

Geochemical Discriminant for Provenance Characterization of Some Clay Deposits in Edo State, Nigeria

Daniel Imariabe Omoruyi^{1*}, Martins Ilevbare², Ayamezimi Oziofu Ehinlaiye¹, Christopher Nnaemeka Akujieze¹

¹Department of Geology, University of Benin, Benin City, Edo State, Nigeria

²Department of Geology, Afe Babalola University, Ado-Ekiti, Ekiti State, Nigeria

INFORMATION

Article history

Received 01 August 2022

Revised 20 September 2022

Accepted 22 September 2022

Keywords

Clay
Mineralogy
Physicochemical characteristics
Weathering indices
Provenance

Contact

*Daniel Imariabe Omoruyi
imariabe.omoruyi@uniben.edu

ABSTRACT

Bulk geochemical analysis was carried out using X-Ray Fluorescence spectrometry and X-Ray diffractometry methods on the samples from some clay deposits from six locations in Edo State, Nigeria, namely Abudu, Arakhuan, Iguoriakhi, Obadolovbiyeyi, Okhoro, Okomu, to infer their provenance, tectonic setting and source-area weathering. The major oxides for SiO₂ in percent are 54.55, 54.52, 54.64, 58.38, 56.38 and 54.64 in Abudu, Arakhuan, Iguoriakhi, Obadolovbiyeyi, Okhoro and Okomu clay respectively. However, it is highest in Obadolovbiyeyi community the average concentration of Al₂O₃ are 29.90%, 28.22%, 28.87%, 18.85%, 28.81% and 28.87% in Abudu, Arakhuan, Iguoriakhi, Obadolovbiyeyi, Okhoro and Okomu clay respectively. The highest percent of Alumina is in Abudu while the lowest concentration of Alumina is in Obadolovbiyeyi; the low Al₂O₃ concentration is due to lower intensity of alterations of the rocks into clays. The clay samples from this study are characterized by low content of Fe₂O₃, TiO₂ and MgO indicating the dominant source from felsic rocks compositions. The result showed that the dominant clay mineral from the diffractogram profiles is kaolinite. Illite, mica and montmorillonite while the non-clay minerals are quartz and feldspar, with the quartz peak being very prominent. The minimum and maximum averages for the clay are Y is 10.50 ppm at Arakhuan clay and 23.81 ppm at Abudu clay. Similarly, for Nb, Ta and Sc minimum and maximum values are Nb (8.62 ppm, 25.50 ppm) for Okhoro and arakhuan clay, Ta (10.11 ppm, 20.85 ppm) for Obadolovbiyeyi and Abudu clay and Sc (66.73 ppm, 71.70 ppm) for Okomu and Iguoriakhi clay. From this study, the maximum concentration of Ni (82.76 ppm) and Co (45.45 ppm) have concentrations way lower than for mafic and Ultramafic, hence, this authenticate its provenance has been from a felsic origin/source.

1. Introduction

Edo State, Nigeria is underlain by Cretaceous to Tertiary Sedimentary formations. These formations contain large clay deposits. Clay deposits around Abudu, Arakhuan, Iguoriakhi, Obadolovbiyeyi, Okhoro, Okomu, are geochemically and mineralogically studied to characterize the provenance and palaeogeography.

Factors such as source rocks, weathering/recycling, grain-size sorting during transport and sedimentation, diagenesis and metamorphism influence the textural and morphology, chemical composition of clastic sedimentary rocks (Taylor

and McLennan, 1985; McLennan et al., 1990, 1993; Cullers and Podkovyrov, 2000, 2002; Lahtinen, 2000). Weathering, erosion, sediment recycling and diagenesis often affect the alkalis (Na₂O and K₂O) and the alkali-earth elements (CaO and MgO); whereas Al₂O₃, TiO₂, the high field strength elements (HFSE) (Co, Sc, Hf, Ta, Nb, Ti and Y) and some other trace elements are geochemically immobile in nature and are widely known as provenance diagnostic (McLennan et al., 1993). Sediments such as clays or shales are often analyzed for their geochemical attributes with the assumption that they match closely average composition of the upper continental crust (Taylor and McLennan, 1985).



Clay minerals typically develop over extended periods of time from the slow chemical weathering of silicate-bearing rocks by diluted solvents and low carbonic acid concentrations. These typically corrosive liquids travel through the rock that is weathering after leaching through the top worn layers. Some clay minerals are created through hydrothermal activity in addition to weathering. Clay deposits come in two different varieties: primary and

secondary. Secondary clays are clays that have been moved from their original place by water erosion and deposited in a new sedimentary deposit. Primary clays are clays that form as residual deposits in soil and remain at the site of formation. Large lakes and marine basins, which are depositional conditions with relatively low energy, are frequently linked with clay deposits (Adewole and Modupe, 2018).

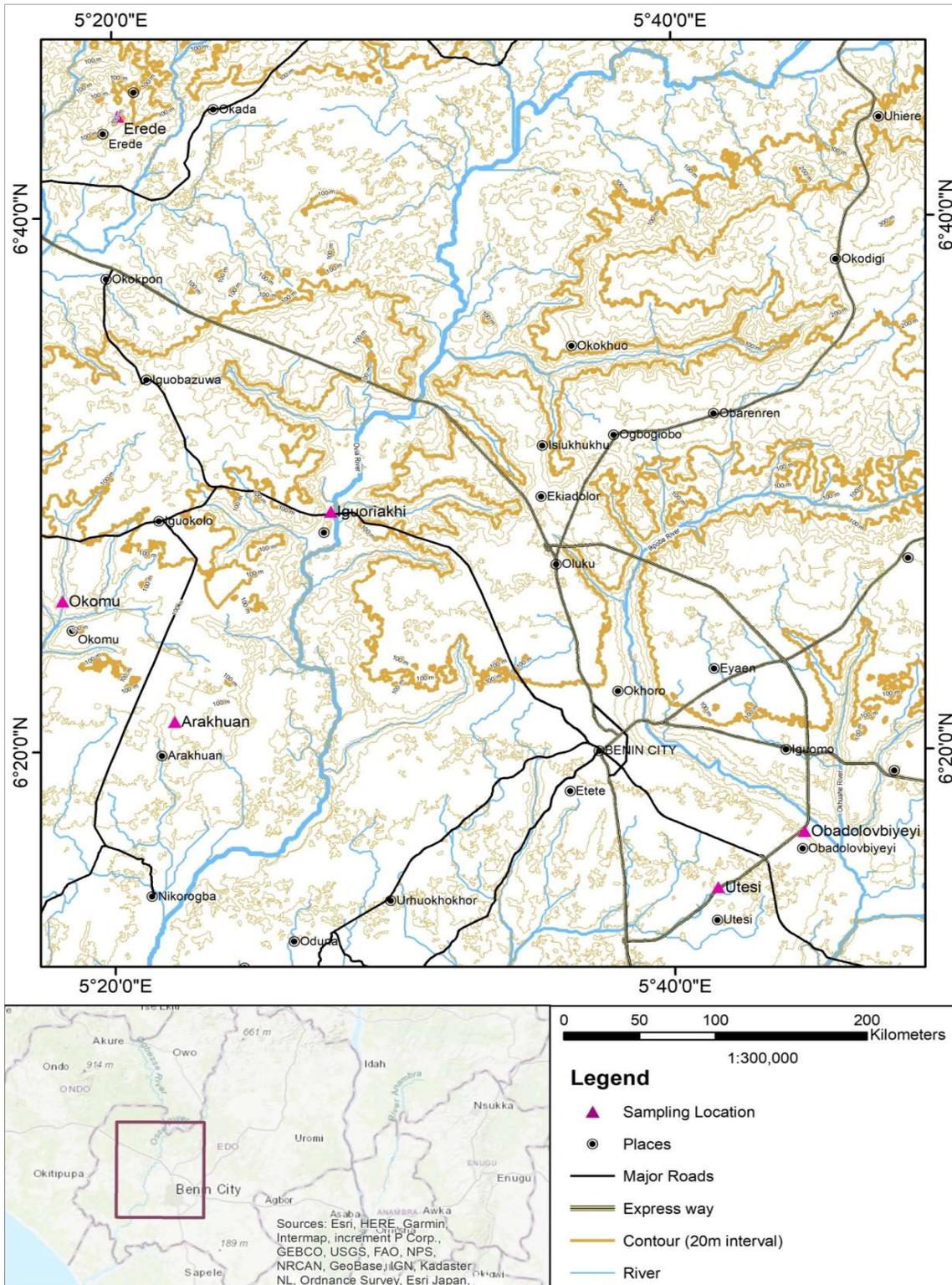


Fig. 1. Location of study area

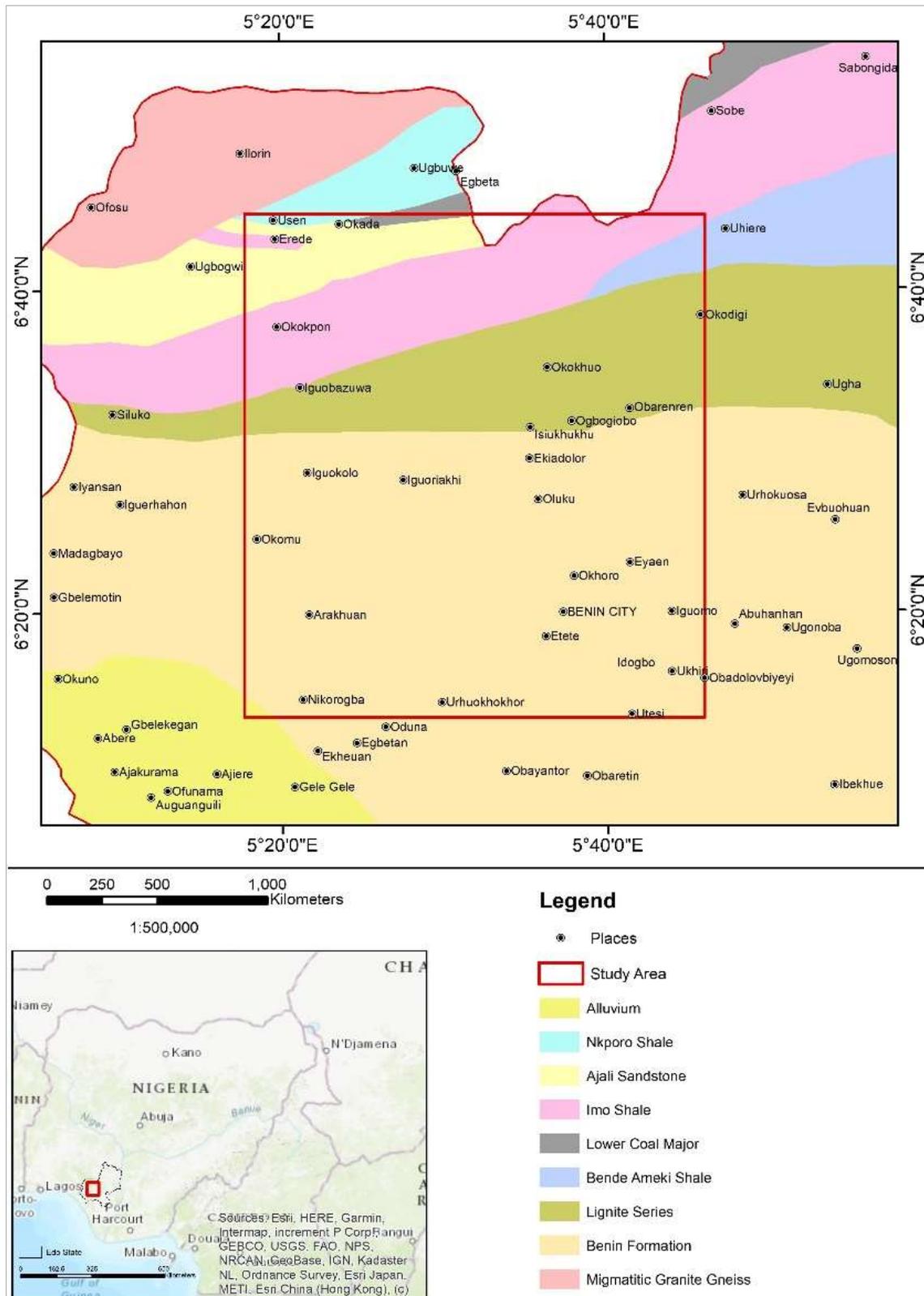


Fig. 2. Geological map of Edo State, Nigeria

Clay has been used in agriculture, industry, and construction from the beginning of time. It is utilized as a building material in the form of sun-dried or burnt brick. Clays play a significant role in a variety of industrial processes, including the production of porcelain, earthenware, and china, as well

as drainage and sewage pipe. For the paper, ceramics, plastics, and rubber industries, clay is a suitable raw material. Drilling muds made of clay and other ingredients protect the cutting tool when drilling. Other applications include the production of fillers, sizings, and sewage purification. Clays

are excellent sources of raw materials from which a variety of household and commercial goods can be produced, (Adeola 2017; Oyinloye 1991). This study reported mineralogy and elements geochemistry of clay in Edo State, Nigeria (Fig. 1) with special emphasis placed on the Provenance and paleogeography of the clay deposits.

2. Geological Setting

Cretaceous to Tertiary Sedimentary formations occupies over eighty percent of Edo State (Fig. 2). Some cretaceous sediments of Anambra Basin and tertiary sediments of Niger Delta sequences are found in the study area. These formations contain clay deposits. The Azagba-Ogwashi Formation has been often spelt as Ogwashi-Asaba Formation consists of clays, sands and grits and seams of lignite alternating with gritty clays. It grades upwards into the Benin Formation. The Ogwashi-Asaba Formation is exposed in stream channels at the northern parts of the Benin Region, west of Ekiadolor-Iwu and 4 km east of Utekon and north of Azalla (Reyment, 1965).

The Benin Formation is assigned to the Oligocene-Pleistocene period in the continent of Africa and to the Oligocene-Pleistocene to recent at the sub oceanic (Short and Stauble, 1967). The formation is characterized by top reddish to reddish brown lateritic massive indurate clay and sand. This is often marked with reticulate mud racks. This cap the underlying more friable pinkish-yellowish white often gravelly-pebble sands clayey soils, sands and clay (Akujieze, 2004). The sedimentary sequences are poorly bedded with discontinuous clay horizons at various depths.

It is estimated to be about 800m thick under Benin City and about 1,830 m near the seashore sections of the formation. They are exposed at various erosion sites, sand quarry sites, and road cuttings. Regionally, the Imo Shale, which sits on top of the Nsukka Formation, reveals a shallow marine shelf environment with preserved foreshore and shoreface sands (Petters and Ekweozor, 1981; Obirike, 2012). It also contains black shales, blue-grey clays, and marl with interspersed

calcareous sandstone, marl, and limestone (Onyekuru, et al., 2018).

According to Obirike et al. (2007) and Onyekuru et al. (2018), regression persisted throughout the Eocene and culminated in the formation of Lower and Middle Eocene deposits, which include the clastic Ameki and Nanka Formations. The transition back to regressive conditions is marked by the progradational Nanka Formation. In the northern parts of the Niger Delta, the Agbada Formation represents the subsurface deposits of the prograding shoreface and river plain, while the Akata Formation refers to the marine Imo Shale counterpart. The Oligocene-Recent Ogwashi-Asaba and Benin Formations dominate the area's uppermost lithostratigraphic units of the stratigraphic succession (Nwajide, 2005; Okoye and Obi, 2011). In the Miocene period, the Niger Delta sediments accumulate and prograde seawards. As a result, the sea level is lowered during the Pleistocene. The Niger River cut wide valleys through its own delta. These troughs are being filled today as the sea level gradually rises (Okoye and Obi, 2011).

3. Materials and Methods

The base map in Fig. 1 indicates that the samples collected were along river courses. Samples were air dried for about two weeks and later disaggregated using Porcelain mortar and pestle. X-ray fluorescence spectrometry and instrumental neutron activation analysis were used for sample preparation, as well as major and trace element analysis, in accordance with Gary (2008). Additionally, X-ray diffraction studies on minerals were conducted as described by Bundy (1993) and Murray and Keller (1993). X-ray diffraction analysis (XRD) was used to determine the mineralogical composition of these samples. Representative samples from six different clay deposits were analyzed to assess their whole-rock geochemical compositions. The major oxides (SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MgO, CaO, Na₂O, K₂O and P₂O₅) as well as some trace elements (Ba, Sr, Cs, Rb, Ta, Nb, Sc, Y, Ni and Co) were determined using Phillips PW-1800 X-ray fluorescence (XRF) analyzer.

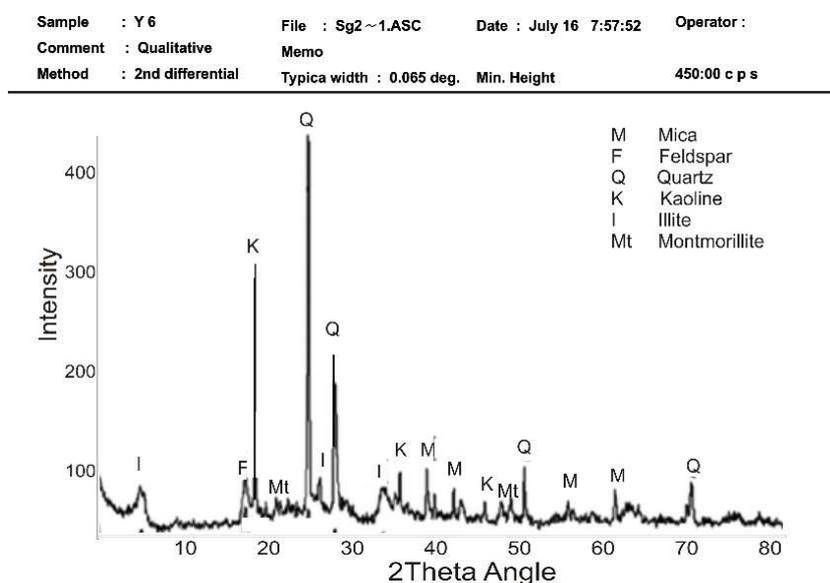


Fig. 3. XRD of Iguoriakhi

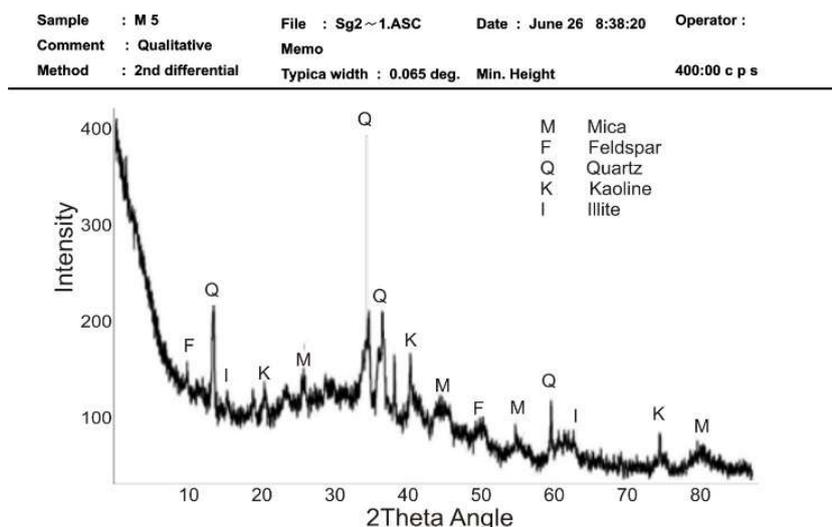


Fig. 4. XRD of Okhoro

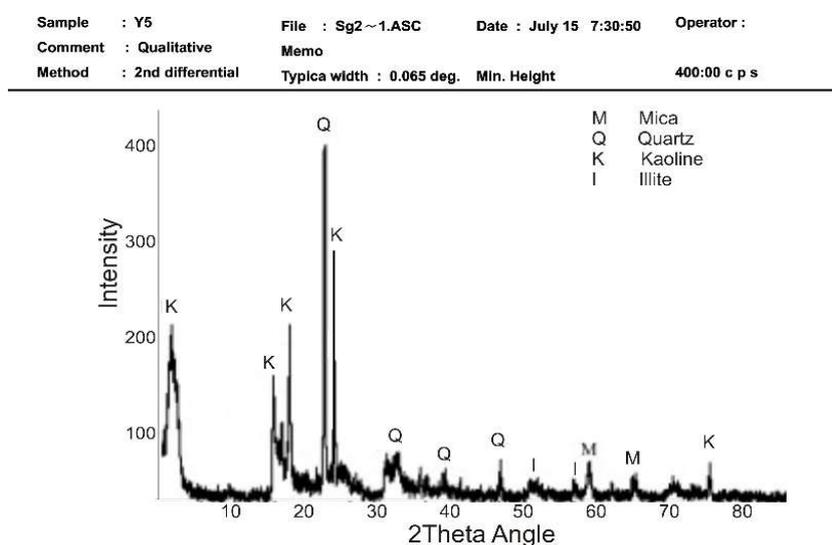


Fig. 5. XRD of Obadolovbiyeyi

4. Results and Discussion

The results obtained from the geochemical analyses are systematically presented. These results have been presented in the order in which the analysis were done and represented using tables and figures geared towards easy and comprehensive data interpretation.

4.1. Degree of Alteration, weathering effect, and maturity

Chemical weathering indices are frequently utilized to quantify changes brought on by chemical weathering in various materials (Birkeland, 1999; Darmody et al., 2005; Ruxton, 1968; Harnois, 1988). The indices are based on the idea that as leaching advances, the ratio between concentrations of mobile (such as SiO₂, CaO, MgO and Na₂O) and immobile (such as Al₂O₃, Fe₂O₃, and TiO₂) elements will gradually decline. Calculating the Chemical Index of Alteration (CIA), where CIA = molar (Al₂O₃ / [Al₂O₃+CaO+Na₂O+K₂O])×100, can help assess the extent of chemical weathering of the sediments' source rocks, according to Nesbitt and Young (1982). The CIA monitors the progressive transformation of potassium feldspars and

plagioclase into clay minerals (Rahman and Suzuki, 2007). When Ca, Na, and K drop as weathering severity increases, this measure is accurate (Duzgoren-Aydin et al., 2002). The only difference between the CIA and the Chemical Index of Weathering (CIW) proposed by Harnois (1988) is the omission of K₂O from the equation: CIW = molar (Al₂O₃ / (Al₂O₃+CaO+Na₂O))×100.

According to McLennan (1983), McLennan (1993) and Mongelli et al. (1996), the interpretation of CIA and CIW is similar, with values of 50 for unweathered upper continental crust and approximately 100 for heavily weathered materials. Low CIA values (i.e 50 or less) also might reflect cool and / or arid conditions. Nesbitt and Young (1982) classified the CIA values as very slightly weathered (50 to 60), slightly weathered (60 to 70), moderately weathered (70 to 80), highly weathered (80 to 90), and extremely weathered (90 to 100). The intensity of the chemical weathering can also be estimated using the Plagioclase Index of Alteration; in molecular proportions: PIA = [(Al₂O₃-K₂O) / (Al₂O₃+CaO*+Na₂O-K₂O)]×100 where CaO* is the CaO residing

only in the silicate fraction and calculated as $\text{CaO}^* = \frac{1}{4} \text{CaO} - 10/3 \text{P}_2\text{O}_5$ (after McLennan et al., 1993). Unweathered plagioclase has PIA value of 50 while Phanerozoic shales have PIA value of 79. Fedo et al. (1995), proposed the PIA as an alternative to the CIW. The PIA can be used to monitor plagioclase weathering because it dissolves quite quickly and is prevalent in silicate. Based on the amount of alkali and alkaline earth elements in the weathering products, Parker's

Weathering Index (WIP) is used to assess the severity of weathering of silicate rocks. The WIP also takes into account certain individual mobility, specifically the mobility of sodium, potassium, magnesium, and calcium, based on the strength of their bonds with oxygen (Parker, 1970). In contrast to how CIA values are produced, the definition of WIP states that smaller WIP values signify stronger chemical weathering.

Table 1. Major and trace elements composition of the clay deposits

	Abd 1	Abd 2	Ara 1	Ara 2	Igk 1	Igk 2	Oby 1	Oby 2	Okhoro 1	Okhoro 2	Okm 1	Okm 2	PAAS
Major Elements (%)													
SiO ₂	52.70	56.40	53.70	55.34	52.90	56.38	49.95	66.80	56.26	56.50	52.94	56.33	64.80
TiO ₂	1.20	1.02	1.23	0.35	1.18	1.04	0.70	0.15	1.25	1.25	1.12	1.06	1.00
Al ₂ O ₃	28.69	29.22	30.20	26.23	28.49	29.24	17.20	20.50	29.22	28.40	28.45	29.29	16.90
Fe ₂ O ₃	3.63	3.67	3.50	2.92	3.65	3.65	4.32	4.08	4.95	4.26	3.65	3.60	7.22
MnO	0.01	0.01	0.01	0.01	0.01	0.01	0.04	0.03	0.08	0.07	0.01	0.01	0.11
MgO	0.08	0.46	0.52	0.65	0.08	0.46	3.55	4.15	4.75	2.05	0.08	0.44	2.20
CaO	1.90	1.45	1.31	0.20	1.90	1.45	2.02	1.69	1.55	1.46	1.96	1.48	1.30
Na ₂ O	0.09	0.28	0.22	0.45	0.05	0.28	1.85	1.65	0.90	0.90	0.07	0.30	1.20
K ₂ O	0.95	0.94	0.90	0.85	0.99	0.94	0.34	0.60	0.98	6.01	0.97	0.94	3.70
P ₂ O ₅	0.01	0.01	0.01	0.05	0.01	0.01	0.30	0.08	0.04	0.05	0.01	0.01	0.16
LOI	10.20	10.55	10.24	11.30	10.20	10.55	0.23	0.04	0.02	0.05	10.20	10.55	-
Weathering Index Ratios													
SiO ₂ /Al ₂ O ₃	1.84	1.93	1.77	2.11	1.86	1.93	2.90	3.26	1.93	1.99	1.86	1.92	-
Al ₂ O ₃ /TiO ₂	23.91	28.65	24.55	74.94	24.14	28.12	24.57	136.67	23.38	22.72	25.40	27.63	-
Log (SiO ₂ /Al ₂ O ₃)	0.26	0.29	0.25	0.32	0.27	0.29	0.46	0.51	0.29	0.30	0.27	0.21	-
Na ₂ O/K ₂ O	0.095	0.30	0.24	0.53	0.05	0.30	5.44	2.75	4.10	0.15	0.07	0.32	-
CIA	93.55	94.09	94.71	95.73	93.47	94.09	87.09	89.18	92.69	80.45	93.38	94.01	77.66
CIW	96.31	96.79	97.25	98.56	96.36	96.80	88.50	91.39	95.43	95.46	96.21	96.71	92.13
PIA	99.04	98.87	99.10	99.73	99.12	98.87	99.94	95.85	98.01	97.79	99.05	98.82	98.79
MIA	87.10	88.18	89.42	91.46	86.94	88.18	74.14	78.36	85.38	60.90	86.76	88.02	55.32
ICV	0.27	0.27	0.25	0.21	0.28	0.27	0.75	0.60	0.49	0.53	0.28	0.27	0.99
Trace element (ppm)													
Ba	862.66	992.54	675.00	685.00	662.61	672.67	1141.00	990.61	960.34	954.26	660.00	692.00	
Sr	185.24	184.06	10.00	12.00	15.62	15.40	189.00	10.0	185.67	188.25	8.00	11.00	
Cs	10.30	10.68	12.00	10.00	12.55	12.25	11.65	11.85	11.30	10.26	10.00	10.00	
Rb	10.55	10.52	125.00	97.00	22.09	24.22	10.00	20.45	10.85	10.50	110.00	98.00	
Ta	21.45	20.25	20.00	8.00	10.42	10.40	20.00	0.33	21.40	20.35	10.00	12.00	
Nb	8.75	8.60	24.00	27.00	22.02	22.02	13.00	10.18	8.99	8.24	20.00	20.00	
Sc	87.20	84.90	65.85	68.55	72.55	70.85	85.45	85.30	84.40	88.60	65.90	67.55	
Y	22.41	25.21	10.00	11.00	14.25	15.22	18.60	19.25	20.48	22.40	12.00	10.00	
Ni	81.60	82.40	30.22	30.15	31.60	31.65	83.00	82.52	70.80	84.20	33.52	32.85	
Co	28.55	30.52	35.40	33.65	23.60	27.20	46.00	44.90	25.83	30.36	26.55	28.35	

Note: Abd: Abudu, Ara: Arakhuan, Igk: Iguoriakhi, Oby: Obadolovbiyeyi, Okh: Okhoro, Okm: Okomu, CIW: Chemical Index of Weathering ($100[\text{Al}_2\text{O}_3]/(\text{Al}_2\text{O}_3+\text{CaO}+\text{Na}_2\text{O})$), CIA: Chemical Index of Alteration ($100[\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3+\text{CaO}+\text{Na}_2\text{O}+\text{K}_2\text{O})]$), PIA: Plagioclase Index of Alteration ($100[(\text{Al}_2\text{O}_3-\text{K}_2\text{O})/(\text{Al}_2\text{O}_3+\text{CaO}+\text{Na}_2\text{O}-\text{K}_2\text{O})]$), ICV: Index of compositional variability ($(\text{Fe}_2\text{O}_3+\text{Na}_2\text{O}+\text{CaO}+\text{MgO}+\text{TiO}_2)/\text{Al}_2\text{O}_3$)

4.2. Mineralogy

The diffraction analysis for three locations (Iguoriakhi, Okhoro and Obadolovbiyeyi) is presented as X-ray diffractograms (Figs. 3-5). The minerals found in the deposits include quartz, feldspar, mica, illite, and montmorillonite. Only kaolinite, illite, montmorillonite, and mica are the main clay minerals, while quartz and feldspar are the non-clay minerals, according to the diffractograms. Due to its remarkable resistance to weathering, quartz is the main non-clay mineral that is found in every horizon in the profiles. Due to their relative crystallinity, quartz has noticeable peaks in the X-ray diffractogram of the clay (Obrike, 2012).

The XRD profiles in a related investigation by Kabeto et al. (2012) demonstrate the presence of kaolinite as a significant

mineral. Based on kaolinite and other related minerals, there are four different forms of clay. Kaolinite is the first mineral, followed by microcline-kaolinite, muscovite-kaolinite, and muscovite-microcline-kaolinite. The clay has been split into three types: 1) kaolinite clay (Fig. 5), 2) mica-kaolinite clay (Fig. 4) and 3) mica-illite-kaolinite clay.

Similarly, the XRD of this investigation indicates a similar mineralogy. Iguoriakhi and Okhoro clay contain the highest concentrations of micas among the peaks, but Obadolovbiyeyi clay has the highest concentration of kaolinite. Feldspar, quartz, and montmorillonite are all associated minerals with the Iguoriakhi clay in all three locations (Fig. 3). Strong and sharp peaks and prominent basal reflections are signs of intermediate to well-formed

crystalline mineral components (Jubril and Amajor, 1991; Obrike et al., 2007; Obrike, 2012).

Some of the samples from Iguoriakhi and Okhoro (Figs. 3-4), for example, revealed brooding of kaolinite reflection, which may indicate the presence of weakly ordered kaolinite (Grim, 1968). According to XRD data, significant amounts of kaolinite were found in the Obadolovbiyeyi samples (Fig. 5). The clay in the study area are thought to have formed through the weathering of silicate minerals in Basement Complex rocks, possibly the adjacent rocks of the Oban Massif, under acidic conditions, based on the presence of non-clay minerals and large amounts of kaolinite (Odigi, 1989; Salihu and Suleiman, 2018).

4.3. Major oxide geochemistry

For the area under study, the metallic oxide and trace element data (Table 1) show that silica (SiO_2) and alumina (Al_2O_3) predominate, followed by Fe_2O_3 , CaO , MgO , TiO_2 , K_2O and Na_2O . There are traces of the residual oxides. Additionally, this outcome is consistent with Kabeto et al. (2012). The geochemical compositions of the clays from the six (6) localities (Abudu, Arakhuan, Iguoriakhu, Obadolovbiyeyi, Okhoro, and Okomu) average 54.55, 54.52, 54.64, 58.38, 56.38, and 54.64 for SiO_2 (in percent), respectively. These silica percentages show that silica is present in nearly comparable amounts throughout the areas. However, the Obadolovbiyeyi village has the highest rate. This could be as a result of the high concentration of quartz found here, as seen in Table 1.

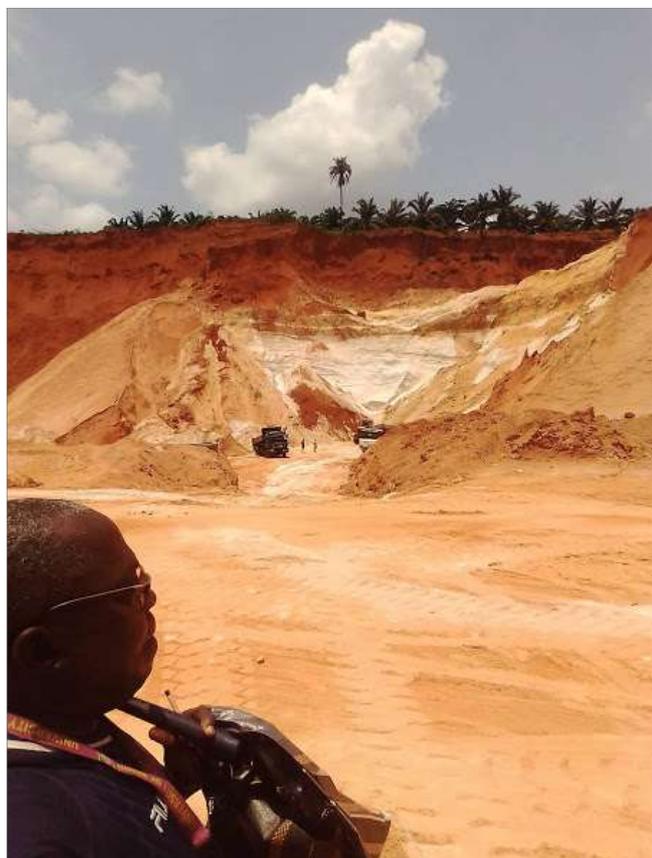


Fig. 6. Clay/sand quarry at Obadolovbiyeyi, Idogbo, Edo State, Nigeria

It is possible that the increased value of 58.38 percent in the clay results from a relative depletion of MnO , MgO , CaO , Na_2O and K_2O in the horizon. Quartz, which is secondary in origin, was likely accumulated from the chemical weathering of rock, creating silicates. The weathering and dissolution of silicate minerals consequently led to the enrichment of SiO_2 and Fe_2O_3 in the topsoil as revealed in Figs. 6-7 (Wang et al., 2011).



Fig. 7. Clay exposure around Okhoro, Edo State, Nigeria

The very low values of CaO , Na_2O , K_2O , MgO and LOI strongly indicate leaching during chemical weathering. The concentration values for CaO are 1.68%, 0.76%, 1.68%, 1.86%, 1.51% and 1.72%, Na_2O are 0.185%, 0.34%, 0.17%, 1.75%, 0.90%, 0.05%, K_2O are 0.95%, 0.88%, 0.97%, 0.47%, 3.50%, 0.49% and MgO are 0.27%, 0.59%, 0.27%, 4.15%, 3.4% and 0.26% in Abudu, Arakhuan, Iguoriakhu, Obadolovbiyeyi, Okhoro and Okomu clay respectively. TiO_2 , P_2O_5 and MnO are relatively low in all the clays but TiO_2 is high in Abudu (1.11%) and Okomu (1.09%) clay.

Iron oxide (Fe_2O_3) is present in clay from Abudu, Arakhuan, Iguoriakhu, Obadolovbiyeyi, Okhoro, and Okomu to varying degrees: 3.65, 3.21, 4.20, 4.52, and 3.63 percent respectively. One of the main oxides in the clay deposits in the research area is iron as Fe_2O_3 . The severe color shifts of the clays from pink to yellow to red and the deposition of iron minerals as cementing elements are likely caused by its high values (>2 percent) in the samples from all sampled locations. Iron oxide (Fe_2O_3), particularly in the samples from Uturu and Ikpankwu, would be a restriction on their usage in the

production of paper, rubber, and white bodies. Significant levels of salt, calcium, and magnesium oxides observed in the deposits would also lessen the clays' vitrification (Obrike, 2012).

The presence of some other constituents like CaO, MgO, MnO, and TiO₂, relative amounts of Al₂O₃, the temperature of firing, and the conditions in the furnace all play important roles in the clays, and they could also pose a challenge to their use as industrial raw materials for the production of paper and rubber (Kreimeyer, 1987; Obrike, 2012; Burhan and Ciftci, 2010). Smectite was not present in the deposits, which was explained by the fact that MgO concentrations were also low. In general, the absence of related carbonate or dolomitization processes in the research area was brought on by the low levels of MgO and CaO. Al₂O₃ is present in clay from Abudu, Arakhuan, Iguoriakhu, Obadolovbiyeyi, Okhoro, and Okomu at average concentrations of 29.90%, 28.22%, 28.87%, 18.85%, 28.81%, and 28.87%, respectively. The lowest concentration of aluminum, or Al₂O₃, is found in Obadolovbiyeyi; Abudu has the highest percentage of aluminum, whereas Abudu has Obadolovbiyeyi's highest percentage of aluminum. Fe₂O₃, TiO₂, and MgO levels in the clay samples from this investigation are low, indicating that felsic rocks compositions are the primary source. Iguoriakhi and Obadolovbiyeyi clay samples' brownish color may be due to their relatively high Fe₂O₃ content (Kabeto et al., 2009; Kabeto, 2010).



Fig. 8. Clay deposit around Abudu, Edo State, Nigeria

Kaolinite and muscovite-kaolinite clays among other forms of clays exhibit low SiO₂ content, as is to be expected. UK clays, on the other hand, have higher SiO₂ and lower Al₂O₃ levels. Al₂O₃, SiO₂, and Fe₂O₃ differ from the perfect kaolin and pure kaolin from the UK and Saudi Arabia respectively, although being comparable to Saudi Arabia's white, red, and grey clays and Nigeria's clays (Mohsen and El-maghraby, 2010; Aref and Rong, 2009; Ehinola et al., 2009). While the high-Al₂O₃ clays have low SiO₂ and high Fe₂O₃ contents, the low-Al₂O₃ clay samples have high SiO₂ and low Fe₂O₃ concentrations. However, the MgO contents of both varieties are comparable. The samples' gritty texture suggests that the

samples' increased sand content may be the cause of their low-Al₂O₃ (Atsbeha, 2011; Murrey, 2007).

4.4. Trace elements geochemistry

Compactible and incompactible trace elements are grouped together in Table 1's analysis of 10 trace elements in clay deposits. Ni, Cu, Cr, and Co are among the trace elements that can be compressed. While Ta, Nb, Sc and Y are High Field Strength Elements (HFSE) with characteristically high ionic radius, the elements Ba, Sr, Cs, and Rb are incompressible. Geochemists refer to the way these trace elements divide up in the solid earth and melt in the Earth's mantle as compactibility. It is a measure of a trace element's ability to replace a main element in a mineral in geochemistry. The least stable within its crystal structure is an element that is incompactible. The mantle is assumed when an element is compactible but does not specify what type of rock it is. Accordingly, incompressible elements are those that are plentiful in continental crust and depleted in the mantle (Heinnonem et al., 2020). The average minimum and maximum averages for the clay samples are Y is 10.50 ppm at Arakhuan clay and 23.81 ppm at Abudu clay. Similarly, for Nb, Ta and Sc minimum and maximum values are Nb (8.62 ppm, 25.50 ppm) for Okhoro and arakhuan clay, Ta (10.11 ppm, 20.85 ppm) for Obadolovbiyeyi and Abudu clay and Sc (66.73 ppm, 71.70 ppm) for Okomu and Iguoriakhu Clay.

The concentration of trace elements in ppm for the clay samples in Abudu, Arakhuan, Iguoriakhu, Obadolovbiyeyi, Okhoro, and Okomu were as follows: Co (28.04 ppm, 34.51 ppm, 25.40 ppm, 45.45 ppm, 28.10 ppm, and 27.45 ppm), Ni (82.00 ppm, 30.19 ppm, The clay's lower Co and Ni values and greater Ba and Sr concentrations point to a felsic source rock (Spalletti et al., 2008).

Elements like Zr, Cr, Fe and Mo are suitable for provenance and tectonic setting determination because of their very limited mobility throughout sedimentary processes, and their brief durations in saltwater, according to Ma et al. (2019), Cai et al. (2018), Uchida et al. (2017) and Ge et al. (2019). As a result of their quantitative transit into clastic deposits during weathering and transport, these components serve as a proxy for the parent material.

According to Garver et al. (1996), Gao et al. (2020) and Armstrong-Altrin et al. (2004), Ni concentrations larger than 200 ppm and Co concentrations greater than 150 ppm are signs of mafic or ultramafic provenance. According to the analysis, the maximum amounts of Ni (82.76 ppm) and Co (45.45 ppm) are much lower than the declared standards for mafic and ultramafic rocks, hence validating the claim that the material originated from a felsic source.

4.5. Weathering history

CaO* is the amount of CaO incorporated in the sediment's silicate fraction, and the main oxides utilized for CIA computation are in molecular ratios. The CIA makes use of the loss of alkali and alkaline earth elements like Na, K and Ca to gauge the extent of chemical weathering of rocks. Generally speaking, a CIA of 45 to 55 denotes no weathering, 60 to 80 denotes moderate chemical weathering, and 80 or

higher denotes substantial chemical weathering (Singh et al., 2005). The average CIA for Abudu, Arakhuan, Iguoriakhu, Obadolovbiyeyi, Okhoro, and Okomu clay is 93.82 percent, 95.22 percent, 93.78 percent, 88.14 percent, 86.57 percent, and 93.70 percent, respectively. Table 1 shows the CIA of the clay and bulk fractions of sediments in this study. For all of the clay, the results indicated CIA values greater than 80, indicating a significant chemical weathering in the study area.



Fig. 9. Clay exposure around Okhoro, Edo State, Nigeria

Referring to the study area's location map (Fig. 1), the amount of chemical weathering of the clay minerals on the ground is revealed by their GPS positioning, with the chemical weathering of the clay being strongest in the Northwestern part of Benin City and decreasing toward the South Eastern part of Benin City. According to Nesbitt, weathering at the incipient stage is indicated by CIA values between 30-55, weathering at the intermediate stage is represented by CIA values between 51-85, and weathering at the advanced stage is indicated by CIA values greater than 85. Again, a CIA of 93.82%, 95.22%, 93.78%, 88.14%, 86.57% and 93.70% for Abudu, Arakhuan, Iguoriakhu, Obadolovbiyeyi, Okhoro and Okomu clay respectively implies that the weathering that resulted in the formation of these clays have reached advanced stage since all the computed CIA values are greater than 85%.

Furthermore, Nesbitt et al. (1982) reported a CIA value of nearly 100 for kaolinite and chlorite and 70 to 75 for average studies whereas Taylor and McLennan (1985) reported a CIA value of 85 to 100 for residual clays.

According to Condie (1993), the majority of post-Archean Shales exhibit moderate Ca, Na and Sr losses due to source weathering, with CIW values ranging from 80 to 95. The clay is once again verified to be kaolinitic clay, which is sourced from post-Archaen shales that have lost their Ca, Na, and Sr due to source weathering. The CIA and CIW of the sediments in this study are greater than those of the sediments proposed by Talor and Mcleenan (1985) and Condie (1993). In order to determine the mineralogical index of alteration

(MIA), Voicu et al. (1997) determined that $MIA = 2 * (CIA - 50)$. In order to evaluate MIA values, it is helpful to consider the following ranges: incipient (0-20%), weak (20-40%), moderate (40-60%), and intense to extreme (60-100%) degree of weathering. The term "100%" refers to a basic material's complete weathering into its equal weathered result (Voicu and Bardoux, 2002).

According to these criteria and applied to the clay sediments of this study, the MIA averages for Abudu, Arakhuan, Iguoriakhu, Obadolovbiyeyi, Okhoro, and Okomu clay are 87.64 percent, 90.23 percent, 87.56 percent, 76.25 percent, 73.14 percent, and 87.39 percent, respectively. These averages lie between 60 and 100 percent, indicating that the clay deposits under study have endured severe to extremely severe weathering conditions. The abundance of alumina in relation to the other major cations in a rock or mineral is measured by a ratio called the Index of Compositional Variability (ICV), which is defined by Cox et al. (1995) as $(Fe_2O_3 + K_2O + Na_2O + CaO + MgO + MnO + TiO_2) / Al_2O_3$.

Silica is not included to avoid quartz dilution issues. Non clay silicates have a greater ICV because they have a lower percentage of Al_2O_3 than clay minerals do in relation to other constituents. The ICV is lowest in the kaolinite group of minerals and continues to decline in the montmorillonite group of clay minerals (Cox et al., 1995). For the clay types Abudu, Arakhuan, Iguoriakhu, Obadolovbiyeyi, Okhoro, and Okomu, the computed averages of the ICV are respectively 0.27, 0.23, 0.51, 0.12, 0.48, and 0.28. These low ICV averages are compatible with clay minerals and with the research of Cox et al. (1995).



Fig. 10. Clay deposit around Arakhuan, Edo State, Nigeria

Additionally, the ICV averages for Iguoriakhi and Obadolovbiyeyi clay are 0.51 (the highest value) and 0.12, respectively (lowest value). The reason for the high value of Iguoriakhi clay is the presence of the clay mineral montmorillonite, which is also supported by the XRD profile (see Fig. 3) that shows montmorillonite as one of the clay minerals. The lowest result, 0.12, indicates that kaolinitic clay predominates at Obadolovbiyeyi. The XRD profile (in

Fig. 5) confirms this once again by demonstrating that kaolin is the dominating clay mineral in the profile.

The CIW values range from 50 for unweathered upper continental crust to roughly 100 for materials that have undergone substantial weathering, with the full elimination of alkali and alkaline-earth elements (McLennan et al., 1983, McLennan, 1993, Mongelli et al., 1996). This is once more confirmed by the XRD profile (in Fig. 5), which shows that kaolin is the dominant clay mineral in the profile.



Fig. 11. Clay deposit around Okomu, Edo State, Nigeria

The relative CIWs are 96.55, 97.91, 96.58, 89.95, 95.45, and 96.46 percent for the clay types Abudu, Arakhuan, Iguoriakhu, Obadolovbiyeyi, Okhoro, and Okomu. These outcomes are once more consistent with badly weathered materials, according to Mogelli et al. (1996), which implies that the clay minerals are chemically matured. This is once more confirmed by the XRD profile (in Fig. 5), which shows that kaolin is the dominant clay mineral in the profile.

The plagioclase index of alteration (PIA; Fedo et al., 1995), which is computed using the following equation (molecular proportions), can also be used to estimate the degree of weathering in the source area: PIA is equal to $[(Al_2O_3 - K_2O)/(Al_2O_3 + CaO + Na_2O - K_2O)] * 100$. The average PIA is 99.14 percent, 99.42 percent, 99.00 percent, 97.90 percent, 97.90 percent and 98.94 percent for Abudu, Arakhuan, Iguoriakhu, Obadolovbiyeyi, Okhoro, and Okomu clay, respectively. These averages are nearly equal to the values for the CIW (Table 1), which serves as a substitute for PIA for all the clay samples analyzed. The XRD profile (in Fig. 5) confirms this once again by demonstrating that kaolin is the dominating clay mineral in the profile. The high PIA obtained suggests an ideal detrital input characterized by strong chemical weathering, which causes all major cations, including Ca^{+2} , K^+ and Na^+ present in feldspar minerals, to hydrate and leach, resulting in the formation of clay minerals (Wang et al., 2011; Sultan and Shazil, 2010; Garrigós et al., 2001).

4.6. Provenance

Since in situ weathering did not produce the majority of the

clay deposits in the study area, geochemical signatures for clastic rocks were employed to determine origin (Madharaju and Ramasamy, 2002; Armstrong-Altrin et al., 2004). Al_2O_3/TiO_2 ratio grows from 3 to 8 for mafic igneous rocks, 8 to 21 for intermediate rocks, and 21 to 70 for felsic igneous rocks. These ratios have also been used to determine the composition of the source rock for the majority of clastic rocks (Hayashi et al., 1997). Al_2O_3/TiO_2 averages for the investigated clay are 24.78, 49.75, 26.13, 80.62, 23.05, and 26.52 for Abudu, Arakhuan, Iguoriakhu, Obadolovbiyeyi, Okhoro, and Okomu clays, respectively. The clay is most likely originated from a felsic igneous rock according to Hayashi et al. (1997).

An exception to this is the Obadolovbiyeyi clay, whose ratio is more than 70, that is 80.62. This incredibly high ratio indicates that it was likely derived from remnants of marine transgressive and regressive phases that were transported and deposited as sediments, which after repeated cycles of sedimentation and subsequent cementation processes became indurated into a claystone in the basin it was deposited, which is indicating a mixed provenance. The average of Na_2O/K_2O ratio of the clay samples for Abudu, Arakhuan, Iguoriakhu, Obadolovbiyeyi, Okhoro and Okomu clay are 0.12, 0.39, 0.18, 4.10, 2.13 and 0.19 respectively. The gross average of the ratio is 1.19, which indicates a felsic source (Akinmosin and Osinowo, 2008; Ibe and Akaolisa, 2010).

The SiO_2/Al_2O_3 ratio of 3.07 (Obadolovbiyeyi clay), 1.96 (Okhoro clay), 1.94 (Arakhuan), 1.90 (both at Abudu and Iguoriakhu clay), and 1.89 (Okomu). Decreasing SiO_2/Al_2O_3 ratio, MgO content (low) and increasing Fe_2O_3 content (Table 1) may also indicate the residual weathered Fe-Mg minerals such as olivine and/or amphibole and pyroxene, which are inherited from moderately weathered granitoids. The low Na_2O , K_2O , MgO, MnO and P_2O_5 and content may also reflect the formation of Al-Si clay such as kaolinite in the finest sediment grain-sized fractions (Ndjigui et al., 2014).

Table 2. Guidelines for chemical classification of quartz

Author	Weathering indices	Quartz type
Lindsey (1999)	$\text{Log}(SiO_2 : Al_2O_3) > 1.50$	Quartz arenite
	$\text{Log}(SiO_2 : Al_2O_3) < 1.00$	Gray wacke
This study	$\text{Log}(SiO_2 : Al_2O_3) = 0.31$	Gray wacke

The $\text{Log}(SiO_2/Al_2O_3)$ for the clay at Abudu, Arakhuan, Iguoriakhu, Obadolovbiyeyi, Okhoro and Okomu clay averages 0.28, 0.29, 0.28, 0.49, 0.3 and 0.24 respectively. Given that all of the clay's averages are smaller than 1, the quartz type in the clay is listed in Table 2 of the Lindsey (1999) chemical classification for quartz as being Graywacke.

This supports the observations made when studying the clay deposits in the field, with a focus on the clay exposures at Okhoro, Iguoriakhu, Arakhuan, and Okomu as seen in the field images (Figs. 6-11). Greywacke is a general term that can be used to describe the fine-grained clay component of the rock as well as its immature side.

The log ($\text{SiO}_2/\text{Al}_2\text{O}_3$) for the clay at Abudu, Arakhuan, Iguoriakhu, Obadolovbiyeyi, Okhoro and Okomu clay averages 0.28, 0.29, 0.28, 0.49, 0.3 and 0.24 respectively. Given that all of the clay's averages are smaller than 1, the quartz type in the clay is listed in Table 2 of the Lindsey (1999) chemical classification for quartz as being Graywacke. This supports the observations made when studying the clay deposits in the field, with a focus on the clay exposures at Okhoro, Iguoriakhu, Arakhuan, and Okomu as seen in the field images (Figs. 6-11). Greywacke is a general term that can be used to describe the fine-grained clay component of the rock as well as its immature side.

5. Conclusion

In other to characterize the provenance of some clay in Edo State a geochemical study was done, and based on that this conclusion may be drawn:

1. The dominant clay mineral from the diffractogram profiles is kaolinite. Illite, mica and montmorillonite were also present but in minor amount while the non-clay minerals are quartz and feldspar, with the quartz peak been very prominent.

2. The concentration of the trace elements in parts per million (ppm) from this study reveals that the clay is sourced from a felsic origin. The alumina-titanium oxide ratio confirms the provenance of the clay as felsic igneous rocks. The silica-alumina ratio of the clay is consistent with those moderately weathered granitoids.

3. The CIA of the clay shows that the clay has undergone strong chemical weathering which is in an advanced stage. The MIA of the clay corroborates the result from the CIA, of clay that has reached an intense to extreme weathering condition.

4. The CIW of the clay, also authenticate the result from the CIA, as highly weathered and chemically matured clay. The PIA, have values that are also consistent with a strong chemical weathering arising from high detrital influx of sediments.

References

- Adeola, A.J., Olaleye, M.A., 2018. Mineralogical and Geochemical Appraisal of Clay Deposits in Papalanto and Its environs, Southwestern, Nigeria. *Earth Science Research* 7 (1), 1-13.
- Akinmosin, A., Osinowo, O.O., 2008. Geochemical and mineralogical composition of Ishara sandstone deposit, SW Nigeria. *Continental Journal of Earth Sciences* 3, 33-39.
- Akujijeze, C.N., 2004. Effects of Anthropogenic Activities (Sand Quarrying and Waste Disposal) on Urban Groundwater System and Aquifer Vulnerability Assessment in Benin City, Edo State, Nigeria. PhD Thesis, University of Benin, Benin City, Nigeria.
- Birkeland, P.W., 1999. *Soils and Geomorphology*, Third edition. New York, Oxford University Press. 430 pp.
- Bundy, W.M., 1993. The diverse industrial applications of kaolin. *Kaolin Genesis and Utilization* (Murray, H. H., Bundy, W., Harvey, C.), Clay Minerals Society Special Publication 1, Boulder, 43-47.
- Burhan, D., Ciftci, E., 2010. The clay minerals observed in the building stones of Aksaray- Guzelyurt area (Central Anatolia-Turkey) and their effects. *International Journal of the Physical Sciences* 5, 1734-1743.
- Cai, L.X., Xiao, G.L., Guo, X.W., Wang, J., Wu, Z.Q., Li, B.G., 2018. Evaluation of upper paleozoic and mesozoic source rock sin well CSDP – 2 and marine oil and gas exploration prospect in the SYCB. *Acta Petrolei Sinica* 39 (6), 660-673.
- Condie, K.C., 1993. Chemical composition and evolution of the upper continental crust Contrasting results from surface samples and shales. *Chemical Geology* 104 (1-4), 1-37.
- Cox, R., Lowe, D.R., Cullers, R. L., 1995. The influence of sediments recycling and basement composition on evolution of mud rock chemistry in the south-western United States. *Geochim Cosmochim Acta* 59, 2919-2940.
- Cullers, R.L., Podkovyrov, V.N., 2000. Geochemistry of the Mesoproterozoic Lakhanda Shales in Southern Yakutia, Russia: Implications for Mineralogical and Provenance Control and Recycling. *Precambrian Research* 104, 77-93.
- Darmody, R.G., Thorn, C.E., Allen, C.E., 2005. Chemical weathering and boulder mantles, Kärkevage, Swedish Lapland. *Geomorphology* 67 (1-2), 159-170.
- Ehinola, O.A., Oladunjoye, M.A., Gbadamosi, T.O., 2009. Chemical composition, geophysical mapping and reserve estimation of clay deposit from parts of Southwestern Nigeria. *Journal of Geology and Mining Research* 3, 57-66.
- Fedo, C.M., Nesbitt, H.W., Young, G.M., 1995. Unraveling the effects of potassium metasomatism in sedimentary rocks and paleosols with implications for paleoweathering conditions and provenance. *Geology* 23 (10), 921-924.
- Gao, X, Zhang, X., Zhu, X., 2020. Provenance and Tectonic implications of paleozoic strata in the south yellow sea Basin, China Reveled from the Bore hole CSDP – 2. *Journal of Ocean University of China* 19, 536-55.
- Gary, S.K., 2008. *Physical and Engineering Geology*; 2nd Edition.
- Ge, Q., Xue, Z.G., Chu, F., 2019. Distribution patterns of major and Trace elements and Provenance of surface sedimentation on the continental shelf of western Guangdong province and Northeastern Hainan Island. *Journal of Ocean University of China* 18, 849-858.
- Grim, R.E., 1968. *The Clay Mineralogy* 2nd edition Mac Graw Hill, New York, pp. 596.
- Harnois, L., 1988. The C. I. W. index: a new chemical index of weathering. *Sedimentary Geology* 55, 319-322.
- Hayashi, K., Fujisawa, H., Holland, H.D., Ohmoto, H., 1997. Geochemistry of 1.9 Ga sedimentary Rocks from Northeastern Labrador, Canada. *Geochimica et Cosmochimica Acta* 61, 4115-4137.
- Heinonem, J.S., Bohrson, W.A., Spera, F.J., Brown, G.A., Scruggs, M.A., Adams, J.V., 2020. Diagnosing open system magmatic processes using the magma chamber Simulator (MCS): Part II trace elements and Isotopes. *Contributions to Mineralogy and Petrology* 175, 105-126.
- Jubril, M.D., Amajor, L.C., 1991. Mineralogical a geochemical Aspects of the Afam clay (Miocene), Eastern Nigeria Delta. *Nigeria Journal Mining and Geology* 27, 95-105.
- Kabeto, K., 2010. Sequential Compositional variation of Ethiopian flood basalt: Implication for Afar plume enriched component. *Momona Ethiopian Journal of Science* 2, 4-25.
- Kabeto, K., Sawada, Y., Roser, B., 2009. Compositional Differences between Felsic Volcanic Rocks from the Margin and Center of the Northern Main Ethiopian Rift. *Momona Ethiopian Journal of Science* 1, 4-35.
- Kabeto, K., Zenebe, A., Bheemalingeswara, K., Atshbeha, K., Gebresilassie, S., Amare, K., 2012. Mineralogical and Geochemical Characterization of Clay and Lacustrine Deposits of Lake Ashenge Basin, Northern Ethiopia: Implication for Industrial Applications. *Momona Ethiopian Journal of Science*

- 4(2), 111-129.
- Madharaju, J., Ramasamy, S., 2002. Petrography and geochemistry of Late Maastrichtian - Early Paleocene sediments of Tiruchirappalli Cretaceous, Tamil Nadu - Paleoweathering and provenance implications. *Journal of the Geological Society of India* 59, 133-142.
- McLennan, S.M., 1993. Weathering and global denudation. *Journal of Geology* 101, 295-303.
- McLennan, S.M., Taylor, S.R., Eriksson, K.A., 1983. Geochemistry of Archean Shales from the Pilbara Supergroup, Western Australia. *Geochimica et Cosmochimica Acta* 47 (7), 1211-1222.
- Mongelli, G., Cullers, R.L., Muelheisen, S., 1996. Geochemistry of Late Cretaceous-Oligocene shales from the Varicolori Formation, southern Apennines, Italy: implications for mineralogical, grain-size control and provenance. *European Journal of Mineralogy* 8, 733-754.
- Murray, H.H., 2007. Clay industry materials and rocks, America Institute of Mining, Metallurgy and Petroleum Engineers, New York. Seeley W series pp. 259-284.
- Murray, H.H., Keller, W.D., 1993. Kaolin, kaolin and kaolin. In: Murray, H. H., Bondy, W. and Harvey, C. (Eds.), *Kaolin Genesis and utilization*. The Clay Mineral Society (Special Publication), Aurora, USA, (1).
- Ndjigui, P.D., Beauvais, A., Fadil-Djenabou, S., Ambrosi, J.P., 2014. Origin and evolution of Ngaye River alluvial sediments, Northern Cameroon: Geochemical constraints. *Journal of African Earth Sciences* 100, 164-187
- Nesbitt, H.W., Young, G.M., 1989. Formation and Diagenesis of Weathering Profiles. *The Journal of Geology* 97, 129-147.
- Nesbitt, H.W., Young, G.M., McLennan, S.M., Keays, R.R., 1982. Effects of chemical Weathering and sorting on the petrogenesis of siliciclastic sediments, with implications for provenance studies. *Journal of Geology* 104:525-542.
- Nwajide, C.S., 2005. A guide to geological field trips to Anambra and related basins in Southeastern Nigeria. Great AP Express Publishers Ltd.
- Obriake, S.E., 2012. Evaluation of Imo clay-shale deposit (Paleocene) from Okada, Edo State, Southwestern Nigeria, as drilling mud clay. *Journal of Applied Technology of Environmental Sanitation* 1 (4), 311-316.
- Obriake, S.E., Osadebe, C.C., Onyeobi, T.U.S., 2007. Mineralogical, geochemical, physical and industrial characteristics of shale from Okada area, southwestern Nigeria. *Journal Mining and Geology* 43 (2), 109-116.
- Odigi, M.I., 1989. Mineralogical and geochemical studies of Tertiary sediments from the eastern Niger Delta and their relationship to petroleum occurrence. *Journal of Petroleum Geology* 10 (1), 101-114.
- Okoye, I.P., Obi, C., 2011. Synthesis and Characterization of Al-Pillared Bentonite Clay Minerals. *Research Journal of Applied Sciences* 6, 447-450.
- Onyekuru, S.O., Iwuoha, P.O., Iwuagwu, C.J., Nwozor, K.K., Opara K.D., 2018. Mineralogical and geochemical properties of Clay deposits in parts of Southeastern Nigeria. *International Journal of Physical Sciences* 13 (14), 217-229
- Oyinloye, A.O., 1991. Application of kaolinitic clays in Industrial Clay technology TERRA. *A Journal of Environmental Concern* 1 (1), 68-72.
- Parker, A., 1970. An index of weathering for silicate rocks. *Geological Magazine* 107, 501-504.
- Petters, S.W., Ekweozor, C.M., 1981. Origin of Cretaceous black shales in the Benue Trough, Nigeria. *Journal of Palaeogeography Palaeoclimatology Palaeoecology* 40, 311-319.
- Rahman, J., Suzuki, S., 2007. Geochemistry of sandstone from the Miocene Surma group, Bengal basin, Bangladesh: Implications for provenance, tectonic setting and weathering. *Geochemical Journal* 41(6), 415-428.
- Reyment, R.A., 1965. Aspects of the Geology of Nigeria. Ibadan University Press, Ibadan.
- Rudnick, R.L., Gao, S., 2003. The Composition of the Continental Crust. In *Treatise on Geochemistry*. Elsevier-Pergamon, Oxford-London, Vol. 3: pp. 1-64.
- Ruxton, B.P., 1968. Measures of the degree of chemical weathering of rocks. *Journal of Geology* 76 (5), 518-527.
- Salihu, S.A., Suleiman, I.Y., 2018. Comparative analysis of physical and chemical characteristics of selected clays deposits found in Kebbi State, Nigeria. *International Journal of Physical Sciences* 13 (10), 163-173.
- Short, K.C., Stauble, A.J., 1967. Outline of the Geology of Onitsha, Owerri and Benue Provinces. Geological Survey of Nigeria, Bulletin No. 21.
- Singh, M., Sharma, M., Tobschall, H.J., 2005. Weathering of the Ganga alluvial plain, northern India: implications from fluvial geochemistry of Gomati River. *Applied Geochemistry* 20, 1-21.
- Taylor, S.R., McLennan, S., 1985. *The Continental Crust: Its Composition and Evolution*: Blackwell, Oxford, 312 p.
- Uchida, E., Osada, K., Nakoa, K., 2017. Major and Trace Element chemical compositional signatures of some granite rocks related to metal mineralization in Japan. *Open Journal of Geology* 7, 559-57.
- Voicu, G., Bardouz, M., Harnois, L., Grepeau, R., 1997. Lithological and geochemical environment of igneous and sedimentary rocks at Omai gold mine, Guyana, South America, *Exploration and Mining Geology* 6, 153-170.
- Wang, H., Liu, Z., Sathiamurthy, E., Colin, C., Li, J., Zhao, Y., 2011. Clay mineralogy and elemental geochemistry of river surface sediments in Malay Peninsula and North Borneo. *Science China: Earth Sciences* 54, 272-282.
- Voicu, G., Bardouz, M., Harnois, L., Grepeau, R., 1997. Lithological and geochemical environment of igneous and sedimentary rocks at Omai gold mine, Guyana, South America, *Exploration and Mining Geology* 6, 153-170.