposits associated with the superficial weathering profile. (a) Hydrated and metahalloysite occurs as nodules, sheets and veins in recent and older Cenozoic weathering profiles. The sheet deposits are massive, jointed, white, yellowish or pink, porous halloysite rock which may occur as a mottled or pallid zone beneath a goethitic, laterite layer or may occur exposed in naturally stripped areas. In some topographically high areas, from which topsoil has been stripped, halloysite rock occurs as the exposed cap to bedrock claystones and these occurrences are believed to be the exposed, lower horizons of partly eroded soil profiles. Halloysite rock of older soil profiles is in some places (Fig. 2, b) concealed by recent talus.

(b) Hydrated halloysite (Fig. 2, h) occurs as white, light yellow or light brown, soap-like, translucent, moist veins commonly filling shrinkage cracks in older, impure halloysite rock formed in both fired and unfired soils. This vein halloysite is the purest found and may be white and massive, or may occur in thin, red, brown and white, colour-banded layers suggesting deposition from gels. It dries to a porcellanitic texture and develops shrinkage cracks on air drying.

(c) Metahalloysite occurs as thin deposits as an intergranular film to kaolinite pellets, and also coating joints and bedding surfaces in bedrock claystones.

Clastic fragments in bedrock. Loughnan and Craig (1960) described the occurrence of a halloysite fraction in the pellet claystones of the hillock known as the Pimple. Some is probably attributable to the joint and other coatings described above but at least part of it has been traced by the writer to rare metahalloysite or partly hydrated halloysite pellets of the same size as the dominant kaolinite pellets of this rock type (Fig. 2, c).

MINERALOGY

The mineralogy of a range of occurrences is summarized on Table 1. The purest occurrence of the mineral is the white, porcellanitic, vein material (Table 2, E) which soon after collection showed a strong 10Å basal spacing, characteristic of hydrated halloysite, in its powder diffraction pattern. At the time of the present study this material had partly dehydrated to metahalloysite though a broad band about 10 Å is still

TABLE 1. MINERALOGY AND ASSOCIATIONS OF HALLOYSITE OCCURRENCE

Specimen No. and locality	Halloysite		Bedrock or Host	
	Character	Mineralogy	Character	Mineralogy
Murulla 1685	White, porcellanitic, vein matter	Hydrated halloysite, metahalloysite	Massive, cream soil horizon, ferruginous capping	Halloysite, α-quartz goethite
Murulla 1685 J	White, light-brown and brown vein matter	Hydrated halloysite, metahalloysite, allophane?	Massive, burnt fossil soil	Metahalloysite; α-cristobalite
Pages River, Murulla 1688	White, porcellanitic vein matter	Hydrated halloysite, metahalloysite	Burnt ash zone	Metahalloysite, α-cristobalite, tridymite
Muswellbrook 1888A	Yellow, soft, internal, porous, clastic fragment	Metahalloysite, α-quartz, Tr. kaolinite	Sedimentary bed of kaolinitic claystone	Kaolinite, α-quartz organic matter; Tr. halloysite
1888B	Joint and bedding coatings	Metahalloysite	Sedimentary bed of kaolinitic claystone	Kaolinite, α-quartz, organic matter; Tr. halloysite
Murulla 1685 Z	Pink, massive, concretionary weathering, soil horizon	Hydrated halloysite, metahalloysite, α-quartz	Unburnt pellet claystone ("tonstein")	Kaolinite, α-quartz, organic matter, Tr. halloysite Tr. goethite
Muswellbrook 1888C	"Inclusion" in buchite	Metahalloysite; α-cristobalite	Buchite	Rock glass, α-cristobalite, enstatite
Murulla 1685 N	Light gray, massive soil horizon	Metahalloysite; α-cristobalite	Naturally fired pellet claystone	Mullite, α-crystobalite, tridymite
Murulla 1685 M	Weathered, exfoliating shells of vitrified claystone of collapse zones	Hydrated halloysite, metahalloysite, α-quartz	Pellet claystone fired to softening point in collapse breccia above burning coal	Structureless, vitrified "mullite" rock

prominent. In this material (Fig. 1, A) metahalloysite is observed to dominate when the much greater intensity of the 001 reflection (10 Å) for the hydrated form (Brindley and Goodyear, 1948), with respect to that of the dehydrated form (7 Å), is taken into account.

It can be reasonably inferred that all Hunter Valley halloysites were once fully hydrated and their present character is a function of the stage reached in progressive dehydration to metahalloysite. The powder diffraction patterns of material from soils (Fig. 1, C) and air dried vein material (Fig. 1, A) accord with those expected for natural, mixed hydrated halloysite-metahalloysite materials that are passing towards equilibrium under conditions of low humidity (Brindley and Goodyear, 1948). The 001 spacing for the hydrated halloysite components range from 10.1 to 9.7 Å (Fig. 1, A and C). The 001 spacings of the metahalloysite components range from 7.5 to 7.3 Å. This data accords with Brindley and Goodyear's experimental data on the shrinkage associated with the decrease of humidity at low temperatures. In material dried at 300°C (Fig. 1, A′) the broad bands in the 10 Å region are lost and a sharp 7.2 Å peak is recorded. The material from exposed, dry, old soil profiles is chiefly metahalloysite with no significant 10 Å peak appearing on the powder diffraction diagram (Fig. 1, B).

TABLE 2. COMPARISON OF ANALYTICAL DATA ON NATURAL AND THEORETICAL MATERIALS

Theoretical Minerals				Natural Materials					
	K	H	M		A	B	C	D	E
SiO_2	46.56	40.86	28.21	SiO_2	45.28	51.70	51.97	41.61	43.78
TiO_2	—	—	—	TiO_2	0.85	1.03	1.70	1.36	0.44
Al_2O_3	39.50	34.66	71.79	Al_2O_3	37.38	43.77	43.00	33.31	37.49
Fe_2O_3	—	—	—	Fe_2O_3	1.61	2.60	2.37	2.34	Tr.
FeO	—	—	—	FeO	0.29	n.d.	n.d.	0.36	n.d.
MgO	—	—	—	MgO	0.15	0.13	0.11	0.12	0.10
CaO	—	—	—	CaO	0.10	0.10	0.12	Tr.	0.10
Na_2O	—	—	—	Na_2O	0.21	0.21	0.22	0.12	0.14
K_2O	—	—	—	K_2O	0.36	0.26	0.36	0.32	0.24
Structural H_2O	13.94	12.23	—	H_2O^+	13.95	Nil	Nil	14.52	13.96
Interlayer H_2O	—	12.24	—	H_2O^-	0.41	0.34	0.47	6.44	3.78
Total	100.00	10.00	100.00	Total	100.59	100.14	100.32	100.50	100.11

Analyses by J. H. Rattigan, except for TiO_2 of E which was determined by the Australian Mineral Development Laboratories.

K—theoretical kaolinite, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$; H—theoretical hydrated halloysite, $Al_2O_3 \cdot SiO_2 \cdot 4H_2O$; M—theoretical 3:2 mullite, $3Al_2O_3 \cdot 2SiO_2$; A—pellet claystone, 1888; B—fired claystone, 1686; C—vitrified claystone, 1685; D—impure halloysite, 1685Z; E—white, porcellanitic vein halloysite, 1685.

All the massive and nodular halloysites of soil profiles are contaminated with silica (Fig. 1, Table 1) which is recorded in several polymorphs from the halloysite deposits. The halloysite of soil profiles not subjected to firing of coal (Fig. 1, C) is distinctive in that quartz in the low thermal state is the invariable contaminant. The halloysite deposits associated with burnt sections of the coal seam at Wingen carry metastable α-cristobalite and tridymite (low) as contaminants (*cf.* Loughnan and Craig, 1960). β-quartz has been identified as a major component of siliceous sinter deposited from fumes issuing from fractures over the seam now burning at Mt. Wingen, but this polymorph does not coexist with halloysite in any sampled occurrence or in soils over cooled sections of the fired region.

GENESIS OF HALLOYSITE

Halloysite was not synthesized in the experiments of Roy and Osborne (1952, 1954) and Roy and Brindley (1956). It was inferred however that halloysite may have an upper stability limit of 175°C at 5,000 psi. It is generally held that halloysite is a product of weathering or supergene processes but some workers seem to demand a structural control for a kaolinite-halloysite transition. Loughnan and Craig (1960, p. 289) consider it doubtful that fired products of kaolinite would recombine with silica and water at low temperature to yield halloysite.

Bates (1952) considered that the kaolinite structure would have to be destroyed by solution before halloysite would form. Bates demanded humid or saturated conditions for halloysite occurrence.

Deer, Howie and Zussman (1963, p. 209) suggest that the most structurally plausible means of halloysite genesis is though the action of sulphate-bearing solutions on kaolinite, leading to gel formation and subsequent recrystallization.

The views summarized above show some contrasting opinions on the factors that may be dominant in halloysite genesis. The writer interprets his data, in terms of aspects of genesis, as follows.

Humid or saturated conditions. Most deposits can be referred to the humid or saturated conditions demanded by Bates (1952). The fossil, lateritic profiles are probably referable to Cainozoic palaeoclimates more humid than those of the present day. Recent vein halloysite (Fig. 2, h) is possibly still forming and samples were moist when collected from the damp subsoil, at 6 inches depth, on hillslopes during an abnormally dry year, and thus these deposits may be related to zones of spring seepage.

Fumes from burning coal are hydrous and the soils above them, and the collapsed zones about them, were subjected to hot, aqueous fluids during coal combustion. The deposits of the ash and collapse-breccia zones of lower cliffs at Pate's River (Fig. 2, e) are now some feet above normal river level but the elevated remnants of perched, gravel terraces indicate that the breccia zones must once have been close to the water table at an ancient river level. The breccia zones probably offered, subsequent to firing, and still offer, excellent channel-ways for groundwater seepages.

The deposits coating joints, fractures and grains of claystones can be related to groundwater percolation.

Compositional control. A dominant control in the Hunter Valley district would appear to be compositional (high total $Al_2O_3+SiO_2$) as only very pure kaolinitic claystones, (Table 2, A) their thermally derived products (Table 2, A–C) and rarely kaolinitic, quartz sandstones are the host rocks for halloysite formation. The limited range of constituents and the "very acid" compositional character of the bedrock would possibly prevent formation of any clay minerals other than kandites but the compositional control does not explain the formation of halloysite rather than kaolinite.

Structural control. The writer's data on occurrence and mineralogy (Table 1 and Fig. 1) suggest that there is no control by mineral structure apparent in halloysite formation as it develops from every fired product of kaolinite and kaolinite-silica rocks including kaolinite, impure halloysite, mullite-cristobalite rock, and structureless, vitrified products. This fact and the fact that vein deposits with a dried gel-like character fill open shrinkage gashes in fired soils, both suggest that a kaolinite-halloysite transition, insofar as such infers a direct mineral structure replacement, does not generally occur. The writer's interpretation of his data accords with the views of Bates (1952) and not Loughnan and Craig (1960).

About fired coal seams halloysite is associated with tridymite and cristobalite and presumably replaces anhydrous, aluminous phases that formed during the thermal reconstitution of claystones. However there is no positive evidence that replacement was controlled by mineral structure. In fact the occurrence of mullite-rock replacement suggests that halloysite was not, as proposed by Loughnan and Craig (1960), necessarily restricted in its replacement to products that were altered within isotherms that reached no more than the metakaolinite structural range in the thermal reconstitution of kaolinite.

The peculiar mineral associations of tridymite and cristobalite with partly hydrated halloysite, first brought to notice by these workers, is probably due to selective replacement at low temperatures of the aluminous phases of thermally dissociated claystones. It follows from studies on the dissociation of kaolinite (cf. Brindley and Nakahira, 1958) that any abundant tridymite and cristobalite in products derived from the simple (non-metasomatic) thermal alteration of such a pure kaolinite rock as that of Table 2, A (or Loughnan and Craig's MB1) must imply that some dissociation of the kaolinite structure has occurred beyond the metakaolinite region. The halloysite of such fired rocks may thus have formed from the aluminous phases silicon spinel or mullite, with the replacement process not involving all the silica phases produced in dissociation.

Sulphate activity. The writer has no evidence to dispute the statement of Deer, Howie and Zussman (1963, p. 209) on halloysite genesis through sulphate activity except that materials other than kaolinite may be attacked.

In the Greta Coal Measures pyrite is abundant in coal seams, in carbonaceous pellet clays and about basic intrusives. Moreover the overlying unit, the marine Maitland Group, has abundant sulphates in the form of gypsum, and originally in the form of glauberite. The firing of coal has led to heated sulphurous fumes and condensates, and of sublimates of elemental sulphur, affecting the fired zones. It may be inferred, therefore that sulphate bearing fluids had some influence in the formation of halloysite deposits associated both with fired and unfired strata.

The temporal relationship between halloysite formation and combustion is not known. Because of thermal stability considerations, and tests on samples about currently burning areas, it is improbable that halloysite formed near the seat of combustion. However "telethermal", sulphate bearing fluids, derived in part from burning coal, acting on permeable ash and collapse zones of burnt out areas, may have contributed to halloysite formation somewhat in the manner proposed by Loughnan and Craig (1960, p. 279) except that mullite and other phases as well as metakaolinite, were probably replaced.

The ash and collapse zones of older fired areas were, and are, permeable zones some of which are near the present watertable. As such they were probably saturated or near saturated for long periods after combustion occurred and it is not possible to state positively that sulphate solutions were an essential factor in halloysite formation. No alunite, alkali or calc-alkali sulphates have yet been found in direct association with halloysite of the Hunter River deposits and the role of sulphates must remain a matter for speculation.

Some anomalies. Those pellets of halloysite which occur with kaolinite in bedrock claystones are somewhat anomalous. It is necessary to explain how such discrete fragments of two kandite clays occur in such close association in the one detrital rock. It seems unlikely that partially hydrated halloysite fragments are from a stripped, Permian soil horizon and were carried with kaolinite pellets to a coal-swamp environment. The limitations of such a theory of origin lie in the dehydration characteristics of halloysite which has been held to be unstable beyond 175°C at 5000 psi, and in the presumed thickness (greater than 5000 feet) of younger strata that overlie the Greta Coal Measures. An alternative explanation is the local action of sulphate waters, derived from pyrite crystals of the claystone, on kaolinite clasts, but this does not explain the occurrence of halloysite "clasts" that are found also in non-pyritic, conglomeratic arenites of the Greta Coal Measures.

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