



Commercially Imported Bentonite Versus Locally Derived Bentonitic Clays: A Comparative Assessment Study of Mineralogy and Geochemical properties, Anambra Basin, Southeastern Nigeria

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ABSTRACT

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This study aimed to investigate the mineralogy and chemical properties of the bentonites from the Imo Shale and Ameki formations, vis-a-vis commercially imported bentonite (CIC), for its suitability in formulation of drilling mud. 50 suspected bentonitic clays were studied, and properties of starting materials were utilized during screening. The CIC and four samples that met the API specification for drilling mud were subjected to X-ray diffraction (XRD) and X-ray fluorescence (XRF) analyses. XRD revealed SPL15 consists: 55% kaolinite, 20% quartz, 15% K-feldspar, and 10% hematite, suggesting kaolinite-type; and SPL6, SPL8, and SPL11 consist: 28-47% kaolinite, 26-32% quartz, and 12-20% nontronite, indicating smectite-type with significant amount of kaolinite co-existing, while the CIC consists of 12% quartz, 10% K-feldspar, 12% calcite, 41% nontronite, and 25% amorphous materials. XRF, showed Al_2O_3 (15.77-25.49) wt%, Fe_2O_3 (6.61-10.01) wt%, SiO_2 (51.67-59.11) wt%, and loss on ignition (7.57-11.22) wt%, indicating variable degrees of alterations. Significant proportion of the CIC exists in an amorphous phase, suspected to be additives. Thus, comparison with the CIC revealed compositional disparity/deficits in the local clays. Consequently, treatment/beneficiations may be necessary to achieve the desired compositions. Based on these results, the primary criteria for the formulation of drilling fluid, using mineralogy and chemical compositions, are achievable.

1. INTRODUCTION

Drilling operations for petroleum and water resources, generally demand huge quantities of drilling mud, which are predominately and frequently imported into the country in past decades. Moreover, there abound several raw clay/shale deposits in various sedimentary basins in Nigeria, which can typically boost and sustain economic growth, and subsequently offer both investment and job opportunities. In this regard, there is an urgent need to redirect research efforts towards sourcing for alternatively efficient-low-cost locally derived bentonitic clays for self-reliance. Thus, the compelling interest in this study is geared toward effective exploitation of the local raw materials for national industrial development.

Meanwhile, several clay deposits have been discovered, their industrial uses investigated and reported in Nigeria [1-7]. These deposits range from lateritic/residual clays from weathered products of basement complexes [3, 4, 7] to those arising from sedimentary units within the various sedimentary basins, as well as those formed along major river channels [1, 5, 6]. A survey carried out by the Nigerian Mining Corporation typically established the presence of bentonitic clay reserves of over 700 million tonnes within Nigeria, with the largest deposit found in Afuze, Edo State, estimated at 70–80 million tonnes [8].

Also, Abia State, which hosts the present study locations, holds about 1% of the total proven bentonite reserves [9]. Ironically, few studies have been done on these clay

compositions and their suitability in the formulation of drilling mud utilized in the drilling industries. Notable is the pioneer works [10, 11] including the recent works [9, 12], which typically assess the suitability of clay deposits from diverse locations within the northeastern and southeastern parts of Nigeria. The ultimate outcomes of these researches revealed that the clays are not directly suitable for oil-drilling mud. However, their essential properties could be improved upon by beneficiation with mixed metal hydroxides, trona, lime (Na_2CO_3), cellulose, etc., therefore recommended its use for drilling water wells [10].

However, mineralogical and geochemical characterization of clay deposits from Imo Shales and some clay deposits in Ameki formation, Anambra Basin southeastern Nigeria for possible use as drilling mud have not been considered.

2. PAGE BRIEF GEOLOGICAL SETTING OF THE STUDY AREA

The study area, along with sample locations are within Latitudes $5^{\circ}26'$ and $5^{\circ}40'$ N and Longitudes $7^{\circ}26'$ and $7^{\circ}43'$ E (Figure 1). It is accessible via Umuahia-Bende, Bende-Arochukwu, and Umuahia-Aba (Ohiya) principal axes, Southeastern Nigeria. It lies within the southern proportion of the Benue Trough, which typically underlies the most extensive parts of Southeastern Nigeria.

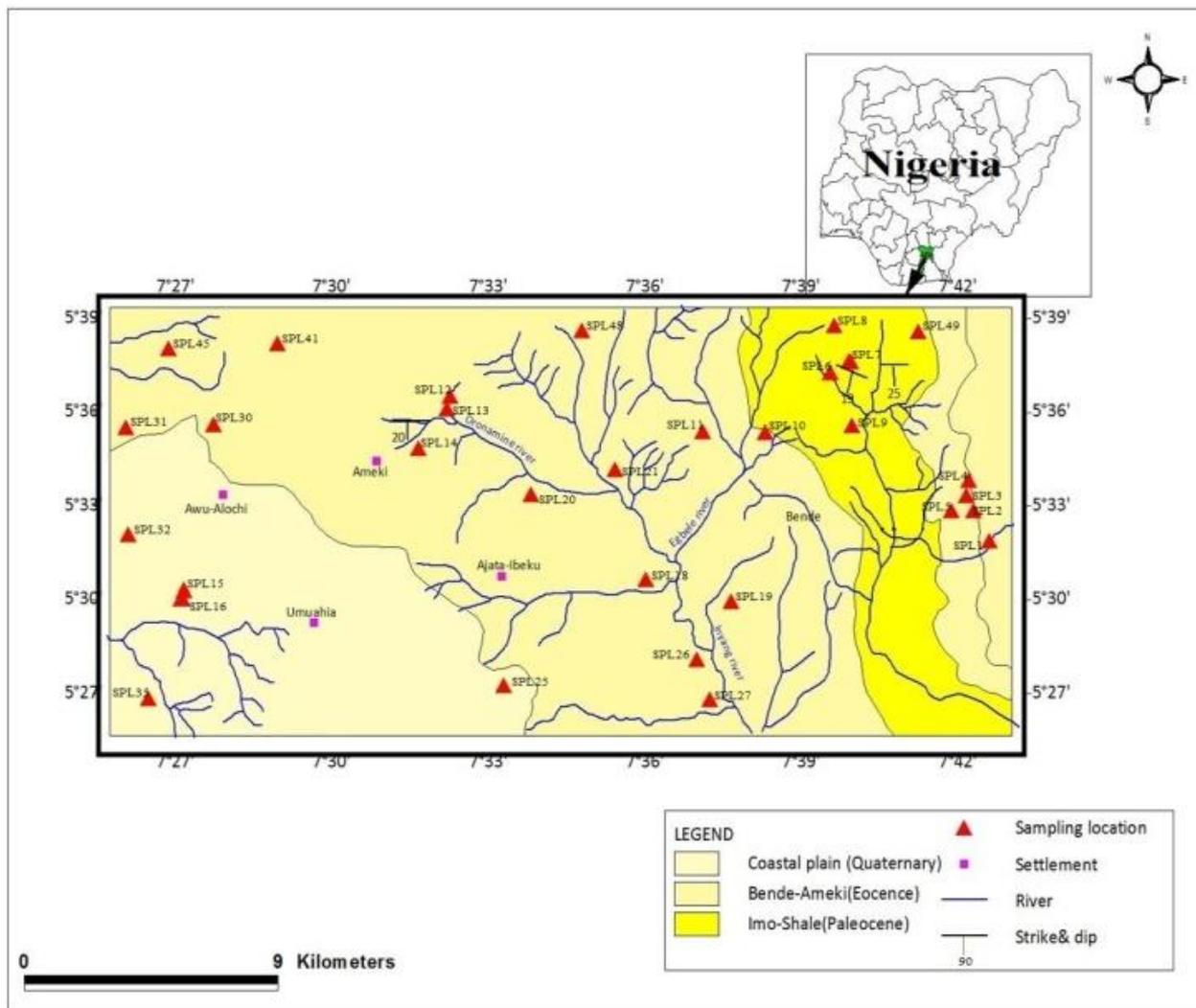


Figure 1. Geological map of the study area showing location of samples

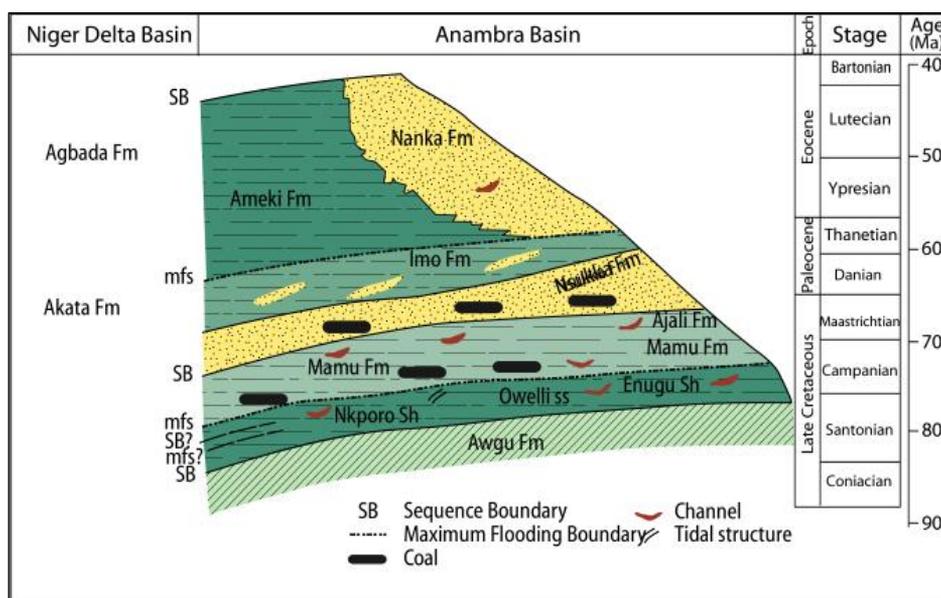


Figure 2. Stratigraphic section of the Anambra Basin from Late Eocene and time equivalent formations in the Niger Delta [14]

The succession has a stratigraphic record of deposits represented by sediments of three distinct marine depositional episodes: the Albian-Cenomanian; Turonian-Santonian as well as Campano-Maastrichtian episodes [13]. The

stratigraphic succession within the confines of the Anambra Basin as part of Southern Benue Trough is typically, presented in Figure 2.

Notwithstanding, the first marine transgression in the

Southern Benue Trough invariably began in the mid-Albian period with the deposition of the Asu River Group, predominantly composed of shales and some mottles of localized sandstone, siltstone, and limestone facies [14, 15]. Besides, the marine transgression that started deposition of sediments in the Anambra Basin proper began in the Campanian period, but lasted briefly, which was immediately followed by a regressive phase. These episodes follow the depositions of Nkporo Shale and its lateral equivalents, the Enugu Shale, including Owelli Sandstone (Nkporo Group), which generally formed the basal beds of the Campanian period.

Moreover, due to large volume of sediments deposition, the broad, shallow sea slowly turned shallower, coupled with gradual/inactive subsidence rate. Thus, the Maastrichtian period quickly initiated the regressive phase that saw the deposition of deltaic fore-sets and flood plain sediments regarding the Mamu Formation (Lower Coal Measures) [15]. The Mamu Formation is overlain by the continental beds of Ajali Sandstone, followed by a unique return to partially paralic conditions along with the deposition of the Nsukka Formation. The emplacement of the Nsukka Formation invariably marked the beginning of the Sokoto transgression and the succeeding documentation of the return to swampy conditions [16].

The Imo Shale overlies the Nsukka Formation. It shows characteristic shallow marine shelf conditions, with foreshore and shoreface sands that are rarely preserved [17]. It typically consists of blue-grey clays, dark-grey and black shales with continuous strips of calcareous sandstone, marl, and limestone [13]. The regressive phase persisted throughout the Eocene period [13], ultimately leading to the emplacement of Lower and Middle Eocene deposits including the clastic Ameki and Nanka Formations. The lithostratigraphic units under investigation include the Imo Shale (Ezinnachi) and Ameki Formation (Ohiya). These are Tertiary formations in the Anambra Basin.

3. MATERIALS AND METHODS

3.1 Field sampling method

Fifty (50) representative fresh clay samples were carefully collected from Imo shale and Ameki Formation at various key locations, where they are typically exposed within the study area. Samples were well labeled and kept for laboratory analyses. The samples were initially air-dried and later pulverized by developing a highly polished surface in the chamber of the specimen holder of the Pw 1800 diffractometer with copper tube anode.

3.2 Analytical methods

50 g of each prepared sample collected from the field were placed in beakers and soaked with de-ionized water of a pH value of 7.0 at room temperature (25°C), stirred properly, and left for 24 hours. The pH meter (PC Testr 35 Multi-Parameter) was used to read off the pH and electrical conductivity values of each sample by deepening the electrodes into the beaker containing de-ionized water together with the sample.

3.2.1 Mineralogical and chemical analyses

The XRD analysis is a rapid and non-destructive technique.

Thus, one commercially imported drilling clay, and four local clay samples from the various study locations, which successfully scaled through the preliminary API standard screening, was analyzed for their mineralogical and chemical characteristics, using X-ray diffraction (XRD) and X-ray Fluorescence (XRF) approaches. The following instrument/conditions were applied: Philips PW1729 X-ray diffractometer, Cu anode X-ray tube, 40 kV 30 mA tube, 40 kV 30 mA tube power, 1 degree 2-theta/min scan speed 5 to 80 degrees 2 theta scan range graphite monochromatic at SpectraChem Analytical, CRL Energy Ltd, New Zealand. Phase identifications and quantification was carried out using Siroquant search/match evaluation. The mineralogy was carried out on unoriented mounts of the total samples.

3.2.2 Chemical analysis

XRF analysis was also conducted on the same samples, to determine the major oxide compositions of the clays, using a Philips PW 1450/20 automatic X-ray fluorescence spectrometer equipped with 60 position sample changer at the same laboratory. Powder samples (<75microns) were dried in an oven at 110°C, and lost on ignition (LOI) was carried out at 1000°C. A total of 10 key major oxides: SiO₂, TiO₂, Al₂O₃, ΣFe₂O₃, MnO, MgO, CaO, Na₂O, K₂O and P₂O₅, and LOI of each sample was equally determined by drying the samples at 110°C overnight followed by calculation of their water and other volatiles content as wt.% at 1000°C. The accuracy of the major element is +2%.

4. RESULTS AND DISCUSSION

4.1 Mineralogical composition

Smectite and kaolinite are the dominant clay minerals in the studied samples. The XRD analysis of a split representing the clay portion of the studied samples based upon template analysis indicated that SPL6, SPL8, and SPL11 and the commercially imported clay (CIC) are smectite-type. Smectite, kaolinite, palygorskite are the main clay minerals identified via the XRD analysis. The rest are non-clay minerals, which are majorly dominated by quartz, calcite, dolomite, K-feldspar (Table 1 & Figure 3).

Although shale/clays are mostly composed of clay minerals, other minerals, such as basanite, and sanidine, were also detected in one sample each. The presence of calcite or dolomite but the absence of pyrogenic minerals in the samples suggests that they might be of sedimentary origin.

Additionally, the SPL15 sample predominately consists of kaolinite, which prominently peaks at 7.23Å, (1.50-7.23Å). Presence of hematite (2.6Å), K-feldspar (3.95Å), and quartz (1.78-4.40Å) were also identified, based on non-destructive XRD analysis, therefore it is typically characterized as kaolinite-type. Moreover, well crystallized Na-smectite is reliably distinguished by a sharp peak at 12.73Å. However, the studied samples generally range from 1.59 to 12.73Å. The samples (SPL6, SPL8, and SPL11), as shown in Table 1 and Figure 3 (c & d), typically indicate the co-existence of smectite and kaolinite minerals as well as other non-clay minerals.

4.2 Chemical compositions

The results of the major element geochemistry, presented in Table 2, show that the analyzed representative clay samples

were dominated by quartz with a correspondingly high proportion of SiO₂ (51.67 -59.11 wt%), while other major oxides were generally less than 50 wt% (Figure 4). It typically correlates positively with the CIC sample (SiO₂, 59.09 wt%; Al₂O₃, 18.53 wt%, and Fe₂O₃, 5.09 wt%), except for the result of the SPL15, which is inconsistent.

Besides, there are depletions in the critical values of SiO₂, MgO, CaO, and Na₂O (51.67; 0.56; 0.01 and 0.05 wt%), respectively. This result strongly corroborates the mineralogical data presented in Table 1. From Table 2, it is apparent that all the samples are moderately rich in SiO₂ (51.67 -59.11 wt%), moderate Al₂O₃ (15.77-25.49 wt%) with SPL15 exceptional value of 25.49 wt% which is conspicuously high, and a wide range of K₂O (0.17-6.06 wt%), suggesting weathered samples. Conversely, they possess low average contents of TiO₂, MnO, CaO, and Na₂O as well as low MgO. The high K₂O/Na₂O ratios are usually attributed to the established presence of K-bearing minerals like K-feldspar and mica, illite, muscovite, biotite [18, 19].

A positive correlation between K₂O and Al₂O₃ (av. 0.037) reasonably implies that the concentrations of K-bearing

minerals wield no significant influence on Al distribution, therefore suggests that the abundance of these elements is primarily uncontrolled by the content of clay minerals, contrary to what is documented elsewhere [18]. However, the contribution from the feldspars is reasonably indicated by their Al₂O₃/SiO₂ ratios [20].

Furthermore, the XRF chemistry revealed a significant concentration of Fe in most samples. The predominant mineral containing Fe that may be present from XRD data is nontronite, which is a Fe bearing smectite. Also noted is the minor presence of palygorskite that peaks at 10.39Å in one sample (Figure 3c). The reflections are sharp and well defined, lessening the likelihood of interlayer clay minerals. Al₂O₃ was enriched in the weathered-sample (SPL15), suggesting that, during the alteration process, mobile elements, like Na, Ca, and K, were probably depleted by meteoric or groundwater. The net results were the concentration of Al₂O₃ and the resultant precipitation of kaolinite clay-type. Conversely, the leaching of alkali elements downward could result in an alkaline environment suitable for the precipitation of smectites.

Table 1. Mineralogical composition of the studied clays and the commercially imported clay (CIC)

Phase name	Formula	SPL6 %	SPL8 %	SPL11 %	SPL15 %	Average	CIC (Wyoming)%
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	30	28	47	55	40.00	-
Quartz	SiO ₂	26	28	32	20	26.50	12
K-feldspar	K(Al,Fe)Si ₂ O ₈	-	-	-	15	15.00	10
Hematite	Fe ₂ O ₃	-	-	-	10	10.00	-
Dolomite	Ca,Mg(CO ₃) ₂	-	18	-	-	18.00	-
Palygorskite	(Mg,Al) ₅ (Si,Al) ₈ O ₂₀ (OH) ₂ .8H ₂ O	-	14	-	-	14.00	-
Nontronite	(Fe,Al)Si ₂ O ₅ (OH).xH ₂ O	20	12	20	-	17.33	41
Bassanite	CaSO ₄ .0.5H ₂ O	-	-	1	-	1.00	-
Sanidine	(Na,K)(Si ₃ Al)O ₈	18	-	-	-	18.00	-
Calcite	CaCO ₃	6	-	-	-	6.00	12
*Amorphous	-	-	-	-	-	-	25
Total	-	100	100	100	100	-	100

Note: * This may compose of non-crystalline materials used in improving the quality of the imported clay.

Table 2. Major oxide compositions of the studied clays and commercially imported clay (CIC)

Oxide (wt%)	SPL6	SPL8	SPL11	SPL15	Av. value	CIC(Wyoming)
SiO₂	57.08	53.70	59.11	51.67	55.39	59.09
Al₂O₃	19.15	15.78	19.69	25.49	20	18.53
Fe₂O₃	7.05	6.62	7.59	10.08	7.84	5.09
MgO	0.78	5.06	1.41	0.56	1.95	3.24
CaO	3.79	4.69	1.99	0.01	2.62	2.25
Na₂O	0.25	0.08	0.07	0.05	0.11	2.71
K₂O	1.07	0.47	0.61	0.79	0.74	0.77
MnO	0.05	0.11	0.07	0.01	0.06	0.06
TiO₂	0.86	1.01	1.15	1.51	1.13	0.78
P₂O₅	0.03	0.23	0.33	0.16	0.19	0.15
S₀₃	1.47	1.03	0.41	0.01	0.73	0.98
LOI	8.42	11.22	7.57	9.66	9.22	6.35
Total	100	100	100	100	100	100
Oxides ratio						
SiO₂/Al₂O₃	3.00	3.45	3.00	2.03		
CaO/Na₂O	18.95	78.17	28.43	0.20		
K₂O/Al₂O₃	0.06	0.03	0.03	0.03		
Fe₂O₃/K₂O	6.65	14.69	12.44	6.63		
CaO/TiO₂	4.41	4.64	1.73	0.01		
MgO/TiO₂	0.91	5.01	1.23	0.36		
Na₂O/TiO₂	0.23	0.06	0.06	0.03		
CIA%	79	75	88	97		

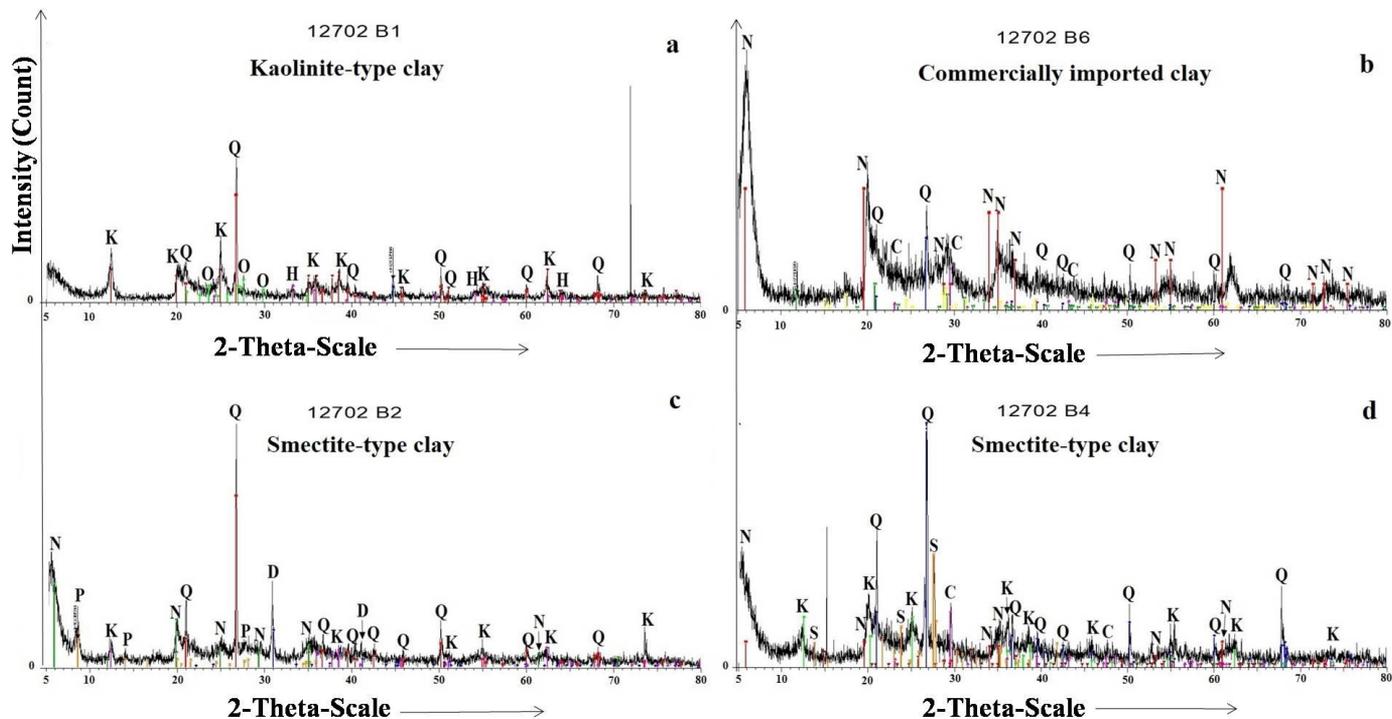


Figure 3. Representative XRD patterns of the local studied and the commercially imported clays

Note: [K= Kaolinite, Q= Quartz, O= K-felspar H= Hematite, D= Dolomite, P= Palygorskite, N= Nontronite, B= Bassanite, C= Calcite, S= Sanidine]

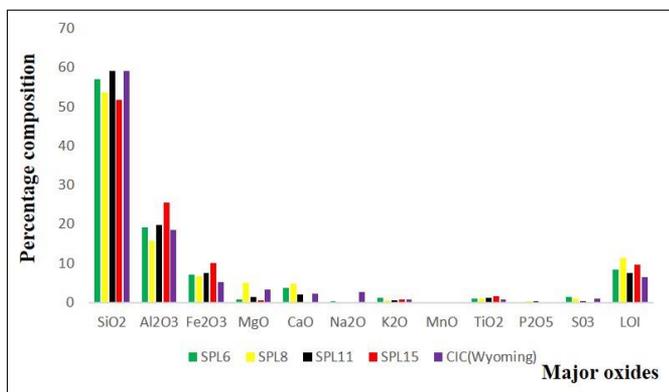


Figure 4. Plot of major oxide compositions of the studied clay in comparison with the CIC

However, the mobility of these critical elements during the wet season could have resulted in an acidic environmental condition suitable for the precipitation of kaolinite in SPL15, where the Al+Fe/Si ratio is enhanced [21-23]. This observation is corroborated by the low pH values recorded. Conversely, the concentration of alkaline elements and elevated Al+Fe could inevitably resulted in an alkaline condition suitable for the precipitation of smectite under drought climatic conditions [24-27]. However, this scenario may possibly suggest the reason why smectite and kaolinite minerals co-existed in some of the studied samples.

Simultaneously, the octahedral composition of smectites as described on an Mg-Al-Fe triangular plot (Figure 5), was performed by integrating fields of various workers [28-33], produced for dioctahedral smectites. SPL6, SPL8, and SPL11 plot close to the Al field next to the Wyoming type montmorillonites. It is significant in that it distinguished the smectite-type of the local clays from the kaolinite-type. Therefore, the region where the three samples plot could be

reasonably regarded as the "nontronite field" in this scheme, as they critically contained a more significant percentage of Fe/Al as compared to CIC, which also may be regarded as Al-Fe rich smectite.

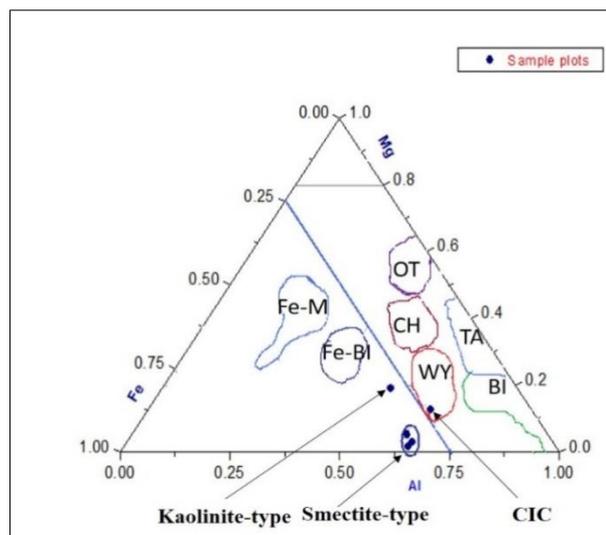


Figure 5. Ternary variation plot of the main octahedral cations for smectites [28-33]

[TA = Tatavilla-and OT = Otoy-type montmorillonites; CH= Cheto-type montmorillonites; Wy = Wyoming-type montmorillonites and Fe-M =Fe-rich varieties; BI= beidellite and Fe-BI = Fe-rich beidellites]

Also, the chemical index of alteration (CIA) proposed by Nesbitt and Young [34], was calculated for the studied samples to establish the extent of alteration/weathering. The CIA varied from (75-97%), this indicates reduction in the contents of alkali and alkaline earth elements (Table 2), as recorded from the studied clays, typically suggesting a relatively intense weathered source area [7]. The significant

presence of kaolinite in the investigated clays could undoubtedly lead to poor rheological properties since such type of clay has low swelling capability.

5. CONCLUSIONS

The mineralogy and chemical compositions of clay/shale samples from part of southeastern Nigeria were successfully assessed and characterized to ascertain their potential use as drilling mud. The results showed, three out of the four analyzed samples are typically characterized, as smectite-type, which relatively correlated with the commercially imported clay, while the other is kaolinite-type. They consist of kaolinite, nontronite (ferric-smectite), and palygorskite clay minerals in addition to other non-clay minerals like quartz, K-feldspar, calcite, dolomite, and iron minerals. Kaolinite and quartz are the most dominant minerals, as they occurred in all the samples.

The outcome of this study broadly demonstrates a wide range of industrial applications of the local clays. Conversely, the considered Nigerian clays are compositionally not comparable to the commercially imported clay, which varies significantly, corroborating observations of earlier workers. A significant proportion of the CIC is contained in an amorphous phase, suspected to be additives applied to improve its quality.

Therefore, it is our view that pre-treatment/processing may undoubtedly help to overcome the compositional disparities/deficits in the local clays. Besides, relevant treatment approaches, preferably a significant level of blending and beneficiation with lime as refining techniques, are therefore recommended. However, the discussed results in light of the mineralogical and chemical properties of the studied clay/shales and the attendant drilling mud challenges are under no circumstances exhaustive. Thus, a sufficiently detailed rheological and filtration characterization, on the samples with a positive prospect, can be seen as a focus for future study.

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