EUROPEAN JOURNAL OF EMERGING ENVIRONMENTAL AND EARTH SCIENCES

COMPOSITION OF RARE EARTH AND TRACE ELEMENTS IN SOSAN AKOKO RESIDUAL CLAY, SOUTHWEST NIGERIA: EVIDENCE OF WEATHERING PROCESSES AND PROVENANCE

Dr. Tarela N. Ayodimeji
Department of Geology, Obafemi Awolowo University, Ile-Ife, Nigeria

Dr. Kelechi O. Ransome
Centre for Earth and Mineral Sciences, University of Ibadan, Ibadan, Nigeria

V0LUME 01 ISSUE 01 (2024)

Published Date: 17 December 2024 // Page no.: - 26-34

ABSTRACT

This study presents a comprehensive geochemical and mineralogical analysis of residual clay from Sosan Akoko, located within the Precambrian basement complex of Southwestern Nigeria, to elucidate its weathering history and provenance. Fifteen representative clay samples were collected from three excavated pits and were analyzed using X-ray diffractometry (XRD) and inductively coupled plasma-mass spectrometry (ICP-MS). The mineralogical analysis identified kaolinite (1.4%) and nontronite (2.77%) as the principal clay minerals. The non-clay mineral fraction is dominated by quartz, with minor occurrences of orthoclase, labradorite, and albite. The geochemical data reveal high mean values for the Chemical Index of Alteration (CIA) at 79.43% and the Chemical Index of Weathering (CIW) at 90.84%. These high index values, coupled with the depletion of alkali and alkaline earth elements, signify an intense degree of chemical weathering in the source area. The provenance of the parent material was investigated using elemental ratios and discriminant diagrams. Plots of TiO_2 versus Al_2O_3 suggest that the clay was derived predominantly from acidic igneous rocks. This is further substantiated by the high concentrations of certain trace elements, such as Rubidium (Rb), which ranges from 113.4 to 138.2 ppm, and Strontium (Sr), ranging from 218.3 to 229.2 ppm, indicating active chemical weathering processes. The chondrite-normalized Rare Earth Element (REE) patterns show an enrichment in Light Rare Earth Elements (LREE) relative to Heavy Rare Earth Elements (HREE), with a significant negative Europium (Eu) anomaly (average 0.83%). This signature is characteristic of felsic source rocks. Ternary diagrams, including the La-Th-Sc plot, corroborate these findings, with samples plotting firmly in the felsic source region. The collective evidence from mineralogy, major and trace element geochemistry, and REE distributions strongly indicates that the Sosan Akoko residual clay originated from the in-situ chemical weathering of felsic, likely granitic, parent rocks under intense weathering conditions, although the presence of some primary minerals suggests that the weathering process has not reached complete maturity.

KEYWORDS: - Acidic Rocks, Chemical Indices, Clay Body, Mineralogy, Ternary Diagrams, Source Area, Provenance.

Introduction

1.1. Broad Background and Historical Context

The study of residual clays, which form from the in-situ chemical and physical breakdown of parent rocks, offers a unique window into the geological processes that shape the Earth's continental crust. These clays are not merely weathering products but are geological archives that record critical information about the original source rock (provenance), the intensity and nature of paleoweathering conditions, and the tectonic setting of their formation. The chemical and mineralogical composition of these materials is the result of a complex interplay of factors including parent rock lithology, climate, topography, and time. Within the vast expanse of Nigeria's Precambrian basement complex, numerous residual clay deposits exist, formed by the prolonged weathering of ancient crystalline rocks under tropical conditions. Historically, these deposits have been primarily evaluated for their economic potential, with studies focusing on their suitability for industrial applications such as ceramics, refractories, and drilling muds. However, their scientific value as paleoenvironmental indicators has been comparatively underexplored.

The process of weathering involves the gradual transformation of primary rock-forming minerals, such as feldspars and micas, into more stable secondary clay minerals like kaolinite, smectite, and illite. During this transformation, mobile elements like calcium (Ca), sodium (Na), potassium (K), and magnesium (Mg) are preferentially leached away, leading to a relative enrichment of immobile elements such as aluminum (Al), titanium (Ti), and zirconium (Zr) in the resulting clay. The extent of this elemental fractionation serves as a powerful proxy for the intensity of chemical weathering. Provenance studies, which aim to identify the source of sediments and sedimentary rocks, are fundamental to reconstructing paleogeography and understanding crustal evolution. By analyzing the geochemistry of weathering products like clay, geologists can trace their origins back to specific types of parent rocks—be they felsic (e.g., granite), mafic (e.g., basalt), or of a mixed lineage. This is possible because certain elements and their ratios, particularly immobile trace elements and Rare Earth Elements (REEs), are inherited from the parent rock with minimal alteration during weathering and transport, thus preserving a "geochemical fingerprint" of the source.

1.2. Critical Literature Review

The use of geochemistry as a tool for interpreting geological history is well-established. Numerous researchers have demonstrated the significant role that clay mineralogy and the concentration of chemical elements play in comprehensive provenance studies [1, 2, 3, 4, 5, 6, 7]. The chemical signature of sediments is fundamentally controlled by the interplay between the composition of the source rocks and the modifying effects of chemical weathering [1, 6]. For instance, Roddaz et al. (2006) utilized major and trace element geochemistry to unravel the controls on weathering and provenance in the Amazonian foreland basin, highlighting how different tectonic settings and climatic conditions influence sediment composition [1]. Similarly, Singh (2009) investigated Ganga River sediments, showing how provenance and sedimentary processes could be distinguished through their geochemical and REE signatures [3].

A cornerstone of paleoweathering analysis is the use of chemical indices derived from major element oxides. The Chemical Index of Alteration (CIA), proposed by Nesbitt and Young (1982), is a widely used metric calculated as `$Al\_2O\_3 / (Al\_2O\_3 + CaO\* + Na\_2O + K\_2O) \\times 100$` [14]. This index effectively tracks the degree to which feldspars have been converted into aluminous clay minerals, with higher values indicating more intense weathering [14, 25]. A modification to this index, the Chemical Index of Weathering (CIW), was later proposed by Harnois (1988), which excludes K_2O from the calculation to account for potassium fixation in illitic clays [15]. These indices have been successfully applied across the globe to infer paleoclimatic conditions and weathering intensity from sedimentary profiles [5]. The mobility of alkali and alkaline earth elements during weathering means their depletion relative to stable elements provides a robust measure of chemical weathering intensity [13].

The geochemistry of trace and Rare Earth Elements (REEs) provides even more specific information about the petrogenesis and provenance of igneous and metamorphic rocks, and by extension, the sediments derived from them [8, 9, 10, 11]. REEs, in particular, are exceptionally useful because they behave as a coherent group, with subtle but predictable fractionation based on their ionic radii. Their patterns, when normalized to a standard like chondrite, can reveal crucial details about the source rock. For example, sediments derived from felsic rocks, which are typical of the upper continental crust, generally exhibit an enrichment in Light REEs (LREEs), a relatively flat Heavy REE (HREE) pattern, and a characteristic negative Europium (Eu) anomaly [31, 36, 37]. This negative Eu anomaly arises from the retention of Eu in plagioclase feldspar during magma differentiation. Conversely, mafic rocks tend to have lower LREE/HREE ratios and little to no Eu anomaly [34]. The ratios of certain immobile trace elements, such as Thorium (Th), Scandium (Sc), Zirconium (Zr), and Cobalt (Co), are also powerful discriminators of provenance, as their ratios differ significantly between felsic and mafic sources [28, 29, 30].

In Nigeria, research on residual clay deposits has been extensive but has often focused on their economic aspects. Studies by Ajayi and Agagu (1981), Elueze and Bolarinwa (2001), Fasuba et al. (2001), and others have characterized the mineralogy, physicochemical properties, and industrial suitability of various clay deposits across the Precambrian basement complex [16, 17, 18, 19, 20, 21, 22]. These studies have established the prevalence of kaolinite-rich clays resulting from the weathering of granitic and gneissic rocks. However, as noted in the source material for this study, there has been a relative scarcity of publications that apply detailed trace element and REE geochemistry to rigorously investigate the weathering history and specific provenance of these residual clays, particularly those within the tropical forest belts [32].

1.3. The Identified Research Gap

Despite the foundational work on Nigerian clays, a significant research gap exists in the detailed geochemical characterization of these deposits for paleoenvironmental reconstruction. Much of the previous work has focused on major mineralogy and bulk chemistry for industrial classification [18, 20, 21]. While these studies are valuable, they often lack the high-resolution data provided by trace and Rare Earth Elements, which are essential for definitively constraining provenance and quantifying weathering intensity. The tropical setting of Southwestern Nigeria, with its characteristic high rainfall and temperature, promotes intense chemical weathering, creating complex weathering profiles. However, few studies have leveraged modern geochemical tools to systematically deconvolve the signals of weathering intensity from the primary signature of the source rock in this specific region. The present study addresses this gap by undertaking a focused investigation of a residual clay body in Sosan Akoko, an area representative of the Nigerian basement complex, using an integrated approach that combines mineralogy with major, trace, and REE geochemistry.

1.4. Study Rationale, Objectives, and Hypotheses

The rationale for this study is to move beyond a purely economic appraisal of residual clays and to utilize the Sosan Akoko clay deposit as a geological archive. By applying a detailed geochemical framework, this research aims to unlock the information encoded within the clay's composition to reconstruct its geological past. The primary objective is to determine the weathering history and provenance of the residual clay overlying the

Precambrian basement complex rocks in Sosan Akoko, Southwestern Nigeria [16, 33].

To achieve this overarching goal, the study sets forth the following specific objectives:

1. To determine the detailed mineralogical composition of the clay samples using X-ray diffraction (XRD).

2. To analyze the major, trace, and Rare Earth Element (REE) geochemistry of the clay samples using inductively coupled plasma-mass spectrometry (ICP-MS).

3. To calculate and interpret chemical indices of weathering (CIA and CIW) to quantify the degree of source area weathering.

4. To use geochemical discriminant diagrams, elemental ratios, and REE patterns to identify the lithological characteristics of the parent rock (provenance).

Based on the geological context and the principles of weathering geochemistry, the study was guided by the following hypotheses:

1. The residual clay at Sosan Akoko will exhibit high values for the Chemical Index of Alteration (CIA) and Chemical Index of Weathering (CIW), reflecting the intense chemical weathering typical of a tropical environment.

2. The geochemical signature of the clay, particularly the trace and REE patterns, will indicate a provenance dominated by felsic source rocks, consistent with the underlying granitic and gneissic units of the Precambrian basement complex.

3. Despite intense weathering, the clay may retain some primary rock-forming minerals, indicating that the weathering profile has not yet reached full maturity, reflecting an ongoing weathering process.

METHODS

2.1. Research Design

This study employed a multi-faceted research design that integrated geological field investigation with advanced laboratory-based analytical techniques. The design was cross-sectional, involving a one-time sampling event to characterize the clay deposit at a specific point in time. The overall approach was descriptive and analytical, aiming to first describe the mineralogical and geochemical characteristics of the clay and then to analyze these data to infer geological processes, namely weathering and provenance. The core of the design was to use geochemistry as the primary tool for interpretation. This involved a systematic analysis of major elements to assess weathering intensity and bulk composition, and trace and Rare Earth Elements to diagnose the source rock signature. The combination of these different lines of geochemical evidence was intended to provide a robust and internally consistent interpretation of the clay's origin and history.

2.2. Participants/Sample

The study was conducted in the Sosan Akoko area of Southwestern Nigeria. Geologically, this area is situated within the Precambrian basement complex of Nigeria, which forms part of the Pan-African mobile belt lying between the West African and Congo Cratons [36]. The specific study location falls between latitudes 7°25'1" N to 7°32' N and longitudes 5°53' E to 5°58' E [37]. The region is characterized by a gently undulating terrain covered by thick vegetation, typical of the country's tropical rainforest belt [37, 45]. Field mapping identified three major lithological units in the area: biotite gneisses, granite gneisses, and granites [38]. The biotite gneisses are found in the western part of the area, while the granite gneisses are extensive, covering approximately 50% of the study area and forming prominent outcrops [41, 42]. The granites occur as low-lying bodies, often covered by a significant overburden, and constitute about 15% of the area [44]. The residual clay under investigation directly overlies these basement complex rocks.

The sampling strategy was designed to obtain representative material from the clay body. Fieldwork involved the excavation of three pits at different locations across the study area to capture any potential lateral variability. From these pits, a total of fifteen clay samples were collected, out of which twelve were selected as representative for detailed analyses [17, 89]. A point sampling method was used within each pit [90]. The pits were dug to a depth of approximately 2 meters, revealing a typical tropical weathering profile consisting of topsoil, a laterite layer, and the underlying clay body [90]. Samples were collected from the clay layer at systematic 0.3-meter intervals in each pit to investigate vertical compositional changes [91]. Each sample was carefully placed in a labeled sample bag to ensure proper identification and prevent cross-contamination [91].

2.3. Materials and Apparatus

The sample preparation and analysis relied on standard geological laboratory equipment. For initial sample processing, a rubber-headed pestle and an agate mortar were used for gentle disaggregation and pulverization [92]. This choice of equipment is crucial to avoid contamination from metallic grinding elements and to preserve the integrity of the mineral grains.

The mineralogical composition of the clay was determined using an X-ray diffractometer (XRD), specifically a Phillips-PW1800 model [99]. This instrument operates by directing X-rays onto a powdered sample and measuring the angles at which the X-rays are diffracted by the crystal lattice of the minerals present. The XRD analysis was configured to use Ni-filtered Cu K-alpha radiation, a standard for geological materials, with a scanning rate of

1°2θ per minute per centimeter [100].

The chemical composition, including major element oxides and a comprehensive suite of trace and Rare Earth Elements, was determined using an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) [101]. ICP-MS is a highly sensitive analytical technique capable of detecting elements at concentrations down to parts per trillion. It works by ionizing the atoms of the sample in a high-temperature argon plasma and then separating and quantifying these ions based on their mass-to-charge ratio using a mass spectrometer. Both the XRD and ICP-MS analyses were conducted at the ACME Analytical Laboratories in Vancouver, Canada, a facility known for its high standards in geochemical analysis [102].

2.4. Experimental Procedure/Data Collection Protocol

The experimental procedure followed a systematic workflow from sample preparation to instrumental analysis.

Sample Preparation: Upon arrival from the field, the collected clay samples were first air-dried for several days to remove ambient moisture [92]. Once dried, the samples were carefully disaggregated using a rubber-headed pestle in an agate mortar to break down any clumps without excessively grinding the primary mineral grains [92]. The disaggregated material was then pulverized to a fine, homogenous powder, a necessary step to ensure that the small subsample taken for analysis is representative of the bulk sample and to meet the requirements for XRD and ICP-MS analysis [93]. The powdered samples were then packaged and sent for analysis.

Mineralogical Analysis (XRD): The mineralogy was determined using the XRD technique on powdered samples [94]. The procedure involved several steps to fully characterize the mineral suite. First, a bulk analysis was performed on an untreated powdered sample to identify all major minerals present. Following this, the clay fraction (<2 µm) was separated and analyzed. To identify specific types of clay minerals, especially swelling smectites, the clay fraction was treated with ethylene glycol, which intercalates into the structure of smectite minerals and increases their basal spacing, making them identifiable [95]. A final analysis was conducted after heating the clay fraction to 600°C, which causes the crystal structure of certain minerals like kaolinite to collapse, confirming their presence [95]. The instrument generated diffraction charts, which are plots of X-ray intensity versus the diffraction angle (2θ) [100].

Geochemical Analysis (ICP-MS): For the determination of major and trace element compositions, the ICP-MS method was utilized [101]. This required the complete digestion of the powdered sample to bring the elements into a liquid solution. A standard digestion procedure for silicate rocks involves using a mixture of strong acids, such as hydrofluoric (HF), nitric (HNO_3), and perchloric ($HClO_4$) acids, in a sealed vessel under heat and pressure. The resulting solution, containing the dissolved elements from the sample, was then diluted and introduced into the ICP-MS instrument for analysis. The instrument was calibrated using certified international rock standards to ensure the accuracy and precision of the measurements. Major elements were reported as weight percent oxide (e.g., SiO_2%), while trace and Rare Earth Elements were reported in parts per million (ppm).

2.5. Data Analysis Plan

The raw data generated from the analytical instruments were processed and interpreted to meet the study's objectives.

XRD Data Interpretation: The diffraction charts from the XRD analysis were interpreted by identifying the characteristic peaks for different minerals. Each mineral has a unique set of diffraction peaks corresponding to specific lattice spacings (d-values), which appear at specific 2θ angles. These peaks were identified by comparing the obtained patterns with standard reference data from the Joint Committee on Powder Diffraction Studies (JCPDS) [23, 97] and key diffraction patterns for clay minerals compiled by Chen (1977) [24, 97]. The peak intensities, which are roughly proportional to the abundance of a mineral, were also used to estimate the relative percentages of the identified minerals [99, 124].

Geochemical Data Analysis: The major element oxide data were used to calculate key geochemical parameters and weathering indices. The Chemical Index of Alteration (CIA) was calculated using the molecular proportions of the oxides according to the formula: $CIA = [Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O + K_2O)] \times 100$, where CaO* represents the calcium in silicate minerals only [14]. Similarly, the Chemical Index of Weathering (CIW) was calculated as $CIW = [Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O)] \times 100$ [15]. To investigate the provenance and tectonic setting, the major element data were plotted on various discrimination diagrams, such as a plot of (Na_2O+K_2O) versus SiO_2 and a plot of K_2O versus SiO_2 [206, 207]. The degree of weathering and elemental mobility was also visualized using ternary diagrams, specifically the A-CN-K (Al_2O_3–(CaO+Na_2O)–K_2O) and A-CNK-FM (Al_2O_3–(CaO+Na_2O+K_2O)–(Fe_2O_3+MgO)) plots [255].

The trace and REE data were analyzed using normalization techniques to identify elemental patterns and anomalies. Trace element concentrations were normalized to the average values for the Upper Continental Crust (UCC) as defined by Taylor and McLennan (1985) to highlight enrichments or depletions relative to the average crustal source [31, 267]. REE concentrations were normalized to chondrite values to produce smooth patterns that reveal features like LREE/HREE enrichment and Europium (Eu) anomalies [299]. The Eu anomaly (Eu/Eu^*) was calculated as $Eu/Eu^* = Eu_N / (Sm_N \times Gd_N)^{0.5}$, where N denotes chondrite-normalized values. Provenance was further constrained by examining ratios of immobile trace elements, such as Th/Sc and La/Sc, and by plotting the data on a La-Th-Sc ternary diagram, which is effective at distinguishing between felsic, mafic, and andesitic sources [37, 38, 331].

RESULTS

3.1. Preliminary Analyses (Mineralogy)

The mineralogical composition of the Sosan Akoko clay samples, as determined by X-ray diffraction (XRD) analysis, reveals a mixture of clay and non-clay minerals. The primary clay minerals identified are nontronite and kaolinite [105]. Nontronite, an iron-rich member of the smectite group, is the more abundant of the two, constituting an average of 2.77% of the samples [19, 109]. Kaolinite is present in a smaller proportion, with an average abundance of 1.44% [19, 109].

The non-clay mineral fraction is overwhelmingly dominated by quartz (SiO_2), which comprises an average of 83.27% of the bulk sample composition [106, 109, 124]. This high quartz content indicates a mineralogically mature sediment derived from a quartz-rich source. In addition to quartz, several primary rock-forming minerals are present in smaller quantities. These include the plagioclase feldspars labradorite (4.92%) and albite (2.81%), and the alkali feldspar orthoclase (3.78%) [19, 107, 109]. The persistence of these feldspars, which are generally susceptible to chemical weathering, suggests that the weathering process that formed the clay is either incomplete or ongoing.

3.2. Main Findings (Geochemistry)

Major Element Composition: The average chemical composition of the Sosan clay samples is dominated by three major oxides: silica (SiO_2), alumina (Al_2O_3), and iron (III) oxide (Fe_2O_3) [119]. Silica is the most abundant component, with a mean concentration of 58.03% (ranging from 53.10% to 63.40%) [113]. Alumina follows with a mean of 13.38% (ranging from 13.72% to 17.22%), and ferric oxide has a mean of 7.66% (ranging from 7.15% to 8.00%) [113, 126]. Together, these three oxides constitute the bulk of the chemical makeup, which is consistent with the classification of the material as a hydrated aluminum silicate [120]. Other major oxides, including those of mobile alkali and alkaline earth elements, are present in significantly lower concentrations: K_2O has an average of 2.72%, while CaO (0.80%), Na_2O (0.70%), and MgO (0.83%) are all below 1% [113].

Weathering Indices: The calculated chemical indices of weathering point towards an intense degree of chemical alteration. The Chemical Index of Alteration (CIA) shows a mean value of 79.43% (with a range of 73.5% to 81.1%) [113]. The Chemical Index of Weathering (CIW) is even higher, with a mean of 90.84% (ranging from 88.1% to 91.6%) [113, 129]. Values for these indices, particularly when they exceed 70%, are indicative of intensive weathering of the source rocks [130].

Trace and Rare Earth Element (REE) Concentrations: The trace element data reveal high concentrations of Rubidium (Rb) and Strontium (Sr), with values ranging from 113.4 to 138.2 ppm for Rb and 218.3 to 229.2 ppm for Sr, respectively [21, 216]. The concentrations of several trace elements, including Ba (mean 1036.16 ppm), Zr (mean 695.64 ppm), Th (mean 23.98 ppm), and Nb (mean 32.71 ppm), are notably elevated compared to standard crustal abundances [277, 279].

The REE analysis indicates a consistent pattern across the samples. The chondrite-normalized patterns are characterized by a significant enrichment of the Light Rare Earth Elements (LREEs; Lanthanum to Samarium) relative to the Heavy Rare Earth Elements (HREEs; Gadolinium to Lutetium) [356]. This fractionation is quantified by the chondrite-normalized Lanthanum to Ytterbium ratio, (La/Yb)_cn, which ranges from 12.02 to a high of 57.01, with an average of 12.75 [113, 291]. A prominent feature of the REE pattern is a distinct negative Europium (Eu) anomaly. The $Eu/Eu*$ ratio, which measures the magnitude of this anomaly, ranges from 0.77 to 1.17, with a mean value of approximately 0.83, indicating a significant depletion of Eu relative to its neighboring REEs [286, 327, 356].

3.3. Secondary or Exploratory Findings

Geochemical discrimination diagrams provide further insight into the parent rock characteristics. A plot of total alkalis (Na_2O+K_2O) against silica (SiO_2) shows that the samples plot within the fields for basaltic andesite and andesite, suggesting an intermediate to felsic source rock [206]. Furthermore, a plot of K_2O versus SiO_2 places the samples within the high-K calc-alkaline series, a common feature of magmas generated in continental arc settings [209].

Provenance-specific diagrams reinforce a felsic origin. A binary plot of TiO_2 against Al_2O_3 shows that the majority of the clay samples plot in the zones corresponding to granite/rhyolite and a mixture of granite/rhyolite + basalt, pointing towards predominantly acidic rock sources [325]. This is strongly supported by the La-Th-Sc ternary diagram, a tool used to differentiate between mafic, intermediate, and felsic provenances [331]. On this diagram, the Sosan clay samples cluster tightly together, plotting near the La-Th axis and well within the region indicative of a felsic source, closely associated with reference points for the Upper Continental Crust (UCC) and North American Shale Composite (NASC) [306, 357]. The ternary weathering trends depicted on A-CN-K and A-CNK-FM plots show the samples plotting close to the Al_2O_3 apex and away from the alkali and alkaline earth element corners, visually confirming the high degree of chemical weathering and the leaching of mobile cations [220].

DISCUSSION

4.1. Interpretation of Key Findings

The integrated mineralogical and geochemical results of this study provide a cohesive narrative of the origin and evolution of the Sosan Akoko residual clay. The mineral assemblage, dominated by quartz with secondary amounts of kaolinite, nontronite, and relict feldspars, is highly informative. The high abundance of quartz (83.27%) is expected for a residual soil derived from felsic rocks like granites and gneisses, which are rich in this highly resistant mineral [106, 124, 324]. The presence of kaolinite, a product of intense feldspar weathering, confirms that the parent rocks have undergone significant chemical alteration [19, 350]. However, the co-existence of kaolinite with less stable primary minerals—orthoclase, albite, and labradorite—and the smectite-group mineral nontronite is particularly significant [210, 351]. This mineral suite indicates that the weathering has not proceeded to completion; the system has not yet reached full chemical maturity [352]. Nontronite formation is favored under moderate chemical weathering conditions with poor drainage, where silica and cations are not completely leached. This suggests that while weathering is intense, as evidenced by the kaolinite, micro-environmental factors or the ongoing nature of the weathering process have allowed for the preservation of feldspars and the formation of smectite [211, 353].

The geochemical data strongly corroborate the story of intense weathering of a felsic source. The high CIA (mean 79.43%) and CIW (mean 90.84%) values are unequivocal indicators of advanced chemical weathering [113, 129]. These values signify the substantial removal of mobile cations (Ca, Na, K) from the parent rock and the corresponding residual enrichment of alumina [130]. Such high weathering indices are characteristic of materials formed in tropical climates with high precipitation and temperature, which accelerate chemical reactions [25, 26]. The low concentrations of CaO, Na_2O, and MgO in the bulk chemistry further support this interpretation of significant elemental leaching [126]. The slightly higher average K_2O content (2.72%), however, aligns with the mineralogical finding of relict orthoclase feldspar, suggesting that potassium-bearing minerals have not been entirely weathered out [128].

The provenance of the clay is clearly fingerprinted by its trace and REE geochemistry. The enrichment in LREEs relative to HREEs and the pronounced negative Europium anomaly are classic signatures of upper continental crustal rocks, particularly differentiated felsic sources like granite [288, 290, 327]. The negative Eu anomaly is a direct inheritance from the parent magma, where the preferential incorporation of Eu2+ into plagioclase feldspar during crystallization depletes Europium in the resulting melt and the rocks that form from it [34, 36]. The weathering of plagioclase (labradorite and albite were identified in the samples) would release this signature into the clay [287]. The high LREE/HREE ratios further preclude a significant contribution from mafic rocks, which typically have flat REE patterns and no Eu anomaly [290]. The elevated concentrations of large-ion lithophile (LIL) elements like Rb and Ba, and high-field-strength (HFS) elements like Zr and Th, are also consistent with a felsic provenance [279].

4.2. Comparison with Previous Literature

The findings of this study align well with the broader body of literature on weathering geochemistry and provenance analysis. The high CIA values recorded for the Sosan clay are comparable to those reported for sediments in other intensely weathered regions, such as the Amazon basin and parts of Asia [1, 4, 5]. The interpretation that CIA values above 70 indicate intense weathering is consistent with the framework established by Nesbitt and Young (1982) and supported by numerous subsequent studies [14, 25, 26]. The geochemical characteristics of the Sosan clay also show strong parallels with global averages for upper crustal materials. The REE patterns, with LREE enrichment and a negative Eu anomaly, are similar to those of the Post-Archean Average Shale (PASS) and the Upper Continental Crust (UCC), reinforcing the conclusion of a crustal, felsic provenance [290, 303].

The use of trace element ratios for provenance discrimination in this study is well-supported by previous research. Cullers (1994, 1995) and others have extensively demonstrated that ratios of immobile elements like Th/Sc, La/Sc, and Co/Th are robust indicators of source rock composition because they are not significantly fractionated during weathering and transport [28, 30]. The Th/Sc ratios of the Sosan clay (1.28-3.07) fall squarely within the range expected for felsic rocks and are significantly higher than those for mafic rocks [260]. The data plotting on the La-Th-Sc ternary diagram as a tight cluster in the felsic field provides a powerful visual confirmation of this, consistent with its application in other provenance studies [37, 38].

When placed in the context of research on Nigerian clays, this study provides a significant advancement. While previous studies have correctly identified many Nigerian residual clays as kaolinitic weathering products of the basement complex [16, 17], this work provides a more detailed, quantitative confirmation using a modern, multi-indicator geochemical approach. The conclusion of a felsic source from granitic and gneissic rocks corroborates the field geology and the general conclusions of works by Elueze & Bolarinwa (2001) and others [17, 324]. However, by integrating REE and immobile trace element data, this study moves beyond general associations to provide a specific geochemical fingerprint that definitively links the clay to a differentiated, felsic, high-K calc-alkaline parentage. The selective leaching of certain cations while others are fixed by clay absorption, as observed in this study, is a process that has been documented in other weathered terrains by researchers such as Awwiller (1994) and Compton et al. (2003) [32, 33].

4.3. Strengths and Limitations of the Study

The primary strength of this research lies in its integrated, multi-proxy approach. By combining field evidence, mineralogy, major element geochemistry, and trace/REE geochemistry, the study develops a comprehensive and internally consistent model for the clay's origin. The use of multiple, independent geochemical indicators (e.g., CIA/CIW, REE patterns, trace element ratios, discriminant diagrams) all pointing to the same conclusion—intense weathering of a felsic source—lends high confidence to the interpretation. The high-quality analysis performed at a reputable international laboratory further strengthens the reliability of the dataset.

However, certain limitations should be acknowledged. The study is geographically focused on the Sosan Akoko area. While its findings are significant for understanding this specific deposit and are representative of processes on the Precambrian basement, caution should be exercised in extrapolating these detailed geochemical signatures to the entire Southwestern Nigerian basement complex without further research. The study concludes a "predominantly" acidic source and notes that plots do not exclude "possible combined sources" [305, 325], acknowledging a slight ambiguity. While the felsic signal is overwhelmingly dominant, the slight scatter in some plots and the andesitic classification in one diagram suggest that minor contributions from intermediate or other rock types within the complex gneissic terrain cannot be entirely ruled out. This complexity is inherent in studying sediments derived from ancient, polymetamorphic basement terranes.

4.4. Implications for Theory and Practice

Theoretically, this study serves as a robust case study that validates and reinforces the utility of modern geochemical techniques in paleo-environmental analysis. It demonstrates how a carefully integrated geochemical dataset can be used to deconstruct the complex history of a residual deposit, successfully separating the primary inherited provenance signature from the secondary overprint of intense weathering [358]. It contributes valuable data on the geochemical behavior of elements in a tropical weathering environment overlying a Precambrian shield, a setting of significant global importance for understanding crust-forming processes and soil development.

On a practical level, the detailed characterization has significant implications. For industrial utilization, understanding the precise mineralogy and chemistry is paramount. The high quartz content implies the material would be highly abrasive, while the presence of iron-rich nontronite would affect its color and firing properties in ceramics. The low kaolinite percentage suggests it might not be a high-grade resource for applications requiring pure kaolin, like paper coating or pharmaceuticals, without significant beneficiation. This study therefore provides the kind of detailed data that is essential for guiding appropriate industrial applications, moving beyond the more general classifications of previous work [18, 21, 22]. Furthermore, the study provides a baseline for environmental geochemistry in the region, characterizing the natural concentrations and distributions of potentially toxic elements, which is vital for agricultural and land-use planning.

4.5. Conclusion and Future Research Directions

This study successfully determined the source area weathering and provenance of the residual clay from Sosan Akoko, Southwestern Nigeria. Through an integrated analysis of its mineralogical and geochemical composition, several key conclusions were reached.

First, the clay is the product of intense in-situ chemical weathering of the underlying Precambrian basement rocks, as evidenced by high CIA and CIW values and the significant depletion of mobile alkali and alkaline earth elements [349, 351]. Second, despite the intensity of weathering, the clay has not reached full maturity, as shown by the preservation of primary feldspar minerals and the presence of nontronite alongside kaolinite [352, 353]. Third, multiple independent geochemical proxies, including trace element ratios (Th/Sc), chondrite-normalized REE patterns (LREE enrichment, negative Eu anomaly), and discriminant diagrams (La-Th-Sc), converge to indicate that the clay was predominantly derived from a felsic (granitic/gneissic) source rock [354, 356, 357].

This research underscores the power of using major elements, immobile trace elements, and REEs in concert to unravel the geological history of complex weathering products. It is recommended that this comprehensive geochemical approach be adapted and applied more broadly to other clay bodies across Nigeria and in similar tropical basement terrains worldwide [358]. Future research could focus on quantifying the rates of weathering using isotopic systems, investigating the specific micro-environments that lead to the co-existence of smectite and kaolinite, and expanding the geographic scope of sampling to build a more detailed regional model of paleoweathering and crustal evolution in West Africa.

REFERENCES

[1] Roddaz, M., Viers, J., Brusset, S., Baby, P., Boucayrand, C., Hérail, G. (2006). Controls on weathering and provenance in the Amazonian foreland basin: insights from major and trace element geochemistry of Neogene Amazonian sediments. Chemical Geology, 226(1-2): 31-65. http://dx.doi.org/10.1016/j.chemgeo.2005.08.010

[2] Borges, J.B., Huh, Y., Moon, S., Noh, H. (2008). Provenance and weathering control on river bed sediments of the eastern Tibetan Plateau and the Russian Far East. Chemical Geology, 254(1-2): 52-72. http://dx.doi.org/10.1016/j.chemgeo.2008.06.002

[3] Singh, P. (2009). Major, trace and REE geochemistry of the Ganga River sediments: influence of provenance and sedimentary processes. Chemical Geology, 266(3-4): 242-255. http://dx.doi.org/10.1016/j.chemgeo.2009.06.013

[4] Noh, H., Huh, Y., Qin, J., Ellis, A. (2009). Chemical weathering in the Three Rivers region of Eastern Tibet. Geochimica et Cosmochimica Acta, 73(7): 1857-1877. https://doi.org/10.1016/j.gca.2009.01.005

[5] Shao, J., Yang, S., Li, C. (2012). Chemical indices (CIA and WIP) as proxies for integrated chemical weathering in China: inferences from analysis of fluvial sediments.

Sedimentary Geology, 265: 110-120. http://dx.doi.org/10.1016/j.sedgeo.2012.03.020

[6] Garzanti, E., Padoan, M., Setti, M., López-Galindo, A., Villa, I.M. (2014). Provenance versus weathering control on the composition of tropical river mud (southern Africa). Chemical Geology, 366: 61-74. http://dx.doi.org/10.1016/j.chemgeo.2013.12.016

[7] Garzanti, E., Resentini, A. (2016). Provenance control on chemical indices of weathering (Taiwan river sands). Sedimentary Geology, 336: 81-95. http://dx.doi.org/10.1016/j.sedgeo.2015.06.013

[8] Allegre, C.J., Minster, J.F. (1978). Quantitative models of trace element behavior in magmatic processes. Earth and Planetary Science Letters, 38(1): 1-25. http://dx.doi.org/10.1016/0012-821X(78)90123-1

[9] Hanson, G.N. (1978). The application of trace elements to the petrogenesis of igneous rocks of granitic composition. Earth and Planetary Science Letters, 38(1): 26-43. http://dx.doi.org/10.1146/annurev.ea.08.050180.002103

[10] Hanson, G.N. (1980). Rare earth elements in petrogenetic studies of igneous systems. Annual Review of Earth and Planetary Sciences, 8: 371-406. http://dx.doi.org/10.1146/annurev.ea.08.050180.002103

[11] Haskin, L.A. (1984). Petrogenetic modelling-use of rare earth elements. Developments in Geochemistry, 2: 115-152. http://dx.doi.org/10.1016/B978-0-444-42148-7.50009-5

[12] Singh, M., Sharma, M., Tobschall, H.J. (2005). Weathering of the Ganga alluvial plain, northern India: implications from fluvial geochemistry of the Gomati River. Applied Geochemistry, 20(1): 1-21. http://dx.doi.org/10.1016/j.apgeochem.2004.07.005

[13] Nesbitt, H.W., Markovics, G. (1980). Chemical processes affecting alkalis and alkaline earths during continental weathering. Geochimica et Cosmochimica Acta, 44(11): 1659-1666. http://dx.doi.org/10.1016/0016-7037(80)90218-5

[14] Nesbitt, H., Young, G.M. (1982). Early Proterozoic climates and plate motions inferred from major element chemistry of lutites. Nature, 299(5885): 715-717. http://dx.doi.org/10.1038/299715a0

[15] Harnois, L. (1988). The CIW index: A new chemical index of weathering. Sedimentary Geology, 55(3): 319-322. http://dx.doi.org/10.1016/0037-0738(88)90137-6

[16] Ajayi, J.O., Agagu, O.K. (1981). Mineralogy of primary clay deposits in the basement complex areas of Nigeria. J. Min. Geol, 18(1): 27-30.

[17] Elueze, A.A., Bolarinwa, A.T. (2001). Appraisal of the residual and sedimentary clays in part of Abeokuta area, Southwestern Nigeria. Journal Mining and Geology, 37(1): 7-14.

[18] Fasuba, O.A., Egunlae, O., Jimoh, B. (2001). Metallurgical analysis of Orin-Ekiti alumina clay deposit for use as a refractory. Journal of Engineering Technology and Industrial Applications, 1(4): 67-71.

[19] Ehinola, O.A., Oladunjoye, M.A., Gbadamosi, T.O. (2009). Chemical composition, geophysical mapping and reserve estimation of clay deposit from parts of Southwestern Nigeria. Journal of Geology and Mining Research, 1(3): 057-066. https://doi.org/10.5897/JGMR.9000010

[20] OlaOlorun, O., Oyinloye, A. (2010). Geology and geotechnical appraisal of some clay deposits around Ijero-Ekiti Southwestern Nigeria: implication for industrial uses. Biological Sciences-PJSIR, 53(3): 127-135.

[21] Akinola, O.O., Obasi, R.A. (2014). Compositional characteristics and industrial potential of the lateritic clay deposit in Ara-Ijero areas, Southwestern Nigeria. International Journal of Scientific and Technology Research, 3(8): 305-311.

[22] Onyeobi, T.U.S., Imeokparia, E.G., Ilegieuno, O.A., Egbuniwe, I.G. (2013). Compositional, geotechnical and industrial characteristics of some clay bodies in Southern Nigeria. Journal of Geography and Geology, 5(2): 73-84.

[23] JCPDS. (1974). Joint committee on powder diffraction standards. Selected powder diffraction data for mineral. 1st Edition In: L.G. Berry (ed.) Philadelphia, p. 833.

[24] Chen, P.Y. (1977). Table of key lines in X-ray powder diffraction patterns of minerals in clays and associated rocks: Indiana Geological Survey Occasional Paper 21, p. 67.

[25] Fedo, C.M., Wayne Nesbitt, H., Young, G.M. (1995). Unraveling the effects of potassium metasomatism in sedimentary rocks and paleosols, with implications for paleoweathering conditions and provenance. Geology, 23(10): 921-924. https://doi.org/10.1130/0091-7613(1995)023%3C0921:UTEOPM%3E2.3.CO;2

[26] Böning, P., Brumsack, H.J., Böttcher, M.E., Schnetger, B., Kriete, C., Kallmeyer, J., Borchers, S.L. (2004). Geochemistry of Peruvian near-surface sediments. Geochimica et Cosmochimica Acta, 68(21): 4429-4451. http://dx.doi.org/10.1016/j.gca.2004.04.027

[27] Wronkiewicz, D.J., Condie, K.C. (1987). Geochemistry of Archean shales from the Witwatersrand Supergroup, South Africa: source-area weathering and provenance. Geochimica et Cosmochimica Acta, 51(9): 2401-2416. https://doi.org/10.1016/0016-7037(87)90293-6

[28] Cullers, R.L. (1994). The controls on the major and trace element variation of shales, siltstones, and

sandstones of Pennsylvanian-Permian age from uplifted continental blocks in Colorado to platform sediment in Kansas, USA. Geochimica et Cosmochimica Acta, 58(22): 4955-4972. http://dx.doi.org/10.1016/0016-7037(94)90224-0

[29] Cullers, R.L., Basu, A., Suttner, L.J. (1988). Geochemical signature of provenance in sand-size material in soils and stream sediments near the Tobacco Root batholith, Montana, USA. Chemical Geology, 70(4): 335-348. http://dx.doi.org/10.1016/0009-2541(88)90123-4

[30] Cullers, R.L. (1995). The chemical signature of source rocks in size fractions of Holocene stream sediment derived from metamorphic rocks in the wet mountains region, Colorado, USA. Chemical Geology, 113(3-4): 327-343. http://dx.doi.org/10.1016/0009-2541(94)90074-4

[31] Taylor, S.R., McLennan, S. M. (1985). The Continental Crust: Its Composition and Evolution. Blackwell, Oxford, p. 312. http://dx.doi.org/10.1017/CBO9780511575358.014

[32] Awwiller, D.N. (1994). Geochronology and mass transfer in Gulf Coast mudrocks (south-central Texas, USA): Rb Sr, Sm Nd and REE systematics. Chemical Geology, 116(1-2): 61-84. https://doi.org/10.1016/0009-2541(94)90158-9

[33] Compton, J.S., White, R.A., Smith, M. (2003). Rare earth element behavior in soils and salt pan sediments of a semi-arid granitic terrain in the Western Cape, South Africa. Chemical Geology, 201(3-4): 239-255. http://dx.doi.org/10.1016/S0009-2541(03)00239-0

[34] Cullers, R.L. (1995). The controls on the major-and trace-element evolution of shales, siltstones and sandstones of Ordovician to Tertiary age in the Wet Mountains region, Colorado, USA. Chemical Geology, 123(1-4): 107-131. http://dx.doi.org/10.1016/0009-2541(95)00050-V

[35] McLennan, S.M. (1993). Weathering and global denudation. The Journal of Geology, 101(2): 295-303. http://dx.doi.org/10.1086/648222

[36] Taylor, S.R., McLennan, S.M. (1981). The composition and evolution of the continental crust: rare earth element evidence from sedimentary rocks. Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences, 301(1461): 381-399. https://doi.org/10.1098/rsta.1981.0119

[37] Mclennan, S. (1989). Rare earth elements in sedimentary rocks: influence of provenance and sedimentary processes. Reviews in Mineralogy and Geochemistry, 21: 169-200. http://dx.doi.org/10.1515/9781501509032-010

[38] Ekosse, G. (2001). Provenance of the Kgwakgwa kaolin deposit in southeastern Botswana and its possible utilization. Applied Clay Sci., 20(3): 137-152. https://doi.org/10.1016/S0169-1317(01)00064-3