

## MINERALOGY OF KAOLIN CLAYS FROM PUGU, TANGANYIKA

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### ABSTRACT

Kaolin clays from Pugu, Tanganyika, have been studied by *x*-ray, thermal, chemical and electron-optical methods. They include deposits of well-crystallized kaolinite and also of the *b*-axis disordered kaolin mineral. The latter give exceptionally clear *x*-ray diagrams which have been studied in greater detail than has previously been possible. Morphologically the disordered kaolin shows small but well-formed hexagonal plates. The cation exchange capacities have been measured and appear to be related to substitutions in both tetrahedral and octahedral lattice positions. The main chemical difference between the ordered and disordered clays appears to lie in the amount of tetrahedral substitution.

### INTRODUCTION

The work described in this paper is the result of a combination of studies which present an unexpected and, in some respects, unusual picture of the mineralogy of kaolinite. Briefly, from a study of a number of kaolin-bearing sediments from Pugu, Tanganyika, two were selected for detailed study. Electron micrographs showed, in one specimen, slightly elongated hexagonal flakes, some showing a re-entrant angle

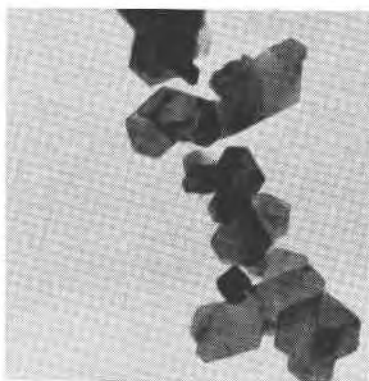


FIG. 1. Electronmicrograph of *Pugu* K Kaolin,  $\times 5000$  enlarged to 20,000, showing one crystal of anatase.

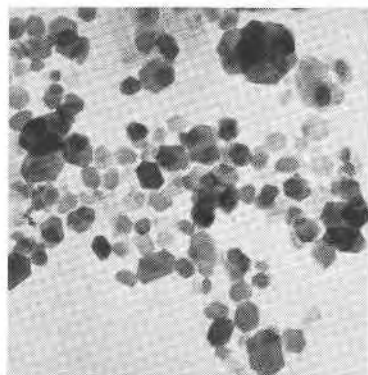


FIG. 2. Electronmicrograph of *Pugu* D Kaolin,  $\times 8000$ , enlarged to 20,000.

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(Fig. 1), and in the other specimen, smaller but extremely regular and uniform hexagons (Fig. 2). X-ray analysis showed the larger flakes to be well crystallized kaolinite, but the smaller flakes gave the type of x-ray powder diagram previously obtained with the disordered kaolin structure found in many fireclays (Brindley and Robinson, 1947a; Brindley, 1951). Relatively pure specimens of both types of kaolin were readily obtained and their chemical composition, cation-exchange capacity, thermal and mechanical properties studied. The kaolin mineral in fireclays is usually associated with considerable quantities of fine-grained quartz and mica, together with other impurities, which have rendered difficult its detailed examination. It was thought to be worthwhile, therefore, to study in some detail these ordered and disordered forms of kaolin.

#### GEOLOGY OF THE DEPOSIT

During the recent exploitation of the massive kaolin-sandstone deposits in the Pugu Hills, west of Dar-es-Salaam, Tanganyika, samples of the rock were taken from Adit "D" west of the present factory and from Adit "K" west of opencast workings previously developed. The samples described came mainly from 40-50 ft. from the portal of Adit "D" and from 120 ft. from the portal of Adit "K"—and for brevity will be referred to hereafter as "*Pugu D*" and "*Pugu K*" respectively.† Because both samples originated from the same series of strata, a brief account of their geology may be given.

The source rocks of the deposits are the Basement Complex (Archaean) rocks, which extend to within 100 miles of Pugu and which consist of a series of migmatites, biotite-gneisses and gneissose granites (Stockley, 1948). Rapid erosion and transportation in the Upper Cretaceous and variations in land level produced a rhythmic succession of sediments, each cycle beginning with micaceous arkose, slightly kaolinized, passing up into deltaic deposits of mica-free arkose, contemporaneously kaolinized *in situ* to a considerable extent (e.g., *Pugu K*), and ending with a deeper, marine facies consisting of kaolin deposited with finer quartz and feldspar sand (e.g., *Pugu D*).

*Pugu K* is a white permeable kaolin-sandstone containing, in the specimen tested, 29.4% kaolin, the remainder being sand grains of a narrow particle size range with a median diameter of 0.28 mm. The sand grains, although highly polished, are not so completely rounded as in some desert sands. Judging from photographs of Davies and Rees (1945), their rugosity or angularity (area divided by area of a sphere of the same mass

† By strange coincidence, the *K* material turns out to be good kaolinite and the *D* material the distorted structure.

(Robertson and Emödi, 1943) ) appears to be about 1.08. Absence of very small sand grains, the narrow particle size range of the grains, the rarity of mica and the presence of sand-blasted pebbles demonstrate that the sand was subjected to aeolian influence by passing through desert conditions on its way to the sea. Accessory minerals include ilmenite and zircon. Hematite and goethite occur as "iron-staining," especially where the overburden is shallow.

*Pugu D* is less white, almost impermeable and very uniform in quality throughout; the kaolin content is 52.8% and the sand grains, with a median diameter of 0.18 mm., have a much wider particle size range.

Similar rocks are the kaolinized fine-grained Keuper arkoses at Hirschau and Schnaittenbach in Bavaria and the coarser-grained arkoses found near Steinfels, Weiherhammer and elsewhere (Zwetsch, 1950). In Georgia, U.S.A., kaolin was also formed in the Upper Cretaceous, but here the sand grains are more angular and there is a great variation in clay content and quality over this area (Mitchell and Henry, 1943; Kesler, 1951).

#### X-RAY ANALYSIS OF PUGU *D* AND *K* CLAYS

X-ray analyses of these materials have been carried out with (a) a 20 cm. diameter, semi-focusing camera, using flat powder specimens, (b) a 19 cm. diameter Unicam instrument, using thin coatings of powder on thin-walled silica tubes of external diameter about 0.025 cm., and (c) the same camera using powders packed in thin silica tubes of internal diameter about 0.03 cm. Methods (a) and (c) require no binding agent; gum-tragacanth was used in (b). Filtered  $\text{CoK}\alpha$  radiation ( $\lambda = 1.78659\text{kX}$ ) was employed.

X-ray powder diagrams are reproduced in Fig. 3; diagrams 1 and 2 of *Pugu K* clay and 3 of *Pugu D* clay were taken by method (b) and are reproduced without change of scale. Diagrams 4 and 5, of *K* and *D* clays respectively, were taken by method (c) and are shown with two-fold enlargements in order to make clear the details of the lower order reflections.

Since the *K* and *D* clays differ in crystal size, it was considered important to determine whether the differences shown in their x-ray diagrams could be attributed to the crystal sizes of the materials. Two fractions of the *K* material were therefore prepared, *K1* and *K2*, with crystal sizes respectively 1.4–0.2  $\mu$  and less than 0.2  $\mu$  equivalent spherical diameter (*e.s.d.*); the corresponding x-ray diagrams are numbers 1 and 2 in Fig. 3. The reflections from the two samples are practically identical. Impurity lines from quartz, indicated in the key by dotted lines marked *Q*, are more prominent in 1 than in 2. The reflections in 2 are somewhat less

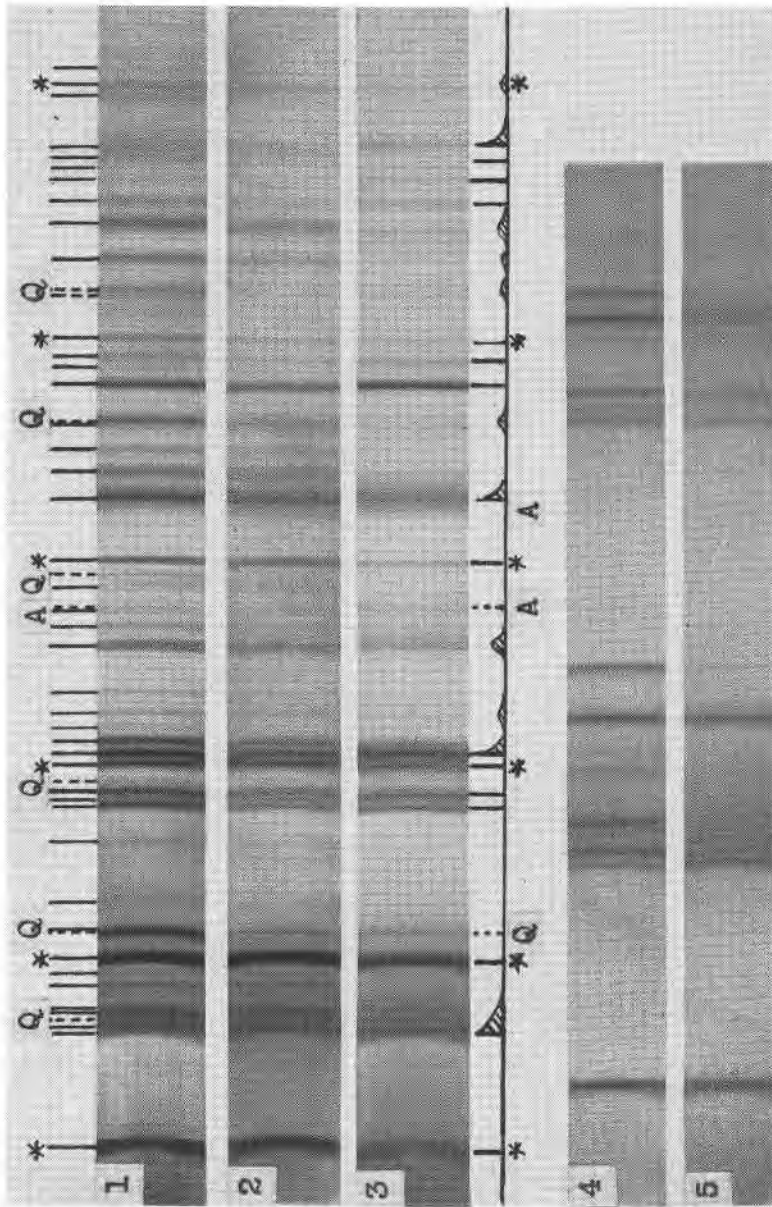


FIG. 3. X-ray powder diagrams of Pugu kaolin clays (19 cm. diameter camera; filtered  $\text{CoK}\alpha$  radiation). (1) *K* clay ( $1.4-0.2\mu$  particle size). (2) *K* clay ( $<0.2\mu$  particle size). (3) *D* clay ( $\times 2$  enlargement). (4) *K* clay ( $\times 2$  enlargement). (5) *D* clay ( $\times 2$  enlargement). *K* = well crystallized kaolinite; *D* = *b*-axis disordered kaolin mineral; *Q* = quartz reflections; *A* = anatase reflections.

sharp than in 1, in accordance with the smaller crystal size of *K2*, and the weakest reflections from *K2* are less easily seen, *but in all essential respects the coarse and fine fractions are crystallographically identical.*

The full pattern of lines from the *K* clay is indicated in the key in diagram 1, with asterisks marking the basal (00*l*) reflections, and *Q* and *A* indicating impurity lines from quartz and anatase. This diagram agreed in all respects with the data of Brindley and Robinson (1946) for well crystallized kaolinite from which the triclinic structure of the mineral was evaluated. The very close triclinic doublet, (111̄) and (1̄11̄), with spacings 4.170 and 4.120kX, which is resolved by the best crystalline kaolinites, is imperfectly resolved by the *Pugu K* clay, but the doublet character is undoubtedly present and can be seen in the enlarged diagram, number 4.

It is concluded that the *Pugu K* clay, both coarse and fine fractions, consists of a well-crystallized kaolinite together with some fine quartz and anatase. The presence of anatase, shown by one or two lines only in diagrams 1–3, was confirmed by heating the clays to about 600° C. to destroy the kaolin mineral, when the full sequence of anatase lines together with quartz lines is observed.

Crystallographic interest centers mainly in the *Pugu D* clay, the *x*-ray diagram of which shows that it is a very good example of the *b*-axis disordered kaolin mineral first discussed by Brindley and Robinson (1947*a*). The sample prepared for *x*-ray analysis is of a high degree of purity and contains no more than a trace of quartz and anatase. The clarity of the diffraction diagram, Nos. 3 and 5 in Fig. 3, is greatly superior to that obtained from the fireclays previously studied and justifies a full description of the results obtained.

The diagrams in Fig. 3 are arranged so as to facilitate the comparison of the diffraction patterns of the well crystallized kaolinite and the *b*-axis disordered mineral. The outstanding feature of the latter is the broadly spreading band of intensity with a sharp low-angle termination at about 4.47 kX, the nature of which is entirely consistent with two-dimensional diffraction from randomly displaced layers. The well-ordered mineral gives a series of lines in this angular range. This difference is clearly shown in figures 4 and 5.

The lattice spacings, estimated reflection intensities, and characteristics of line profiles, such as sharp, broad or diffused, are tabulated in Table 1 together with the calculated spacings and indices. The following lattice parameters were used:

$$\begin{array}{ll} a & 5.14(7) \text{ kX} \\ b & 8.91(5) \\ c & 7.38(0) \end{array} \quad \beta = 104.5^\circ$$

TABLE 1. X-RAY DATA FOR PUGU D CLAY, A *b*-AXIS DISORDERED KAOLIN MINERAL

<i>hkl</i>	<i>d</i> , in kX		<i>I</i> (est.)	Characteristics of line profiles
	Calculated	Observed		
001	7.145	7.17	10	sharp
"02"	4.457	4.47	8	band, strongly diffused to higher angles
002	3.572	3.577	10+	sharp
20 $\bar{1}$	2.560	2.560	8	sharp
130	2.552			
13 $\bar{1}$	2.507	2.497	8	sharp
200	2.491			
003	2.382	2.381	8	sharp
20 $\bar{2}$	2.336	2.336	9	diffused to higher angles
131	2.311			
13 $\bar{2}$	2.215	2.202	1	very broad
201	2.188			
20 $\bar{3}$	1.988	1.985	4	diffused to higher angles
132	1.961			
13 $\bar{3}$	1.865	—	—	not observed
202	1.839			
004	1.786	1.786	4	sharp
20 $\bar{4}$	1.662	1.663	5	diffused to higher angles
133	1.639			
13 $\bar{4}$	1.560	1.538	1	diffused to lower angles
203	1.540			
060	1.486	1.485	10	sharp
33 $\bar{1}$	1.485			
33 $\bar{2}$	1.459	1.455	3	broad
061	1.454			
330	1.450			
005	1.429	1.429	2	sharp

TABLE 1—Continued

<i>hkl</i>	<i>d</i> , in kX		<i>I</i> (est.)	Characteristics of line profiles
	Calculated	Observed		
20 $\bar{5}$ 134	1.400 1.382	—	—	not observed
33 $\bar{3}$ 062 331	1.379 1.372 1.364	1.372	1	broad
13 $\bar{5}$	1.321	1.336	1	
204	1.305	1.307	1	very broad, spreading towards lower angles
26 $\bar{1}$ 40 $\bar{1}$	1.2850 1.2827	1.2847	3	moderately sharp
33 $\bar{4}$ 063 332	1.2695 1.2605 1.2515	1.2624	1	
26 $\bar{2}$ 400	1.2537 1.2457	1.2476	$\frac{1}{2}$	
40 $\bar{3}$ 261	1.2385 1.2291	1.2345	3	diffused to higher angles
006	1.1908	1.1918	1	

Additional observed lines, all very weak, of uncertain indices:  
 $d=1.112, 1.042, 1.032, 1.022, 0.972, 0.958$  kX.

On the basis of the earlier work the unit cell is assumed monoclinic with  $\beta=104.5^\circ$ . A mean value of  $c \sin \beta$  is obtained from the  $00l$  spacings ( $l$  ranging from 1 to 6), viz., 7.145 kX. The  $b$  parameter is calculated from  $d(060)=1.485(8)$  kX and the  $a$  parameter is taken to be  $b/\sqrt{3}$ .

The results in Table 1 confirm and amplify the earlier data and the conclusions drawn therefrom. Altogether 23 reflections are now indexed and 6 higher orders of uncertain indices are recorded, as compared, in the earlier work, with 14 indexed reflections and two others which probably did not arise from the kaolin mineral. Of the 23 indexed reflections, 22 are of the type  $(hkl)$  with  $k=3n$ , where  $n=0, 3$  or 6. The only reflection observed with  $k \neq 3n$  is indexed as "02" and is the 'two-dimensional'  $hk$  band with its characteristic intensity distribution. The results support the earlier conclusion that the distortion consists of largely random dis-

placements of the structural layers parallel to  $b$  and of integral multiples of  $b/3$ .

One aspect of the data given in Table 1 calls for comment, namely the fact that most of the observed reflections correspond to two or three calculated reflections in close proximity such as doublets of the type  $(20l)$ ,  $(13\bar{l}+1)$ . The question arises whether a more appropriate choice of axes or parameters would bring these calculated groups of lines into coincidence. It should be noted, in the first place, that the  $\beta$ -angle,  $104.5^\circ$ , corresponds very closely with a relative shift of successive structural layers by  $-a/3$  along the  $a$ -axis. If the displacement is *exactly*  $-a/3$ , then  $\beta$  is given by  $\cos \beta = -a/3c$ , which leads to a value for  $\beta$  of  $103.5^\circ$ . With this value of  $\beta$  and with the axial ratio  $b/a = \sqrt{3}$ , the groups of closely spaced lines are brought into coincidence. Under these conditions a hexagonal cell embracing three structural layers exists which is related to the monoclinic cell by the following transformation matrix

$$\begin{vmatrix} 1 & 0 & 0 \\ -\frac{1}{2} & \frac{1}{2} & 0 \\ 1 & 0 & 3 \end{vmatrix}$$

so that if  $HKL$  are the hexagonal indices, then  $H=h$ ,  $K=-h/2+k/2$ , and  $L=h+3l$ , and the hexagonal parameters are  $a_h=5.14(7)\text{kX}$  and  $c_h=21.43(5)\text{kX}$ . The available evidence suggests that  $\beta=104.5^\circ$  is in better agreement with the observations than is the ideal value  $103.5^\circ$  and that the structure is, therefore, more appropriately regarded as being monoclinic, or at least pseudo-monoclinic, than hexagonal. Although it has not been found possible to photograph the calculated doublets and triplets, even at the higher angles where greater resolving power obtains, the diffusion of many of the reflections shown in diagram 3 of figure 3 suggests that the lattice is not based on a clearly defined hexagonal cell. Indeed, this would not be expected since in kaolinite there is a clear evidence that the lattice is triclinic, the translation from layer to layer being only approximately  $-a/3$  along the  $a$ -axis together with a small translation along the  $b$ -axis making the angle  $\alpha=91.8^\circ$ .

Thus, the  $x$ -ray evidence shows that the *Pugu D* clay is a  $b$ -axis disordered mineral of the type described by Brindley and Robinson (1947 *a*); the previous data are confirmed and amplified by the exceptionally clear diffraction diagrams obtained with this clay.

#### DIFFERENTIAL THERMAL ANALYSIS OF PUGU CLAYS

The apparatus used for this investigation has already been fully described (Mackenzie, 1952), so it need only be noted that, (*a*) all temperatures quoted refer to the sample, since the temperature thermocouple was positioned in this material; (*b*) differing bulk densities pre-



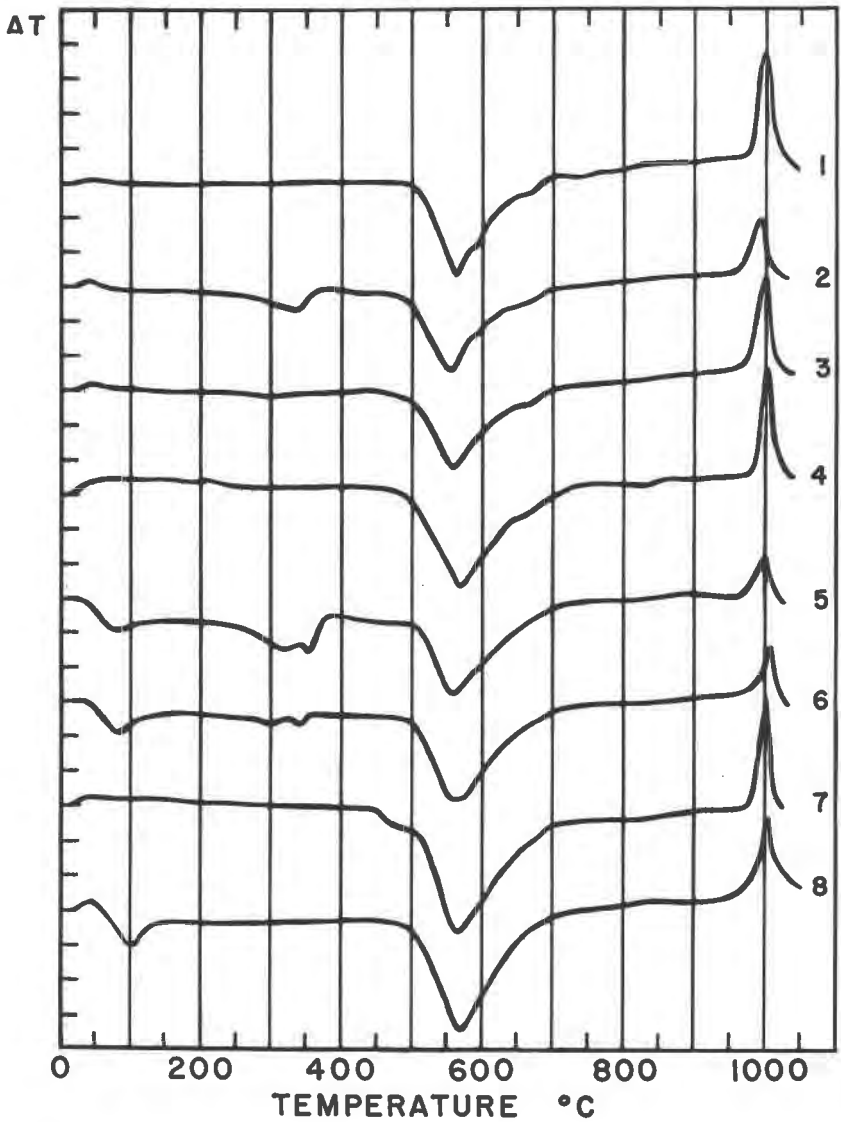


FIG. 4. Thermograms for colored samples of *Pugu* Kaolin. Data are given in Table 2 under the following curve Nos.: 1-253; 2-256; 3-252; 4-251; 5-259; 6-257; 7-314; 8-254.

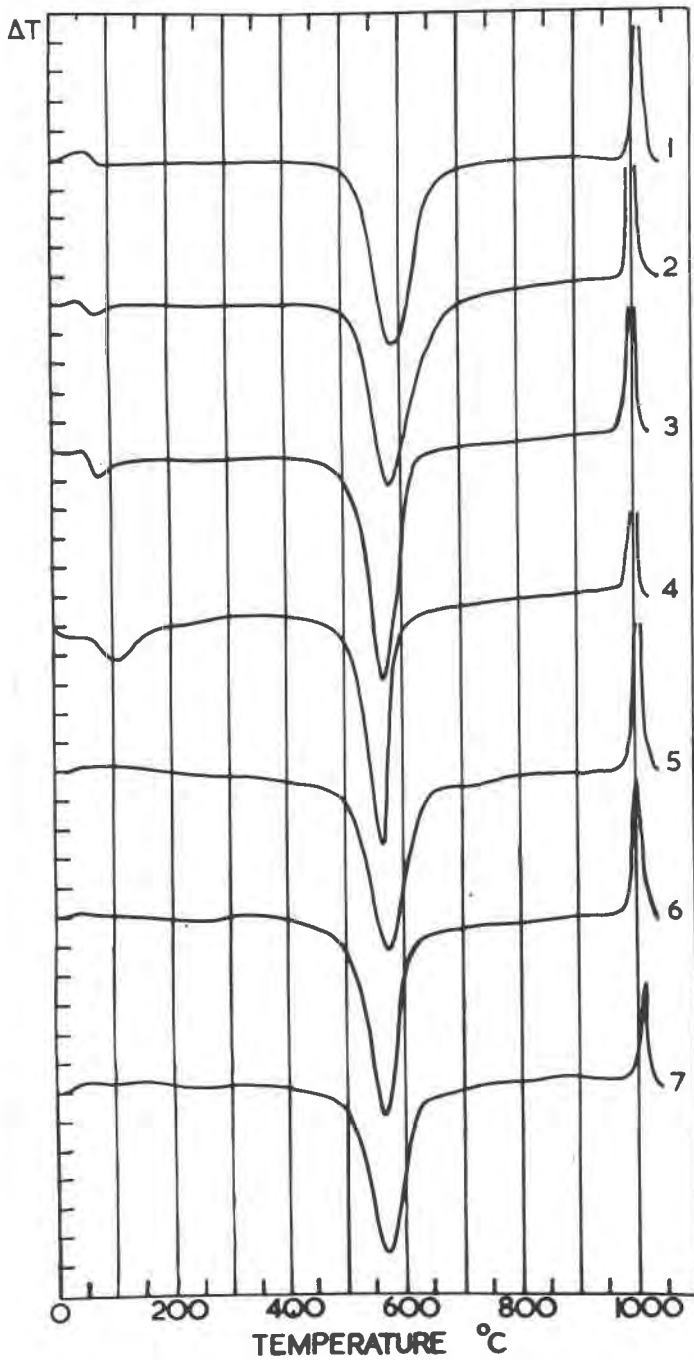


FIG. 5. Thermograms for some kaolin and halloysite samples. Data are given in Table 2 under the following curve Nos.: 1-249; 2-213; 3-379; 4-282; 5-416; 6-414; 7-418.

TABLE 2. THERMAL DATA FOR KAOLIN SAMPLES

Curve No.	Sample No. or Description	Color	Audit	Sample Wt. (g.)	T(endo) ° C.	$\Delta T(\text{endo})$ ° C.	Area (endo) mm. <sup>2</sup>	Wt. of reacting material (g.)	Per cent reacting material*	T(exo) ° C.
249	Cornish Kaolinite	White	—	0.20	588	12.7	1036	0.190	95	1008
309	50% Cornish Kaolinite	White	—	0.20	570	7.3	550	0.102	51	1005
192	25% Cornish Kaolinite	White	—	0.20	557	3.6	254	0.047	23	992
254	<i>Lithomarge</i>	White	—	0.20	571	6.2	537	0.100	50	1002
313	1	White	K	0.20	582	12.4	1014	0.186	(93)	994
314	7	White with pink staining	K	0.25	567	6.6	628	0.117	47	998
259	17	Yellow-stained material	K	0.17	558	4.3	313	0.058	34	1000
257	17	Red with yellow stains	K	0.20	563	4.9	456	0.086	43	1007
253	6	White	C	0.20	563	5.4	395	0.074	37	997
256	6	Yellow-stained material	C	0.19	557	4.4	353	0.066	35	993
251	6	Red surface clay	C	0.20	570	5.8	529	0.098	49	1002
252	6	Deep red	C	0.20	560	4.4	374	0.070	35	998
416	Pugu K1 (1.4-0.2 $\mu$ )	White	K	0.14	571	11.2	753	0.139	99	1003
414	Pugu K2 (<0.2 $\mu$ )	White	K	0.14	566	12.8	743	0.136	97	1001
418	Cornish K $\phi$ (<0.4 $\mu$ )	White	—	0.14	571	11.1	745	0.137	98	1010
379	5	White	D	0.18	569	15.5	937	0.175	(97)	997
282	Halloysite (Iowa)	White	—	0.20	560	16.0	720	0.200	(100)	997
383	50% Halloysite (Iowa)	White	—	0.20	543	7.8	356	0.099	50	1005
385	25% Halloysite (Iowa)	White	—	0.20	532	4.0	166	0.046	23	1004

\* Values in parentheses are assumed percentages from which other percentages are calculated; values for curves 313 and 379 are those given by other methods (see Table 5).

cluded use of a constant amount for all determinations, although 0.20 g. samples were used wherever possible.

In order to characterize the materials responsible for the red and yellow staining on some of the clay samples, the first specimens examined were a range of colored clays from Adits *C*, *D* and *K*, (Fig. 4). Yellow-stained samples apparently contained goethite (peak at about 350° C.), with, in the Adit *C* sample (curve 2), possibly some boehmite (peak at 595° C.), and in the Adit *K* samples (curves 5 and 6) a small amount of gibbsite (peak at about 320° C.). The concentrations of these minerals were in all cases low—never more than about 5%. Since red-stained material (curves 3 and 4) did not show the presence of any hydrous oxide, the iron must presumably be present as hematite. At about 665° C., colored clays from Adits *C* and *K* (curves 1–7) showed a small peak, possibly due to a trace of illite. Quartz, if present, would not be observable on any of these thermograms.

It is well recognized that the thermal effects given by members of the kaolin group serve to distinguish them reasonably distinctly—*e.g.* increasing disorder in the lattice (*i.e.* from kaolinite to halloysite) causes a decrease in the temperature of the principal endothermic peak and an increase in its asymmetry (Grimshaw *et al.*, 1945; Brindley and Robinson, 1947*a*). A simple method of numerically evaluating this latter effect has recently been proposed by Bramao *et al.* (1952). In interpreting such thermal data, however, other factors affecting peak temperature and shape, *e.g.* the amount and the particle size of the reactant, must also be considered and, if necessary, allowed for. In the present set of experiments the sample weight was not always constant and consequently correction for the effect of this factor must be made before a rigorous comparison of curves in Figs. 4 and 5 can be attempted.

From the sample-weight data in Table 2, it will be observed that the peak temperatures in column 6 will be slightly too low for curves 256, 259 and 379 and too high for 314. Although the conditions prevailing here are not identical with those normally obtaining when the sample is diluted with foreign material, and the sample weight kept constant, it is considered sufficiently accurate, in view of the relatively small differences in sample weight, to employ the weight of reactant as determined by the ratio of the area under the peak on each curve to the peak area for the pure material (the usual relationship for determination of amount of reactant: see MacKenzie, 1952) for correlation with peak temperature (Fig. 6). As, from all available data, the material which gave curve 379 would appear to be practically pure, the amount of reactant here cannot be calculated as an area percentage and it was considered little error would arise by considering the amount of reactant to be 0.175g.—the

weight derived from other measurements (Table 5). The correlation of peak temperature with amount of reactant (Fig. 6) indicates that all the *Pugu C* and *K* samples are reasonably similar to Cornish kaolinite. The slightly lower peak temperature for *Pugu K* than for Cornish kaolinite tends to suggest that it is rather less well-crystallized, while the slightly higher peak temperatures for the sample labelled *Lithomarge*—a compact segregation of kaolinite—and for the red surface clay from sample 6, *Adit C*, seems to indicate, if anything, rather better crystallized material. The differences are slight, however, and broken lines have been inserted to cover what might well be the kaolinite region. The point for *Pugu D* falls well outside this region and, in fact, lies intermediate between the kaolinite and halloysite regions—*i.e.* in the position which should correspond to that for the disordered form of kaolinite found in many fireclays.

In view of the difference in particle size of *Pugu K* and *D* clays it is necessary, however, to examine closely the effects of such variation before drawing any definite conclusions. For this purpose thermograms were obtained for the samples *K1* ( $1.4\text{--}0.2\ \mu$ , *e.s.d.*) and *K2* ( $<0.2\ \mu$ , *e.s.d.*)—see *x*-ray section—and for *K6*, a  $<0.4\ \mu$ , *e.s.d.* fraction of a Cornish kaolinite (curves 5, 6 and 7, Fig. 5). To avoid confusion, the data

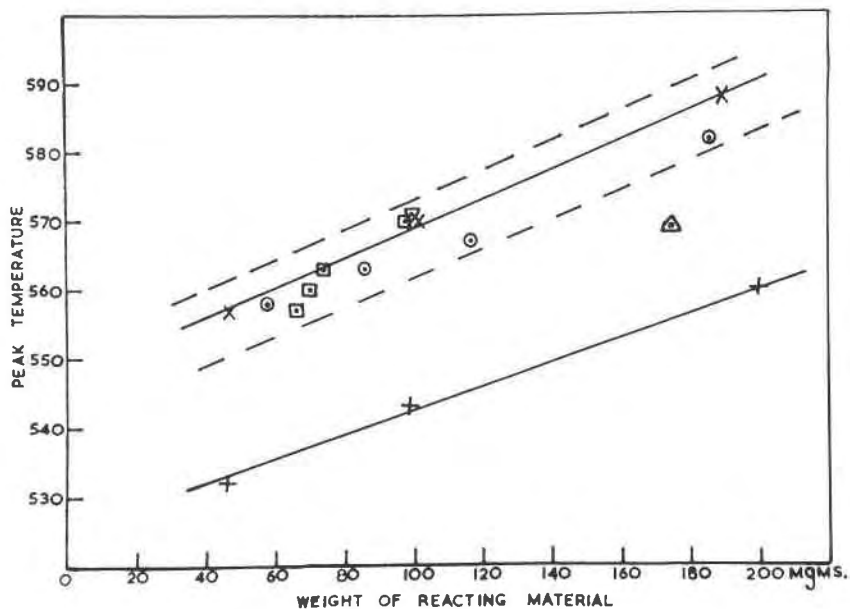


FIG. 6. Relationship between peak temperature and amount of reacting material for various samples: X = Cornish kaolinite; O = *Pugu K*; □ = *Pugu C*; ▽ = "*Lithomarge*"; △ = *Pugu D*; + = Iowa halloysite.

TABLE 3. SLOPE RATIOS FOR KAOLIN SAMPLES

Curve Number	Sample Number or Description	Slope Ratio
249	Cornish Kaolinite	0.95
309	Cornish Kaolinite 50%	0.93
192	Cornish Kaolinite 25%	0.91
254	"Lithomarge"	0.96
313	1 } 7 } Pugu K 17 } 17 }	0.81
314		0.64
259		0.60
257		0.64
253	6 } 6 } Pugu C 6 } 6 }	0.82
256		0.86
252		0.76
251		0.73
416	Pugu K1 (1.4-0.2 $\mu$ )	1.05
414	Pugu K2 (<0.2 $\mu$ )	1.26
418	Cornish K 6 (<0.4 $\mu$ )	1.26
379	5 Pugu D	1.26
282	Halloysite (Iowa)	1.97
383	Halloysite (Iowa) 50%	1.87
385	Halloysite (Iowa) 25%	1.95

for these samples are not plotted on Fig. 6, but from Table 2 it will be appreciated that while both *K1* and *K6*, fall within the kaolinite region, *K2* falls outside. However, although the particle size of *K2* is almost identical with that of *Pugu D* (Meldau and Robertson, 1952), the peak temperature for *K2* is not sufficiently low (by about 5°) to bring it into line with the value for *Pugu D* and, consequently, one seems justified in definitely distinguishing *Pugu K* and *Pugu D* clays.

The "slope ratio" of the thermogram (*i.e.*  $\tan \alpha / \tan \beta$ , where  $\alpha$  is the angle between the perpendicular to the peak and the tangent to the descending side and  $\beta$  the corresponding angle on the ascending side) has recently been proposed (Bramao *et al.*, 1952) as a convenient means of distinguishing members of the kaolin series, provided the particle sizes are reasonably uniform, as kaolinite normally has a smaller slope ratio than halloysite. It has been pointed out, however, that very finely divided kaolinite might give a slope ratio in the halloysite region, although there is little possibility of the reverse happening. The present series of minerals gives values (Table 3) which are of little use in sepa-

rating kaolinite and the disordered form of kaolinite since *K2*, *K6* and *Pugu D* (curve 379), all of a similar particle-size, have slope ratios which are virtually identical. It would appear, therefore, that particle-size is relatively more important in determining the asymmetry of the peak than order or disorder in the lattice—except insofar as order or disorder may encourage or discourage the growth of larger particles. In halloysite, with a very high slope ratio, for example, the sheets are considered to be randomly stacked and here the “crystal” determining the asymmetry of the peak may indeed be the single sheet. From Table 3,

TABLE 4. CHEMICAL ANALYSES OF SEPARATED PUGU KAOLINS

	1	2
SiO <sub>2</sub>	44.59	48.14
TiO <sub>2</sub>	1.38	0.76
Al <sub>2</sub> O <sub>3</sub>	38.12	35.74
Fe <sub>2</sub> O <sub>3</sub>	1.43	1.45
FeO	nil	nil
MgO	0.06	0.11
CaO	0.10	0.19
Na <sub>2</sub> O	0.12	0.04
K <sub>2</sub> O	0.08	0.14
H <sub>2</sub> O+105° C.	13.91	13.14
H <sub>2</sub> O-105° C.	0.71	0.48
SO <sub>3</sub>	0.09	0.05
P <sub>2</sub> O <sub>5</sub>	trace	nil
Cl	nil	nil
	100.59	100.14
Fe <sub>2</sub> O <sub>3</sub> in residue after extraction	1.15	1.05
Total exchange capacity	7.4 m.e./100 g.	4.6 m.e./100 g.
Exchangeable H <sup>+</sup> ions	2.46 m.e./100 g.	0.0 m.e./100 g.

1. *Pugu D* Kaolin.

2. *Pugu K* Kaolin.

Analyst: A. H. Clarke, M.Sc. (Geochemical Laboratories Ltd.)

however, it would appear that all samples from Adits *C* and *K* are somewhat coarse in particle-size, while *lithomarge* is of the same particle size order as the Cornish kaolinite.

In conclusion, therefore, the thermal analysis results agree with the *x*-ray ones in placing *Pugu K* in the kaolinite group and *Pugu D* in the disordered lattice group and, in addition, demonstrate that, of all the samples from this deposit studied, this seems to be the only one with a disordered lattice. These samples have also provided additional data regarding the effect of particle size upon thermograms of kaolin minerals.

## CHEMICAL DATA

Samples of *Pugu K* and *Pugu D* of less than  $5\mu$  *e.s.d.* were separated from the crude rock by the usual sedimentation procedure using ammonia as the dispersing agent for *Pugu K* and ammonia together with some tetrasodium pyrophosphate for *Pugu D*, and were subjected to chemical analysis (Table 4). The free iron oxides in these samples were determined by the sodium hydrosulphite method (Galabutskaya and Govorova, 1934; Mackenzie and Mitchell), and the cation-exchange capacity was determined by the micro-method of Mackenzie (1951). The exchangeable  $H^+$  was determined from direct titration measurements on the original sandstone.

In calculating the mineralogical analysis, titania was assumed to be anatase, since this mineral was detected by *x*-ray diffraction; the iron oxide made soluble by sodium hydrosulphite was assumed to be goethite, as shown by differential thermal analysis of yellow-stained material; sulfur dioxide may reasonably be ascribed to gypsum. As mica is very rare, and feldspar occurs in the sand,  $K^+$  is probably present in feldspar. The small amount of  $Na^+$  added as pyrophosphate was subtracted from the *Pugu D* analysis, and a correction made for the  $NH_4^+$  (0.04%) replacing  $H^+$ . The sum of the analyzed constituents exceeds 100% by 0.55% (after correcting for ammonia) in *Pugu D* kaolin; it was considered probable that an error of this size had arisen in the determination of one rather than of a number of elements. A preliminary calculation threw suspicion on alumina, so the excess was subtracted from the percentage of alumina in the analysis. No correction was made with *Pugu K*.

With these assumptions, the chemical analysis of *Pugu D* kaolin was

TABLE 5. MINERALOGICAL ANALYSES OF PUGU KAOLINS

	<i>Pugu D</i> Kaolin %	<i>Pugu K</i> Kaolin %
Kaolin mineral	96.93	92.40
Quartz	—	5.13
Anatase	1.38	0.83
Orthoclase	0.47	0.76
Moisture (70–105° C.)	0.71	0.48
Goethite	0.31	0.44
Gypsum	0.19	0.10
	99.99	100.14
Mineral impurities	2.35	7.26
Mineral impurities without quartz	2.35	2.13



TABLE 6. IONIC CONSTITUTION OF THE CLAY MINERALS,  
ON BASIS OF O=5.000

	Theoretical for Kaolinite	<i>Pugu D</i> Kaolin	<i>Pugu K</i> Kaolin
Mg/2	—	0.002	0.002
Ca/2	—	0.004	0.003
Na	—	0.008	0.004
H	—	0.007	—
		0.021	0.009
Al	2.0	1.958	1.957
Fe <sup>+3</sup>	—	0.039	0.037
Mg	—	0.003	0.005
		2.000	1.999
Al	—	0.018	0.009
Si	2.0	1.982	1.991
		2.000	2.000
O	5.0	5.000	5.000
OH	4.0	4.122	4.092
		9.122	9.092

employed to calculate the mineralogical composition and the ionic constitution of the clay minerals (Tables 5 and 6). The cation-exchange capacity calculated from the ionic constitution is 7.53 *m.e./100 g.* of dry clay, which is in excellent agreement with the measured value of 7.4 *m.e./100 g.*, a value which, since it was determined by the micro-method, is probably 1–2% low. With no assumptions as to the excess alumina, however, the calculated cation-exchange capacity is 10.9 *m.e./100 g.*, which is not in accord with the measured value, and which suggests that the above assumptions are valid. If it is assumed that there is the same correspondence between measured and calculated values for *Pugu K*, it is possible to calculate the amount of free silica left by imperfect dispersion. In this connection, it may be remarked that the samples submitted to thermal and *x*-ray analysis, although from the same rock, had been better dispersed before separating.

Also from the ionic constitution of the clay minerals (Table 6), it would appear that there is greater Al<sup>+3</sup> for Si<sup>+4</sup> substitution in *Pugu D* than in *Pugu K* kaolin, that *Pugu D* contains more exchangeable Na<sup>+</sup> (reflecting perhaps its more decidedly marine origin) and also H<sup>+</sup> ions, and that *Pugu D* appears to have 0.122 more hydroxyls than is required by the formula Al<sub>2</sub>(Si<sub>2</sub>O<sub>5</sub>)(OH)<sub>4</sub> and *Pugu K* 0.092 hydroxyls in excess.

#### ELECTRON-OPTICAL STUDIES

Electron micrographs of *Pugu K* and *D* kaolins, of the paper-coating kaolin *Hydratex No. 2* from Georgia, U.S.A., and of Cornish *Low Viscosity S.P.S.* china clay were obtained, and the *D*-clay crystals were also

TABLE 7. MICROMERITIC MEASUREMENTS OF SOME KAOLIN MINERALS

	<i>Pugu D</i> Kaolin	<i>Pugu K</i> Kaolin	Georgia <i>Hydratex</i> No. 2 Kaolin	Cornwall <i>Low Viscosity</i> <i>China Clay</i>
Length, average, m $\mu$	196	512	247	518
Breadth, average, m $\mu$ (at 90° to length)	152	348	180	360
Thickness, average, m $\mu$	22.3	ca. 67.2	—	—
Length/breadth	1.29	1.47	1.37	1.44
Elongation	1.12	1.27	1.19	1.24
Rugosity	1.9	ca. 1.8	1.7	ca. 2.1
Specific surface, m <sup>2</sup> /g.	44.9	15.3	—	—

palladium-shadowed for thickness measurement. The results of micrometric measurements on these electron-micrographs have already been published (Meldau and Robertson, 1952) and, together with the values for more recently determined parameters and with measurements for other kaolins, are collected in Table 7. It should be noted the "elongation" is expressed as the *ratio of the crystal length to the crystal breadth divided by 1.155* (the ratio for a true hexagon). No values for the specific surface of *Hydratex No. 2* or of *Cornish Low Viscosity S.P.S. china clay* are available, but for comparative purposes may be cited the values found by Vassiliou and White (1948) for *Cornish Supreme china clay* using a moisture capillarity/temperature technique, and those of Carman and Malherbe (1950) for an unnamed Cornish china clay using nitrogen adsorption and air permeability—namely, 23 m<sup>2</sup>/g. and 11.4 m<sup>2</sup>/g., respectively.

Electron-optical studies show that about 98% of *Pugu D* crystals are euhedral. In Georgia kaolin the smallest crystals (<0.5  $\mu$ ) are euhedral, but large crystals approaching 1  $\mu$  in diameter almost all have one re-entrant angle. In *Cornish Low Viscosity S.P.S. china clay*, euhedral crystals are rare, and large crystals often have more than one re-entrant angle or even a jagged, broken edge. These observations amplify those of Clark (1950), who showed that crystals of plastic china clay from Cornwall are thinner and more irregular than in the low viscosity types; and that Zettlitz kaolin is so irregular in outline that crystal angles are rarely seen. Meldau and Robertson (1952) gave some evidence that the viscosity of deflocculated kaolin slips was closely related to rugosity, but not to exchange capacity.

#### *Gold sol adsorption*

Electron micrographs showed that unprotected gold sol particles are particularly strongly attracted to the corners and edges of *Pugu D* clay,

whilst relatively fewer are attracted to the *Georgia* kaolin crystals, many remaining near the crystals without being influenced by them. *Low Viscosity S.P.S.* china clay is more weakly attracting still, except at jagged broken crystal edges where the gold particles form a thickly-studded fringe. Gold particles are also attracted preferentially to re-entrant angles.

These observations confirm that *Pugu D* kaolin is very well crystallized, the electrostatic charge being mainly concentrated at the 6 corners. In less perfect crystals the charge is distributed among many points along a longer perimeter and is therefore weaker, while broken crystals have many points of high charge because of unsatisfied valence bonds and consequently attract many gold particles.

### *Impurities*

In view of observations on the occurrence of titania as anatase in fireclays and in sedimentary kaolin (Brindley and Robinson, 1947*b*; Nagelschmidt *et al.*, 1949) the electron-micrographs were scanned for this mineral. Opaque isometric crystals showing hexagonal, and occasionally square and triangular outlines were considered to be anatase (Fig. 1); and this was confirmed by *x*-ray examination in the case of *Pugu D*. It was estimated by counting that anatase crystals are about twice as common in the *Georgia* kaolin as in the *Pugu* kaolins.

Large clouds of 1  $\mu$  diameter and extreme thinness, seen in both *D* and *K* clays are believed to be a hydrated iron compound: a coral-like fragment was unidentified, but an opaque sphere may possibly be hematite. Otherwise the *Pugu* and *Georgia* clays appear to be practically monomineralic, whereas the *Cornish* clay shows considerable numbers of wavy mica crystals.

## GENERAL DISCUSSION AND CONCLUSIONS

Both *x*-ray diffraction and differential thermal analysis show that *Pugu D* kaolin is the disordered type of kaolin mineral found in many fireclays, and that *Pugu K* kaolin is a well-crystallized kaolinite in which the structural layers are much more regularly superposed, but possibly not so regularly as in the best specimens of kaolinite. Although *Pugu D* shows a high degree of structural irregularity, it is morphologically very perfect; indeed, the crystals are more nearly hexagonal than in any other clay known to us. On the other hand, *Pugu K* is more perfect structurally but less perfect in crystal shape. The two types are regarded as having been formed under different conditions; it seems reasonable to suppose that fine-grained euhedral crystals of *b*-axis disordered

kaolin will not develop into larger grained crystals of well-ordered kaolinite having re-entrant angles. Indeed, if one accepts the dislocation hypothesis of crystal growth as recently discussed by Dekeyser and Amelinckx (1951, 1952) it is quite inconceivable that a disordered system could, with further growth, develop into an ordered one.

The *Pugu D* clay provided an excellent  $x$ -ray diagram of a  $b$ -axis disordered mineral of a high degree of purity which confirmed and amplified earlier data and the conclusions drawn therefrom. On the other hand, the differential thermal results amply demonstrated the difficulties which may arise in attempting to distinguish members of a series when particle-size effects are superimposed. Although it has proved possible, even when the samples were relatively impure, to distinguish kaolinite from  $b$ -axis disordered kaolin, further study of the thermal effects in the kaolin series arising from order and disorder in the lattice and from particle-size differences would appear very desirable.

As the separated clays were remarkably free from impurities, evaluation of their chemical composition was possible. From this, and other evidence, it seems probable that the cation-exchange capacities of these clays arise from substitutions in both the tetrahedral and octahedral positions in the lattice rather than from valences at the edges of the crystals—*e.g.*, observed and calculated exchange capacities for *Pugu D* agree almost exactly if certain reasonable assumptions are made, and although the area of "edge" faces per gram for *Pugu D* is 4.0 times as great as for *Pugu K* the exchange capacity is only 1.61 times as great.

The chemical calculations show that, while the degree of substitution in the silica layer is about twice as great in the  $b$ -axis disordered as in the ordered mineral, there is relatively little difference in substitution in the octahedral layer, *viz.*, about 1.93% of these positions are occupied by  $\text{Fe}^{+3}$  and 0.15% by  $\text{Mg}^{+2}$  in *Pugu D* compared with about 1.85% and 0.28% respectively, in *Pugu K*. The main difference, chemically, between the clays, therefore, appears to lie in the amount of tetrahedral substitution.

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