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ARTICLE

Paleo-environmental conditions, paleoclimatic significance and effects of weathering on clay deposits in the Lower Benue Trough, Nigeria. Mineralogical approach

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ABSTRACT

Combined methods for mineralogical identifications were used to characterise the clay deposits within the Lower Benue Trough of Nigeria to interpret paleo-environmental conditions, the paleoclimatic significance of the trough, and effects of weathering on the minerals as factors that favour its deposition/accumulation within the trough which host other important industrial minerals like coal, barite, limestone etc. Bulk-sample random-powder XRD data and data for clay fractions deposited onto zero-background quartz plates were measured. The samples contained kaolinite, vermiculite, and traces of smectite, and the non-clay phases included quartz, microcline, and muscovite. All samples were unaffected after glycolation, confirming the absence of significant smectite. Muscovite was characterized by the nature of its 10 Å basal peak with a width of <0.10° 2θ, which was very sharp. DTA/TGA results support the presence of kaolinite, and the characteristic kaolinite O-H, Al-OH, Si-OH and Si-O-Al FTIR bands also confirmed its presence. Vermicular and book-like morphologies were observed under the SEM, typical of kaolinitic clay from in situ alteration. High kaolinite abundance in these sediments is consistent with intense weathering of parent rocks rich in Al under wet/tropical paleo-climatic conditions with fresh and/or brackish water conditions in a continental setting. The variety of observed morphologies suggests that the deposits suffered more of chemical weathering. The clay deposits in Lower Benue Trough are quartz-rich, kaolinitic and derived from the chemical weathering of Al-rich source rocks.

1. Introduction

Clays are earthly and naturally fine-grained inorganic polymineralic materials of < 2 μm in size. The layered structures of these hydrated aluminosilicates clay minerals determine their characteristic chemical and physical properties of the clays which are formed as a result of chemical weathering of pre-existing crystalline rocks and feldspar minerals under warm tropical and subtropical climatic conditions or as a result of the hydrothermal alteration [1].

The basic structure of layer silicates and all silicates ion

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(SiO_4^{4-}), where the silicon occupies the tetrahedral site. The aluminium ion (Al^{3+}) can substitute for Si^{4+}, but it is generally located in the octahedral sheet. Their characteristic auto construction form the unit cell of layering to yield; 1:1 type of clay minerals that consist both tetrahedral and octahedral sheets to form; kaolinite–serpentinite, kaolinite and halloysite clay minerals [2] and 2:1 types of clay minerals that have two tetrahedrally coordinated sheets of cations both positioned in between the octahedral sheet to form illite, montmorillonite, chlorite [3, 4, 5]. The major geological process that is responsible for the compositional trend of clay rich sediments is chemical weathering although the parent rock in some instances weathers into soils and clays by combined action of biological, chemical and physical weathering [6,7]. It has been proven that imprints of the original composition of the precursor are readily preserved in the sediments [8, 9, 10].

In this present investigation, representative sedimentary clay samples from Mamu/Ajali and Enugu/Nkporo Formations within the Lower Benue Trough were examined mineralogically using combined methods: X-ray diffraction (XRD), differential thermal analysis (DTA), thermogravimetry (TGA) and scanning electron microscope (SEM) were employed to understand significant compositional changes in response to subtle changes in conditions of the clay through the use of DTA/TGA techniques, interpret the paleoenvironment and paleoclimate conditions from the clay assemblages and to understand the change in mineral morphology associated with weathering under different climatic conditions

2. Location and geological description

The study area is located between latitude 6°00' - 8°00' N and longitude 6°50' - 8°00' E (Figure 1). The area is connected by tarred road, which leads from Aloji to Ofejiji, Udanebiomi, Abocho, Agbenema, Eke-efe, Otukpa, Okpokwu and Enugu (Figure 2). The roads are motorable all the year round. Clay samples were collected from road cuts. Total area covered for this investigation is 25,134.84km^2 (Figures 1 and 2).

Distributions of clay mineral of Cretaceous (Campanian-Maastrichtian) age in different geological situation that occurred in the Lower Benue Trough of Nigeria were studied (Figures 1 and 3).

Description of the unit starts with sedimentation in the Lower Benue Trough which commenced with the: Marine Albian Asu River Group, this constitutes the shales, limestones and lenses of sandstone within the Abakaliki Formation from the area of Abakaliki and the limestone of Mfamosing in the flank of Calabar [11] (Figures 4 and 5). Following this formation, Ezeaku Shales and the Makurdi Formation of Turonian occurred. The Ezeaku Shales is characterized with the presence of thick flaggy (calcareous and non-calcareous) shales, sandy and calcareous sandstones with shelly limestones. Outcrops of this formation are prominent towards the south area of Oturkpo division (Egedde-Oju area) with about 304.8 meters thick in the area and reaches 609.6 meters. Below the Ezeaku Formation is the marine Nkalagu Formation (black shales, limestones and siltsones) Cenomanian – Turonian. Deformation during the Mid-Santonian in the Benue Trough led to the displacement of the major depositional axis westward leading to the formation of the Anambra Basin. Therefore, Anambra Basin constitute the Post-deformational sedimentation in the Lower Benue Trough and sedimentation within the Anambra Basin commenced with the Campanian-Maastrichtian marine and paralic shales of the Enugu and Nkporo Formations, this is followed by the coal measures of the Mamu Formation. The Ajali and Owelli Formations is characterized by the presence of fluviodeltaic sandstones that lie conformably on the Mamu Formation and its lateral equivalents are constituted in most places. During the epoch of overall regression of the Nkporo cycle, coal-bearing Mamu Formation and the Ajali Sandstone accumulated. The Mamu Formation is characterized by a narrow strip trending north-south from the flank of Calabar, going west around the plateau of Ankpa and terminates close to River Niger at Idah [12] (Figures 4 and 5). During the Paleocene, another onset of transgression in the Anambra Basin was marked by the Nsukka Formation and the Imo shale while the regressive conditions was returned during Eocene by the mark of Nanka sands. These Nanka Formation gives an excellent opportunity to study deposits of tidal origin. Well-exposed, strongly assymetrical sandwaves suggest the predominance of flood-tidal currents over weak ebbreverse currents. The presence of the latter are only suggested by the bundling of lamine separated outcrop of the Nanka Formation is the Umunya section, 18km from the Niger bridge at Onitsha on the Enugu – Onitsha express-way (Figures 3,4 and 5).

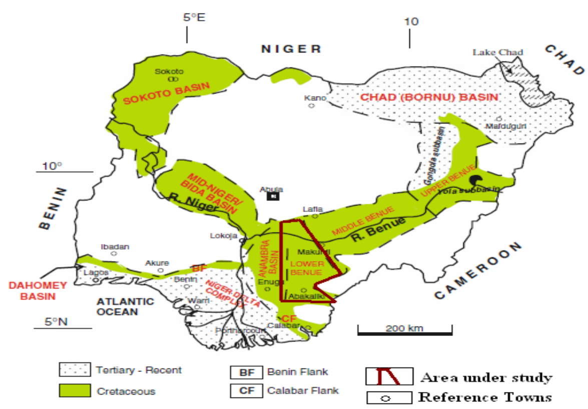


Figure 1. The position of Lower Benue Trough within the map of Nigeria [12]

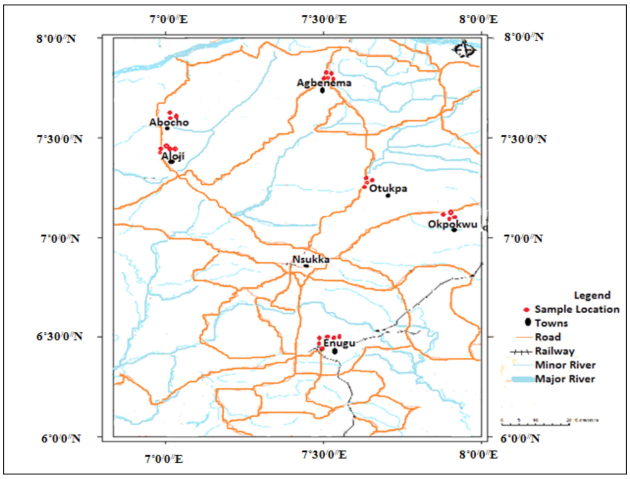


Figure 2. Sample location on a sketch map of the study area

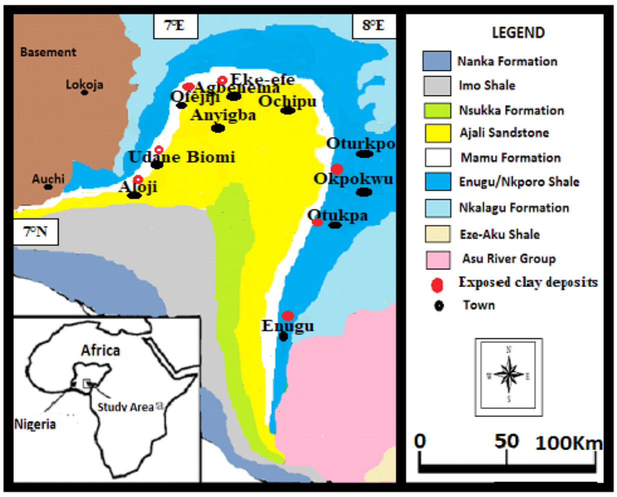


Figure 3. Location of exposures on the geologic map of Lower Benue Trough [13]

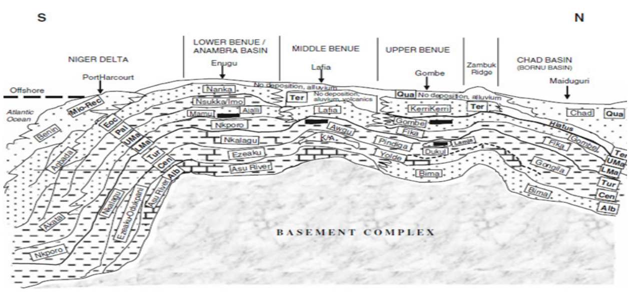


Figure 4. The N–S stratigraphic cross-section across the Benue Trough [12]

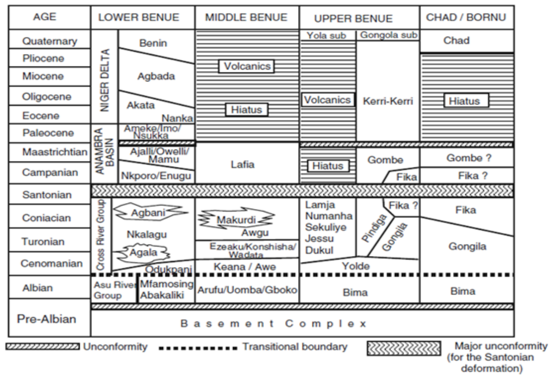
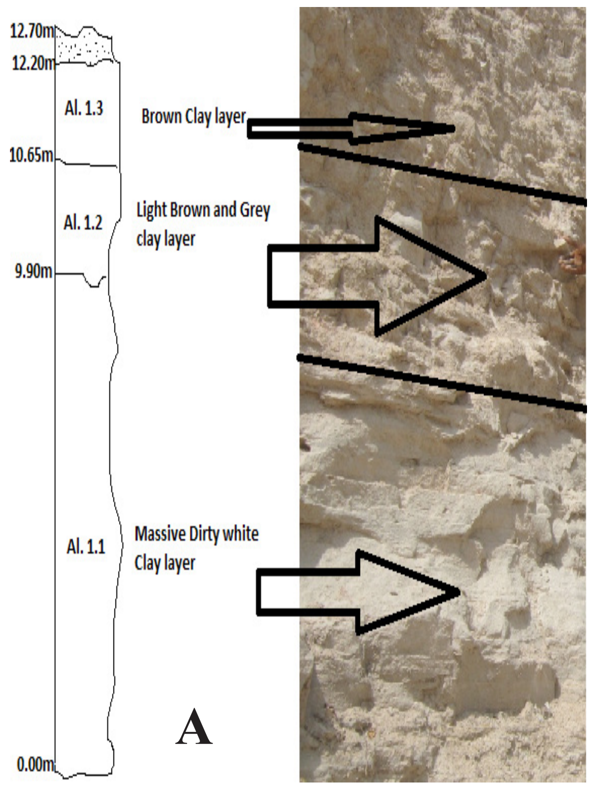


Figure 5. The Benue Trough: Its stratigraphic successions [14, 15]

3. Materials and methods of study

Thirty four (34) clay samples representing different vertical sections of the exposures in Aloji, Agbenema, Ochipu, Otukpo, Okpokwu from Mamu/Ajali Formation and Enugu from Enugu/Nkporo Formation within the Lower Benue Trough were collected with effort made by avoiding weathered horizons (Figures 2, 3 and 6). The samples were pulverized and packaged for XRD, scanning electron microscope (SEM), differential thermal/thermogravimetric analysis (DTA/TGA), and fourier transform infra-red analysis (FTIR) at the Geological Sciences Department, Indiana University, Bloomington, Indiana, U.S.A.



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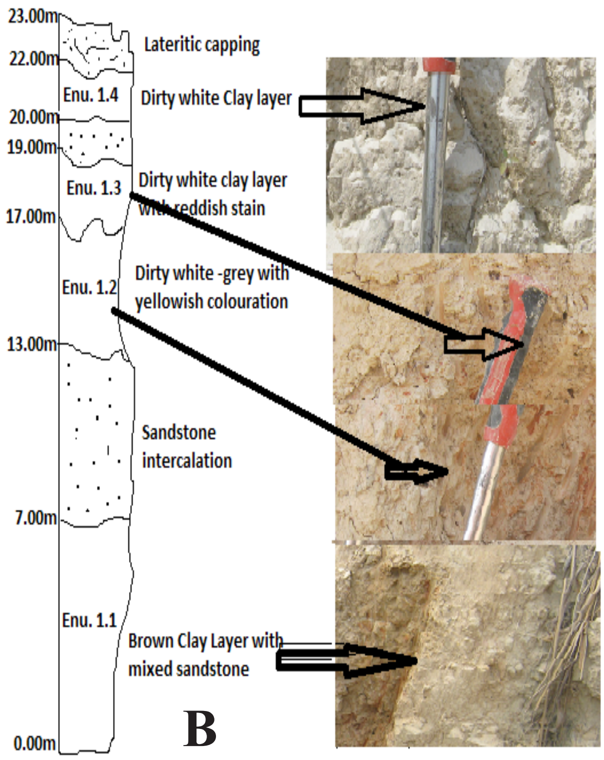

Figure 6. Sample points of clay deposits

Note: (A) at Aloji along Ayingba-Itobe road, Mamu/Ajali Formation (7°24'45″ N and 6°56'17″ E) and (B) along the Abakaliki - Onitsha road, within Iva Valley, Enugu/Nkporo Formation (06°27'54.6" N and 7°27'17.1" E)[13].

X-ray diffraction analysis was performed using a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (45 kV, 35 mA), step-scanning from 2°-70° and counting for 2 sec per 0.02° step. Data were analyzed using Bruker AXS Eva and Topas software. Both randomly oriented mounts and oriented mounts were carried out and the relative phase amounts (weight %) was estimated using the Rietveld refinement method [16, 17].

In this work random orientation of the clay sample was achieved by allowing the free fall of the powdered raw clay samples into a 1 mm deep cavity in a Ti sample mount, thereby minimizing preferential orientation of clay crystallites while for the orient mount, the clay samples were prepared as follows: separation of fine fraction from the raw clay based on Stokes law settling in an aqueous. The method of separation involves placing a sample in the blender with distilled water, filling the blender about 1/3 full, and blending the sample for 10 minutes to disaggregate the material. All preparation steps to this point served to produce a disaggregated suspension of the material that is suitable for further size separation via settling and centrifuging. The content was poured into a beaker for sedimentation over about 24 hours. Turbid liquid in middle or upper was then poured into a centrifuge tube and centrifuge at 8000 r/min for 45 min. The residues in bottom of the tube was collected and spread on a glass dish for air dry. 5g of dried fine clay sample was then dispersed in distilled water for preparation of clay slurry. The clay slurry was sedimented onto a zero-background quartz plate to prepare an orient mount. The sample was dried on the quartz plate at room temperature and analyzed. The analyzed sample was exposed to ethylene glycol vapor for a minimum of 24 hours and then analyzed again.

The thermoanalytical methods complement the X- ray diffraction analysis (XRD). Thermal analysis (DTA/TGA) were carried out using a SDT 2960 Simultaneous DSC/TGA analyzer at a heating rate of 10°C/min in the range ambient to 900°C with alumina as standard. Size separated < 2 μm samples were used for thermal analysis.

The morphology and texture of the clay particles were determined by scanning electron microscopy using an environmental SEM Scanning Electron Microscope (FEI Quanta 400 FEG) which requires no coating.

The fourier transform infra red (FITR) spectra of the samples were recorded between 4000 and 400 cm^{-1} on Nicolet 6700 FITR spectroscope. The size separated < 2 m samples were dispersed in KBr in the ratio (1:200) and are pressed into discs at high pressure to obtain the transparent disc which was then placed in the sample compartment for scanning.

4. Results and Discussion

XRD data for clay samples from Lower Benue Trough, measured over the region from 2-70°2θ, revealed two clay minerals (Figure 7). These include dominant kaolinite with peaks at 12.4°, 25° and 38° 2 – Theta, followed by traces of vermiculite with peak at at 6.1° 2 – Theta and non clay minerals include dominant quartz with peaks at 21°, 27°, 37°, 44°, 50° and 60° 2 - Theta while muscovite peaks were recorded at 8.9° and 17°, microcline occur at 27° and 30° 2 – Theta values correspondingly (Figure 7; Table 1). The clay samples are very similar in compositional trend. All the investigated clay samples were characterised by the presence of kaolinite, which constitute between 40-60 % , of all the clay and presence of high composition of quartz (50-69 %; Table 1) accounts for their grittiness. The presence of negligible peaks of microcline (1 – 5 %) and muscovite (1 – 8 %) in the raw clay samples (Figure 7; Table 1) suggests intense weathering of the parent rock to form the clay deposits. The presence of traces of vermiculite indicates alteration of biotite in the felsic protoliths to vermiculite.

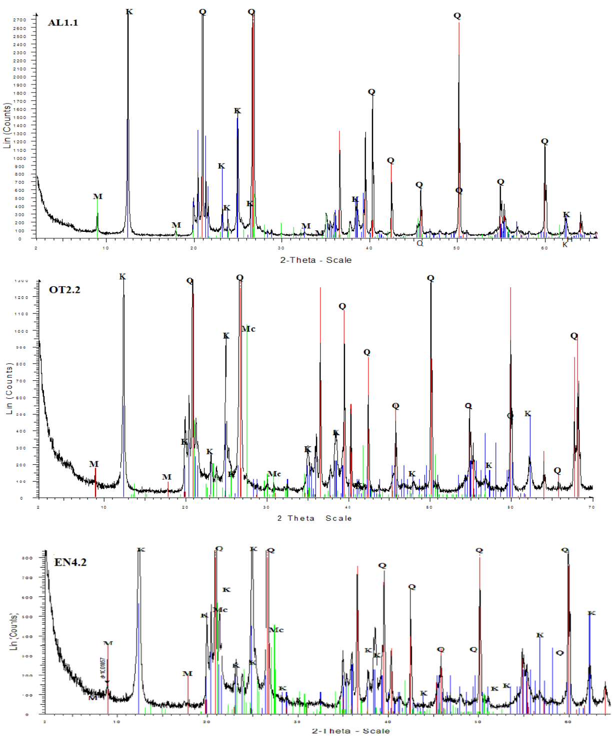

Figure 7. X-ray diffractogram of raw clay sample from Aloji (AL1.1), Oturkpa (OT1.1) and Enugu (EN4.3) within the Lower Benue Trough, Nigeria K - Kaolinite, M - Muscovite, Q - Quartz

XRD data were obtained for oriented aggregates over a 2θ range from 2 - 70° after the samples were (i) air dried and (ii) glycolated. Data for air-dried samples revealed the presence of kaolinite at 12.4°, 25° and 38° 2θ and traces of vermiculite at 2θ value of 6.1° (Figure 8; Table 2). Quartz peaks are mostly at 21°, 27°, 37°, 44°, 50° and 60° 2θ values while muscovite occur at 8.9° and 17°, microcline at 27° and 30° 2θ values (Figure 8; Table 2), All the investigated air-dried samples contained abundant kaolinite (39 -79 %) but poor in quartz (17 – 40 %) compared to the raw clay samples with kaolinite of 40 – 60 %, quartz 50 - 69 %.

Muscovite, a 2:1, dioctahedral mica, was observed at 8.9° to 17° 2 - Theta. Illite and muscovite were distigushed using the method that starts that very sharp 1st order basal peak with a width of <0.10° 2θ is related to muscovite and broad peaks to Illite [18, 19] (Figure 8). The presence of muscovite (1 – 8 %) and traces of microcline (1 – 7 %) suggest felsic source rock that suffered incipient weathering and moderate distance of transportation (Table 2).

The mineralogy of the solvated, ethylene glycol treated clay samples showed that the kaolinite peaks at 12.4°, 25° and 38° 2θ values, in all samples, were not affected (Figure 8). Vermiculite also showed no shift in the 6.1 2θ peak (Figure 8). The observed feldspar and muscovite peaks

Table 1. Mineralogical composition (% vol.) of raw clay deposits from different locations within the Lower Benue Trough, Nigeria

Sample No.→ Minerals↓	AL1.1	AL1.2	AL1.3	AL2.1	AL2.2	AL2.4	AL2.5	OF1.3	OF2.1	OF2.2
Quartz	46	50	48	54	52	53	55	50	50	49
Microcline	3	5	3	----	---	2	3	2	2	4
Kaolinite	46	45	46	42	44	45	40	44	46	44
Vermiculite	---	---	--	---	---	---	---	---	---	---
Muscovite	5	---	3	4	4	---	2	4	2	3
Total	100	100	100	100	100	100	100	100	100	100

SampleNo →Elements ↓	OF2.3	OF2.4	OF2.5	AG1.1	AG1.2	AG2.2	AG2.1	OT1.1	OT1.2	OT2.1	OT2.2
Quartz	50	57	53	50	48	52	49	49	**50**	**48**	**45**
Microcline	3	-----	----	5		3	3	--	--	---	--
Kaolinite	43	41	44	43	49	40	42	46	45	50	48
Vermiculite	----	----	----	2	1	2	3	3	2	2	4
Muscovite	4	---	3	---	2	3	4	2	1	---	3
Total	100	100	100	100	100	100	100	100	100	100	100

Mamu/Ajali Formation clay:
Aloji samples
AL1.1, AL1.2, AL1.3, AL2.1, AL2.2, AL. 2.4 and AL2.5.
Ofejiji samples
OF1.1, OF1.3, OF2.1, OF2.2, OF2.3, OF2.4 and OF2.5.
Agbenema samples
AG1.1, AG1.2, AG2.1 and AG2.2.
Oturkpa samples
OT1.1 and OT1.2, OT2.1, OT2.2.

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in raw and air dried samples were retained in the treated samples (Figure 8).

Data obtained from the raw clay samples of Aloji, Ofejiji, Agbenema, Oturkpa, Okpokwu and Enugu of Mamu/Ajali and Enugu/Nkporo Formations shows that the clay deposits are kaolinitic with appreciable amounts of microcline and muscovite and very high quartz content. The presence of kaolinite, quartz and muscovite suggests derivation of the clays from felsic rocks in a continental environment.

Table 1. Cont.

SampleNo →Elements ↓	OK1.1	OK1.2	OK3.1	OK3.2	EN2.1	EN2.2	EN3.1	EN3.2	EN4.1	EN4.2	EN4.3
Quartz	44	47	49	47	47	44	43	45	37	39	43
Microcline	---	4	3	3	---	---	4	---	---	4	3
Kaolinite	45	47	46	47	46	49	47	48	55	50	47
Vermiculite	---	2	---	---	---	3	2	3	4	---	3
Muscovite	8	---	2	1	6	3	3	2	2	5	---
Ilmenite	---	---	---	---	---	---	---	---	---	---	3
Total	97	100	100	100	100	100	100	100	100	100	100

Mamu/Ajali Formation clay samples:
Okpokwu - OK 1.1, OK1.2, OK. 3.1and OK3.2.
Enugu/Nkporo Formation clay samples:
Enugu - EN2.1, EN2.2, EN3.1, EN3.2, EN4.1, EN4.2 and EN4.3.
Okpokwu - OK 1.1, OK1.2, OK. 3.1and OK3.2.
Enugu/Nkporo Formation clay samples:
Enugu - EN2.1, EN2.2, EN3.1, EN3.2, EN4.1, EN4.2 and EN4.3.

Table 2. Mineralogical composition (% vol.) of <2µm clay fractions from Mamu/Ajali and Enugu/Nkporo Formation within the Lower Benue Trough, Nigeria

Sample No→ Minerals↓	AL 1.1	AL 1.2	AL 1.3	AL2.1	AL2.2	AL2.3	OF2.1	OF 2.2	OF2.3	AG1.1	AG1.2	AG 2.1	AG2.2
Quartz	48	31	35	40	40	44	38	34	37	40	43	45	41
Microcline	2	3	8	5	2	--	2	4	2	3	2	3	2
Kaolinite	39	53	45	52	50	49	55	59	58	50	54	47	50
Vermiculite	3	1	4	--	3	4	3	1	--	--	---	---	---
Muscovite	6	9	8	3	5	3	2	1	3	7	1	5	7
Total	100	100	100	100	100	100	100	100	100	100	100	100	100

SampleNo → Elements ↓	OT1.1	OT1.2	OK1.1	OK1.2	OK3.1	OK3.2	EN2.1	EN2.2	EN3.1	EN3.3	EN4.1	EN4.2	EN4.3
Quartz	30	35	27	36	35	33	30	25	21	28	20	28	17
Microcline	--	4	3	3	----	---	--	---	2		4	2	2
Kaolinite	65	58	69	57	62	58	63	65	73	70	73	62	79
Vermiculite	3	2	--	3	1	6	---	2	---	---	---	2	---
Muscovite	2	--	1	1	--	2	6	8	4	2	3	6	2
Total	100	99	100	100	98	100	99	100	100	100	100	100	100

Mamu/Ajali Formation clay samples:
Aloji - AL1.1, AL1.2, AL1.3, AL2.1, AL2.1 and AL2.3.
Ofejiji - OF2.1, OF2.2 and OF 2.3.
Agbenema - AG1.1, AG1.2, AG2.1 and AG2.2.
Oturkpa - OT1.1, OT1.2, OT2.1 and OT2.2.
Okpokwu - OK1.1, OK1.2, OK3.1 and OK3.2.
Enugu/Nkporo Formation clay samples:
Enugu - EN2.1, EN2.2 EN3.1, EN3.2, EN4.1, EN4.2 and EN4.3.

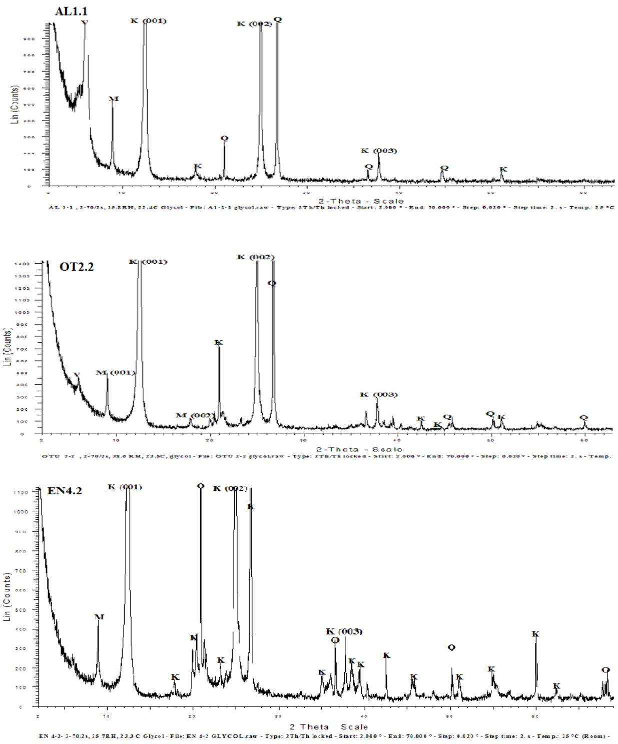

Figure 8. X-ray diffractogram of glycolated <2 **μ**m clay samples from Aloji (AL1.1), Oturkpa

Note: (OK2.2) of Mamu/Ajali Formation and Enugu (EN4.2) within the Lower Benue Trough,Nigeria. V - Vermiculite, M - Muscovite, K - Kaolinite, Q - Quartz

The thermal properties of the investigated clay were undertaken using differential thermal and thermogravimetric analysis (DTA and TGA). The characteristic patterns of the fine fractions (< 2 m) and loss in volume is presented in Figures 19 to 21 and Table 2 accordingly. DTA and TGA curves of the clay samples are given for the temperature range of 10-900°C. The first endothermic peak observed within the range of 138 – 154°C is due to the elimination of hygroscopic and zeolitic waters; the second endothermic peak observed within the range of 408.41 to 519.67°C is due to dehydroxylation [20, 21]. The last endothermic peak between 860 to 900°C is followed by an exothermic peak due to recrystallization into a possible new phase formation known as mullite [21].

The weight loss during thermogravimetric analysis revealed that samples from Mamu/Ajali Formation ranged between 0.76 to 1.26 mg (Figure 9a and Table 3) while those of Enugu/Nkporo Formation is 1.21 to 2.11 mg (Figure 9b and Table 3). The slightly higher values of the Enugu/Nkporo Formation samples could be attributed to presence of higher finer particles with organic matter. Weight loss for all the clay samples were recorded between 499 °C and 504 °C, probably due to large organic matter decomposition with loss in weight increasing with temperature. This is consistent with author 21 assertion that kaolinites undergoes dehydroxylation at 408°C to 520°C to form metakaolin. The thermogravimetric patterns (Figures 9a – c; Table 3) of the fine (<2μm) clay sample is generally consistent with the results of the mineralogy.

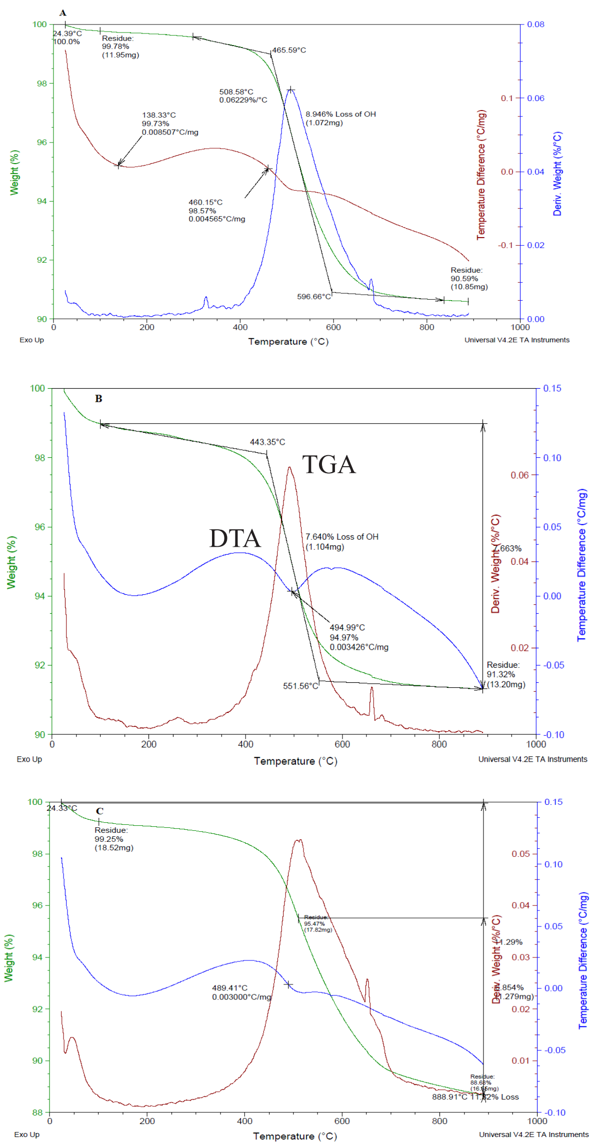

Figure 9. DTA/TGA curves for <2**μ**m clay fraction from (A): Aloji (AL1.1) (B): Okpokwu (OK1.1) of Mamu/Ajali Formation and (C): Enugu (EN.4.2) of Enugu/Nkporo within the Lower Benue Trough, Nigeria

The mineralogical and structural data obtained from the XRD and DTA-TGA were complemented with FTIR. Fine (< 2μm) clay samples from Aloji (AL1.1, AL1.2, AL1.3), Oturkpa (OT2.2), Okpokwu (OK1.1) and Enugu (EN2.1, EN3.1, EN4.2, EN4.3) within the Lower Benue Trough

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Table 3. Weight loss (% vol.) of representative clay sample from Mamu/Ajali and Enugu/Nkporo Formation, Lower Benue Trough, Nigeria

Sample No:	AL1.1	AL1.2	AL2.2	EK1.2	OK1.1	OT2.2	EN2.1	EN3.1	EN4.2	EN.4.3
Initial Vol.(mg)	11.98	13.36	13.01	15.52	14.46	13.45	11.57	18.66	12.86	14.63
Residue(mg)	10.85	12.60	12.10	14.22	13.20	12.27	10.25	16.55	11.15	13.42
Vol. Loss(mg)	1.13	0.76	0.91	1.30	1.26	1.18	1.32	2.11	1.71	1.21
Loss OH(Wt %)	9.41	5.68	6.94	7.98	7.66	8.10	10.35	11.29	12.67	8.17

Mamu/Ajali Formation clay samples:
Aloji - AL1.1, AL1.2, AL2.2; Okpokwu - OK1.1; Oturkpa - OT2.2
Enugu/Nkporo Formation clay samples:
Enugu - EN2.1 and EN3.1.

were subjected to IR spectral studies.

The charateristic infrared spectra of the sampled clay is presented in Figures 10 a – c and Table 4 revealed Al – O - H stretching at 3659.51 cm^{-1} to 3696.20 cm^{-1} bands, typical of kaolin group, 3621.22 cm^{-1} and 3622.12 cm^{-1} infers OH stretching and bands between 3438.28 cm^{-1} and 3447.25 cm^{-1} reflects absorption of water (H – O – H) within the crystal layers of the clay mineral, but this was absent in one sample from Aloji (AL1.1), this suggest presence of high quartz (Figure 10a). A C – H stretching occured at 2925.97 cm^{-1} in one sample from Enugu (EN3.1) (Figure 20c, Table 4), inferring presence of organic matters. Bands ranging from 1625.47 cm^{-1} – 1628.25 cm^{-1} observed in all the investigated samples except for two samples from Aloji (AL1.1 and AL1.2) describes the presence of water (H – O – H bending of water), another, typical spectrum kaolin was observed within the range from 1104.00 cm^{-1} to 1110.08 cm^{-1} with an AL – O – H stretching characteristic. From 915.12 cm^{-1} to 918.10 cm^{-1}, which is close to the proposed value of 912 cm^{-1} reflects OH – deformation linked to th $2Al^{2+}$ while the bands varying from 689.76 cm^{-1} to 790.41 cm^{-1} reflects abundance of quartz (Figure 10 a – c; Table 4.4). The bands between 538.17 cm^{-1} and 542.45 cm^{-1} close to the proposed 537 cm^{-1} reveals the presence of Fe_2O_3 and Si – O – Al stretching but 457.24 to 471.11 cm^{-1} spectrum bands signify Si – O – Si bending.

Si-O and Al-OH functional groups are in the 1000cm^{-1} and 500 cm^{-1} region. Muscovite and possibly quartz interference was observed at 1032.16 in Oturkpa (OT2.2), 1034.21 in Okpokwu (OK1.1) , 1030.06 and 1033.52 in Enugu (EN3.1 and EN4.2) for the studied clay samples. The corresponding bands at 915.78 – 918.17 cm^{-1} infer Al-OH bending vibrations but 784.76 -789.78 cm^{-1} suggest Si-O-Si inter tetrahedral bridging bonds in SiO_2 for typical kaolinitic clay minerals. The bands between 1625.94 – 1888.91 cm^{-1} signifies the region were OH deformation of water is found (Table 4). The FTIR results corroborated the quartz-rich, kaolinitic clay results obtained from the XRD data of the clay deposits.

The obtained FTIR bands of the clay samples were compared with a proposed typical kaolinitic spectrum[22] as shown in table 4.

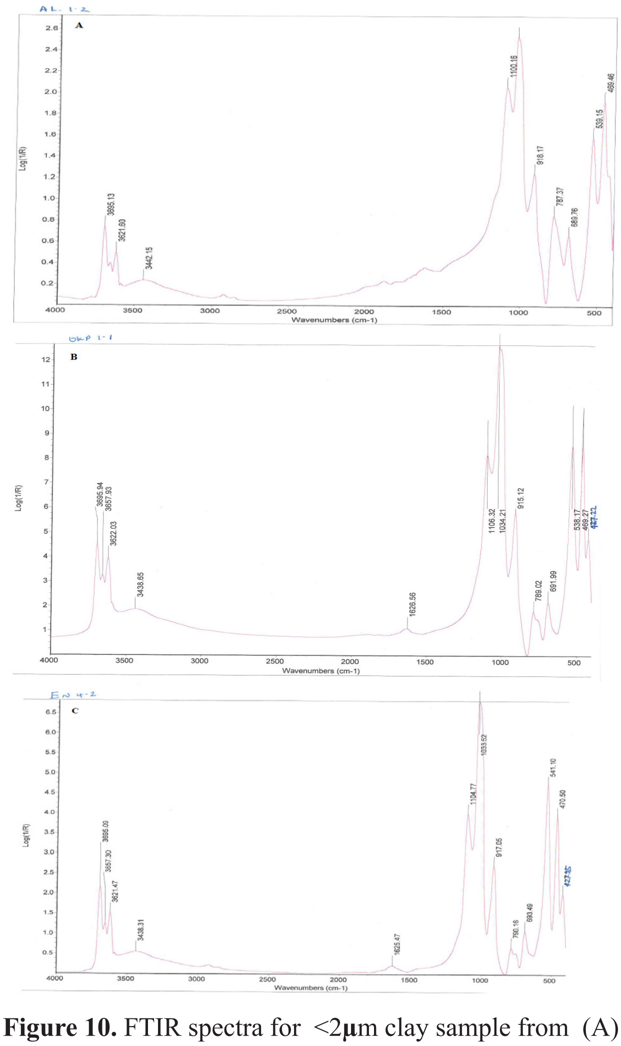

Figure 10. FTIR spectra for <2μm clay sample from (A): Aloji (AL1.2) and (B): Okpokwu (OK1.1) of Mamu/Ajali Formation and (C): Enugu (EN4.2), Enugu/Nkporo Formation within the Lower Benue Trough, Nigeria

Table 4. Wavenumbers of clay samples from Mamu/Ajali and Enugu/Nkporo Formations from Lower Benue Trough compared to theoretical kaolin

Theoretical Kaolin	AL. 1.1	AL. 1.2	Al.1.3	EK.1.2	EN.2.1	EN. 4.3	EN.4.2	EN.3.1	OK.1.1	OT2.2	Assignments
3694	3694.59	3695.13	3695.49	3695.17	3696.20	3693.58	3695.09	3694.71	3695.94	3694.81	Al---O-H stretching
3650	3659.51	----	3657.63		3656.53	3659.82	3657.30	3658.74	3657.93	3659.02	Al---O-H stretching
3620	3621.70	3621.60	3622.14	3621.59	3621.69	3620.66	3621.47	3621.20	3622.03	3621.44	OH Stretching, Crystalline hydroxyl
				3591.55	3593.15	3589.07		3590.16		3591.19	OH Stretching, Crystalline hydroxyl
		3442.15	3443.30	3443.09	3447.25	3445.42	3438.31	3443.04	3438.65	3438.28	H-O-H stretching, Absorbed water
				2924.68				2925.97			C-H stretching
				2857.54							C-H stretching
			1625.94	1625.76	1628.25	1625.53	1625.47	1624.73	1626.56	1626.08	H-O-H bending of water
----	1149										
1114	1110.08		1104.00	1109.87	1110.90	1104.29	1104.77	1106.94	1106.32	1107.91	Al---O-H stretching
					1087.37						Si-O quartz
					1071.80						Si-O quartz
1032				1037.77	1037.00		1033.52	1030.06	1034.21	1032.16	Si-O stretching, Clay minerals
1010	1001.13	110.16		1009.88	1007.89					1015.07	Si-O stretching
912	916.45	918.17	917.41	915.78	915.14	918.10	917.05	916.96	915.12	916.49	OH deformation, linked to $2Al^{3-}$
790	788.92	787.37	784.76	789.78	789.65	789.55	790.16	790.60	789.02	790.41	Si-O quartz
693		689.76	693.35	692.91	692.45	692.27	693.49	693.17	691.99	693.55	Si-O quartz
				580.96							
537	542.45	539.15	538.95	543.15	539.08	542.27	541.10	541.13	538.17	538.88	Fe-O, Fe_2O_3, Si-O-Al stretching
	480.43										
468	457.24	469.46	470.16	468.79	468.93	471.11	470.50	470.63	469.27	470.21	Si-O-Si bending
	443.13										
430						428.58	427.85		427.22	426.98	
				418.33							

Mamu/Ajali Formation samples:
Aloji – AL1.1, AL1.2, AL1.3, Eke-efe – EK1.2, OK1.1, OT2.2.
Enugu/Nkporo Formation samples:
Enugu – EN3.1, EN4.2, EN4.3

Scanning electron micrographs were obtained for sample Aloji (AL1.1), Oturkpa (OT2.2) from Mamu/Ajali Formation, Enugu (EN4.2 and EN4.3) from Enugu/Nkporo Formation within the Lower Benue Trough. Fine (<2μm) clay samples were used for the SEM analysis. The micrographs provided the informations on the physical, geochemical processes and the environment in the genesis of the sedimentary clays.

The vermicular and book-like morphological characterstic under the SEM (Figures 11a, b, c and d), suggest a typical kaolinitic feature for the clays under investigation, generated from weathering processes [23, 24]. A face-to-face pattern of arrangement of platy crystals was observed in all the analyzed samples, this infers grains of kaolinite (Figure 11a). The irregular angular kaolinite edge is characteristic of actively growing crystals [23]. A swirl-like texture of muscovite was observed more in samples from Otukpa (OT2.2), and Enugu (Figure 11c) in association with face-to-face arrangement of kaolinitic grains and vermiculite, suggesting their detrital origin [24]. In the sed-

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imentary clay, finer clay grains are agglomerated as they are deposited by the cementing effect of organic matter thereby giving a flower - like appearance (Figure 11b). Two types of grains were observed, infering the diversity of the environment for their formation. Smaller kaolinite grains surround larger grains of smooth edges (Figure 11b). These bimodal features indicate that the finer grains are recrystallized product while the coarser grains are of detrital origin. Such a texture in kaolinite occurs due to incipient formation of this particular mineral in a waterlaiden condition from silicate parent material [23] (Figure 11 d).

The clay morphology reflected varied characteristic shapes in different environment of deposition within the Lower Benue Trough. A characterised thin plates and embayed edge was observed in all the clay samples (Figures 11c and d), suggesting that the clay underwent relatively stronger chemical weathering than physical weathering.

This study have proven that there is no evidence of the role of diagenesis in the formation of the clay minerals in the study area because there no observed change in the morphology of kaolinitic clay from aggregates of books to individual blockier crystals and on that basis, it can be an important tool in paleoclimatic studies [25] (Figures 11 a, b, c and d).

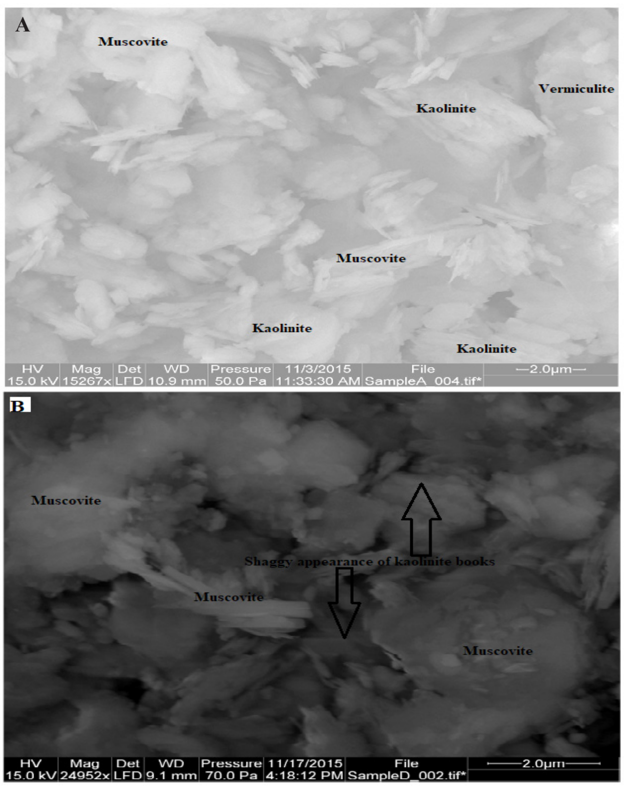

Figure 11 a, b. Scanning electron micrographs of clay samples from Mamu/Ajali Formation, Lower Benue Trough, Nigeria

Note: A = Aloji (Al.1.1), showing vermicular and book- like kaolinites having thin plates and embayed edge in association with detrital muscovite and B = Oturkpa (OT2.2) showing shaggy appearance of kaolinite books with thin plates within muscovite matrix showing flower/swirl – like structures.

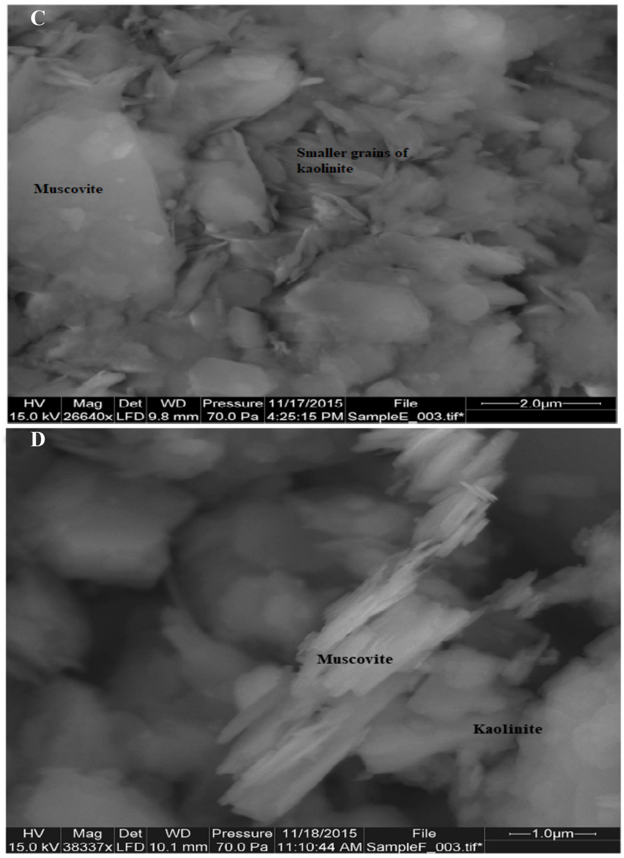

Figure 11 c, d. Scanning electron micrographs of clay sample from Enugu/Nkporo Formation, Lower Benue Trough

Note: (C) EN4.2 showing the smaller grains of kaolinite grains surrounding larger muscovite grains and (D) EN4.3 Muscovite surrounded by grains of kaolinite.

4.1 Paleo-environmental Conditions

The XRD, TGA/DTA, FT-IR and SEM result confirms that the clay deposits in Aloji, Ofejii, Udane-Biomi, Agbenema, Oturkpa, Okpokwu from Mamu/Ajali Formation and Enugu from Enugu/Nkporo Formation are largely dominated by kaolinites with traces of vermiculite. This reveals that both formations are characterised by high compositional value of kaolinitic clay mineral from continental marginal setting compared to clay types like illite and smectite of marine marginal setting. It is also known that kaolinite concentration is more in sediments close to the shore compared illites and smectites that increases in composition with distance from the shoreline [26].

Base on the dominant kaolinitic clay mineral which was probably derived from weathered crystalline rocks

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containing K-feldspar (microcline) and muscovite, suggestive of the basement rocks surrounding the trough, such as the Eastern Nigeria, North central Nigeria and the Oban Massif [12] a continental environment can be envisaged as probable depositional environment for the two formations.

4.2 Paleoclimatic Significance

Clay minerals are significant tool widely used in interpreting, understanding and solving problems such as tectonics, source rock, zonation, age, metamorphism, oil exploration and its latest application is in the area of paleoclimatic studies. It is worthy of note that climate major controlling factor over the clay type that can be formed at a particular point in time in a given location; base on this, clay minerals can be a powerful tool in paleoclimatic studies inorder to recognize warm and humid climatic condition typical for the formation of kaolinitic clay minerals, or dry seasons, for illite or smectite formation because these two-layer/three-layer ratios of clay minerals are conditioned by climate [27]. Therefore, since the dominant clay mineral recorded is kaolinite and its formation is conditioned by warm, humid, acidic and high leaching conditions. Under such conditions of climate, hydrogen ions increases within that environment to produce kaolinite while characteristic ions like K^+, Na^+, Ca^{2+} and Fe^{2+}) are leached away leading to lose of smectite and illite clay minerals. Although diagenetic processes can favour the formation of kaolinitic minerals, such processes will hinder its use as a paleoclimatic tool. During diagenesis, morphologically, the kaolinite changes from aggregates of book like form to blocks of individual crystals. However, this study have proven that there is no evidence of diagenesis in the formation of the studied clay minerals in both Formations of Ajali/Mamu and Enugu/Nkporo within the Lower Benue Trough. The presence vermiculite, suggest high precipitation and chemical weathering of biotite and other intermediate weathering products [28]. It is also supported by the observed varied thin shapes of kaolinitic clay minerals under the SEM with embayed edge, suggest that the clay underwent relative stronger chemical weathering conditions than physical weathering.

Based on the dominant clay mineral recorded, it shows that the Ajali/Mamu and Enugu/Nkporo within the Lower Benue Trough were deposited under conditions of warm and humid climate.

4.3 Weathering Effect

The observed clay morphology varied remarkably in shape from one depositional environment to another. Some of the clays occurred as thin plates with embayed edge, suggesting the clay underwent relative stronger chemical weathering and displayed thicker plates indicates a condition of dominative physical weathering. These characteristics suggest that the clay underwent to some extend chemical weathering. These shape changes reflected the changing weathering conditions, and suggested that climate played an important role in these variation of mineral morphology with the gross genetic environment during formation of the clay. Controlling environmental factors for kaolinization include parent material and concentration of ions in the fluids of kaolinization [24]. SEM observations show that the clay deposits of the Lower Benue Trough consist of many stacks or books of kaolinite flakes, a typical feature of kaolinite generated from the process of weathering [22, 23] (Figures 11 a, b c and d).

High content of quartz observed in the raw clay samples (Table 1) must be as a result of renewed tectonic activity within the Lower Benue Trough during the mid Santonia when there was a displacement of the major depositional axis westward [12] which disturbs the sedimentation dynamics, possibly resulting in sediment mixing and reworking.

5. Conclusion

Clay mineral assemblage from Ajali/Mamu and Enugu/Nkporo Formations within the Lower Benue Trough have being used to elucidate the paleo-environmental conditions, paleoclimatic significance and effect of weathering during their formations.

Mineralogical analysis using XRD, DTA/TGA, FTIR and SEM methods of analysis revealed that the bulk mineral composition of the clay samples are kaolinite and vermiculite as the mineral phase and microcline, muscovite and quartz as non clay phases. The dominant clay minerals kaolinites with traces of vermiculite; suggested to be as a result of some controlling factors like source rock, climatic conditions, size sorting and environment of deposition. The dominance of kaolinites suggests that the clays are deposited in an environment that correspond to continental setting, its dominance also reflects that they must have being subjected to strong chemical weathering with very good leaching, favoured by tropical to sub-tropical humid climates as observed mophologically under the SEM. This evaluation has proven that despite that both formations are in different stratigraphic locations, they were both deposited relatively under similar conditions of climate and environment. Therefore, the clay deposits in the Lower Benue Trough are quartz-

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rich and kaolinitic in nature derived from the chemical weathering of Al-rich source rocks under wet/tropical paleo-climatic conditions with fresh and/or brackish water conditions in a continental setting.

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