

FURTHER CORRELATIONS OF KAOLINITE CRYSTALLINITY WITH CHEMICAL AND PHYSICAL PROPERTIES

by

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ABSTRACT

Previous work has demonstrated that the degree of crystal perfection in kaolinite can be correlated with many physical properties. In this paper some further relationships are shown, including surface area, base exchange capacity, total percentage of iron and titanium, and high-temperature mullitization. Surface area, base exchange capacity, and the total amount of iron and titanium in the clay increase as the degree of crystal perfection decreases.

INTRODUCTION

Brindley and Robinson (1946) first pointed out that many x-ray diffraction patterns of kaolinite showed significant differences because of variations in the stacking arrangement of the unit cells. These stacking variations were reflected mostly in the diffraction peaks hkl where $k \neq 3$. Murray and Lyons (1956) studied several sedimentary kaolins from Georgia and South Carolina and correlated the "degree of crystallinity" with such physical data as particle size distribution, aqueous viscosity, brightness, and resistivity. This paper is a continuation of the above mentioned study.

The term "degree of crystallinity" or "degree of crystal perfection" was used in the first paper and was based upon the amount of stacking disorder as indicated by the x-ray diffraction pattern. There has been some dissatisfaction with this term, and perhaps because the differences that are seen on the x-ray diffraction diagram are mostly stacking variations, more descriptive terms might be used, such as "well stacked," "moderately stacked," and "poorly stacked." However, for continuity with the previous paper, the terms "well, medium, and poorly crystallized" will be used.

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DISCUSSION

The base exchange capacity of kaolinite is low compared with that of the other minerals (Grim, 1953, p. 129). Very careful base exchange determinations, however, reveal differences in many kaolinites. The exchange capacity

of twelve different kaolinites collected from the Cretaceous Tuscaloosa formation in Georgia and South Carolina shows a five-fold variation in the milliequivalents per 100 g. As shown on Fig. 1, the base exchange capacity correlates almost perfectly with degree of crystallinity. Well-crystallized kaolins have a very low base exchange capacity, and those that are poorly crystallized have the higher base exchange capacity. Some of the kaolins in Georgia contain small quantities of montmorillonite, and these, of course, would give abnormally high results. Two of the samples studied did contain montmorillonite, and these had exchange capacities of 5 and 7; therefore they were not included on the plot of Fig. 1. The relationship between base

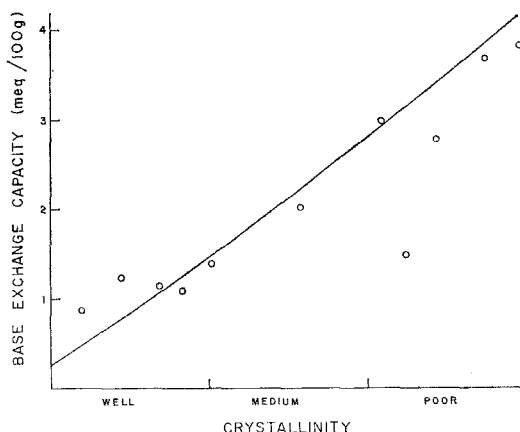


FIGURE 1.—Relationship between crystallinity and base exchange capacity.

exchange capacity and degree of crystallinity is one that would be expected because if the kaolins were disordered in the stacking, then there would be more exposed charged sites for exchange to take place. Schofield and Samson (1955) and others recently have indicated that exchange is due to substitution within the lattice, and that broken bonds are a relatively minor cause of base exchange.

Another property that was correlated with degree of crystallinity was surface area, measured by the BET method in square meters per gram. Figure 2 shows that surface areas range from 8 to 27 m²/g, and the well-crystallized kaolins have a smaller surface area than the poorly crystallized kaolins. Again this correlation would be expected because the imperfectly stacked poorly crystallized kaolins would, of course, have more surface area than the well crystallized books of kaolin.

Two impurities in kaolinite which are somewhat deleterious to their use in paper and other end uses are minerals containing iron and titanium. Chemical

analyses of all the samples that were studied for this paper revealed a correlation between the total amount of Fe_2O_3 and TiO_2 and the degree of crystallinity. The well crystallized kaolins contained the smallest quantity of these two oxides, and the poorly crystallized kaolins contained the largest amount.

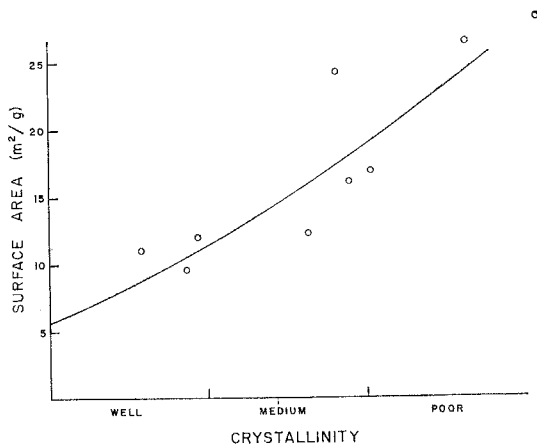


FIGURE 2.—Relationship between crystallinity and surface area.

The ratio of Fe_2O_3 to TiO_2 was consistently highest in the poorly crystallized specimens. It is not known how or why this relationship occurs. One possibility is that because the poorly crystallized kaolins have more surface area and higher exchange capacity, more iron oxide and titanium oxide are crystallized on the surfaces of the clay. However, it is felt that most of the iron and titanium is tied up in discrete minerals, as ilmenite and leucoxene. The relationship shown in Fig. 3 needs further study and may have geological significance.

Another property that was noted in this study was the correlation between degree of crystallinity and the amount of dispersing agent necessary to achieve the minimum viscosity. The previous study (Murray and Lyons, 1956, p. 36) showed that the viscosity correlated with the degree of crystallinity. In the viscosity determinations, the incremental dosage percentage of dispersing agent (in this case a sodium polyphosphate) is always precisely measured and recorded and particular note thereof is taken when the minimum viscosity is achieved. The kaolins that were well crystallized required much less dispersing agent to achieve minimum viscosity than the poorly crystallized kaolins. Again, this can be related—at least in part—to the exchange capacity and surface area of the kaolin. The relationship between crystallinity and the amount of dispersant needed to achieve minimum viscosity is shown on Fig. 4.

Another property that was measured was the uncalendered gloss of each of these kaolins after they were applied in the form of coatings to paper. Gloss is an important property in the paper industry, and in many instances paper companies pay a premium for clays that will give a high gloss. Gloss

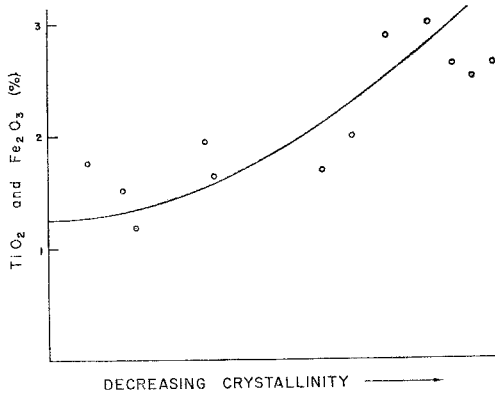


FIGURE 3.—Relationship between total iron plus titanium and crystallinity.

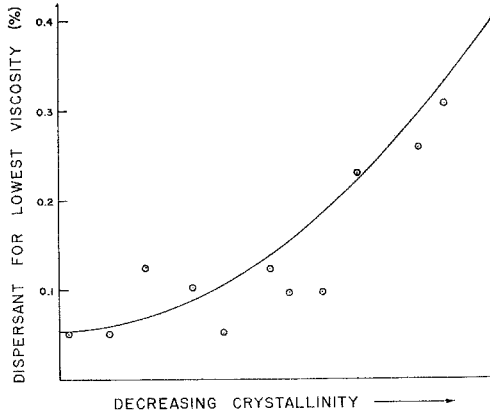


FIGURE 4.—Relationship between crystallinity and total dispersant for minimum viscosity.

is measured as the percent reflectance at a specified angle (TAPPI Method T-424 M-52, 1952). Figure 5 shows the general relationship between gloss and degree of crystallinity. The poorly crystalline kaolins give the highest gloss, and the well crystallized kaolin the lowest gloss. The reason for this is probably that the poorly crystallized kaolins are thinner flakes and therefore more

readily orient parallel to the sheet and form a smoother surface, whereas the well-crystallized kaolins are "blocky" and form a more uneven surface.

The degree of crystallinity is also related to the development of mullite at high temperature. Johns (1953) suggested a relationship between mullitization and kaolinite crystallinity. Recently Brindley and Nakahira (1959) have reviewed the kaolinite-mullite reaction series and have indicated the structural transformation from kaolin to the mullite phase.

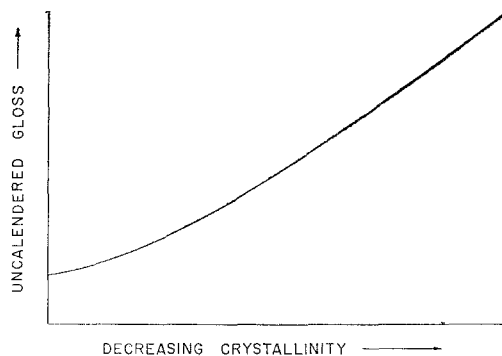


FIGURE 5.—Relationship between crystallinity and uncalendered gloss.

The present authors have noted that in well-crystallized specimens that have been made into briquettes and fired, electron micrographs of exposed fracture faces show a definite hexagonal pattern of the mullite crystals (Plate 1). The single plates and the poorly crystallized kaolins do not, in general, show this nice hexagonal net of mullite crystals.

Another interesting relationship is that the fired specimens of well crystallized kaolins show intermediate-sized mullite needles (Plate 2). Plate 3 is a specimen from a poorly crystallized kaolin. The mullite crystals are larger and do not show the orientation parallel to the hexagonal net similar to the well crystallized kaolins. This relationship, which needs further study and amplification, has been noted in many different specimens and electron micrographs.

Finally, there is a relationship between degree of crystallization and occurrence of large stacks. In deposits which are composed of well-crystallized kaolins, there is a predominance of large stacks similar to that shown in Plate 4. In the poorly crystallized kaolins, there do not seem to be many of these thick books, or stacks, with the largest dimension parallel to the *c* axis. In the poorly crystallized deposits, the kaolin is either an agglomeration of plates that are not stacked in a precise manner or else it consists of relatively thin aggregations of overlapping plates (Plate 5), reminiscent of a slate roof.

Several geological studies have been made on the Tuscaloosa formation in this area, and it is interesting to make geological speculations, although it

is not known precisely how these kaolins were formed. There has to be a reason why certain deposits are well crystallized and contain the beautiful vermicular stacks of well-crystallized kaolin, and why others contain only the thin plates and are poorly crystallized. Both types of deposits contain quartz, ilmenite, leucoxene, and other accessory minerals, so that it does not appear to be a diagenetic difference. The evidence seems to indicate that the original formation of the kaolinite on the crystalline rocks exerted the primary control over the degree of crystallinity. Sand (1956, p. 37) has suggested that the thick, well-crystallized books or stacks form from mica, and that the thin poorly crystallized plates form from feldspar. This is an excellent suggestion and seems to be a plausible explanation, but will require additional study to be proved or disproved. It is known that the well-crystallized kaolins, i.e. the stacks, will become disordered and appear similar to a poorly crystallized kaolin after many hours of grinding in a ball mill. W. F. Bradley (personal communication) has suggested that perhaps the poorly crystalline kaolins went through attrition during their transport and that this is the reason that there are no stacks in the deposits, and, therefore, they are disordered along the *c* axis. The present authors feel, however, that the stacking variation that is reflected by the degree of crystallinity is basically the result of disorder within the unit lattice of the kaolinite. Only precise and detailed studies will reveal whether or not this is the case.

SUMMARY

The degree of crystallinity of kaolinite varies significantly and can be related to many properties of the kaolinite. Surface area, base exchange capacity, and amount of iron and titanium all increase with decreasing crystallinity. The amount of dispersing agent necessary to achieve the lowest viscosity increases with decreasing crystallinity. The uncalendered papermaking gloss increases with decreasing crystallinity. The well-crystallized kaolins develop an intermediate sized mullite needle which tends to reflect the hexagonal outline of the kaolin crystals. The poorly crystallized kaolins, at fairly high temperatures, form larger mullite crystals, which do not follow this hexagonal net. The deposits in which well crystallized kaolins are found contain a significant proportion of stacks or books of kaolin, whereas the poorly crystalline deposits contain a dearth of these large stacks or books. Further work can reveal some interesting geological implications which may shed some light on the original formation of the kaolinites, and also indicate the diagenetic environment.

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PLATE 1.—Electron micrograph showing oriented mullite needles after firing to 1300°C (17,300 ×).

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PLATE 2.—Mullite crystals developed from well-crystallized kaolin at 1400°C (13,800 ×).

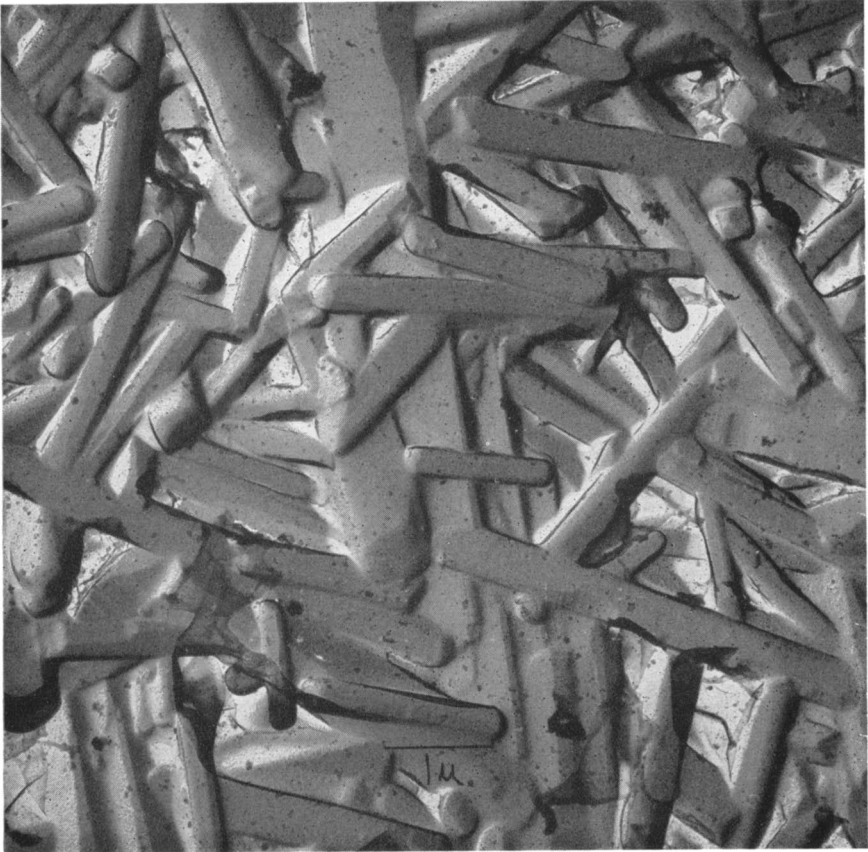


PLATE 3.—Mullite crystals developed from poorly crystallized kaolin at 1400°C (13,800 ×).

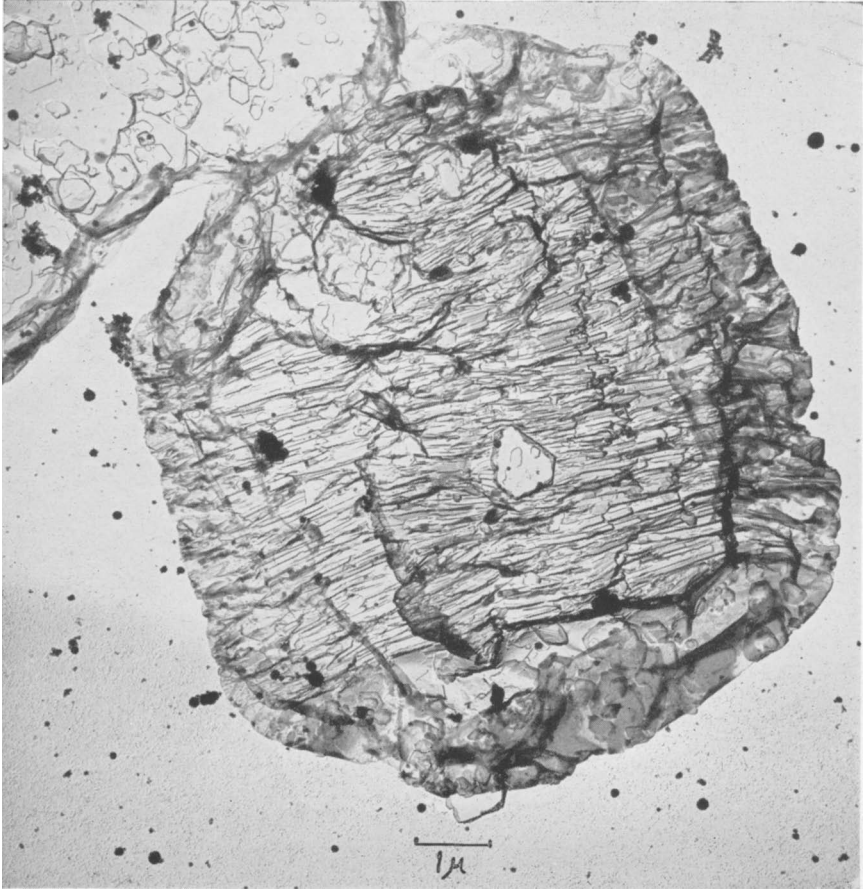


PLATE 4.—Kaolin stacks—well crystallized (10,000 \times).

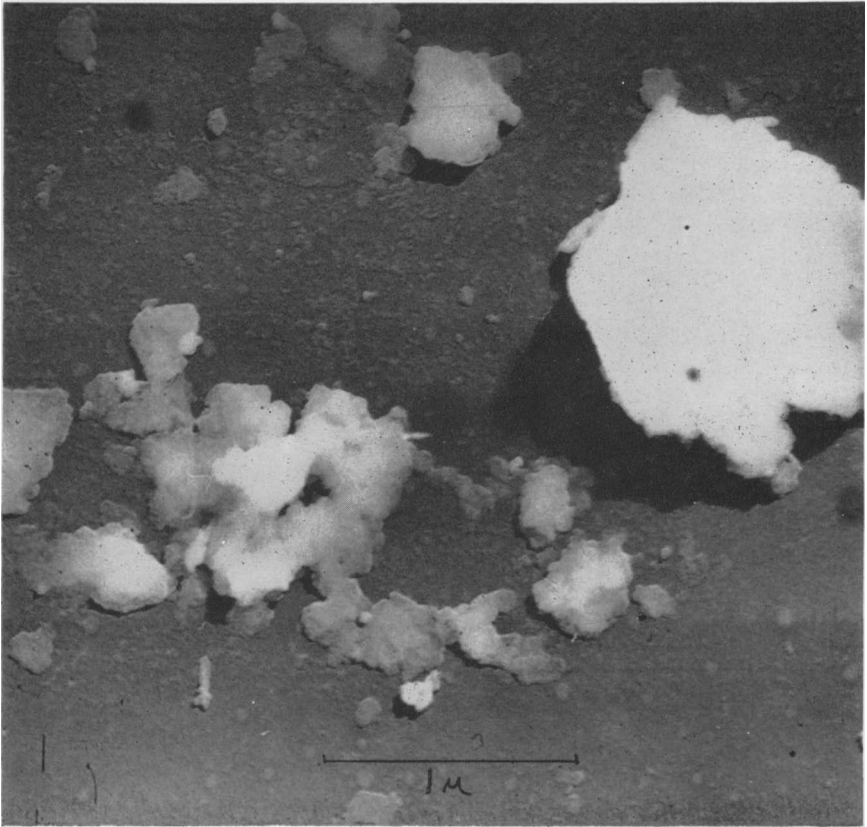


PLATE 5.—Kaolin stacks and plates—poorly crystallized (32,400 ×).

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