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Determination of the Composition of Clay and Shale and Their Industrial Potential Associated with the Ameki Formation in Nsugbe and Its Environs, Southeastern Nigeria

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Abstract
Clays possess various industrially significant properties, including plasticity, adsorptivity, ion exchange capacity and shrink-swell potential. This research aims to determine the composition and industrial potential of clay and shale associated with the Ameki Formation in Nsugbe and its environs, Southeastern Nigeria. A total of eight soil samples were collected from four locations and analyzed using X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD) to assess their mineralogical and chemical properties. These analyses provide critical insights into resource quality and industrial suitability. The XRF data indicate that both shale and clay samples are rich in silicate minerals, as evidenced by high SiO_2 concentrations. The clay samples exhibit a higher Al_2O_3 content, suggesting a greater proportion of clay minerals, whereas the shale samples contain higher levels of Fe_2O_3 and TiO_2, pointing to the presence of Iron-rich minerals and Titanium-bearing phases. The presence of sulfur in both shale and clay, particularly in certain high concentration samples, suggests a possible marine or anoxic depositional environment. Variations in trace element concentrations across the samples likely reflect differences in sediment provenance and depositional conditions. The data also suggest varying degrees of diagenesis, with shale samples indicating a more mature, Iron-rich environment, while clay samples display characteristics of a more weathered or kaolinitic composition. The XRD quantitative analysis identified minerals such as Quartz, Orthoclase, Clinochlore, Albite, Garnet, Vermiculite, Nacrite, Kaolinite, and Rutile, among others. These findings indicate that the Nsugbe clay and shale deposits have significant industrial potential, particularly for use in refractories, bricks, pottery, and ceramics. Long-term monitoring of the Nsugbe deposits can provide insights into sustainable extraction practices. Collaborative efforts with industries could further increase the economic value of these resources while ensuring environmental sustainability, ultimately benefiting the local community.

Keywords
Silicate minerals, X-Ray Fluorescence, X-Ray Diffraction, Nsugbe, clay

1. Introduction

Clay and shale represent the most abundant sedimentary rocks, accounting for approximately 60% of the Earth's Crust. Clay, composed of ultra-fine-grained sediment with colloidal-sized particles measuring less than 2 µm, forms from the decomposition of feldspar minerals. Shale, a fine-grained, laminated rock derived from compacted muds, consists primarily of clay and silt-sized particles. These layers are rich in quartz and clay minerals, characterized by water-resistant properties due to low water saturation coefficients and high organic matter content. Magnetic minerals in shale, present in trace concentrations, undergo alteration during early diagenesis, forming magnetic Nano-minerals. Clay mineral compositions in soil reflect their weathering and deposition history. For example, residual soils from basalt predominantly contain illite and montmorillonite, while granite-derived feldspar weathers into kaolinite. Clays exhibit various industrially significant properties, including plasticity, adsorptivity, ion exchange capacity and shrink-swell potential. These characteristics make clay essential for industries such as ceramics, pottery, water purification, and pollutant remediation. Weathering processes are influenced by factors such as rainfall, temperature, and vegetation. The ion exchange properties of clay minerals, such as montmorillonite, make them highly reactive and valuable for environmental applications like water purification. Mineralogical transformations, such as the alteration of feldspar to kaolinite or montmorillonite to bauxite, demonstrate the role of weathering, climate, and tectonics in shaping these deposits.

Onyekuru et al. (2018) investigated the mineralogical and geochemical properties of clay deposits in parts of Southeastern Nigeria. Their findings indicate that, when compared with other reference clays and standard specifications, the clay deposits in the study area exhibit characteristics suitable for economic and certain engineering applications. Nfor (2009) studied the paleo-depositional environmental characteristics of the Nsugbe area and its environs in Anambra State, Southeastern Nigeria, using pebble morphometric analysis. The results show that the average lengths of the long, intermediate, and short axes of the pebbles are 25 mm, 18 mm, and 11.3 mm, respectively. These findings suggest a predominantly fluviatile depositional environment with some influence of a beach/littoral setting. In a separate study, Nfor (2008) examined the stratigraphic nomenclatural procedures of the Lower Benue-Anambra Basin, focusing on Nsugbe as a distinct formation. The study revealed that the lithology of Nsugbe is characterized by highly ferruginized sandstone, which differs significantly from the Nana Sand, known for being friable and unconsolidated.

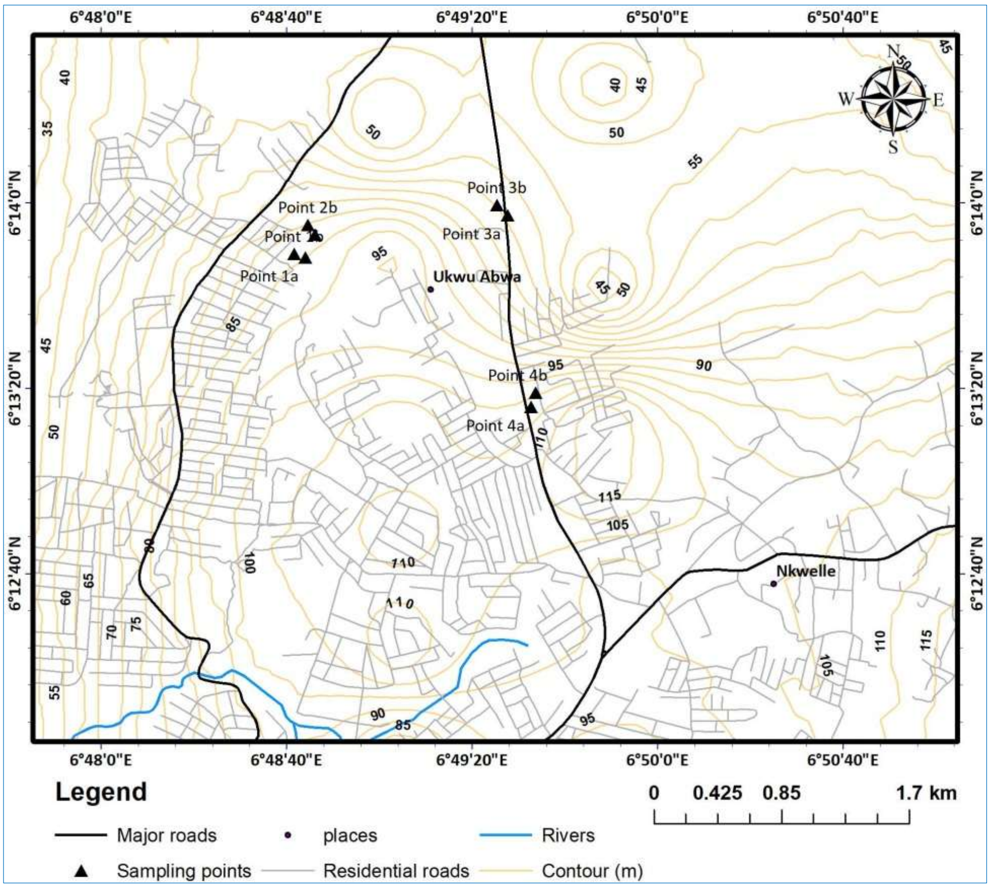

Fig. 1. Base map of the study area

Understanding the diagenetic transformation of magnetic minerals in shale provides insights into the paleoenvironmental conditions and diagenetic history. The industrial relevance of clays stems from their structural and compositional adaptability, making them a cornerstone for sustainable technologies like carbon sequestration and waste management. Shale's organic matter and magnetic mineral content suggest significant potential for hydrocarbon exploration and reconstructing past environmental conditions. The aim of this research is to determine the composition and industrial potential of clay and shale associated with the Ameki Formation in Nsugbe and its environs, Southeastern Nigeria.

2. Description of Study Area

The study focuses on Nsugbe and its environs within the Anambra Basin, southeastern Nigeria. This area is geographically bounded by coordinates 6°48′0″E to 6°50′40″E and 6°12′40″N to 6°14′0″N as shown in Fig. 1. The region features diverse lithologies, including ferruginized sandstone, shale, siltstone, and clay deposits, forming part of the Ameki Formation. The area's economy is supported by oil and gas exploration, agriculture, and commerce. The climate alternates between a wet season (April to October) and a dry season (November to March), with average temperatures around 27.5°C and 79% humidity (Manpower Nigeria, 2022).

The study area is located within the Anambra Basin, a sub-basin of the Lower Benue Trough. Sedimentation in the Lower Benue Trough began during the Albian with the deposition of the Asu River Group, consisting of shales, limestones, and sandstone lenses. Pyroclastic deposits from the Aptian to Early Albian have also been reported (Ojoh, 1992).

Overlying the Asu River Group are the Cenomanian-Turonian Nkalagu Formation, composed of black shales, limestones, and siltstones, and the interbedded regressive sandstones of the Agala and Agbani Formations. Mid-Santonian tectonic activities shifted the depositional axis westward, forming the Anambra Basin. Subsequent Campanian-Maastrichtian sedimentation in the Anambra Basin began with the marine and paralic shales of the Enugu and Nkporo Formations, followed by the coal measures of the Mamu Formation and the fluviodeltaic sandstones of the Ajali and Owelli Formations. In the Paleocene, marine shales of the Imo and Nsukka Formations were deposited, capped by the Eocene Nanka Sandstone (Reyment, 1965). Downward into the Niger Delta, these formations transition into the Akata Shale and Agbada Formation, which are Paleogene equivalents of the Anambra Basin. Shales like Nkporo and Enugu represent shallow marine and marsh environments, while the Mamu Formation and Ajali Sandstone reflect regressive depositional phases. There is notable exposure of Nkporo Shale (Best viewed at Leru village, 72 km south of Enugu); Enugu Shale (Found near the Onitsha-Road Flyover in Enugu) and Mamu Formation (Exposed at Miliken Hills, Enugu) in Anambra. The organic-rich shales of the Anambra Basin hold potential as hydrocarbon sources but are only locally expected to reach maturity levels for hydrocarbon expulsion.

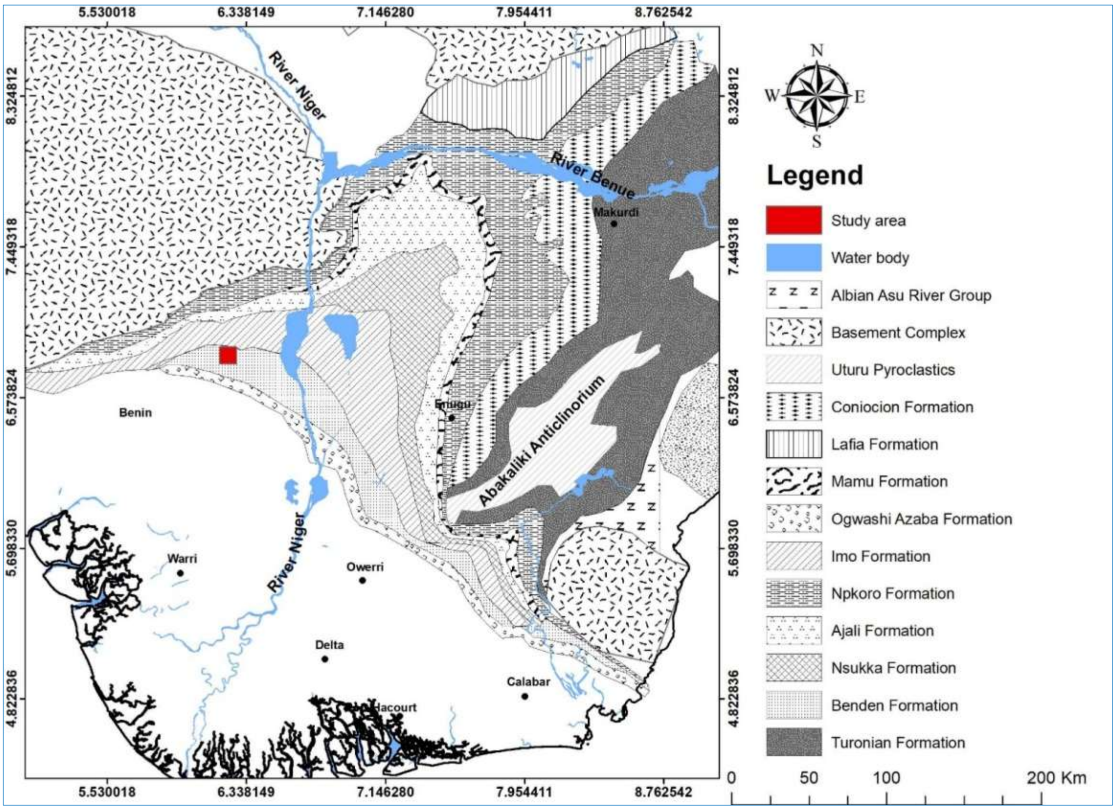

Fig. 2. Field photographs of Okomu Coastal Plain Sands, Nigeria

The geological diversity of Nsugbe's lithologies hints at complex depositional and tectonic processes that shaped the region. These characteristics, coupled with climatic conditions, influence the weathering rates and subsequent mineralogy of the clays and shales, impacting their industrial applications. The Nsugbe area lies within the Anambra Basin, part of Nigeria's Lower Benue Trough. This sedimentary basin experienced deposition phases influenced by marine transgressions and regressions during the Cretaceous and Paleogene periods.

There is notable exposure of Nanka Formation (best observed at the Umunya section, 18 km from the Niger Bridge) at Onitsha. Major lithological units include Imo Shale (Marine shale deposits from the Paleocene) and Nanka Sandstone (Eocene tidal deposits marked by sand waves and mud drapes). Local lithologies identified include ferruginized sandstone, shale, and clay (Ikechukwu, 2017). These formations highlight depositional environments ranging from shallow marine to fluviodeltaic settings. The interplay of marine and fluvial processes in the Anambra Basin underlines the significance of stratigraphic studies for resource evaluation. Identifying the transition zones between lithologies is crucial for accurately targeting economically valuable formations as shown in Fig. 2.

3. Materials and Methods

3.1. Sample Collection

Eight soil samples were collected from four locations using GPS for accurate georeferencing. Samples were handled to prevent contamination, using non-metallic tools and stored in polyethylene bags for laboratory analysis. The rock samples were analyzed at National Steel Raw Materials Exploratory Agency in Nigeria. Table 1 shows the sampling locations with their coordination points.

3.2. Methods

X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD are methods used to analyze the soil samples collected from the study to understand the mineralogical and chemical properties of Clays and Shales. It will also enable precise evaluation of resource quality and industrial suitability.

3.2.1. X-Ray Fluorescence (XRF)

Used to determine elemental composition by analyzing secondary X-rays emitted when samples are excited by a primary X-ray source. The following steps are taken while analyzing the samples, which are: Sample grinding, sieving, and pellet pressing with wax additives. Results are processed using Genius IF XRF and analyzed via specialized software.

3.2.2. X-Ray Diffraction (XRD)

Identifies mineralogical composition by observing diffracted X-rays through a crystal lattice. The following steps are taken during analyzing the samples. Crushing, grinding and sieving to prepare powdered samples, which are analyzed using Rigaku Miniflex XRD equipment.

4. Presentation of Results, Interpretation and Discussion

4.1. XRF Quantitative Analysis Summary of Shale Samples

4.1.1. Silicon Dioxide (SiO_2)

The SiO_2 concentration varies from 48.29% to 56.84% across the different samples, with a mean concentration of 51.16%. SiO_2 is often abundant in shale and indicates the presence of quartz and other silicate minerals, which are common in sedimentary rocks.

4.1.2. Iron Oxide (Fe_2O_3)

The concentration of Fe_2O_3 fluctuates significantly, from 7.10% to 17.97%, with a mean of 11.99%. Fe_2O_3 is a major component of iron-bearing minerals and may suggest shale's iron content, which can be indicative of its source rock or diagenetic history.

Table 1. Sampling locations with their Coordination points

Sample location	Coordinate points		Elevation	No. samples collected
Location 1 (Ota Queen River)	6°13′48.222″N	6°48′44.022″E	37m	Two (High side)
Location 2 (Ota Queen River)	6°13′53.19″N	6°48′46.098″E	20m	Two (Low Side)
Location 3 (Ukwu Abwa Road)	6°13′57.372″N	6°49′27.696″E	68m	Two
Location 4 (Nkisi Road)	6°13′16.02″N	6°49′32.772″E	88m	Two

Table 2. XRF Quantitative Analysis of shale and clay samples

S/N	Oxides	Shale Samples					Clay Samples				
		Conc. Wt. %	Conc. Wt.%	Conc. Wt. %	Conc. Wt. %	Mean Conc. Wt. %	Conc. Wt. %	Conc. Wt.%	Conc. Wt. %	Conc. Wt. %	Mean Conc. Wt.%
1	SiO_2	49.65	48.288	56.844	49.858	51.16	44.046	56.589	57.298	42.207	50.035
2	V_2O_5	0.135	0.207	0.15	0.16	0.163	0.125	0.264	0.229	0.132	0.1875
3	Cr_2O_3	0.051	0.034	0.04	0.021	0.0365	0.042	0.047	0.038	0.037	0.041
4	MnO	0.16	0.166	0.041	0.077	0.111	0.051	0.043	0.038	0.257	0.09725
5	Fe_2O_3	17.972	14.805	4.514	10.683	11.993	25.656	9.189	6.22	20.415	15.37
6	Co_3O_4	0.077	0.059	0.008	0.041	0.0462	0.121	0.0035	0.023	0.113	0.065125
7	NiO	0.012	0.01	0.008	0.01	0.01	0	0.007	0.007	0.01	0.006
8	CuO	0.046	0.047	0.035	0.04	0.042	0.045	0.062	0.048	0.05	0.05125
9	Nb_2O_3	0.012	0.031	0.015	0.022	0.02	0.012	0.05	0.037	0.027	0.0315
10	CaO	0.418	1.011	0.079	0.538	0.5115	0.156	0.045	0.061	1.689	0.48775
11	K_2O	1.28	0.98	0.463	0.837	0.89	0.306	1.147	1.519	0.918	0.9725
12	TiO_2	1.846	3.362	2.908	3.044	2.79	2.168	5.028	4.651	3.149	3.749
13	Al_2O_3	27.522	23.455	33.713	26.355	27.761	25.342	25.534	28.528	24.019	25.85575
14	Ta_2O_5	0.021	0.022	0.02	0.006	0.0172	0.586	0.471	0	0	0.26425
15	ZnO	0.014	0.O56	0.007	0.047	0.0227	0.008	0.032	0.016	0.049	0.02625
16	Ag_2O	0.022	0.077	0.025	0.023	0.0367	0	0.015	0.057	0.046	0.0295
17	Cl	0.534	0.747	O.589	0.576	0.125	0.129	0.281	0.225	0.172	0.20175
18	ZrO_2	0.125	0.162	0.102	0.111	0.619	0.538	0.642	0.041	0.714	0.48375
19	MoO_3	0	0.006	0.004	0.002	0.003	0.002	0.003	0.008	0.004	0.00425
20	P_2O_5	0	0.017	0.139	0.171	0.0817	0.179	0.032	0	0	0.05275
21	SO_3	0	6.524	0.265	7.347	3.534	0.346	0.265	0.164	5.894	1.66725
22	BaO	0.103	0	0.031	0.031	0.0412	0.136	0.208	0.104	0.074	0.1305
23	Ta_2O_5						0	0.011	0.041	0.027	0.01975
24	WO_3						0.006	0	0	0	0.0015

Table 3. XRD Quantitative Analysis Data showing weight % of minerals with 2ϴ° from samples 1 to 8

Sampling Points	Minerals of Samples Analyzed	Peak Point by Weight %	Formula	2ϴ°
Sample 1 (Shale)	Quartz	53	SiO_2	20.87
	Orthoclase	37	$Al_2O_3.K_2O_6.SiO_2$	25.25
	Clinochlore	5.9	Al-Fe-SiO_2-OH	12.77
	Albite	1.9	$NaAlSi_3O_8$	30.21
	Vermiculite	1.2	Na-K-Al-O-Si·12H_2O	59.3
	Garnet	1.02	3(Ca, Fe, Mg)O·(Al, Fe)	34.24
Sample 2 (Shale)	Quartz	39	SiO_2	25.24
	Orthoclase	3	$Al_2O_3.K_2O_6.SiO_2$	20.93
	Clinochlore	35	Al-Fe-SiO_2-OH	13.50
	Albite	1.5	$NaAlSi_3O_8$	30.05
	Nacrite	0.2	$H_4Al_2Si_2O_9$	25.15
	Garnet	20.7	3(Ca, Fe, Mg)O·(Al, Fe)	55.15
Sample 3 (Shale)	Quartz	56	SiO_2	68.44
	Orthoclase	11.5	$Al_2O_3.K_2O_6.SiO_2$	21.21
	Kaolinite	14.9	$Al_4(OH)_8(Si_4O_{10})$	20.2
	Albite	7.8	$NaAlSi_3O_8$	24.42
	Nacrite	5.1	$H_4Al_2Si_2O_9$	36.83
	Garnet	0.9	3(Ca, Fe, Mg)O·(Al, Fe)	60.23
	Illite	4.3	$K(Al, Fe)_2AlSi_3O_{10}(OH)_2$	25.32
Sample 4 (Shale)	Quartz	50	SiO_2	60.27
	Orthoclase	17	$Al_2O_3.K_2O_6.SiO_2$	21.32
	Clinochlore	2	Al-Fe-SiO_2-OH	19.31
	Albite	17	$NaAlSi_3O_8$	68.11
	Sodalite	12	$Al_6Na_8Si_6O_{24}Cl_2$	24.77
	Garnet	1.1	3(Ca, Fe, Mg)O·(Al, Fe)	49.2
	Illite	0.007	$K(Al, Fe)_2AlSi_3O_{10}(OH)_2$	36
Sample 5 (Clay)	Quartz	32.9	SiO_2	26.65
	Orthoclase	33.3	$Al_2O_3.K_2O_6.SiO_2$	28.5
	Montmorillonite-Chlorite	0.1	Na-Ca-Al-Si_4O_{14}.O	27.05
	Garnet	17.9	3(Ca, Fe, Mg)O·(Al, Fe)	34.15
	Hematite	15.9	Fe_2O_3	32.75
Sample 6 (Clay)	Quartz	24	SiO_2	24.75
	Orthoclase	26	$Al_2O_3.K_2O_6.SiO_2$	25.52
	Clinochlore	10	Al-Fe-SiO_2-OH	12.76
	Albite	14	$NaAlSi_3O_8$	21.54
	Rutile	3	TiO_2	27.35
	Garnet	13	3(Ca, Fe, Mg)O·(Al, Fe)	34.05
	Vermiculite	10	Na-K-Al-O-Si·12H_2O	27.55
Sample 7 (Clay)	Quartz	30	SiO_2	38.7
	Orthoclase	1.3	$Al_2O_3.K_2O_6.SiO_2$	27.04
	Clinochlore	39	Al-Fe-SiO_2-OH	12.84
	Albite	16	$NaAlSi_3O_8$	21.35
	Rutile	1	TiO_2	27.05
	Garnet	3.5	3(Ca, Fe, Mg)O·(Al, Fe)	21.65
	Vermiculite	4	Na-K-Al-O-Si·12H_2O	68.42
	Muscovite	5	$KAl(Si_3Al)O_{10}(OH,F)_2$	25.41
Sample 8 (Clay)	Quartz	8	SiO_2	—
	Orthoclase	5	$Al_2O_3.K_2O_6.SiO_2$	21.36
	Clinochlore	54	Al-Fe-SiO_2-OH	5.88
	Albite	19	$NaAlSi_3O_8$	27.65
	Rutile	4	TiO_2	24.16
	Osumilite	7	K-Na-Ca-Mg-Fe-Al-SiO	21.36
	Garnet	3.2	3(Ca, Fe, Mg)O·(Al, Fe)	34.37

4.1.3. Aluminum Oxide (Al_2O_3)

The values for Al_2O_3 are relatively stable, ranging from 19.45% to 33.71%, with a mean of 27.76%. Al_2O_3 is commonly associated with clay and feldspars, suggesting that the shale may contain a significant amount of clay minerals or feldspathic components.

4.1.4. Calcium Oxide (CaO)

The CaO concentration shows variation, with the highest value (1.38%) in sample 4 and the lowest value (0.08%) in sample 3, resulting in a mean concentration of 0.51%. CaO is typically associated with calcite or dolomite and indicates the potential presence of carbonate minerals in the shale.

4.1.5. Titanium Dioxide (TiO_2)

TiO_2 is another important oxide, with concentrations ranging from 1.81% to 3.36%. This oxide is often associated with minerals like rutile, anatase, and ilmenite, which are relatively stable under oxidizing conditions.

4.1.6. Other Elements (V_2O_5, Cr_2O_3, MnO, Co_3O_4, NiO, CuO, etc.)

These trace elements occur at low concentrations and may provide insight into the trace mineral composition and possible geochemical conditions during sediment deposition. For example, vanadium (V) and chromium (Cr) concentrations are higher in the shale samples and may indicate the influence of specific depositional environments or diagenesis.

4.1.7. Sulfur (SO_3)

The concentration of SO3 in the shale samples is notably higher in Sample 4 (6.91%) and Sample 3 (6.24%), with a mean of 3.53%. The presence of sulfur can be an indication of organic material or sulfide minerals, and elevated sulfur levels could suggest anoxic depositional conditions or marine influence.

4.2. XRF Quantitative Analysis Summary of Clay Samples

4.2.1. Silicon Dioxide (SiO_2)

The SiO_2 concentrations for the clay samples vary from 42.21% to 68.91%, with a mean of 50.04%. This is indicative of the dominant silicate minerals like quartz in the clay samples. High SiO_2 content is typical of clays that are derived from weathered feldspar and other silicate parent rocks.

4.2.2. Iron Oxide (Fe_2O_3)

The Fe_2O_3 content in the clay samples ranges from 4.21% to 25.66%, with a mean of 15.37%. The variability of Fe_2O_3 concentrations suggests that the clay samples may have been subjected to varying levels of weathering and iron-rich mineral deposition.

4.2.3. Aluminum Oxide (Al_2O_3)

The concentrations of Al_2O_3 in the clay samples range from 18.32% to 28.53%, with a mean of 25.86%. Al_2O_3 is typically associated with kaolinite, feldspar, and other alumino-silicate minerals, which are common in clay deposits.

4.2.4. Calcium Oxide (CaO)

The CaO concentration in the clay samples varies significantly, from 0.05% to 2.41%, with a mean of 0.49%. The presence of CaO in clay may indicate the presence of carbonates, which can affect the clay's plasticity and overall properties.

4.2.5. Titanium Dioxide (TiO_2)

TiO_2 ranges from 2.23% to 5.03%, with a mean of 3.75%. TiO_2 is often associated with ilmenite and rutile, which are relatively stable minerals that can provide insights into the clay's source region.

4.2.6. Other Elements (V_2O_5, Cr_2O_3, MnO, NiO, CuO, etc.)

Similar to the shale samples, trace elements in the clay samples are present in relatively low concentrations, though Mn concentrations are notably higher in sample 8 (0.199%) compared to other samples. This could indicate localized sources of Mn.

4.2.7. Sulfate (SO_3)

Sample 8 has a very high sulfur content (5.9%), significantly higher than the other clay samples (mean of 1.67%). This suggests that sample 8 may have been influenced by anoxic conditions or marine influence with higher organic matter. From the XRF data, we can infer that both shale and clay samples are rich in silicate minerals, as indicated by the high concentrations of SiO_2. The clay samples show a higher content of Al_2O_3, suggesting a greater proportion of clay minerals, while the shale samples show higher concentrations of Fe_2O_3 and TiO_2, pointing to the presence of Iron-rich minerals and titanium-bearing phases as shown in Table 2. The presence of sulfur in both shale and clay samples, particularly in the higher concentrations in certain samples, suggests a possible marine or anoxic depositional environment. The variability in trace elements across the samples could also reflect differences in sediment provenance and the specific depositional conditions at each sampling point. The shale and clay samples seem to have undergone varying levels of diagenesis, with the shale samples indicating a more mature or Iron-rich environment and the clay samples showing a slightly more weathered or kaolinitic composition.

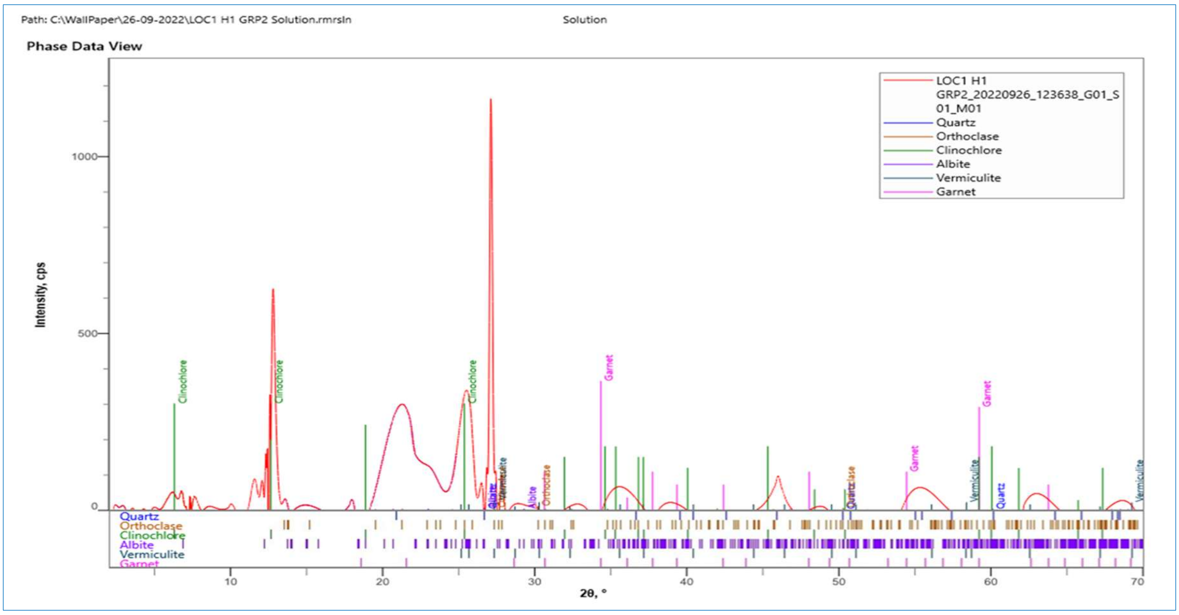

Fig. 3. XRD qualitative analysis peak plot of intensity (cps) against 2Θ° of sample 1

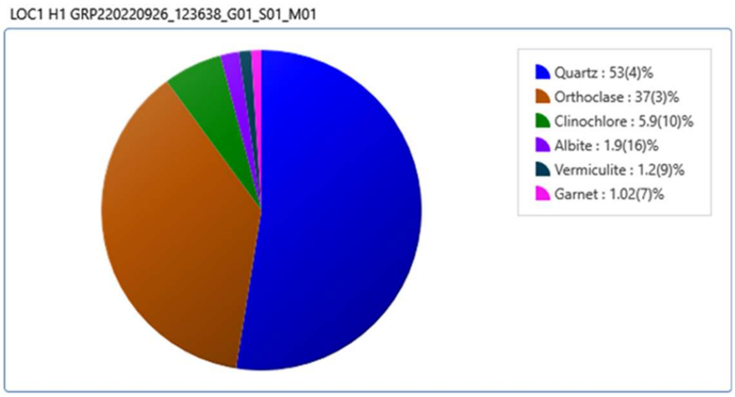

Fig. 4. XRD quantitative analysis pic chart weight % of minerals in sample 1

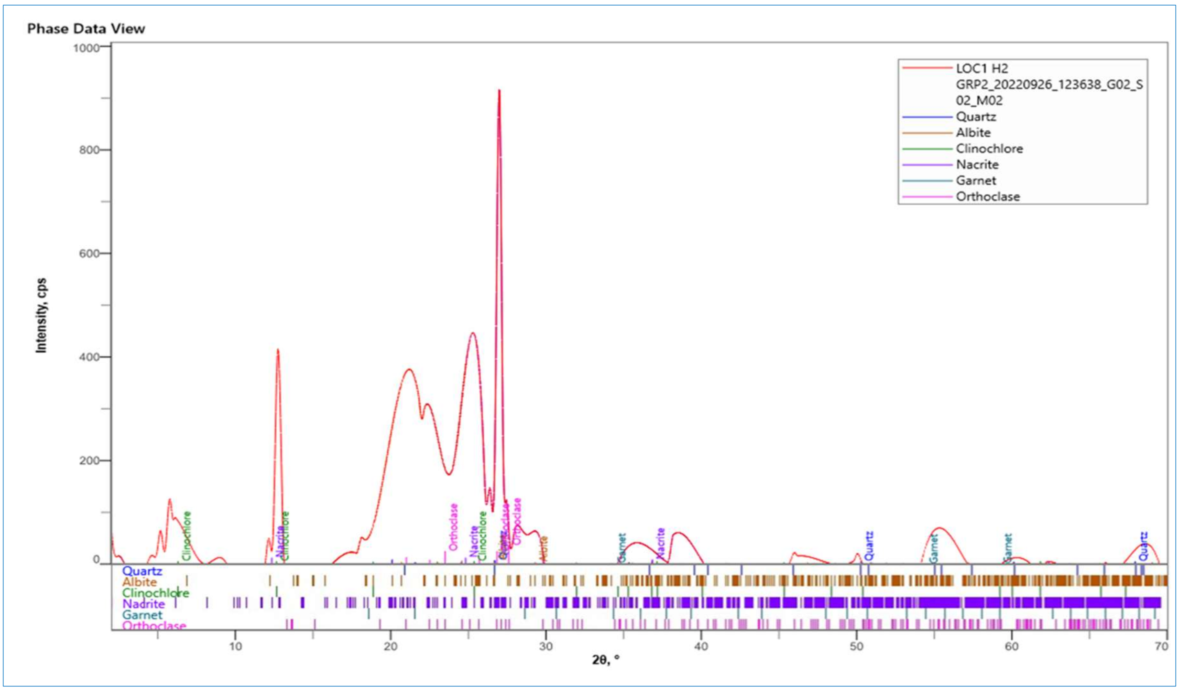

Fig. 5. XRD qualitative analysis peak plot of intensity (cps) against 2ϴ° sample 2

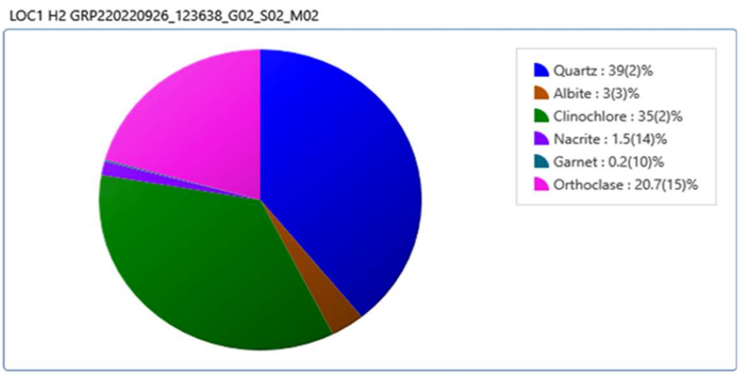

Fig. 6. XRD quantitative analysis pic chart weight % of minerals in sample 2

4.3. XRD Quantitative Analysis Summary of Shale and Clay

Tables 3 provide the XRD quantitative analysis data for the various mineral components found in samples 1 through 8. Figs. 3 to 19 show the XRD qualitative analysis peak plot of intensity (cps) against 2ϴ° and XRD quantitative analysis pic chart weight % of minerals of sample 1 through 8. It includes the weight percentages of each mineral, the chemical formula, and the corresponding peak 2θ° values, which reflect the diffraction angles for these minerals. The minerals identified across the samples include Quartz, Orthoclase, Clinochlore, Albite, Garnet, and various other minerals such as Vermiculite, Nacrite, Kaolinite, and Rutile, among others. The 2θ° values assist in the precise identification of each mineral phase in the samples.

Quartz is the most dominant mineral across all samples, with its peak percentage by weight ranging from 8% in sample 8 to 56% in sample 3. This is expected, as quartz is a common constituent of shale and clay deposits. Its high abundance in many of the samples suggests that the rocks are largely composed of siliceous material.

Orthoclase (a type of feldspar) also appears consistently across all samples, with its peak percentage varying from 1.3% in Sample 7 to 37% in sample 1. Its presence indicates a feldspathic nature of the samples, and its varying abundance may reflect differences in the degree of alteration or mineralization.

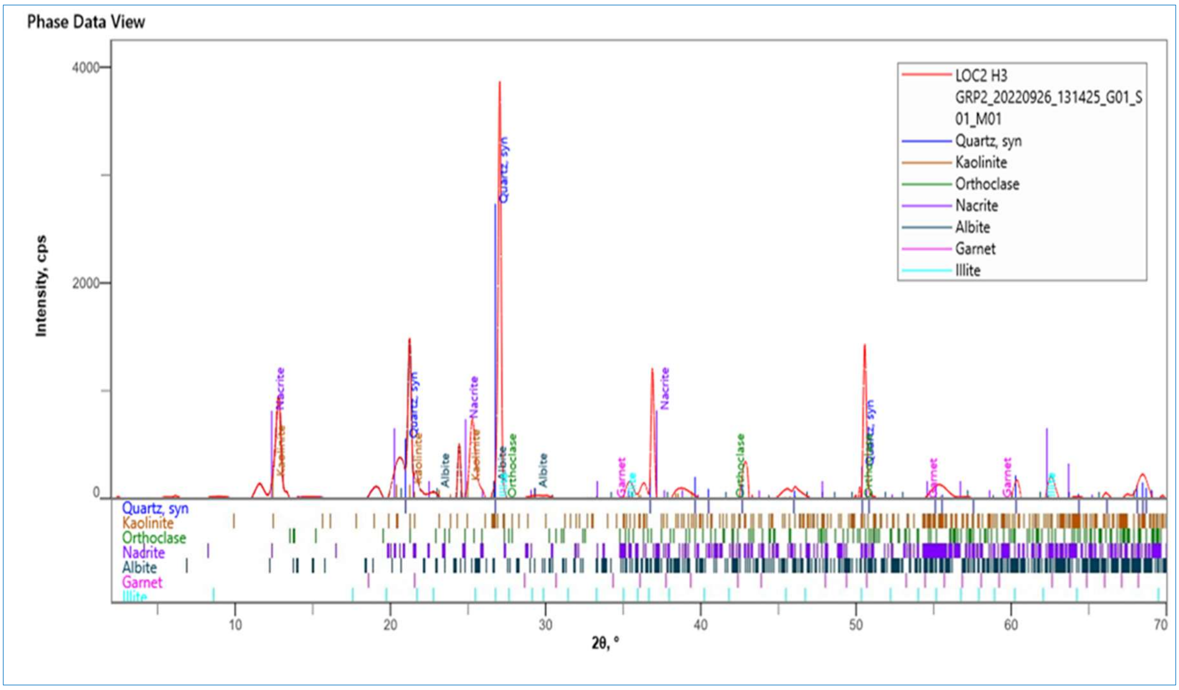

Fig. 7. XRD qualitative analysis peak plot of intensity (cps) against 2Ɵ° sample 3

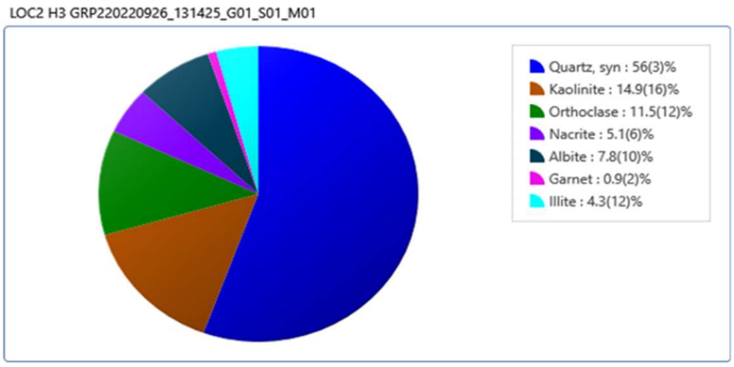

Fig. 8. XRD quantitative analysis pic chart weight % of minerals in sample 3

Clinochlore (a type of chlorite) is present in varying quantities, with Sample 8 having the highest percentage (54%). Clinochlore is often associated with low-grade metamorphism, so its abundance suggests some metamorphic influence on the samples.

Albite (Sodium-rich feldspar) appears in most of the samples, with relatively high concentrations, particularly in sample 1 (1.9%) and sample 4 (17%). The presence of albite may reflect both primary and secondary mineralization processes in these samples.

Garnet is consistently found in all the samples, but in very small quantities, ranging from 0.9% in sample 3 to 20.7% in sample 2. Garnet's presence is notable, as it is often used as an indicator of metamorphic conditions.

The presence of garnet suggests that some of the samples may have been subjected to metamorphism, though its low abundance suggests it is not a dominant phase.

Vermiculite is found in samples such as sample 1 (1.2%) and sample 6 (10%). Vermiculite is a hydrated phyllosilicate mineral, typically forming under specific weather conditions. Its presence may indicate a more altered or weathered environment.

Nacrite (a type of kaolinite) appears in samples 2 and 3 in very small quantities (0.2% and 5.1%, respectively). Nacrite forms in low-temperature; low-pressure conditions and its presence may indicate some weathering or alteration of feldspathic material.

Kaolinite is found in sample 3 (14.9%) and is typical of clay-rich sedimentary rocks, often forming in tropical weathering environments. The high percentage in sample 3 suggests that this sample may be derived from a more weathered source.

Sodalite, present in sample 4 (12%), is a rare mineral typically associated with alkaline igneous rocks. Its presence in this sample may reflect some interaction with alkali-rich fluids or a specific source material.

Hematite is present in sample 5 (15.9%), a mineral indicative of oxidizing conditions. Its presence suggests that some of the samples may have experienced more oxidizing conditions during their formation.

Rutile is found in sample 6 (3%) and sample 7 (1%), which is a titanium oxide mineral typically forming under high-temperature conditions, possibly reflecting the influence of igneous processes or high-temperature alteration.

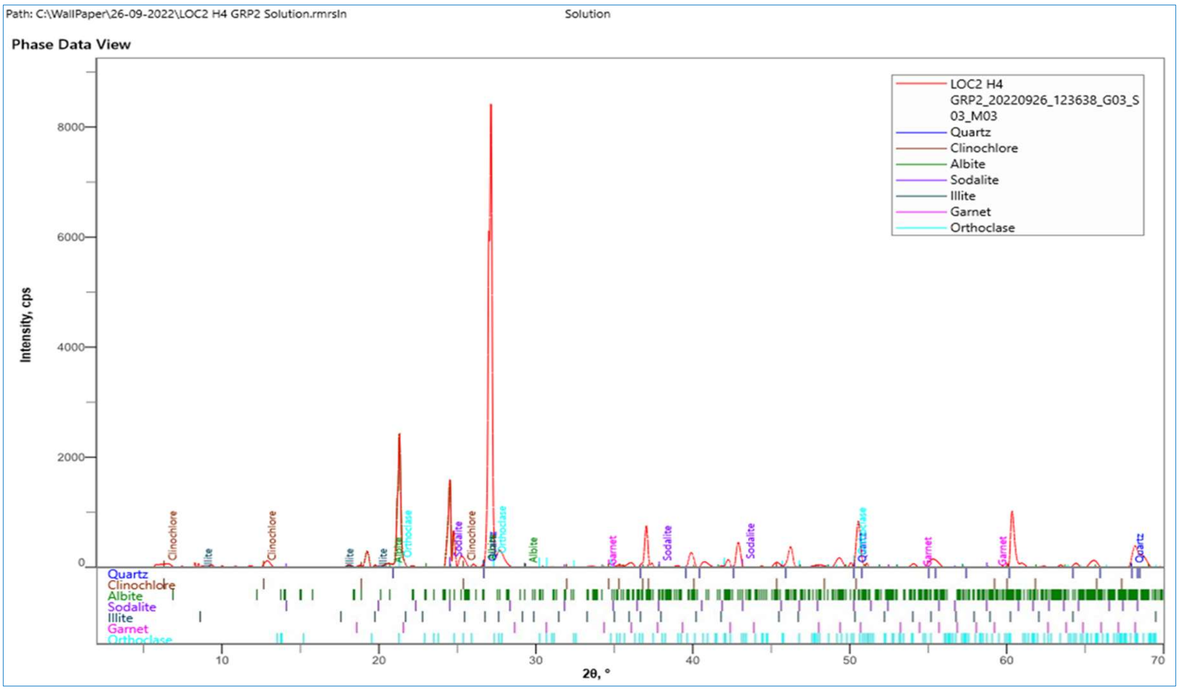

Fig. 9. XRD qualitative analysis peak plot of intensity (cps) against 2ϴ° sample 4

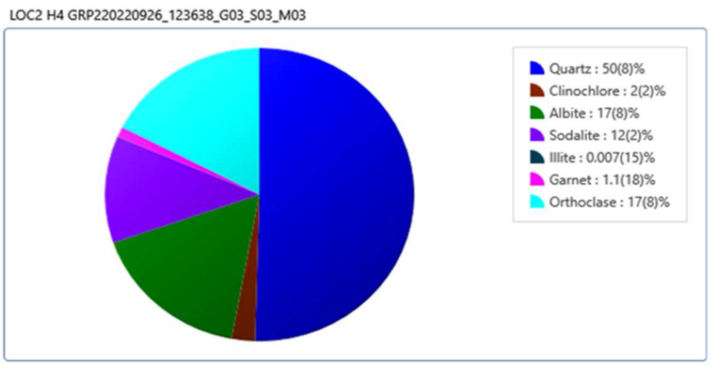

Fig. 10. XRD quantitative analysis pic chart weight % of minerals in sample 4

Muscovite (a type of mica) is present in sample 7 (5%), and it typically forms under low to medium-grade metamorphic conditions. Its presence suggests a possible metamorphic influence on this sample.

Osumilite, found in sample 8 (7%), is a rare mineral typically associated with high-pressure conditions, but its presence here is minimal and does not suggest significant high-pressure metamorphism.

Sample 3 contains the highest percentage of quartz (56%), followed by kaolinite (14.9%) and orthoclase (11.5%), which could suggest more mature, weathered shale with some influence of low-temperature alteration or weathering processes. Sample 1 (shale) has a high percentage of orthoclase (37%) and quartz (53%), indicating a predominantly siliceous nature with some feldspathic influence. Sample 8 (clay) stands out with its high content of clinochlore (54%), suggesting some metamorphic influence, possibly a metamorphosed clay.

The Garnet content across samples remains relatively low (ranging from 0.9% to 20.7%), reflecting its minor but notable role, likely indicating some degree of metamorphism. Vermiculite and nacrite are more abundant in the clay samples (samples 5, 6, 7, and 8), which suggests a greater degree of weathering and clay formation in these samples. The XRD analysis of these samples indicates a mix of igneous, metamorphic, and weathering influences, with siliceous (quartz) and feldspathic (orthoclase) minerals predominating in most samples. The presence of clay minerals (kaolinite, clinochlore, vermiculite) suggests alteration or weathering processes, with possible low- to medium-grade metamorphism influencing some samples.

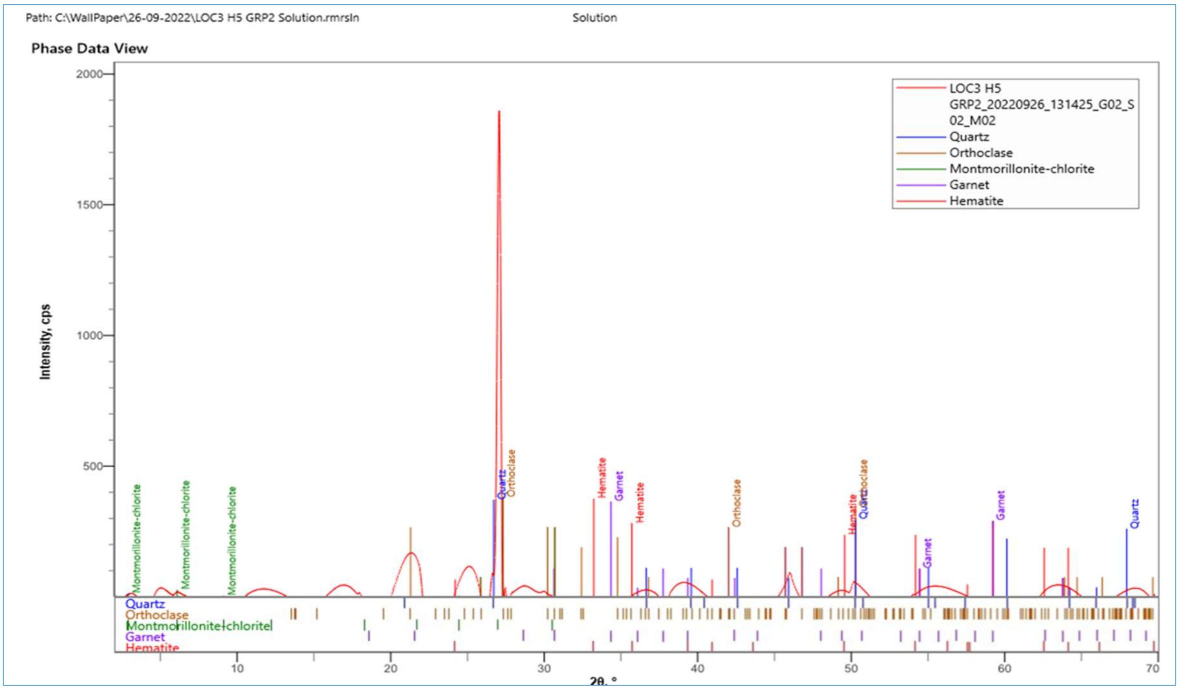

Fig. 11. XRD qualitative analysis peak plot of intensity (cps) against 2ϴ° sample 5

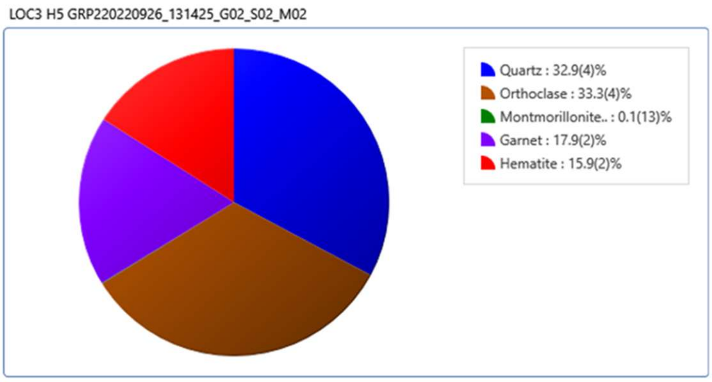

Fig. 12. XRD quantitative analysis pic chart weight % of minerals in sample 5

5. Discussion

5.1. Mineralogical and Chemical Analysis

The mineralogical analysis of the shale and clay samples from the Nsugba area reveals a diverse array of minerals, each offering insights into the depositional environment, origin, and potential industrial uses of the deposits. The key findings and their implications for the industrial potential of the samples are summarized below.

Quartz, orthoclase, and garnet are present in all the analyzed samples, with quartz being the most abundant. This suggests that the clays were primarily derived from stable, weathered materials from older rock formations (e.g., granite or gneiss), which is consistent with the area's geological history.

Quartz is a hard, durable mineral, contributing to the overall strength and abrasion resistance of the clays, making them suitable for industrial applications such as brick production and possibly ceramics.

5.1.1. Clinochlore

Found in samples 1, 2, 4, 6, 7, and 8, Clinochlore indicates that the clays are primarily unweathered, fine-grained materials. This suggests a relatively stable environment of deposition with minimal weathering or alteration. This mineral's presence in the clays may enhance their plasticity, making them suitable for ceramics and pottery production.

5.1.2. Kaolinite and Montmorillonite-Chlorite

These minerals, particularly in samples 3 and 5, suggest the presence of authigenic clays, which are formed under diagenetic or post-depositional conditions, and they are primarily cementing materials. Kaolinite is often associated with weathering under acidic conditions, indicating that these samples might have originated from weathered Basement Complex rocks. These clays are fine-grained and suitable for ceramics, refractories, and other products requiring fine textures.

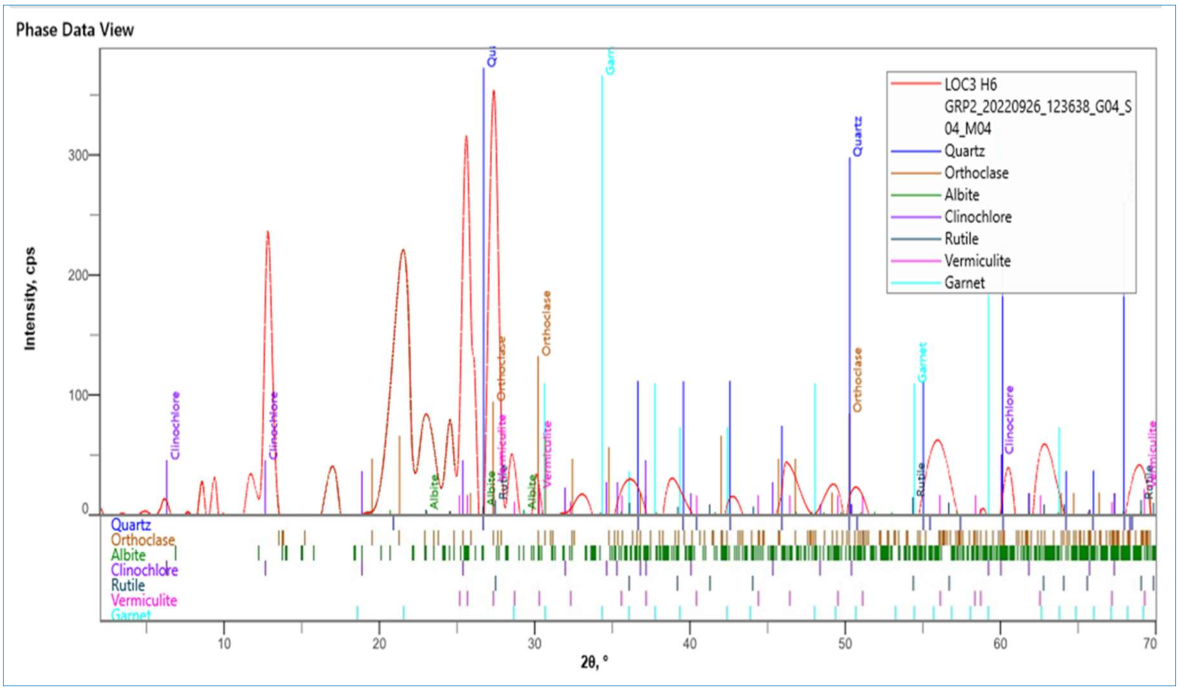

Fig. 13. XRD qualitative analysis peak plot of intensity (cps) against 2ϴ° sample 6

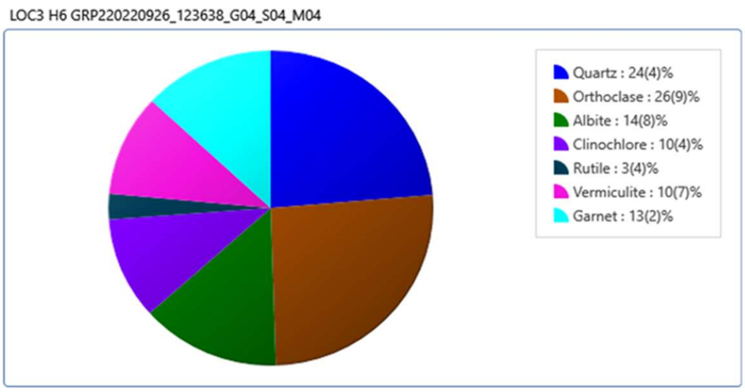

Fig. 14. XRD quantitative analysis pic chart weight % of minerals in sample 6

5.1.3. Illite

Present in samples 3 and 4, illite suggests that the clays are highly plastic and have a low K_2O content (0.306-1.517 wt. %), which can make them problematic for certain uses such as foundation materials. Illite-rich clays may lead to foundation instability in construction, as the high plasticity can result in swelling or shrinkage when exposed to moisture, a concern for geotechnical applications.

5.1.4. Sodalite

The presence of Sodalite in sample 4 indicates that the clay has a metasomatic origin, which typically forms in conditions of high pressure and low temperature (below 600°C). This suggests that this clay may have been influenced by hydrothermal activity and could have potential for high-temperature applications, such as in the production of specialized refractories.

5.1.5. Hematite

Hematite, found only in sample 6, is an Iron oxide mineral that significantly influences the color of the clay, contributing to its red, yellow, or pink hues. The presence of hematite and its high Fe_2O_3 content in sample 6 is likely responsible for the concretion formation in the Nsugba section, which may be of interest for color-specific products in the ceramics industry.

5.1.6. Other Minerals

Nacrite, Vermiculite, Rutile, Muscovite, and Osumilite are present in specific samples. These minerals suggest variations in the depositional environments and indicate that some samples may be suitable for high-temperature applications like refractories, ceramics, and pottery.

5.2. Chemical Composition and Industrial Potential

Clay's unique properties, including plasticity, adsorptivity, and shrink-swell capacity, make it versatile for various industries: *Plasticity* (ideal for ceramics and pottery), adsorptivity (useful in water purification and pollutant removal) and shrink-swell capacity (important for soil stabilization and geotechnical projects).

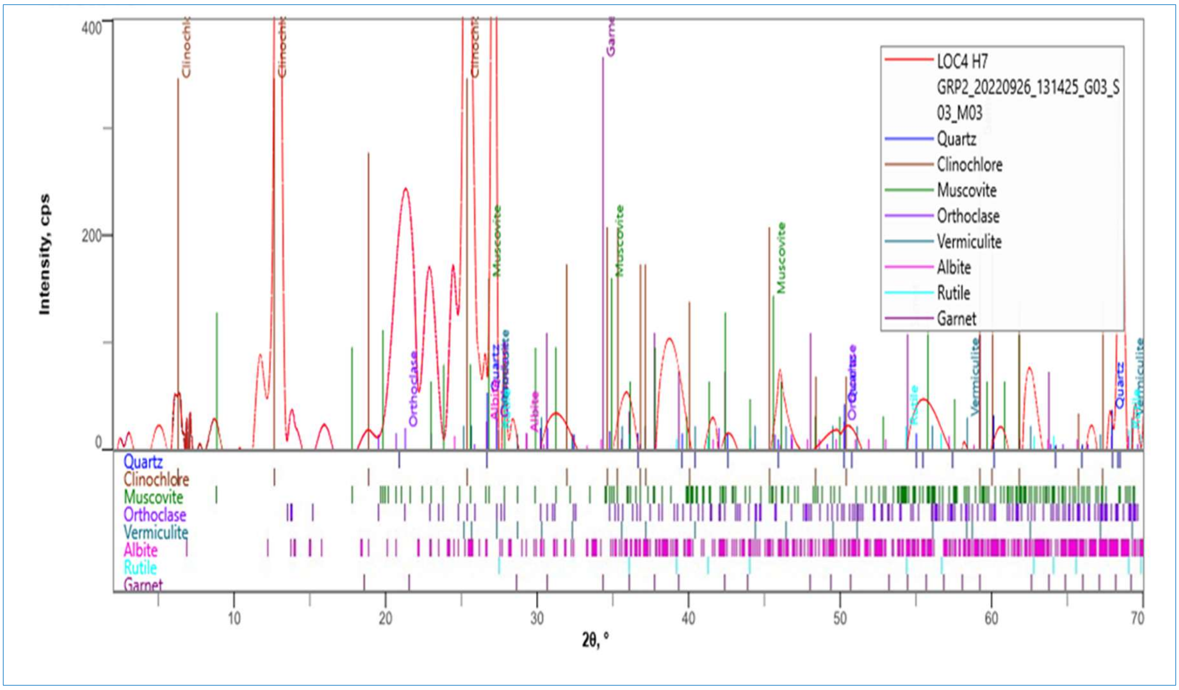

Fig. 15. XRD qualitative analysis peak plot of intensity (cps) against 2ϴ° sample 7

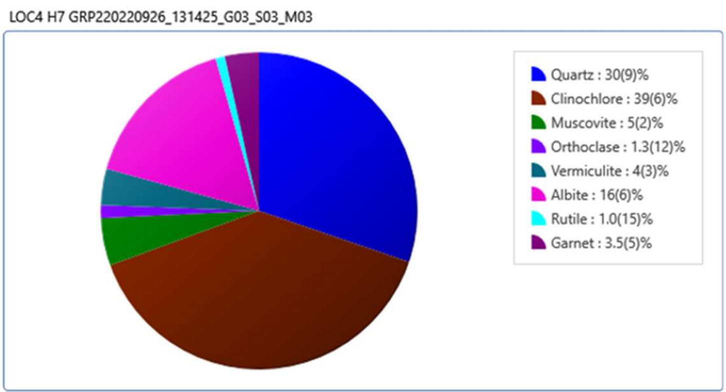

Fig. 16. XRD quantitative analysis pic chart weight % of minerals in sample 7

Studies, such as those by Emmanuel et al. (2015) and Benjamin et al. (2019), confirm the suitability of clays for producing ceramics, paint, glass, and refractory bricks. However, high iron oxide content could limit applications like high-grade cement production. Beneficiation processes can refine clay and shale deposits, improving their quality and expanding their industrial use. The chemical analysis shows that the shale and clay deposits are rich in SiO_2 (Silicon Dioxide), Al_2O_3 (Aluminum Oxide), and Fe_2O_3 (Iron Oxide), with other notable elements including TiO_2 (Titanium Dioxide), MnO (Manganese Oxide), MgO (Magnesium Oxide), and CaO (Calcium Oxide). These elements are crucial for various industrial applications: SiO_2 and Al_2O_3 are key components in the production of ceramics, bricks, and refractories, as they provide the required strength and thermal stability; Fe_2O_3 is important for coloring ceramics and can also contribute to the production of refractory bricks that can withstand high temperatures and the presence of TiO_2, MnO, MgO, and CaO suggests that the clays may also be useful for specialized ceramics or other refractory products that require these specific oxides as shown in Table 4 and 5.

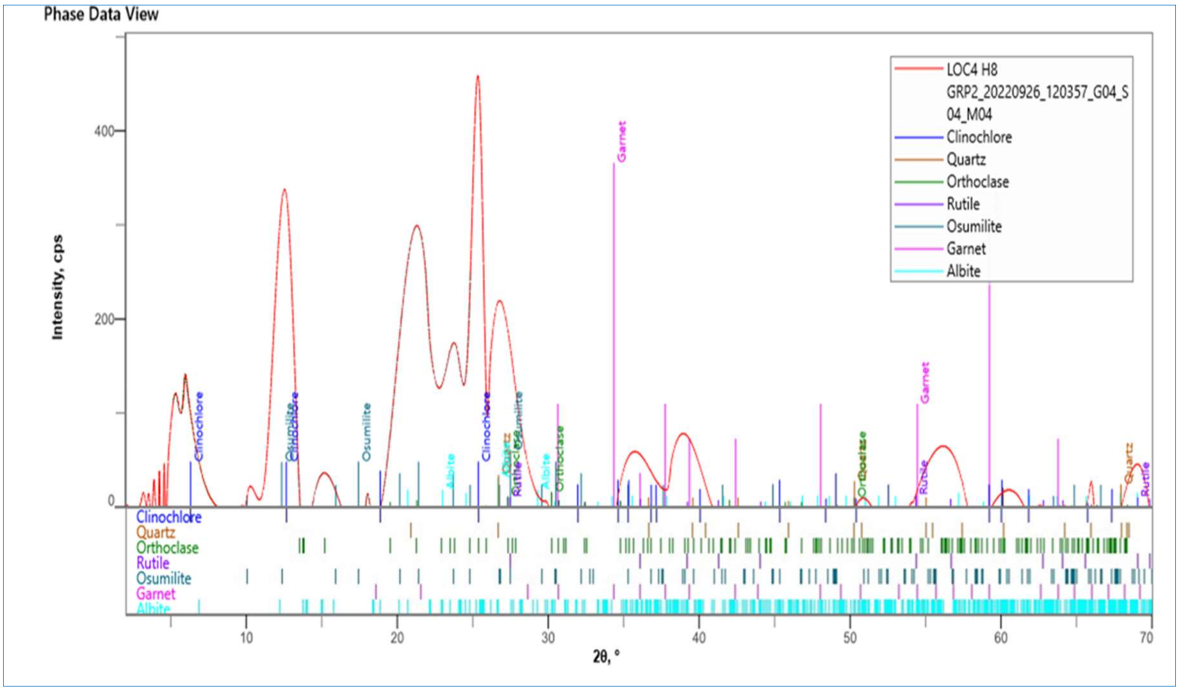

Fig. 17. XRD qualitative analysis peak plot of intensity (cps) against 2ϴ° sample 8

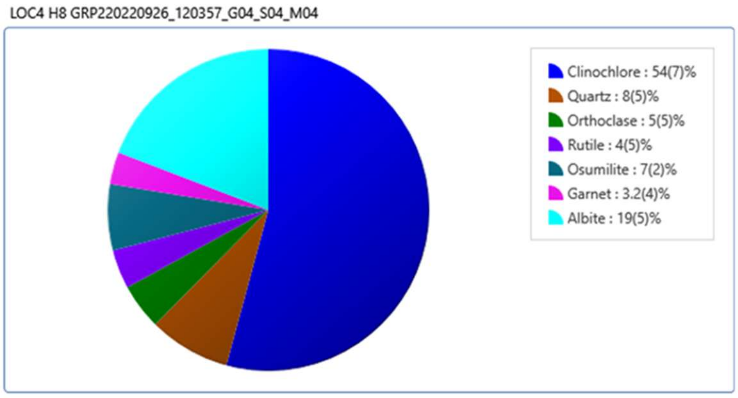

Fig. 18. XRD qualitative analysis peak plot of intensity (cps) against 2ϴ° sample 8

5.2.1. Silicon Dioxide (SiO_2)

For Sample 1-4, the mean concentration of SiO_2 is 51.16%, which is within the range of known reference clays used for various industrial purposes (e.g., Afikpo Shale: 59.81%, Florida Active Kaolinite: 57.67%) and for Sample 5-8, the mean concentration is 50.035%, which is again close to the reference values for industrial use, such as Refractory Bricks (51.70%), and Ceramics (67.50%).

Industrial Implication: The high SiO_2 content is favorable for industries like ceramics and refractory brick manufacturing, as SiO_2 is an essential component for both due to its role in providing structural integrity and heat resistance.

5.2.2. Aluminum Oxide (Al_2O_3)

For samples 1-4, the mean concentration of Al_2O_3 is 27.76%, which is similar to the reference value for Afikpo Shale (21.76%) and within the range for other industrial uses like Refractory Bricks (25.44%) and Ceramics (26.50%) and for Sample 5-8, mean concentration is 25.86%, close to the reference values for Refractory Bricks (25.44%) and Ceramics (26.50%).

Industrial Implication: Al_2O_3 is critical for ceramics and refractory materials as it imparts thermal stability. The values suggest these samples could be suitable for both industries.

5.2.3. Iron Oxide (Fe_2O_3)

For Sample 1-4, the mean concentration is 11.99%, which is higher than the Afikpo Shale (3.02%) and falls within the range for refractory bricks (25.44%), ceramics (0.5-1.20%), and paper (0.43%) and for samples 5-8, mean concentration is 15.37%, which is higher than Afikpo Shale (3.02%) and aligns with refractory bricks (25.44%) and ceramics (0.5-1.20%).

Industrial Implication: While Fe_2O_3 in higher concentrations may be undesirable in some industrial applications (like ceramics or paper), it is useful in specific applications, especially in refractory bricks, where it can contribute to the material's strength and hardness.

5.2.4. Magnesium Oxide (MgO)

For Sample 1-4, No significant MgO content and for samples 5-8, mean concentration is 0.26%, which is within the acceptable range for refractory bricks (0.5-1.20%) and ceramics (0.1-0.19%).

Industrial Implication: MgO contributes to the refractory properties of clays. The low content in the samples suggests limited suitability for certain refractory applications, but they can still be used in ceramics where low MgO content is acceptable.

5.2.5. Calcium Oxide (CaO)

For sample 1-4, the mean concentration is 0.51%, which is within the range for Refractory Bricks (0.2-0.7%) and for sample 5-8, mean concentration is 0.49%, which is again within the acceptable range for Refractory Bricks (0.2-0.7%). *Industrial Implication*: CaO is often used in the production of bricks and refractories. The levels in the samples indicate that they can be used in industries that require moderate lime content.

5.2.6. Sodium Oxide (Na_2O)

For Sample 1-4, No significant Na_2O content. Sample 5-8: Some content of Na2O is observed (e.g., 0.47%).

Industrial Implication: Na_2O is beneficial in some ceramics, but excessive amounts may hinder the clay's performance. The low levels in the samples indicate these clays are suitable for industries that require lower sodium oxide concentrations.

5.2.7. Potassium Oxide (K_2O)

For Sample 1-4, the mean concentration is 0.98%, which is within the acceptable range for Refractory Bricks (0.87%) and for Sample 5-8, mean concentration is 0.97%, which again falls within the range for Refractory Bricks (0.87%).

Industrial Implication: K_2O is beneficial in ceramics for improving workability and other properties. The values in both sample sets suggest they could be used in ceramic production.

5.2.8. Titanium Oxide (TiO_2)

For Sample 1-4, the mean concentration is 2.79%, which is within the range for Refractory Bricks (1.0-2.80%) and for Sample 5-8, mean concentration is 3.75%, which is slightly higher than the reference range but still acceptable for some industrial uses like ceramics and refractories.

Industrial Implication: TiO_2 contributes to the color and opacity of ceramic products and can improve the refractoriness of bricks. The samples may be suitable for industries requiring titanium oxide.

Table 4. Chemical composition of some known reference shale and clay samples for samples 1-8 (Onyekure et al., 2018)

Major Oxides	Mean Conc. Wt. % Samples 1-4	Mean Conc. Wt. % Samples 5-8	Afikpo Shale (Arua and Onyeoku,1978)	Afam Clay (Jubril and Amajor, 1991)	Plastic Fire Clay of Louis (Huber, 1985)	Florida Active Kaolinite (Huber, 1985)	Maastrichtian Clayin Bida Basin (Olusola et.al. 2011)	Dukku Clay Kebbi State (Salihu and Suleiman, 2018)
SiO_2	51.16	50.035	59.81	42.2	57.67	5	63.3	55.59
Al_2O_3	27.761	25.8557	21.76	26.2	24	2.92	24.6	35.5
Fe_2O_3	11.993	15.37	3.02	5.1	3.23	9.42	1.6	4.5
MgO	-	0.2642	1.45	0.7	0.3	3.65	0.06	1.9
CaO	0.511	0.4877	1.32	1.6	0.7	0.08	0.04	2.1
Na_2O	-		0.47	2.9	0.2	1.91	0.07	-
K_2O	0.98	0.9725	0.87	8.3	0.5	0.03	0.32	-
TiO_2	2.79	3.749	0.92	-	-	0.98	1.75	0.02
P_2O_5	0.0817	0.0527	-	-	-	1.18	0.07	-
MnO	0.111	0.0972	nd	0.03	-	0.002	0.01	-
H_2O			-	-	10.5	10.19	-	-

5.2.9. Phosphorus Pentoxide (P_2O_5) and Manganese Oxide (MnO)

Both are present in very low concentrations in the samples (0.08% for P_2O_5 and 0.11% for MnO in sample 1-4).

Industrial Implication: These oxides generally do not significantly influence industrial potential, as their concentrations are below levels that would affect material performance for most industrial applications. The chemical composition of samples 1-4 and Samples 5-8 generally shows that these shales and clay deposits are suitable for industrial uses, including ceramics, refractory bricks, and possibly paper production. The main contributors to their industrial value are their high SiO_2 and Al_2O_3 contents, which are key components in the production of refractory materials and ceramics. However, their Fe_2O_3 content may limit their use in certain applications where lower iron content is preferred (e.g., paper production). Overall, these deposits have considerable potential as raw materials for various industrial products as shown in Table 4 and 5.

Suitability for Industrial Uses: The shale and clay deposits from samples 1-4 and Samples 5-8 exhibit a composition that makes them suitable for ceramics and refractory bricks. The high levels of SiO_2, Al_2O_3, and TiO_2, along with moderate amounts of K_2O, make these deposits ideal for these industries.

However, their relatively high Fe_2O_3 content may limit their use in industries like ceramics or paper production, which require low iron concentrations.

Best Industrial Fit: These clays are best suited for high-temperature applications like refractory bricks, which benefit from their strength and thermal stability. The ceramics industry can also use these clays, particularly where moderate iron oxide levels are acceptable and where potassium content is beneficial for molding and shaping.

Table 5. Standard specifications of the concentration in % of oxides in shale and clay for industrial uses for samples 1-8 (Onyekure et al., 2018)

Major Oxides	Mean Conc. Wt.% samples 1-4	Mean Conc. Wt.% samples 5-8	Refractory bricks (Parker, 1967)	Ceramics (Singer and Sunja 1971)	Rubby (Keller, 1964)	Paper (Keller, 1964)	Brick Clay (Murray, 1960)	Refractory Bricks and Ceramics (Malu et al., 2013)
SiO_2	51.16	50.035	51.7	67.5	44.9	45.90-48.5	38.67	68.478
Al_2O_3	27.761	25.8557	25.44	26.5	32.35	33.5-36.1	9.45	14.942
Fe_2O_3	11.993	15.37	25.44	0.5-1.20	0.43	0.30-0.60	2.7	11.143
MgO	-	0.2642	0.5-1.20	0.1-0.19	Tr	-	8.5	1.615
CaO	0.511	0.4877	0.2-0.70	0.18-0.30	Tr	0.0-0.50	15.84	0.034
Na_2O	-		0.8-3.50	0.20-1.50	0.14	0.0-1.6	2.76	2.045
K_2O	0.98	0.9725	-	1.10-3.10	0.28	0.0-1.6	2.76	-
TiO_2	2.79	3.749	1.0-2.80	0.10-1.0	1.8	0.0-1.70	-	-
P_2O_5	0.0817	0.0527	-	-	-	-	-	-
MnO	0.111	0.0972	-	-	-	-	-	-
H_2O			-	-	-	-	3.04	-

However, it is noted that the industrial specifications of the clays in the study area may not fully match the high standards of commercially marketed European and Asian counterparts, primarily due to the higher iron oxide content, which may affect the color and workability of the clays for certain products. The shale and clay deposits in the study area have significant industrial potential, particularly to produce refractory bricks and cement. However, the high iron oxide content poses some challenges, especially for ceramics, where lower iron oxide content is preferred for high-quality products. The alumina-iron ratio is generally favorable for cement production, and the deposits could be utilized in cement manufacturing, particularly where the iron oxide content is not excessively high. Overall, these clays offer promising prospects for various industrial applications, though care must be taken to manage the high iron oxide content for certain uses as shown in Table 4 and 5.

6. Conclusion

The clays and shales in the Nsugbe area contain industrially valuable minerals, making them suitable for refractory, ceramic, and other applications. Future studies should expand sampling coverage and explore beneficiation techniques to reduce iron oxide content. XRF analysis reveals that both clay and shale samples are rich in silicate minerals, with high SiO_2 concentrations. Clay samples contain more Al_2O_3, indicating higher clay mineral content, while shale samples have increased Fe_2O_3 and TiO_2, suggesting iron-rich and titanium-bearing phases.

The presence of sulfur hints at a marine or an anoxic depositional environment. Variations in trace elements reflect differences in sediment provenance and depositional conditions.

XRD analysis shows influences from igneous, metamorphic, and weathering processes, with quartz, feldspar (orthoclase), and clay minerals (kaolinite, clinochlore, vermiculite) dominating.

Shale and clay deposits (samples 1-8) are well-suited for ceramics and refractory bricks due to high SiO_2, Al_2O_3 and TiO_2 content.

Moderate K_2O levels make the clay ideal for molding and shaping in ceramics and high Fe_2O_3 content may limit applications in industries requiring low iron levels, such as ceramics and paper production. These clays are best suited for high-temperature applications like refractory bricks, where their strength and thermal stability are advantageous.

7. Recommendation

Research and Improvement: It is recommended that further research be conducted to improve the quality of the clay materials. Such research could focus on reducing Iron oxide content in some samples or enhancing the plasticity of the clays to make them more suitable for a broader range of industrial applications.

Economic Impact: By improving the quality of the clays, it is possible to enhance the economic viability of local clay industries, thereby benefiting the local economy in Nsugba and the surrounding areas.

Comparative Studies: More comparative studies should be conducted to explore the specific uses of these clays in refractory, pottery, bricks, and ceramics production, taking into account factors like temperature resistance, plasticity, and coloration.

The discovery of oil and gas near Nsugbe has spurred local economic activities in agriculture and commerce. However, sustainable resource extraction practices are essential to balance economic growth with environmental conservation. Collaborative research between industry and academia can maximize the economic benefits of clay and shale resources while addressing environmental concerns.

Long-term monitoring of the Nsugbe deposits can provide insights into sustainable extraction practices. Collaborative efforts with industries can further enhance the economic value of these resources while ensuring environmental conservation.

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