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Mineralogy, Physicochemical Characteristics and Industrial Potential of Some Residual Clay Deposits within Ekiti State, Southwestern Nigeria

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Abstract

Residual clay deposits overlying Precambrian Basement Complex situated at Orin, Igbara Odo, Ikere and Ado Ekiti were investigated using several analytical techniques. Field evidence supported by mineralogical and physicochemical analyses suggests that the kaolinitic clay deposits is a product of hydrothermal and in-situ weathering of aplite, and granite. Kaolinite is the predominant clay mineral of the studied clay deposits with subordinate quartz, potassium iron oxide and aluminium phosphatic minerals. There is localised occurrence of halloysite. The absence of vanadium in the EDS data of rolled into tubes kaolinite sheets of Ado Ekiti clay match up with XRF data. This result trend combined with field observation suggests that clay bodies formed from weathering of feldspar is deficient in vanadium. The study suggests that morphology of kaolinitic minerals is influenced by the kind of parent material (i.e. feldspars or micas) and degree of chemical weathering. The pH values of pore water from clay samples range from 7.14 - 9.08. The electrical conductivities (EC) of the clay/water slurries (S/L ratio) range from 0.004mS/cm – 3.02mS/cm. The oxidation reduction potential (ORP) values range between -62.4 and – 6.8 for the solids or slurries prepared with water. The dissolved oxygen (DO) values range from 6.73ppm – 7.26ppm for solids or slurries prepared with water. The loss on ignition ranges from 2.24-13.39. The SiO_2/Al_2O_3 molar ratio of 1.40 and 1.50 for Orin and Ikere clay bodies indicated that a 1:1 clay mineral was the dominant component. The high chemical index of alteration (CIA = 77.97~98.64) and chemical index of weathering (CIW = 97.21~99.93) values probably indicated the complete weathering of feldspars to kaolinite. The weathering index of Parker (WIP) values grouped the analysed clay samples into moderate to intense degree of weathering. This observation is confirmed by the absence of detrital feldspar in the XRD spectra peak. Factor analysis showed enrichment and depletion of major and trace elements which could be attributed to moderate to intense leaching conditions of the presumed parent material. The data shows explicit relationship between the clayeyness value (Al_2O_3/SiO_2 ratio), the relative base loss (RBL) and the cation exchange capacity (CEC). Cluster analysis of major and trace elements showed two groups of chemical differences amongst the elements in the clays; moderate and intense degree of weathered clays. Nevertheless, the variations in the degree of weathering or leaching process have greater contribution to clay deposits differentiation. Assessment of the industrial potential of the studied clay bodies based on their physical and chemical characteristics revealed that they are suitable for the production of refractory bricks and ceramics. Suitable processing would be compulsory if they are to meet the requirements for other industrial applications, such as rubber, paper, paint, cosmetics, and fertilizer industries.

Keywords: Clay; Mineralogy; Physicochemical characteristics; Weathering indices; Pore water; Multivariable analysis; Igbara Odo Ekiti; Ikere Ekiti; Ado Ekiti.

1.1 Introduction

Clay minerals are seldom mono-mineralic and have no genetic significance, as it is used for residual weathering products, hydrothermally altered products, and sedimentary deposits (Murrey, 2007). These minerals occur under a fairly limited range of geologic environments which include soil horizons, continental and marine sediments, geothermal fields, volcanic deposits, and weathering rock formations. In general, they form where rocks are in contact with water, air, or steam and the type of clay however is controlled by the composition of pre-existing rock mineralogy (Kabeto et al., 2012). Several studies show that clays preserve a geochemical 'fingerprint' specifically few trace elements of the parent rocks from which they were formed (Mosser, 1980; Mosser et al., 1991). Some specific physical and chemical properties of kaolin are dependent on the environment of deposition, geological origin, geographic source and the material method at the end of processing (Murray and Kogel, 2005).

Superficial clay deposit is formed from the weathering of Precambrian Basement rocks. One major progenitor of clay deposits is feldspar, which is a common mineral in many granitic rocks like granite pegmatite. Furthermore, clay deposits are common in areas where hydrothermal alteration leads to high level of kaolinization, which characterizes area where Pan-African magmatism is prevalent (Okunlola, 2008). The type of clay that formed is not only a function of the nature of parent rock but also the intensity of weathering and the length of time during which it occurred (Akinola and Obasi, 2014). Clay deposits are widely distributed on the Precambrian Basement Complex of Nigeria (Ajayi and Agagu, 1981; Emofurieta and Salami, 1988). Interestingly, various researchers have looked at some of these clays from different perspectives (Ajayi and Agagu, 1981; Ehinola et al., 2009; Olaolorun and Oyinloye, 2010; Onyeobi et al., 2013). For example, Ajayi and Agagu (1981) carried out mineralogical analyses of primary clay deposits from seven localities representing different rocks in the Nigerian Basement Complex and found that the deposits that weathered from granites, gneisses, pegmatites and schists consisted mainly of kaolinite and trace proportions of montmorillonite and illite while deposits weathered from calc-silicate rocks contained high proportions of montmorillonite.

The clay deposits from Ekiti and its environs were distinguished by the geology viz: the Ado Ekiti clay bodies are underlain by quartzite and charnockites; Igbara Odo clay bodies covered quartzite and migmatite rocks; Orin and Ikere clay bodies were underlain by the charnockites. However, comprehensive studies are not yet been taken up on these clay deposits in terms of mapping, characterization, quality and quantity. The growing demand for mineral exploration and the mineral resource utilization for speedy development of the country, efforts are being made to delineate the areas potential for mineral resources for detailed studies and exploitation. The present work is an outcome of one such effort conducted in and around Ekiti and its environs to study the clay deposits in terms of their distribution, mineralogy, geochemistry, quantity and quality. The paper presents the mineralogy and physicochemical characteristics of eleven clay deposits at Ekiti Environs in South Western Nigeria with a view to evaluate their economic potentials, as a contribution to the nation's industrial raw materials database. Furthermore, the study explores multivariable statistical approach for evaluating obtained geochemical data to reveal differences and variables that have greater contribution to the clay differentiation.

1.2 Clay minerals and weathering index

Soils derived from weathering of igneous, sedimentary, and metamorphic rocks are different from one another due to the nature and mineral constituents of parent rocks. Other factors, generally with lesser controlling effects are climate, topographic setting, organisms and time (Retallack, 1990). Weathering results in the alteration of rocks and minerals and decomposition and/or modification of rocks and minerals to more stable forms at or near the surface environment (Buol et al., 1989). The major chemical weathering processes of soil formation include hydrolysis, oxidation-reduction, dissolution/precipitation, and hydration (Buol et al., 1989). The products of weathering result in accumulation of resistant minerals, and the formation of new clay minerals and iron oxides in soils (Khamchanh-Kanhalangsy, 1997). The net effect of chemical weathering, then, is the conversion of feldspar to smectite and, with continued and/or more intense leaching, Al-rich clays such as gibbsite and kaolinite (Tosca et al., 2010).

Clay minerals belong to the phyllosilicate group. As a distinguishing feature, they are few micrometers maximum in size and their preferred formation occurs under surface (laterites, soils, sediments) or subsurface (diagenesis, hydrothermal alterations) conditions (Meunier, 2004). Clay minerals are secondary minerals derived from chemical alteration of mostly feldspars and micas in parent material. These minerals are dominantly alumino silicates made up of tetrahedron and octahedron sheets constituting a unit cell. Their manner of auto-construction and habit form the unit cell characterized by layering yielding 1:1 and 2:1 classes of clay minerals. The 1:1 clays consist of tetrahedral and octahedral sheets forming kaolinite–serpentinite clay minerals and some of the members are kaolinite and halloysite (Meunier, 2004). The 2:1 clay minerals have two tetrahedrally coordinated sheets of cations both sandwiching an octahedral sheet. This classification has six groups: pyrophyllite, talc, smectites, vermiculites, micas, and chlorites. Clay minerals can be categorized into four subgroups: (1) kaolinite; (2) smectite (montmorillonite, saponite); (3) mica (illite), and (4) chlorite (Shichi and Takagi, 2000; Nayak and Singh, 2007; Burhan et al., 2010).

Clay minerals may be significant indicators of earth processes such as climate and weathering. They form through a range which involves at one extreme the action of compressed water or vapor at a temperature of several hundred degrees centigrade, and at the other extreme, the action of atmospheric agencies (i.e. CO_2, O_2 and rainwater) at an ordinary temperature. Clay minerals are formed by hypogene processes due to the action of gases, vapors, or solutions that originate below and force their way upward through rocks of the earth's crust. Most of the elements of the clay minerals are contributed by the invaded rocks; few, other than water, are derived from deeper sources.

A number of authors have proposed some weathering indices for weathering profiles developed on natural rocks. For example Nesbitt and Young (1982) proposed weathering index (CIA) to estimate paleoclimate from Early Proterozoic sediments of the Huronian Supergroup, the north shore of lake Huron. It is expressed in Eq. (1). CIA is interpreted as an indicator of conversion degree from feldspars to clay such as kaolinite. The assumed immobility of Al and higher mobility of Na, K, and Ca, makes CIA increases with the increase of weathering degree.

Harnois (1988) suggested weathering index (CIW) which modified CIA. CIW eliminated K_2O from the equation of CIA and is expressed in Eq. (2). The assumed immobility of Al and higher mobility of Na, K, and Ca, makes CIW increases with the increase of weathering degree. In the case of K-feldspar rich rock, CIW might have a tendency to show larger values even for unweathered rock because CIW does not account for the behaviour of Al which is associated with K-feldspar.

Parker (1970) suggested weathering index (WIP) for silicate rocks based on element mobility, which was related to bond strength of each element (Na, K, Mg, and Ca) with oxygen. It is ex-pressed by the sum of alkali and alkaline earth element composition ratio (Eq. (3). WIP does not need to assume Al immobility during the weathering. Because mobile elements (Na, K, Mg, and Ca) will be leached during the weathering, values of all terms in Eq. (3) will decrease correspondingly. Therefore, smaller value of WIP means larger weathering degree. Gill and Yemane (1996) in their study measured the degree of chemical weathering (or leaching) in the soil profile by observing molecular weathering ratios otherwise known as relative base loss (RBL) expressed in equation 4.

2. Sampling location and Geology of the study area

The study area lies within latitudes 7°23′ and 7°52′N and longitudes 4°58′ and 5°31′E, covering about 4344 km^2 (Fig. 1). The humid tropical climate has high mean annual temperature of 27^{o}C and an annual average rainfall of 1500 mm. The area is located in the southwestern sector of the Nigerian Basement Complex which formed the southern part of the Trans-Saharan mobile belt of Neo-proterozoic (750 - 500Ma) age (Caby, 1989) (Fig. 1). The geology of Nigeria is dominated by sedimentary and crystalline basement complex formations which occur in almost equal proportions all over the country (Durotoye, 1983; Rahaman and Malomo, 1983; McCurry, 1989; Shitta, 2007). The sediment is mainly Upper Cretaceous to recent in age while the Basement Complex rocks are thought to be Precambrian. The Precambrian Basement Complex is characterized by the occurrence of migmatite-gneiss complex, metasediments (supracrustal rocks) consisting of heterogeneous lithology of schistose assemblages known as the schist belts and the intruding Older Granite. The Younger Granite is Jurassic in age and occurs in Jos Plateau in the north central part of the country. Systematic mapping of the area revealed three main lithologic units: migmatites, metasediments, and intrusives. They comprise five distinguishable lithologies: migmatite-gneiss, quartzite/Quartz-Schist, granite with aplitic intrusion in some places and charnockite (Fig. 1). Migmatite covered a greater portion of the area and the older granite and charnockites intruded into the migmatite – gneiss-quartzite complex.

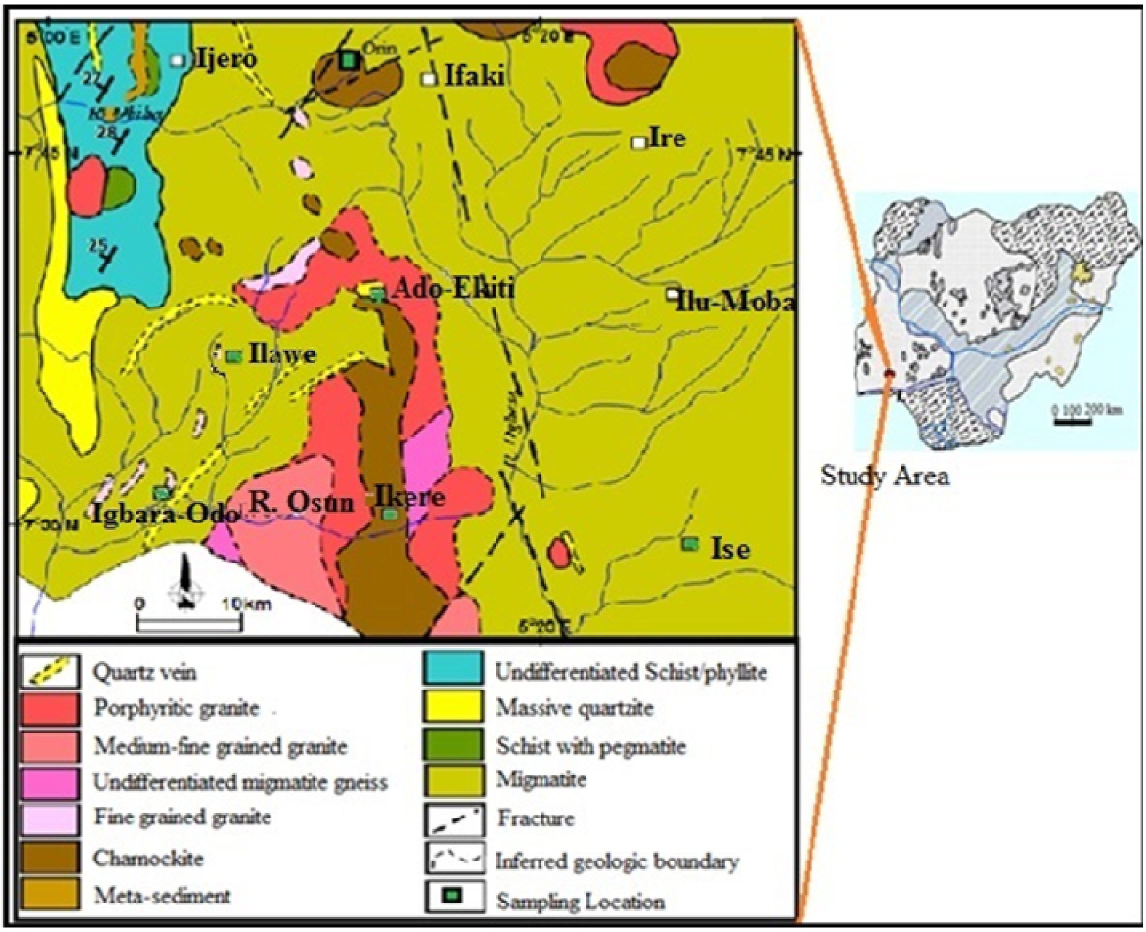

Figure 1. Geologic Map of study area (Modified from Talabi and Tijani, 2010).

Three principal petrographic varieties of granites were recognized in the zone, the fine-grained biotite granite, medium to coarse grained, non-porphyritic biotite – hornblende granite and coarse – porphyritic biotite-hornblende granite. These varieties are common in Ado, Ikere, Iyin and in the north-eastern part of the area (Fig. 1). Charnockites, dark-green, to greenish-grey rock of fine, medium-coarse grained texture are common in Ado, Ikere, and on the north-eastern part of the study area especially at Itapa, Ire and Ilumoba areas. Two types of charnockitic occurrence have been observed. The charnockites that occur along the margins of Older Granitic bodies especially the porphyritic granites as exemplified by charnockitic outcrops in Ado, Ikere and Igbara-Odo areas (Fig. 1). The other occurrence comprise of charnockites aligned in a NE-SW direction as shown at Oye, Itapa and Ijelu areas. The contact between charnockites and the surrounding rocks is variable. In some places on the one hand, gradational contact was observed between the charnockites and the surrounding Older Granites, while on the other hand the contact is abrupt between gneisses and charnockitic rocks (Fig. 1). At Ifaki, the charnockites show cross-cutting intrusive contacts with surrounding rocks, while at Ikere, the charnockite occur on slightly weathered surfaces which have been broken up into xenolithic blocks by a foliated porphyritic granite. Furthermore, on the fresh surfaces, it is difficult to distinguish the contact between granite and charnockite because the feldspars of the granite have the same greenish colour as those of the charnockite (Fig. 1).

Quartzites form eroded hills. The quartzite exhibits white to gray colour due to iron oxides. A few good massive quartzite outcrops rising up to 100 metres above the surrounding terrain occurs around Ado-Ekiti, while the ones at Ikogosi are highly schistose with muscovite flakes scattering on its environment (Fig. 1). However, around the south western part of Ilawe the quartzite forms rubbles. Quartzite resistant to weathering forms ridges and hilltops (Fig. 1). The nearly pure silica content of the rock provides little to soil formation and therefore the quartzite ridges are often bare or covered with only a very thin layer of soil and little vegetation.

3. Sampling and Analytical methods

Representative samples were collected from Orin, Igbara Odo, Ikere and Ado Ekiti clay deposits adopting point sampling method. Altogether, four disturbed samples representative of each clay deposit, were collected from freshly exposed surfaces, and then taken to the laboratory in sealed polythene bags to prevent contamination and loss of moisture. The unsieved samples were then prepared for analyses by crushing using a jaw crusher, followed by milling which was accomplished by gently grinding the sample carefully, so as not to destroy the structure of the constituent minerals. Prepared samples were oven-dried at 100 ºC for 12 hours before various tests were conducted on them.

3.1 Pore water chemistry of clay samples

The pH of interstitial/pore water was determined using 1:10 core/water ratio. Ten grams of each clay samples were weighed and put in a beaker and suspended in 100 ml of ultra-pure water. The mixture was then agitated carefully for 30 mins, and allowed to settle for 15 min. The pH and electrical conductivity (EC) of the supernatant were measured by using a Hanna HI 9828 pH meter with portable pH/EC/TDS/DO/ORP/Temperature probe. The pH meter was calibrated before use with buffer solution of pH 4.0 and 7.0, and with a conductivity standard of 12.88 mS/cm at room temperature. Triplicate samples measurements were taken at room temperature.

3.2 Cation Exchange Capacity (CEC)

The cation exchange capacity (CEC) was determined by the ammonium acetate method using buffered at pH 8.2. Oven dried clay samples (0.5g) were weighed into a 50 ml centrifuge tube and extracted using 25 ml aliquots of 1.0 M ammonium acetate. The mixture was shaken for 15 minutes and then centrifuged (at 3000 rpm) for 20 minutes. The procedure was repeated four times to give 100 ml of supernatant, which was filtered through 0.45 µm pore cellulose acetate membrane. The concentration of the exchangeable cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) was determined by inductively coupled plasma mass spectrometry (Agilent7500ce). The results in ppm were then converted to meq per 100 g of the sample following the method of Radojevic and Bashkin (1999).

3.3 XRD analysis

The mineralogical compositions were determined by X-ray diffraction (XRD) analysis. A Philips PANalytical instrument equipped with a pw 3830 X-ray generator operated at 40 kV and 25 mA was used. The samples were oven-dried at 100°C for 12 hours to remove the adsorbed water. The samples were pressed into rectangular aluminium sample holders using an alcohol wiped spatula and then clipped into the instrument sample holder. The representative clay samples were step-scanned from 5 to 85 degrees 2 theta scale at intervals of 0.02 and counted for 0.5 sec per step. The XRD analyses were carried out at the iTHEMBA laboratories, Cape Town, South Africa.

3.4 Morphological analysis

The representative clay samples were oven-dried at 105°C for 12 hours and aluminium and carbon coated. The scanning electron microscope/electron dispersive x-ray spectroscopy (SEM/EDS) analysis was carried out with analytical Leica/Leo S440 Scanning Electron Microscope equipped with a Fissons Quantum EDS detector, using Sigma software, under 20 KV at a working distance of about 25 mm. EDS spectrum was collected over 60 seconds. FEI Nova Nano SEM 230 (both instruments are located at Electron Microscope Unit, University of Cape Town, South Africa), equipped with an Oxford X- max detector and INCA software was used for the elemental analysis (quantitative work by energy dispersive X-ray analyses). The EDS analysis was carried out at 20 Kv and 5 mm working distance.

3.5 XRF analysis

The bulk chemical compositions of the clay samples were determined by X-ray fluorescence (XRF) analysis. Samples were oven-dried at 100°C for 12 hours for adsorbed water measurements, and crushed. The powdered samples were then mixed with a binder (ratio of 1: 9 in grams of C-wax and EMU powder) at a ratio of 2: 9 (2 gram binder and 9 gram sample). The powder mixture was then pelletized at a pressure of 15 Kbars for 1 minute. Loss on ignition (LOI) experiment was performed prior to major element analysis. The XRF analyses were carried out at the Geology department of the University of the Western Cape, South Africa. A Phillips PANalytical PW1480 X-ray fluorescence spectrometer using a Rhodium Tube as the X-ray source was used. The technique reports concentration as % oxides for major elements and ppm for minor elements.

3.5.1 Data treatment and multivariate statistical methods

Multivariate statistical method was applied on the bulk chemical data from XRF analysis (i.e. major oxides mass %) using SPSS-17.0 statistical software. Varimax rotated factor analysis was performed on correlation matrix of reorganized data. The variance, cumulative, and extraction sums of square loadings of the variables with Eigen-values were computed. Rotation of the axis defined by factor analysis produced a new set of factors, each one involving primarily a sub-set of the original variables with a little overlap as possible, so that the original variables were divided into groups. The factor analysis of the present data set further sorted by the contribution of less significant variables (< 0.4 factor score). A varimax rotation of the different varifactors of eigen-value greater than 1, were further cleaned up by this technique and in varifactors original variables participated more clearly. Liu et al. (2003a) classified the factor loading as “strong”, “moderate”, and “weak”, corresponding to absolute loading values of > 0.75, 0.75–0.50, and 0.50–0.40, respectively. Factor and cluster analyses were combined to assess the degree of major component matrix dissolution and determination of chemical processes. Hierarchical agglomerative clustering was performed on data normalized to z scores and unit variance using squared Euclidean distances as the measure of similarity (Massart et al., 1988). Wards method was selected because it possesses a small space distorting effect, uses more information on cluster contents than other methods (Helena et al., 1999), and has been proven to be an extremely powerful grouping mechanism (Willet, 1987). This multivariate statistical approach enables the description of the best discriminatory parameters of the studied clays.

4. Results and discussion

4.1 Geochemistry of clay deposits

Table 1 presents the results of chemical analysis showing the different oxide forms of the major elements contained in the studied clay bodies. For comparison, typical composition of china clay (SCC), plastic fire clay (PFC), Afam clay (AFC), an average clay-shale (AVCS), Iyuku clay, Ubiaja clays (i.e. UBJ_R and UBJ_G), Ijero clay, Ara clay and Iluno clay are also shown in Table 2. For the studied clays, variability of silica content is obvious, where the Orin Ekiti clay shows lowest value (40.43%) and Ado Ekiti clay with the highest value (74.98%). However, the alumina contents of Igbara Odo and Ado Ekiti clays are relatively low compared to a typical china clay, Afam clay, Iyuku clay, Ubiaja clays, Ijero clay, Ara clay and Iluno clay` the values ranging from 14.14 - 16.58% and 12.19 – 13.54% respectively. The Fe_2O_3 concentrations range from as low as 3.49% for the Ado Ekiti clay to as high as 17.60% for the Ikere clay reflecting the higher degree of oxidation in the latter. Furthermore, the Fe_2O_3 contents are relatively high in most clay bodies compared to a typical China clay, Afam, clay, Iyuku clay, Ubiaja clays, Ijero clay, Ara clay and Iluno clay (Table 2).

TiO_2 contents range from as low as 1.52% in the Ado Ekiti clay to as high as 2.43% in the Ikere Ekiti clay. Nevertheless, the TiO_2 contents are relatively high compared to Iyuku clay, Ijero clay, Ara clay, Iluno clay and China clay but lower than Ubiaja clays (Table 2). The alkalis (K_2O, Na_2O) as well as CaO, MgO and MnO which occur in relatively insignificant proportions are in the range 0.02 to 3.63% that is indicative of the moderate to high degree of weathering, under tropical conditions, from which the clay deposits resulted.

The chemical analyses show major variations of SiO_2 and Al_2O_3 contents between the clay samples with the Ado Ekiti clay being the most siliceous. The SiO_2:Al_2O_3 ratio range from as low as 1.39 % in the Orin Ekiti clay to as high as 5.80% in the Ado Ekiti clay. However, the SiO_2:Al_2O_3 ratio is relatively high compared to China clay (Table 2). The Al_2O_3:SiO_2 ratio or relative "clayeyness" suggests significant clay accumulation especially in the Orin and Ikere Ekiti clay. The SiO_2/Al_2O_3 molar ratio of 1.40 and 1.50 for Orin and Ikere clay bodies indicated that a 1:1 clay mineral was the dominant component. The K_2O/Na_2O ratio range from as low as 6.54 % in the Orin Ekiti clay to as high as 19.81% in the Ikere Ekiti clay. However, the entire K_2O/Na_2O ratio in the studied clay is relatively high compared to China clay except Ikere clay. No evidence of salinization (shown in the Na_2O/K_2O ratio) in the studied clays.

The LOI range from as low as 2.52 % in the Ado Ekiti clay to as high as 11.27% in the Ikere Ekiti clay. However, the LOI in the studied clay is relatively low compared to China clay. The sum of Fe_2O_3, MnO and TiO_2 range from as low as 5.04% in the Ado Ekiti clay to as high as 2.15% in the Ikere clay but all the values are higher than China clay. The chemistry of the clays is dominated by Si and Al. Table 1 shows depletion of the soluble elements Ca, Na and K relative to Al and, in some cases, Fe. This is attributed to weathering which has proceeded to a stage where a major part of alkali and alkaline earth elements were removed. Mineralogically, progressive Al-enrichment is reflected by the formation of smectite and Al-bearing clay minerals in the residual weathered materials (Nesbitt and Young, 1989; Nesbitt and Markovics, 1997).

The chemical composition of the studied clay deposits is given in Table 1. Two methods used in measuring the degree of weathering can be obtained by calculation of the chemical index of alteration (CIA) (Nesbitt and Young, 1982, 1984) and chemical index of weathering (CIW) (Harnois, 1988) using molecular proportions. In the CIA equation, CaO* is the amount of CaO incorporated in the silicate fraction of the studied clay samples. Correction for CaO from carbonate contribution was not done for the studied clay samples since there was no CO_2 data. Thus, to compute for CaO* from the silicate fraction, the assumption proposed by Bock et al. (1998) was adopted. In this regard, CaO values were accepted only if $CaO \leq Na_2O$; consequently, when $CaO > Na_2O$, it was assumed that the concentration of CaO equals that of Na_2O (Bock et al., 1998). However, only Igbara Odo clay showed CaO contents higher than Na_2O. As a result, the chemical index of alteration (CIA) was calculated for the studied clays as shown in Table 1. The CIA values of the studied clays suggest variation in the degree of weathering: the Igbara Odo and Ado Ekiti clays are moderate chemically weathered. While Orin and Ikere Ekiti clays are intense chemically weathered and leached. The moderate chemical weathering conditions were the most conducive to smectite mineral generation; more intense weathering and leaching conditions of presumed parent material leading to residual enrichment of Al-rich products before burial metamorphism (Tosca et al., 2010).

The high CIA and CIW values in the studied clay probably reflect the absence of detrital feldspar as revealed XRD spectra analysis (Figure 2). Schulze (1989), suggested that minerals are indicators of the amount of weathering that has taken place and the presence or absence of, gives information as to how soils formed. CIA are reflected mainly by changes in the proportion of feldspars and clay minerals or caused by grain size sorting during original deposition of the parent material for the profile (Nesbitt and Young, 1982). Variability in the values of CIA and CIW in the studied clay might due to topography which led to increased physical erosion of uplifted terrains. Tosca et al. (2010) observed that increased physical erosion of uplifted terrains would tend to drive CIA lower, allowing for a greater proportion of igneous/detrital clay relative to clay formed through weathering in the regolith.

Parker (1970) suggested weathering index (WIP) for silicate rocks based on element mobility, which was related to bond strength of each element (Na, K, Mg, and Ca) with oxygen. It is ex-pressed by the sum of alkali and alkaline earth element composition ratio. In the studied clay samples, the weathering index of Parker (WIP) of the Orin and Ikere Ekiti clays are indicative of intense degree of weathering. Conversely, WIP values of Igbara Odo and Ado Ekiti clay suggests moderate degree of weathering.

Other method used in measuring the degree of chemical weathering included observing molecular weathering ratios as given by Gill and Yemane (1996). For example, in the studied clay the relative base loss (RBL) is very strong (Table 1).

Table 1. Major (wt %) and trace (ppm) elements contents and other chemical parameter of the studied clay bodies from Ekiti Environs (*LOI = Loss on Ignition; CIA = Chemical Index of Alteration; RBL = Relative Base Loss; CEC (meq) = Cation Exchange Capacity).*

Major elements (wt %)	Orin		Igbara Odo		Ikere		Ado	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean
SiO_2	32.48 - 45.70	40.43	63.85-70.27	58.18	35.74 -45.42	40.58	73.38-75.92	74.98
Al_2O_3	21.07 - 33.18	29.09	14.14-16.58	19.94	25.02 - 29.05	27.03	12.19-13.54	12.92
Fe_2O_3	8.30 - 25.61	15.76	6.36-7.27	9.80	11.79 - 23.41	17.60	1.65-6.95	3.49
MnO	0.03 - 0.12	0.08	0.04-0.04	0.05	0.04 - 0.20	0.12	0.02-0.04	0.03
MgO	0.06 - 3.51	0.94	0.41-0.61	0.65	0.32 - 0.67	0.49	0.25-0.42	0.36
CaO	0.00 - 0.01	0.00	0.17-0.34	0.17	0.00 - 0.01	0.00	0.06-0.23	0.16
Na_2O	0.02 - 0.49	0.14	0.11-0.17	0.14	0.02 - 0.02	0.02	0.05-0.33	0.22
K_2O	0.01 - 3.27	0.91	2.07-3.64	2.21	0.34 - 0.36	0.35	0.82-5.05	3.63
TiO_2	0.79 - 3.99	2.01	1.03-2.41	1.81	1.44 - 3.42	2.43	0.72-3.07	1.52
P_2O_5	0.08 - 0.18	0.12	0.05-0.07	0.08	0.12 - 0.19	0.15	0.05-0.08	0.06
SO_3	0.01 - 0.03	0.02	0.00-0.01	0.01	0.00 - 0.01	0.01	0.00-0.01	0.01
LOI	5.57 - 13.39	10.44	3.93-6.38	6.92	11.16 - 11.38	11.27	2.24-3.07	2.52
Total	99.85-100.04	99.94	99.95-99.98	99.96	99.92 - 100.18	100.05	99.81-99.99	99.90
SiO_2/Al_2O_3	1.30-1.54	1.40	3.85-4.97	4.41	1.43-1.56	1.50	5.59-6.02	5.81
Al_2O_3/SiO_2	0.65 - 0.77	0.72	0.20-0.26	0.39	0.64 - 0.70	0.67	0.17-0.18	0.17
Na_2O/K_2O	0.01 - 2.70	1.13	0.05-0.05	0.41	0.04 - 0.06	0.05	0.06-0.06	0.06
CIA	86.42 - 99.91	95.91	81.33 - 86.64	83.99	98.51 - 98.77	98.64	70.21-92.88	77.97
CIW	98.44 - 99.94	99.53	97.02-98.07	98.21	99.93 - 99.94	99.93	96.07-99.11	97.21
WIP	0.34 - 30.25	9.09	17.89-31.24	19.41	3.19 - 3.73	3.46	7.23-42.84	30.97
RBL	3.09 - 206.72	94.38	5.11-3.48	34.32	23.95 - 42.86	33.41	2.20-10.13	4.86
CEC (meq)	14.70 - 16.94	16.39	6.84-8.95	10.73	16.79 -18.79	17.79	7.72-8.15	7.93
Trace elements (ppm)								
	Orin		Igbara Odo		Ikere		Ado	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Ba	44 - 1461	431.75	335-460	408.92	286 - 1407	846.50	220-683	519.00
Ce	22 - 492	194.75	67-178	146.58	73 - 250	161.50	4.00-40	19.67
Co	5.00 - 45	19.67	8-11.	12.89	1.00 - 71	36.00	1.00-2.00	1.50
Ni	37 - 113	69.75	38-40	49.25	38 - 74	56.00	34-39	36.33
Pb	14 - 34	22.75	26-28	25.58	32 - 55	43.50	15-25	21.33
Rb	6 - 161	47.25	82-152	93.75	18 - 19	18.50	38-172	125.67
Sr	3.00 - 43	16.5	63-84	54.50	64 - 87	75.50	58-112	91.00
V	111 - 342	166.5	117-222	168.50	139 - 325	232.00	57-331	152.00
Y	25 - 188	86.75	41541	16.50	77 - 282	179.50	26-38	30.33
Zn	61 - 232	173.75	28-39	80.25	71 - 232	151.50	14-23	18.33
Zr	381 - 2638	1168	358-929	818.33	641 - 992	781.50	640-1237	880.33

Eq. 1. $CIA = [Al_2O_3/ (Al_2O_3+CaO^*+Na_2O+K_2O)]*100$ *(where CaO* represents silicates only).*

Eq. 2. $CIW = [Al_2O_3/ (Al_2O_3+CaO''+Na_2O)]*100.$

Eq. 3. $WIP = 2Na_2O/0.35 + MgO/0.90 +2K_2O/0.25 + CaO/0.7$, *and*

Eq. 4. Relative Base Loss $(RBL) = (Al_2O_3)/(CaO+MgO+Na_2O+K_2O).$

The high relative base loss of Orin, Igbara Odo and Ikere Ekiti clays are likely due to erosion and topographic settings. However, the relatively low RBL of Ado Ekiti clay is attributed to its siliceous nature. Such strong loss of mobile cations and clay enrichment is typical of soils that form in warm tropical and subtropical environments (Brady, 1990). According to Gill and Yemane (1996) these values indicate removal of mobile cations by extreme leaching conditions.

The distribution of trace elements in Orin, Igbara Odo, Ikere and Ado Ekiti clay bodies are shown in Table 1. Vanadium (V^{4+}) is more concentrated in Ikere clay which is relatively rich in Fe_2O_3 and TiO_2 content (Table 1). Trace elements such as Co, Ni, Y and Pb show similar concentration range in the studied clay bodies. Zirconium is more concentrated in Orin clay its distribution pattern suggests concentration during the course of intense chemical weathering of parent material. The relatively high concentration of Rb and Sr in the Ado Ekiti clay suggest ongoing chemical weathering of the studied clay body.

Table 3 shows the results of the randomised block design model used for both major and trace elements obtained from the studied clay samples using X-ray fluorescence analysis (Table 1). In the case of both major and trace elements content of studied clay samples, the F-value is greater than F-critical on the rows (i.e. sampling sites). On the contrary, the F-value is less than F-critical on the columns (i.e. geochemical variables). This result trend suggests that the underlain basement rocks of the studied clay deposits show little contribution to their differentiation. However, the variations in the degree of weathering or leaching process have greater contribution to clay deposits differentiation (Table 2).

4.2 Cation exchange capacity

Table 1 shows the cation exchange capacity (CEC) of the clay bodies. For the studied clays, the variability of CEC is obvious where Ado Ekiti clay show lowest value (7.93 meq/100g) and Ikere Ekiti clay with the highest value (17.79 meq/100g). Table 1 shows explicit relationship amongst the amount of clayeness (Al_2O_3/SiO_2 ratio), relative base loss (RBL) and the cation exchange capacity (CEC). Accordingly, the observed variability of CEC in the studied clay bodies could be attributed to the concentration of alumina (Al_2O_3) and amount of clayeness. Grim (1968) reported that the cation exchange capacity of kaolinite is considerably less than that of smectite, in the order of 2–10 meq/100 g, depending on the particle size, but the rate of the exchange reaction is rapid, almost instantaneous.

4.3 Pore water chemistry

Table 4 shows results of interstitial pore water for the clay samples. For the studied clays, variability of pH is evident, where both Ikere and Ado Ekiti clay show lowest value (7.91) and Orin Ekiti clay with the highest value (8.88). The pH values of the Orin and Igbara Odo Ekiti clay indicate alkaline medium but Ikere and Ado Ekiti clay suggests nearly neutral medium (Table 3). The relatively low pH value of Ikere and Ado Ekiti clay implies effect of ongoing weathering which could lead to flushing of soluble basic constituents in the clay bodies.

The electrical conductivities (EC) of Igbara Odo Ekiti clay show lowest value (0.007 mS/cm) and Ikere and Ado Ekiti with the highest value (0.02 mS/cm). Accordingly, the total dissolved solids (TDS) of the Igbara Odo Ekiti show lowest value (3.50 ppm) and Ikere and Ado Ekiti clay with the highest values (9.50 ppm).

The oxidation reduction potential (ORP) value of Orin Ekiti clay shows lowest value (-34.5) and Ikere and Ado Ekiti with the highest value (-5.40). The dissolved oxygen (DO) of Ikere and Ado Ekiti clay show lowest value (6.86 ppm) and Orin and Igbara Odo Ekiti clay bodies with the highest value (7.19 ppm). The ORP and DO generally decrease with depth except where a perched water table is present. Variability of ORP and DO values in the clay bodies is partly attributed to variations in the saturation level (i.e. dampness) of clay bodies due to fluctuation in the water table. In addition, a relative increase of ORD and DO in the Orin and Igbara Odo Ekiti clay deposits could be ascribed to plants photosynthesis.

Table 2. Comparison of the average chemical composition of the studied clays with average chemical composition of other types of clay

Major oxides (wt %)	Orin	Igbara Odo	Ikere	Ado	Ara clay (Akinola & Obasi, 2014).	Ara clay (Olaolorun & Oyinloye, 2010).	Ijero clay (Olaolorun & Oyinloye, 2010).	Iluno clay (Olaolorun & Oyinloye, 2010).	Iyuku clay (Onyeobi et al., 2013)	Ubiaja$_R$ clay (Onyeobi et al., 2013)	Ubiaja$_G$ clay (Onyeobi et al., 2013)	Average clay-shale (Pettijohn, 1957). AVCS	Afam clay (Jubril & Amajor, 1991). AFC	Florida non - active kaolinite (Huber, 1985).	Florida active kaolinite (Huber, 1985).	Plastic Fire clay St.Louis (Huber, 1985) PFC	China clay. GTY (Huber, 1985). SCC
SiO_2	40.43	58.18	40.58	74.98	48.50	51.95	50.97	44.63	64.45	55.8	50.41	58.1	42.20	45.57	52.92	57.67	46.88
Al_2O_3	29.09	19.94	27.03	12.92	28.82	22.42	23.19	40.38	20.28	27.5	31.62	15.4	26.2	38.45	9.42	24.00	37.65
TiO_2	2.01	1.81	2.43	1.52	1.02	1.25	0.99	0.13	0.84	2.58	2.73	-	-	0.01	1.18	-	0.09
Fe_2O_3	15.76	9.80	17.60	3.49	9.84	7.72	7.29	0.26	0.63	3.15	2.43	4.24	5.1	0.75	3.65	3.23	0.88
CaO	0.00	0.17	0.00	0.16	0.58	0.23	0.24	0.07	0.28	0.09	0.11	3.11	1.6	-	1.91	0.70	0.03
MgO	0.94	0.65	0.49	0.36	0.96	0.76	1.46	0.21	0.12	0.12	0.17	2.44	0.7	0.05	0.08	0.30	0.13
K_2O	0.91	2.21	0.35	3.63	2.49	2.86	3.20	0.52	0.42	0.25	0.29	3.24	8.3	0.06	0.98	0.50	1.6
Na_2O	0.14	0.14	0.02	0.22	0.23	0.19	0.70	0.04	0.18	0.01	0.02	1.3	2.9	-	0.03	0.20	0.21
MnO	0.08	0.05	0.12	0.03	0.03	0.04	0.12	0.01	0.01	0.04	0.02	-	0.03	-	-	-	-
Cr_2O_3	-	-	-	-	0.02	0.02	0.01	0.01	-	-	-	-	-	-	-	-	-
P_2O_5	0.12	0.06	0.15	0.06	0.12	0.09	0.12	0.04	-	0.11	0.14	-	-	-	0.02	-	-
SO_3	0.02	0.01	0.01	0.01	-	-	-	-	-	-	-	-	-	-	-	-	-
H_2O^+	10.44	6.92	11.27	2.52	-	12.30	11.47	14.10	12.02	9.82	10.23	-	-	-	10.19	10.50	12.45
SiO_2/Al_2O_3	1.39	2.92	1.50	5.80	2.09	2.32	2.20	1.11	3.18	2.03	1.59	3.77	1.61	1.19	5.62	2.40	1.25
K_2O/Na_2O	6.54	15.97	19.81	16.23	10.83	15.05	4.57	14.44	2.33	25.00	14.50	2.49	2.86	-	32.67	2.50	7.62
$Fe_2O_3+MnO+TiO_2$	17.85	11.66	20.15	5.04	10.89	9.01	8.40	0.40	1.48	5.77	5.18	4.24	5.13	0.76	4.83	3.23	0.97

Table 3. Major and Trace elements using randomised block design model

Major elements						
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	31075.7	11	2825.07	69.19	3.3E-44	1.88
Columns	0.0086	10	0.00086	2.1E-05	1	1.92
Error	4491.32	110	40.83			
Total	35567.1	131				

Trace elements						
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	8603978	10	860398	12.82	4.1E-14	1.93
Columns	554362	10	55436.2	0.83	0.60	1.93
Error	6710234	100	67102.3			
Total	1.6E+07	120				

Table 4. Interstitial pore water results for studied clay bodies (n = 3)

Measurement parameters	Orin		Igbara Odo		Ikere		Ado	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean
pH	8.73 - 9.08	8.88	8.42 - 8.72	8.57	7.14 - 8.67	7.91	8.52 - 9.04	7.91
EC (mS/cm)	0.01 - 0.03	0.02	0.004 - 0.01	0.007	0.01 - 0.03	0.02	0.11 - 3.02	0.02
TDS (ppm)	3.00 - 16	8.75	2.00 - 5.00	3.50	3 - 9.50	9.50	53 - 1509	9.50
ORP	-51.7 - 5.1	-34.15	-36 - 6.8	-14.60	-14.6 - 3.8	-5.40	-62.4 - 41.7	-5.40
DO (ppm)	7.15 - 7.22	7.19	7.12 - 7.26	7.19	6.86 - 6.99	6.86	6.76 - 7.19	6.86

4.4 Clay mineralogy

The XRD patterns of all studied clay bodies indicate the predominating presence of quartz and kaolinite with minor quantities of potassium iron oxide and aluminium phosphatic minerals (Figure 2). Identification of secondary minerals was difficult because their peaks tended to be obscured by the greater peaks of the major minerals (i.e. quartz and kaolinite). All the studied clay bodies are rich in quartz and kaolinite which suggest felsic sources. Kaolinite is formed by the decomposition of orthoclase feldspar in granite. All the studied clay bodies consist of minor quantities of potassium iron oxide and aluminium phosphatic minerals. These minerals are the product of chemical interaction between the leached solutions from the upper layer of the soil overburden and kaolinitic clay. The association of potassium iron oxide + kaolinite + aluminium phosphatic minerals reflects erosion and transport of laterites under tropical climates. The small amounts of these accessory minerals in the studied clay bodies would perhaps be attributed to well drained and less susceptibility to water of kaolinitic clay. The terrigenous character of these studied clay bodies is shown by high content of quartz and the less oxygenated conditions by the presence of potassium iron oxide.

Variability in the crystallinity of the minerals in the clay bodies are inferred from XRD peak intensities; with Igbara-Odo clay exhibited the least crystallinity and Orin clay body showed the highest crystallinity (Figure 2). Accordingly, the variations in the crystallinity suggest variations in the proportion of quartz and kaolinite in the clay bodies. This observed trend is in good agreement with the previous work by Mahjoor et al. (2009).

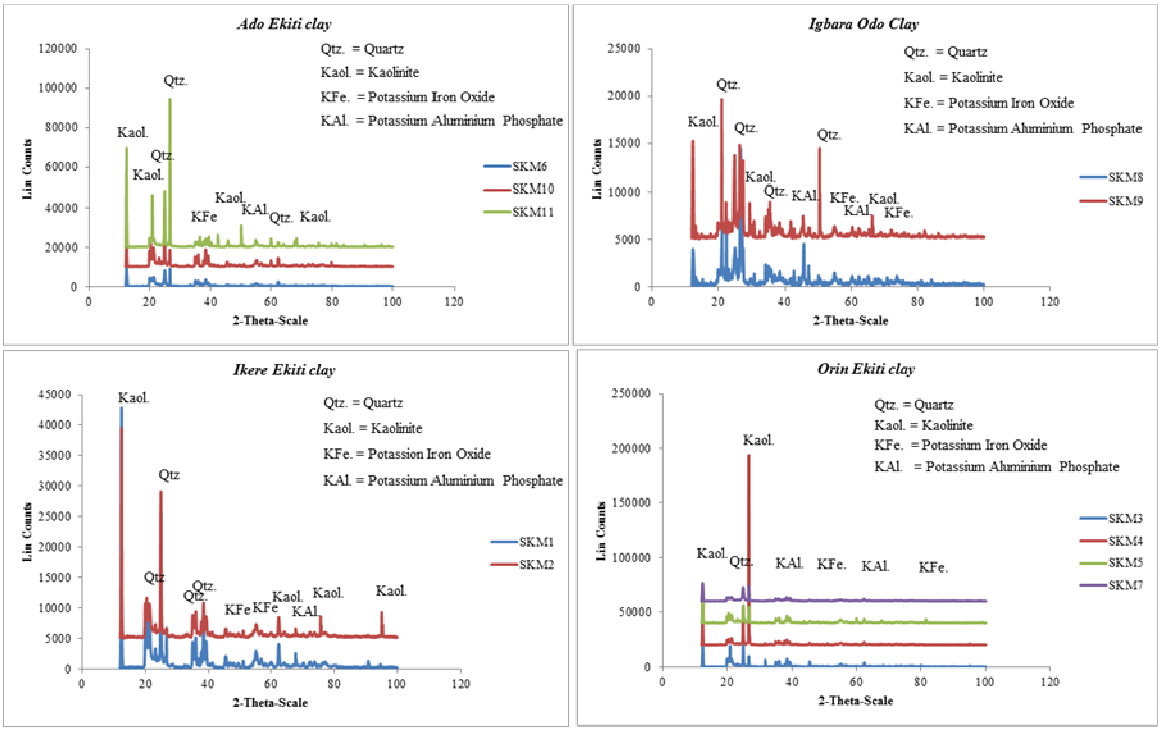

Figure 2: X-ray diffraction spectra of studied clay bodies.

4.5 SEM micrograph of clay samples

SEM micrographs and corresponding EDS spectra revealed that the microstructure of Ikere Ekiti clay (code-named SKM1), Orin Ekiti clay (code-named SKM4), Igbara Odo clay (code-named SKM8) and Ado Ekiti clay (code-named SKM11) comprised clay agglomerates with typical rolled into tubes kaolinites sheets and flakes of fine clay particles (Fig. 4). Kaolinite sheets were rolled into tubes because of the strain caused by lattice mismatches closely aligned silicon dioxide and aluminum oxide layers (Nicolini et al., 2009). The higher EDS peak intensities for aluminium than silicon indicated that the spectra were collected from the clay particles (Igbal and Lee, 2000; Hag et al., 2009). The presence of Pd, Yb, Eu, Sb, and Os in addition to Al, Si, Ti and Fe suggests variation in the purity of different clay samples (Figs. 3 & 4).

The EDS spectra show presence of V in the Ikere Ekiti clay (code-named SKM1), Orin Ekiti clay (code-named SKM4) and Igbara Odo clay (code-named SKM8) but clearly absent in the Ado Ekiti clay (code-named SKM11) (Figs. 3 & 4). The absence of vanadium in the EDS data of rolled into tubes kaolinite sheets of Ado Ekiti clay match up with XRF data. The field evidence and EDS data suggest that kaolinitic clay bodies from Ikere, Orin and Igbara Odo are somewhat formed from intense chemical weathering actions of micas than orthoclase feldspar. On the contrary, the EDS data suggest that Ado Ekiti clay body is formed from weathering of orthoclase feldspars. Orthoclase feldspars can be transformed into kaolinite or amorphous silico-aluminic phases by hydrolysis depending on weathering conditions. The amorphous phase can become kaolinite or halloysite according to its crystalline predisposition and nucleation influence (Iglesia and Galan, 1975). It is noted by Rankama & Sahama (1950) that feldspars are virtually devoid of vanadium. On the contrary, micas commonly show V^{4+} and V^{5+} in replacement for Fe^{3+} and Al^{3+} (Sears, 1958). Keller et al. (1981) reported that vanadium contained in the mica may inhibit the development of well crystallized kaolinitic flakes derived from it. Accordingly, the absence of vanadium would support the argument of development of well crystallized kaolinite from feldspars regardless of intermediate alteration phases (Keller et al., 1981).

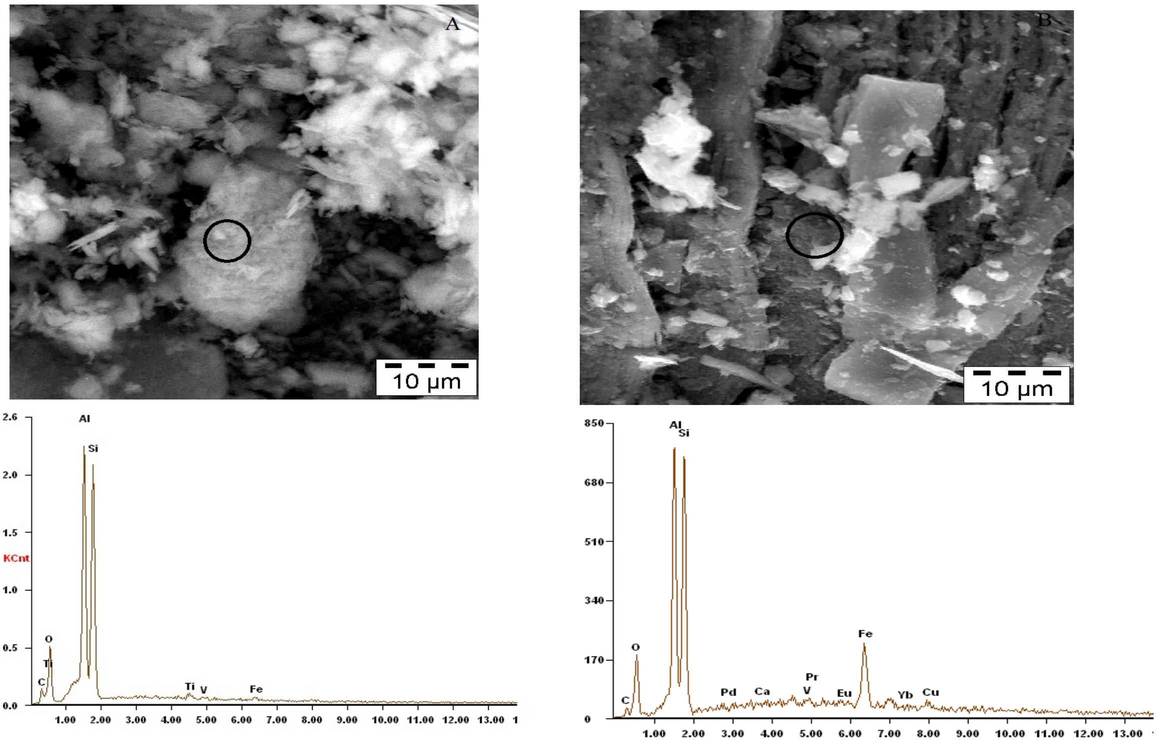

Figure 3: SEM micrograph of some selected clay samples (A = *elongated kaolin in a sample taken at Igbara Odo clay; B = a representative of oriented tubes and small platy fragments of kaolin in sample taken at Ikere clay*). *Note the presence of vanadium in the corresponding EDS spectrum.*

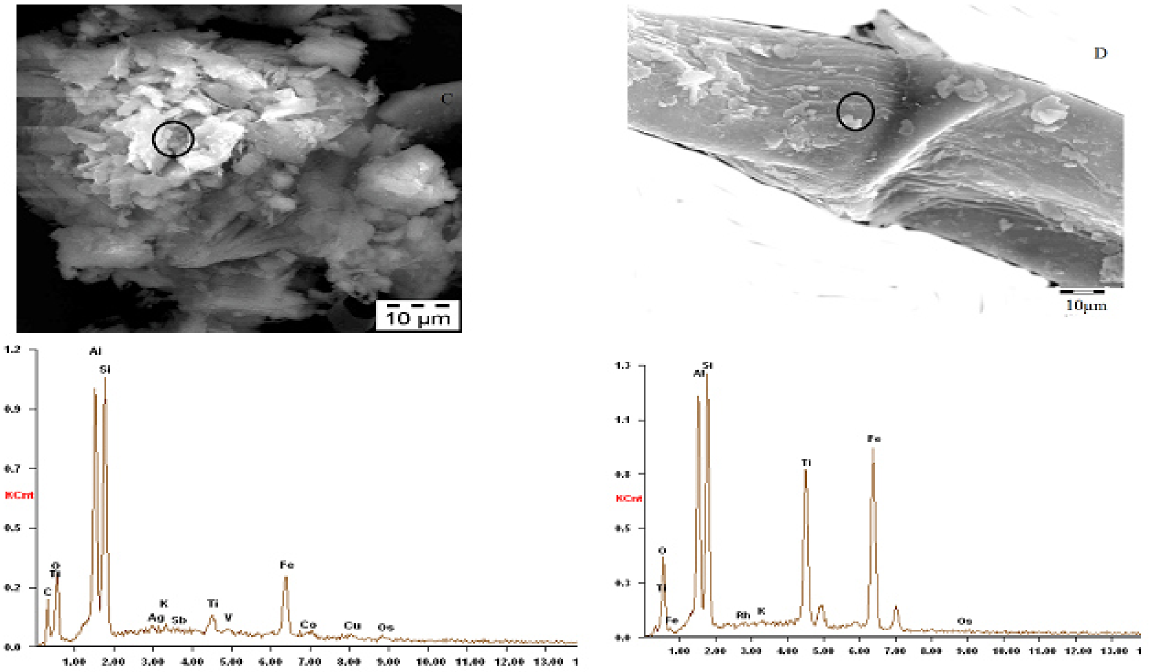

Figure 4: SEM micrograph of some selected clay samples (*C=Assemblage of plate-like hexagonal kaolinite in sample taken at Orin Ekiti clay; D = rolled into tubes kaolinite sheets in a sample taken at Ado Ekiti clay*). *Note the absence of vanadium in the corresponding EDS spectrum.*

Consequently the morphology of kaolinitic minerals may be influenced by the kind of parent material and degree of chemical weathering. In nature, the halloysite-ordered kaolinite transformation will take place when it is subjected to intense weathering actions in the presence of Al-complexes and with partial washing of silica.

4.6 Multivariate analysis

4.6.1 Cluster analysis

The relationship among the studied clay samples obtained through cluster analysis synthesized by the dendrogram plots (distance cluster combination) is shown in Figure 5. This gives evidence on the degree of chemical weathering of the clay samples. Multivariate statistical evaluation of the obtained data based on dendrogram cluster analysis using major elements, trace elements and LOI as variables; classified the clay samples into two cluster groups (Figure 5).

Cluster group I comprise of Igbara-Odo Ekiti clay (code-named SKM8 and SKM9) and Ado Ekiti clay (code-named SKM6 and SKM11). Cluster group II include Ikere Ekiti clay (code-named SKM1 and SKM2) and Orin Ekiti clay (code-named SKM3, SKM4 and SKM5) (Figure 5). The discriminant function analysis performed by comparing structure matrix to functional group centroid, showed strong association of SiO_2, CaO, Na_2O, K_2O, SO_3, Ce, Rb, Zn, Ba, Y, and Ni with clay samples in the group I. On the contrary, TiO_2, P_2O_5, Al_2O_3, Fe_2O_3, MnO, MgO, LOI, Pb, V, Zr, Co and Sr showed weak association with core ash samples in the Group II at Function I. The groups are 100 % different from each other.

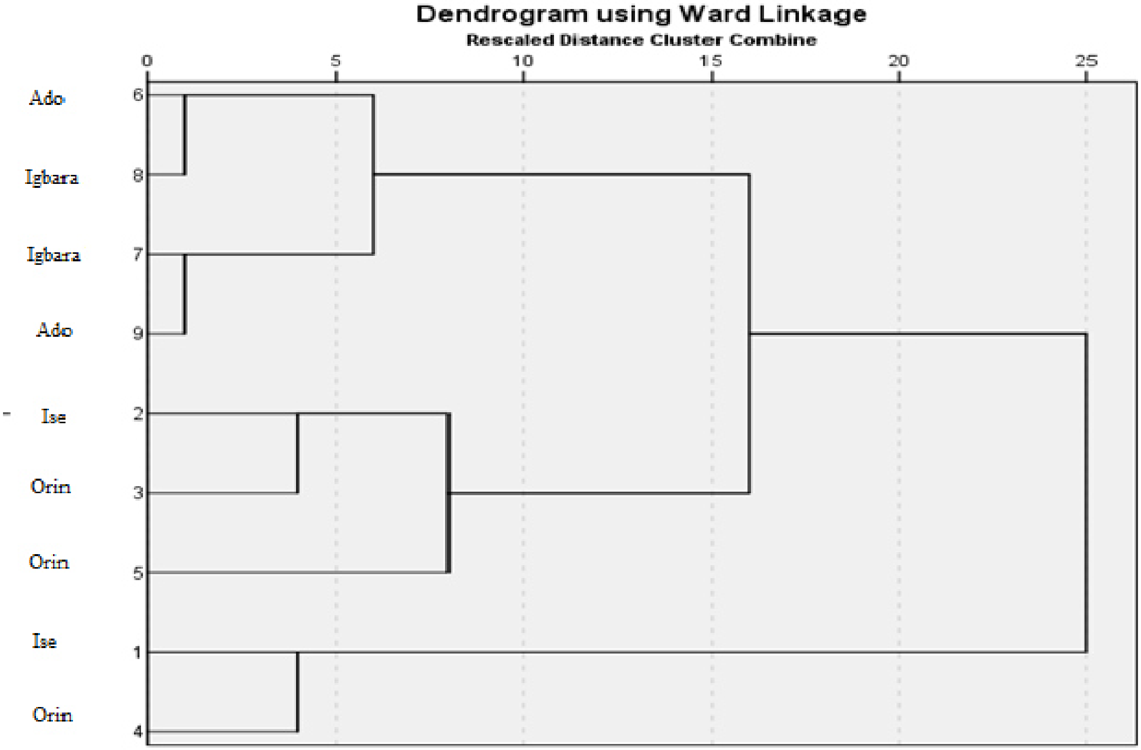

Figure 5: Dendrogram cluster analysis of studied clay bodies using major elements (wt %), trace elements (ppm) and loss on ignition as variables.

4.6.2 Factor analysis

The results of the varimax rotated factor loadings matrix and commonalities were obtained from principal component analysis (PCA). PCA is a statistical tool used to assess metal behaviour in earth materials (Liu et al., 2003b). The PCA is applied to detect the hidden structure and associations of elements in the data set, in an attempt to explain the influence of latent factors on the data distribution (Simeonov et al., 2000; Krishna et al., 2011). The rotated component matrix for the essential elements showed six components (Table 5).

Component I has a total variance of 43.77% and considerable enrichment of MnO, TiO_2, P_2O_5, Fe_2O_3, Co, Ba, Y, Zn, Ni, V and relative depletion of SiO_2 content. Component II accounts for 23.35% of total variance and significant enrichment of MgO, CaO, K_2O, Ba, Rb and Sr. The second component has weak loadings of these variables; LOI, SO_3, Al_2O_3 and Zr. The third component holds a total variance of 13.55% and enrichment of MgO, SO_3, Al_2O_3, Fe_2O_3, Zn, and Ni but depleted in Sr, CaO and SiO_2. The fourth component contains a total variance of 8.1% with enrichment of Na_2O, LOI, SO_3 and Ce but show depletion of SiO_2 and Zr. The fifth component comprises a total variance of 5.09% with enrichment of MgO, TiO_2 and V but show depletion of Al_2O_3 content. The sixth component includes a total variance of 4.43% with enrichment of Sr but depleted of Na_2O, SO_3 and Ce. This observed enrichment and depletion trend could be attributed to intense but differential leaching conditions of the presumed parent material.

Table 5. Varimax Rotated Factor Loadings Matrix and Communalities Obtained from Principal Component Analysis for the Studied Major Elements in the Clay bodies

Variables	Comp. I	Comp. II	Comp. III	Comp.IV	Comp.V	Comp.VI	Communalities
SiO_2	-0.58		-0.58	-0.45			0.99
Al_2O_3		-0.60	0.52		-0.43		1.00
Fe_2O_3	0.74		0.55				0.99
MnO	0.93						0.99
Na_2O				0.57		-0.61	0.93
MgO		0.55	0.52		0.49		0.99
TiO_2	0.51				0.81		0.99
K_2O		0.97					0.98
P_2O_5	0.75						0.99
SO_3		-0.50	0.43	0.44		-0.45	0.99
CaO		0.66	-0.51				0.83
LOI		-0.40		0.78			0.99
Ni	0.60		0.75				1.00
Co	0.94						0.99
Ba	0.80	0.43					0.98
Pb						0.99	0.99
Y	0.93						0.98
Zn	0.66		0.64				1.00
Rb		1.00					0.99
Sr		0.49	-0.69			0.51	0.98
Zr		-0.51		-0.85			0.99
V	0.44				0.89		0.99
Ce				0.73		-0.51	0.98
EV	10.07	5.37	3.117	1.86	1.17	1.02	
VAR (%)	43.77	23.35	13.55	8.1	5.09	4.43	
CVAR (%)	43.77	67.12	80.67	88.77	93.86	98.30	

4.7 Industrial potential of the clay deposits

The physico-chemical characteristics and mineralogical composition constitute essential parameters in the appraisal of the suitability of clays as industrial raw materials. A comparison of the chemical composition of the clay bodies studied with the chemical specification of some industrial clays (Table 6) shows clearly that the Orin clay and Igbara Odo clays are suitable for the production of refractory bricks (Parker, 1967) and rubber and paper (Keller, 1964).

In this regard the alumina content of the two clay bodies and silica content of Orin clay are too low. Furthermore, the concentrations of CaO, MgO, Na_2O and K_2O for all the four clays are in excess of the requirements for the production of rubber and paper (Keller, 1964). Their effect would be to lower the vitrification of the clays without necessarily detracting from their refractoriness (Onyeobi et al., 2013). There is a close chemical compositional similarity between Orin, Igbara Odo and Ikere Ekiti clay bodies and plastic fire clay of St. Louis (Huber, 1985) except for considerable differences in K_2O/Na_2O, $Fe_2O_3+MnO+TiO_2$ and silica/alumina ratios. This clearly shows that the Orin, Igbara Odo and Ikere Ekiti clay are fire clay. Economically, good quality fire clays are used for the production of refractories in the iron and steel industries (e.g. crucibles, furnace linings etc).

Nevertheless, the use of the Orin, Igbara Odo and Ikere Ekiti clays in the pottery industry for the manufacture of sanitary ware, glazing tiles and acid-proof products would depend on the level of beneficiation feasible to turn them into good quality fire clays. For example, Orin, Igbara Odo and Ikere Ekiti clays are unsuitable for glazed products on account of its objectionably high amount of Fe_2O_3 impurities which would cause undesirable brown colourations.

Conversely, the Ado Ekiti clay will probably exhibit attributes analogous with those of plastic fire clay upon the removal (through filtration) of the silty/sandy quartz particles that make it gritty. This would reduce the SiO_2/Al_2O_3 ratio thereby enhancing the alumina content in relative terms. Subsequent blending with appropriate quantities of clay with high content of alumina will add to its refractory nature.

5. Summary and conclusions

There is common occurrence of clay bodies in the studied areas. Field evidence supported by mineralogical and chemical analyses indicated that the clay bodies are product of hydrothermal fluid and in-situ weathering of aplite, fine grained biotite granite, medium to coarse grained, non-porphyritic biotite – hornblende granite and coarse – porphyritic biotite - hornblende granite. Kaolinite is the major clay mineral of the studied clay deposits with a smaller amount quantity of quartz, potassium iron oxide and potassium aluminum phosphate. The spectra peak in the XRD data are are not attributable to feldspars indicating intense weathering of feldspar in the parent materials.

The high chemical index of alteration (CIA), chemical index of weathering (CIW) and the weathering index of Parker (WIP) values probably indicated the intense degree of weathering. The SiO_2/Al_2O_3 molar ratio of 1.40 and 1.50 for Orin and Ikere clay bodies indicated that a 1:1 clay mineral was the dominant component. The study reveals clear relationship amongst the amount clayeyness (Al_2O_3/SiO_2 ratio), relative base loss (RBL) and the cation exchange capacity (CEC). There is localized occurrence of halloysite. The absence of vanadium in the EDS data of rolled into tubes kaolinite sheets of Ado Ekiti clay match up with XRF data.

This result trend combined with field observation suggests that clay body formed from weathering of feldspar is deficient in vanadium. The morphology of kaolinitic minerals may be influenced by the kind of parent material (i.e. feldspars or micas) and degree of chemical weathering. A multivariate statistical analysis elucidated the geochemical evolution of the studied clays and indicated that the variation in the geochemical data is controlled by six components. Therefore the geochemical indices show differences and variables that have greater contribution to clay deposits differentiation. Appraisal of the industrial potential of the studied clay bodies based on their physical and chemical characteristics revealed that they are suitable for the production of refractory bricks and ceramics. Appropriate processing would be necessary if they are to meet requirements for other industrial applications, such as rubber, paper, paint, cosmetics and fertilizer industries.

Table 6. Major elemental oxides of the tested samples compared with similar clay and industrial specification

Major oxides (wt%)	Orin	Igbara Odo	Ikere	Ado	Samples As Brick clay (Murray, 1960)	Reference Rubber (Keller, 1964)	Reference Refactories bricks (Parker, 1967)	Ceramics (Singer & Songa, 1971)	Samples As coating (Anon, 1972)	Samples As filler (Anon, 1972)	Pharmaceutical (Todd, 1975)	Agricultural (Huber, 1985)	Fertilizer (NAFCON, 1985)
SiO_2	40.43	58.18	40.58	74.98	38.67	44.90	51 - 70	67.50	47.80	48.70	47.00	49.88	46.07
Al_2O_3	29.09	19.94	27.03	12.92	9.45	32.35	28 - 44	26.50	37.00	36.00	40.00	37.65	38.07
TiO_2	2.01	1.81	2.43	1.52	-	1.80	1.0 - 2.80	0.10 - 1.0	0.03	0.05	-	0.09	0.50
Fe_2O_3	15.76	9.80	17.60	3.49	2.70	0.48	0.5 - 2.40	0.5 - 1.20	0.58	0.82	-	0.88	0.33
CaO	0.00	0.17	0.00	0.16	15.84	Tr	0.1 - 0.2	0.18 - 0.30	0.04	0.06	-	0.03	0.38
MgO	0.94	0.65	0.49	0.36	8.50	Tr	0.2 - 0.7	0.1 - 0.19	0.16	0.25	-	0.13	0.01
K_2O	0.91	2.21	0.35	3.63	2.76	0.28	-	1.10 - 3.10	1.10	2.12	-	1.6	0.43
Na_2O	0.14	0.14	0.02	0.22	2.76	0.14	0.8 - 3.50	0.20 - 1.50	0.10	0.10	-	0.21	0.27
MnO	0.08	0.05	0.12	0.03	-	-	-	-	-	-	-	-	-
P_2O_5	0.12	0.08	0.15	0.06	-	-	-	-	-	-	-	-	-
SO_3	0.02	0.01	0.01	0.01	-	-	-	-	-	-	-	-	-
H_2O^+	10.44	6.92	11.27	2.52	-	-	-	-	-	-	13.00	12.45	13.47
SiO_2/Al_2O_3	1.39	2.92	1.50	5.80	4.09	1.39	-	2.55	1.29	1.35	1.18	1.32	1.21
Al_2O_3/SiO_2	0.72	0.34	0.67	0.17	0.24	0.72	-	0.39	0.77	0.74	0.85	0.75	0.83
K_2O/Na_2O	6.54	15.97	19.81	16.23	1.00	2.00	-	-	11	21.2	-	7.62	1.59
$Fe_2O_3+MnO+TiO_2$	17.85	11.66	20.15	5.04	2.70	2.28	-	-	0.61	0.87	-	0.97	0.83

Adapted from Emofurieta et al. (1992); Olaolorun and Oyinloye (2010); Onyeobi et al. (2013); Akinola and Obasi (2014).

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