THE KAOLINS:
MINERALOGY, DEPOSITS, USES

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SYNOPSIS

The mineralogical section of the paper highlights the difficulties encountered in classifying the kaolinite group of minerals, and gives details of the various characterization methods used.
The section concerned with deposits deals with the origin of the ores, without discussing genetic characteristics.
The section dealing with economics specifies the different grades required by users, and also gives information on the use of kaolins, especially in the paper industry.

INTRODUCTION

The geologist who begins a study of the economics of a large deposit of clay must be able to rapidly identify both the nature and the structure of the different kinds of clay minerals found. Because of the importance of a mineralogical diagnosis, the first section of this paper consists of a review of characterization standards of modern methods of investigating the kaolinite-group ores.

In the second section theories on the origin of pure kaolin deposits are reviewed, and some of the petrographic problems are also mentioned.

The third section considers kaolin as a polyvalent raw material and specifications and grades are given for known uses.

PART ONE
MINERALOGY OF THE KAOLINITE GROUP

For a little over a century, kaolin minerals have been subjected to a progressive and intensive study for fundamental and applied purposes, using various methods of investigation: X-ray diffracto-

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metry (on random powder and oriented aggregates), thermal analyses (differential D.T.A., thermoponderal TPA, thermogravimetric TGA), infra-red spectroscopy, and electron microscopy. Analytical methods have become more accurate, and the resulting data have been integrated and oriented towards a better classification system for the kaolinites.

With the development and improvement in investigational methods and techniques, and owing to the discovery of new kaolin species, many of the earlier classification systems are now either somewhat out of date, incomplete, confused, or even contradictory.

As a consequence, various authors have used different descriptive terms (kaolinite, anauxite, pholerite, halloysite . . .), and have applied different meanings to their terms.

Many species or varieties exist inside the kaolinite group. The best known are: kaolinites, halloysite, metahalloysite, and fire-clay. Dickite and nacrite also fall into the kaolin mineral group, although these well-crystallized minerals are rarely identified in clay minerals and are generated in specific hydrothermal conditions, such as during the kaolinization of granites.

Thus, apart from the two latter minerals, routine or detailed investigations depend upon structural characterization (X-ray, IR) and morphological examination (electron microscopy).

Previously it was accepted that a platy hexagonal morphology was necessary for a well-crystallized kaolinite, and that a tubular morphology was found only in badly crystallized or disordered kaolinite minerals (halloysite).

Since about 1960 it has been established that such a simple rule could no longer be systematically applied, as the kaolin minerals may exhibit specific

characteristics that belong to extreme varieties (e.g. well-crystallized kaolinite with rolled morphology; badly crystallized kaolinite with nearly hexagonal shaped particles). As a consequence, the traditional couple 'crystallinite-morphology' should not be used in the usual way, e.g. 'platy hexagonal well-crystallized kaolinite' or 'tubular badly crystallized halloysite'. Rigid classification becomes questionable. But no general agreement has so far been reached among clay mineralogists regarding the identification and nomenclature of kaolin minerals. A suggestion by Brown[19] for a group name, kandites, has not been generally accepted.

In some species (halloysite, for example), the degree of hydration must be considered, as there exist fully hydrated forms, as well as partially or completely dehydrated ones.

In other cases, confusion can arise because a monomineralic phase may exhibit aspects of several species. Crystallinity, ordering-disordering, and morphology may vary within the same monomineralic phase as a result of the occurrence of a more-or-less wide range in the granulometry of particles. In other instances, a natural mixture of minerals may occur, in which both platy hexagonal and tubular morphologies appear, and all typical features are removed in a X-ray pattern or an electronmicrograph when an analysis of a clay phase shows it to be polymineralic.

STRUCTURE — MORPHOLOGY — CLASSIFICATION

This section is not intended to be an exhaustive discussion, as the subject is widely covered in the literature, and the most important papers are listed in the bibliography.

The structure of kaolinite has been outlined by Pauling[81], detailed by Gruner[39], and later revised by Brindley and his colleagues[10-15]. Kaolinite was structurally restudied by Newham[70], Brindley and Nakahira[14], Zvyagin[106], Drits and Kashaev[29], Bailey[1] and several other authors whose names are not reported in this brief historical background.

In the ideal form, kaolinite consists of a platy-hexagonal-particle assemblage with a structure that

FIGURE 1 Sheet and layer structure of kaolinite

is rather simple in comparison to other clay minerals.

A silica tetrahedral sheet and an alumina octahedral sheet are combined into a single unit (Figure 1), with the tips of the silica tetrahedrons and one of the layers of the octahedral sheet forming a common layer. The atomic distribution and links are illustrated in Figure 2. The structural layer shows a high degree of regularity in stacking, which may be shown in a powder diffractogram by a number of clearly defined reflexions. The sheet dimensions of tetrahedral and octahedral units are sufficiently alike in the a-b dimensions so that a combination of attached octahedral-tetrahedral layers is formed, with vertical stacking distributed along the c-axis, giving a basal spacing of about 7Å (elementary thickness of the layer). Varieties of the kaolin species are based on variations of this basal spacing (which can lie at peaks between 7 and 10Å for the fully hydrated form) and in the isomorphous replacement of Fe-Al into the layers.

As already pointed out, dickite and nacrite have been placed in the kaolin-group minerals because their structure is somewhat similar to kaolinite. Dickite and nacrite differ from kaolinite in the stacking of layers and in Al in the octahedral position. In dickite, the unit cell is composed of two unit layers instead of one. In nacrite, the unit cell has six unit layers; each of which has the kaolinite arrangement. For the two discrete minerals, dickite and nacrite, the basal spacing is also at a peak of approximately 7Å and their particles are morphologically of a well-crystallized material. Under the polarizing microscope, optical characteristics are frequently obtained because these minerals have well-developed, large-sized crystals, which is a characteristic rarely found in kaolinite.

Occasionally, kaolinite-type clay minerals have been found with a considerably higher molecular ratio of silica to alumina than is found in kaolinite. This mineral has been described as 'anauxite' but may be considered as a mixture of kaolinite and silica (kaolinite with double silica tetrahedral sheets randomly interlayered into the kaolinite unit cell).

In its most characteristic form, halloysite is traditionally considered to consist of rounded lath-like tubular or rolled particles. The structural layers scatter X-rays in a wide and incoherent manner from layer to layer (Brindley and Robinson[17]). Combinations of this incoherent character and the curvature of layers causes diffraction bands instead of well-defined reflexions.

Brindley and de Souza Santos[18] have published an 'evolutionary set' of characters (X-ray diffraction-morphology), which show four steps or stages in kaolinite minerals (Figure 3) from a well-formed platy kaolinite to a highly disordered tubular halloysite. The use of the electron microscope and X-ray diffractometry does provide some basic data, but, since imperfections have been discovered in the morphology-crystallization relationship, the preliminary investigation proposed by Brindley et al[18] must be used with caution, and should not
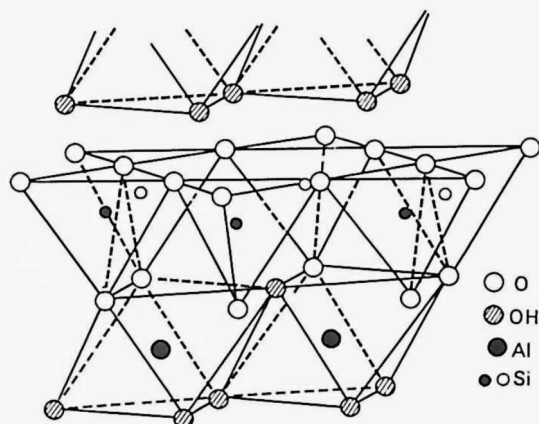
$$2\ [Al_2(OH)_4 . Si_2O_5]$$

Tricline $a_0 = 5{,}14$ Å, $b_0 = 8{,}93$ Å, $c_0 = 7{,}37$ Å

$\alpha = 91°\ 48'$, $\beta = 104°\ 30'$, $\delta = 90°$

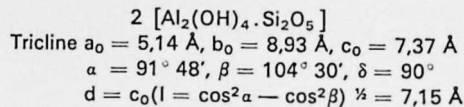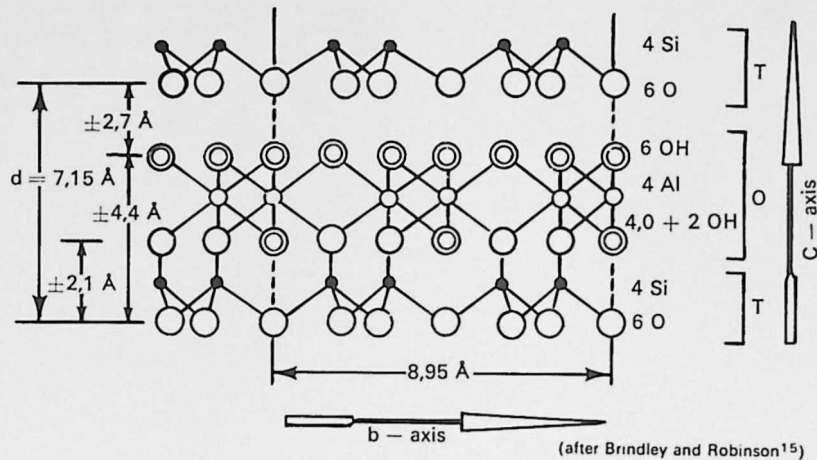$d = c_0(I = \cos^2\alpha - \cos^2\beta)\ ^{1/2} = 7{,}15$ Å

FIGURE 2   Electron micrograph of kaolinite

be considered as an absolute criterion. A mineral that exhibits a tubular morphology and a well-crystallized X-ray pattern cannot be placed in such a simple but rigid classification scheme.

When disordered stacking of layers occurs with respect to the b-axis, or to both the b- and a-axis, it is believed that a wide range of degrees exist in the stacking order-disorder and might also exist between fully-ordered, one-dimensional disordered, and fully disordered types.

It is logical to have in the kaolinite group a complete morphological series from hexagonal plates to elongated plates to laths with hexagonal tendencies to curved laths to tubes to more amorphous curls and rounded grains of allophane[4].

An excellent review and critique of the problems involved in the nomenclature and classification of the kaolinite group has been published by Douillet and Nicolas[28], who propose an interesting classification scheme. It has the great merit of allowing for

bined in the same monomineralic phase.

Douillet and Nicolas[28] proposed that the three sets of characteristics be combined and integrated into a proper classification scheme:

- *hydration form:* all minerals with a peak of 7Å basal spacing should be designated as kaolinite; those with a higher basal spacing (up to 10Å) will be hydrokaolinite
- *morphology:* a set of descriptive terms may be used independantly of the real structural nature of the mineral investigated: platy, rolled, curved, tubular, lathed, rounded
- *degree and regularity of crystallinity:* minerals could be classified as either well, intermediate, bad, or poorly ordered; the final choice would depend on X-ray diffraction data or any other method of analysis (IR, thermal).

Finally, this simple nomenclature would allow for the integration of all types of kaolinite into two groups:

Group	d(001)	Crystallinity	Degree of hydration	Morphology	Mineralogy
1	7Å	Excellent	Excellent	Hexagonal	Dickite, nacrite
11	7-10Å	Variable	Variable	Variable	7Å kaolinite, 10Å hydrokaolinite

the classification of all structural-morphological 'kaolinites'. The authors consider that the difficulties in most schemes are related to two factors: the wide range of descriptive terms and the structural-morphological classification attempted by several authors, although kaolinite is a unique mineral with varying morphologies, crystallinity, and hydration forms. It thus exhibits peculiar features according to the local conditions; alternatively it may display a set of distinct characteristics com-

This scheme has value in that it does not lead to a rigid classification, and all known types of kaolinite fit into the classification; there is also a place for any discovered in the future: platy hexagonal, badly crystallized kaolinite; fibrous, more-or-less well-crystallized kaolinite; tubular, badly crystallyzed hydrokaolinite; tubular, well-crystallized kaolinite. Other symbols may be added when necessary, such as IT or pM (triclinic, monoclinic, and pseudomonoclinic).
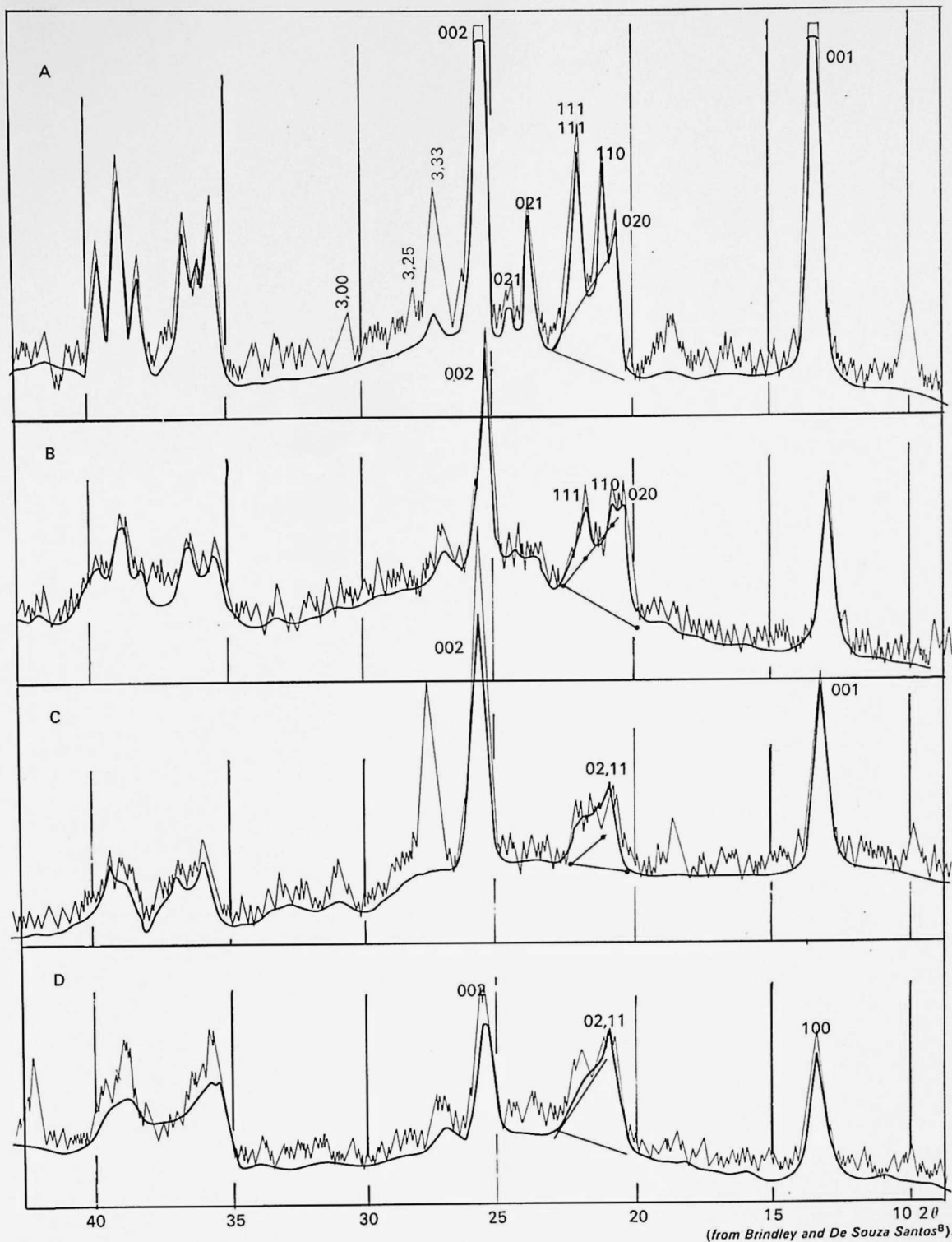
FIGURE 3 X-ray powder diffraction patterns of monomineralic kaolin minerals. (A) Well-ordered, well-formed platy material, enhanced basal reflexions (kaolinite). (B) Platy material with b-axis disordered sequence, enhanced basal reflexions (disordered kaolinite). (C) Layer sequence partially disordered with respect to both a- and b-axes, little enhancement of basal reflexions, rolled forms (halloysite). (D) Highly disordered layer sequence, no enhancement of basal reflexions, tubular form (halloysite).

EXAMINATION AND DIAGNOSTIC METHODS

Diffraction

X-ray patterns are used in the identification of kaolinite minerals, from either oriented aggregates or from a random powder preparation.

In clay mineralogy, one of the methods of analysis consists of an X-ray pattern of an oriented aggregate of the minus-two-microns fraction. This method enhances preferentially all 002 reflexions and either decreases or suppresses all (hk) reflexions. In the case of the kaolinite minerals, diffractogram patterns show a sequence of (001) reflexions: the (001) peak at 7Å for kaolinite and at 10Å for hydrokaolinite. A heating treatment at 80 to 110°C irreversibly changes the basal spacing of hydrokaolinite from 10Å to 7Å.

Kaolinite peaks at 7Å (001) and 3,58Å (002) are stable after glycol solvation and acid attack, but are suppressed from the X-ray diffractogram after heat treatment at 500°C (complete dehydroxylation). In monomineralic phases, the existence of (001) reflexions establishes the presence of kaolinite. In the case of a polymineralic composition, where kaolinite appears as one of the components, identification problems arise from the coexistence of certain clay minerals, particularly chlorites. This latter mineral is effectively characterized by a (001) sequence of reflexions at peaks of 14, 7, 4,7, and 3,53Å.

The 7 and 3,53Å peaks, in particular, interfere with those of kaolinite. Many methods have been proposed for distinguishing between them, but there is no absolute criterion.

It is possible to use an acid attack (boiling HCl), which destroys chlorite and leaves the kaolinite intact. Where an equal content of kaolinite and chlorite exists, and when these minerals are well-crystallized, a doublet occurs at a peak of 3,53 to 3,58Å. The 14Å and 4,7Å peaks are, of course sufficient in themselves to indicate the presence of chlorite (Mg type, whereas in Fe-type 14 and 7Å peaks are of very low intensity), but this would not disprove the presence of kaolinite.

The poorly crystallized forms of those minerals must also be considered; these forms are revealed in diffractogram patterns by asymmetric reflexions and a lowering in intensities of the (hkl) reflexions.

Again, in the case of a mixture of poorly crystallized forms, such asymmetries at a peak of 3,5Å (toward the high-angle side) may mask the doublet found at a peak of 3,5Å.

It has also been proposed that some supplementary tests with hydrazine will displace the 7Å-peak kaolinite reflexion to a peak of 10,4Å, leaving intact the 7Å-chlorite reflexion in its correct position. But it also appears that hydrazine could react differentially leaving some very fine kaolinite particles ($< 1\mu$) at the 7Å-peak instead of displacing the entire 7Å initial reflexion at 10,4Å, as occurs in large-sized particles.

Range et al[84] have proposed a classification scheme for kaolinites based on degrees of lattice disorder, using the effect of reaction with hydrazine, water, ethylene glycol, and glycerol on the basal spacing, i.e. a displacement or otherwise of the 7 to 10,4Å peak. The behaviour of kaolinite after successive replacement and leaching will give one or other of the above products, and the authors show how a distinction can be made and how a five-fold classification scheme can be derived.

The proposed procedure and the results are schematically shown in Table 1.

Kaolinite-hydrokaolinite minerals may also be distinguished by the sequence of (hkl) reflexions from a random powder diffractogram. There is normally no difficulty in carrying out this investigation in the monomineralic phase.

In the polymineralic phase, this technique is somewhat questionable as many reflexions from other components usually interfere in some parts of the X-ray pattern.

Random powder diffractograms are preferred for the identification of the composition of the mineral (nacrite, dickite, kaolinite, etc.), for polymorphism, for crystallinity, and for order-disorder purposes, as specific (hk) reflexions are then considered.

Table 2 shows the X-ray data for kaolinite, dickite, and nacrite. Among the reflexions listed, some are peculiar to each of the three minerals.

Nacrite is readily distinguished, but for kaolinite and dickite, some reflexions are characterized by either their occurrence or their intensities (Table 3).

Table 4 shows the (hkl) reflexions that allow a rather rapid differentiation between kaolinite, fire-clay, and hydrokaolinite (halloysite). From kaolinite to hydrokaolinite, there is a marked diminution of the (hk) reflexions that appear in the X-ray pattern.

For the three minerals, the basal spacing (001) is at a peak at about 7Å (7,15Å for kaolinite and fire-clay; 7,2 to 7,5Å for hydrokaolinite), and the (002) reflexion is centred about a peak of 3,57Å.

More important differences occur in the presence or absence of some specific reflexions. It appears that kaolinite minerals have the most complete X-ray pattern. The fire-clay type shows the complete set of reflexions but a decrease in intensities, and this diminution in intensity reaches a maximum in the case of hydrokaolinite.

Basal reflexions at peaks of 7 and 3,5Å are generally sharp and intense for kaolinite; they decrease in intensity for fire-clay, and become less intense, enlarged, and asymmetric for hydrokaolinite.

Kaolinite has a characteristic reflexions sequence between 4,35 and 3,75Å, which becomes resolved into a diffraction band at about 4,1Å in fire-clay; it is suppressed in the case of hydrokaolinite.

Kaolinite is characterized by three well-defined triplets at (4,35; 4,17; 4,12Å); (2,55; 2,52; 2,48Å), and (2,37; 2,33; 2,38Å). The most crystallized type may even show the 4,12Å reflexion duplicated as a doublet.

The triplets of kaolinite are more or less replaced by doublets in fire-clay minerals and by a single enlarged reflexion from some hydrokaolinites.

TABLE 1

REACTION TYPES OF KAOLINITE GROUP ACCORDING TO THEIR BEHAVIOUR TOWARDS HYDRAZINE HYDRATE, WATER, ETHYLENE GLYCOL AND GLYCOL LEACHINGS

(*after Range, Range and Weiss,*[85])

PROCEDURE	OBSERVED BASAL SPACING (in Å)				
Drying at 110°C			7,2 — 7,3		
Hydrazine hydrate (65°C, 7 days)	10,4	10,4	9,5 — 9,6	7,2 — 7,3	10,0 — 10,2
Leaching of hydrazine with water	7,2	10,4	10,2 sharp + 8 broad	—	9,85
Replacement of water by ethylene glycol	7,2	10,85			10,85
Replacement of water by glycerol	7,2	7,2	7,2		11,1
TYPES OF KAOLINITE	I No or relatively little disorder	II Medium to strong dis.	III	IV Fire-Clay	Halloysite-Hydrokaolinite

TABLE 2

DIFFRACTION DATA FOR WELL-CRYSTALIZED KAOLINITE, DICKITE AND NACRITE

Kaolinite (G. W. Brindley and K. Robinson, 1946)			Dickite (R. E. Newham and G. W. Brindley, 1956)			Nacrite (Von Knorring et al, 1952)		
hkl	d . Å	I	hkl	d . Å	I	hkl	d . Å	I
001	7,15	10	002	7,16	10	002	7,17	10
020	4,45	4	020	4,46	0,5			
			110	4,44	4			
1$\bar{1}$0	4,35	6	11$\bar{1}$	4,37	4	11$\bar{1}$	4,41	7
$\bar{1}$1$\bar{1}$	4,17	6	021	4,27	3			
1$\bar{1}\bar{1}$	4,12	3	111	4,13	7	112 ; 200	4,12	3
02$\bar{1}$	3,84	4	11$\bar{2}$	3,95	2			
021	3,734	2	022	3,795	6			
002	3,566	10	004	3,587	10	004	3,577	10
111	3,365	4	11$\bar{3}$	3,427	3			
11$\bar{2}$	3,138	2	023	3,272	2			
1$\bar{1}$2	3,091	2	113	3,101	2	202	3,04 — 3,08	1,3
			11$\bar{4}$	2,938	2	113	2,917	0,5
022	2,748	2	024	2,794	·2			
20$\bar{1}$; 130 ; 1$\bar{3}$0	2,553	8	13$\bar{1}$; 200	2,560	4	020 ; 31$\bar{2}$; 206	2,578	3
13$\bar{1}$; 1$\bar{1}$2	2,521	4	131 ; 20$\bar{2}$	2,51	5			
13$\bar{1}$; 112 ; 200	2,486	9				31$\bar{3}$; 021 ; 31$\bar{1}$	2,502	3
003	2,374	7	006	2,40	1	022 ; 31$\bar{4}$	2,438	7
20$\bar{2}$; 1$\bar{3}$1 ; 11$\bar{3}$	2,331	10	13$\bar{3}$; 202	2,322	9	11$\bar{6}$	2,33	2
131	2,284	9						
1$\bar{3}\bar{2}$; $\bar{2}\bar{2}$0	2,182	3	133 ; 20$\bar{4}$	2,212	2	311	2,237	0,5
02$\bar{3}$; 041	2,127	2						
20$\bar{3}$; 1$\bar{3}$2	1,985	7	13$\bar{5}$; 204	1,975	5	222 ; 20$\bar{8}$	1,982	0,5
132 ; 221	1,935	4	223	1,937	1	22$\bar{5}$; 317 ; 116	1,921	2
13$\bar{3}$	1,892	2	044	1,898	2			
$\bar{1}$3$\bar{3}$; 202	1,835	4						
11$\bar{4}$	1,809	2	13$\bar{6}$; 224	1,805	1	22$\bar{6}$	1,818	2
004	1,778	5	008	1,785	1	008	1,792	3
1$\bar{5}$0 ; 24$\bar{1}$; 3$\bar{1}\bar{1}$	1,682	2	24$\bar{1}$	1,686	1			
2$\bar{4}$0 ; 15$\bar{1}$; 20$\bar{4}$	1,659	8	13$\bar{7}$; 206	1,652	5	22$\bar{7}$	1,668	3
133 ; 24$\bar{2}$; 310	1,616	6	15$\bar{3}$	1,613	1	133	1,617	0,6
15$\bar{2}$; 24$\bar{1}$; 13$\bar{4}$	1,581	4	314	1,586	1			
203 ; 241	1,539	5	137 ; 20$\bar{8}$	1,555	4			
060 ; 33$\bar{1}$	1,486	9	060 ; 33$\bar{1}$	1,489	5	51$\bar{8}$	1,488	5

TABLE 3

CHARACTERISTIC REFLEXIONS FOR KAOLINITE AND DICKITE
(*after Douillet and Nicolas*[28])

	Kaolinite		Dickite	
Peculiar reflections	4,18	5	4,27	3
	3,84	4	3,95	2 — 3
	3,74	2		
	3,37	4	3,42	3
	3,14	3	3,26	2
	2,75	3	2,79	2
Common reflections but with different intensities	4,13	3	4,13	6 — 7
	1,94	4 — 7	1,94	1 — 2
	1,78	4 — 5	1,78	1 — 4
	1,62	6 — 8	1,62	1
Supplementary reflections	2,29	8	2,93	1 — 2
	1,84	4		
	Refl.	Intens.	Refl.	Intens.

TABLE 4

DIFFRACTION DATA FOR KAOLINITE, FIRE-CLAY AND HYDROKAOLINITE
(*after Douillet and Nicolas*[28])

Kaolinite			Fire-clay		Hydrokaolinite Halloysite		
hkl	d . Å	I	d . Å	I	001 ou h ; k	d . Å	I
001	7,15	10	7,15	10	001	7,2 — 7,5	8
020	4,45	4	4,45	8	02,11	4,42	10
1$\bar{1}$0	4,35	6	(4,36	2)			
11$\bar{1}$	4,17	6					
1$\bar{1}\bar{1}$	4,12	3	(4,14	2)			
02$\bar{1}$	3,837	4					
021	3,734	2					
002	3,566	10	3,57	10	002	3,578	8
111	3,365	4					
$\bar{1}$1$\bar{2}$	3,138	2					
$\bar{1}$1$\bar{2}$	3,091	2					
022	2,748	2	Doublet				
20$\bar{1}$; 130 ; 1$\bar{3}$0	2,553	8	2,55	7	13,20	2,579	7
1$\bar{3}\bar{1}$; 1$\bar{1}$2	2,52	4					
1$\bar{3}\bar{1}$; 112 ; 200	2,486	9	2 50	7			
003	2,374	7	2,375	7	003	2,403	2
2$\bar{0}\bar{2}$; 1$\bar{3}$1 ; 11$\bar{3}$	2,331	10	2,325	8			
131	2,284	9	Doublet				
1$\bar{3}\bar{2}$; 2$\bar{2}$0	2,182	3			04,22	2,218	1
02$\bar{3}$; 041	2,127	2					
20$\bar{3}$; 1$\bar{3}$2	1,985	7	1,977	4			
132 ; 221	1,935	4					
13$\bar{3}$	1,892	2					
1$\bar{3}\bar{3}$; 202	1,835	4					
11$\bar{4}$	1,809	2					
004	1,778	5	1,785	3	004	1,80	1
1$\bar{5}$0 ; 24$\bar{1}$; 3$\bar{1}\bar{1}$	1,682	2					
2$\bar{4}$0 ; 1$\bar{5}$1 ; 20$\bar{4}$	1,659	8	1,657	2	31 ; 15 ; 24	1,678	5
133 ; 24$\bar{2}$; 310	1,616	6					
15$\bar{2}$; 2$\bar{4}$1 ; 13$\bar{4}$	1,581	4					
203 ; 241	1,539	5	1,541	1			
060 ; 33$\bar{1}$	1,486	9	1,486	8	06 ; 33	1,481	8
06$\bar{1}$; 11$\bar{5}$	1,464	2	1,457	2			
061	1,449	4					
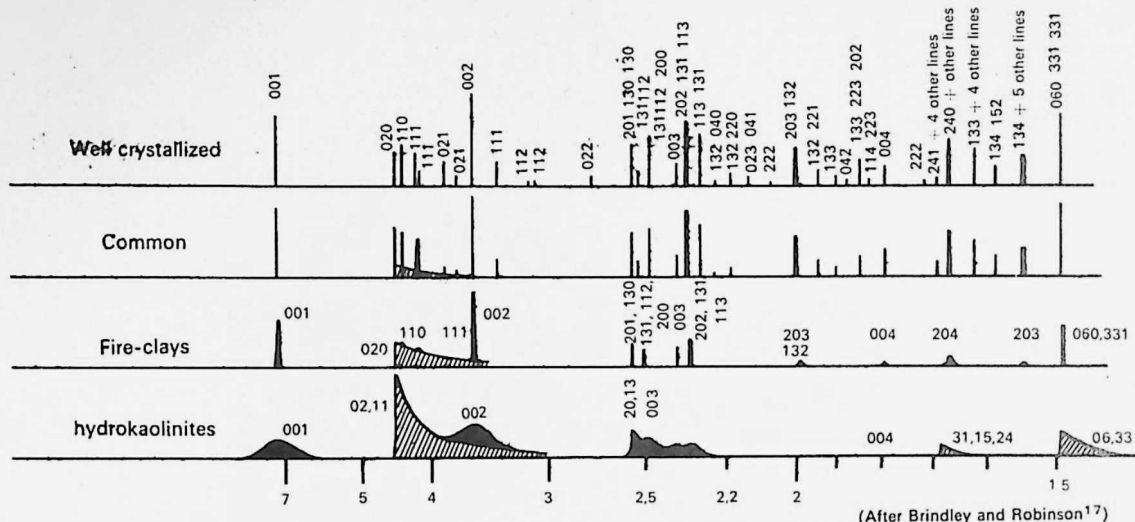
FIGURE 4   Schematic Debye-Scherrer X-ray monogram

(After Brindley and Robinson[17])

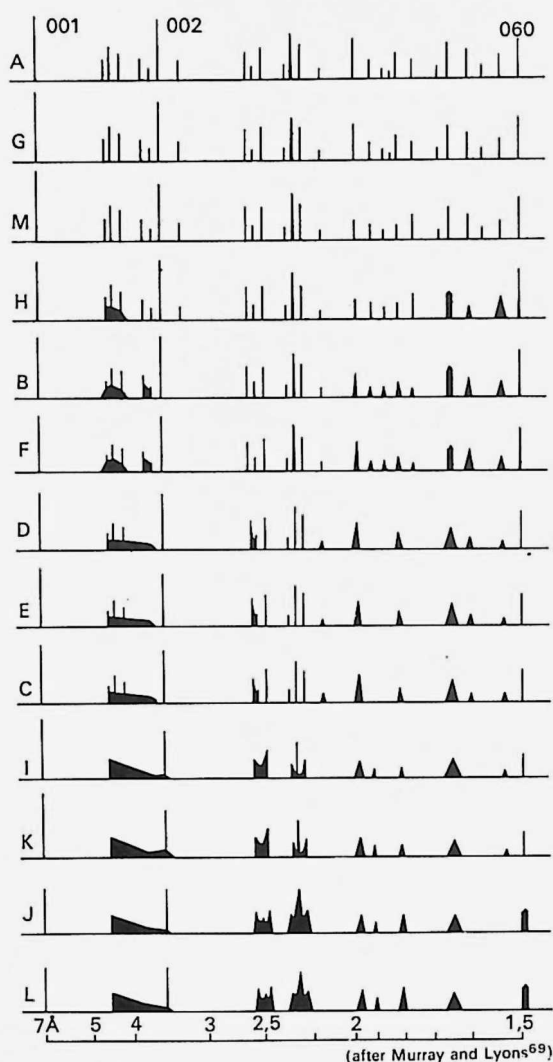(after Murray and Lyons[69])

FIGURE 5   Crystallinity degrees in kaolinite

Brindley and Robinson[17] have published a schematic chart for distinguishing between well-crystallized kaolinite, 'common' kaolinite, fire-clays, and hydrokaolinites (Figure 4).

A simple routine identification comprises at least a set of three combined criteria: electronmicrographs, oriented aggregate, and random powder diffractograms (see Table 5).

Crystallinity indexes or order-disorder criteria have been attractive analytical tools, and useful techniques, because of their importance in industry. Murray and Lyons[68] have proposed a set of 13 diffractograms in which a progressive decrease in crystallinity is shown (Figure 5). The classification is based on the changes in facies and intensities of the (hk1) reflexions, particularly within enlargements of reflexions, replacement of triplets by doublets, or by a single reflexion.

From such a gradation, it would logically be accepted that it would be easy to identify the degree of crystallinity. In fact, if it is accepted that the decrease in crystallinity is based on the common and parallel substitution of the three characteristic triplets by doublets and then by single reflexions. Experience with the Belgian kaolins indicates that this method is invalid. For example, a mono-mineralic kaolinite phase shows the first well-defined triplet, but the other two are transformed into single but enlarged reflexions. These differences cannot be integrated into Murray and Lyon's classification scheme.

Hinckley[42] and Range and Weiss[84] also proposed a crystallinity index measurement, but their methods were based on the ratio values of the intensities of the first triplet reflexions (see Figure 6).

Electronic microscopy

The literature gives a large number of electron microscopic pictures, mainly because the structure of the kaolinite-hydrokaolinite minerals are easily recognized (platy, rolled, tubular particles, etc.). Beutelspacher and Van der Marel[8] published an atlas that is recommended as a laboratory tool.

TABLE 5

ROUTINE IDENTIFICATION FOR KAOLINITE-HYDROKAOLINITE MINERALS

| | Kaolinite s.s.- | Disordered Kaolinite | (Métahalloysite) | Hydrokaolinite | |
				(hydrated Hall.)	(dehydrated Hall.)
Electronic Microscope	Platy hexagonal particles	Hexagonal but smaller particles		Tubes, rolled	
X-Ray powder	7,15Å and 3,56Å sharp, symmetric intense	7,1Å and 3,56Å sharp but less intense	7,15-7, 5Å enlarged	10Å intense symmetric or not (collapses irreversibly to 7 upon heating)	Diffraction band or single enlarged reflexion centred about 7,3Å often extending with its foot to Å
	4,43-4,35-4, 15Å distinct, well defined and always less intense than 7,15 and 3,56Å	4,43-4,12Å resolved often into a continuous band whereas some reflexions may still be apparent depending on the order-disorder	Large very asymmetric diffraction band between 4,4Å and 4Å; equal to greater intensity compared to 7Å	Large very asymmetric diffraction band between 4,4Å and 4Å often more intense than 10A	Large asymmetric diffraction band from 4,4 to 4Å more intense than the one of hydrated form
	Characteristic triplets at: (2,56-2,52-2,49Å) and (2,38-2,34-2,29Å)	Doublets at (2,56-2,5Å) and (2,37-2,33Å)	Continuous enlarged reflexion from 2,5 to 2,3Å x where 2,56-2,5Å and 2,32Å reflexions may be apparent	Band between 2,55-2,5Å often equal in intensity as for 3,3Å but half intense of the 4,4-4Å diffraction band Band at 2,36Å generally less intense than 2,55-2,5Å one	Band 2,55-2,5Å with 2,5Å reflexion often clearly defined Weak 2,40Å The 2,36Å band is more intense than the one of hydrated form. 3,6Å less intense relatively to the 4,4-4Å band
Oriented aggregates	7,1Å and 3,56Å enhanced in intensity 4,43-4,35-4,1Å almost withdrawn	7,1 and 3,56Å more intense Band 4,43-4,12Å lowered in intensity	Intensity of 4,4-4Å band equal or more important than for 7,2Å	Same as for powder X-ray pattern. When heated to 80-110°C, 10Å and 3,3Å reflexions are irreversibly replaced by 7A and 3,5Å reflexions. 3,6Å and 2,4Å reflexions are new.	

Scanning-electronic apparatus was recently introduced as a routine investigation technique and will certainly provide new and more accurate data.

In the present paper, no attempt has been made to cover the full range of kaolinite morphologies. A set of 12 representative electronmicrographs are shown as illustrative of the range. (See Figure 16).

Thermal investigations

DTA (Figure 7) and TPA (Figure 8) techniques are the normal methods used as investigational tools for kaolinite materials.

Generally DTA curves show endothermic and exothermic peaks as typical features. Those trends may be described as follows:

■ the first endothermic peak is more or less intense. It occurs between 100 and 150°C when hygroscopic water is removed.

■ the second intense endothermic peak occurs between 550 and 700°C, depending upon the nature of the mineral. This thermal event is related to the removal of the OH links into the octahedral sheet.

■ a third endothermic peak may occur between 840 and 920°C.

■ a characteristic exothermic peak, generally intense, occurs between 950 and 1020°C. It is related to the recrystallization of α-alumina and mullite.

Chemical compositions

The chemical characterization of the kaolinites is based on the ratio of SiO_2 to Al_2O_3, and on the hydration state.

Table 6 indicates some of the limits of composition.

INFRARED SPECTRA

Several aspects may be considered in discussing the infrared spectra of minerals. The problem of the interpretation of the spectra (namely the
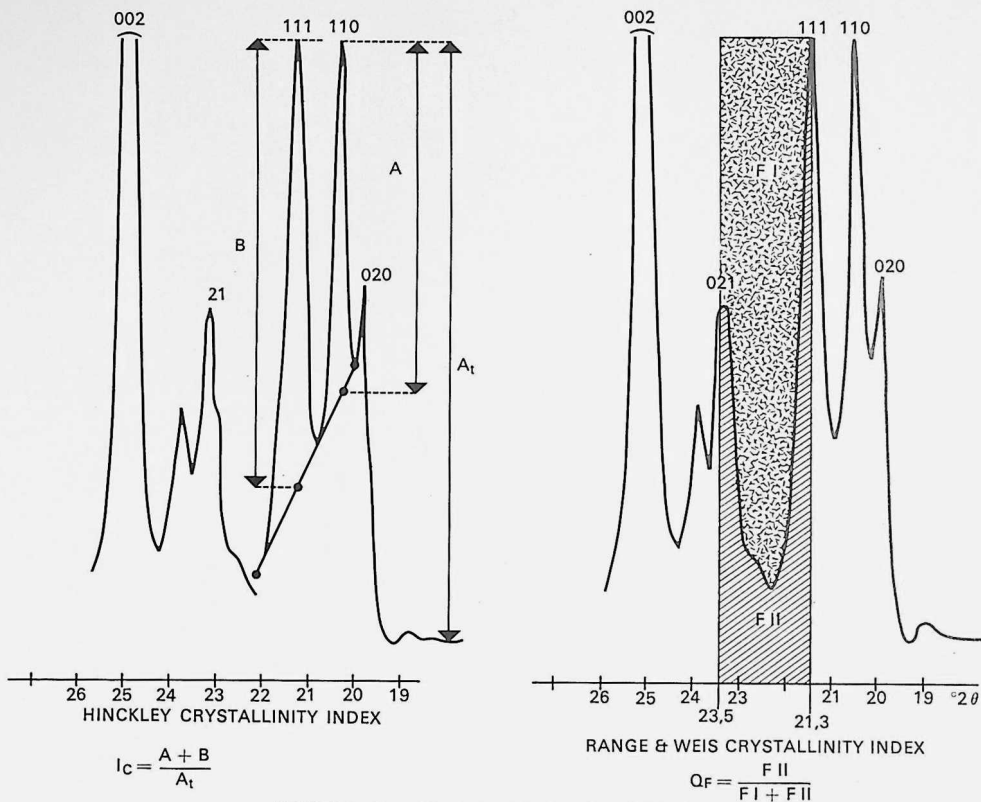
$$I_C = \frac{A + B}{A_t}$$

HINCKLEY CRYSTALLINITY INDEX

RANGE & WEIS CRYSTALLINITY INDEX

$$Q_F = \frac{F\,II}{F\,I + F\,II}$$

FIGURE 6   Crystallinity of kaolinite minerals (Oret).

TABLE 6

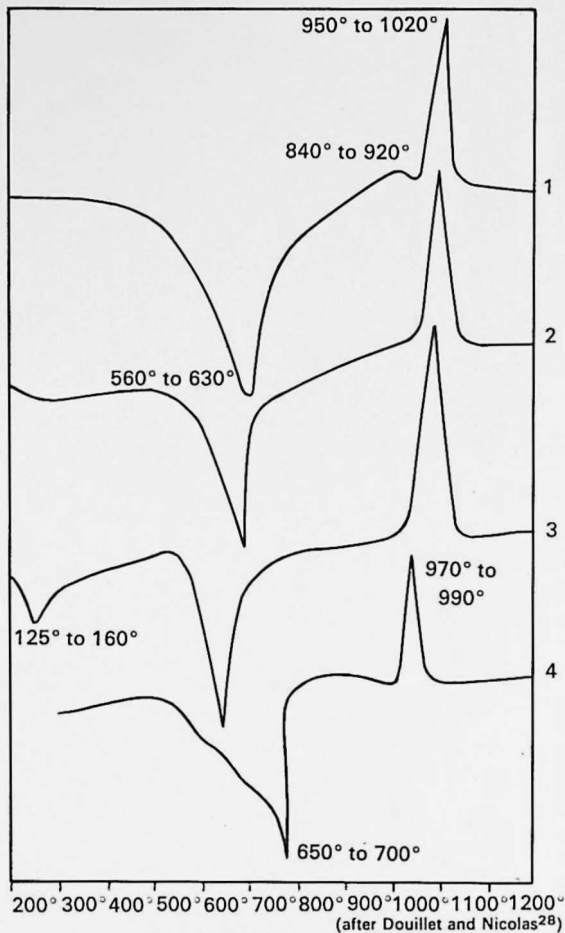### CHEMICAL COMPOSITION VARIATIONS IN KAOLIN MINERALS

(after Douillet and Nicolas[28])

Oxides %	Kaolinites Nacrites	Hydrokaolinites	Dickites
SiO_2	44 to 48	37 to 44	40 to 46
Al_2O_3	36 to 40	30 to 36	35 to 40
Fe_2O_3	< 1,5	< 1,5	< 1,5
FeO	< 0,3	< 0,3	< 0,3
MgO	< 0,5	< 0,5	< 0,5
CaO	< 0,5	< 0,5	< 0,5
Na_2O	< 0,5	< 0,5	< 0,5
K_2O	< 2,5	< 2,5	< 2,5
TiO_2	< 2,5	< 2,5	< 2,5
H_2O-	11 to 15	20 to 28	11 to 20

assignment of the bands to the various motions of the crystal lattice) is a specifically spectroscopic problem and is too complicated to be discussed here.

Two different regions may be considered in the infrared spectrum of layer silicates: the high-frequency region (4000 to 3000 cm^{-1}), where the bands are related to the stretching vibrations of the O-H bonds; the investigation of this region provides data about the structural role of the -O-H groups, which information is not obtained from X-ray diffractometry; and the medium- and low-frequency region (below 1200 cm^{-1}), where the origin of the bands is more complex and, in fact, non-evident: these bands may be due to bending motions of the -O-H bonds, or to various motions of the silicon-oxygen, or cation-oxygen bonds, or finally to more complex vibrations originating from the combination of the preceding ones. These problems have already been discussed[32,33,78,79,90] and are beyond the scope of this paper.

Two main points will be briefly discussed here, namely

o the differences between the spectra of different minerals that are otherwise structurally related; and

o the variations in the spectrum of a given mineral as a function of the perfection of its crystal structure.

950° to 1020°

840° to 920°

560° to 630°

125° to 160°

970° to 990°

650° to 700°

200° 300° 400° 500° 600° 700° 800° 900° 1000° 1100° 1200°

(after Douillet and Nicolas[28])

1. Well crystallized kaolinite
2. Poorly crystallized kaolinite
3. Hydrokaolinite

FIGURE 7 Typical D.T.A. curves

In connexion with these points, some very general remarks should be made: the absorption frequencies observed in the infrared spectrum are primarily determined by the masses of the atoms and by the bonding forces between them; but these frequencies are also influenced by other factors such as the symmetry of the crystal.

Thus, two compounds with the same chemical formula, but different structures, will have some absorption *regions* in common, but will differ in the details of the spectrum.

These differences may be quite large if the structures are drastically different; and conversely, polymorphic phases characterized by minor structural differences will give very similar infrared spectra.

This is well illustrated by a comparison of the spectra of kaolinite, nacrite, and dickite: these minerals are characterized by the same chemical formula and the same type of layer structure, but show a difference in the stacking of the layers. The infrared spectra of kaolinite and nacrite are very similar[33]. The situation is nearly the same for kaolinite and dickite (Figure 9): apart from some

differences in the shape of the bands, the spectra are again very similar. This great similarity comes from the fact that the atomic arrangement and the bonding forces *within a layer* are essentially the same. The most specific differences appear in the high-frequency region (3800 to 3000 cm^{-1}), which is related to the O-H stretching vibrations.

On the other hand, any kind of disorder is necessarily associated with an irregular distribution of the bonding forces, and thus will emphasize a more-or-less important broadening of the absorption bands. These disorder effects may be related to small imperfections of the crystal structure, to isomorphic replacement of some cations, to a disordered distribution of some cations (the Si-Al case being the most widely represented in mineralogy), or finally to a nearly complete position disordering leading to the so-called amorphous state. Some of these effects are illustrated by the infrared spectra of halloysite and montmorillonite.

Apart from the occurrence of interlayer water (which is, in any case, easily removed without fundamental alteration of the structure), halloysite is chemically and structurally very similar to the series kaolinite-nacrite-dickite, the main difference being a disordered stacking of the layers. The infrared spectrum (Figure 10) is accordingly similar to that of kaolinite, but with some broadening of the bands. This broadening is particularly evident in the 110 to 1000 cm^{-1} region. Likewise, there are some characteristic modifications in the number and relative intensities of the O-H bands observed in the 3800 to 3000 cm^{-1} region.
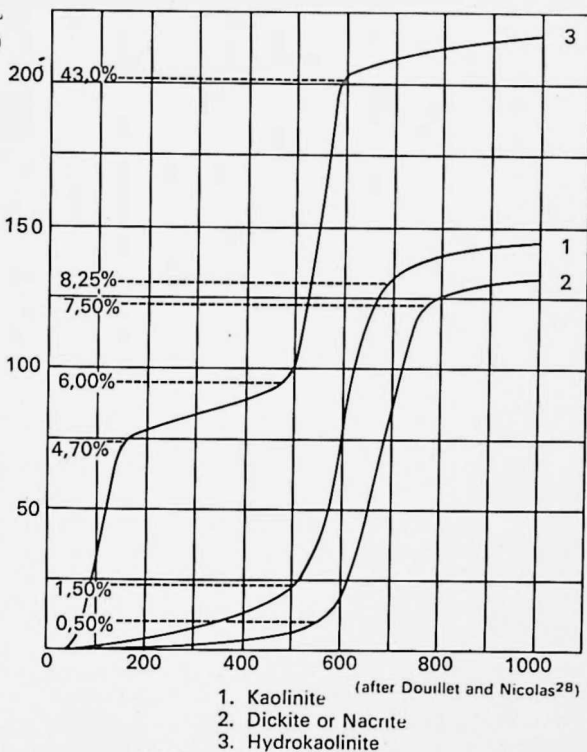
1. Kaolinite
2. Dickite or Nacrite
3. Hydrokaolinite

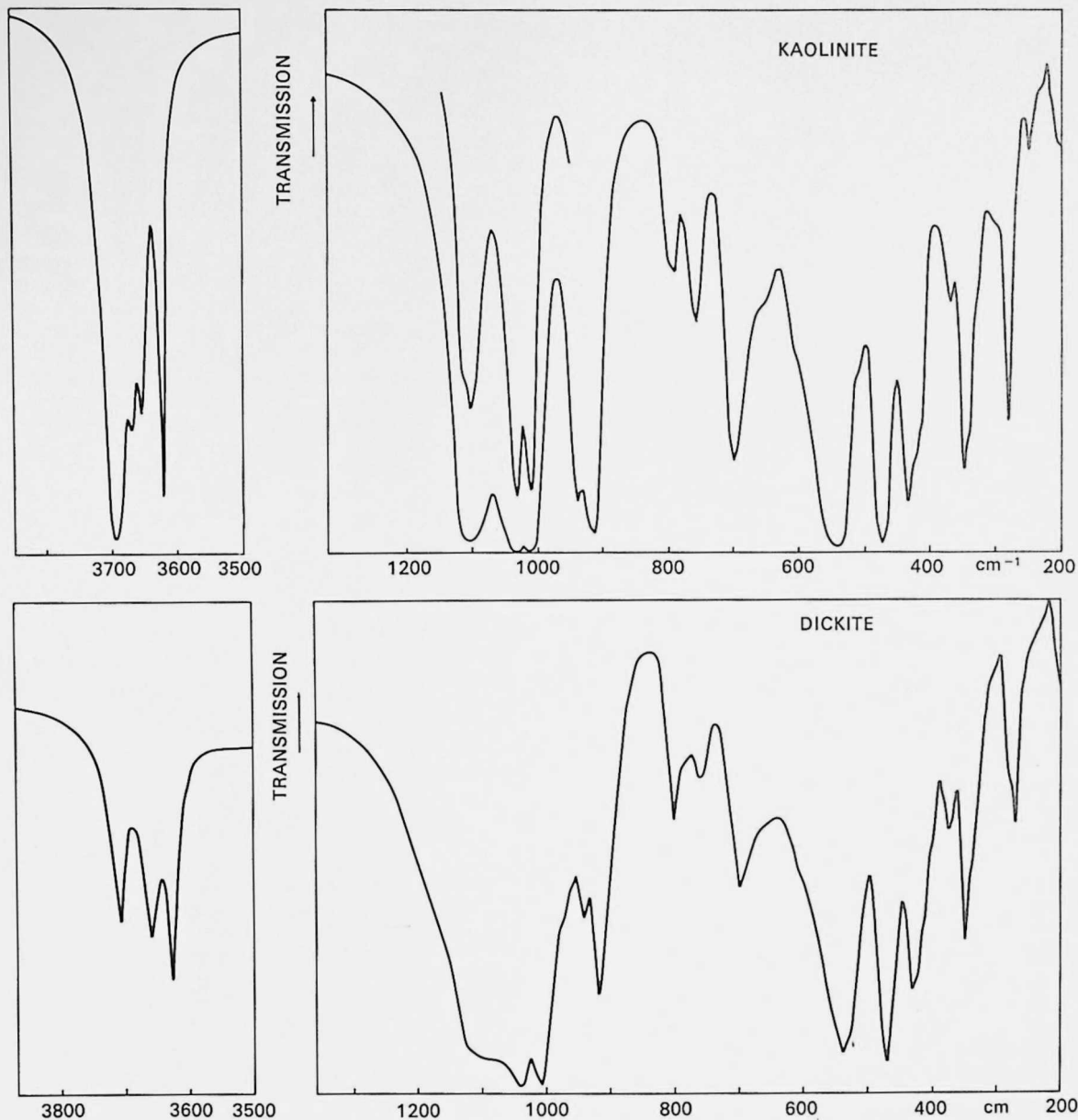(after Douillet and Nicolas[28])

FIGURE 8 Thermoponderal curves

FIGURE 9   Compared IR spectra of Kaolinite and Dickite.

A further example of disorder is offered by montmorillonite, but here, the disorder has several simultaneous origins, namely the isomorphic replacement of some cations, the disordered cationic distribution over available crystallographic sites, the variable water content, and the lack of stacking order. As a consequence of this fairly high degree of disorder, only a few broad bands appear in the infrared spectrum (Figure 11).

Finally, the relationship between the infrared spectrum and the crystal imperfections of kaolinite is considered. This problem has already been investigated for the high-frequency bands originating from the O-H groups: the 2 weak bands near 3670 and 3650 cm^{-1} are fairly sensitive to crystal imperfection[62], and a very careful investigation of the intensity ratio of the 3695 and 3625 cm^{-1} bands may give information on the type of kaolinite, its degree of crystallinity and the shape of the particles[81]. It should be pointed out, however, that this information can be obtained only by working under carefully controlled specific conditions.

More generally, such results on the behaviour of the O-H bands are significant only if the resolving power of the spectrometer is rather good, a condition that is not always fulfilled with routine spectrometers.

In fact, variations in the infrared spectrum as a function of the crystal perfection of kaolinite are not restricted to the high-frequency region, but
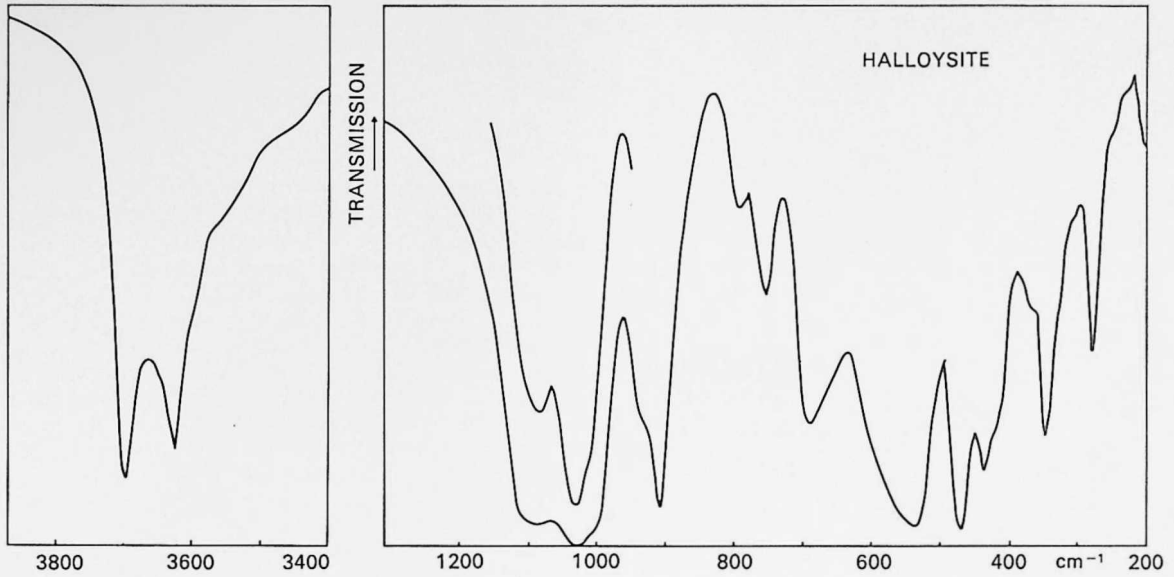
FIGURE 10   Small broadening of the bands as a result of stacking disorder.
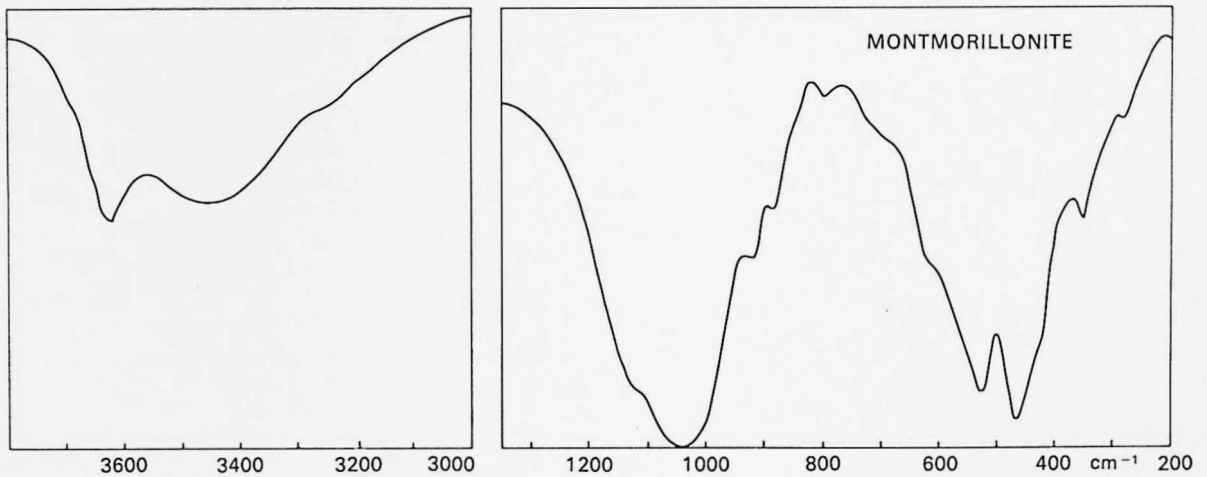

FIGURE 11   General broadening of the bands in the IR spectrum of Montmorillonite.

may also be found in the medium-frequency region: some bands will appear, either as a separate peak, or as a shoulder, depending on the crystal perfection of the sample (Figure 12).

In conclusion, it appears from the published data on the infrared spectrum of layer silicates, and from the examples quoted in this paper, that, in conjunction with other methods, infrared spectroscopy may supply useful information about the nature and crystal perfection of layer silicates.
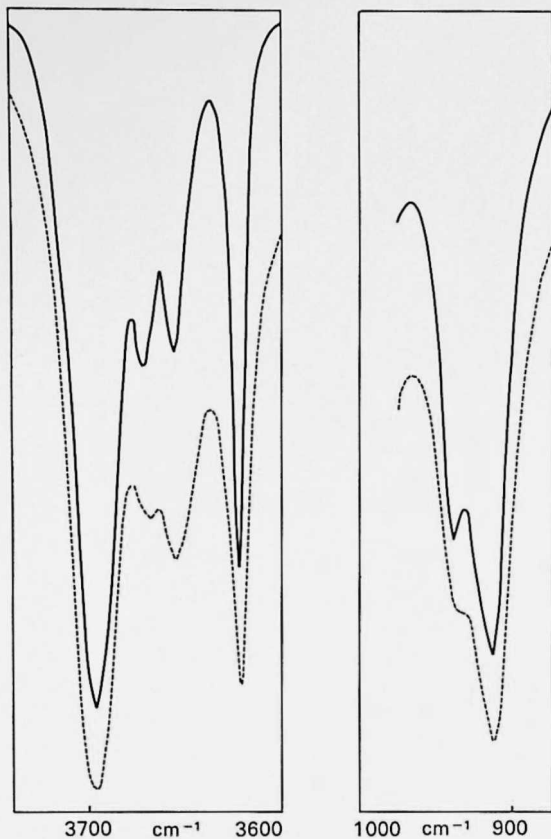
FIGURE 12 *Changes of particular bands in the IR spectrum of Kaolinite as a result of crystal imperfection. Full lines: well crystallized Kaolinite. Dotted lines: poorly crystallized Kaolinite.*

PART TWO
GENESIS — PETROGRAPHY

The kaolinites can be synthesized by the use of an acid hydrothermal method on an amorphous material[2,259]. The laboratory process seems to indicate silicification and the progressive information of an aluminous support[88].

On the other hand, in the natural state, kaolinite does not seem to precipitate from aqueous solutions, but is the result of a secondary mineralization related to the chemical weathering of a feldspathic-parent rock.

The feldspathic rocks undergo a weathering process as follows:

- complete leaching of alkaline and alkaline-earth elements (potassium, lithium, sodium, magnesium, calcium);
- partial mobilization of iron, titanium, and of the silica of silicates;
- passing through an amorphous phase turning to a composition near that of kaolinite, by progressive removal of silica[26];
- authigenic crystallization of aluminosilicates more or less hydrated: kaolinites and hydro-kaolinites.

The importance of the kaolinizing weathering strongly depends on ecological parameters such as pH (acid) and Eh (reducing) and on the influence of the environment (leaching of the silica)[65,76,105].

Fluids of various sorts are liable to carry out weathering:

- surface waters (meteoric or streaming waters) produce a leaching of parent-rock *per descensum* and a weathering of supergene type;
- juvenile waters (hydrothermal fluids), the final stage of acid magma differentiation, produce a parent-rock leaching *per ascensum* and an hydrothermal weathering that is often associated with metallic mineralization. The composition of juvenile waters remains a mystery and their existence itself is in dispute. The origin, the mode of conveyance, and the deposition of the metals they carry are also debatable[58].

Connate waters, originating on the surface, can, through their composition, temperature, or acidity, while percolating down, affect rocks encountered while percolating. The circulation of this third type of water produces a form of leaching sometimes defined as 'lateral'. At present, some schools of thought tend to attribute hydrothermal occurrences to the action of heated percolating waters.

It is difficult to determine what type(s) of water(s) is (are) responsible for the genesis of such kaolin deposits and reference is made to the discussions that were raised in connexion with the kaolin deposits in (or from) variscan granites in France and Czechoslovakia[53,54,71,72].

The arguments about the various theses are founded on a series of observations and criteria that can be summarized as follows:

- attempts by paleoclimatic research to prove that kaolins were formed during a biostatic age;
- morphological studies concerned with the deposits indicate that the mineralization develops with depth or, on the contrary, that its progressive extinction suggests a kaolinization *per descendum;*
- when analysing mineralogical populations, one notes that the orthoclase albite-lithic micas-tourmaline-topaz-sericite-cassiterite-fluorite-quartz associations show evidence of the importance of deuteric magmatism[57]. On the other hand, goethite-magnetite-ilmenite-rutile associations are peculiar to supergene profiles;
- the morphology of quartz and tourmaline grains that are more or less cracked and corroded, and encrusted with organic material, may suggest that they once belonged to levels close to the surface[53];
- decrepitometric measurements and analyses of fluid inclusions in quartz and fluorite tend to show that the material was subjected to temperatures above normal[72];
- radiometric analyses of hydroxyls are allied to thermal arguments, related to the argillaceous minerals themselves.

Parent-rocks and autochthonous kaolins

Large autochthonous kaolin deposits are often derived from intrusive magmatic bodies such as granites, tonalites, diorites, aplites, and pegmatites (Galicia, Spain; Cornwall, U.K.; Bohemia, C.S.S.R.); and kaolin deposits that are derived from extrusive magmatic rocks: rhyolites, pyroclastics, and tuffs are known in Japan.

The weathering of feldspathic gneiss can result in small and impure kaolinic clay concentrations. Their economic value is minimal (Mysore, India).

Finally, small deposits in sedimentary feldspathic rocks occur in the Ardennes, Belgium[100]: arkoses, feldspar quartzite.

Detrital kaolinites and their evolution

Some of the kaolin deposits that are among the most important in the world have an allochthonous origin (Georgia, South Carolina, U.S.A.; Bavaria, GFR). After having been formed by a leaching action on granite mother-rock, the clay particles reach transportation and sedimentation phases in sandy layers that are more-or-less rich in clay particles. These clay particles could have undergone different transformations during their travels; they can undergo more changes in situ, for example, of a supergene nature.

The case of the United States South-east kaolins is unusual, as they were formed at the expense of some backland granites; sandy sediments associated with primary clay portion laid down upon piedmont extended along the cretaceous shore. These sediments (resistant minerals, clay particles, residual feldspars) then underwent important changes within the micro-channels of a delta. The still-fresh material and the primary clay portion developed into fairly well crystallized kaolinite. Nowadays kaolins occur as irregular shaped lenses in the Tuscaloosa cretaceous sands[2,38].

WORKING AND PROCESSING

Kaolins are worked in an open-quarry system by dry-cutting or hydromonitor; the paper grades require special protection against pollution from humic acid and weathering.

The ores are treated by dry or wet processes or are roasted. Dry treatment (air-floated grade, dry process) is applied to loading kaolins (rubber, paint, paper): the ore is simply crushed and jigged, and then made up into specific mixtures.

The wet treatment (water-washed grade, wet process) concerns the higher grade kaolins meant for coating purposes. The ore is stocked in tanks in which it flocculates (sluffy or slip). Introducing a deflocculating agent (for instance sodium phosphate) changes the mud into blunging. Major polluters (quartz, micas) are removed in a degritting stage. After a granulometric classification by centrifugation, iron is removed in a bleaching stage. Sometimes, the removal of anatase by ultraflotation is necessary.

The kaolin is then filtered and once again floated before final drying. Kaolins principally intended for the pottery industry are roasted. At a temperature of about 1000°C, kaolinite changes to mullite, cristoballite, and/or spinel.

Information regarding plants and kaolins flowsheet and the geographic distribution of exploitable deposits appears in a number of issues of *Industrial minerals* that are devoted to a review of kaolins throughout the world[45-48].

PART THREE
INDUSTRIAL USES OF THE KAOLINS

In 1972, World consumption of kaolin was three million tonnes and a forecast by the U.S. Bureau of Mines[24] indicates that World demand in the year 2000 could reach 6,5 to 10 million tons.

The kaolins are cheap and widely spread over the World, and are used for many different purposes according to their chemical or physical properties.

Kaolin is also a source of alumina. Those kaolins that contain 40 to 45 per cent silica and 30 to 40 per cent alumina with low alkalis content (Table 6) are among the most important raw materials for the pottery, refractory, and glass industries. The chemical composition of the ores is important and purchasers are especially careful to obtain quantitative analyses of alumina, silica, alkalis, iron, magnesium, and titanium, as well as loss on ignition. As an alumina source, kaolin competes against bauxite and sillimanite in their high-temperature forms: mullite and alumina. Kaolin, because of its contribution to the homogeneity and fluidity of silicate melts, is used for fibre glass and dielectric chinaware. High-temperature fire bricks require kaolin as the source of alumina.

Buyers of kaolin usually check for the quantity of alumina and the absence of alkalis, and it is also desirable that they test the hydration degree of the argillaceous minerals. A comparison between the kaolinite dehydration curves on the one hand and the hydrokaolinite curves on the other hand (Figure 9) clearly shows how differently those materials behave in the presence of heat[36,37].

The X-ray diffraction process appears to be suitable (Table 5) for continuous quality control tests to ensure that the specifications of new supplies are to the standard required.

Kaolin : load

Rubber, paint, varnish, or plastic manufacturers are appreciative of the fact that in kaolin they have an inert material, fine grained, opaque, and possessing useful rheological properties. The kaolins are used to supply a low-cost load increase in the volume and weight of manufactured articles. In this field, they face competition from talc, barium sulphate, diatomite, and calcium carbonate (whiting, ground calcium carbonate, or precipitated calcium carbonate).

The user must pay attention to the degree of hydration of clays with regard to the surface

properties, and accordingly the viscosity of 'kaolin milks' is directly related to the position of hydroxyls. The second point of interest is the size and shape of the kaolin particles; these structural features have a fundamental influence on the behaviour of kaolins in suspension.

According to the complexity of the loading process in which kaolin will be used, the buyers insist on either granulometry curves or electron microscope pictures of the material.

Kaolin : pigment

At present it is estimated that 65 per cent of the United States kaolin production and 75 per cent of the European kaolin production are used in paper mills.

Paper is made of a cellulose or textile fibrous wood. Interstices are filled with an initial kaolin deposit (loading kaolin), which is also the support for a second layer consisting of a really opaque film made of high-grade kaolin and used as a pigment. Paper kaolins must conform to the following five technological criteria: whiteness, brightness, granulometry, viscosity, and pH. The five criteria are the subject of routine measurements in specialized laboratories[31]. The whiteness, the brightness, and the gloss partially depend on the pureness of the raw material (absence of iron and titanium).

Secondary kaolins often contain 1,5 to 2,6 per cent of titanium oxides (in the form of ultra-fine anatase associated with goethite) whereas primary kaolins (Cornwall type) are free from these impurities. The occurrence of anatase plus goethite is probably contemporary with secondary kaolinite. It could be an authigenetic crystallization of the iron and titanium removed during the diagenesis[27] of the ilmenite detrital grains.

The roasting of kaolin increases the brightness but also results in the destruction of crystalline structures and definitely affects the valuable rheological properties of crude kaolin[52].

A too-high or irregular viscosity of particle-rich suspensions (65 per cent of solids or more, Figure 13) is one of the most critical problems of
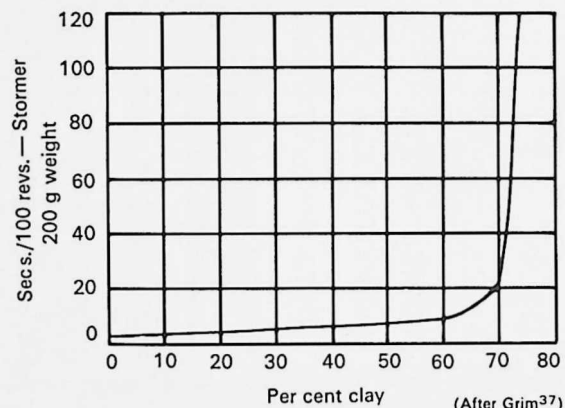
these coating kaolins, which need to spread in much the same way that milk spreads, on a support made by the kaolin[104]. Viscosity is closely related to the surface state of the particles in suspension.

If the kaolin contains an exchangeable-cation bearing phase — montmorillonite, illite, or micas — a change in the surface condition (surface area and base exchange capacity) could appear, and result in disturbances in the viscosity of the material when it is in suspension.

Five per cent of quartz will not disturb the rheological properties of kaolin, but only one or two per cent of montmorillonite or mica is sufficient to cause viscosity problems in the clay-water suspension (Figure 14).
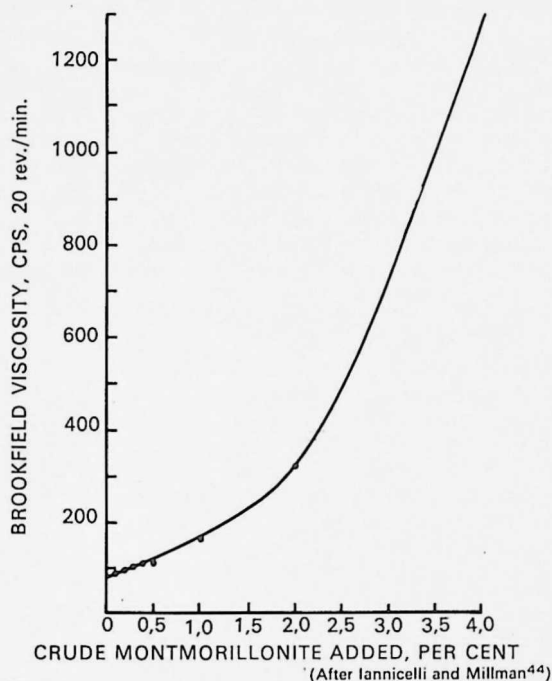
FIGURE 14 Effect of montmorillonite additions on viscosity of clay-water suspensions 70 per cent solids

(After Iannicelli and Millman[44])

Muscovite flakes are more coarsely grained than clays and are generally removed at the screening stage, but montmorillonite is different; they can reach several per cent in the finest portion (less than two microns) of the best kaolin ores[21].

In the case of pure kaolinite suspensions, surface conditions are determined by size criteria (grain size, stacking degree), by crystallochemical criteria (electro-kinetic potential, crystallinity), and by morphological criteria.

The grain-size analysis of a coating kaolin shows a size less than 2 microns for most of its components (75 to 95 per cent). But, should the thin kaolinite flakes tend to behave like book leaves (a and b crystallographic axes being the growth directions of the stacks), putting the material in suspension adversely affects viscosity.

FIGURE 13 Effect of clay concentration on flow characteristics of kaolin water-system

Robertson and Emmodi[86] attempted to take this tendency to stack into account, and introduced the idea of rugosity to both viscosity and stack volume.

The delimination process is an important phase in the wet processing of coating kaolins. The use of powerful dispersives, associated with attrition grinding, will tend to reduce the stacks to a set of individual thin flakes that will settle perfectly flat on their support[43].

Several American authors[68,69,77] found a relationship between the state of the surface of kaolins and the stacking mode of the kaolinite slabs. They call this mineralogical character crystalline perfection degree, or crystallinity (Figure 15). Because of the lack of precision of the

maximal dispersion speed correspond to maximal values of the zeta potential[30].

Finally a morphological investigation of the less-viscous coating kaolins with the electron microscope shows that they are composed of hexagonal platy flakes (Figure 16: 1 to 3).

On the other hand, the particles of hydrokaolinite occur as tubes (Figure 16: 10 to 12). Their poor properties in suspension are well known.

Robertson[85] recently suggested that the pictures shown in Figure 16 (4 to 9) could be artefacts of the hexagonal thin flakes.

FIGURE 15 Relationship between crystallinity and base exchange capacity.

processes pointed out in the first part of this paper, the crystallinity measurements do not seem to be useful as routine tests in specialized laboratories. The crystalline perfection is not even mentioned in the technical data published by China Clay producers.

The particles of a kaolin in suspension achieve some hydrolysis by the absorption of water molecules. The importance of this hydrolysis is connected with the stacking behaviour of the kaolinite and thus with its crystallinity grade.

The plate surfaces of the crystalline assemblages bristle with acid radicals, whereas the edges get a positive charge. The degree of dissociation of the acid radicals confers a characteristic pH to the aqueous suspension.

The presence of marginal cations is responsible for the flocculation of the kaolinite-water system and the task of dispersive agents such as tripolyphosphates is mainly to neutralize the positive charges fringing the crystalline faces[76].

The negative charge aquired by the kaolinite particles (zeta potential) may be the subject of experimental measurements[101]. The values of the electro-kinetic potential provide important information concerning rheological properties, since, depending on pH, the minimal viscosity and the

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FIGURE 16 **1.** Well-crystallized hexagonal shaped particles of kaolinite from Brittany, France. X23 700 **2.** Kaolinite and mica flakes from a hydrothermally weathered granite in Brittany, France. X23 000 **3.** Kaolinite particles (below 1 micron) extracted from a altered granite (Cornwall, U.K.). X23 700 **4.**Well-crystallized kaolinite from tertiary sandy sediments in Southern Belgium. X30 000
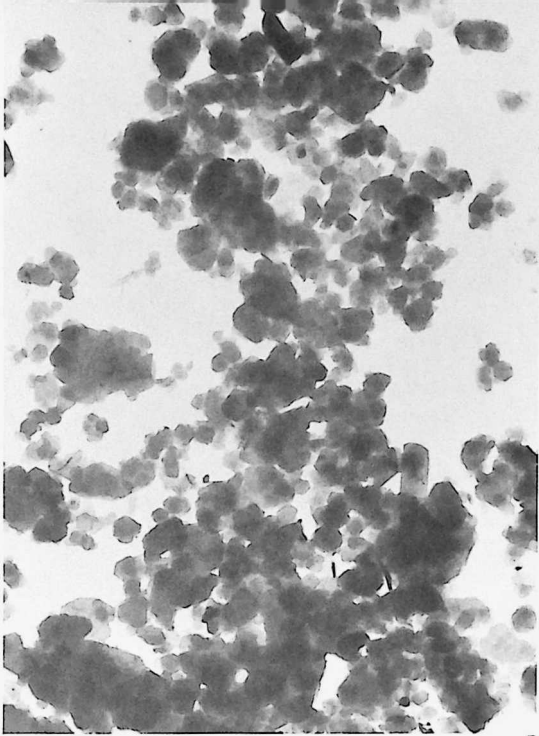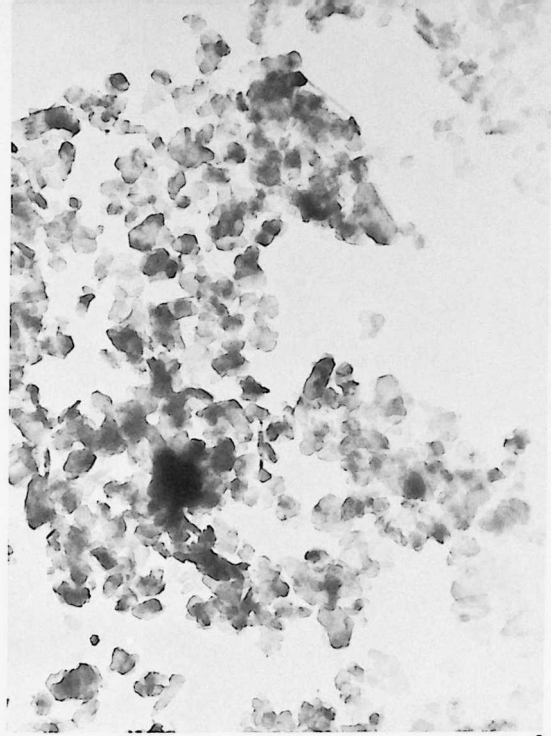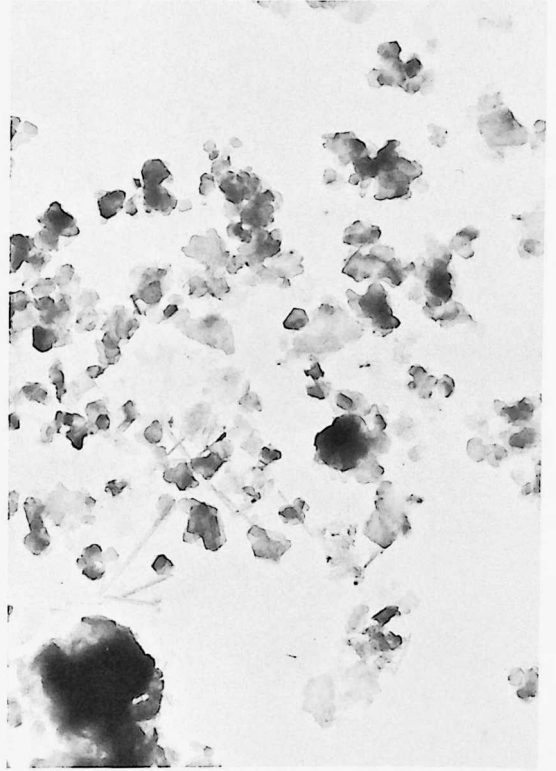
FIGURE 16 **5.** *Partially b-axis disordered kaolinite particles from tertiary sands in Oret (Belgium) X30 000* **6.** *Partially b-axis disordered kaolinite from tertiary residual clayey layers in Oret (Belgium) X30 000* **7.** *Mixture of sericite (lathe-shaped particles) and badly crystallized kaolinite from tertiary weathered Cambrian arkosic quartzite in Ardennes, Belgium. X30 000* **8.** *Mixture of badly crystallized kaolinite with some tubular forms (Germany) X23 700*
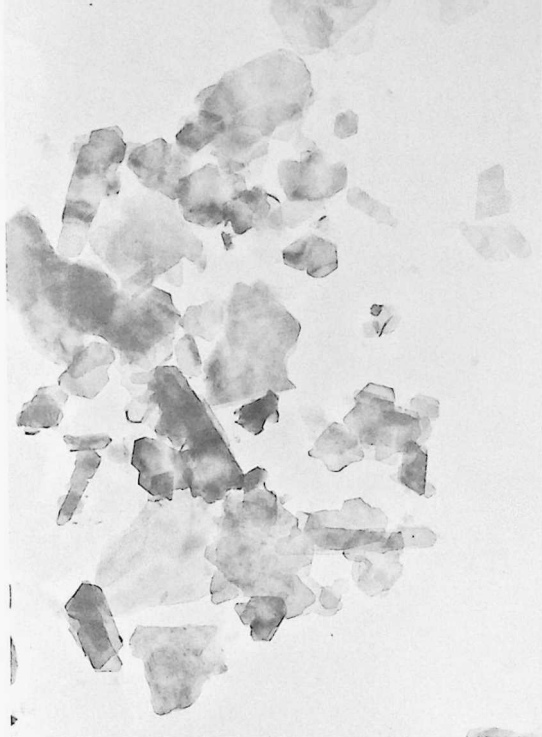
FIGURE 16   9. Kaolinite with muscovite particles from Germany X30 000 10. Tubular form (Halloysite from Utah (U.S.A.) X23 700 11. Tubular form (Halloysite) from Indiana (U.S.A.) X23 700 12. Illite and kaolinite, with goethite, from sandy layer in the residual tertiary cover of Southern Belgium. X30 000.

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