

## The natural conversion of ordered kaolinite to halloysite (10Å) at Burning Mountain near Wingen, New South Wales

F. C. LOUGHNAN AND F. IVOR ROBERTS

School of Applied Geology  
The University of New South Wales  
New South Wales, Australia

### Abstract

In the vicinity of Burning Mountain, New South Wales, an unusually thick sequence of kaolinite clayrocks (flint clays) has been considerably altered by heat from the natural combustion of coal seams. Recent quarrying operations in the area have exposed excellent sections through the metamorphosed succession and it is evident that in the high temperature zone above the burnt seams ordered kaolinite of the clayrocks has been converted to mullite and cristobalite. Below the seams, however, the temperatures were considerably lower and metakaolin resulted. Much of the metakaolin has subsequently been rehydroxylated by groundwater to yield halloysite (10Å) and this reaction is continuing at the present time. To determine the reason for development of halloysite (10Å) instead of kaolinite as the rehydroxylated product, a study has been undertaken of the various intermediate phases in the reaction sequence *ordered kaolinite* → *metakaolin* → *halloysite (10Å)*. Attempts have also been made to reproduce the rehydroxylation reaction in the laboratory by relatively mild hydrothermal treatment and whereas these have proven unsuccessful to date, it would appear that the upper temperature limit for development of halloysite (10Å) does not lie much above ambient conditions.

### Introduction

Primarily because of the significance to ceramics, thermal reactions involving ordered kaolinite have been studied by many workers over the past several decades and it has been established that the mineral, held at a temperature a little above 400°C for a protracted period, is dehydroxylated to form an X-ray amorphous phase termed *metakaolin* (Roy and Osborn, 1954). At somewhat higher temperatures however, an assemblage of mullite and cristobalite results. Nevertheless, controversy still persists, particularly with respect to the structure of metakaolin and other intermediate phases that may develop in this reaction sequence. Thus, according to Brindley and Nakahira (1959), metakaolin occurs up to about 925°C at which temperature it is converted to a silica-alumina spinel ( $2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ ) and at approximately 1050°C this spinel breaks down to yield mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) and cristobalite ( $\text{SiO}_2$ ). However, Delmon *et al.* (1979, p. 642) considered from results of density and radial electron distribution studies of the phase changes in well-ordered kaolinite

between 925°C and 950°C, that the data are "completely incompatible with the hypothesis that a mixed Si-Al spinel phase forms". These authors contended rather that extensive segregation of silica and alumina occurs with the latter being mostly in the *gamma* form. Pertinent in this respect, Blaszcak and Pampuch (1972) undertook chemical and infrared absorption studies of the decomposition products of kaolinite and concluded the results indicated segregation of silica and alumina at temperatures as low as 500°C to 600°C.

Roy *et al.* (1955) and Brindley and Nakahira (1959), nevertheless, have shown by electron diffraction and X-ray diffraction techniques respectively, that single crystals of kaolinite converted to metakaolin retain the *a* and *b* lattice parameters of the original kaolinite up to at least 880°C and that the principal structural change involved in the conversion is a shift in the aluminum from octahedral to tetrahedral coordination with oxygen. Accompanying this change the *c*-axis periodicity is destroyed. Subsequently, Percival and Duncan (1974) verified the

structural model of Brindley and Nakahira (1959) by means of infrared absorption spectroscopy.

That at least some remnants of the kaolinite structure persist in metakaolin seems evident from the ease with which kaolinite can be reconstituted from metakaolin by relatively mild hydrothermal treatment (van Nieuwenberg and Pieters, 1929; Hill, 1954; Saalfeld, 1955; Roy and Brindley, 1955). Moreover, since variations in the calcination temperature within the range of 405°–850°C appear to have little effect on the rate of rehydroxylation, presumably these remnant structures persist to at least 850°C. Reconstitution of kaolinite from metakaolin has mostly been carried out in autoclaves in which the  $P_{H_2O}$  is dependent on the temperature. But, in the apparatus employed by Roy and Brindley (1955), pressure was varied independently of the temperature and, from the results, these authors concluded that the  $P_{H_2O}$  is much less important than temperature in influencing the rate of the reaction.

Roy and Brindley (1955) also examined the thermal decomposition of nacrite, dickite, disordered kaolinite and halloysite and found that these minerals respond in a manner similar to well-ordered kaolinite when subjected to temperatures in the range of 405°–850°C. They also found that whereas each of the "meta" phases can be rehydroxylated under relatively mild hydrothermal conditions, the reactions are considerably slower than those for well-ordered kaolin and, irrespective of the structure of the original kandite, the rehydroxylated product is invariably kaolinite.

Nevertheless, several natural occurrences of halloysite (10Å) have been recorded where it has been contended that the mineral originated through the rehydroxylation of metakaolin. Thus, Loughnan and Craig (1960) described a relatively thick zone of halloysite (10Å) containing cristobalite and tridymite in places, overlying kaolinite clayrocks or flint clays near Muswellbrook, New South Wales. Mullite and cristobalite occur above the halloysite zone and it was believed heat from combustion of a coal seam altered the overlying clayrocks to mullite and cristobalite whereas similar strata below the seam were subjected to much lower temperatures, sufficient only to promote conversion of the kaolinite to metakaolin. Halloysite (10Å) was considered to have formed from metakaolin by a rehydroxylation process. Bardossy *et al.* (1970) invoked a similar mechanism to account for the presence of halloysite (10Å) in the Bédarioux bauxite deposit of southern France although these authors attributed the kaolinite-me-

takaolin conversion to heat from intrusion of a basaltic dyke.

Metakaolin was not encountered in either of these deposits, however, and since the proposed mechanism is obviously at variance with the experimental data of Roy and Brindley (1955) and others, doubt remained. In an attempt to resolve this enigma therefore, a further study has been undertaken with attention being focussed on the Burning Mountain area near Wingen where recent quarrying operations have exposed excellent sections of the metamorphic zones associated with the natural combustion of coal seams.

### Geological setting

At Burning Mountain in the upper Hunter Valley of New South Wales (Fig. 1) coal seams of the Early Permian Koogah Formation are on fire and probably have been for the past 15,000 years (Loughnan, 1973). The Koogah Formation is restricted in outcrop to the area immediately northeast of Wingen where it can be traced along the limbs of the Sandy Creek Syncline and Pages River Anticline for a distance of 16 km and is truncated at both ends by faults (Manser, 1967). Near Burning Mountain and in the quarries to the northeast the dip is 20° to 30° toward the northwest but on the eastern side of the Sandy Creek Syncline it approaches the vertical and in places is slightly overturned. The unit varies in thickness from about 50 m in the vicinity of Burning Mountain to more than 200 m in the eastern exposures and is of nonmarine origin, comprising for the most part thick massive beds of kaolinite clayrocks or flint clays that range in texture from very fine grained to conglomeratic and coarsely brecciated with clasts measuring nearly 2 cm across. Kaolinite, which has an ordered structure (Hinckley Index >1.3), is frequently the only mineral detectable in these clayrocks by either chemical or X-ray means although locally boehmite or quartz may be present as major constituents and anatase, siderite, hematite and gibbsite are not uncommon accessories.

Associated with the massive beds of kaolinite clayrocks are lenticular coal seams, which in the eastern part may attain a thickness of 25 m although throughout most of the area they rarely exceed 2 m. From the few available analyses of the coal a high sulphur content is indicated and probably ignition of the seams resulted from heat generated by oxidation of pyrite. Only the uppermost seams have been affected in this manner and combustion has progressed in a general southwesterly direction leaving unburnt segments in its wake. These segments probably owe

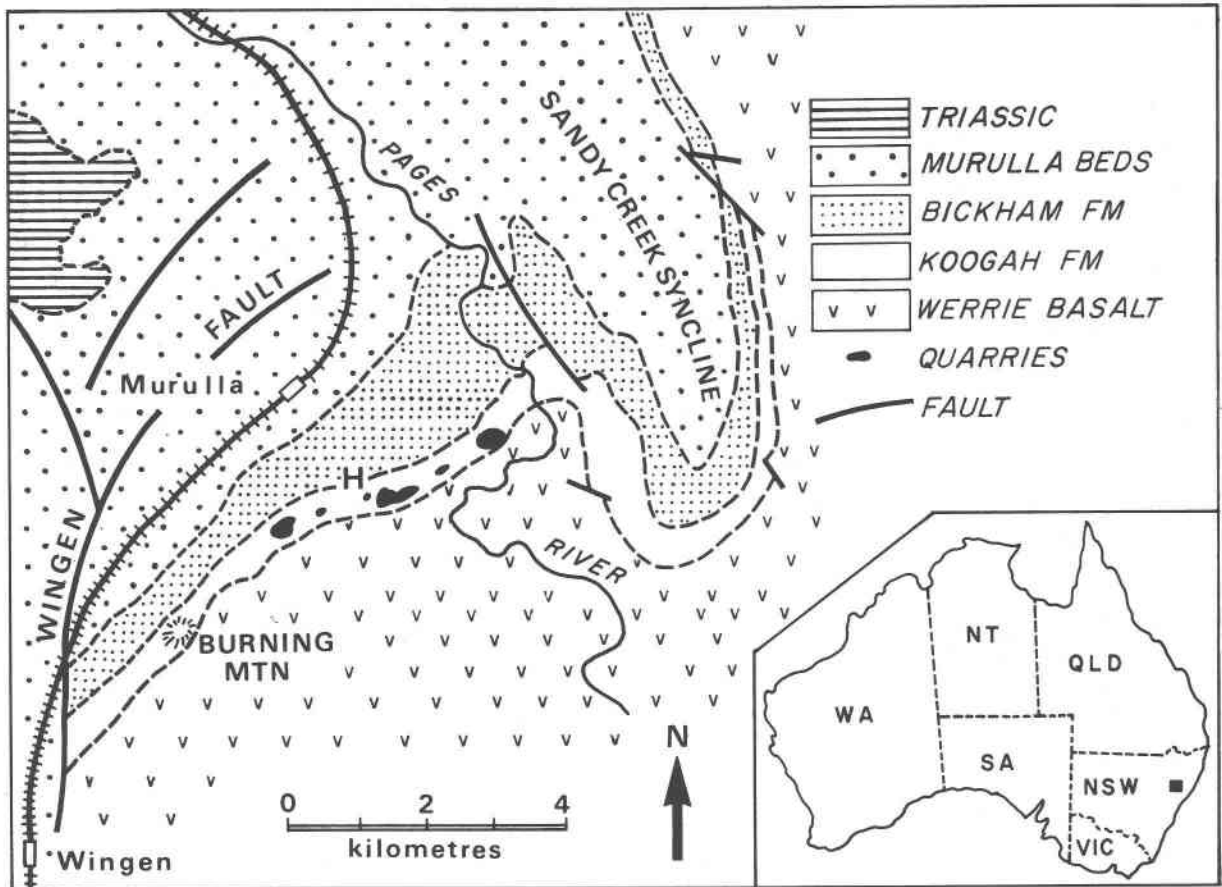


Fig. 1. Geological sketch map of the Burning Mountain area near Wingen. H denotes the "Halloysite" quarry.

their preservation to saturation by groundwater at the critical periods. The combustion site is currently advancing at the rate of one meter per year.

The Koogah Formation is underlain by the Werrie Basalts, which have a thickness of about 1800 meters and are composed of basic to intermediate lavas with minor amounts of pyroclastic and epiclastic sedimentary rocks. The volcanic rocks were intensely weathered prior to deposition of the Koogah Formation and remnants of a once thick paleosol generally separate the two units.

Conglomerate, sandstone and shale of the marine Bickham Formation conformably overlie the Koogah Formation and these are succeeded in turn by a second coal-bearing sequence of Late Permian age designated the Murulla Beds by Manser (1967).

#### Combustion metamorphism of the kaolinite clayrocks

In the area 2 to 5 km northeast of Burning Mountain, exploitation of natural chamotte (calcined kaolinite clayrock) for use in the production of refrac-

tories has yielded a number of excellent exposures of the burnt coal seams and attendant zones of metamorphosed kaolinite clayrock. A generalized section through these zones is shown diagrammatically in Figure 2 and it will be observed that the uppermost has a thickness ranging up to 15 m, depending upon the extent of erosion, and comprises mainly dense, hard blocks of mullite, cristobalite and tridymite with sporadic hematite lenses. The cristobalite is generally present in the *alpha* form but in several samples it has an X-ray diffraction pattern akin to that of the *beta* variety, which according to Sosman (1955), is unstable below 280°C and at 200°C should invert instantaneously to the *alpha* structure. However, this type of phenomenon has been noted previously by Flörke (1955), who attributed it to disordering in the *alpha* cristobalite lattice. Tridymite is considerably less abundant than cristobalite and unlike the latter, has probably been derived entirely from sporadic quartz grains in the original kaolinite clayrocks. The temperatures attained in this zone were well in excess

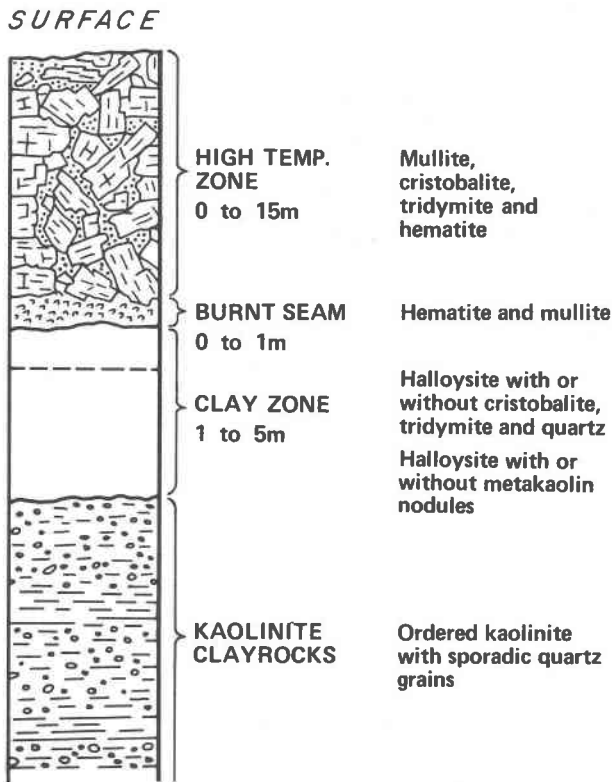


Fig. 2. A generalized section through the metamorphosed zones.

of 1000°C and, since some of the altered clayrocks in close proximity to the burnt seam have apparently suffered plastic deformation, conceivably in places they reached 1750°C, the softening point of the material.

The original coal seam is now represented by a zone up to a meter thick, consisting of massive and vesicular hematite with disseminated fragments of mullite rock. The latter were probably dislodged from the roof during collapse of the seam and became embedded in the iron oxide, which at the time was in a molten or quasi-molten state.

A clearly defined surface separates the burnt seam from the underlying clay zone, which is white, light grey or less commonly reddish in color, and varies up to several meters thick. Halloysite (10Å) is the dominant crystalline phase in this zone and frequently constitutes more than 95% of the material. Nevertheless, in the upper 30 cm cristobalite and tridymite may be present in addition to halloysite (10Å), and quartz grains, some of which are rimmed with cristobalite, have also been encountered. This intimate association of cristobalite, tridymite and halloysite

(10Å) is incongruous in that the minimum temperature for conversion of quartz to cristobalite and tridymite is 867°C (Sosman, 1955) whereas, according to Roy and Osborn (1954), the upper limit of stability for halloysite (10Å) is 175°C and indeed, from more recent work by Minato and Aoki (1978), it is probably well below this temperature. The clay zone may pass down into unaltered kaolinite clayrock although frequently it is underlain by mullite-cristobalite rock resulting from combustion of a second coal seam.

Closely spaced veins, about a centimeter across and also composed of halloysite (10Å), intersect the clay zone in places. The vein halloysite differs however from that of the host rock in being brittle and unusually dense and in having a porcelaneous appearance on the fracture surfaces. These veins do not extend into the burnt seam or mullite-rich zones.

#### Origin of the clay zone

Whereas the succession described above characterizes alteration of the kaolinite clayrocks throughout much of the area, in the "Halloysite" quarry (Fig. 1), which has been opened primarily for the production of absorbent clay, the kaolinite clayrocks are succeeded by a zone nearly 10 m thick, composed predominantly of rounded nodules, which measure up to 30 cm in diameter, separated by light colored clay (Fig. 3). The clayrocks forming the floor of the quarry vary in texture from fine grained to coarsely brecciated and are essentially monomineralic, consisting of ordered kaolinite (Fig. 5). But, although the nodules have the same textural features as the kaolinite clayrocks, they are considerably harder, comprise material that is amorphous to X-radiation and significantly have the infrared absorption spectrum of metakaolin. Indeed, as far as can be determined, this is the first recorded natural occurrence of metakaolin. Nevertheless, some of the nodules have softer and lighter colored rims (Fig. 4) and these pass outward into the internodular clay, which is composed of halloysite (10Å) and is in the form of ex-foliated layers encompassing the nodules. At this location the upper part of the succession has been eroded and only a few large boulders of mullite-cristobalite rock strewn over the surface attest to the former existence of a high temperature zone.

Since the nodular metakaolin is obviously an intermediate phase in the transition of ordered kaolinite to halloysite (10Å), X-ray diffraction, differential thermal and infrared absorption studies were undertaken of a series of samples across one of these nodules to gain a better understanding of the processes

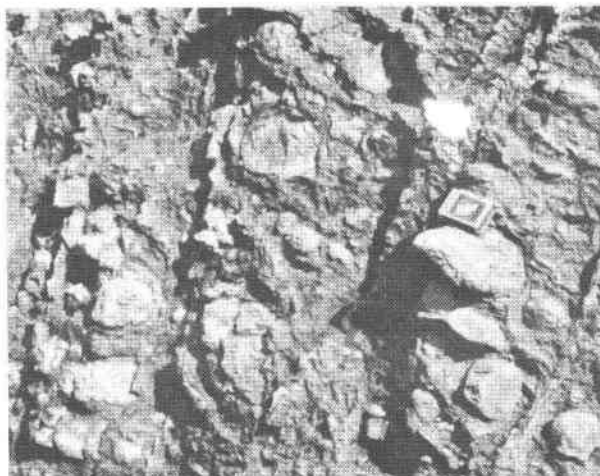


Fig. 3. Nodular metakaolin and internodular halloysite (10Å) exposed on wall of the "Halloysite" quarry.

involved. Some of these results are presented in Figures 5, 6 and 7 respectively, and it will be observed that there is a progressive increase in the halloysite content at the expense of metakaolin as the outer rim is approached. Analyses of a representative sample of the underlying kaolinite clayrocks have also been included for comparison.

In addition, transmission electron micrographs were obtained for the core and rim of the nodular material as well as the internodular halloysite (10Å). The metakaolin constituting the core is mostly in the form of plates, some of which have a regular and in part, hexagonal morphology (Fig. 8a) presumably inherited from the kaolinite of the parent clayrocks. The halloysite composing the bulk of the nodule rim

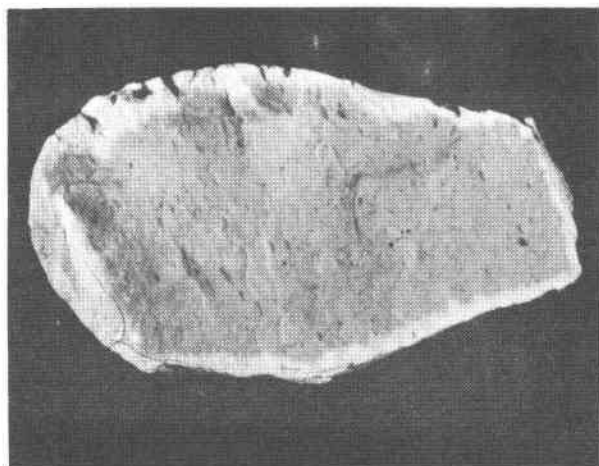


Fig. 4. A metakaolin nodule with lighter colored rim composed mainly of halloysite (10Å). Nodule is 6 cm long.

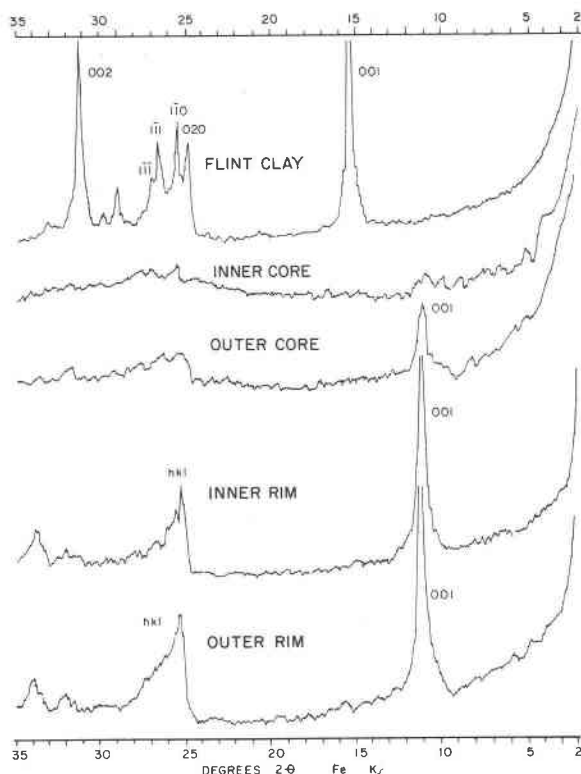


Fig. 5. X-ray diffraction data for samples of kaolinite clayrock, and core and rim of a metakaolin nodule.

on the other hand, has a spheroidal structure (Fig. 8b) similar to that described by Askenasy *et al.* (1973) and Dixon and McKee (1974). These spheroids comprise concentric layers with sporadic interlayer partings, and at the exterior, tend toward a shell-like appearance. The closely associated internodular halloysite in contrast, is mostly tubular (Fig. 8c) and as such closely resembles the vein halloysite (Fig. 8d). These tubes have maximum electron density at the margins and probably represent elongated plates that have been furled from opposite sides (Wilke *et al.*, 1978).

From the chemical analyses (Table 1) it is evident that the alteration of metakaolin to halloysite (10Å) has been accomplished through the uptake of an appreciable quantity of water and this has led to an increase in volume and development of the exfoliated layers about the remnant metakaolin nodules. Since these processes are continuing at the present time in areas far removed from the combustion site, the water is undoubtedly of meteoric origin.

It is apparent therefore, that the clay zone has originated from the kaolinite clayrocks by a two-stage process involving initial dehydroxylation of ordered

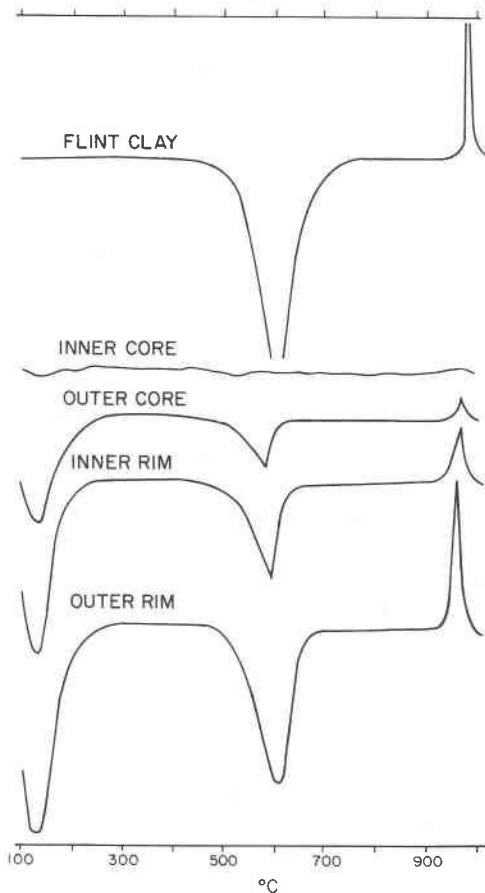


Fig. 6. Differential thermal data for samples of kaolinite clayrock, and core and rim of a metakaolin nodule.

kaolinite under the influence of heat from combustion of an overlying coal seam to yield metakaolin, and subsequent slow rehydroxylation of the metakaolin through reaction with groundwater leading to crystallization of halloysite ( $10\text{\AA}$ ). The temperatures experienced in the clay zone ranged from a little above  $400^{\circ}\text{C}$  at the transition of the clayrocks to metakaolin, to more than  $867^{\circ}\text{C}$  immediately below the burning coal where quartz was altered, at least in part, to cristobalite and tridymite. But, since mullite has not been encountered in this zone, the metakaolin-mullite conversion temperature was not reached at any point.

The reason for the development of halloysite instead of kaolinite as the rehydroxylated product is not understood, for not only has halloysite defied all attempts at synthesis to date but furthermore, from studies by Roy and Brindley (1955) and others, kaolinite seems to be the stable structure resulting from

rehydroxylation of the meta phase of all kandite minerals. Roy and Brindley did detect differences in the behavior of the "meta" phases on hydrothermal treatment and suggested that these could be attributed to variations in the crystal structure of the parent mineral and the condition under which dehydroxylation was effected. An attempt was made therefore to determine whether these factors had played a decisive role in the preferential crystallization of halloysite ( $10\text{\AA}$ ) in the clay zone at Burning Mountain. To this end, samples of kaolinite clayrock and internodular halloysite, both previously calcined at  $500^{\circ}\text{C}$  and  $800^{\circ}\text{C}$  for 24 hours, together with one of the natural metakaolin were held in autoclaves with excess water at  $350^{\circ}\text{C}$  for 7 days. The X-ray diffraction traces for the products are shown in Figure 9 and it is apparent that although all of the "meta" phases yielded kaolinite, that derived from the natural metakaolin is the most poorly ordered. The reason for this is not clear. Possibly it is due to a struc-

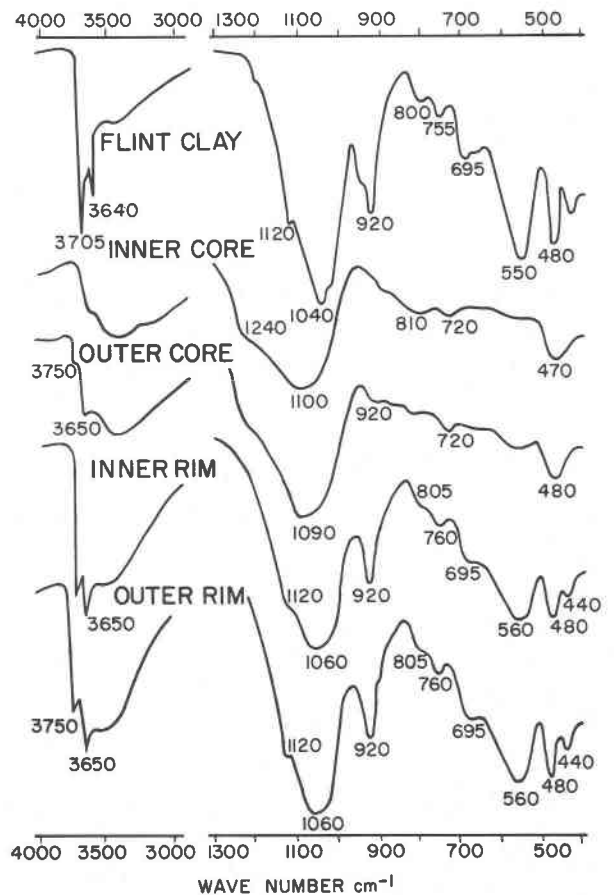


Fig. 7. Infrared absorption data for samples of the kaolinite clayrock, and core and rim of a metakaolin nodule.

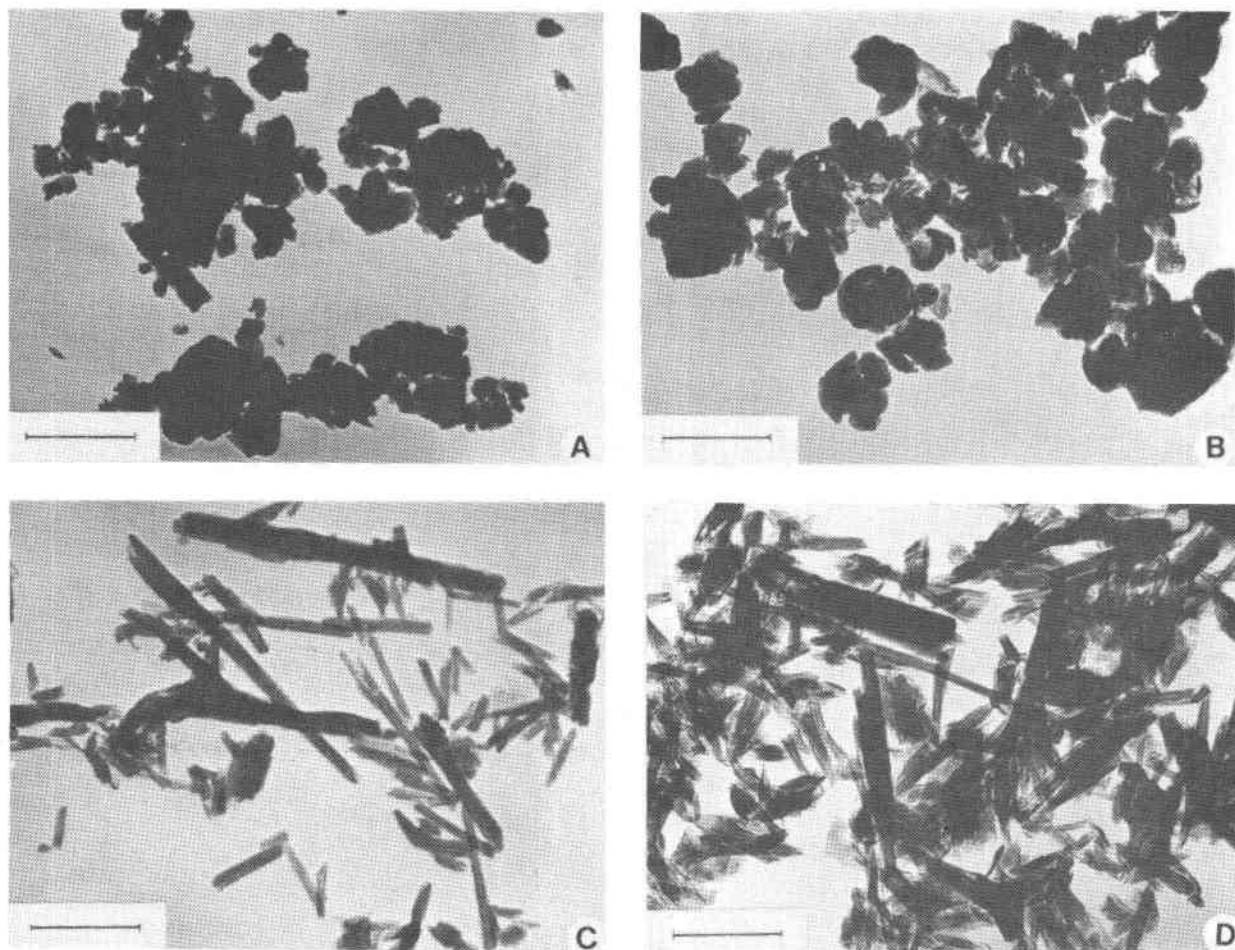


Fig. 8. (a) Transmission electron micrograph of the metakaolin. (Bar = 0.5 microns); (b) Transmission electron micrograph of the halloysite (10Å) forming rim of metakaolin nodule. (Bar = 0.5 microns); (c) Transmission electron micrograph of the internodular halloysite (10Å). (Bar = 0.5 microns); (d) Transmission electron micrograph of the vein halloysite (10Å). (Bar = 0.5 microns).

tural difference arising from the conditions under which the natural metakaolin formed. Significant in this respect, the natural metakaolin does have a distinctive differential thermal curve in that the high temperature exotherm is absent (Fig. 10). Nevertheless, such differences were not detected by infrared absorption spectroscopy. Moreover, if the natural metakaolin is subjected to hydrothermal treatment at 143°C for much longer periods (Fig. 9), well-ordered kaolinite results.

Presumably the inability to form halloysite (10Å) in these runs is due to temperature-pressure conditions outside the stability field for the mineral and certainly the work of Minato and Aoki (1978) substantiates this conclusion. A further attempt was therefore made to synthesize the mineral through rehydroxylation of the natural metakaolin in an auto-

clave at  $95^{\circ} \pm 2^{\circ}\text{C}$  over a period of 20 weeks but kaolinite was again the product (Fig. 9). However, the reconstituted mineral has a disordered structure and apparently at this temperature a much longer period is necessary for development of ordered kaolinite. From these results it is evident that the upper limit of formation for halloysite (10Å) does not lie much above ambient temperature.

#### Origin of the vein halloysite

As noted above, halloysite (10Å) also occurs as thin veins, which appear to infill contraction fractures in the clay zone but unlike that constituting the host rock the vein halloysite has a compact, porcelainous texture. Presumably it was emplaced during cooling of the metakaolin and, as such, is unrelated in origin to the zone halloysite.

Table 1. Chemical analyses

	1	2	3	4	5	6	7
SiO <sub>2</sub>	45.05	50.05	38.22	37.45	49.9	39.78	51.90
Al <sub>2</sub> O <sub>3</sub>	37.22	39.97	31.03	30.11	31.4	32.26	43.04
Fe <sub>2</sub> O <sub>3</sub>	0.65	1.34	1.53	0.96	1.53	0.37	1.48
TiO <sub>2</sub>	1.47	1.36	1.79	1.21	2.20	0.06	2.21
CaO	0.13	0.08	0.15	0.13	0.05	0.14	0.14
MgO	0.00	0.07	0.00	0.07	0.05	0.00	0.00
K <sub>2</sub> O	0.01	0.14	0.03	0.06	-	0.01	0.02
Na <sub>2</sub> O	0.00	0.17	0.04	0.22	-	0.00	0.05
H <sub>2</sub> O <sup>+</sup>	13.37	3.21	10.69	10.39	10.54	11.99	0.99
H <sub>2</sub> O <sup>-</sup>	1.95	3.28	17.33	19.90	4.17	15.02	0.31
Total	99.85	99.67	100.81	100.50	99.7	99.63	100.14

Analyst:- I. E. Wainwright

1. Kaolinite clayrock 2. Core of metakaolin nodule  
3. Rim of metakaolin nodule 4. Intermodular halloysite  
5. Halloysite with cristobalite and tridymite 6. Vein halloysite  
7. Mullite-cristobalite rock.

At the present combustion site sulphur and sulphate minerals are being deposited about the vents and conceivably similar solfataric activity has been responsible for development of the vein halloysite. Adjacent to the burning seam, heated and superheated fluids charged with sulphate ions probably attacked and dissolved in part the altered kaolinite clayrocks; but as these fluids migrated to distant, cooler regions, they became supersaturated with respect to silica and alumina and precipitation ensued. Finally crystallization of this precipitate yielded halloysite (10Å).

### Conclusions

From the study of the halloysite (10Å) associated with kaolinite clayrocks and burnt coal seams in the Burning Mountain area near Wingen it is possible to draw the following conclusions:

1. The halloysite (10Å) developed from ordered kaolinite of the clayrocks by two separate mechanisms. That constituting the thick, persistent clay zone below the burnt coal seam evolved through the initial conversion of the kaolinite to metakaolin, by heat from combustion of the coal, and the subsequent rehydroxylation of the metakaolin through reaction with groundwaters. The halloysite (10Å) forming the thin veins, on the other hand, is probably the product of solfataric activity.

2. The temperatures attained in the halloysite-rich clay zone ranged from a little above 400°C at the

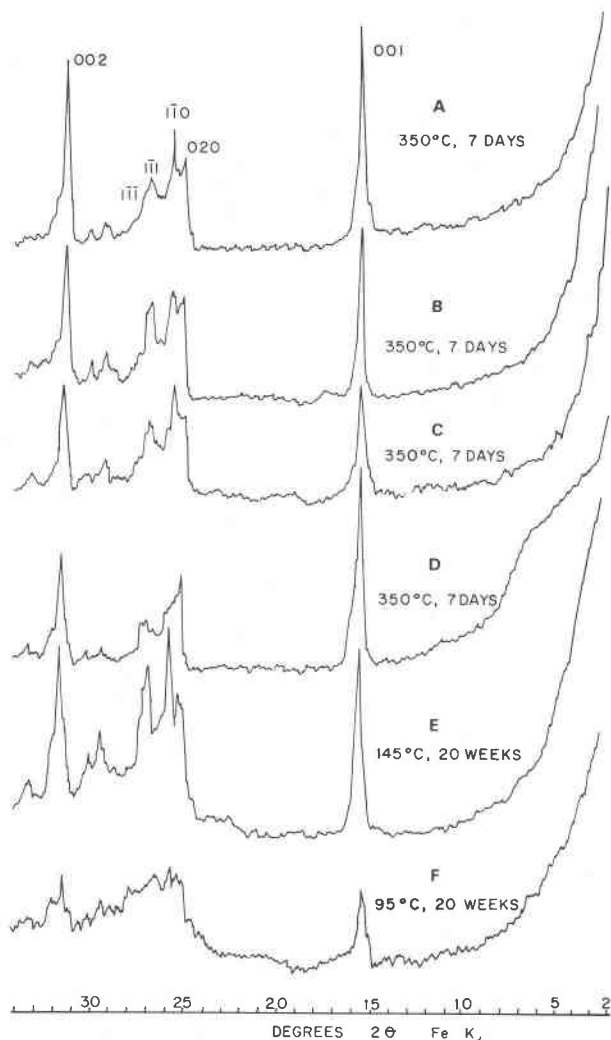


Fig. 9. X-ray diffraction traces of the rehydroxylated products. Autoclave conditions shown. A. Kaolinite clayrock precalcined at 500°C for 24 hours. B. Kaolinite clayrock precalcined at 800°C for 24 hrs. C. Intermodular halloysite precalcined at 800°C for 24 hrs. D, E and F. Natural metakaolin.

base to about 950°C immediately below the combustion zone. But, above the burnt seam they were considerably higher, sufficient to convert the kaolinite clayrocks to an assemblage of mullite and cristobalite with or without tridymite, and probably reached 1750°C in places.

3. The reason for the development of halloysite (10Å) instead of kaolinite as the rehydroxylated phase in the clay zone is not clear particularly since all attempts to synthesize halloysite (10Å) from the naturally occurring metakaolin by hydrothermal means have proven unsuccessful. From the results, however, it would appear that the upper temperature



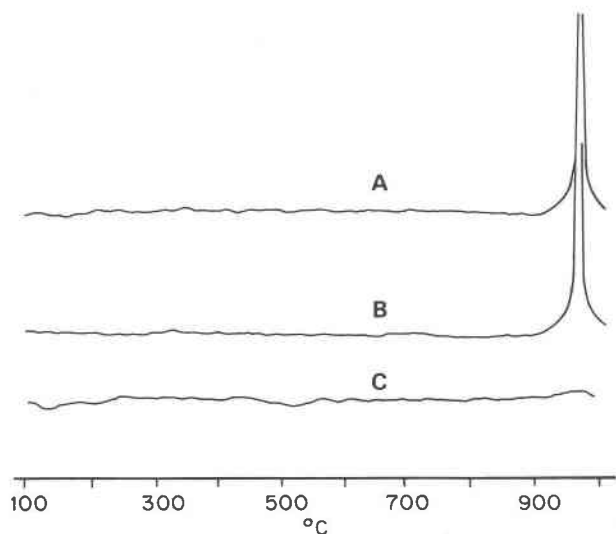


Fig. 10. Differential thermal curves for "meta" phases. A. Kaolinite clayrock precalcined at 800°C. B. Internodular halloysite precalcined at 800°C. C. Natural metakaolin.

limit for development of halloysite does not lie much above ambient conditions.

4. As far as can be determined this is the first record of naturally-occurring metakaolin.

#### Acknowledgments

We are much indebted to I. E. Wainwright for the chemical analyses, M. K. Withers for advice on the infrared absorption data and A. S. Malin and V. Piegerova for use of the transmission electron microscope.

#### References

- Arkenasy, P. E., Dixon, J. B. and McKee, T. R. (1973) Spheroidal halloysite in a Guatemalan soil. *Proceedings of Soil Society of America*, 37, 799-803.
- Bardossy, G., Mesko, L., Panto, G. and Sargo, C. (1970) Le metamorphisme de contact de la bauxite de Bédarieux et quelques aspects généraux du metamorphisme des bauxites. *Bulletin de Societe Geologie de France*, 12, 856-869.
- Blaszczak, K. and Pampuch, R. (1972) Study of the reaction series kaolinite-metakaolin by infrared spectroscopy and acid dissolution technique. *Mineralogia Polonica*, 3, 4-19.
- Brindley, G. W. and Nakahira, M. (1959) The kaolinite-mullite reaction series: II Metakaolin. *Journal of the American Ceramic Society*, 42, 314-318.

- Delmon, B., Herbillon, A. J., Leonard, A. J. and Bulens, M. (1979) Critical assessment of the joint use of various physico-chemical techniques in the study of the thermal transformation of kaolin. In M. M. Mortland and V. C. Farmer Eds., 6th International Clay Conference (1978), *Developments in Sedimentology* 27, Elsevier, 639-648.
- Dixon, J. B. and McKee, T. R. (1974) Internal and external morphology of tubular and spheroidal halloysite particles. *Clays and Clay Minerals*, 22, 127-137.
- Flörke, O. W. (1955) Zur frage des "hoch" Cristobalit in opalen, bentoniten und glassern. *Neues Jarbuch Mineralogische Monatshefte*, 217-233.
- Hill, R. D. (1953) The rehydration of fired clay and associated minerals. *Transactions of British Ceramic Society*, 52, 589-613.
- Loughnan, F. C. (1973) Kaolinite clayrocks of the Koogah Formation, New South Wales. *Journal of Geological Society of Australia*, 20, 329-341.
- Loughnan, F. C. and Craig, D. C. (1960) An occurrence of fully hydrated halloysite at Muswellbrook, New South Wales, *American Mineralogist*, 45, 783-790.
- Manser, W. (1968) Geological map of New England 1:100,000, Wingen sheet. University of New England Publication, Armidale, N.S.W.
- Minato, H. and Aoki, M. (1979) Rate of transformation of halloysite to metahalloysite under hydrothermal conditions. In M. M. Mortland and V. C. Farmer Eds. 6th International Clay Conference, *Developments in Sedimentology* 27, Elsevier, 619-627.
- Percival, H. J. and Duncan, J. F. (1974) Interpretation of the kaolinite-mullite reaction sequence from infrared absorption spectra. *Journal of the American Ceramic Society*, 57, 57-61.
- Roy, R. and Brindley, G. W. (1955) Study of hydrothermal reconstitution of the kaolin minerals. *Clay Minerals*, 4th National Conference, National Academy of Science 456, 125-132.
- Roy, R. and Osborn, E. F. (1954) The system alumina-silica-water. *American Mineralogist*, 39, 853-885.
- Roy, R., Roy, D. M. and Francis, E. E. (1955) New data on the thermal decomposition of kaolinite and halloysite. *Journal of the American Ceramic Society*, 38, 198-205.
- Saalfeld, H. (1955) Hydrothermale bildung von tonmineralen aus metakaolin. *Berichte Deutsche Keramische Gesellschaft*, 52, 150-152.
- Sosman, R. B. (1955) New and old phases of silica. *Transactions of British Ceramic Society*, 54, 655-670.
- Van Nieuwenberg, C. J. and Pieters, H. A. (1929) Rehydration of metakaolin and synthesis of kaolin. *Berichte Deutsche Keramische Gesellschaft*, 10, 260-263.
- Wilke, B. M., Schwertman, u. and Murad, E. (1978) An occurrence of polymorphic halloysite in granite saprolite of Bayerischer Wald, Germany. *Clay Minerals*, 13, 67-77.

*Manuscript received, January 5, 1981;  
accepted for publication, April 28, 1981.*