

A STUDY OF THE HYDROTHERMAL RECONSTITUTION OF THE KAOLIN MINERALS¹

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ABSTRACT

The progressive reconstitution of the thermally decomposed members of the kaolin group (the so-called "meta" phases) has been studied as a function of time, temperature and water vapor pressure of reconstitution, with a view to determining the extent of "pseudomorphism" after the parent structure. The nature of the dehydroxylated dickite which shows a 14A reflection has been investigated further but no additional x-ray data characteristic of a 14A-type structure can be found.

The sequence of rehydration shows that all the meta phases tend to form kaolinite, but the actual sequence of events depends on the parent material. Under the proper conditions well-crystallized kaolinite is obtained from all the meta phases. However, the original minerals themselves could not be converted directly to kaolinite within the time limits of the experiments.

INTRODUCTION

The kaolin minerals kaolinite, dickite, nacrite, and metahalloysite, have essentially the same chemical composition, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, and are composed of structurally similar layers. The first three of these minerals are morphologically similar and have a platy habit; metahalloysite appears to have a rolled or tubular form. In addition to these four specific forms, there exist also crystallographically disordered forms, notably of kaolinite; these seem to be common in fire clays, and show a platy habit. The hydroxyl groups are removed from these structures at temperatures around 550° to 650° C, being lower for the finer-grained materials and probably also for the less well-crystallized forms, and higher for the larger and better-crystallized materials.

In general a highly disordered phase is formed after loss of hydroxyls from the structure, but the fact that some order is preserved has been shown by Brindley and Hunter (1955) working with single crystals of nacrite, and by Roy, Roy, and Francis (1955) using single-crystal electron diffraction data from kaolinite. More recently a new phenomenon has been reported for dickite by Hill (1955), who found that on careful heating to 700° C, a reflection appeared at a spacing of 14 Å. (This is not to be confused with the 14 Å parameter of the structure which normally does not appear as a reflection.) The existence of this effect called for further investigation.

The present work was aimed at elucidating two problems: (1) The nature of the structural reorganization in dickite which gives rise to the 14 Å reflection and the possibility that an aluminian chlorite might be formed; and (2) the nature of the meta phases following complete loss of hydroxyl units from the

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kaolin minerals. Specifically we have attempted to answer the following questions:

(a) Is there one modification which is demonstrably more stable at low temperatures (e.g., 350° C) to which the other forms will revert with appropriate thermal or hydrothermal treatment?

(b) After removal of hydroxyl groups to form the herein called meta phases, meta-kaolinite, meta-dickite, meta-metahalloysite, etc., are the resulting meta phases identical?

(c) Closely related to (b) and perhaps the only way to answer (b) is the following question: If hydrothermal treatments are applied to the meta phases, are the original phases reestablished or are the end products all the same?

There is not much previous work in this field. The note by Hill has already been mentioned. Saalfeld (1955) in a brief communication noted that dehydroxylated kaolinite could be reconstituted under mild hydrothermal treatment to give a phase resembling the disordered fire-clay mineral; he used 300° C and 1400 p.s.i. water vapor pressure, but the duration of the experiment is not stated. He refers also to earlier experiments by Nieuwenburg and Pieters, and by Gillard. Roy and Osborn (1954) were able to synthesize only one of the kaolin polymorphs (kaolinite) in several hundred hydrothermal runs under a wide range of *p-t* conditions from a variety of starting materials, all of which were amorphous or largely amorphous to x-rays, including meta-kaolinite.

EXPERIMENTAL

Samples of kaolinite, (well crystallized, from Macon, Ga.), dickite (see below), nacrite (Brand, Saxony), halloysite, (Eureka, Utah) and the "fire-clay"-type disordered kaolinite (Pugu, Tanganyika) were selected and their powder x-ray patterns checked. Part of each was dehydroxylated by successive heating at 575°, 610°, and 710° C except for the dickite (see below) and halloysite which was heated only to 610° C to avoid formation of $\gamma\text{-Al}_2\text{O}_3$. The samples were then treated under hydrothermal conditions of independently controlled temperature and pressure in previously described equipment (Roy and Osborn, 1952, 1954).

RESULTS

The Modified Form of Dickite

Four separate dickites from the following localities have been examined: (1) Pottsville, Pennsylvania; (2) Ouray, Colorado; (3) Schuylkill County, Pennsylvania; and (4) unknown.

The development of a 14 A reflection seems to depend upon the particle size of the mineral and on the temperature and time of heating; coarse particles show the effect at higher temperatures (around 700° C), whereas with fine particles the effect is obtained at temperatures around 600° C. Long runs at 700° C with fine particles tend to destroy the effect.

These experiments, in which temperature, time, and particle size were varied, were undertaken with a view to obtaining the modified structure in a better-organized form so that the structural details could be examined. In this we have been unsuccessful. By analogy with the earlier work of Nelson and Roy (1954)

in which trioctahedral 7 Å type minerals were converted hydrothermally to minerals of a 14 Å type, hydrothermal heating conditions were also applied to dickite. It was thought that the presence of a water vapor atmosphere at the temperature of transformation might inhibit the normal dehydration and facilitate the reconstitution to an aluminian chlorite. Hill, working with a dickite from Ouray (Colo.), found that after heating at 700° C a 14 Å spacing was obtained with no higher orders, but when "rehydrated in saturated steam at 200° C for 54 hours there were, in addition, higher orders at 7.15 Å and 3.57 Å."

In our experiments we have failed to find any additional evidence of such a transformation other than the appearance of the 14 Å line itself, which we have confirmed in a number of experiments. Conditions of dry heating can be found under which the x-ray diagrams show reflections around 7.2 and 3.6 Å, and at first sight these may be regarded as the higher orders of the 14 Å line (Fig. 1); however, they are almost certainly due to incomplete conversion of the ordinary dickite structure, since further treatment eliminates them. Similarly mild hydrothermal treatment also may be made to yield 7.2 and 3.6 Å lines in addition to the 14 Å, as Hill found, but this we believe is due essentially to partial reconversion toward a kaolin-type mineral (actually kaolinite rather than dickite; see below). These results, being essentially negative, may carry less conviction than a positive result. However, we would emphasize that in any further experiments on this phenomenon considerable care must be exercised in the interpretation of reflections which may seem to be higher orders of the 14 Å reflection while in fact they are only indications of a mixture of phases.

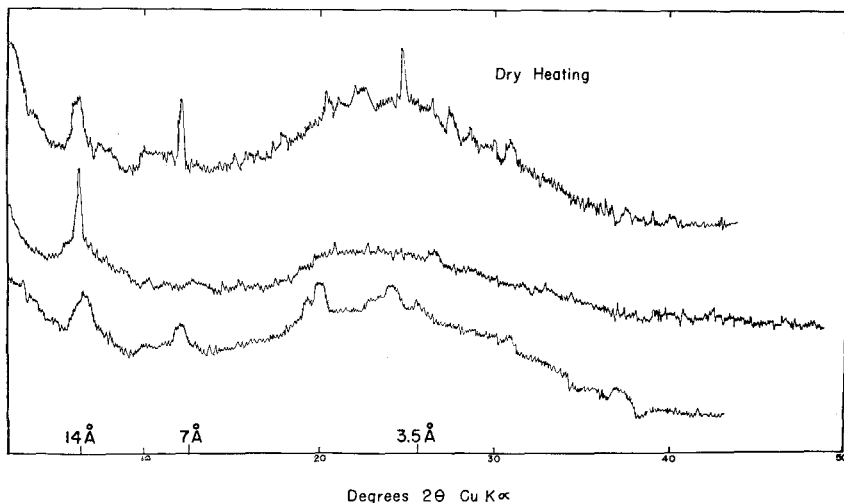


FIGURE 1. — X-ray diffractometer traces of: (a) Dickite partially converted to meta-dickite showing the appearance of a 14Å reflection and showing the last traces of the original dickite pattern; (b) dickite showing typical development of 14Å reflection formed by further heat treatment of (a); (c) comparable (?) effect obtained with chrysotile; see Nelson and Roy (1954).

Nature of the Meta Phases

Hydrothermal treatment of the original mineral. — The following treatments were applied to kaolinite, dickite, metahalloysite and a disordered kaolinite, (specimen from Pugu, Tanganyika; Robertson, Brindley, and Mackenzie, 1954): (i) Heat treatment at 370° C, at 20,000 p.s.i. water vapor pressure for 26 days. (ii) Heat treatment at 390° C, at 39,000 p.s.i. water vapor pressure for 13 days. Kaolinite, dickite, nacrite, and metahalloysite showed no semblance of change; no *marked* change occurred in the disordered kaolinite, and there was certainly no conversion to a well-ordered structure.

These experiments in themselves failed to show that one form is demonstrably more stable than the others.

Hydrothermal treatment of the meta phases. — A direct detailed study of the meta phases themselves still awaits careful examination. We have studied the question indirectly by considering the reactions of the meta phases to hydrothermal treatment.

The experiments show that the meta phases do not revert to the initial phases when treated hydrothermally, but eventually revert to kaolinite or a close approximation to kaolinite. The process by which they revert, however, seems to differ for the different meta phases.

Hydrothermal treatment at 200° C and 2000 p.s.i. water vapor pressure leads to the following results: After eight hours there is little change; only the basal reflections from the meta-dickite begin to show rather weakly. After 24 hours, basal reflections begin to show from the meta-kaolinite and meta-dickite, but no change is shown by meta-metahalloysite (Fig. 2). After treatment for one week, there is a marked transformation of meta-kaolinite back to kaolinite, with development of prominent basal reflections and some tendency towards three-dimensional order as shown by *hkl* reflections beginning to appear (Fig. 3). Meta-dickite still shows very little diffraction evidence other than the basal lines; presumably the layers have developed a parallel orientation, but three-dimensional order is slow to develop. Meta-metahalloysite, on the other hand, seems very slow to develop any layer parallelism, but diffraction bands suggesting development within the layers begin to appear.

Hydrothermal treatment at 370° C and water vapor pressures of 20,000 p.s.i. shows very much more rapid reaction. After only eight hours treatment (Fig. 4), meta-kaolinite shows considerable conversion toward a well-ordered kaolinite. Meta-dickite shows good basal reflections and two-dimensional scattering from the layers is also quite clear, but there is little three-dimensional order. Meta-metahalloysite still shows scarcely any basal reflections, though the layers show some development, which is indicated by the two-dimensional scattering.

With longer periods of treatment under these conditions, the change of meta-kaolinite to kaolinite continues to keep ahead of the other changes, meta-dickite changes rather slowly towards a well-ordered kaolinite, while meta-metahalloysite moves even more slowly towards an ordered kaolinite. In runs of more than a week at temperatures near 350° to 375° C and pressures of about 20,000 p.s.i. the reconstitution of all the meta phases to kaolinite is fairly complete, as shown in Figure 5.

The influence of pressure was shown to be less important than temperature since runs at 370° C and 2000 p.s.i. gave results quite similar to those at 20,000 p.s.i. and showed much faster reaction than the runs at 200° C and 2000 p.s.i.

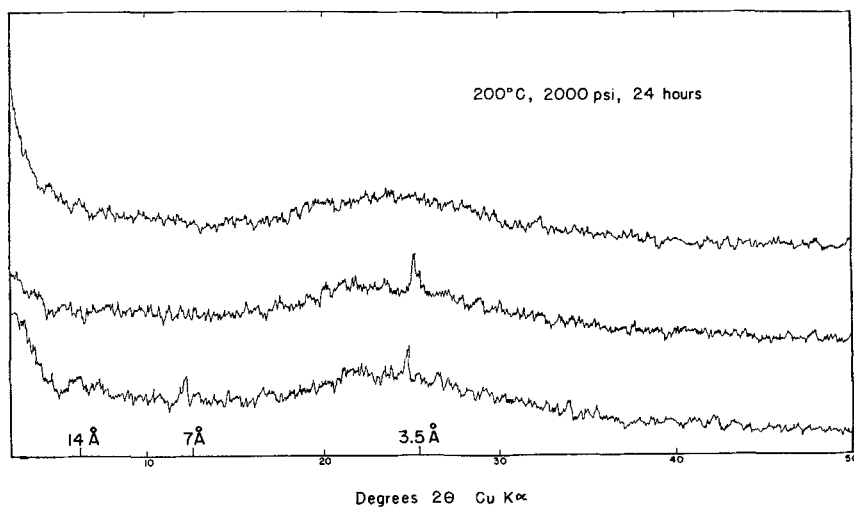


FIGURE 2.—Diffractometer traces showing results of hydrothermal treatment of meta phases under the mildest conditions (200° C, 2000 p.s.i. for 24 hours). Note destruction of 14Å dickite reflection even under these mild conditions.

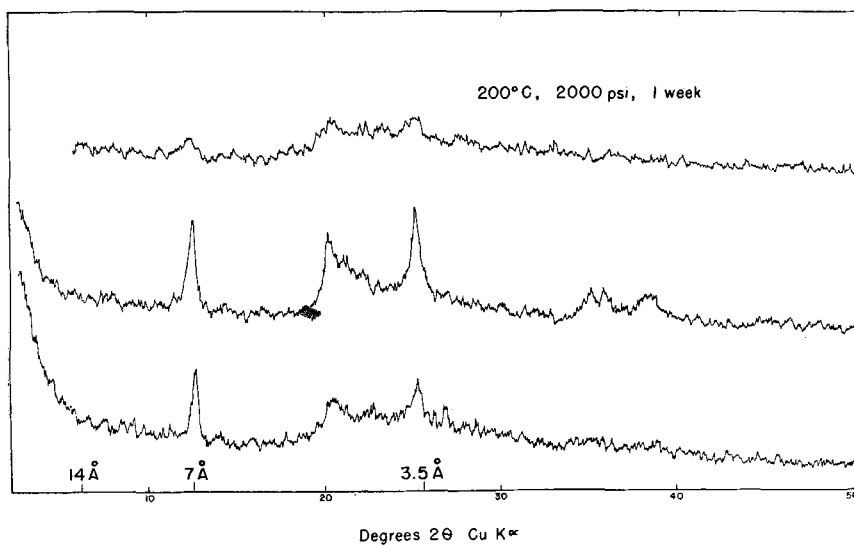


FIGURE 3.—Diffractometer traces showing results of hydrothermal treatment of meta phases for a longer period of time (200° C, 2000 p.s.i., one week). Note most rapid reconversion of meta-kaolinite and least rapid conversion of meta-metahalloysite and absence of basal reflections.

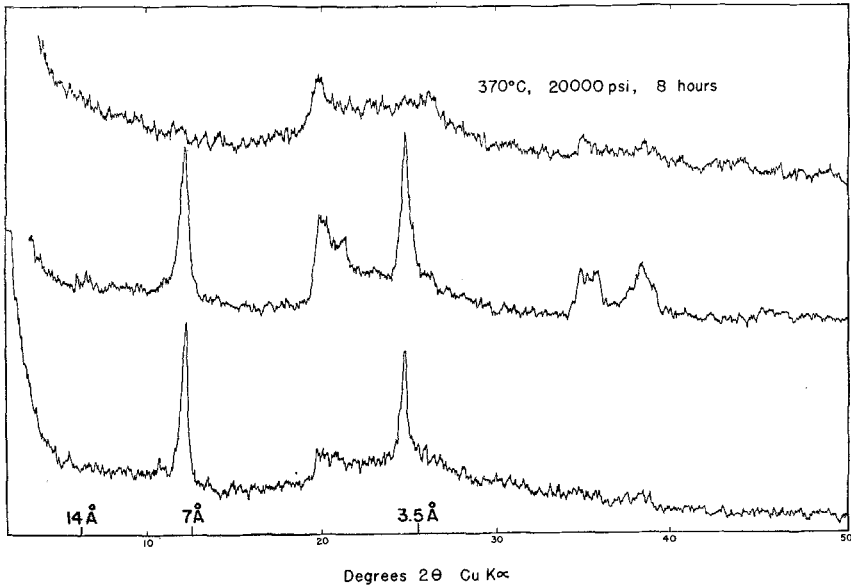


FIGURE 4. — Results of higher temperature, higher pressure hydrothermal treatment (370°, 20,000 p.s.i., eight hours). Note marked development of only basal reflection in meta-dickite, absence of basal reflections in meta-metahalloysite and a close approach to a full diffraction pattern of kaolinite. Note that meta-kaolinite yields the best final product.

DISCUSSION

While further work should be done with other specimens and different conditions of dehydration and reconstitution, the main outlines now seem clear.

All the kaolin minerals, after dehydration, are eventually reconstituted as kaolinite. Although it is doubtful whether the final product in all cases will have good three-dimensional order, there is no uncertainty about the direction in which the reconstitution goes. Kaolinite is the end product and dickite and halloysite are not reconstituted under the conditions of these experiments.

It is also clear that the meta phases must retain marked differences, for in no other way can we explain different behavior on hydrothermal treatment. Meta-dickite presumably retains some platy characteristics since the layers reform rather easily. The arrangement of the Al ions is different in dickite and kaolinite; this must persist into the meta phases since the reconstitution of meta-dickite to kaolinite is much more difficult than that of meta-kaolinite to kaolinite. Likewise, meta-metahalloysite must retain some of the features of metahalloysite connected with the curved layers, since its reconstitution to kaolinite takes place with considerable difficulty, especially as regards the parallelism of the layers. In other words, the dehydroxylation of the platy polymorphs must cause considerable rupturing of interlayer bonds and consequent disorder in any stacking of the layers, whereas in metahalloysite dehydroxylation apparently causes much more drastic rupturing in the plane of the sheets.

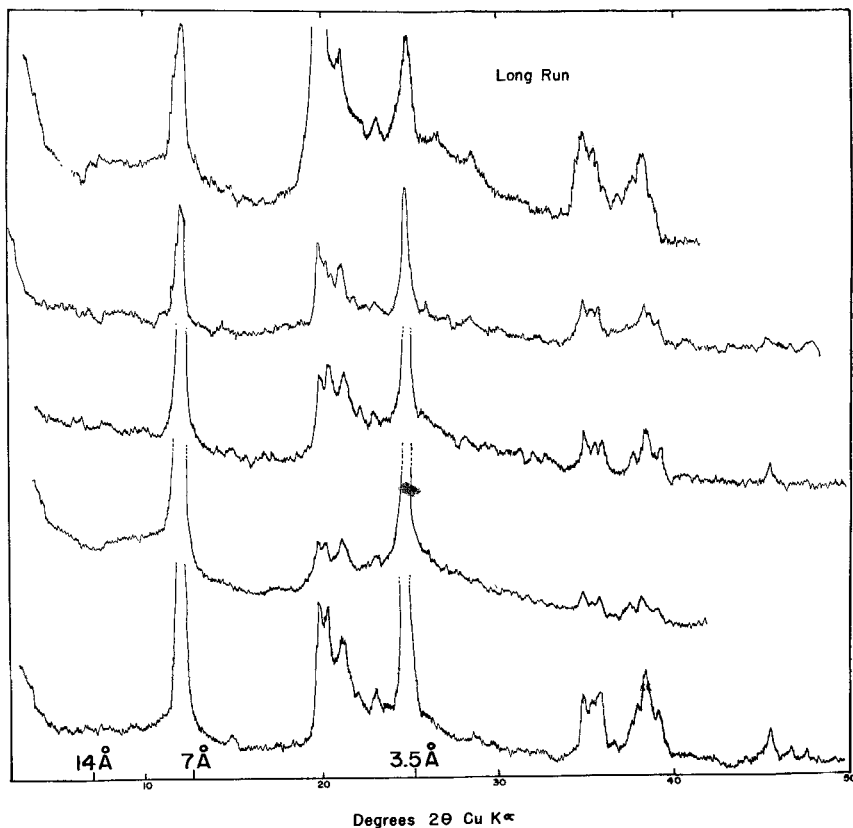


FIGURE 5. — Results of extended run at 370° C and 20,000 p.s.i. showing more or less complete conversion of the different meta phases to a fairly well-ordered kaolinite. Note that meta-kaolinite yields the best final product.

These results also emphasize, we believe, the fact that it is no longer useful to report merely the use of “hydrothermal conditions.” The temperature, pressure and time of reaction are such important variables that the term “hydrothermal conditions” serves only to describe the general type of reaction attempted.

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REFERENCES

- Brindley, G. W., and Hunter, K., 1955, The thermal reactions of nacrite and the formation of metakaolin, γ -alumina, and mullite: *Min. Mag.*, v. 30, p. 574-584.
- Hill, R. D., 1955, 14 A spacings in kaolin minerals: *Acta Cryst.*, v. 8, p. 120.
- Nelson, B. W., and Roy, Rustum, 1954, New data on the composition and identification of chlorites: in *Clays and clay minerals*, Natl. Acad. Sci.—Natl. Res. Council Pub. 327, p. 335-348.
- Robertson, R. H. S., Brindley, G. W., and Mackenzie, R. C., 1954, Mineralogy of kaolin clays from Pugu, Tanganyika: *Amer. Min.*, v. 39, p. 118-138.
- Roy, Rustum, and Osborn, E. F., 1952, Some simple aids in the hydrothermal investigation of mineral systems: *Econ. Geol.*, v. 47, p. 717-721.
- , 1954, The system alumina-silica-water: *Amer. Min.*, v. 39, p. 853-885.
- Roy, Rustum, Roy, D. M., and Francis, E. E., 1955, New data on thermal decomposition of kaolinite and halloysite: *J. Amer. Cer. Soc.*, v. 38, p. 198-205.
- Saalfeld, H., 1955, Hydrothermale Bildung von Tonmineralen aus Metakaolin: *Deut. Keram. Gesell.*, v. 52, p. 150-152.