VARIABILITY IN "CRYSTALLINITY" VALUES AMONG THE KAOLIN DEPOSITS OF THE COASTAL PLAIN OF GEORGIA AND SOUTH CAROLINA

by

DAVID N. HINCKLEY
AC Spark Plug Division, General Motors Corp., Flint, Michigan

ABSTRACT

Quantitative measurement of the relative degree of crystal perfection among 144 samples of Coastal Plain kaolin shows that the deposits are nonhomogeneous with respect to crystallinity and that the hard and soft types can be distinguished at the 0.95 probability level by an analysis of variance. The nonhomogeneity of the deposits and the distinction between the hard and soft types agrees with the results obtained for other properties not reported here. Although on the basis of pulverizing ease there may be a single population with hard and soft end members, in terms of origin the evidence indicates the existence of two distinct clay populations.

INTRODUCTION

Differences among the kaolin deposits of the Coastal Plain of Georgia and South Carolina have been pointed out by numerous investigators ever since the deposits came under the appraising eye of G. E. Ladd (Ladd, 1898). These early-noticed megascopic differences, principally in texture, hardness, and mineral and chemical impurities, were supplemented by a knowledge of crystallinity differences in 1943 when Klinefelter (Klinefelter, O'Meara, Truesdell, and Gottlieb, 1943) noticed marked differences between the X-ray patterns of the hard and soft clay types. Differences in degree of crystallinity, also noted by subsequent investigators, were effectively illustrated by Murray and Lyons (1956) when they included the Coastal Plain kaolins with other kaolins from various parts of the world and ranked their X-ray patterns according to sharpness and resolution.

The present study is concerned with the variability in the degree of crystal perfection among the kaolin deposits and has as a point of departure the differentiation made by clay pit operators between the hard and the soft clay types and has as objectives obtaining answers to two specific questions: (1) Are the deposits homogeneous with respect to degree of crystal perfection? (2) Can the hard and soft clay types be distinguished on the basis of this variable?

SAMPLING PLAN

Sample material was supplied by several clay companies and consisted of eight drill cores taken in pairs from four commercially active clay deposits, two hard type and two soft type. The clay deposit was designated by the company supplying the core as "hard" or "soft" even though some differences were known to exist within each deposit.

Samples were selected from the cores according to a sampling plan associated with an experimental design set up to answer the questions previously mentioned. The sampling plan, a nested type, required that each core be arbitrarily divided into thirds, and that two 6-in. samples be taken at random from each third. Each 6-in. sample was then divided into three 2-in. subsamples providing eighteen distributed subsamples from each core or a total of 144 2-in. subsamples from the eight cores.

DEGREE OF CRYSTALLINITY

For the purposes of this study it was necessary to obtain a more quantitative, less subjective measure of the differences in crystallinity than is provided by visual inspection and ranking of X-ray patterns.

The problem of obtaining suitable data was two-fold: First, to find a method for keeping preferred orientation at a minimum and, second, to select peaks similar in their response to preferred orientation and having relative intensities indicative of the state of crystal perfection.

Sample Preparation

Two methods were found to be successful in keeping preferred orientation at a minimum. A "slab" method preserves the original, usually unoriented condition of the sample. This is accomplished by simply cutting from the sample a small slab of clay about 2 cm square and 2 mm thick, glueing this wafer to a suitable holder, planing it smooth with the edge of a new glass microscope slide, and removing the disturbed upper layers by alternately pressing and lifting Scotch Tape from the surface.

The second method consists of mixing finely ground thermoplastic organic cement* with the powdered clay to make a mixture 30 per cent by weight. After thoroughly mixing, the mixture was slowly heated on a glass or metal plate until the cement softened and could be blended into the clay. The mixture was worked with a spatula for several minutes while in this plastic state and then allowed to cool. (Brindley and Kurtossy (1961) have recently improved this method by dissolving the Lakeside in dioxane and evaporating off the solvent when a homogeneous mixture is obtained.) The resulting product, usually in tablet form but exhibiting considerable variation in cohesiveness, was pulverized to pass 80 mesh and then placed in X-ray sample

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* The cement used was "Lakeside No. 70C" supplied by Hugh Courtright & Co., 7652 Vincennes Ave., Chicago 20, Ill.

holders. Examination under a petrographic microscope shows that the agglomerated clay particles or pellets are noticeably equidimensional and show no birefringent effects indicative of preferential orientation. Because of its relative ease, the "slab" method was used for most of the sample preparation.

Crystallinity Measurement

The peaks on the X-ray diffractometer tracing which were selected for measurement to indicate the relative degree of crystal perfection are the $1\bar{1}0$ and the $11\bar{1}$ at 20.4° and 21.3° 2θ, respectively, with CuKα radiation. The method described in detail elsewhere (Bates and Hinckley, 1959) consists of forming a ratio from the heights of the $1\bar{1}0$ and the $11\bar{1}$ peaks above a line drawn from the trough between the 020–$1\bar{1}0$ peaks to the background just beyond the $11\bar{1}$ peak (about 22° 2θ). These measurements are combined to form the numerator and are divided by the height of the $1\bar{1}0$ peak above general background. Figure 1 indicates the relationships involved.

As crystal perfection improves, principally because of less random shifts of $nb_0/3$ along b (Brindley, 1951), the resolution of $1\bar{1}0$ and $11\bar{1}$ is improved. The better resolution of the $1\bar{1}0$ causes the trough between it and the 020 to deepen resulting in an increase in the measured height of the $1\bar{1}0$ and the $11\bar{1}$ (A and B, Fig. 1). The denominator, the total height above background of the $1\bar{1}0$ reflection, provides a measure of absolute intensity and the ratio formed, called the crystallinity index, is suitable for comparing crystal perfection between samples.

A quartz peak of moderate intensity occurs at 20.8° 2θ, about midway between the $1\bar{1}0$ and the $11\bar{1}$. Ordinarily the amount of quartz present is small and this peak caused no adverse effects.

A ranking method for indicating relative degree of crystallinity, of the same general type described by Murray and Lyons (1956), was developed as a check on the effectiveness of the crystallinity index. Figure 2 is a plot of class value versus crystallinity index for the 108 samples on which this was tried. A phi medial correlation coefficient (Quenouille, 1952) of 0.85 is obtained indicating that about 72 per cent of the variation is common to both measurements.

A comparison of the crystallinity index to an index for crystallinity produced by a method described by Johns and Murray* was also made. A correlation coefficient of $\phi r = 0.85$ was obtained for this relationship indicating the same general variations in degree of crystal perfection are being measured. There are two advantages to the method used in this study. First, the crystallinity index values have a greater spread and do not include zero, and, second, the peaks under consideration occur within a shorter angular range.

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* The method of Johns and Murray consists of obtaining a ratio of the $02\bar{1}$ reflection with the 060 reflection. Personal communication H. H. Murray, October 1959.

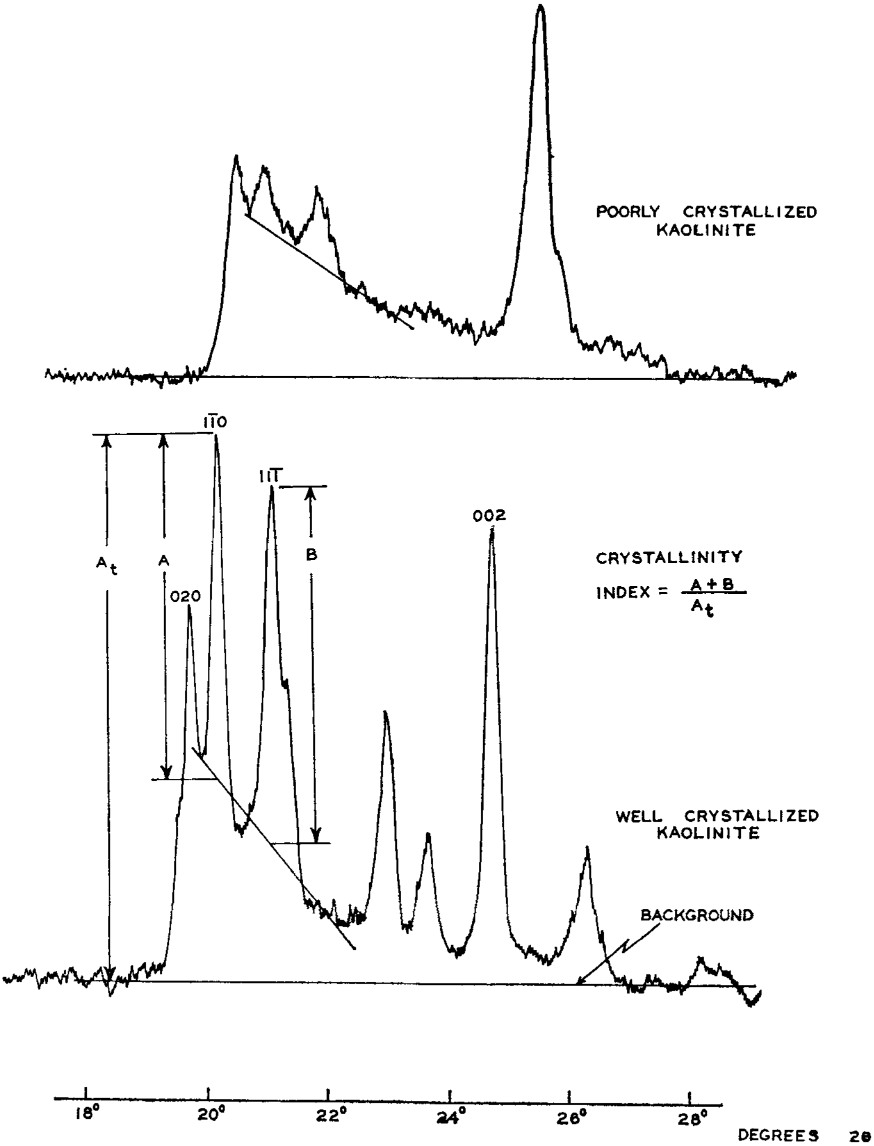

Figure 1.—Crystallinity index for kaolinite.

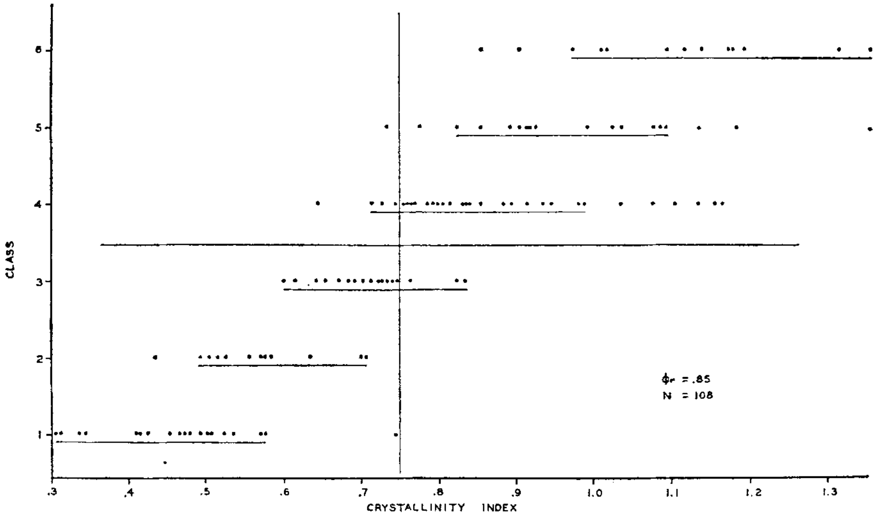

Figure 2.—Correlation: Class vs. Crystallinity index.

DISCUSSION OF RESULTS

The data from which the frequency distributions (Fig. 3) and the analysis of variance (Table 1) are derived are not presented here, but are available elsewhere (Hinckley, 1961).

Table 1.—Analysis of Variance of Crystallinity

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	*F* Ratio
Types	1	73,486.18	73,486.18	19.81*
Pits	2	7,417.01	3,708.50	8.36**
Cores	4	891.69	222.92	1
Thirds	16	10,252.78	640.80	1.83
Samples	24	8,369.83	348.74	5.02***
Subsamples	96	6,662.33	69.40	
Total	143	107,079.82		

N = 144 C.T. = 677,466.17 * = Significant at 0.95

The frequency distribution is bimodal, and the analysis of variance indicates that the deposits are non-homogeneous and that the types differ significantly. Compared to the relatively small variation among subsamples from within a 6-in. core sample the variability is large among samples, among thirds of cores, among cores, among pits, and among clay types. Despite the

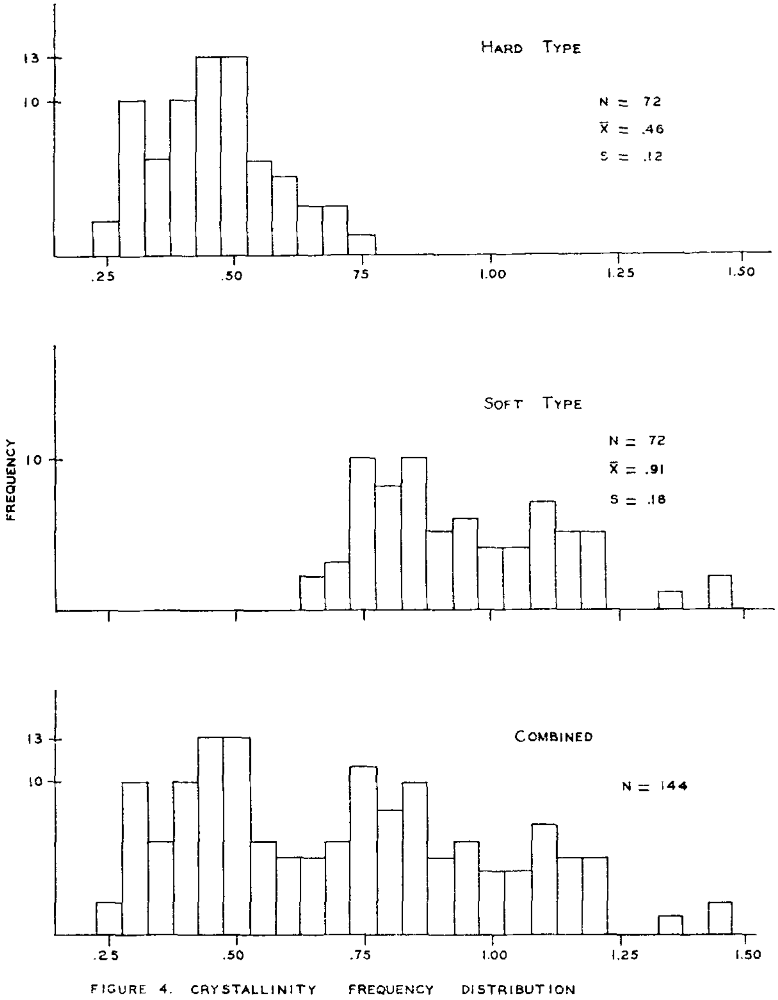

Figure 3.—Crystallinity frequency distribution.

large variability among pits within the same type (significant at the 99 per cent level) the differences between the hard and soft clay types are sufficiently large to allow them to be differentiated at the 95 per cent level.

During the sampling process similarities in the sequence of certain megascopic features were noticed in the pairs of cores from pit 1. These features, principally differences in texture, grit content, and color, delineated zones which appeared to have counterparts in the adjacent core. Samples in addition to those required by the sampling plan were taken to ascertain whether these megascopically observable zones were also zones with respect to crystallinity. In the case of pit 1, where the cores were drilled relatively close together, the zones were significantly different. The cores, compared zone by zone by a paired "t" test, did not differ significantly. This is a situation which would be expected if the deposits were layered. These results, however, were not duplicated in another soft type clay deposit, not described here, in which the cores were drilled farther apart. These situations corroborate the evidence for non-homogeneity shown to exist within the clay deposits by the analysis of variance.

It is not possible to say whether or not the hard and soft types represent the end members of a single population of kaolin or whether they are from separate and distinct kaolin populations. The work of Klinefelter *et al.* (1943) and additional work connected with this study but reported elsewhere (Hinckley, 1961), however, indicate that while on the basis of pulverizing ease there may be a single population with hard and soft end members, the distribution of crystallinity values and other properties suggest the existence of two distinct clay populations.

REFERENCES

Bates, T. F., and Hinckley, D. N. (1959) Mineralogy and petrology of the kaolin clays of the Piedmont and Coastal Plain regions of southeastern United States: *Progress Report,* 1 June, 1958–1 June, 1959, The Pennsylvania State University, University Park, Pa.

Brindley, G. W. (1951) The kaolin minerals: In "X-ray identification and crystal structures of clay minerals": *Mineralogy Society of Great Britain Monograph,* Chap. 2, pp.32–75.

Brindley, G. W., and Kurtossy, S. S. (1961) Quantitative determination of kaolinite by X-ray diffraction: *Amer. Min.*, v.46, pp.1205–1215.

Hinckley, D. N. (1961) Mineralogy and petrology of the kaolin clays of the Piedmont and Coastal Plain regions of southeastern United States: *Technical Report,* The Mineral Industries Experiment Station, College of Mineral Industries, The Pennsylvania State University, University Park, Pennsylvania, Data Appendix A, Sampling plan 3, p.17.

Klinefelter, T. A., O'Meara, R. C., Truesdell, G. C., and Gottlieb, S. (1943) Hard and soft kaolins of Georgia: *U.S. Bur. Mines Rept. Inv.* 3682, 20pp.

Ladd, G. E. (1898) A preliminary report on a part of the clays of Georgia: *Georgia Geo. Survey Bull. 6-A*, 203pp.

Murray, H. H., and Lyons, S. C. (1956) Correlation of paper-coating quality with degree of crystal perfection of kaolinite: in *Clays and Clay Minerals,* Natl. Res. Council, pub. 456, pp.31–40.

Quenouille, M. H. (1952) *Associated Measurements:* Butterworth's Scientific Publications, London, England, p.37.