An X-ray examination of an exceptionally well crystallized kaolinite.

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Summary. Specimens of kaolinite have been found in inclusions in the ferruginous deposits on the Yorkshire Coast, just north of Scalby. The excellent quality of the X-ray powder pattern suggests that this kaolinite is better crystalline than kaolinites from other localities. Although the lattice constants of the Scalby material are considered to be identical with those previously published for kaolinite, minor differences in the intensities of the X-ray reflections do occur and may be due to a less distorted structural layer in the Scalby kaolinite.

THE material described in this paper was collected from inclusions in the ferruginous deposits on the Yorkshire coast, just north of Scalby. X-ray examination by the powder method revealed that the mineral was kaolinite, whilst observation under the microscope indicated that the crystallite size was ~ 30–$50\,\mu$. The unusual sharpness of the kaolinite reflections in the powder pattern and the relatively large particle size suggest that the kaolinite from this locality is probably better crystalline than any previously reported.

Each kaolinite inclusion was flanked by a layer (a few millimetres thick) of dark brown material, the whole being embedded in a reddish-brown matrix. X-ray powder photographs taken with Co-$K\alpha$ radiation showed that the main constituent of the dark brown material was goethite and that of the reddish-brown chalybite; in each material rather coarse quartz was found in small quantities. The powder pattern of the kaolinite contained a few reflections in excess of those reported by Brindley and Robinson (1946) for kaolinites from other localities. These reflections could not be attributed to any impurity and, in fact, could be explained by supposing that reflections previously recorded as single in the kaolinite pattern were actually resolved in the powder pattern of the Scalby material. This might be expected because the Scalby kaolinite is not so finely divided as other kaolinites, and because the

X-ray technique employed by the authors (see next section) is capable of higher resolution than the one used by Brindley and Robinson.

Two subsidiary tests also suggested that the sample of Scalby material examined was indeed free from impurity. In the first, the sample was treated with hot dilute HCl for several hours without any change occurring in the X-ray pattern. In the second, the sample was heated for three to four hours at 575° C. with a complete disappearance of the accepted kaolinite reflections and also of the additional lines found in the powder pattern of the untreated specimen. Although it can be concluded with some certainty that the sample investigated was pure kaolinite, it must be mentioned that samples from some inclusions were found to contain minor amounts of free quartz.

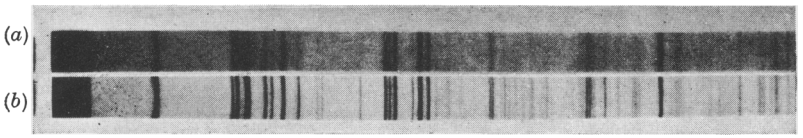

FIG. 1. X-ray powder photographs of (*a*) Cornish kaolinite, (*b*) Scalby kaolinite. Cu-$K\alpha$ radiation, camera diameter 22·9 cm.

The X-ray data. X-ray powder photographs were taken with crystal-monochromatized Cu-$K\alpha$ radiation with a Guinier-type transmission camera of 22·9 cm. effective diameter. The camera was calibrated by mixing aluminium powder with the specimen being X-rayed. Fig. 1*b* shows a typical photograph of the Scalby material, whilst for comparison, fig. 1*a* shows a photograph of a good quality kaolinite from Cornwall. It will be evident that the X-ray reflections from the Scalby kaolinite are sharper than their counterparts from the Cornish specimen. Further, it will be noticed that reflections which appear broad in fig. 1*a* are usually resolved into two reflections in fig. 1*b*. In the case of the Cornish kaolinite, the focusing properties of the X-ray camera did not resolve any reflections that had not previously been resolved by the technique employed by Brindley and Robinson. It thus appears that the greater resolution in the pattern of the Scalby material has arisen mainly because of the larger crystallite size.

The measured spacings and visually estimated intensities of the reflections from the Scalby kaolinite are compared with the corresponding data of Brindley and Robinson in columns B and A, respectively, of table I. Apart from the resolution of certain reflections in the X-ray pattern of the Scalby material, there is little difference between the two

TABLE I. Comparison of powder data of Scalby kaolinite (col. B) with Brindley and Robinson's data (col. A) and with the calculated spacings for a cell having a 5·155, b 8·959, c 7·407 Å., α 91·68°, β 104·87°, γ 89·94° (col. C).

A			B			C
I	$d_{obs.}$	hkl	I	$d_{obs.}$	hkl	$d_{calc.}$
vvs	7·16Å.	001	*vvs*	7·17Å.	001	7·16Å.
m^-	4·46	020	m^-	4·478	020	4·478
m	4·36	$1\bar{1}0$	*s*	4·366	$1\bar{1}0$	4·366
			Tr.	—	110	4·341
m	4·18	$11\bar{1}$	m^+	4·186	$11\bar{1}$	4·180
w^+	4·13	$1\bar{1}\bar{1}$	m^-	4·139	$1\bar{1}\bar{1}$	4·134
wm	3·845	$02\bar{1}$	*m*	3·847	$02\bar{1}$	3·848
w	3·742	021	w^+	3·745	021	3·745
vvs	3·573	002	*vs*	3·579	002	3·578
			Tr.	—	$1\bar{1}1$	3·421
wm	3·372	111	m^-	3·376	111	3·373
w	3·144	$11\bar{2}$	*w*	3·155	$11\bar{2}$	3·155
w	3·097	$1\bar{1}2$	*w*	3·107	$1\bar{1}2$	3·106
w	2·754	022	*w*	2·754	022	2·755
ms	2·558	$1\bar{3}0$ $20\bar{1}$ 130	m^-	2·566	$1\bar{3}0$ $20\bar{1}$	2·568 2·566
			w^+	2·553	130	2·553
wm	2·526	$13\bar{1}$ $1\bar{1}2$	m^-	2·535	$13\bar{1}$	2·534
			vw	2·519	$1\bar{1}2$	2·520
s	2·491	$13\bar{1}$ 200 112	$m^+(r)$	2·495	$13\bar{1}$ 200 112	2·504 2·491 2·486
ms	2·379	003	w^+	2·385	003	2·385
vs	2·336	$20\bar{2}$ $13\bar{1}$ $11\bar{3}$	*m*	2·347	$20\bar{2}$	2·346
			m	2·338	$13\bar{1}$ $11\bar{3}$	2·339
s	2·289	$1\bar{1}3$ 131	*Tr*	—	$1\bar{1}3$	2·307
			m	2·293	131	2·293

Tr, trace reflection.
r, just resolved by eye into two reflections.

sets of data. All the reflections in column B can be accounted for by a unit cell with parameters a 5·155 Å., b 8·959 Å., c 7·407 Å., α $91{\cdot}6_8°$, β $104{\cdot}8_7°$, and γ $89{\cdot}9_4°$; the calculated spacings for this cell are given in column C of table I. The cell agrees, within the limits of experimental error, with that calculated by Newnham (1956) by a least-squares method using Brindley and Robinson's data. Apparently Newnham (private communication) quoted his axial parameters in Å. when in fact they were in kX-units, and this error was carried forward to a later publication by Brindley and Nakahira (1958). The actual parameters of Newnham's cell are a 5·149 Å., b 8·950 Å., c 7·386 Å., α 91·6°, β 104·8°, and γ 89·9°.

Although the lattice of the Scalby kaolinite is indistinguishable from that of other kaolinites, at least as far as the accuracy of the present data is concerned, differences do occur in the relative intensities of some of the reflections. Figs. 2*a* and 2*b* show microphotometer traces of reflec-

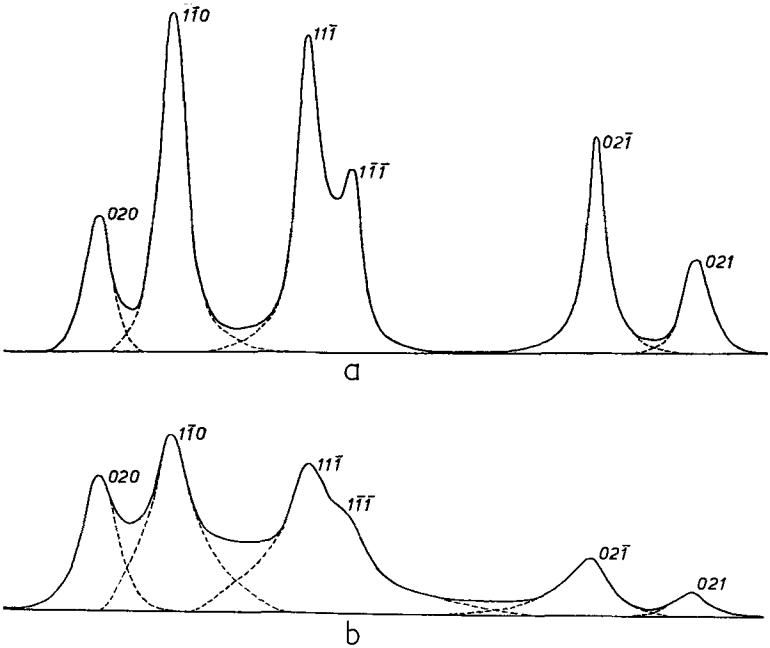

FIG. 2. Microphotometer trace of reflections from (*a*) Scalby kaolinite, (*b*) Cornish kaolinite.

tions, within the range 4·48 Å. to 3·74 Å., from the Scalby and Cornish kaolinites respectively. It is quite noticeable that in the case of the latter, the intensity of the 020 reflection is greater than that of the 02$\bar{1}$, whereas in the Scalby pattern the reverse is true. This is perhaps the most obvious difference, but others do occur. It is not thought that the intensity data have been modified significantly by possible preferred orientation in the particular form of specimen used in the present technique. This is supported by the facts that the relative intensities of the reflections from the Cornish kaolinite agree very well with those obtained for a number of kaolinites by Brindley and Nakahira using a diffractometer method, and that X-ray photographs of the Scalby material taken with a 19-cm. diameter Debye-Scherrer camera showed the same pattern of intensities as was obtained using the Guinier-type camera.

Discussion of the kaolin-type layer in the Scalby mineral. According to the conclusions reached by Brindley and Nakahira, the intensity differences in the X-ray data of the Scalby and Cornish kaolinites could possibly be due to a smaller degree of distortion in the structural layer of the Scalby mineral. Brindley and Nakahira explained the triclinic nature of kaolinite by considering the kaolin layer to have the same degree of distortion, regarding rotations of Si–O tetrahedra and Al–O(OH) octahedra, as was found to occur in dickite by Newnham and Brindley (1956). They also found that a dickite-type layer led to an improvement on earlier calculations in the agreement between the calculated and observed intensities in the kaolinite powder pattern, and that rather better agreement was possible if one considered an even more distorted layer than that found in dickite.

Calculated relative intensities (taken from Brindley and Nakahira's paper) of a series of kaolinite reflections are given in columns A and C of table II; the data in column A are for a structure based on the dickite-

TABLE II. Comparison of calculated and observed intensities for kaolinites from Scalby and Cornwall.

	A.	B.	C.	D.
hkl.	$I_{calc.}$	$I_{obs.}$	$I_{calc.}$	$I_{obs.}$
020	100	10	100	10
$1\bar{1}0$	273	27	215	22
110	9		2	
$11\bar{1}$	292	36	205	25
$1\bar{1}\bar{1}$	133		96	
$02\bar{1}$	219	16	104	6
021	67	7	49	3

Columns A and C give calculated values of $F^2\phi(\theta)$ for structures based on a dickite-type layer and on a more distorted layer respectively, ϕ (θ) being the polarization and Lorentz factor.

Columns B and D give the observed intensities for the Scalby and Cornish kaolinites, respectively.

Data in each column are scaled so that the intensity of the 020 reflection is taken as standard.

type layer and those in column C for a structure with a more distorted layer. It will be seen that the observed intensities for the Scalby kaolinite (column B, table II) are, in general, in better agreement with the calculated values in column A, whilst those for the Cornish kaolinite (column D, table II) are more consistent with the data in column C. This suggests, though very tentatively in view of the small number of reflections considered, that the kaolin layer in the Scalby material is less

distorted than that in the Cornish kaolinite, or apparently in kaolinites that have been investigated previously.

Because of the inadequate resolving power of the microphotometer used in this work, it did not seem worthwhile to attempt to measure quantitatively the intensities of the other reflections considered by Brindley and Nakahira. Nevertheless these are explained qualitatively by the above conclusions.

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