# The thermal reactions of nacrite and the formation of metakaolin, γ-alumina, and mullite.[1]

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## 1. INTRODUCTION.

FOR many years, a number of problems have persisted concerning the reactions which occur and the products which form when kaolinite and kaolin clays are heated to progressively higher temperatures. Between approximately 550° and 900° C., X-ray powder diagrams of kaolinite show mainly a broad band indicating either an amorphous, or a highly disordered, or a very finely dispersed state. The product is generally called metakaolin. At temperatures above 950° C. γ-alumina and mullite are formed. In some cases they appear together; in others, the appearance of mullite is delayed. The relations of these products to each other and to the original kaolinite have received various interpretations and the course of the reaction is still disputed. Following an examination of nacrite from Hirvivaara, Finland (von Knorring, Brindley, and Hunter, 1952), we considered that a single crystal study of its thermal reactions might throw further light on those of kaolinite. The two minerals have a similar lamellar morphology and are composed of silicate layers having the same structure and the same chemical composition; they differ only in the stacking arrangements of the layers and in crystal size. The dehydration of nacrite follows a similar course to that of kaolinite and the ultimate products of decomposition are the same for the two minerals. It seems reasonable to suppose that their thermal reactions will be closely similar, though the particular temperatures at which reactions proceed may depend on crystal size.

## 2. Experimental procedure.

Flakes of nacrite, about 0·2–0·5 mm. in size, were selected which, under the microscope and from X-ray rotation diagrams (fig. 1a), appeared to be of good crystalline quality. The best crystals showed a mosaic texture of the kind previously described for brucite (Brindley and Ogilvie, 1952) and which appears to be common for layer silicates. The a- and b-axes of a flake were determined prior to heat-treatment and subsequently they could be recognized by reference to irregularities in the outline of the flake. For X-ray study the crystals were mounted with shellac on fine glass fibres. For heat-treatment they were removed by alcohol from the shellac-coated fibres and placed in a platinum container. One flake was given as many as 20 heat-treatments between 500° and 1200° C. at about 50° intervals, each lasting 2–3 hours. The temperature was raised at the rate of about 15° C./min. and after treatment the crystals were cooled slowly in the furnace. Other flakes were heated directly to a particular temperature.

## 3. Results.

### (a) The metakaolin range, approximately 650–900° C.

Rotation diagrams about the b-axis (b 5·15 Å. for nacrite) showed no more than a slight weakening of the reflections up to about 650° C., but at 670° C. a marked change occurred. The majority of the reflections then disappeared; those remaining (fig. 1b) formed a hexagonal pattern which, in terms of the a- and b-axes of nacrite, are indexed as 200, 110, 310. A rotation diagram about the normal to the flake, approximately c, showed streaks parallel to the rotation axis which could be indexed as 20l, 11l. No evidence was obtained for regularity normal to the flake surface. As the temperature was progressively raised, the hexagonal pattern of spots became weaker and a diffuse halo increased in intensity. The spot pattern was clearly visible up to 880° C. (fig. 1c).

The interpretation placed on these results is that, following the expulsion of the (OH) radicals from the structure, the layers retain a relict structure of hexagonal type having no detectable regularity from one layer to another. Since the (OH) radicals are expelled from the octahedral aluminium layer, it seems likely that the residual structural regularity is maintained by the Si–O hexagonal network. The relation of the Al atoms to this network, which has not yet been established, is
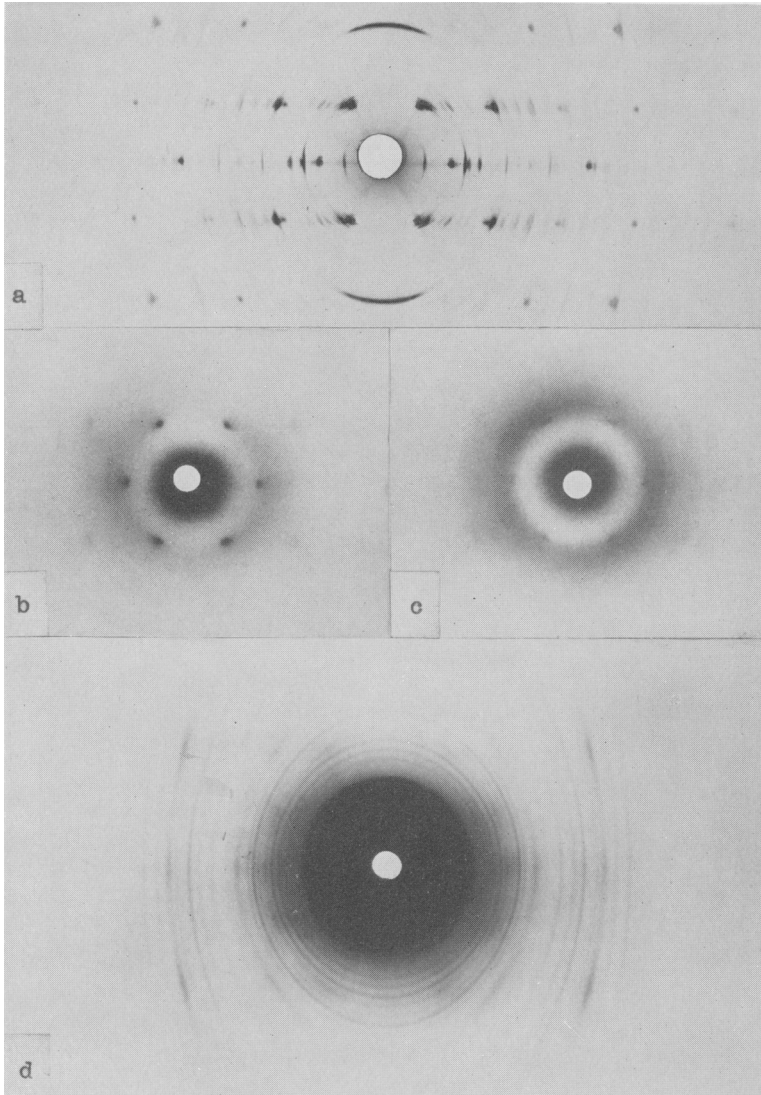
FIG. 1. (a) b-axis rotation diagram of nacrite. (b) b-axis diagram of the *same* nacrite crystal after heating to 670° C. (c) b-axis diagram of the *same* nacrite crystal after heating to 880° C. (d) a-axis rotation diagram of the *same* nacrite crystal after heating to 950° C.

discussed later. The results show clearly the persistence of a partially ordered phase up to about 900° C. which may be appropriately called metakaolin.

### (b) *Formation of γ-alumina and mullite in the range 950–1150° C.*

No one disputes that mullite is the main product which ultimately forms on firing kaolinite to temperatures well above 1000° C. and the same is true for nacrite. The role of γ-alumina which forms at about 950° C. but disappears at higher temperatures and the true character of the exothermic reaction at about 950° C. have been much disputed.

The present work shows that when a single crystal flake is heat-treated at 950° C., the subsequent X-ray rotation diagram (fig. 1$d$, a rotation diagram about the $a$-axis of nacrite) contains a clear powder diagram in which a few lines show marked increases of intensity in particular directions indicating preferential orientation. The majority of the lines have a smooth distribution of intensity and can be attri-buted unambiguously to mullite; they correspond to a random distribu-tion of small crystals. The lines showing orientation effects correspond to γ-alumina. This is a cubic, spinel-type structure giving relatively few strong lines. The following can be clearly recognized: 400 (I, 10; $d$ 1·978); 440 (I, 10; $d$ 1·387); 311 (I, 8; $d$ 2·40); and 220 (I, 2; $d$ 2·79), where I is the relative intensity given by Rooksby (1951) and $d$ is the measured spacing. The variability of γ-alumina has been commented on by Bradley and Grim (1951) and interpreted in some detail by Ervin (1952); in the present work it has not been possible to study the γ-alumina in detail owing to the numerical preponderance of mullite lines in the X-ray diagram.

The evidence is conclusive that in these experiments γ-alumina forms with preferential orientation relative to the nacrite and the mullite has random orientation. This situation persists to 1150° C.

The presence of finely divided cristobalite is shown by a diffuse line at about 4·1 Å. corresponding to the strongest cristobalite reflection.

### (c) *The second recrystallization at about 1150° C.*

The X-ray diagram clarifies considerably when the flake is heated to about 1150° C. The lines associated with γ-alumina which show marked orientation effects disappear at this temperature, the mullite pattern becomes clearer and more lines are visible. The pattern is still that of a random powder. It seems that the γ-alumina combines with cristobalite to produce more mullite. The greater clarity of the X-ray diagram

suggests not only *more* mullite, but a *better crystalline* product. Persistence of the 4·1 Å. line indicates that excess silica remains as cristobalite.

### (d) Orientation of γ-alumina.

The enhanced line intensities due to orientation (fig. 1*d*) have the appearance of a blurred rotation diagram with zero, first-, and second-order layer lines. The corresponding axis periodicities, which can be determined only very approximately, are 5·4 Å. from the first-order, and $2 \times 2.78 = 5.56$ Å. from the second-order layers. Taking the cubic cell parameter of γ-alumina as 7·88 Å. (Rooksby, 1951), we find the repeat distances [100] 7·88, [110] 11·14, and [111] 13·64 Å. The observed value admits of only one simple interpretation, viz. [220]. If [110] is the orientation axis, we expect to find only the even-order layers corresponding to $(h+k) = 0, 2, 4$, since γ-alumina is based on a face-centred lattice. This explains why we find the even-order repeat distances and not the odd-orders.

The details of the orientation diagram are fully consistent with this interpretation. The four reflections which are clearly recognized have the indices {220}, {311}, {400}, and {440}. The zero-order layer, with $h+k = 0$, shows $(2\bar{2}0)$, $(1\bar{1}3)$, (004), and $(4\bar{4}0)$. The first observed layer, with $h+k = 2$, shows only (202) and (113) or $(3\bar{1}1)$, and no reflections of type {400} and {440}. The second observed layer, with $h+k = 4$, shows (220), (131), (400), and (404).

The clearest orientation diagram was obtained by rotation about the *a*-axis of a flake of nacrite heated directly to 950° C. Rotation about *b* showed an appreciable enhancement of only the 440 reflection and on the equatorial level only. It appears that there is essentially a single orientation axis and that a fibre texture develops with [110] of γ-alumina parallel to *a* of nacrite.

## 4. Discussion of the present results in relation to the general problem of the thermal behaviour of kaolin clays.

### (a) Metakaolin.

The present work shows clearly the persistence of some degree of crystalline order in the metakaolin phase. Its precise character is not established and the available diffraction data are wholly insufficient for a detailed analysis. It must be of hexagonal type and most probably takes the form of more or less flat Si–O hexagonal networks with little or no regularity between neighbouring networks. Previous workers

have come to somewhat similar conclusions and have advanced hypotheses regarding the relation between the Si–O network and the dehydrated alumina sheet of the kaolin structure.

In the earlier investigations, summarized by Richardson (1951), the diffraction band was considered to indicate an amorphous or nearly amorphous solid. More recent investigators have recognized that metakaolin is at least partially ordered. Tscheischwili, Büssem, and Weyl (1939), using crystal-reflected X-rays and a vacuum camera, observed the persistence of $hk0$ reflections from kaolinite far beyond the temperature at which dehydration occurs; these observations are in complete agreement with the present results for nacrite. They considered the diffraction band was very similar to that from silica-glass and concluded that the disordered part of the structure had a similar short-range order with both Si and Al ions tetrahedrally co-ordinated. They also suggested a model for the ordered metakaolin structure having the same Si–O tetrahedral layer as in kaolinite co-ordinated with an Al–O tetrahedral layer; the latter tetrahedra are, however, very distorted and the Al–O distance, about 1·85 Å., is considerably greater than that generally found.

In a very detailed investigation, hitherto largely unknown due to war-time conditions, Eitel and Kedesdy (1944) (see also Eitel, 1954, pp. 1116–8) followed the thermal transformations of kaolinite by electron microscopy and electron diffraction. They showed the persistence of crystalline form up to high temperatures and observed the diffraction lines from metakaolin found by Tscheischwili et al. and in the present work.

Independently, Comeforo, Fischer, and Bradley (1948) recognized that the X-ray diffraction band from metakaolin is 'more distinct than such bands from strictly amorphous solids' and also noted the persistence of external form by use of the electron microscope. They therefore considered that metakaolin had some residual structure and, on the basis of a general comparison of metakaolin with anhydrous pyrophyllite, they considered that 'it does not seem improbable' that there are 'coordinated strings of alumina octahedra, with some buckling of the silica layer'. Roy, Roy, and Francis (1954), using electron microscopy and electron diffraction, have confirmed the persistence of hexagonal morphological form into the metakaolin phase and have observed single-crystal diffractions from the metakaolin in exact agreement with the data for nacrite.

There is abundant evidence, therefore, for the persistence of morpho-

logical form and residual crystalline order in metakaolin. The details of the crystalline order can only be tentatively suggested. Since the alumina layer of the kaolin structure must be modified by the dehydration process, it is reasonable to attribute residual order to the Si–O networks. Brindley and Youell (1951) have shown that when chlorites are subjected to acid attack, the Si–O sheets remain largely intact after the dissolution of the octahedral layers. Of the two suggestions put forward for the arrangement of the Al and O ions in metakaolin, that given by Comeforo et al. is the more plausible, since it is related to structures suggested for aluminium-montmorillonites and for pyrophyllite. In no case, however, is the evidence for the Al–O arrangement very detailed, and for metakaolin the suggestion is little more than a hypothesis. It has, however, been linked up with the process of mullite formation and this will be discussed in later paragraphs.

In concluding this section, it can be said that there is now ample evidence for residual structure in metakaolin most probably associated with the hexagonal Si–O layers. Suggestions which have been put forward regarding the disposition of the Al and O ions are largely unproved hypotheses.

### (b)  The formation of γ-alumina and mullite.

The major problem is the nature of the reactions by which these products are formed. Their simultaneous or almost simultaneous appearance in some experiments and the delayed, sometimes long delayed, appearance of mullite in other experiments have been difficult to understand, and although recent investigations have shed light on these apparent anomalies, the problem still is not fully elucidated. Conclusions drawn from a restricted range of observations have frequently been diametrically opposed.

One line of thought, initiated by Comeforo, Fischer, and Bradley (1948), treats the formation of γ-alumina as incidental to the main reaction process. They believed they had evidence from electron microscope observations that mullite needles develop with orientations related to the initial kaolinite flakes and on this basis took the extreme view that 'any γ-alumina which may have been observed in special instances is therefore only incidental and is not a step in the major reaction series of the firing process'. Since γ-alumina has been observed in practically all investigations of fired kaolin minerals and often prior to the formation of mullite, it is a misrepresentation to suggest that it 'may have been observed in special instances'.

The question whether mullite develops with special orientations relative to the parent material is of basic importance. Comeforo et al. regarded the ordered formation of mullite as proceeding from an ordered arrangement of Al octahedra in metakaolin, and subsequent workers (Johns, 1953; Glass, 1954) have developed this line of thought. However, other electron microscope studies by Eitel and Kedesdy (1944) did not show any orientation of the mullite. They obtained very clear micrographs of well-crystallized kaolinite heated progressively to 1200° C. Since the original paper is now almost unobtainable, their own description may usefully be quoted:

'Die bei 950 und 1000° gebrannten Präparate gleichen im wesentlichen der Brennstufe von 900° in der Ausbildung der körnigen Oberflächenstruktur, ohne daß sich irgendeine Orientierung der Teilchen erkennen läßt. Es ist nicht zu bezweifeln, daß hier bereits die ersten Kristallkeime des neugebildeten Mullits vorliegen. Da diese Kriställchen beim Brennen des Kaolins nicht aus der Schmelze entstehen, sondern durch Reaktion im festen Zustand, kann man die bekannte nadelige Form der Mullitkristalle nicht ohne weiteres erwarten. Die tafligen Pseudomorphosen nach Kaolin haben selbst bei einer Exposition der Präparate bei 1100° (Abb. 3) noch einen bemerkenswerten Zusammenhalt. Die Kanten der hexagonalen Formen sind allerdings nicht mehr so scharf, sondern ausgefranst, und besonders fällt auf, daß die vordem so gleichmäßig durchsichtigen Tafeln stofflich auch stark heterogen erscheinen.

Bei 1200° (Abb. 4) sind die großen Tafeln in kleinste Bruchstücke zerfallen, welche völlig körnige Stuktur zeigen. Auffallend sind vor allem die kurzprismatischen Individuen, die auf Mullit hindeuten, sowie deutlich erkennbare reguläre Formen von freier Kieselsäure in Form des Cristobalits.'

Although they observed the persistence of the outlines of kaolinite flakes up to 1100° C., they did not record any oriented development of mullite. Brief reference may be made to a study of muscovite heated to temperatures ranging 1000°–1200° C. by Sundius and Byström (1953). After heating to 1000° C., they observed that 'some of the [mullite] needles were irregularly distributed, but others formed star-shaped aggregates, giving the appearance of a hexagonal pattern'. The situation in muscovite is not exactly the same as that in kaolin minerals and such evidence can be accepted only very tentatively.

However, the ideas advanced by Comeforo et al. have stimulated further investigations into the relation between the crystallinity of kaolin minerals and the formation of mullite. The hypothesis that metakaolin contains 'coordinated strings of alumina octahedra' which can be incorporated easily in a mullite structure suggests that a well-ordered kaolin mineral may form mullite more readily (i.e. at a lower temperature, or in greater quantity) than one with disordered layers. This idea has been developed at length by Johns (1953), and his

experiments together with more extensive investigations by Glass (1954) have yielded results in accord with this general picture. Thus Glass reports that 'the amount of mullite detected at the exothermic peak decreases as the structure becomes more random, and the thermal peak decreases in intensity. The $b_0/3$ shifts in kaolinite evidently cause the development of smaller mullite nuclei with resultant decrease in thermal intensity.'

In the light of these results, a single crystal of nacrite, the best crystallized of all the kaolin minerals and having no admixed impurities, would be expected to reveal most clearly the mode of formation of mullite. The present experiments show that the mullite always forms with random orientation from nacrite. At present there appears to be no other *direct* evidence for the oriented formation of mullite from kaolin minerals than the observations of Comeforo et al. The *indirect* evidence from the work of Johns and of Glass may be capable of an alternative interpretation. It seems very desirable, therefore, that further electron microscope observations should be made and, in particular, a *statistical* assessment of the orientation should be undertaken.

Glass emphasizes that the morphology of kaolin minerals and the presence of mica impurities have marked influences on the development of mullite. It is well established that in the case of halloysite only $\gamma$-alumina can be detected in materials heated just beyond the exothermic reaction (Richardson, 1951; Richardson and Wilde, 1952; Glass, 1954). Colegrave and Rigby (1952) quenched material to room-temperature which had been heated in differential thermal apparatus just beyond the exothermic reaction, and they recorded only $\gamma$-alumina. Similar experiments by Insley and Ewell (1935) gave the same result; they also showed that by prolonged heating the $\gamma$-alumina could be formed at $50°$ C. lower temperature. Experiments of this kind have led to the conclusion that the exothermic reaction is due to $\gamma$-alumina and that '$\gamma$-alumina is the precursor to mullite formation' (Colegrave and Rigby, 1952, p. 366). Comeforo, Fischer, and Bradley (1948) emphasized that the magnitude of the exothermic effect can hardly be attributed to a poorly crystalline phase such as $\gamma$-alumina and that it can only arise from the formation of a close-packed phase such as mullite. We agree with this general interpretation, but it is still necessary to explain the apparent absence of mullite after the exothermic effect. In agreement with Glass, we suggest that the mullite nuclei may have formed but not grown to a sufficient size to be observed by X-rays. Glass relates the non-development of the mullite to impedance by $\gamma$-alumina. This may

well be true, but a further point for consideration is that poorly crystalline parent material may produce many more nuclei than well crystallized material. A few nuclei may grow to larger size than a large number of competing nuclei. Other examples can be quoted of the slow appearance of a new phase in X-ray diagrams after an exothermic reaction, e.g. the development of olivine from chlorites.

From these considerations of our own work on nacrite and recent investigations of kaolinite and kaolin clays by others, we draw the following conclusions:

(i) At about 900° C. $\gamma$-alumina develops from metakaolin with an orientation related to that of the parent mineral. This is made possible by persistence of order through the metakaolin range.

(ii) At about the same temperature or a little higher, mullite nuclei form, giving rise to the exothermic reaction observed thermally. The growth of the mullite nuclei to crystals of a size observable by X-rays seems to depend on the crystallinity of the parent material and of the metakaolin. The mullite develops without preferential orientation which may be related to the nuclei forming when the metakaolin residual structure finally breaks down, i.e. at the time when $\gamma$-alumina is forming or has just formed. We agree with Glass that *at this stage* $\gamma$-alumina is not part of the main reaction series. Uncombined silica appears to have the cristobalite form.

(iii) The retardation of mullite formation when the parent mineral is disordered seems well established and the data for nacrite fit into the general scheme in this respect.

(iv) At higher temperatures, about 1150° C. in the nacrite experiments, the $\gamma$-alumina combines with silica to form further mullite, still with random orientation.

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