Research Article

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Mineral Constituents and Kaolinite Crystallinity of the <2 μm Fraction of Cretaceous-Paleogene/Neogene Kaolins from Eastern Dahomey and Niger Delta Basins, Nigeria

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Abstract: This study examines the mineral composition and kaolinite crystallinity of Cretaceous and Paleogene/Neogene kaolins from Nigeria based on X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy data of the <2 μm fraction. The purpose of this was to assess the minerals present, structural order, and possible industrial applications of the kaolins. A total of twenty-eight (28) samples comprising of fifteen (15) Cretaceous and thirteen (13) Paleogene/Neogene kaolins were analysed. The XRD results showed that both the Cretaceous and Paleogene/Neogene kaolins have kaolinite as the dominant phase followed by quartz with anatase, hematite, and goethite occurring in minor quantities. Based on the mineralogical composition, the Paleogene/Neogene deposits were classified as sandy kaolin and the Cretaceous deposits were classified as pure kaolin. The kaolinite structural order for the Cretaceous pure kaolin was higher than that obtained for the Paleogene/Neogene sandy kaolin with more quartz, iron, and titanium oxides. The economic consideration of the deposits showed that the sandy kaolin type can be used in pigment industrial applications whereas the pure kaolin type can be used in refractory, fiberglass, and ceramic industrial applications.

Keywords: Kaolin, mineralogy, XRD, FTIR, structural order, applications

1 Introduction

Kaolin minerals include kaolinite, dickite, nacrite, and halloysite, respectively. Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) is the most common kaolin mineral with the theoretical chemical composition: 46.54% SiO_2 , 39.50% Al_2O_3 , and 13.96% H_2O [1]. Kaolinite has 1:1 ratio of tetrahedral and octahedral layers continuous in the z- and x- axes directions, respectively, and stacked above each other in the y-direction. Kaolinite is one of the most important industrial clay minerals useful to man with a wide range of applications as raw material in ceramics, paper filling and coating, refractory, fiberglass, cement, rubber and plastics, cosmetics, paint, catalyst, pharmaceutical and agriculture [2, 3] because of its relatively low cost and easy availability. Its application is a function of its physical and chemical characteristics in relation to requirements of the end user [1]. The physical and chemical properties of kaolinite are strongly influenced by its structural order [4]. Structural defects in the kaolinite crystal structure have been attributed to a large number of stacking faults that may appear during its formation and growth. The knowledge of variations in the kaolinite structure is important in assessing its correlation with plasticity, brightness, and viscosity [5]. In addition, the degree of defects in kaolinites for use in manufacturing of ceramics is linked to the mineralogical assemblage, structural order, and thermal stability of the material [6]. In view of its wide applications, the occurrence of kaolin is worth proper physico-chemical, mineralogical and chemical investigations.

The X-ray diffractometry (XRD) technique has been well used for mineralogical identifications and in the examination of the structural disorder or crystallinity of kaolinite based on XRD-derived crystallinity indices such as Hinckley indices [5, 7]. The Fourier transform infrared (FTIR) spectroscopy is an alternative method in the determination of kaolinite disorder degree based on differences in the position and relative intensity of OH stretching and

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bending bands in the IR spectrum [8]. Vaculikova [4] proposed two approaches in determining the degree of structural disorder of kaolinites from IR spectra, namely, empirical approach (IR-E) and numerical approach (IR-N). The IR-E is based on resolution and relative intensities of bands in OH stretching and bending region whereas IR-N is based on crystallinity indices (CI) calculated from the intensities selected vibration models and structural OH bands.

Most of the sedimentary kaolins in the world, geologically occur as Cretaceous and Paleogene/Neogene argillaceous sediments [9]. Ekosse [2] with this in mind advocated that kaolin exploration in Africa should be focused on investigating Cretaceous and Paleogene/Neogene argillaceous sediments. In Nigeria, many of the Cretaceous-Paleogene/Neogene kaolin deposits occur within the sedimentary basins which are believed to be filled with Cretaceous-Recent sediments except for some Paleogene/Neogene kaolin occurring within the Jos Plateau in areas underlain by the Younger Granites. Quite a number of the kaolin deposits in Nigeria with estimated reserve of three (3) billion tonnes have not been properly evaluated in detail for industrial purposes [10]. Nigeria is a mono-economic nation with petroleum contributing the largest percentage of her foreign exchange earnings and revenues. Considering the current dwindling of oil prices and the gradual reduction of its oil reserve, diversifying the economy of Nigeria therefore calls for systematic investigation and characterisation of the vast occurrence of kaolinitic clays [2, 11]. This paper seeks to assess the mineralogy and structural order of some potential kaolin deposits in Nigeria using both XRD and FTIR techniques. This is considered essential in boosting the nation's economy.

2 Materials and Methods

2.1 Study Areas

Four Cretaceous-Paleogene/Neogene kaolin deposits in Nigeria were selected for this study, namely,

1. The Cretaceous Lakiri and Eruku kaolins occur within Ise Formation of the Abeokuta Group in the Eastern Dahomey Basin (Fig. 1). The Abeokuta Group has three formations, namely, Ise Formation (oldest), Afowo Formation, and Araromi Formation (youngest). The Ise Formation is a sequence of continental sands, grits and siltstones with a basal conglomerate overlying the Basement Complex. Interbedded kaolinitic clays occur up to metres in some places. Sporomorphs recovered from the shell-BP paleontologists

including *Cicatricosisporites* sp. cf. *C. mohrioides*, *Pilosporites trichopapillosus*, *Klukisporites pseudoreticulatus*, *Aequitriradites* aff. *verucosus* and *Stapilinisporites caminus* indicate an Early Cretaceous (probably Valanginian – Barremian) age for the formation [12].

2. The Paleogene/Neogene Ubulu-Uku and Awo-Omama kaolins occur within the Ogwashi-Asaba Formation of Niger Delta Basin (Fig. 2). The Ogwashi-Asaba Formation consists of white, blue, and pink clays, cross-bedded sands, carbonaceous mudstones, shales and seams of lignite. The type locality is at Eke Mgbalingba in Ogwashi-Asaba, Delta State but extends from Okitipupa Ridge through Onitsha, Ozubulu, Nnewi, Ikot Ekpene, Uyo, and Calabar where it is overlapped by the Benin Formation. Ogwashi-Asaba Formation contains some plant remains, which indicate an Oligocene – Miocene age and a continental environment of deposition for it [13].

Figure 1: Geologic Map of Eastern Dahomey Basin showing the study areas [14].

2.2 Sampling

To avoid contaminations from recent weathering products or external leached materials, the outcrop faces were dug back to at least 60 cm to gain access to fresh surfaces before sampling. Twenty-eight (28) bulk representative kaolin samples composed of nine (9) from Eruku (EP), and six (6) from Lakiri (LP) deposits at 2 m interval, respectively; six (6) from Awo-Omama (AL), seven (7) from Ubulu Uku (UL) deposits at 1 m interval, respectively (Fig. 3) were collected, stored in polythene bags carefully labeled, and transported to the laboratory for XRD and FTIR analyses.

Figure 2: Geologic Map of Niger Delta Basin showing the study areas [13].

Figure 3: Vertical profiles showing sampling depths and lithologic units of the studied kaolin deposit.

2.3 Sample Preparation and Clay Fraction Analyses

The $<2 \mu\text{m}$ fraction was obtained based on the principle of sedimentation according to Stoke's law which allow individual spherical particles to fall freely at a steady velocity under the influence of gravity, resisted only by the viscous drag of the medium [15]. The mineralogy of the $<2 \mu\text{m}$ fraction of the kaolins was determined by using the

XRD method after the removal of organic matter [16]. In order not to alter the kaolinite crystallinity, the dried samples were gently crushed in an agate mortar to a fine texture [17]. The powder samples were scanned in the Bruker AXS D8 Advance PSD system which was operated at 40 kV and 40 mA, using a Cu-K α radiation, graphite monochromator by taking recordings at step size of $0.02^\circ 2\theta$ scanned from 2 to $32^\circ 2\theta$ with a counting time of 2 s/step.

The mineral phases were identified using Bruker EVA software and compared with data and patterns available in the Mineral Powder Diffraction File [18] for confirmation. The relative phase amounts (weight %) were estimated using the Rietveld method. The infrared spectra (IR) were obtained using a Bruker Alpha Platinum-ATR spectrometer. To achieve high quality spectra, good contact between the sample and ATR crystal was ensured. The Bruker's spectroscopy software OPUS allowed real time monitoring of the spectral quality after applying pressure on the sample. The IR peaks were reported based on % transmittance to given wavelengths. The crystallinity of $<2 \mu\text{m}$ fraction of the studied kaolins was evaluated using the Hinckley Index (HI) [5, 19] from X-ray diffractogram, IR - empirical (IR-E) and IR - numerical (IR-N) approaches [4] from IR spectra. The HI computation is illustrated in Fig. 4. Normal HI values ranges from <0.5 (disordered) to 1.5 (ordered) [5]. The IR-N approach is based on crystallinity indices CI_1 and CI_2 defined as $CI_1 = I(v_1)/I(v_3)$ and $CI_2 = I(v_4)/I(v_1)$ where $I(v_1)$ and $I(v_4)$ are intensities of OH stretching bands at $3691/3689 \text{ cm}^{-1}$ and 3619 cm^{-1} , respectively, and $I(v_3)$ is the intensity of OH bending band at 912 cm^{-1} . The kaolinite structures are classified as poorly ordered, if $CI_1 < 0.7$ and $CI_2 > 1.2$; partially ordered; if $0.7 < CI_1 < 0.8$ and $0.9 < CI_2 < 1.2$; and ordered, if $CI_1 > 0.8$ and $CI_2 < 0.9$ [20, 21].

3 Results and Discussion

3.1 X-ray Diffraction

The X-ray diffractograms for the $<2 \mu\text{m}$ fraction were not significantly different, hence only one per deposit is presented for Awo-Omama, Ubulu-Uku, Eruku, and Lakiri deposits, respectively, (Figs 5 and 6). Tables 1 and 2 give the summary of mineral constituents contained in the different $<2 \mu\text{m}$ fraction kaolin samples. Of all the minerals present, kaolinite alone constitutes between 67 – 91 % in the Paleogene/Neogene deposits and 87 – 99 % in the Cretaceous deposits. Quartz and anatase on the other hand, varies from 4 – 28 % and 1 – 6 % in Paleogene/Neogene deposits and 1 – 6 % and 1 – 8 % in Cretaceous deposits,

Figure 4: Calculation of the HI from the ratio of the height above background of the $\bar{1}10$ (A) and $\bar{1}1\bar{1}$ (B) peaks above the band of overlapping peaks occurring between 20–23° compared to the total height of the $\bar{1}10$ above background (At). The abscissa is in terms of 2 theta and the ordinate is on a relative scale [7].

respectively. Hematite and goethite were present in minor quantities. The Cretaceous deposits generally show less quartz contents and higher kaolinite contents compared to the Paleogene/Neogene deposits. The presence of anatase, hematite, and goethite coupled with the absence of pyrite and marcasite indicate that kaolin is associated with oxidizing depositional environment [22, 23]. The average kaolinite percentages obtained for the Paleogene/Neogene (82 %) were comparable to the value reported for Cretaceous Red Sea kaolins in Egypt (84 %) [24] whereas the 96 % average percentage for the Cretaceous deposits is comparable to those reported for the <5 μm fraction of Paleogene/Neogene Maoming kaolins (97%) in China [25], <4 μm fraction of Paleogene/Neogene Georgia kaolins (98%) in the USA and Cretaceous Poveda kaolins in Spain [5]. A plot of the average percentages of minerals present in each of the deposits on the ternary diagram for general mineralogical classification of economic kaolin deposits categorised the deposits into kaolin types (Fig. 7). The Paleogene/Neogene Awo-Omama and Ubulu-Uku deposits plotted in the region of sandy kaolin whereas the Cretaceous Eruku and Lakiri deposits plotted in the region of pure kaolin show a decrease in quartz content with age.

The calculated Hinckley index (HI) percentages from the XRD pattern of the <2 μm fraction are presented in Tables 1 and 2. The HI values obtained for the kaolinites from Awo-Omama range between 0.27 and 0.41 with an average value of 0.31, which corresponds to low kaolinite struc-

Figure 5: Representative X-ray diffractogram of the <2 μm fraction of the kaolin from Awo-Omama (AL1 2m) and Ubulu-Uku (UL2 0m) deposits showing kaolinite (k), quartz (q), anatase (a), and hematite (h).

Figure 6: Representative X-ray diffractogram of the <2 μm fraction of the kaolin from Eruku (EP2 4m) and Lakiri (LP1 4m) deposits showing kaolinite (k), quartz (q), and hematite (h).

Figure 7: Kaolin type mineralogical classification for the deposits [26].

tural order whereas the HI values for the kaolinites from Ubulu-Uku, Eruku, and Lakiri ranges from 0.58 and 1.36 with an average value of 0.97; 0.8 and 1.38 with an average value of 0.98; and 0.75 and 1.09 with an average value of 0.99, respectively, which is classified under the medium to high kaolinite structural order. From the average HI values, the kaolinites are partially ordered except for the Awo-

Table 1: Mineral constituents and HI of the <2 μm fraction of the kaolin from Awo-Omama and Ubulu-Uku Paleogene/Neogene kaolin deposits.

Sample ID	Kaolinite %	Quartz %	Anatase %	Hematite %	Goethite %	HI
CF AL1 0m	91	4	3	2	-	0.28
CF AL1 1m	68	27	5	-	-	0.30
CF AL1 2m	75	20	5	-	-	0.41
CF AL2 0m	89	4	6	1	-	0.29
CF AL2 1m	79	15	6	-	-	0.28
CF AL2 2m	90	5	5	-	-	0.27
CF UL1 0m	67	28	3	-	2	0.58
CF UL1 1m	76	20	-	-	4	1
CF UL1 2m	90	10	-	-	-	1.05
CF UL2 0m	74	24	1	-	1	0.68
CF UL2 1m	84	15	-	-	1	0.92
CF UL2 2m	90	9	1	-	-	1.36
CF UL2 3m	88	11	-	-	1	1.17
Average	82	15	4	1	2	0.61
Max	91	28	6	2	4	1.36
Min	67	4	1	1	1	0.27

Table 2: Mineral constituents and HI of the <2 μm fraction of the kaolin from Eruku and Lakiri Cretaceous kaolin deposits.

Sample ID	Kaolinite %	Quartz %	Anatase %	Hematite %	Goethite %	HI
CF EP1 0m	94.31	1	5	-	-	0.94
CF EP1 2m	96.49	2	1	-	-	0.86
CF EP1 4m	97.3	1	2	-	-	1
CF EP2 0m	97.5	1	1	1	-	0.8
CF EP2 2m	97.31	1	2	-	-	1.07
CF EP2 4m	88.28	2	8	1	1	1.38
CF EP3 0m	92.15	6	1	-	1	0.95
CF EP3 2m	86.71	5	5	1	2	0.86
CF EP3 4m	96.89	-	1	-	2	1
CF LP1 0m	95.74	-	4	-	-	0.75
CF LP1 2m	99.06	-	1	-	-	1.09
CF LP1 4m	98.85	-	1	-	-	1
CF LP2 0m	98.93	-	1	-	-	1.03
CF LP2 2m	99.03	-	1	-	-	1
CF LP2 4m	98.82	-	1	-	-	1.05
Average	95.82	2	2	1	2	0.98
Max	99.06	6	8	1	2	1.38
Min	86.71	1	1	1	1	0.75

Omama kaolinites. The increasing kaolinite structural order is Awo-Omama (with least structural orderliness) < Ubulu-Uku < Eruku < Lakiri (with best structural orderliness). This implies that the Cretaceous kaolinites are more ordered than the Paleogene/Neogene kaolinites. The average HI value of 0.75 obtained for the <2 μm fraction of Cre-

taceous Red Sea kaolinites in Egypt [24] is lower than the average values obtained for Ubulu-Uku, Eruku, and Lakiri deposits. Kaolins that have undergone more intense oxidative weathering typically contain a higher percentage of well-ordered kaolinite and therefore a higher HI value [23].

Table 3: Position and assignment of IR bands of the <2 μm kaolin fraction from Awo-Omama and theoretical kaolinite.

Theoretical Kaolinite	AL1 0m	AL1 1m	AL1 2m	AL2 0m	AL2 1m	AL2 2m	Assignment
3691 - 89	3690	3692	3690	3690	3690	3690	Al—O-H stretching of inner surface hydroxyl groups
3669	3669	3670	3669	3669	3670	3669	Al—O-H stretching of inner surface hydroxyl groups
3651	3651	3649	3649	3650	3650	3650	Al—O-H stretching of inner surface hydroxyl groups
3619	3620	3620	3621	3621	3621	3621	Al—O-H stretching of inner hydroxyl groups
1115 - 14	1116	1116	1118	1116	1116	1116	Si-O stretching (Longitudinal mode)
1028 - 27	1026	1026	1028	1026	1026	1026	In-plane Si-O stretching
1005 - 04	999	999	997	1002	999	997	In-plane Si-O stretching
937 - 935	938	938	938	936	936	938	OH deformation of inner surface hydroxyl groups
912	910	912	912	912	912	910	OH deformation of inner hydroxyl groups
789 - 788	794	798	798	791	795	796	OH deformation linked to Al, Mg
751 - 750	751	751	749	750	753	749	Si-O perpendicular
684 - 681	689	691	696	683	687	691	Si-O perpendicular
541	520	529	528	520	530	530	Fe-O, Fe_2O_3 , Ti-O; Si-O-Al stretching

3.2 FTIR Spectroscopy

The IR spectra for the <2 μm kaolin fraction from Awo-Omama, Ubulu-Uku, Eruku, and Lakiri deposits are presented in Figs. 8 – 11. The summary of the assignment of the absorption bands in measured IR is presented in Tables 3-6.

Figure 8: The IR spectra of the <2 μm kaolin fraction from Awo-Omama between 3900 to 3550 cm^{-1} and 1200 to 500 cm^{-1} .

The identification of absorption bands at about 3691/3689, 3669, 3651/3650, and 3619 by visual estimation (IR-E) can be used to infer kaolinite structural order [4, 8]. According to the IR-E classification, kaolinite structure is considered ordered, if the four OH stretching and bending bands were clearly resolved; partially ordered, if the individual OH bands at 3669, 3651/3650 and 937/935 cm^{-1} could be identified but intensities were low; and poorly ordered, if only one band near 3660 cm^{-1} or inflexions near 3669 cm^{-1} , 3651/3650 cm^{-1} and 937/935 cm^{-1} were observed in the spectra [4]. From the IR spectra obtained for

Figure 9: The IR spectra of the <2 μm kaolin fraction from Ubulu-Uku between 3900 to 3550 cm^{-1} and 1200 to 500 cm^{-1} . **Figure 10:** The IR spectra of the <2 μm kaolin fraction from Eruku between 3900 to 3550 cm^{-1} and 1200 to 500 cm^{-1} .

the samples, the four bands in the OH stretching region were observed with the 3669 band showing weak inflexions which is more pronounced particularly for the <2 μm kaolin fraction from Awo-Omama deposit (Fig. 8). This indicates partially ordered structure for the samples. Based on the IR spectrum for the deposits, the order of increasing

Table 4: Position and assignment of IR bands of the <2 μm kaolin fraction from Ubulu-Uku and theoretical kaolinite.

Theoretical Kaolinite	UL1 0m	UL1 1m	UL1 2m	UL2 0m	UL2 1m	UL2 2m	UL2 3m	Assignment
3691 - 89	3692	3692	3688	3692	3692	3688	3690	Al—O-H stretching of inner surface hydroxyl groups
3669	3669	3670	3668	3667	3668	3668	3670	Al—O-H stretching of inner surface hydroxyl groups
3651	3652	3651	3651	3651	3649	3651	3651	Al—O-H stretching of inner surface hydroxyl groups
3619	3621	3621	3619	3621	3621	3621	3619	Al—O-H stretching of inner hydroxyl groups
1115 - 14	1116	1116	1116	1116	1116	1116	1116	Si-O stretching (Longitudinal mode)
1028 - 27	1026	1028	1026	1026	1026	1024	1028	In-plane Si-O stretching
1005 - 04	1000	1000	1000	1002	1000	997	1002	In-plane Si-O stretching
937 - 935	938	938	938	936	938	936	936	OH deformation of inner surface hydroxyl groups
912	912	910	914	912	912	912	912	OH deformation of inner hydroxyl groups
789 - 788	798	800	798	798	798	798	798	OH deformation linked to Al, Mg
751 - 750	752	753	751	751	751	751	751	Si-O perpendicular
684 - 681	689	689	692	687	687	687	687	Si-O perpendicular
541	530	532	528	530	528	526	528	Fe-O, Fe ₂ O ₃ , Ti-O; Si-O-Al stretching

Table 5: Position and assignment of IR bands of the <2 μm kaolin fraction from Lakiri and theoretical kaolinite.

Theoretical Kaolinite	LP1 0m	LP1 2m	LP1 4m	LP2 0m	LP2 2m	LP2 4m	Assignment
3691 - 89	3688	3686	3686	3686	3688	3688	Al—O-H stretching of inner surface hydroxyl groups
3669	3669	3670	3669	3670	3669	3670	Al—O-H stretching of inner surface hydroxyl groups
3651	3651	3653	3651	3651	3651	3651	Al—O-H stretching of inner surface hydroxyl groups
3619	3619	3619	3619	3619	3619	3619	Al—O-H stretching of inner hydroxyl groups
1115 - 14	1114	1116	1114	1116	1114	1116	Si-O stretching (Longitudinal mode)
1028 - 27	1023	1026	1026	1023	1026	1026	In-plane Si-O stretching
1005 - 04	1000	1000	1000	1000	1000	998	In-plane Si-O stretching
937 - 935	938	938	938	938	938	940	OH deformation of inner surface hydroxyl groups
912	912	912	912	914	912	912	OH deformation of inner hydroxyl groups
789 - 788	794	791	796	796	793	793	OH deformation linked to Al, Mg
751 - 750	749	753	753	753	751	751	Si-O perpendicular
684 - 681	689	689	692	687	687	687	Si-O perpendicular
541	524	524	530	522	526	528	Fe-O, Fe ₂ O ₃ , Ti-O; Si-O-Al stretching

structural order is Awo-Omama, Ubulu-Uku, Eruku, and Lakiri deposits, respectively. Characteristic bands at 1116-1114 and 692-683 indicative of quartz interference in the samples were identified. Muscovite interference was identified in all the samples at bands between 1028-1023 cm^{-1} . The 500-600 cm^{-1} bands due to the presence of iron oxide and Ti-O bond vibrations [27] were prominent at bands between 532-520 cm^{-1} in all the samples. From the foregoing, it therefore means that the IR spectra showed the presence of kaolinite, quartz, muscovite, hematite, goethite,

and anatase in the samples, most of which had earlier been identified by XRD in some of the samples. This further demonstrates the complementary role of both FTIR and XRD techniques in characterising kaolin clay fraction, though the latter did not show the presence of muscovite in the samples.

The calculated CI_1 and CI_2 values obtained for the kaolinites correspond to partially ordered structures based on the IR-N classification (Table 7). There is an agreement between the IR-E and IR-N classifications in that the kaoli-

Table 6: Position and assignment of IR bands of the <2 μm kaolin fraction from Eruku and theoretical kaolinite.

Theoretical Kaolinite	EP1 0m	EP1 2m	EP1 4m	EP2 0m	EP2 2m	EP2 4m	EP3 0m	EP3 2m	EP3 4m	Assignment
3691 - 89	3688	3688	3688	3688	3686	3688	3688	3688	3686	Al—O-H stretching of inner surface hydroxyl groups
3669	3669	3670	3670	3670	3670	3670	3670	3670	3670	Al—O-H stretching of inner surface hydroxyl groups
3651	3651	3651	3651	3651	3651	3651	3651	3651	3651	Al—O-H stretching of inner surface hydroxyl groups
3619	3619	3619	3619	3619	3619	3619	3621	3619	3619	Al—O-H stretching of inner hydroxyl groups
1115 - 14	1116	1114	1114	1114	1114	1114	1116	1116	1114	Si-O stretching (Longitudinal mode)
1028 - 27	1026	1024	1026	1026	1026	1026	1026	1024	1024	In-plane Si-O stretching
1005 - 04	999	998	1002	1000	1000	1002	1000	1000	1000	In-plane Si-O stretching
937 - 935	938	938	940	938	936	938	936	938	936	OH deformation of inner surface hydroxyl groups
912	912	910	914	912	912	912	912	912	912	OH deformation of inner hydroxyl groups
789 - 788	796	791	794	791	791	791	791	791	793	OH deformation linked to Al, Mg
751 - 750	749	751	749	751	751	751	751	751	751	Si-O perpendicular
684 - 681	691	691	696	683	687	691	683	687	691	Si-O perpendicular
541	526	528	522	522	522	528	524	526	526	Fe-O, Fe_2O_3 , Ti-O; Si-O-Al stretching

Table 7: The structural order of kaolinite samples using IR-N classification.

Deposit	Age	Average Cl_1	IR-N Average Cl_2	Class
Awo-Omama (n=6)	Paleogene/Neogene	3.36	1.02	pa-o
Ubulu-Uku (n=7)	Paleogene/Neogene	3.12	1.05	pa-o
	Average	3.24	1.04	pa-o
Eruku (n=9)	Cretaceous	2.99	1.03	pa-o
Lakiri (n=6)	Cretaceous	3.10	1.03	pa-o
	Average	3.04	1.03	pa-o

Figure 11: The IR spectra of the <2 μm kaolin fraction from Lakiri between 3900 to 3550 cm^{-1} and 1200 to 500 cm^{-1} .

nite structures were classified as partially ordered. This

agreement is due to the absence of clay minerals like illite or smectite which could affect the IR pattern in OH stretching and bending region [4]. The IR and HI classifications agree with each other for the Ubulu-Uku, Eruku, and Lakiri deposits except for Awo-Omama deposit. This accordance further confirm that FTIR is a sensitive tool in the estimation of kaolinite crystallinity [28].

3.3 Industrial Applications

The industrial utility of kaolin is determined by its physico-chemical, mineralogical, and geochemical characteristics. The <2 μm fraction is important in accessing the industrial applications of kaolins because most applications require between 40 – 95 % clay fraction [29].

Based on the mineralogical composition (Fig. 12), the pure kaolin type deposits will possibly be useful as raw materials for refractory, fiberglass and ceramic applications whereas the sandy kaolin type deposit will possibly be useful for pigment applications. For the pure kaolin-type, the major colouring minerals are anatase, hematite, and goethite. The presence of Fe and Ti phases could cause whiteness problem in ceramics [30]. This deduction can be substantiated by matching the chemistry of these kaolin samples with various industrial specifications.

Figure 12: Possible industrial applications of the kaolin based on their mineralogical classification [26] described in Fig. 7.

4 Conclusions

The mineralogical analyses carried out on the <2 μm kaolin fraction from Awo-Omama, Ubulu-Uku, Eruku, and Lakiri deposits show them to be essentially kaolinitic with other mineral constituents such as quartz, anatase, goethite, and hematite in that decreasing order. Based on the mineralogical classification (Pruett, 2016), the Paleogene/Neogene Awo-Omama and Ubulu-Uku deposits are classified as sandy kaolin and the Cretaceous Eruku and Lakiri deposits are classified as pure kaolin type.

The kaolinite structural order from the XRD based HI method and the FTIR based IR-E and IR-N methods in increasing orderliness is Awo-Omama (with least structural orderliness) < Ubulu-Uku < Eruku < Lakiri (with best structural orderliness). This implies that the pure kaolin type have higher kaolinite structural order than the sandy kaolin type. From the mineralogy and kaolinite structural order, it can be deduced that the pure kaolin type have undergone more intense oxidative weathering.

The economic consideration of the deposits showed that the sandy kaolin type can be used in pigment industrial applications whereas the pure kaolin type can be used in refractory, fiberglass, and ceramic industrial applications. However, more knowledge on the chemistry is important for efficient mineral separation using magnetic, flotation and selective flocculation methods. This can also give more geologic insight into the evolution of the kaolin deposits and improve the traditional kaolin applications.

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