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

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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 Osborne, 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, Blaszczak 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 that both of these minerals are formed by rehydroxylation of disordered kaolinite. Nevertheles, 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.

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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 weathed-
ered prior to deposition of the Koogah Formation
and remnants of a once thick paleosol generally sepa-
rate the two units.

Conglomerate, sandstone and shale of the marine
Bickham Formation conformably overlie the Koog-
gh 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 Moun-
tain, exploitation of natural chamotte (calcined ka-
olinite 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 meta-
morphosed kaolinite clayrock. A generalized section
through these zones is shown diagramatically in Fig-
ure 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 spo-
radic 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 in-
stantaneously 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
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 exfoliated 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
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 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
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 (10Å). The temperatures experienced in the clay zone ranged from a little above 400°C at the transition of the clayrocks to metakaolin, to more than 867°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 (10Å) in the clay zone at Burning Mountain. To this end, samples of kaolinite clayrock and internodular halloysite, both previously calcined at 500°C and 800°C for 24 hours, together with one of the natural metakaolin were held in autoclaves with excess water at 350°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-
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 autoclave at 95°±2°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, pellaneous 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

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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 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.

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References


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