



Integrated Major Oxide Geochemistry, Contamination Factor and Pollution Load Index for Evaluating Geogenic Enrichment in the Ikole–Itapaji Basement Complex, Southwestern Nigeria

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Received: 29 Jul 2026; Received in revised form: 22 Aug 2026; Accepted: 27 Aug 2026; Available online: 03 Oct 2026

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Abstract— The Ikole–Itapaji Basement Complex, southwestern Nigeria, comprises diverse crystalline rocks that influence both regional geochemical characteristics and environmental quality. This study integrated major oxide geochemistry, sequential extraction, Contamination Factor (CF), and Pollution Load Index (PLI) to evaluate geogenic enrichment and the environmental behaviour of trace elements within the study area. Geological mapping was conducted, during which thirty-five fresh rock samples representing the major lithological units were collected. Following detailed megascopic examination, twenty representative rock samples were selected for whole-rock major oxide geochemical analyses, while seventeen representative soil/sediment samples were analysed for environmental geochemical assessment. Major oxide analyses were carried out using Inductively Coupled Plasma–Mass Spectrometry (ICP–MS) following lithium metaborate fusion combined with multi-acid digestion ($\text{HCl-HNO}_3\text{-HClO}_4$), with analytical quality assured through certified reference materials, analytical blanks, duplicate samples, and internal laboratory standards. The soil/sediment samples were subjected to a seven-step modified Tessier sequential extraction procedure to determine trace-element partitioning among water-soluble, exchangeable, carbonate-bound, Fe–Mn oxide-bound, organic-bound, sulfide-bound, and residual fractions. Contamination Factor and Pollution Load Index were subsequently computed using average shale background values to evaluate elemental enrichment and environmental quality. The area is underlain by migmatite, granite gneiss, coarse porphyroblastic gneiss, granite, pegmatite, and charnockite. Major oxide geochemistry indicates predominantly calc-alkaline, magnesian, and metaluminous to weakly peraluminous compositions, reflecting magmatic differentiation and fractional crystallization within the Precambrian Basement Complex. Sequential extraction results reveal that most trace elements are concentrated within the Fe–Mn oxide, sulfide-bound, and residual fractions, indicating strong lithogenic control and generally low environmental mobility. Although CF identifies localized enrichment of Cd and Pb at a few sampling locations, PLI values indicate that most sites remain within the unpolluted to moderately polluted category. Overall, the study demonstrates that the geochemistry of the Ikole–Itapaji Basement Complex is primarily controlled by parent-rock composition, while localized enrichment of Cd and Pb highlights the need for periodic environmental monitoring to safeguard ecosystem integrity and public health.



Keywords— Ikole–Itapaji Basement Complex, major oxide geochemistry, sequential extraction, contamination factor, pollution load index, geogenic enrichment, environmental assessment.

I. INTRODUCTION

Major oxide geochemistry is one of the most fundamental approaches for characterizing rock composition, classifying lithological units, interpreting magmatic evolution, and understanding crustal differentiation within crystalline basement terrains. The concentrations of major oxides, including SiO₂, Al₂O₃, Fe₂O₃, MgO, CaO, Na₂O, K₂O, TiO₂, MnO, and P₂O₅, provide important information on mineralogical composition, weathering intensity, magma evolution, and tectonic setting (Shand, 1943; Peccerillo & Taylor, 1976; Frost et al., 2001; Frost & Frost, 2011). Consequently, major-oxide geochemistry has become an indispensable tool in geological investigations and mineral exploration, particularly within Precambrian basement complexes, where lithological diversity reflects prolonged tectono-magmatic evolution.

The Nigerian Basement Complex constitutes part of the Pan-African Mobile Belt. It is composed predominantly of migmatite–gneiss complexes, schist belts, Older Granites, charnockitic bodies, and pegmatitic intrusions emplaced during the Pan-African orogeny (Rahaman, 1988; Oyinloye, 2011). These lithological units have experienced multiple episodes of deformation, metamorphism, magmatism, hydrothermal alteration, and tropical weathering, resulting in considerable geochemical variability and natural enrichment of several major and trace elements. As weathering progresses, elements released from crystalline rocks become incorporated into soils and surface materials, where they may influence environmental quality depending on their abundance, mobility, and bioavailability.

Evaluating elemental enrichment within basement terrains requires not only an understanding of their geochemical composition but also an assessment of their environmental significance. Geogenic enrichment, arising from natural geological processes, may produce elevated elemental concentrations comparable to those observed in contaminated environments. Therefore, distinguishing natural geogenic signatures from anthropogenic contamination is essential for environmental assessment, mineral exploration, and sustainable land management (Kabata-Pendias, 2011; Reimann & de Caritat, 2005; Reimann & de Caritat, 2012; Alloway, 2013).

Environmental pollution indices have become widely accepted tools for assessing elemental enrichment in geological materials. The Contamination Factor (CF) quantitatively evaluates the degree of enrichment of individual elements relative to background concentrations, whereas the Pollution Load Index (PLI) provides an integrated measure of the cumulative pollution status of an area (Hakanson, 1980; Birth, 2003). Although originally developed for environmental studies of soils and

sediments, these indices have increasingly been applied in geological investigations to differentiate naturally enriched basement terrains from areas affected by anthropogenic pollution and to establish geochemical baseline conditions for environmental monitoring (Förstner & Wittmann, 2012; Wei & Yang, 2010).

While CF and PLI provide valuable information on the degree of elemental enrichment, they do not indicate the chemical forms in which elements occur or their potential mobility within the environment. Sequential extraction techniques complement these pollution indices by partitioning elements into operationally defined geochemical fractions, namely water-soluble, exchangeable, carbonate-bound, Fe–Mn oxide-bound, organic-bound, sulfide/strongly bound, and residual phases. These fractions provide critical information on elemental mobility, bioavailability, and environmental behaviour. Elements occurring within the water-soluble and exchangeable fractions are generally more mobile and readily available for biological uptake, whereas those associated with the residual fraction are strongly incorporated within mineral lattices and therefore exhibit low mobility under natural environmental conditions (Tessier et al., 1979; Filgueiras et al., 2002; Davidson et al., 1998; De Matteis et al., 2023; Çelebi, 2024; Firmino et al., 2025).

The Ikole–Itapaji Basement Complex of southwestern Nigeria consists predominantly of migmatites, granite gneisses, granites, pegmatites, and charnockitic rocks that have undergone prolonged tectono-magmatic evolution and weathering. Previous investigations within the area have largely concentrated on geological mapping, litho-structural characterization, aeromagnetic interpretation, radiometric analysis, and mineral exploration (Ojo et al., 2024; Adetunla et al., 2025; Ogah & Abubakar, 2024; Salako et al., 2024). Although these studies have significantly improved the understanding of the geological framework and mineral potential of the area, little attention has been given to integrating major oxide geochemistry with environmental pollution indices and sequential extraction techniques to evaluate geogenic enrichment, elemental mobility, and their environmental implications. Such integration provides a more comprehensive understanding of whether elevated elemental concentrations reflect natural geological processes or constitute potential environmental concerns.

This study therefore integrates major oxide geochemistry, sequential extraction, Contamination Factor (CF), and Pollution Load Index (PLI) to evaluate geogenic enrichment, elemental partitioning, and the environmental implications of naturally occurring elements within the

Ikole–Itapaji Basement Complex, Southwestern Nigeria. The study establishes baseline geochemical conditions, assesses elemental mobility through sequential extraction, and provides valuable information for sustainable mineral exploration, environmental monitoring, and future land-use planning within the study area.

This study aims to integrate major oxide geochemistry, sequential extraction, Contamination Factor (CF), and Pollution Load Index (PLI) to evaluate geogenic enrichment, elemental mobility, and their environmental implications within the Ikole–Itapaji Basement Complex, Southwestern Nigeria.

To achieve this aim, the study seeks to:

1. Determine the major oxide composition of the basement rocks within the study area.
2. Evaluate the geochemical characteristics and petrogenetic affinities of the rocks using major oxide data.
3. Characterize the partitioning of elements into water-soluble, exchangeable, carbonate-bound, Fe–Mn oxide-bound, organic-bound, sulfide/strongly bound, and residual fractions using sequential extraction.
4. Calculate the Contamination Factor (CF) of the investigated elements to assess their degree of geogenic enrichment.
5. Determine the Pollution Load Index (PLI) to evaluate the overall geochemical enrichment status of the study area.
6. Assess elemental mobility, bioavailability, and potential environmental implications by integrating sequential extraction results with CF and PLI.
7. Distinguish between natural geogenic enrichment and possible environmental contamination and establish a baseline for future environmental monitoring and sustainable mineral exploration.

1.1 Study Area

Figure 1 illustrates the geographical location of the Ikole–Itapaji study area within Ekiti State, southwestern Nigeria. The inset map of Nigeria shows the position of Ekiti State in the southwestern region of the country, while the highlighted rectangle delineates the study area. The area lies within the Precambrian Basement Complex of southwestern Nigeria, which forms part of the Pan-African Mobile Belt. The Basement Complex is composed predominantly of migmatite–gneiss complexes, Older Granites, charnockitic bodies, pegmatites, and minor metasedimentary rocks that were emplaced and reworked

during the Pan-African orogeny through multiple episodes of magmatism, metamorphism, deformation, and hydrothermal activity (Rahaman, 1988; Oyinloye, 2011).

The enlarged topographic map indicates that the study area extends approximately between latitudes 7°47'N and 8°05'N and longitudes 5°26'E and 5°34'E, covering an estimated surface area of about 590 km². The terrain is rugged and undulating, consisting of numerous hills, ridges, valleys, and lowlands that are characteristic of crystalline basement environments. Closely spaced contour lines represent areas of steep slopes and resistant rock units, whereas widely spaced contours indicate relatively gentle terrain. These geomorphological variations are primarily controlled by differences in lithology, structural deformation, and the differential weathering of basement rocks (Ojo et al., 2024).

The drainage pattern is predominantly dendritic, indicating that stream development is mainly influenced by the regional topographic gradient and the relatively homogeneous crystalline basement. However, local changes in drainage orientation reflect the influence of fractures, joints, faults, and other structural discontinuities that serve as zones of weakness within the Basement Complex. These structures enhance weathering, groundwater circulation, and the migration of dissolved elements released during rock alteration, thereby influencing the geochemical evolution of soils and surface materials (Adetunla et al., 2025).

The study area is readily accessible through a network of major and minor roads linking Ikole-Ekiti and Itapaji, thereby facilitating geological mapping, structural measurements, and representative rock-sample collection. The abundance of fresh outcrops, combined with rugged topography and an extensive drainage network, provides favourable conditions for major oxide geochemical investigations, sequential extraction studies, and the assessment of geogenic elemental enrichment and environmental quality within the Basement Complex (Ogah & Abubakar, 2024; Salako et al., 2024).

Overall, the geological and physiographic characteristics of the Ikole–Itapaji area typify the crystalline Basement Complex of southwestern Nigeria. The combination of diverse lithological units, pronounced topographic relief, structural complexity, and active weathering processes provides an ideal natural laboratory for investigating major oxide geochemistry, elemental partitioning through sequential extraction into water-soluble, exchangeable, carbonate-bound, Fe–Mn oxide-bound, organic-bound, sulfide/strongly bound, and residual fractions, as well as evaluating geogenic enrichment using Contamination Factor (CF) and Pollution Load Index (PLI). This

integrated approach provides valuable insight into elemental mobility, environmental behaviour, and the

natural geochemical baseline of the study area.

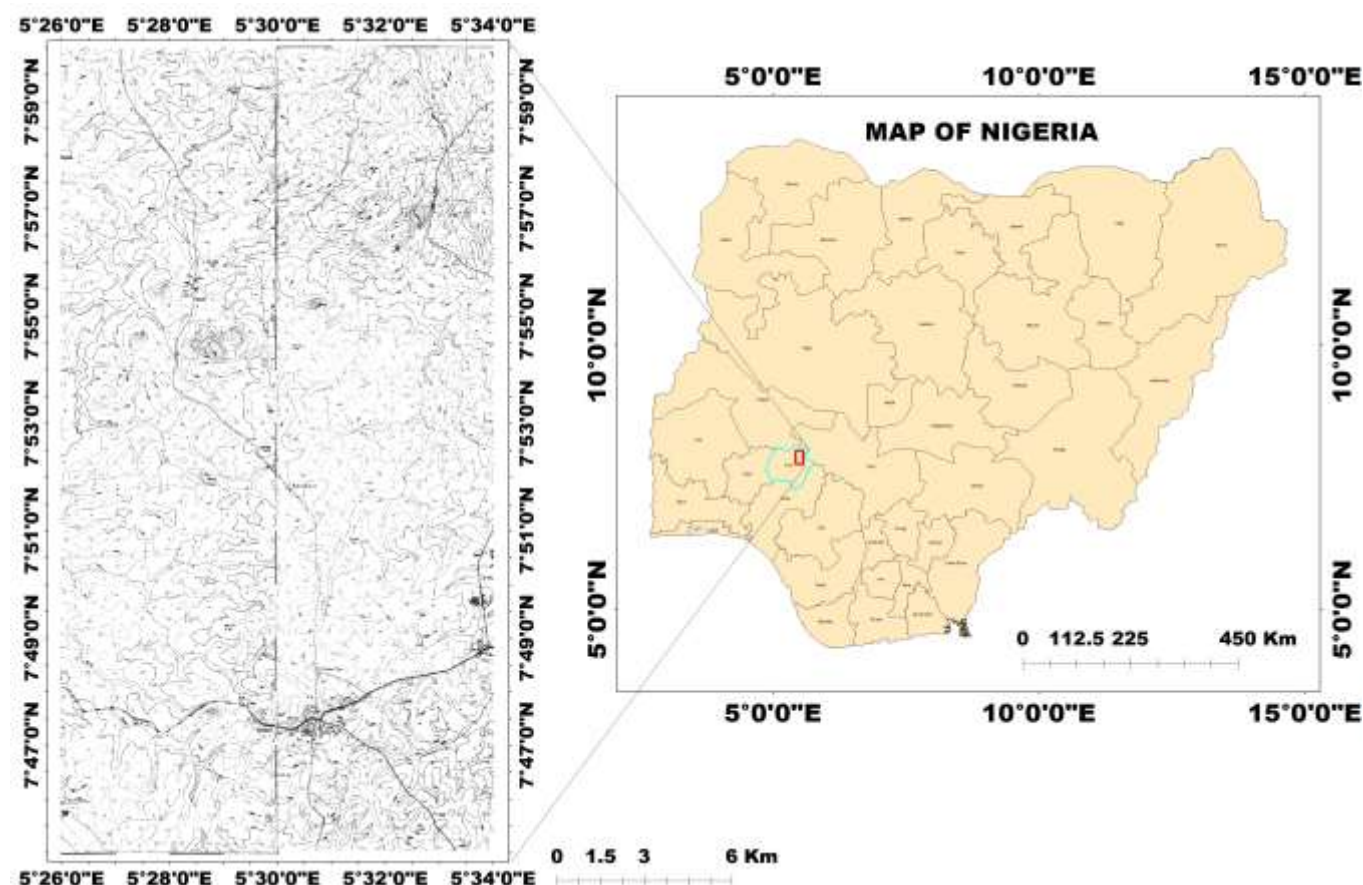


Fig.1. Location and topographic map of the Ikole–Itapaji area, Ekiti State, southwestern Nigeria, illustrating the geographical extent, drainage network, road accessibility, and topographic relief of the study area.

II. GEOLOGICAL SETTING

The study area is situated within the Precambrian Basement Complex of southwestern Nigeria, which forms part of the Pan-African Mobile Belt between the West African and Congo Cratons. This crystalline basement terrain is composed predominantly of ancient metamorphic and igneous rocks that contrast sharply with the surrounding sedimentary basins of Nigeria. The Basement Complex evolved through several tectono-magmatic events, including the Liberian, Eburnean, and Pan-African orogenies, which collectively produced extensive deformation, regional metamorphism, migmatization, granitic magmatism, and hydrothermal activity (Rahaman, 1988; Oyinloye, 2011). These geological processes resulted in the formation of the major lithological assemblages that characterize the Nigerian Basement Complex, including the migmatite–gneiss complex, Older Granites, charnockitic bodies, pegmatites, and minor metasedimentary rocks.

The Ikole–Itapaji area is underlain predominantly by migmatites, granite gneisses, granites, pegmatites, and charnockitic rocks that exhibit varying degrees of deformation and weathering. These lithological units display distinct mineralogical and geochemical characteristics that influence their major oxide composition and the natural distribution of chemical elements released during weathering. The contrasting mineral assemblages and weathering behaviours of these rocks contribute significantly to geogenic elemental enrichment and the chemical composition of the overlying soils and regolith (Kabata-Pendias, 2011; Reimann & de Caritat, 2012).

Structurally, the study area is characterized by well-developed foliations, joints, fractures, faults, and shear zones, which predominantly trend NE–SW and NW–SE in response to Pan-African tectonic deformation. These structural features have influenced magmatic emplacement, fluid circulation, weathering, and mineralization within the Basement Complex. They also enhance rock permeability, thereby promoting

groundwater movement and accelerating geochemical alteration processes that influence elemental redistribution during weathering (Adetunla et al., 2025; Ogah & Abubakar, 2024).

The occurrence of pegmatitic intrusions, quartz veins, and structurally controlled granitic bodies further reflects the prolonged tectono-magmatic evolution of the area. These lithological and structural features contribute to the natural enrichment of major and trace elements and provide favourable conditions for the development of geogenic geochemical anomalies. Recent integrated geological and geophysical investigations have demonstrated that the Ikole–Itapaji Basement Complex possesses considerable

mineral resource potential associated with structurally controlled crystalline rocks (Ojo et al., 2024; Salako et al., 2024).

The geological framework of the study area therefore represents a complex interaction between lithology, tectonic deformation, magmatism, weathering, and hydrothermal processes. This complexity makes the Ikole–Itapaji Basement Complex an ideal environment for investigating major oxide geochemistry, sequential extraction of geochemical fractions, and the application of Contamination Factor (CF) and Pollution Load Index (PLI) to distinguish natural geogenic enrichment from potential environmental contamination (Fig. 2).

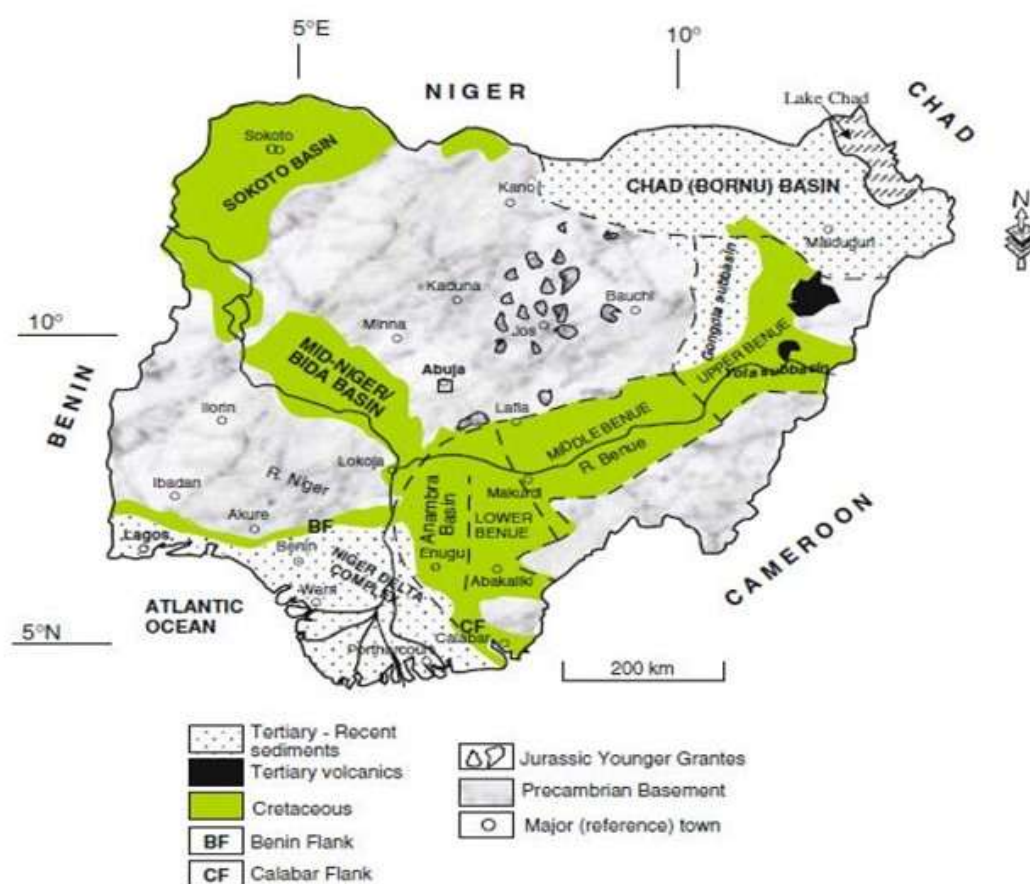


Fig.2: Geological map of Nigeria showing the distribution of major lithological units, including the Precambrian Basement Complex and surrounding sedimentary basins (Sokoto, Chad, Bida, and Benue Trough). The study area (Ikole–Itapaji, southwestern Nigeria) is located within the Basement Complex.

The topographic map (Figure 3) illustrates the spatial distribution of geological sampling locations across the Ikole–Itapaji–Bolorunduro–Odo Oro area. The sampling points are systematically distributed from the southern sector around Ikole and Odo Oro through Bolorunduro to the northern part around Itapaji, ensuring adequate

representation of the major lithological units within the study area. This broad spatial coverage provides a reliable framework for major oxide geochemical analysis, sequential extraction, and the assessment of geogenic enrichment using Contamination Factor (CF) and Pollution Load Index (PLI) (Ogah & Abubakar, 2024).

Sampling density is relatively higher around Itapaji and Bolorunduro, where rugged topography and elevated terrain provide abundant exposures of fresh crystalline basement rocks suitable for representative sampling. In contrast, fewer sampling locations occur around Odo Oro and parts of Ikole, where gentle relief, thicker weathered

overburden, and vegetation locally limit rock exposure. Nevertheless, the sampling strategy ensured adequate coverage of all major lithological units and geomorphological settings within the study area (Ojo et al., 2024).

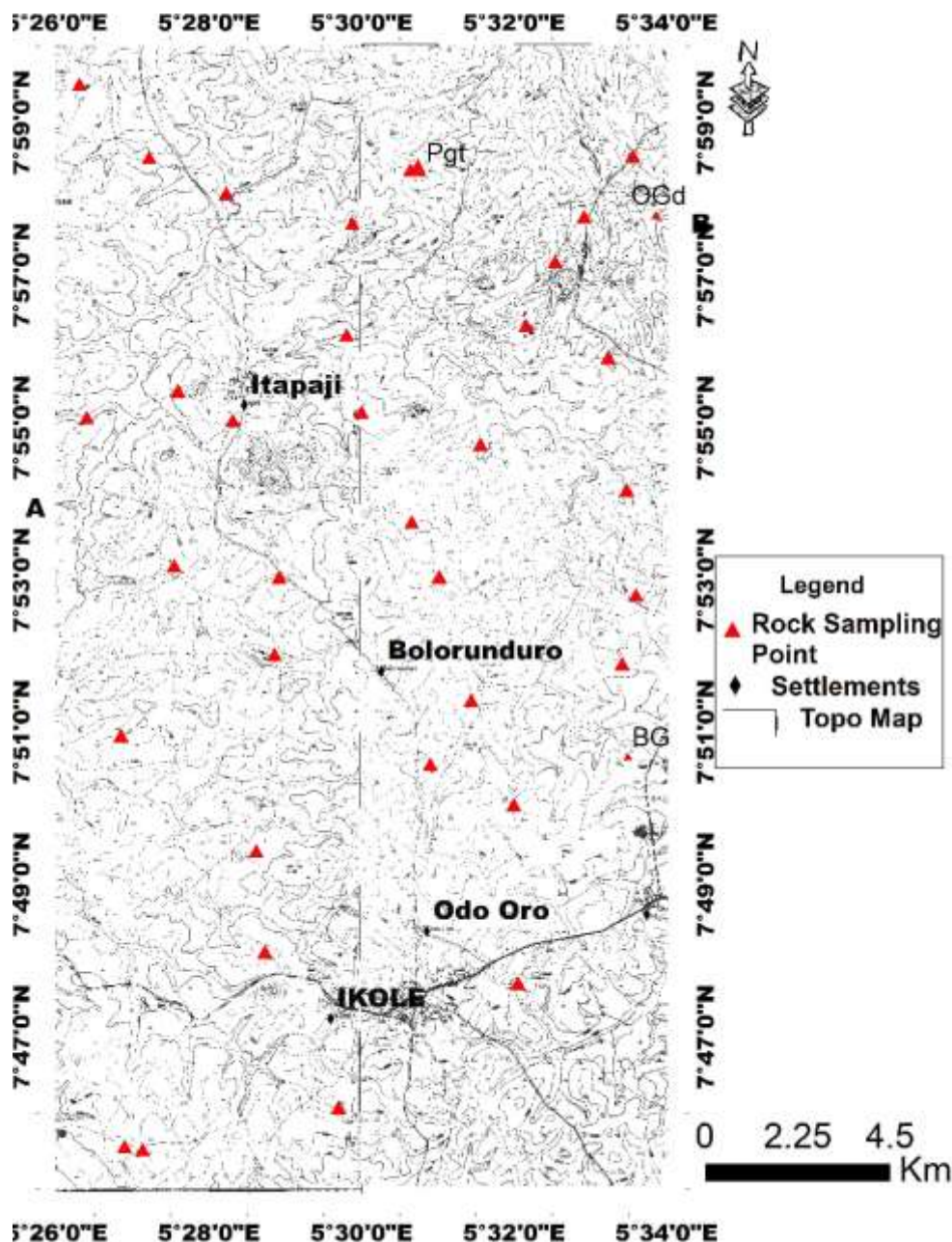


Fig.3. Topographic map of the Ikole–Itapaji–Ake-Ako area, Southwestern Nigeria, showing the distribution of geological sampling points used for geological mapping, structural measurements, and petrographic investigations. The sampling locations provide representative coverage of the major basement rock units across the study area.

The sampling locations extend across hills, ridges, valleys, and gently undulating terrains, thereby minimizing spatial bias and capturing the effects of lithology, weathering, and topography on the geochemical characteristics of the basement rocks. This representative distribution enhances

the reliability of major oxide analyses and provides an appropriate basis for evaluating natural geogenic enrichment and elemental mobility through sequential extraction studies (Kabata-Pendias, 2011; Reimann & de Caritat, 2012).

Furthermore, the sampling programme encompasses the principal crystalline rock units, including migmatite, granite gneiss, coarse porphyroblastic gneiss, granite, pegmatite, and charnockite, ensuring that the geochemical dataset adequately reflects the lithological diversity of the Ikole–Itapaji Basement Complex. This comprehensive coverage provides a robust basis for interpreting major oxide variations, calculating Contamination Factor (CF) and Pollution Load Index (PLI), evaluating elemental partitioning into water-soluble, exchangeable, carbonate-bound, Fe–Mn oxide-bound, organic-bound, sulfide/strongly bound, and residual fractions, and establishing the natural geochemical baseline of the study area (Adetunla et al., 2025).

Overall, the systematic distribution of sampling locations provides a representative dataset for evaluating the geochemistry of the crystalline basement rocks and their environmental significance. The combination of extensive spatial coverage, lithological representation, and varying topographic settings establishes a sound foundation for investigating petrogenesis, geogenic elemental enrichment, elemental mobility, and the environmental implications of naturally occurring chemical constituents within the Ikole–Itapaji Basement Complex.

The geological map and accompanying cross-section (Figure 4) reveal that the Ikole–Itapaji–Ake-Ako area is underlain predominantly by rocks of the Precambrian Basement Complex comprising migmatite (Mg), granite gneiss (GG), charnockite (Ch), granodiorite (OGd), and minor pegmatite intrusions. The spatial distribution of these lithologies indicates a complex geological history involving high-grade metamorphism, partial melting, magmatic emplacement, and crustal reworking during the Pan-African tectonothermal event (Rahaman, 1988; Oyinloye, 2011).

The geological map shows that granite gneiss constitutes the dominant lithological unit, occupying a large proportion of the central and northern parts of the study area. This unit extends continuously from Itapaji through Bolorunduro towards the northeastern portion of the map, suggesting that granite gneiss forms the principal basement framework of the area. Field observations and petrographic characteristics indicate that the granite gneiss is composed predominantly of quartz, feldspar, biotite, and muscovite, reflecting amphibolite- to granulite-facies metamorphic conditions typical of the Nigerian Basement Complex (Rahaman, 1988; Oyinloye, 2011).

Migmatite occurs extensively in the southern portion of the study area around Ikole and Odo Oro. Its widespread distribution reflects extensive partial melting and anatexis within the basement rocks. The gradational contact

observed between migmatite and granite gneiss suggests a shared tectonometamorphic history, with the migmatites representing zones of more intense metamorphic reworking and crustal melting during the Pan-African orogeny (Rahaman, 1988; Oyinloye, 2011).

The charnockite body exposed in the southwestern portion of the map occurs as a relatively restricted lithological unit enclosed within the surrounding granite gneiss. Its limited areal extent suggests emplacement or preservation as an isolated deep-crustal body. Charnockitic rocks are generally associated with high-temperature metamorphism and deep crustal processes, indicating that parts of the study area experienced elevated thermal conditions during crustal evolution (Rahaman, 1988; Adetunla et al., 2025).

The granodiorite body located in the northeastern section of the map forms a discrete intrusive mass. The geological cross-section demonstrates that the granodiorite extends to depth, confirming its emplacement as a plutonic intrusion within the surrounding granite gneiss. Pegmatite veins associated with the granodiorite represent late-stage magmatic differentiates formed from residual silica-rich melts during the final stages of crystallization, reflecting continued magmatic evolution of the basement complex (Rahaman, 1988; Oyinloye, 2011).

The geological cross-section along A–B (Figure 4) illustrates the subsurface relationships between the major lithological units. Granite gneiss occupies much of the intermediate crustal section and overlies a broad migmatitic basement. The irregular contact between the granite gneiss and migmatite reflects differential melting, metamorphic segregation, and prolonged crustal evolution. The continuity of the migmatite beneath most of the profile indicates that it represents one of the oldest exposed basement units within the study area (Rahaman, 1988).

The cross-section further demonstrates that the granodiorite intrusion cuts across the surrounding granite gneiss in the northeastern segment of the profile, confirming that the granodiorite is younger than its host rock. The pegmatite body emplaced within the granodiorite represents a younger magmatic phase produced through crystallization of residual melts enriched in incompatible elements. Such pegmatitic intrusions commonly record the final stages of granitic differentiation and may locally concentrate economically important elements (Oyinloye, 2011; Adetunla et al., 2025).

From a geological evolution perspective, the study area records multiple episodes of crustal development. The migmatites represent the oldest basement components formed through high-grade metamorphism and partial melting. These rocks were subsequently reworked into

granite gneiss during regional tectonometamorphic events. Charnockitic bodies developed under high-temperature crustal conditions, whereas granodioritic intrusions and pegmatites represent younger magmatic phases associated with crustal melting and magmatic differentiation during the Pan-African orogeny (Rahaman, 1988; Oyinloye, 2011). These lithological variations provide the geochemical framework controlling the distribution of major oxides and the natural geogenic enrichment evaluated using Contamination Factor (CF) and Pollution Load Index (PLI).

The geological architecture depicted by the map and cross-section demonstrates that the Ikole–Itapaji–Ake-Ako area forms part of a deeply reworked Precambrian basement terrane characterized by extensive migmatization, granitoid emplacement, and localized charnockitic development. The intimate association of these lithologies records repeated episodes of metamorphism, partial melting, magmatism, and crustal stabilization, which collectively govern the present-day distribution of major oxide compositions and the geogenic elemental enrichment within the study area (Rahaman, 1988; Oyinloye, 2011; Adetunla et al., 2025).

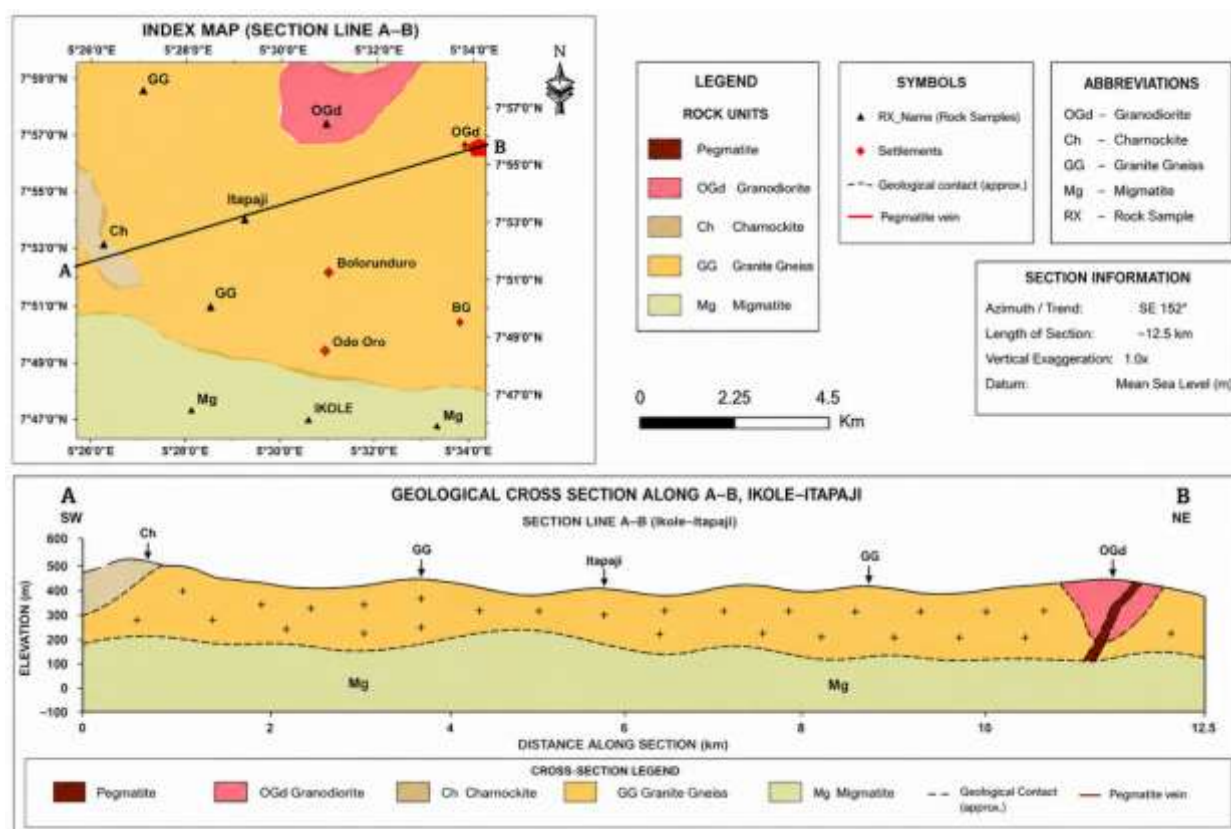


Fig. 4. Geological cross-section along A–B across the Ikole–Itapaji area, showing the subsurface relationships between migmatite, granite gneiss, charnockite, granodiorite, and pegmatite units. The section reveals a migmatitic basement overlain by granite gneiss and intruded by younger granodiorite and pegmatite bodies. The geometry of the rock units reflects prolonged crustal evolution involving metamorphism, partial melting, and magmatic emplacement within the Precambrian Basement Complex.

III. MATERIALS AND METHODS

3.1 Materials

The materials used for this study comprised field and laboratory equipment required for geological mapping, rock and soil/sediment sample collection, whole-rock major oxide geochemical analyses, and geogenic enrichment assessment. Field equipment included a 1:25,000-scale topographic map of the Ikole–Itapaji–Ake-Ako area, a Brunton compass clinometer, a Garmin

GPSMAP 64s handheld Global Positioning System (GPS), geological hammer, chisel, hand lens, measuring tape, sample bags, permanent markers, field notebook, digital camera, and personal protective equipment comprising safety boots, reflective jacket, hand gloves, and safety helmet. These materials facilitated geological mapping, structural observations, accurate location referencing, documentation of field observations, and the collection of representative rock and soil/sediment samples.

Laboratory equipment comprised a diamond rock-cutting machine, jaw crusher, pulverizing machine, analytical weighing balance, drying oven, laboratory sieves, and computer software for geochemical data processing, statistical analysis, and graphical presentation. Whole-rock major oxide and soil/sediment geochemical analyses were carried out at ACME Analytical Laboratories (Bureau Veritas Commodities Canada Ltd.), Vancouver, Canada, using Inductively Coupled Plasma–Mass Spectrometry (ICP–MS).

3.2 Geological Mapping and Sample Collection

The investigation commenced with a reconnaissance survey using a 1:25,000-scale topographic map to obtain preliminary information on accessibility, drainage pattern, topography, and distribution of rock exposures within the Ikole–Itapaji–Ake-Ako area. The reconnaissance survey formed the basis for planning detailed geological traverses and ensuring adequate spatial coverage during field investigations.

Detailed geological mapping was subsequently carried out along accessible roads, footpaths, stream channels, farm tracks, and exposed rock outcrops. Lithological characteristics including colour, grain size, texture, mineral composition, weathering characteristics, and field relationships were carefully observed and documented. Structural features such as foliations, joints, fractures, folds, quartz veins, mineral lineations, and shear zones were identified, while their strike and dip were measured using a Brunton compass clinometer. Geographic coordinates and elevations were recorded using a Garmin GPSMAP 64s handheld GPS receiver, and representative field photographs were taken to document significant geological features. The geological observations formed the basis for the geological map and subsequent geochemical interpretations.

A total of thirty-five (35) fresh rock samples representing the major lithological units encountered during geological mapping, including migmatite, granite gneiss, coarse porphyroblastic gneiss, granite, pegmatite, and charnockite, were collected from different locations across the study area. Following detailed megascopic examination, twenty (20) representative rock samples were selected for whole-rock major oxide geochemical analyses based on the following criteria:

1. Representation of all the major lithological units identified during geological mapping.
2. Freshness of the rock samples, with preference given to fresh, unweathered, and minimally altered specimens.

3. Lithological and mineralogical diversity to ensure adequate representation of the compositional variability of the different rock units within the study area.
4. Megascopic textural variability, including differences in grain size, mineral fabric, and weathering characteristics.
5. Structural characteristics, particularly representative foliations, mineral banding, folds, quartz veins, fractures, and shear fabrics.
6. Spatial distribution to ensure adequate geographical representation of the different lithological units across the study area.
7. Elimination of duplicate samples exhibiting similar lithological, mineralogical, and structural characteristics from the same locality to avoid analytical redundancy while maintaining representative coverage.

This selection procedure ensured that the analysed rock samples adequately represented the lithological, structural, and compositional variability of the crystalline basement rocks within the study area.

In addition, seventeen (17) representative soil/sediment samples were collected from selected locations across the study area to evaluate the degree of geogenic enrichment using Contamination Factor (CF) and Pollution Load Index (PLI). The samples were collected from the near-surface horizon after removing organic debris and other surface contaminants. The collected samples were air-dried at room temperature, gently disaggregated, homogenized, and sieved through a 63 μm mesh to obtain the fine-grained fraction suitable for geochemical analysis.

3.3 Sample Preparation and Geochemical Analysis

Fresh portions of the selected rock samples were cleaned to remove weathered surfaces before being reduced to smaller fragments using a jaw crusher and subsequently pulverized into fine homogeneous powders. The prepared soil/sediment samples were similarly homogenized after drying and sieving to obtain representative analytical aliquots. Both rock and soil/sediment samples were packaged and submitted to ACME Analytical Laboratories (Bureau Veritas Commodities Canada Ltd.), Vancouver, Canada, for geochemical analysis.

Major oxide analyses were carried out using Inductively Coupled Plasma–Mass Spectrometry (ICP–MS) following partial multi-acid digestion with hydrochloric acid (HCl), nitric acid (HNO_3), and perchloric acid (HClO_4), combined with lithium metaborate fusion. The lithium metaborate fusion technique ensured complete dissolution of refractory silicate minerals, while the acid digestion

enhanced the extraction and determination of the major rock-forming oxides. Quality assurance and quality control (QA/QC) procedures included the analysis of certified reference materials, analytical blanks, duplicate samples, and internal laboratory standards to ensure the accuracy, precision, and reliability of the analytical results.

3.4 Major Oxide Geochemical Evaluation

Whole-rock major oxide data obtained from the twenty representative rock samples were evaluated to characterize the chemical composition, magmatic affinity, and geochemical evolution of the basement rocks. Major oxide variation diagrams (Harker plots) were employed to evaluate compositional trends and magmatic differentiation among the investigated lithologies. The degree of alumina saturation was assessed using the A/CNK–A/NK diagram after Shand (1943), while magmatic affinity was evaluated using the Fe-number [FeOt/(FeOt + MgO)] versus SiO₂ discrimination diagram proposed by Frost et al. (2001). These geochemical evaluations provided the basis for interpreting petrogenesis and crustal evolution within the study area.

3.5 Contamination Factor (CF)

The Contamination Factor (CF) was employed to evaluate the degree of geogenic enrichment in the analysed soil/sediment samples relative to average shale background concentrations following Hakanson (1980). The contamination factor was calculated as:

$$CF = C_{\text{sample}} / C_{\text{background}} \quad (1)$$

where:

- C_{sample} is the measured concentration of the investigated major oxide in the soil/sediment sample.
- C_{background} is the corresponding average shale background concentration (Turekian & Wedepohl, 1961).

The calculated CF values were interpreted as follows:

- CF < 1: Low contamination
- 1 ≤ CF < 3: Moderate contamination
- 3 ≤ CF < 6: Considerable contamination
- CF ≥ 6: Very high contamination

3.6 Pollution Load Index (PLI)

The Pollution Load Index (PLI) was used to evaluate the overall degree of geogenic enrichment within the study area based on the analysed soil/sediment samples. The index was calculated as:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{(1/n)} \quad (2)$$

where:

- CF₁–CF_n represent the contamination factors of the investigated major oxides.
- n is the total number of investigated oxides.

The calculated PLI values were interpreted as follows:

- PLI < 1: Background or unpolluted condition.
- PLI = 1: Baseline geochemical condition.
- PLI > 1: Progressive geogenic enrichment above background concentrations.

Table 1. Average shale values used as background concentrations for Contamination Factor (CF) and Pollution Load Index (PLI) calculations (after Turekian and Wedepohl, 1961).

S/N	Element	Average shale value (mg/kg)
1	Fe	47,200
2	Mn	850
3	Pb	20
4	Cu	45
5	Zn	95
6	Ni	68
7	Co	19
8	Cr	90
9	Cd	0.30

IV. RESULTS AND DISCUSSION

4.1 Sequential extraction techniques

4.1.1 Water-soluble Phase

The water-soluble phase represents the most mobile and readily bioavailable fraction of metals in soils and weathered rocks. In natural environments, this fraction is generally very low because most metals remain strongly bound within mineral lattices or secondary mineral phases (Kabata-Pendias, 2011; Alloway, 2013; Filgueiras et al., 2002).

Results in Table 2a show consistently low concentrations of all analysed metals across samples (SQ1–SQ17), indicating limited metal dissolution and mobility. Iron (Fe) records the highest concentrations (2.873–7.427 mg/kg), followed by Mn (1.742–3.128 mg/kg), reflecting their natural abundance in the basement rocks. Copper, Zn, Pb, Ni, Co, Cr, and Cd occur at comparatively low

concentrations, suggesting that their distribution is primarily controlled by natural weathering rather than anthropogenic contamination (Reimann & de Caritat, 2005).

The statistical summary in Table 2b confirms this trend, with mean concentrations following the order Fe > Mn > Cu ≈ Zn > Pb > Co ≈ Ni > Cr > Cd. Similarly, Figure 5 shows a uniform spatial distribution of the analysed metals, with no pronounced enrichment or pollution hotspots across the study area.

From an environmental perspective, the low concentrations in the water-soluble fraction indicate limited metal mobility and bioavailability, suggesting minimal immediate risk to groundwater, agricultural soils, and the local population. Overall, the water-soluble phase reflects predominantly geogenic metal occurrence and indicates that the study area presently poses low environmental and human health risk under existing conditions (De Matteis et al., 2023; Wei & Yang, 2010).

Table 2a. Heavy metals concentration in the water-soluble phase (mg/kg) of sediments/soils from the Ikole–Itapaji area, Southwestern Nigeria. This fraction represents the most mobile and immediately bioavailable portion of trace metals, reflecting their potential short-term environmental availability and mobility in the near-surface environment.

Samples	Fe (mg/Kg)	Mn (mg/Kg)	Pb (mg/Kg)	Cu (mg/Kg)	Zn (mg/Kg)	Ni (mg/Kg)	Co (mg/Kg)	Cr (mg/Kg)	Cd (mg/Kg)
SQ 1	6.321	2.087	0.077	0.681	0.572	0.054	0.062	0.023	0.004
SQ 2	6.128	2.063	0.072	0.631	0.509	0.059	0.063	0.021	0.003
SQ 3	7.427	3.108	0.083	0.724	0.592	0.063	0.069	0.028	0.005
SQ 4	7.129	3.099	0.081	0.711	0.579	0.061	0.066	0.025	0.005
SQ 6	5.873	2.145	0.094	0.742	0.582	0.063	0.067	0.029	0.006
SQ7	4.568	1.958	0.064	0.465	0.368	0.043	0.048	0.016	0.003
SQ 8	6.409	2.056	0.076	0.641	0.539	0.052	0.063	0.022	0.004
SQ 10	2.873	1.742	0.049	0.163	0.126	0.034	0.037	0.013	0.002
SQ 11	3.208	1.839	0.056	0.218	0.189	0.041	0.045	0.015	0.003
SQ 12	5.175	2.094	0.086	0.598	0.565	0.061	0.057	0.024	0.005
SQ 13	5.387	2.109	0.087	0.605	0.591	0.063	0.054	0.026	0.005
SQ 14	6.125	2.135	0.092	0.676	0.608	0.067	0.061	0.029	0.006
SQ 15	7.105	3.128	0.091	0.624	0.573	0.056	0.054	0.031	0.006
SQ 16	5.891	2.207	0.095	0.673	0.606	0.065	0.059	0.034	0.007
SQ 17	5.006	1.876	0.098	0.659	0.627	0.064	0.062	0.033	0.007

Table 2b. Statistical summary of the heavy metals concentration in the water-soluble phase (mg/kg). This table presents the minimum, maximum, and mean concentrations of the selected metals across all samples in the study area. It provides a simplified statistical overview of metal distribution and mobility within the most labile geochemical fraction of the soil–sediment system.

Metal	Fe	Mn	Pb	Cu	Zn	Ni	Co	Cr	Cd
Min	2.873	1.742	0.049	0.163	0.126	0.034	0.037	0.013	0.002
Max	7.427	3.128	0.098	0.742	0.627	0.067	0.069	0.034	0.007
Mean	5.642	2.243	0.080	0.587	0.508	0.056	0.058	0.025	0.005

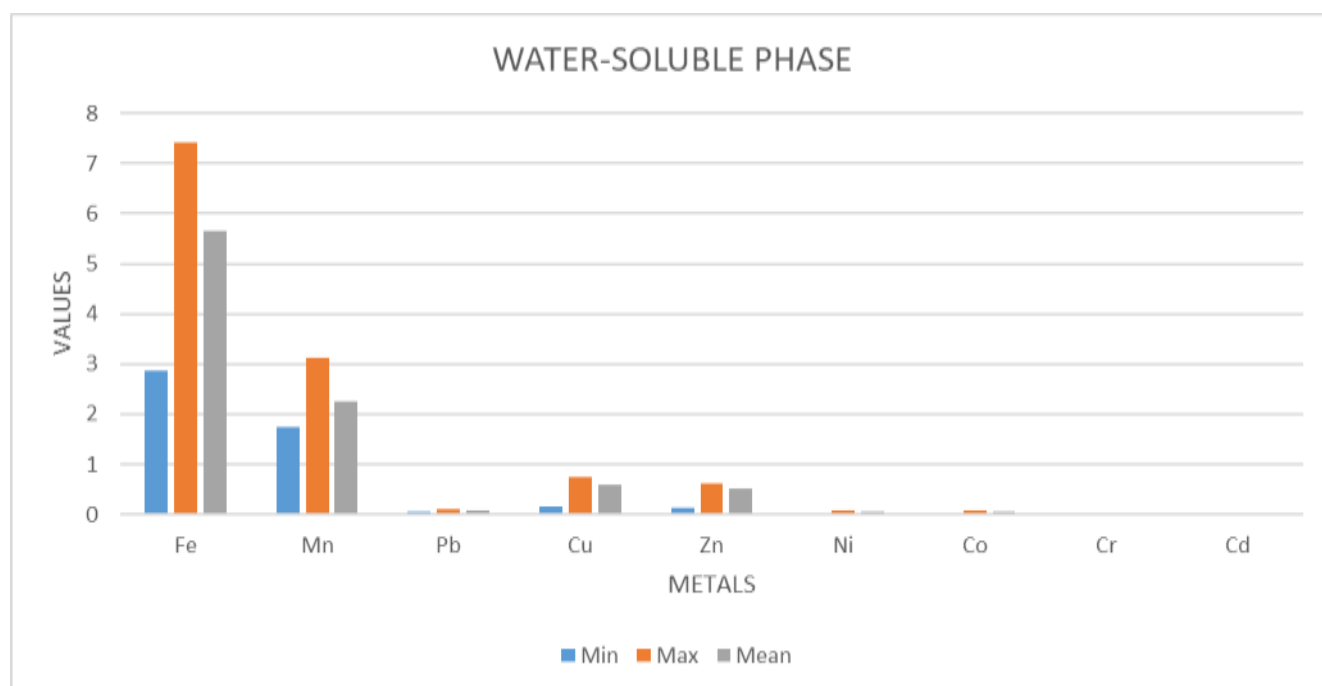


Fig.5. Cluster column chart of heavy metal concentrations in the water-soluble phase (mg/kg). The figure illustrates the comparative distribution of selected metals across all samples, highlighting variations in their mobility and relative abundance within the most labile geochemical fraction.

4.1.2 The Exchangeable Phase

The exchangeable phase contains metals weakly adsorbed onto soil particles and represents a potentially mobile fraction that can be released under changes in pH or ionic conditions (Kabata-Pendias, 2011; Alloway, 2013). Table 3a shows higher metal concentrations than the water-soluble phase, indicating greater but reversible metal retention. Iron (5.731–10.742 mg/kg) and Mn (1.342–3.127 mg/kg) dominate, while Cu and Zn occur in moderate concentrations. Pb and Cd remain low but exhibit slight enrichment, whereas Ni, Co, and Cr are consistently low.

The statistical summary Table 3b confirms the abundance order of Fe > Mn > Cu > Zn > Pb > Ni > Co > Cr > Cd,

Table 3a: Exchangeable phase of the heavy metal concentrations in soil samples (mg/kg). The table presents the distribution of Fe, Mn, Pb, Cu, Zn, Ni, Co, Cr, and Cd across all sampling locations, reflecting metals weakly bound to soil exchange sites and their potential environmental mobility.

Samples	Fe (mg/Kg)	Mn (mg/Kg)	Pb (mg/Kg)	Cu (mg/Kg)	Zn (mg/Kg)	Ni (mg/Kg)	Co (mg/Kg)	Cr (mg/Kg)	Cd (mg/Kg)
SQ 1	8.084	1.875	0.098	0.789	0.701	0.072	0.071	0.031	0.007
SQ 2	8.005	1.802	0.097	0.712	0.685	0.073	0.069	0.032	0.005
SQ 3	10.742	2.085	0.102	0.826	0.732	0.081	0.075	0.037	0.029
SQ 4	10.488	2.016	0.108	0.813	0.735	0.085	0.076	0.037	0.028
SQ 6	6.402	2.073	0.112	0.839	0.784	0.082	0.073	0.042	0.009
SQ7	6.023	1.762	0.082	0.619	0.586	0.065	0.059	0.025	0.005

reflecting strong lithological control. Figure 6 similarly shows the dominance of Fe and Mn with moderate Cu and Zn enrichment, while the remaining metals display relatively uniform distributions across the sampling locations.

Overall, the exchangeable phase indicates limited metal mobility and low environmental risk under present conditions. However, the slight enrichment of Pb and Cd suggests that future soil acidification or environmental disturbance could enhance their mobility, posing potential risks to groundwater quality, agricultural soils, and the health of residents through long-term exposure (Reimann & de Caritat, 2005; Alloway, 2013).

SQ 8	8.787	1.904	0.126	0.804	0.721	0.075	0.073	0.034	0.026
SQ 10	5.731	1.342	0.085	0.279	0.261	0.067	0.072	0.026	0.004
SQ 11	6.174	1.563	0.096	0.351	0.31	0.071	0.072	0.029	0.005
SQ 12	7.787	2.012	0.113	0.801	0.721	0.094	0.087	0.038	0.009
SQ 13	7.819	2.105	0.109	0.799	0.726	0.097	0.085	0.042	0.01
SQ 14	8.534	3.083	0.138	0.902	0.846	0.102	0.095	0.051	0.017
SQ 15	10.231	3.127	0.146	0.927	0.872	0.117	0.102	0.054	0.021
SQ 16	7.118	2.105	0.128	0.942	0.839	0.112	0.11	0.059	0.028
SQ 17	6.104	2.098	0.131	0.967	0.886	0.132	0.121	0.061	0.026

Table 3b: Statistical summary of the heavy metals concentration in the exchangeable phase (mg/kg). This table presents the minimum, maximum, and mean concentrations of selected metals across all samples in the exchangeable fraction. It highlights the variability and relative mobility of metals weakly bound to soil exchange sites, which are potentially available for environmental release.

Metal	Fe	Mn	Pb	Cu	Zn	Ni	Co	Cr	Cd
Min	5.731	1.342	0.082	0.279	0.261	0.065	0.059	0.025	0.004
Max	10.742	3.127	0.146	0.967	0.886	0.132	0.121	0.061	0.029
Mean	7.869	2.064	0.111	0.758	0.694	0.088	0.083	0.040	0.015

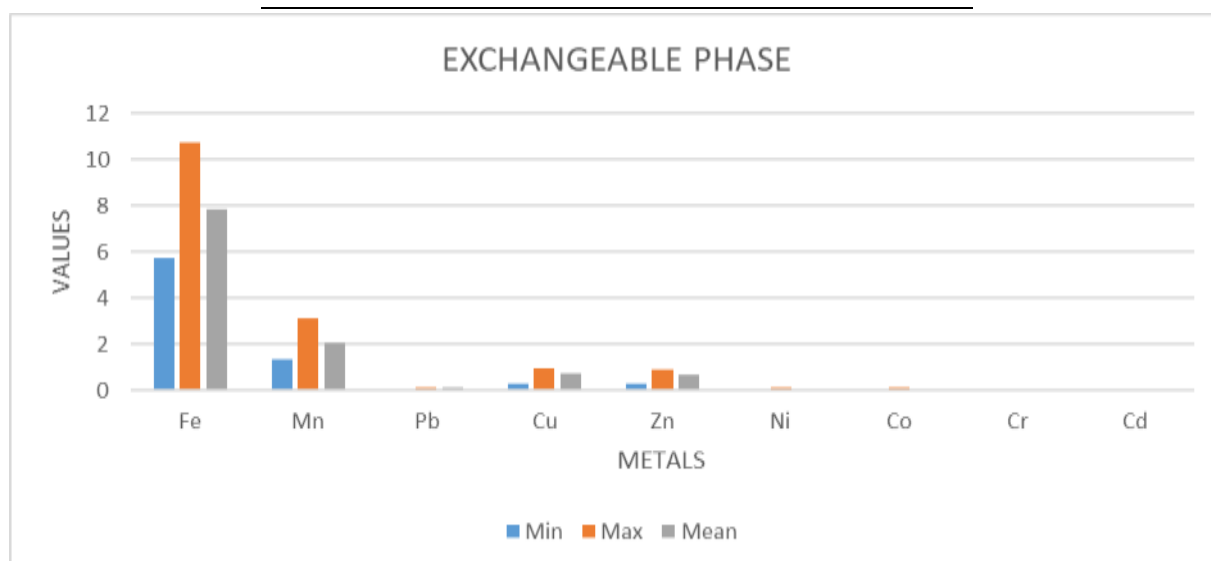


Fig.6. Cluster column chart of heavy metal concentrations in the exchangeable phase (mg/kg). The figure illustrates the comparative distribution of metals across all samples in the exchangeable fraction, highlighting variations in their relative mobility and binding strength to soil exchange sites.

4.1.3 The carbonate-bound phase

The carbonate-bound phase consists of metals associated with carbonate minerals and is susceptible to release under acidic conditions due to carbonate dissolution (Kabata-Pendias, 2011; Alloway, 2013). Table 4a shows a marked increase in metal concentrations compared to the previous fractions, indicating stronger incorporation into carbonate

phases. Iron (36.325–66.488 mg/kg) and Mn (23.728–38.019 mg/kg) are the dominant metals, followed by Zn and Cu, while Pb exhibits moderate enrichment. Nickel, Co, Cr, and Cd occur at comparatively lower concentrations.

The statistical summary in Table 4b confirms the abundance order of Fe > Mn > Zn > Pb > Cu > Ni > Co >

Cr > Cd, reflecting the natural geochemical composition of the basement rocks. Figure 7 also shows higher concentrations around samples SQ3, SQ4, and SQ15, with lower values at SQ10, indicating lithological variation rather than anthropogenic contamination.

Overall, the carbonate-bound phase represents a relatively stable metal reservoir under existing environmental

conditions. However, increased soil acidity could enhance the release of carbonate-bound metals, potentially affecting soil quality and groundwater. The current distribution nevertheless suggests predominantly geogenic enrichment with low environmental and human health risk to residents of the study area.

Table 4a. Heavy metal concentrations in the carbonate-bound phase (mg/kg). The table shows the distribution of metals associated with carbonate minerals across all samples, reflecting their relative stability and potential release under acidic environmental conditions.

Samples	Fe (mg/Kg)	Mn (mg/Kg)	Pb (mg/Kg)	Cu (mg/Kg)	Zn (mg/Kg)	Ni (mg/Kg)	Co (mg/Kg)	Cr (mg/Kg)	Cd (mg/Kg)
SQ 1	40.129	25.207	2.279	2.439	13.226	2.147	1.701	0.531	0.069
SQ 2	41.052	25.422	2.142	2.197	13.055	2.132	1.626	0.625	0.065
SQ 3	65.246	37.529	3.217	2.826	18.614	2.704	2.002	0.954	0.089
SQ 4	66.488	38.019	3.832	3.213	18.901	3.125	2.106	1.005	0.103
SQ 6	38.615	24.234	1.715	2.327	13.178	2.362	1.448	0.603	0.059
SQ7	38.247	24.127	1.665	2.401	13.218	2.295	1.353	0.616	0.055
SQ 8	41.271	25.431	3.102	2.424	13.286	2.149	1.747	1.103	0.072
SQ 10	36.325	23.728	1.025	1.112	12.521	1.891	0.829	0.518	0.054
SQ 11	37.623	24.061	2.611	2.103	12.101	2.047	1.521	0.556	0.055
SQ 12	39.114	25.716	3.112	2.518	12.224	2.104	1.687	0.738	0.069
SQ 13	38.864	24.612	3.109	2.429	12.138	2.049	1.716	0.742	0.071
SQ 14	41.451	26.128	2.234	2.657	13.441	2.162	1.392	0.671	0.077
SQ 15	46.539	37.423	3.627	2.985	19.807	3.127	2.108	1.054	0.121
SQ 16	41.318	25.035	2.512	2.548	13.033	2.102	1.711	1.005	0.098
SQ 17	38.712	24.291	2.271	2.462	12.987	1.937	1.491	0.657	0.097

Table 4b. Statistical summary of the heavy metals in the carbonate-bound phase (mg/kg). The table presents the minimum, maximum, and mean concentrations of metals associated with carbonate fractions, highlighting their relative enrichment and stability within this geochemical phase.

	Metal Fe	Mn	Pb	Cu	Zn	Ni	Co	Cr	Cd
Min	36.325	23.728	1.025	1.112	12.101	1.891	0.829	0.518	0.054
Max	66.488	38.019	3.832	3.213	19.807	3.127	2.108	1.103	0.121
Mean	43.580	26.998	2.630	2.450	13.915	2.235	1.629	0.758	0.078

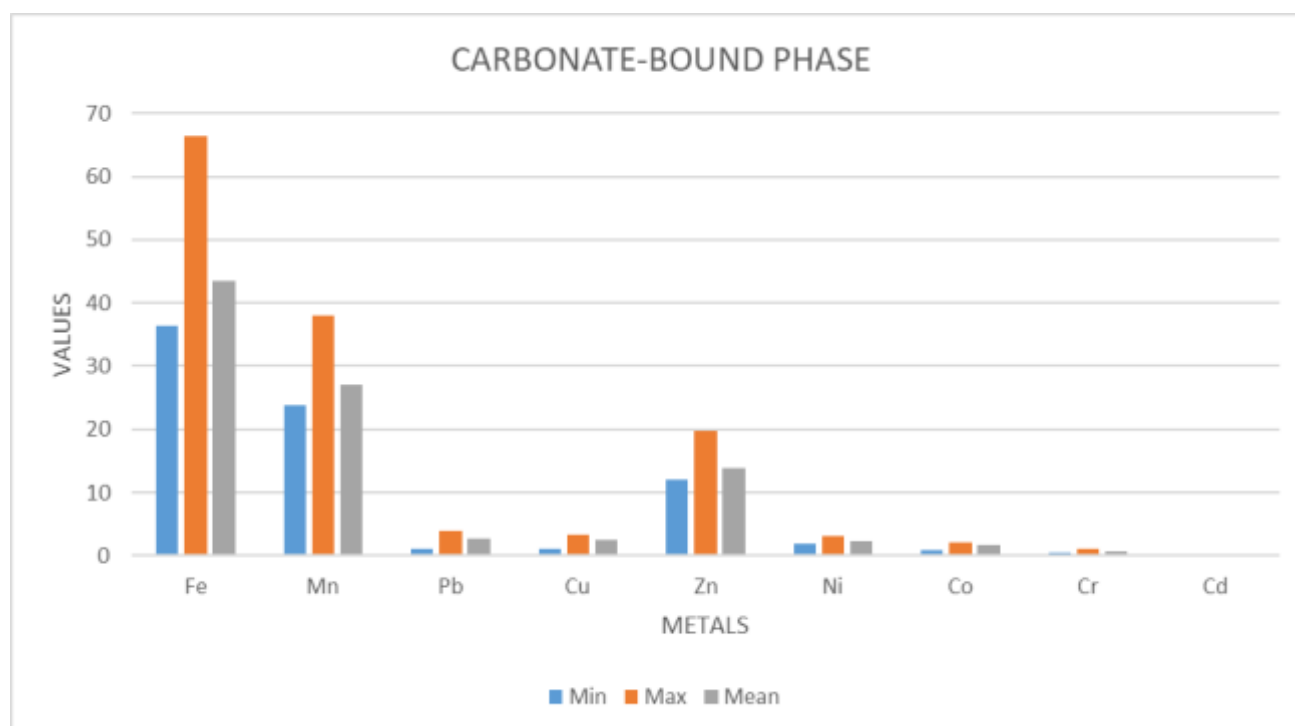


Fig. 7. Cluster column chart of the heavy metal concentrations in the carbonate-bound phase (mg/kg). The figure illustrates the comparative distribution of metals across all samples, highlighting their relative enrichment and association with carbonate minerals within this geochemical fraction.

4.1.4 The Fe–Mn oxide phase

The Fe–Mn oxide phase represents an important metal-binding fraction because iron and manganese oxides possess high adsorption capacities and effectively retain trace metals within soils (Kabata-Pendias, 2011; Alloway, 2013). Tables 5a and 5b show that Fe (303.187–476.031 mg/kg) and Mn (139.204–267.163 mg/kg) dominate this fraction, indicating that Fe–Mn oxides are the principal sinks for trace metals in the study area. Zinc, Pb, Cu, and Ni also occur at relatively higher concentrations, whereas Co, Cr, and Cd are comparatively lower.

The statistical summary confirms the abundance order of Fe > Mn > Zn > Pb > Cu > Ni > Co > Cr > Cd, while samples SQ3, SQ4, and SQ15 exhibit relatively higher

concentrations than SQ10, reflecting lithological variation and natural adsorption processes. The strong association of these metals with Fe–Mn oxides indicates efficient immobilization under the prevailing environmental conditions (Tessier et al., 1979).

Overall, the Fe–Mn oxide phase serves as a major geochemical reservoir that limits metal mobility and reduces their immediate availability to plants and groundwater. However, changes in redox conditions could release these adsorbed metals into the environment. Under the current conditions, the results suggest predominantly geogenic enrichment and a generally low environmental and human health risk to the local population.

Table 5a: Heavy metal concentrations in the Fe–Mn oxide phase (mg/kg). The table presents the distribution of metals associated with iron and manganese oxides across all samples, reflecting their strong adsorption capacity and role as key geochemical sinks for trace elements.

Samples	Fe (mg/Kg)	Mn (mg/Kg)	Pb (mg/Kg)	Cu (mg/Kg)	Zn (mg/Kg)	Ni (mg/Kg)	Co (mg/Kg)	Cr (mg/Kg)	Cd (mg/Kg)
SQ 1	354.813	152.227	25.711	13.403	63.866	19.181	10.271	6.361	0.621
SQ 2	361.558	175.129	22.019	15.019	63.545	20.196	11.287	6.185	0.657
SQ 3	435.209	237.214	33.277	20.236	74.091	22.573	14.263	9.159	1.872
SQ 4	446.513	241.116	35.332	21.873	77.129	26.103	14.742	10.015	1.983
SQ 6	362.145	154.434	26.072	12.615	63.071	20.032	10.481	5.235	0.598

SQ7	358.903	149.828	21.612	13.211	63.242	18.269	9.593	6.062	0.615
SQ 8	371.874	185.401	26.128	14.029	70.008	20.542	11.792	8.187	1.328
SQ 10	303.187	139.204	16.623	11.197	54.584	16.352	6.282	4.815	0.574
SQ 11	337.217	144.436	18.217	12.018	58.611	19.142	8.027	5.251	0.591
SQ 12	349.812	147.164	23.712	16.182	62.202	20.017	10.019	6.131	0.691
SQ 13	345.875	147.119	23.389	16.429	62.138	20.049	9.948	5.782	0.711
SQ 14	360.158	176.524	25.304	15.173	63.493	21.366	11.097	7.176	0.877
SQ 15	476.031	267.163	36.125	22.957	75.937	25.183	13.162	10.254	2.021
SQ 16	361.521	155.003	22.574	14.348	64.113	19.179	11.201	7.012	0.798
SQ 17	338.019	142.401	17.753	12.967	59.285	18.331	10.096	8.954	0.917

Table 5b: Statistical summary of the heavy metals concentration in the Fe–Mn oxide phase (mg/kg). The table shows the minimum, maximum, and mean concentrations of metals bound to Fe–Mn oxides, highlighting their significant enrichment and strong affinity for adsorption within this geochemical fraction.

Metal	Fe	Mn	Pb	Cu	Zn	Ni	Co	Cr	Cd
Min	303.187	139.204	16.623	11.197	54.584	16.352	6.282	4.815	0.574
Max	476.031	267.163	36.125	22.957	77.129	26.103	14.742	10.254	2.021
Mean	370.456	173.958	24.790	15.977	65.554	20.454	10.751	7.122	0.923

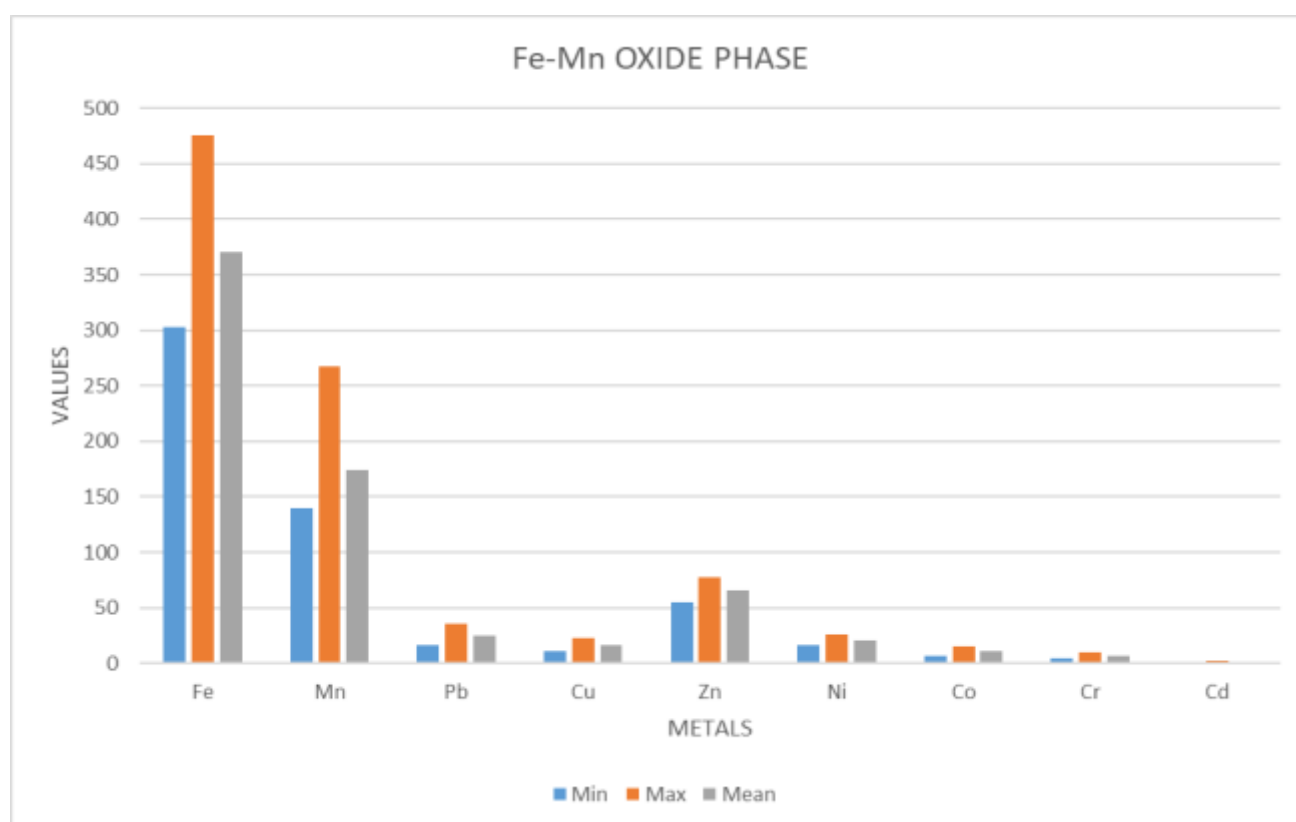


Figure 8. Cluster column chart of the heavy metal concentrations in the Fe–Mn oxide phase (mg/kg). The figure illustrates the comparative distribution of metals across all samples, highlighting strong enrichment and adsorption of trace elements onto Fe–Mn oxide phases within the study area.

4.1.5 The organic matter–bound phase

The organic matter–bound phase comprises metals complexed with organic materials such as humic substances and decomposed plant residues, serving as an important reservoir that regulates metal retention and release during organic matter decomposition (Kaiser & Kalbitz, 2012; Liu et al., 2022). Table 6a shows that Fe (148.854–356.163 mg/kg) and Mn (55.772–89.112 mg/kg) dominate this fraction, while Zn and Cu exhibit relatively high concentrations due to their strong affinity for organic compounds. Lead, Ni, Co, Cr, and Cd occur at comparatively lower concentrations.

The statistical summary in Table 6b indicates the abundance order of Fe > Mn > Zn > Cu > Ni ≈ Pb > Co >

Table 6a: Heavy metals concentrations in the organic matter–bound phase (mg/kg). The table shows the distribution of metals associated with organic matter across all samples, reflecting their affinity for organic complexation and potential release during organic matter decomposition.

Samples	Fe (mg/Kg)	Mn (mg/Kg)	Pb (mg/Kg)	Cu (mg/Kg)	Zn (mg/Kg)	Ni (mg/Kg)	Co (mg/Kg)	Cr (mg/Kg)	Cd (mg/Kg)
SQ 1	182.012	75.224	12.172	20.032	33.213	12.817	6.915	5.503	0.453
SQ 2	181.654	78.127	13.181	20.215	33.158	13.102	6.429	6.232	0.485
SQ 3	335.147	87.225	14.137	22.864	37.685	16.214	8.105	6.954	0.981
SQ 4	341.401	89.112	16.562	23.509	40.021	18.121	9.012	7.051	1.128
SQ 6	164.319	64.435	10.345	15.861	27.183	10.129	4.971	4.672	0.429
SQ7	168.247	64.247	10.631	15.539	28.011	10.216	5.056	4.956	0.433
SQ 8	189.074	81.236	13.123	20.421	33.786	13.014	6.747	6.143	0.472
SQ 10	148.854	55.772	9.926	14.158	24.128	8.997	4.635	4.329	0.414
SQ 11	152.627	57.201	10.011	15.141	25.091	9.089	4.921	4.457	0.425
SQ 12	169.612	65.236	11.162	16.214	25.274	10.176	5.068	4.781	0.446
SQ 13	169.881	64.837	11.134	16.452	25.181	10.089	5.112	8.714	0.451
SQ 14	180.575	76.294	12.634	21.052	32.846	12.763	6.557	5.773	0.472
SQ 15	356.163	87.826	15.663	24.486	40.372	18.522	9.138	7.074	1.221
SQ 16	185.052	75.135	12.246	20.415	33.325	13.012	6.751	6.028	0.482
SQ 17	168.176	65.095	10.773	15.404	28.197	10.332	6.904	6.193	0.462

Table 6b: Statistical summary of the heavy metals in the organic matter–bound phase (mg/kg). The table presents the minimum, maximum, and mean concentrations of metals associated with organic matter, indicating their degree of complexation and relative stability within this geochemical fraction.

Metal	Fe	Mn	Pb	Cu	Zn	Ni	Co	Cr	Cd
Min	148.854	55.772	9.926	14.158	24.128	8.997	4.635	4.329	0.414
Max	356.163	89.112	16.562	24.486	40.372	18.522	9.138	8.714	1.221
Mean	206.186	72.467	12.247	18.784	31.165	12.440	6.421	5.924	0.584

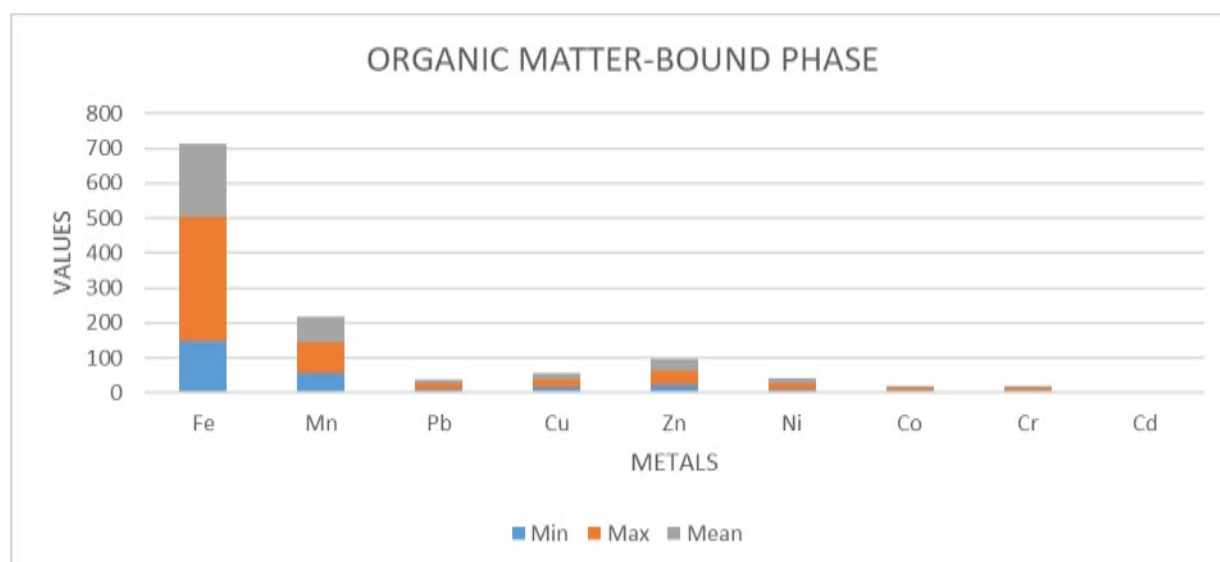


Fig. 9. Cluster column chart of the heavy metal concentrations in the organic matter-bound phase (mg/kg). The figure illustrates the distribution of metals across all samples, highlighting their association with organic matter and relative enrichment through complexation with organic ligands.

4.1.6 The sulfide/strongly bound phase

The sulfide/strongly bound phase represents metals incorporated into sulfide minerals and resistant mineral lattices, making it one of the most stable and least mobile geochemical fractions (Tessier et al., 1979; Davidson et al., 1998). Table 7a shows that Fe (184.382–353.506 mg/kg) and Mn (75.148–150.084 mg/kg) dominate this phase, while Zn, Cu, and Pb exhibit moderate enrichment, indicating their affinity for sulfide-bearing minerals. Nickel, Co, Cr, and Cd occur at comparatively lower concentrations.

The statistical summary in Table 7b confirms the abundance order of Fe > Mn > Zn > Cu > Pb > Ni > Co >

Cr > Cd. Higher concentrations recorded in samples SQ3, SQ4, and SQ15 suggest localized sulfide enrichment related to lithological variations rather than anthropogenic inputs. Figure 10 similarly highlights the dominance of Fe and Mn across the study area.

Overall, the sulfide/strongly bound phase represents a stable geochemical reservoir with very low metal mobility under present conditions. Although oxidation could release some of these metals into the environment, the current distribution indicates predominantly geogenic enrichment and poses minimal environmental and human health risk to the local population (Hakanson, 1980; Davidson et al., 1998).

Table 7a: Heavy metal concentrations in the sulfide/strongly bound phase (mg/kg). The table shows metals strongly associated with sulfide minerals and resistant phases, reflecting their low mobility and long-term geochemical stability within the soil matrix.

Samples	Fe (mg/Kg)	Mn (mg/Kg)	Pb (mg/Kg)	Cu (mg/Kg)	Zn (mg/Kg)	Ni (mg/Kg)	Co (mg/Kg)	Cr (mg/Kg)	Cd (mg/Kg)
SQ 1	251.118	105.746	18.723	14.103	31.411	11.652	6.342	5.126	0.343
SQ 2	252.049	108.224	17.916	14.321	30.782	11.761	6.226	5.472	0.345
SQ 3	345.371	147.602	24.432	20.438	35.255	15.004	7.752	6.159	0.798
SQ 4	352.217	147.916	25.543	20.825	36.126	15.243	8.116	6.458	1.128
SQ 6	184.382	83.239	12.621	13.127	26.134	9.827	4.279	4.174	0.312
SQ7	186.641	84.043	12.584	13.312	26.187	10.022	4.853	4.956	0.331
SQ 8	262.248	115.741	19.251	14.329	31.732	12.021	6.349	5.765	0.372
SQ 10	201.508	75.148	11.016	12.503	22.101	8.217	4.251	4.329	0.314
SQ 11	205.421	77.713	11.172	13.008	23.061	8.734	4.584	4.457	0.325

SQ 12	216.142	85.062	11.729	13.543	27.658	10.964	5.866	4.586	0.337
SQ 13	217.618	84.927	11.972	13.729	27.851	11.492	5.982	8.148	0.421
SQ 14	250.354	106.109	18.649	15.021	30.496	12.035	6.264	5.228	0.432
SQ 15	353.506	150.084	25.791	22.129	37.022	15.232	8.335	6.784	1.147
SQ 16	253.127	107.732	18.069	16.011	32.029	12.022	6.016	5.822	0.441
SQ 17	184.783	85.106	11.967	12.938	25.867	10.112	5.241	5.013	0.437

Table 7b: Statistical summary of the heavy metals concentration in the sulfide/strongly bound phase (mg/kg). This table presents the minimum, maximum, and mean concentrations of metals strongly bound within sulfide and resistant mineral phases, indicating their low mobility and high geochemical stability.

Metal	Fe	Mn	Pb	Cu	Zn	Ni	Co	Cr	Cd
Min	184.382	75.148	11.016	12.503	22.101	8.217	4.251	4.174	0.312
Max	353.506	150.084	25.791	22.129	37.022	15.243	8.335	8.148	1.147
Mean	247.766	104.293	16.762	15.289	29.581	11.623	6.030	5.498	0.499

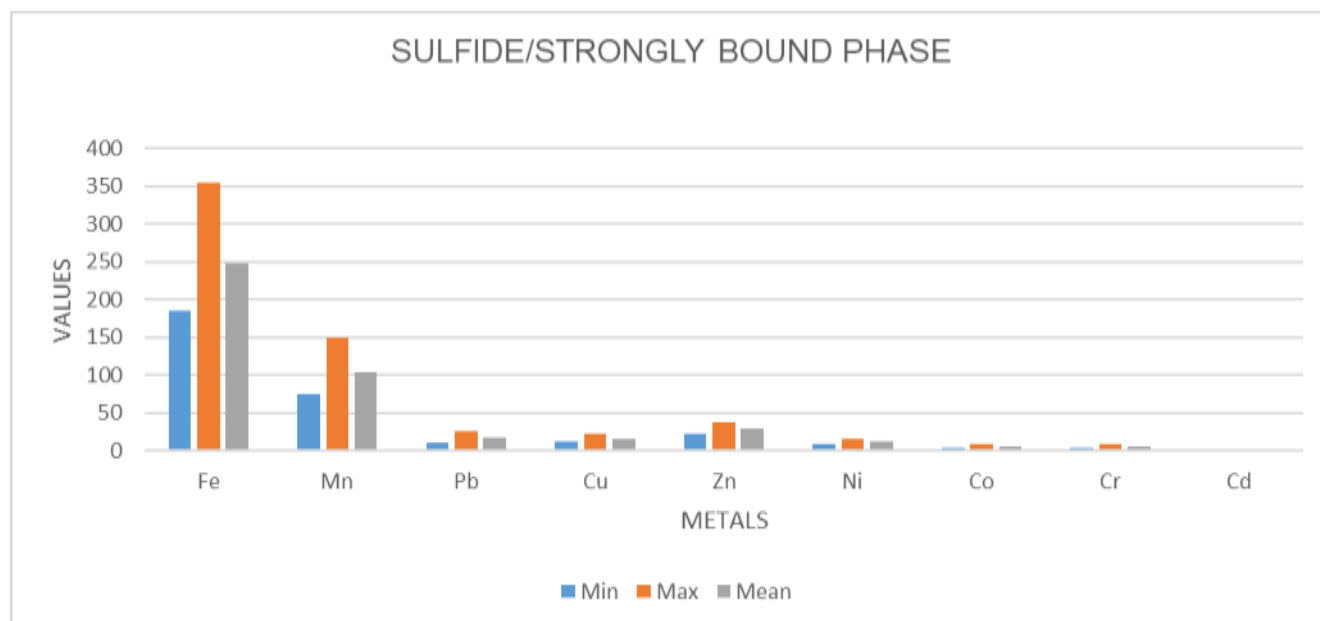


Fig.10. Cluster column chart of the heavy metal concentrations in the sulfide/strongly bound phase (mg/kg). The figure illustrates the distribution of metals strongly bound to sulfide and resistant mineral phases across all samples, highlighting their relative stability and low mobility in the geochemical system.

4.1.7 The residual phase

The residual phase represents metals incorporated within primary and secondary mineral lattices and is regarded as the most stable and least mobile fraction under natural environmental conditions (Tessier et al., 1979; Kabata-Pendias, 2011). Table 8a shows that Fe (12,532.459–16,416.143 mg/kg) and Mn (769.814–946.516 mg/kg) dominate this fraction, confirming strong lithogenic control. Zinc, Cr, Cu, Ni, Co, and Pb also occur at relatively higher concentrations, reflecting structural

incorporation within silicate minerals, whereas Cd remains consistently low.

The statistical summary in Table 8b indicates the abundance order of Fe > Mn > Zn > Cr > Cu > Ni > Co > Pb > Cd. Higher concentrations observed in samples SQ3, SQ4, SQ14, and SQ15 reflect variations in parent rock composition, while lower values in SQ6, SQ10, and SQ13 are consistent with more felsic lithologies. Figure 11

further confirms the dominance of Fe and Mn and the stable distribution of the remaining metals.

Overall, the residual phase represents a long-term geochemical reservoir with negligible metal mobility under present conditions. The predominance of metals in

this fraction indicates that their distribution is controlled mainly by the natural composition of the basement rocks, posing minimal environmental and human health risk to residents of the study area (Alloway, 2013).

Table 8a: Heavy metal concentrations in the residual phase (mg/kg). The table shows metals strongly locked within primary and secondary mineral lattices, representing the most stable and least mobile geochemical fraction in the soil system.

Samples	Fe (mg/Kg)	Mn (mg/Kg)	Pb (mg/Kg)	Cu (mg/Kg)	Zn (mg/Kg)	Ni (mg/Kg)	Co (mg/Kg)	Cr (mg/Kg)	Cd (mg/Kg)
SQ 1	13124.153	851.125	37.231	51.609	86.332	31.861	18.715	66.322	0.597
SQ 2	13231.582	862.197	35.793	52.096	84.809	32.168	19.207	66.188	0.553
SQ 3	16265.625	946.516	40.714	62.631	95.119	42.732	23.061	78.751	1.177
SQ 4	16416.143	941.849	42.028	61.979	97.151	43.833	23.146	80.015	1.185
SQ 6	15693.198	874.034	38.624	56.235	93.009	40.635	21.081	72.231	0.682
SQ7	12758.903	780.623	32.627	53.018	66.745	30.561	13.196	57.592	0.414
SQ 8	14753.727	865.106	36.942	54.723	88.126	34.642	20.731	68.685	1.127
SQ 10	12593.684	789.702	30.574	51.052	65.905	29.364	14.211	55.885	0.534
SQ 11	12682.363	776.937	31.077	51.031	68.016	29.902	13.723	55.759	0.511
SQ 12	14723.794	867.369	38.362	56.387	86.972	34.558	20.148	69.101	0.746
SQ 13	12532.459	769.814	30.984	52.125	68.132	32.092	13.741	55.704	0.642
SQ 14	15562.525	876.614	39.072	58.521	90.165	38.965	22.094	73.672	0.779
SQ 15	15469.538	872.607	40.729	57.985	92.007	39.018	21.628	71.961	1.302
SQ 16	13063.523	856.735	35.071	53.081	84.717	35.109	18.591	67.412	0.698
SQ 17	13274.221	842.699	34.866	52.983	85.458	35.238	18.793	66.923	0.602

Table 8b: Statistical summary of heavy metals in the residual phase (mg/kg). This table presents the minimum, maximum, and mean concentrations of metals retained in the residual fraction, representing the most stable and structurally bound geochemical pool in the soil matrix.

Metal	Fe	Mn	Pb	Cu	Zn	Ni	Co	Cr	Cd
Min	12532.459	769.814	30.574	51.031	65.905	29.364	13.196	55.704	0.414
Max	16416.143	946.516	42.028	62.631	97.151	43.833	23.146	80.015	1.302
Mean	14143.029	851.595	36.313	55.030	83.511	35.379	18.804	67.080	0.770

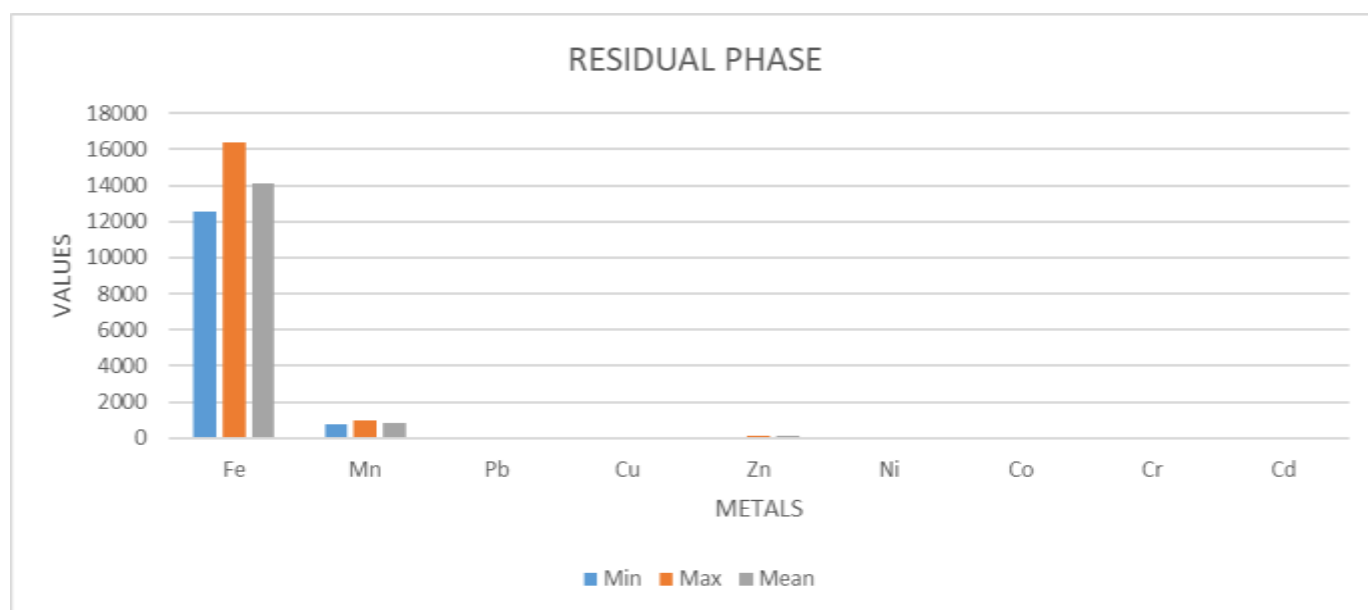


Fig.11. Cluster column chart of the heavy metal concentrations in the residual phase (mg/kg). The figure illustrates the distribution of metals in the residual fraction, highlighting their strong lithogenic control and dominance within primary mineral structures across all samples.

4.2 Contamination factor (CF) of heavy metals in soils of the study area

The Contamination Factor (CF) values presented in Table 9 and Figure 12 indicate varying degrees of heavy metal enrichment across the 17 sampling locations (SQ1–SQ17). Cadmium (Cd) records the highest CF values, with severe contamination at SQ3 (5.92), SQ4 (6.08), and SQ15 (6.20), while Pb also exhibits considerable contamination, with CF values ranging from 2.42 to 4.20. These patterns suggest localized metal enrichment within the study area.

Comparison with the geological setting indicates that samples collected from migmatite and granite gneiss terrains generally exhibit higher Cd concentrations, reflecting the influence of parent rock composition.

Table 9. Contamination factor (CF) of heavy metals in soils of the study area, indicating the degree of metal enrichment relative to background concentrations and providing an assessment of the level of soil contamination across the sampled locations.

Sample	Fe	Mn	Pb	Cu	Zn	Ni	Co	Cr	Cd
SQ1	0.315	1.34	3.29	2.13	2.04	1.06	1.17	0.88	3.31
SQ2	0.318	1.37	3.20	2.17	2.02	1.09	1.19	0.91	3.17
SQ3	0.396	1.67	4.03	2.64	2.38	1.29	1.39	1.17	5.92
SQ4	0.401	1.68	4.20	2.67	2.43	1.35	1.42	1.21	6.08
SQ6	0.324	1.33	3.38	2.25	2.22	1.17	1.13	1.01	3.79
SQ7	0.290	1.18	2.82	2.02	1.85	0.97	0.92	0.83	2.68
SQ8	0.351	1.47	3.66	2.31	2.23	1.18	1.22	1.09	5.03

Sample	Fe	Mn	Pb	Cu	Zn	Ni	Co	Cr	Cd
SQ10	0.273	1.06	2.42	1.73	1.57	0.86	0.74	0.76	2.21
SQ11	0.281	1.10	2.57	1.84	1.66	0.91	0.81	0.79	2.36
SQ12	0.338	1.34	3.41	2.22	2.19	1.14	1.13	1.03	3.88
SQ13	0.339	1.33	3.39	2.23	2.23	1.16	1.11	1.08	4.05
SQ14	0.372	1.60	3.73	2.46	2.33	1.24	1.20	1.13	4.32
SQ15	0.395	1.71	4.10	2.61	2.41	1.31	1.21	1.22	6.20
SQ16	0.342	1.36	3.27	2.30	2.22	1.19	1.18	1.12	4.51
SQ17	0.319	1.29	3.18	2.19	2.17	1.16	1.17	1.10	4.36

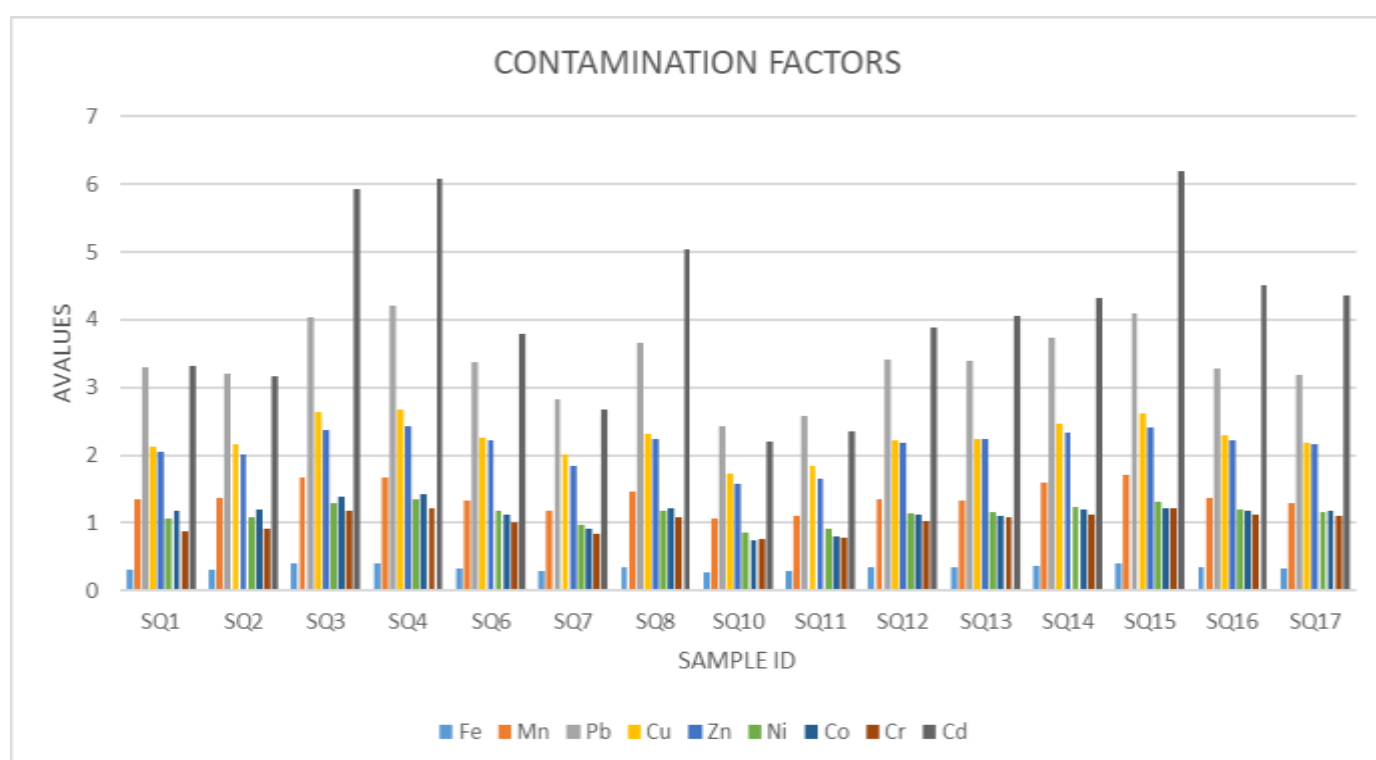


Fig.12: Clustered column chart showing the contamination factor of heavy metals in soil of the study area

4.3 Pollution Load Index (PLI) of heavy metals in soils from the study area

The Pollution Load Index (PLI) provides an integrated assessment of overall heavy metal contamination by combining the contributions of all analyzed elements at each sampling location. From Table 10 and Figure 13, the spatial variation of soil quality across the study area can be effectively evaluated.

In general, the PLI interpretation follows the standard classification where $PLI = 1$ indicates baseline conditions, $PLI > 1$ reflects progressive soil deterioration due to pollution, and $PLI < 1$ suggests unpolluted or near-pristine

conditions (Tessier et al., 1979; Förstner & Wittmann, 2012). Based on Table 10, most sampling points exhibit PLI values greater than 1, indicating widespread deterioration of soil quality and confirming the presence of significant heavy metal stress across the study area (Hakanson, (1980).

Spatially, Figure 13 reveals distinct contamination hotspots, with the highest PLI values recorded at SQ15 (1.45), SQ4 (1.41), and SQ3 (1.38). These locations coincide with areas of more intense human activity and possible lithological influence from Migmatite–Gneiss transitions, which may enhance metal retention and accumulation (Reimann & de Caritat, 2005). In contrast,

lower PLI values at SQ9 (0.85), SQ10 (0.86), and SQ11 (0.90) suggest relatively unpolluted conditions, likely reflecting reduced anthropogenic disturbance or more effective natural dispersion mechanisms.

The combined interpretation of Table 10 and Figure 13 shows that soil contamination in the study area is spatially variable but generally elevated, with clear evidence of localized hotspots. This pattern reflects the combined influence of geogenic background variability and anthropogenic inputs, consistent with established soil geochemical behavior in complex terrains (Reimann & de Caritat, 2005; Förstner & Wittmann, 2012).

Table 10. Pollution Load Index (PLI) of heavy metals in soils from the study area, providing an integrated assessment of the overall level of soil contamination based on the combined contribution of all analyzed heavy metals across the sampled locations.

Sample	PLI
SQ1	1.12
SQ2	1.11
SQ3	1.38
SQ4	1.41
SQ6	1.15
SQ7	0.98
SQ8	1.27
SQ9	0.85
SQ10	0.86
SQ11	0.90
SQ12	1.18
SQ13	1.20
SQ14	1.31
SQ15	1.45
SQ16	1.29
SQ17	1.22

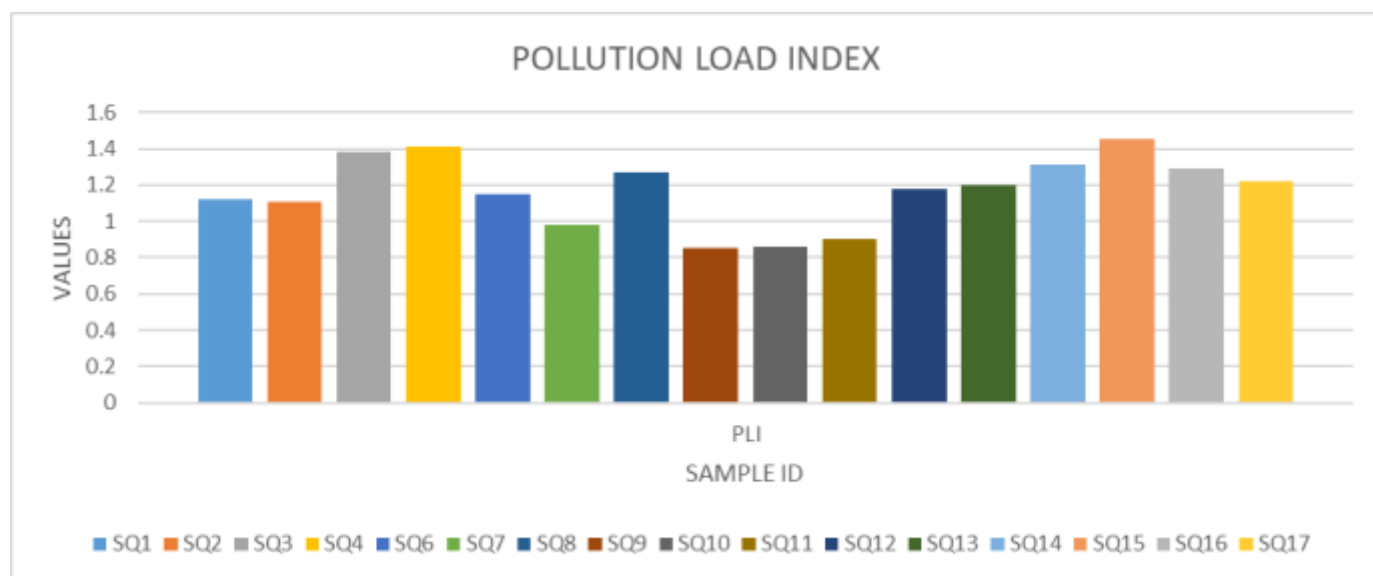


Fig.13: Clustered column chart showing the pollution load index of heavy metals in soil of the study area.

4.4 Major oxides geochemistry (Charnockite)

The Harker variation diagrams (Figure 14) illustrate the relationship between SiO_2 and the major oxides (Al_2O_3 , MgO , CaO , Na_2O , K_2O , TiO_2 , P_2O_5 , and FeOt) for the charnockitic rocks from the Ikole–Itapaji–Ake-Ako area. Although only a few samples were analysed, the diagrams display coherent geochemical trends that provide insight into the magmatic evolution of the rocks.

MgO , CaO , TiO_2 , and FeOt decrease with increasing SiO_2 , indicating progressive depletion of ferromagnesian components during magmatic differentiation. This trend is consistent with fractional crystallization involving the early removal of pyroxene, amphibole, biotite, Fe–Ti oxides, and calcic plagioclase from the evolving magma. The decline in CaO further reflects continuous plagioclase fractionation, while the decrease in TiO_2 and FeOt suggests crystallization of Fe–Ti oxide minerals (Frost et al., 2001).

Conversely, K_2O , Na_2O , Al_2O_3 , and P_2O_5 show positive correlations with increasing SiO_2 . The enrichment of K_2O and Na_2O indicates increasing concentrations of alkali feldspars during the later stages of magmatic evolution, whereas the slight increase in Al_2O_3 reflects the dominance of feldspar-rich felsic assemblages. The progressive increase in P_2O_5 is attributed to the delayed crystallization of apatite, allowing phosphorus to accumulate in the residual melt before saturation (Frost & Frost, 2011).

Overall, the Harker variation patterns indicate that the charnockitic rocks evolved through fractional crystallization of a common parental magma, producing progressively silica-rich and compositionally evolved rocks. These trends are consistent with the magmatic evolution of granitoid suites within the Pan-African Basement Complex of southwestern Nigeria (Rahaman, 1988; Oyinloye, 2011).

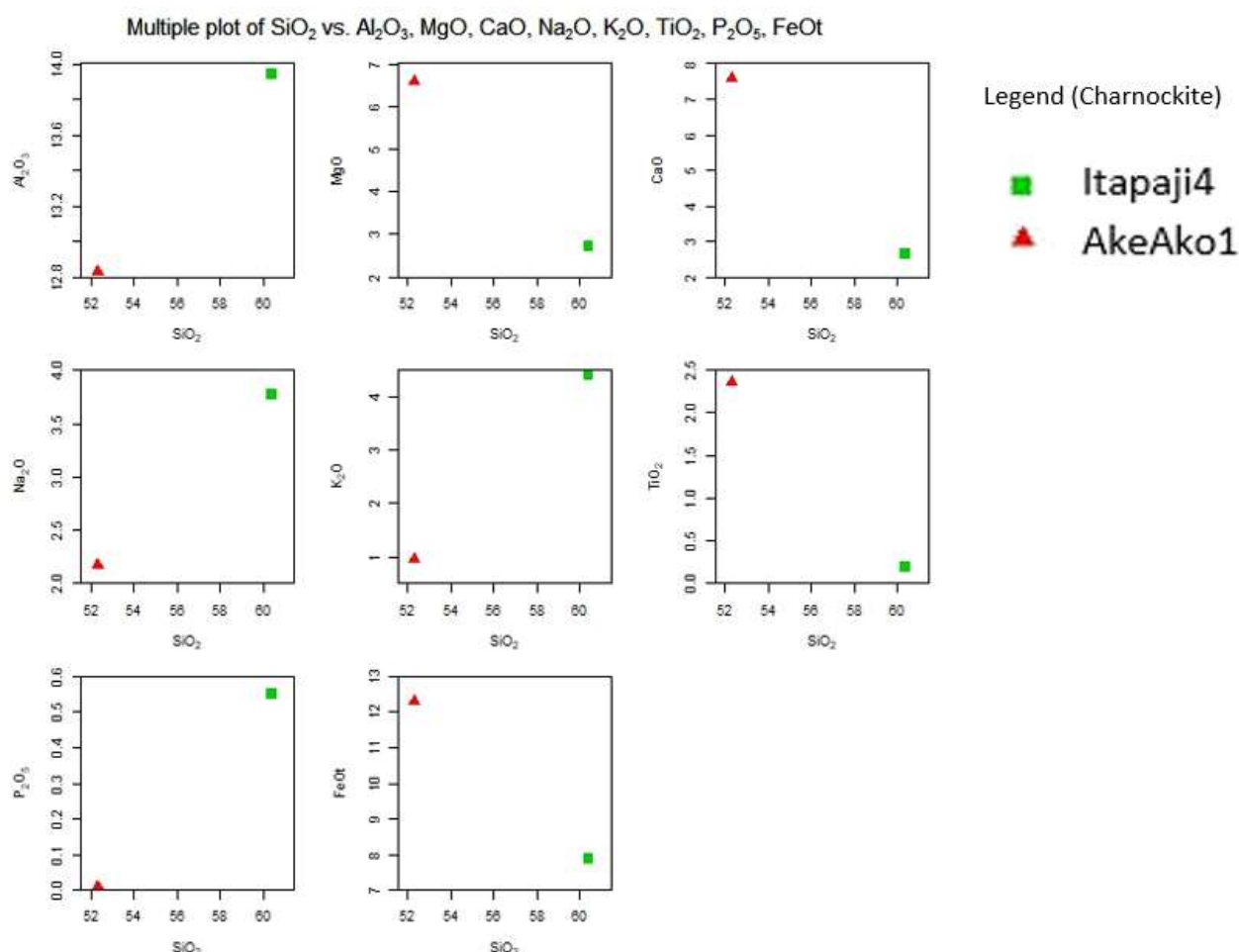


Fig. 14. Harker variation diagrams showing the relationships between SiO_2 and the major oxides (Al_2O_3 , MgO , CaO , Na_2O , K_2O , TiO_2 , P_2O_5 , and FeOt) for the charnockitic rocks from the Ikole–Itapaji–Ake-Ako area. The diagrams indicate systematic geochemical variations consistent with fractional crystallization and progressive magmatic differentiation (after Peccerillo & Taylor, 1976).

The A/CNK–A/NK diagram (Figure 15), proposed by Shand (1943), is widely used to classify granitoids according to their alumina saturation characteristics. The diagram distinguishes peralkaline, metaluminous, and peraluminous rocks based on the molecular proportions of Al_2O_3 , CaO , Na_2O , and K_2O . The two analysed charnockitic samples from the Ikole–Itapaji–Ake-Ako area plot within the metaluminous field, indicating that the rocks contain sufficient Ca, Na, and K relative to Al to accommodate aluminium within feldspars and ferromagnesian minerals without forming peraluminous phases (Shand, 1943).

The Itapaji4 sample plots close to the boundary between the metaluminous and peralkaline fields ($\text{A/CNK} \approx 0.88$), whereas the AkeAko1 sample lies more centrally within the metaluminous field ($\text{A/CNK} \approx 0.70$). Both samples have A/CNK values below 1.0, confirming their metaluminous character. Such compositions are typically associated with granitoids dominated by plagioclase,

hornblende, biotite, and pyroxene, reflecting magmas derived from mantle or lower crustal sources with limited crustal contamination (Frost et al., 2001).

The absence of peraluminous compositions indicates that the parental magma was not significantly enriched in aluminium through extensive crustal melting or sedimentary assimilation. Instead, the metaluminous nature of the charnockites suggests evolution through fractional crystallization of feldspars and ferromagnesian minerals. This interpretation is consistent with the evolution of Pan-African granitoids within the southwestern Nigerian Basement Complex (Rahaman, 1988; Oyinloye, 2011; Frost & Frost, 2011).

Overall, the clustering of both samples within the metaluminous field indicates a common magmatic affinity and supports their derivation from a genetically related parental magma that evolved primarily through fractional crystallization.

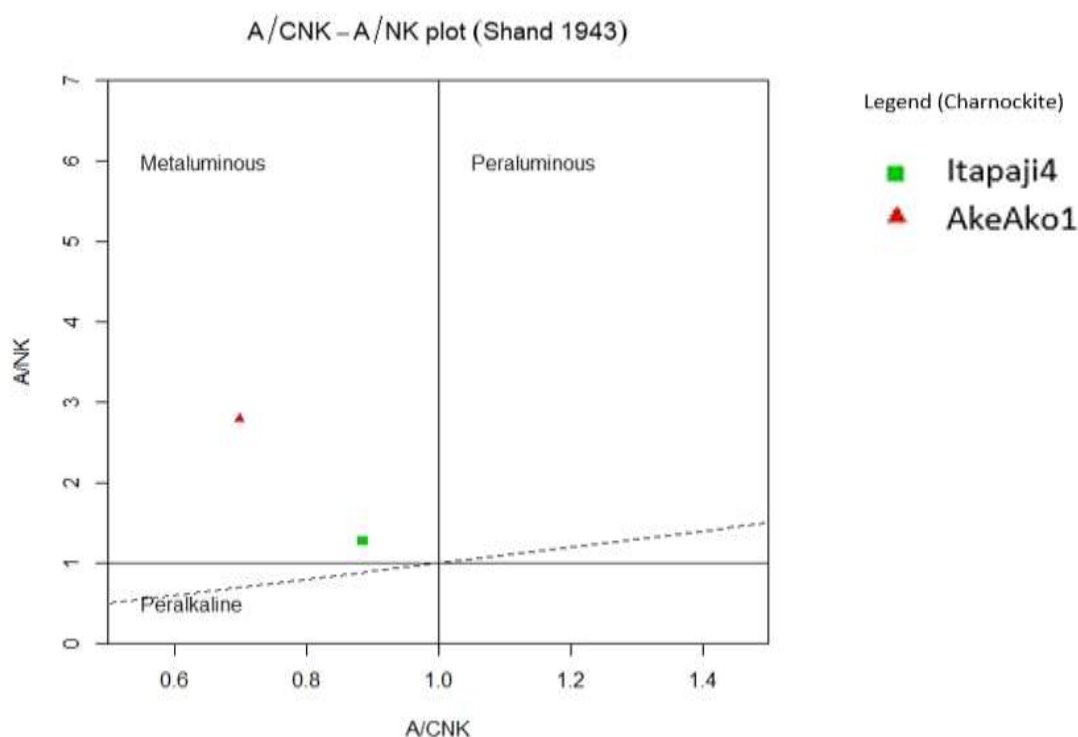


Fig. 15. A/CNK–A/NK alumina saturation diagram after Shand (1943) showing that the analyzed charnockitic samples from the Ikole–Itapaji–Ake-Ako area plot within the metaluminous field, indicating crystallization from mantle-influenced magmas with limited crustal contamination.

The Fe-number versus SiO_2 diagram (Figure 16), proposed by Frost et al. (2001), classifies granitoid rocks into ferroan and magnesian series based on the ratio $\text{FeOt}/(\text{FeOt} + \text{MgO})$. This classification provides important information on magma evolution, oxidation

state, and tectonic affinity. The analysed charnockitic samples from the Ikole–Itapaji–Ake-Ako area plot on opposite sides of the discrimination boundary, indicating subtle variations in their magmatic evolution (Frost et al., 2001).

The Itapaji4 sample plots within the ferroan field, indicating enrichment of total iron relative to magnesium. Ferroan granitoids are generally associated with iron-rich magmas that evolve through extensive fractional crystallization under relatively reduced conditions. Such granitoids commonly occur in post-collisional or within-plate tectonic environments where prolonged magmatic differentiation favours iron enrichment in the residual melt (Frost & Frost, 2011).

In contrast, the AkeAko1 sample plots within the magnesian field, indicating relatively higher magnesium contents compared to total iron. Magnesian granitoids are typically derived from relatively oxidized magmatic systems in which early crystallization of Fe–Ti oxides restricts iron enrichment while preserving higher Mg

contents. These granitoids are commonly associated with calc-alkaline magmatic suites formed in convergent margin settings (Peccerillo & Taylor, 1976; Frost et al., 2001).

The close proximity of both samples to the ferroan–magnesian boundary suggests that the charnockitic suite exhibits transitional geochemical characteristics rather than representing two distinct magma series. The observed variation is most likely related to differences in fractional crystallization, oxidation conditions, or minor compositional heterogeneity within a common parental magma. This interpretation is consistent with the Pan-African evolution of granitoids within the southwestern Nigerian Basement Complex (Rahaman, 1988; Oyinloye, 2011).

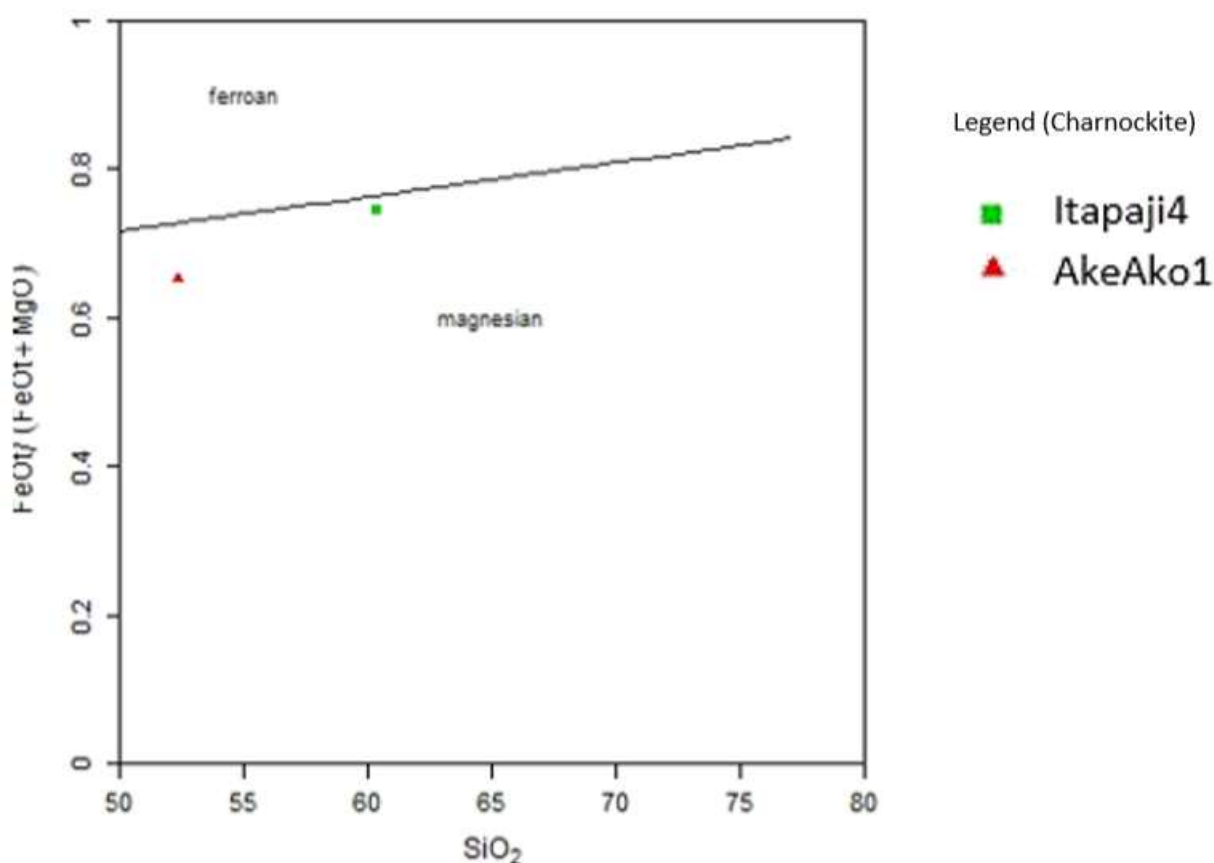


Fig. 16. Fe-number ($\text{FeOt} / (\text{FeOt} + \text{MgO})$) versus SiO_2 discrimination diagram after Frost et al. (2001) showing that the charnockitic samples from the Ikole–Itapaji–Ake-Ako area exhibit both ferroan and magnesian affinities, indicating variations in iron enrichment during magmatic differentiation.

4.5 Major oxide geochemistry (Granite)

The Harker variation diagrams (Figure 17) show the relationships between SiO_2 and the major oxides (Al_2O_3 , MgO , CaO , Na_2O , K_2O , TiO_2 , P_2O_5 , and FeOt) for the Igbona–Ikole granite samples. The sample with higher SiO_2 (Igbona–Ikole 2) exhibits lower Al_2O_3 and FeOt contents, indicating progressive depletion of ferromagnesian minerals and feldspars during fractional crystallization. These trends are consistent with magmatic differentiation commonly observed in felsic granitoids (Frost et al., 2001; Frost & Frost, 2011).

In contrast, Igbona–Ikole 2 shows slightly higher MgO , CaO , K_2O , TiO_2 , and P_2O_5 contents than Igbona–Ikole 1.

Considering the limited number of analysed samples, these variations likely reflect local compositional differences rather than systematic magmatic trends. The high silica contents (68–72 wt.% SiO_2) indicate that both samples represent evolved felsic granites derived from a common calc-alkaline magma (Rahaman, 1988; Oyinloye, 2011).

Overall, the Harker variation patterns support the results of the AFM, TAS, A/CNK–A/NK, and Fe-number classification diagrams, indicating that the Igbona–Ikole granites evolved through fractional crystallization and belong to a calc-alkaline granitoid suite emplaced during the Pan-African tectono-magmatic event (Peccerillo & Taylor, 1976; Frost et al., 2001).

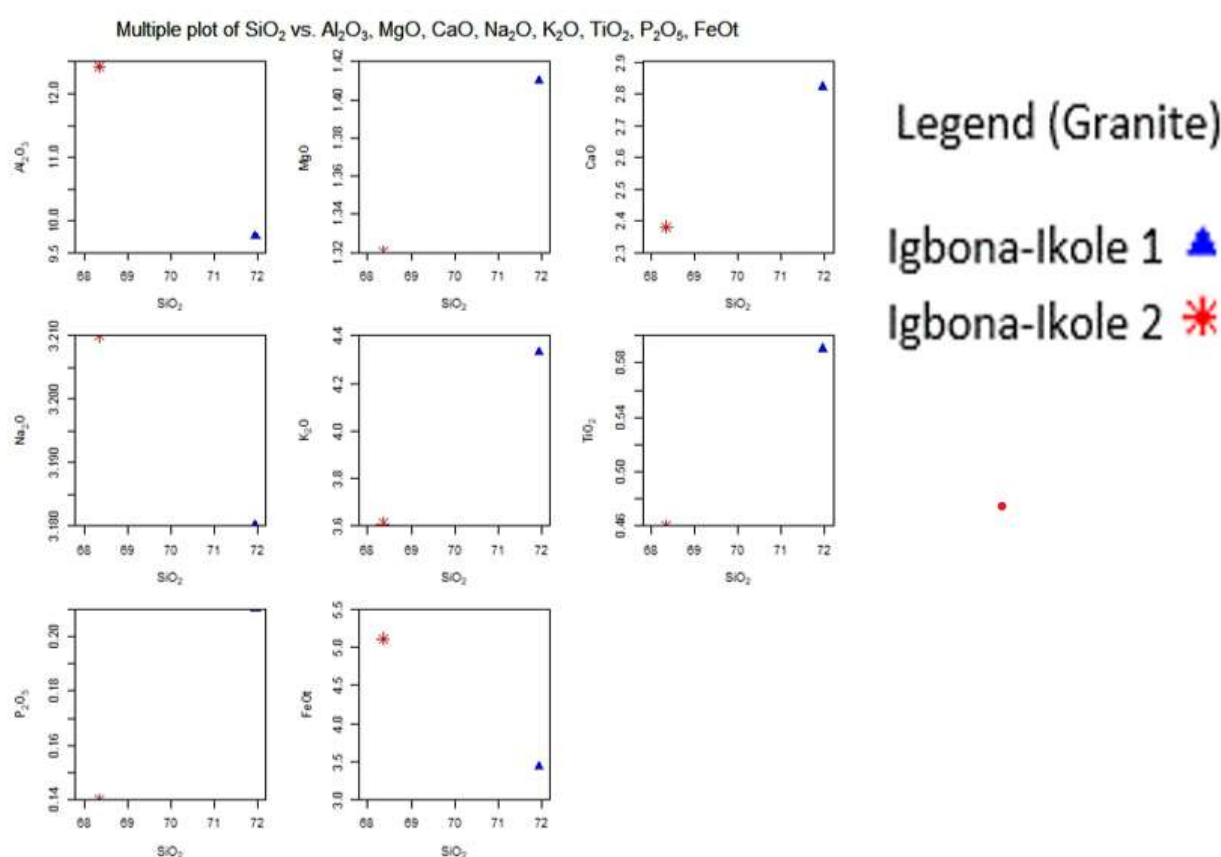


Fig. 17. Harker variation diagrams showing the relationships between SiO_2 and the major oxides (Al_2O_3 , MgO , CaO , Na_2O , K_2O , TiO_2 , P_2O_5 , and FeOt) for the granitic rocks from the Ikole–Itapaji–Ake-Ako area. The observed geochemical variations suggest progressive fractional crystallization and magmatic differentiation (after Peccerillo & Taylor, 1976).

The A/CNK–A/NK diagram (Figure 18), after Shand (1943), classifies the granite samples according to their alumina saturation characteristics using the molecular proportions of Al_2O_3 , CaO , Na_2O , and K_2O . The two analyzed granite samples exhibit slight compositional

variation, plotting within the metaluminous and weakly peraluminous fields.

The Igbona–Ikole 2 sample plots within the metaluminous field ($\text{A/CNK} < 1.0$), indicating that aluminium is balanced by Ca, Na, and K and is mainly hosted in feldspars and ferromagnesian minerals. In contrast, the

Igbona–Ikole 1 sample plots within the weakly peraluminous field, suggesting a slight excess of aluminium that may reflect limited crustal assimilation or partial melting of aluminous crustal materials during magma evolution. These characteristics are consistent with progressive fractional crystallization accompanied by minor crustal interaction in granitoid magmas (Shand, 1943; Frost et al., 2001; Frost & Frost, 2011).

The close proximity of the two samples indicates that the granites are genetically related and most likely evolved from a common parental magma, with the observed variation reflecting different degrees of magmatic differentiation rather than distinct magma sources (Peccerillo & Taylor, 1976; Frost & Frost, 2011).

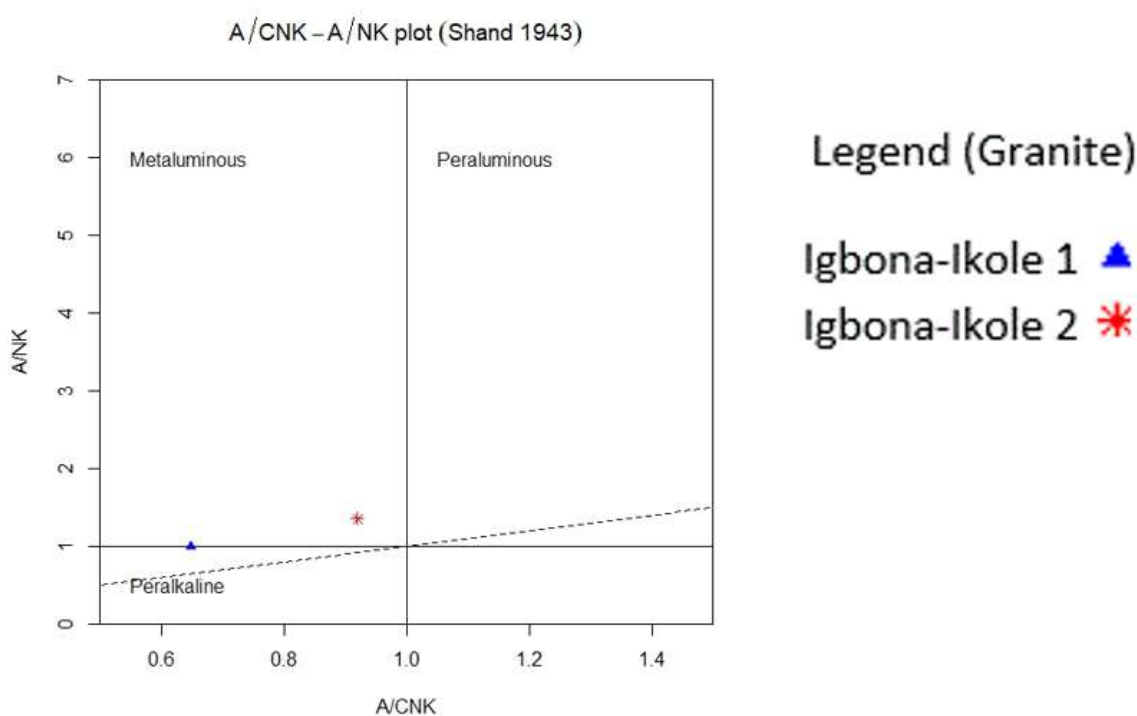


Fig.18. A/CNK–A/NK alumina saturation diagram showing the alumina saturation characteristics of the granitic rocks from the Ikole–Itapaji–Ake-Ako area. The samples plot within the metaluminous and weakly peraluminous fields, indicating evolution through fractional crystallization with limited crustal contamination (after Shand, 1943).

The Fe-number versus SiO_2 diagram (Figure 19), after Frost et al. (2001), classifies the granite samples according to their $\text{FeO}t/(\text{FeO}t + \text{MgO})$ ratios. Both Igbona–Ikole 1 and Igbona–Ikole 2 plot within the magnesian field, indicating that the granitic suite possesses a magnesian affinity typical of calc-alkaline granitoids (Frost et al., 2001; Frost & Frost, 2011).

Igbona–Ikole 2 plots well within the magnesian field, whereas Igbona–Ikole 1 lies close to the ferroan–magnesian boundary but remains magnesian. This slight variation suggests minor differences in iron enrichment

during magma evolution while indicating that both samples are genetically related and evolved through progressive fractional crystallization.

The magnesian affinity implies crystallization under relatively oxidizing conditions, where early removal of Fe–Ti oxides limited iron enrichment in the residual magma. This interpretation is consistent with the calc-alkaline nature of the granites and supports emplacement within a convergent to post-collisional tectonic setting (Frost et al., 2001; Frost & Frost, 2011; Shand, 1943).

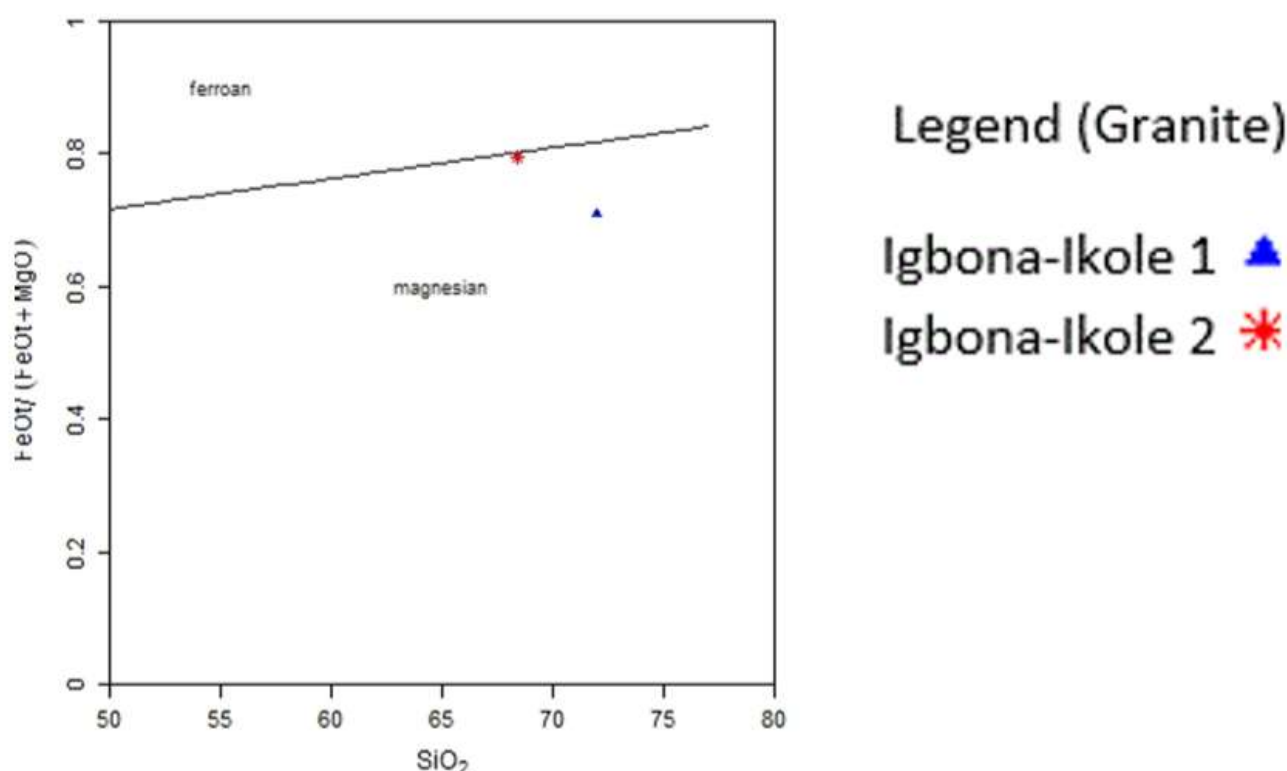


Fig.19. Fe-number ($\text{FeOt}/(\text{FeOt} + \text{MgO})$) versus SiO_2 discrimination diagram after Frost et al. (2001) showing that the granitic rocks from the Ikole–Itapaji–Ake-Ako area plot within the magnesian field, indicating evolution under relatively oxidizing conditions through fractional crystallization.

4.6 Major oxide geochemistry (Granite Gneiss)

The Harker variation diagrams (Figure 20) illustrate the relationships between SiO_2 and the major oxides for the granite gneiss samples from the Ikole–Itapaji–Ake-Ako area. Most major oxides (Al_2O_3 , MgO , CaO , Na_2O , K_2O , TiO_2 , P_2O_5 , and FeOt) generally decrease with increasing SiO_2 , indicating progressive magmatic differentiation. Samples with lower silica contents contain higher MgO , CaO , and FeOt , whereas the high-silica samples are depleted in these oxides, reflecting fractional crystallization of ferromagnesian minerals, plagioclase, Fe–Ti oxides, and apatite (Frost et al., 2001; Frost & Frost, 2011).

Although slight scatter is observed for Na_2O and K_2O , the overall geochemical trends indicate evolution from a

common calc-alkaline parental magma. Minor deviations are expected because the samples were collected from different outcrops that have experienced varying degrees of deformation and metamorphic overprinting within the Pan-African Basement Complex (Rahaman, 1988; Oyinloye, 2011).

Overall, the Harker variation patterns indicate that the granite gneiss represents differentiated felsic magmas that evolved through progressive fractional crystallization before regional metamorphism. This interpretation agrees with the AFM, TAS, A/CNK–A/NK, and Fe-number classification diagrams, which collectively indicate calc-alkaline affinity and predominantly metaluminous to weakly peraluminous compositions (Peccerillo & Taylor, 1976; Frost et al., 2001).

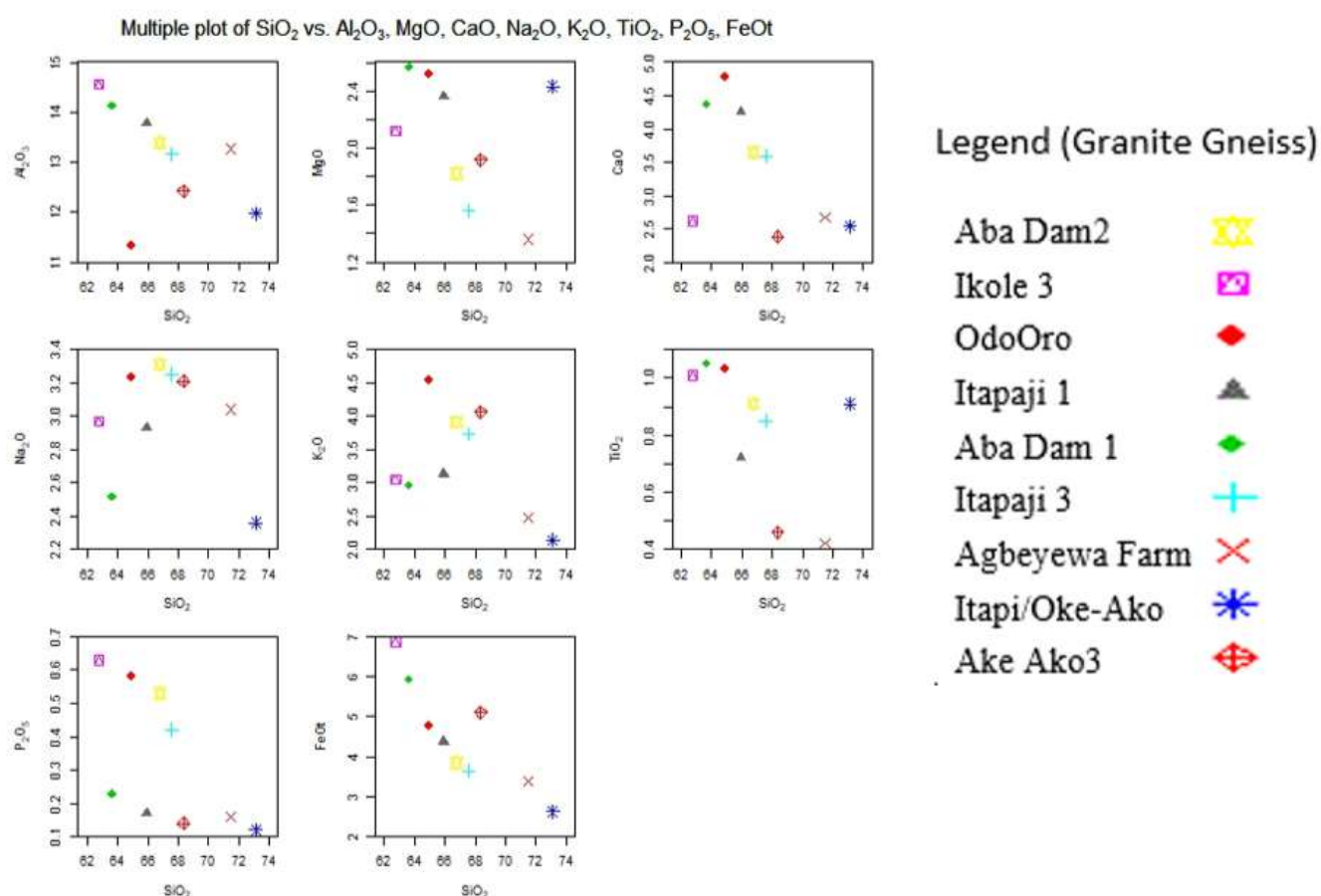


Fig.20. Harker variation diagrams showing the relationships between SiO_2 and the major oxides (Al_2O_3 , MgO , CaO , Na_2O , K_2O , TiO_2 , P_2O_5 , and FeO) for the granite gneisses from the Ikole–Itapaji–Ake-Ako area. The diagrams indicate systematic geochemical variations consistent with progressive fractional crystallization and magmatic differentiation (after Peccerillo & Taylor, 1976).

The A/CNK–A/NK diagram (Figure 21), after Shand (1943), classifies the granite gneiss samples according to their alumina saturation characteristics. The samples are distributed within both the metaluminous and weakly peraluminous fields, indicating slight compositional variation during magma evolution. Most samples plot within the metaluminous field ($\text{A/CNK} < 1.0$), suggesting that aluminium is mainly accommodated within feldspars and ferromagnesian minerals, a characteristic of I-type granitoids (Shand, 1943; Frost et al., 2001).

The Ayewagba and Itapi/OkeA samples plot within the weakly peraluminous field ($\text{A/CNK} > 1.0$), indicating a

slight excess of aluminium that may reflect advanced fractional crystallization and limited crustal assimilation. Such compositions are commonly associated with evolved granitoid magmas emplaced during the Pan-African orogeny (Rahaman, 1988; Oyinloye, 2011).

Overall, the clustering of samples near the $\text{A/CNK} = 1.0$ boundary suggests that the granite gneisses evolved from a common parental magma, with the observed variation resulting from progressive differentiation and minor crustal interaction rather than distinct magma sources (Frost & Frost, 2011; Peccerillo & Taylor, 1976).

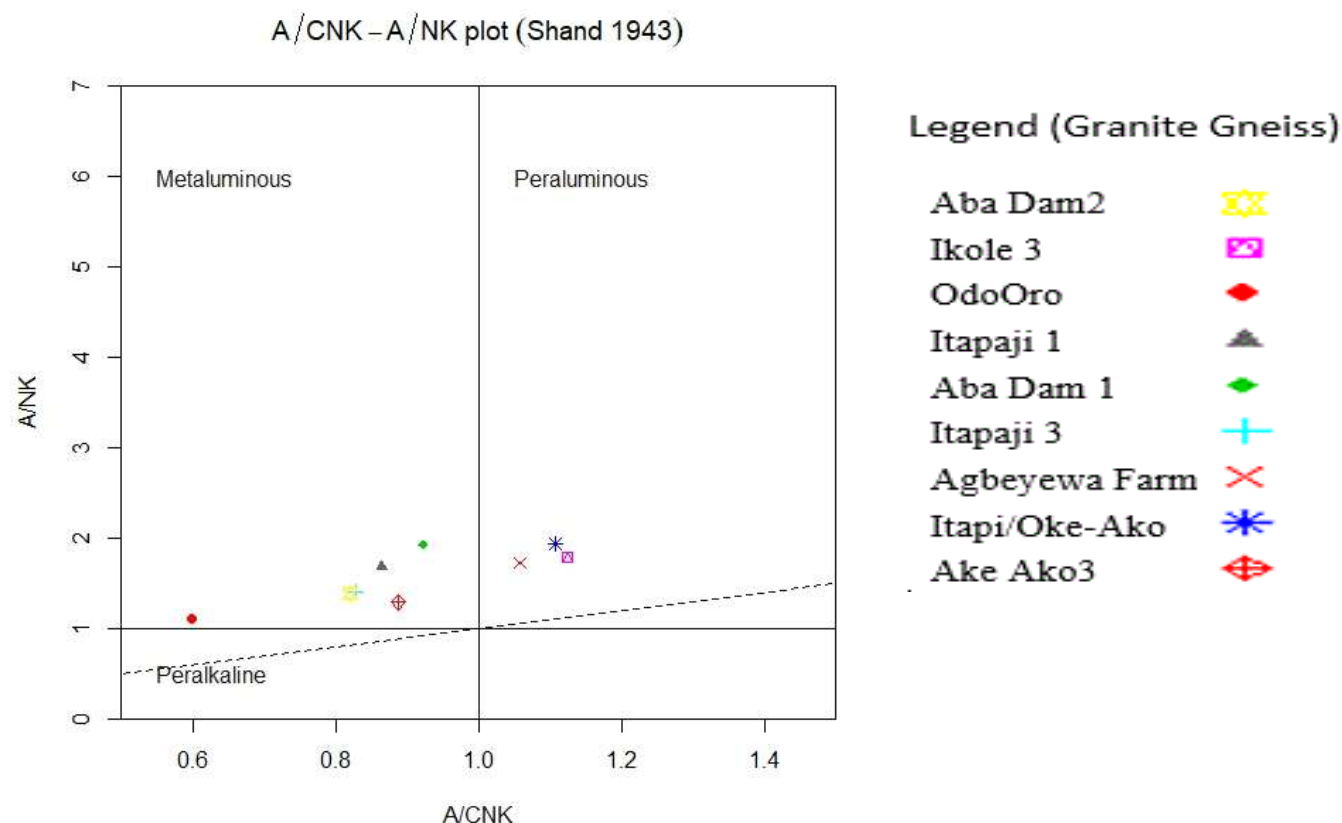


Fig.21. A/CNK–A/NK alumina saturation diagram showing that the granite gneisses from the Ikole–Itapaji–Ake-Ako area are predominantly metaluminous with a few weakly peraluminous samples, indicating evolution through fractional crystallization with minor crustal contamination (after Shand, 1943).

The Fe-number versus SiO₂ diagram (Figure 22), after Frost et al. (2001), classifies the granite gneiss samples into ferroan and magnesian series. Most of the samples plot within the magnesian field, indicating limited iron enrichment during magma evolution. This suggests crystallization under relatively oxidizing conditions typical of calc-alkaline granitoid suites (Frost et al., 2001; Frost & Frost, 2011).

The Ikole 3 sample plots close to the ferroan–magnesian boundary but remains within the magnesian field, indicating only slight iron enrichment relative to the other

samples. This variation is interpreted as the result of progressive fractional crystallization rather than evidence for a separate magma series (Rahaman, 1988; Oyinloye, 2011).

Overall, the predominance of magnesian compositions supports the Harker and A/CNK–A/NK interpretations, indicating that the granite gneisses evolved from a common calc-alkaline parental magma through fractional crystallization with only limited crustal contamination (Peccerillo & Taylor, 1976; Frost et al., 2001).

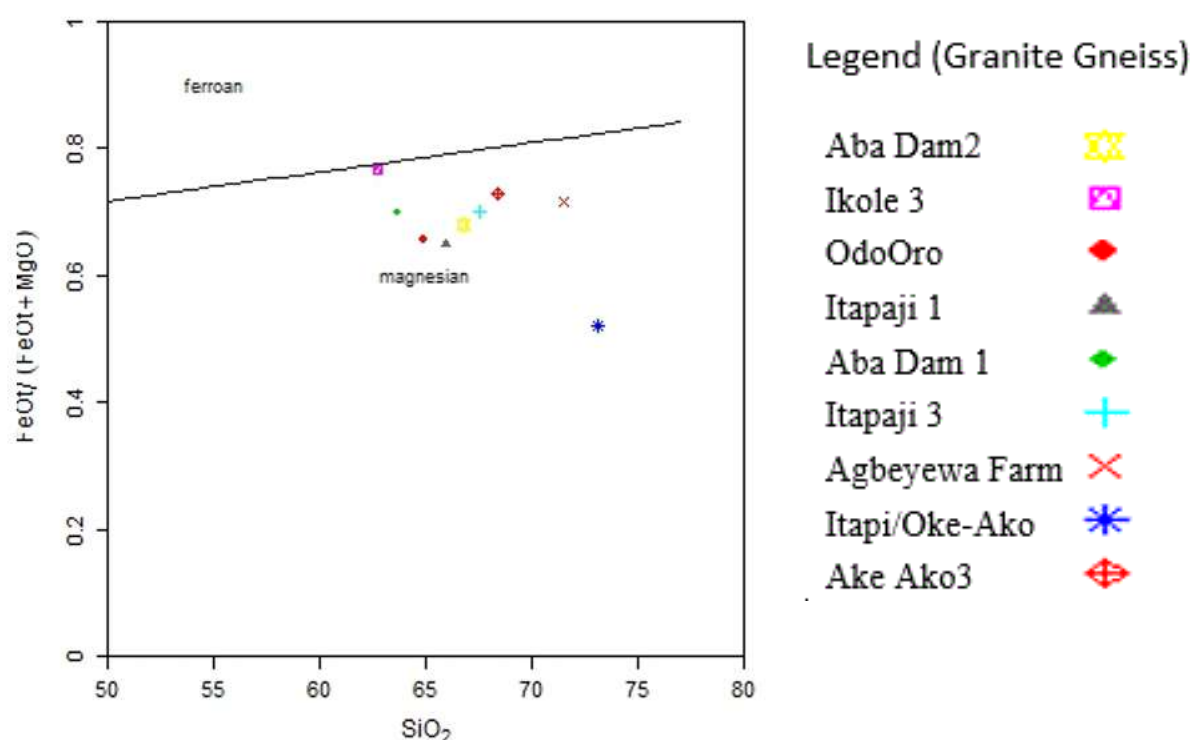


Fig. 22. Fe-number ($\text{FeOt} / (\text{FeOt} + \text{MgO})$) versus SiO_2 discrimination diagram after Frost et al. (2001) showing that the granite gneisses from the Ikole–Itapaji–Ake-Ako area are predominantly magnesian, indicating evolution under relatively oxidizing conditions through progressive fractional crystallization

4.7 Major oxide geochemistry (Migmatite)

The Harker variation diagrams (Figure 23) illustrate the relationships between SiO_2 and the major oxides for the migmatite samples from the Ikole–Itapaji–Ake-Ako area. The diagrams show systematic geochemical trends typical of differentiated felsic magmas. The Ikole 4 sample, with the lowest SiO_2 content, contains the highest concentrations of Al_2O_3 , MgO , CaO , Na_2O , TiO_2 , and FeOt , indicating a relatively primitive composition enriched in ferromagnesian minerals and calcic plagioclase (Rahaman, 1988; Oyinloye, 2011).

In contrast, the Ikole 1 and Ikole 2 samples show higher SiO_2 contents accompanied by decreases in MgO , CaO ,

TiO_2 , and FeOt , reflecting progressive fractional crystallization of amphibole, biotite, plagioclase, and Fe–Ti oxides. Al_2O_3 and Na_2O also decrease slightly with increasing silica, whereas K_2O increases, indicating enrichment of K-feldspar during the later stages of magma evolution (Frost et al., 2001; Frost & Frost, 2011).

Overall, the Harker variation patterns indicate that the migmatites evolved through progressive fractional crystallization from a common felsic parental magma, consistent with the prolonged magmatic evolution and crustal reworking associated with the Pan-African Basement Complex (Peccerillo & Taylor, 1976; Rahaman, 1988).

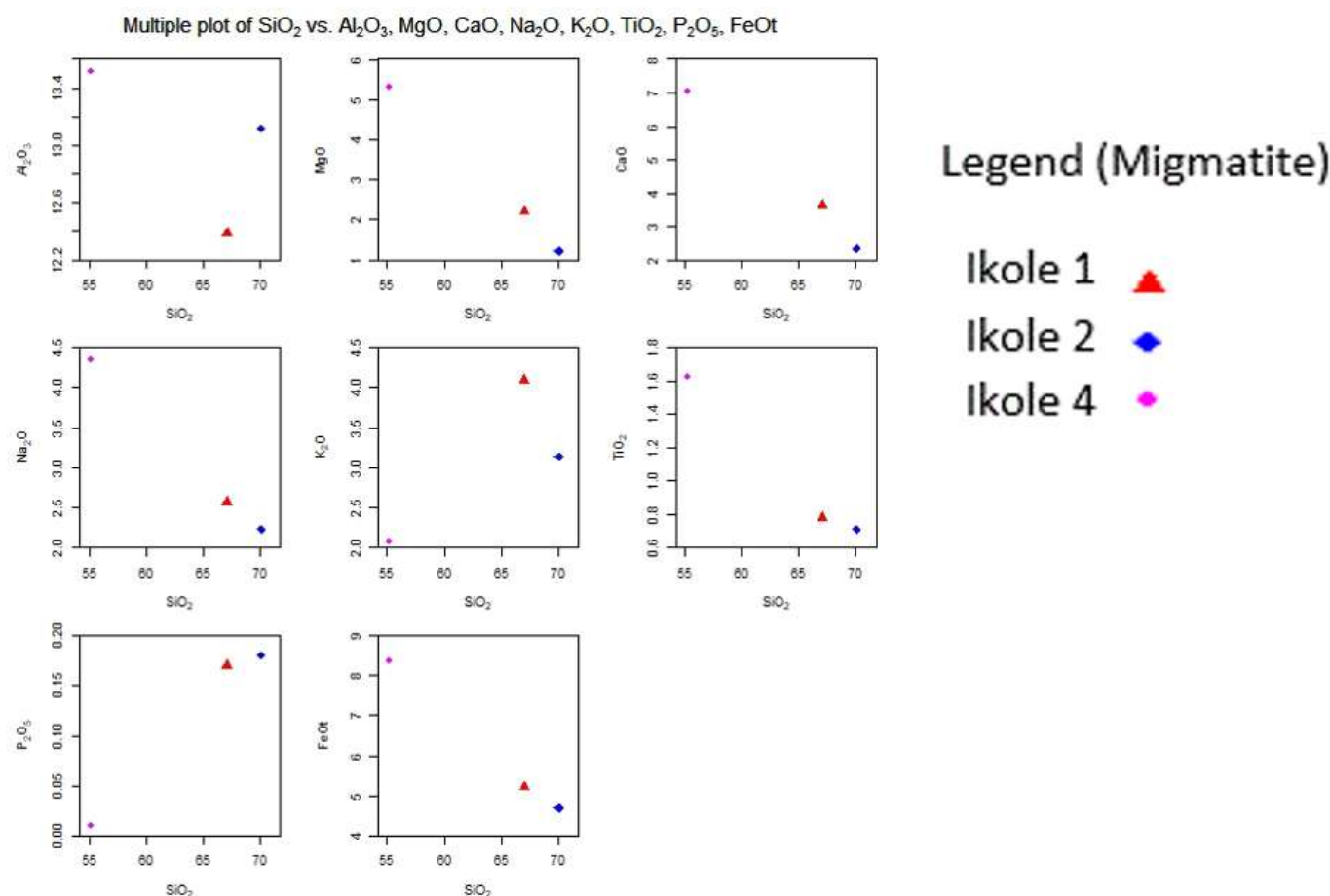


Fig. 23. Harker variation diagrams showing the relationships between SiO_2 and the major oxides (Al_2O_3 , MgO , CaO , Na_2O , K_2O , TiO_2 , P_2O_5 , and FeOt) for the migmatites from the Ikole–Itapaji–Ake-Ako area. The observed geochemical variations indicate progressive fractional crystallization and magmatic differentiation (after Peccerillo & Taylor, 1976).

The A/CNK–A/NK diagram (Figure 24), after Shand (1943), classifies the migmatite samples according to their alumina saturation characteristics. The samples plot within both the metaluminous and weakly peraluminous fields, indicating slight compositional variation during magma evolution. Ikole 1 and Ikole 4 are metaluminous ($\text{A/CNK} < 1.0$), suggesting that aluminium is mainly accommodated within feldspars and ferromagnesian minerals, whereas Ikole 2 is weakly peraluminous ($\text{A/CNK} > 1.0$), indicating a slight excess of aluminium (Shand, 1943; Frost et al., 2001).

The weakly peraluminous nature of the Ikole 2 sample suggests limited crustal contribution through partial

melting or minor crustal assimilation during magmatic evolution, while the metaluminous samples reflect evolution dominated by fractional crystallization. These characteristics are consistent with granitoid magmatism within the Pan-African Basement Complex (Rahaman, 1988; Oyinloye, 2011).

Overall, the close distribution of the samples around the metaluminous–peraluminous boundary indicates that the migmatites evolved from a common parental magma, with the observed variations reflecting progressive differentiation and localized crustal reworking rather than distinct magma sources (Frost & Frost, 2011; Peccerillo & Taylor, 1976).

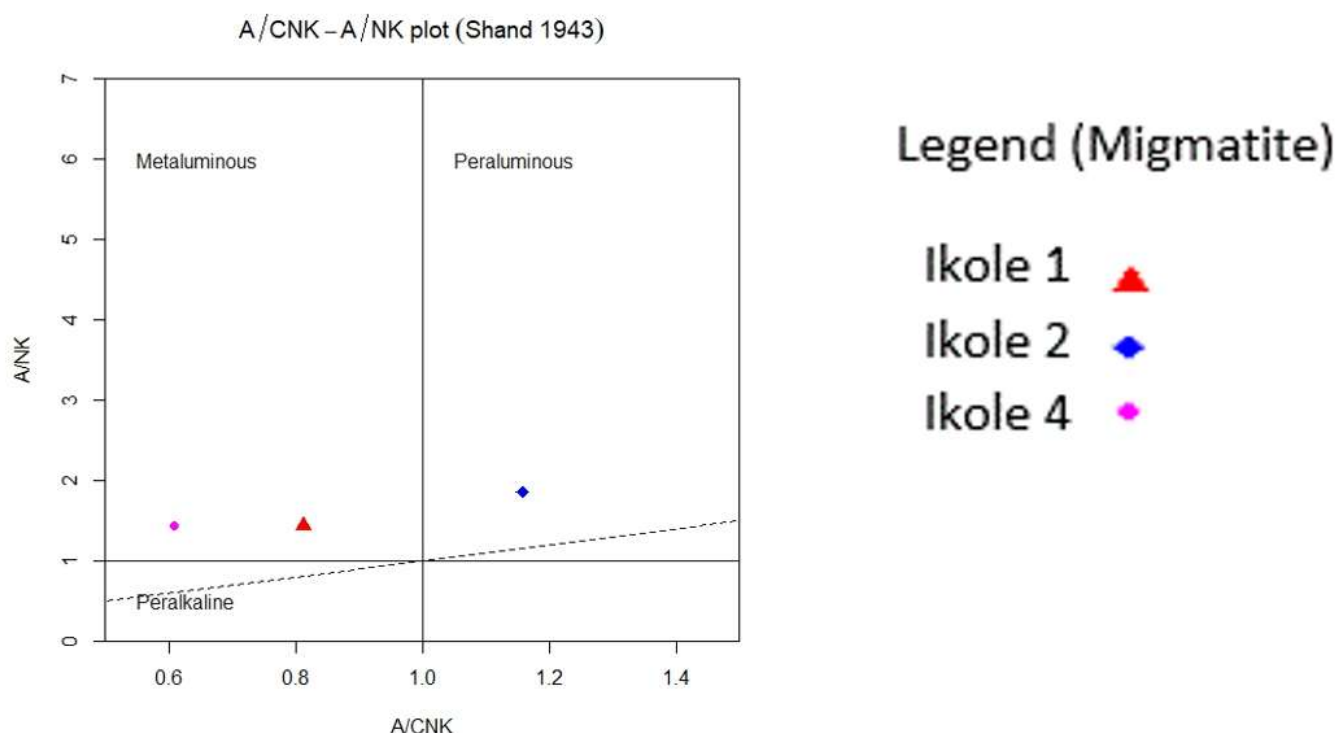


Fig.24. A/CNK–A/NK alumina saturation diagram showing that the migmatites from the Ikole–Itapaji–Ake-Ako area are predominantly metaluminous with one weakly peraluminous sample, indicating evolution through fractional crystallization accompanied by limited crustal contamination (after Shand, 1943).

The Fe-number versus SiO₂ diagram (Figure 25), after Frost et al. (2001), classifies the migmatite samples into ferroan and magnesian series. All the analyzed samples plot within the magnesian field, indicating a consistent magnesian affinity and limited iron enrichment during magma evolution. Although Ikole 2 plots close to the ferroan–magnesian boundary, it remains within the magnesian field, reflecting only minor compositional variation (Frost et al., 2001; Frost & Frost, 2011).

The predominance of magnesian compositions suggests that the parental magma evolved under relatively oxidizing conditions, where early crystallization of Fe–Ti oxides

restricted iron enrichment in the residual melt. This geochemical signature is typical of calc-alkaline granitoids emplaced during the Pan-African tectono-magmatic evolution of the Nigerian Basement Complex (Rahaman, 1988; Oyinloye, 2011).

Overall, the close clustering of the samples within the magnesian field supports derivation from a common parental magma and agrees with the Harker and A/CNK–A/NK diagrams, which indicate progressive fractional crystallization with only minor crustal interaction (Peccerillo & Taylor, 1976; Frost et al., 2001).

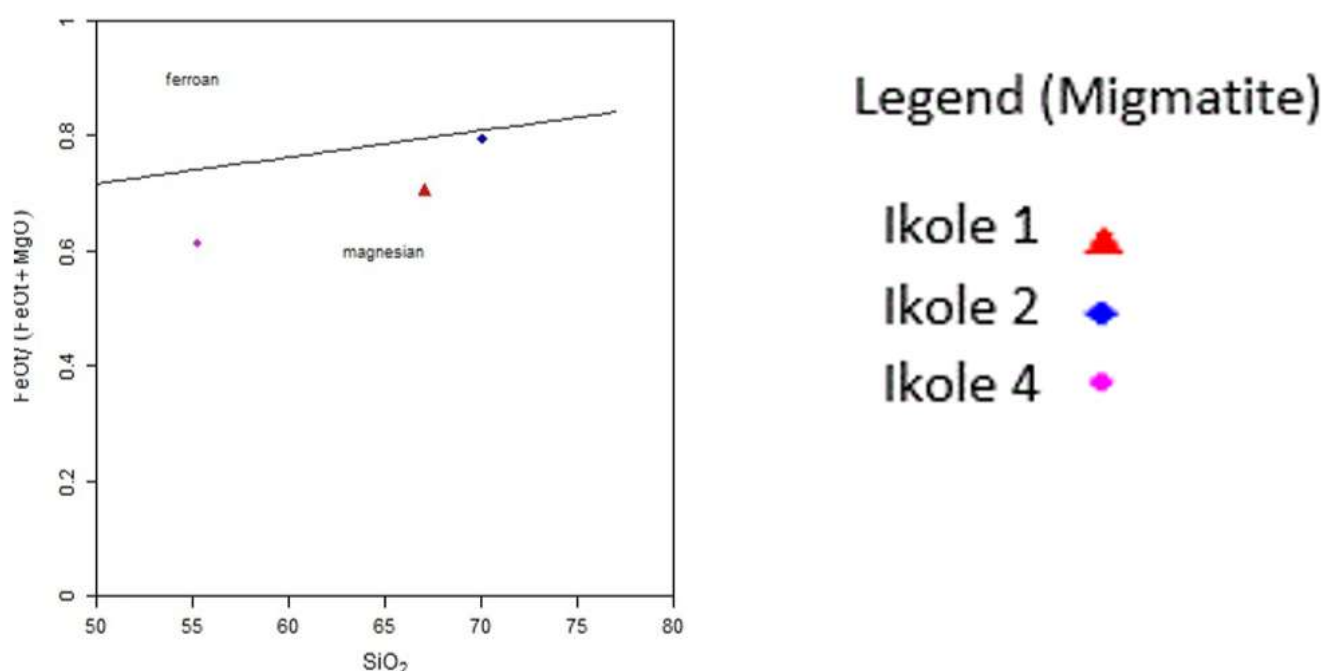


Fig.25. Fe-number ($\text{FeOt}/(\text{FeOt} + \text{MgO})$) versus SiO_2 discrimination diagram after Frost et al. (2001) showing that the migmatites from the Ikole–Itapaji–Ake-Ako area plot within the magnesian field, indicating evolution under relatively oxidizing conditions through progressive fractional crystallization.

4.8 Major oxide geochemistry (Pegmatite)

The Harker variation diagrams (Figure 26) illustrate the relationships between SiO_2 and the major oxides for the pegmatite samples from the Ikole–Itapaji–Ake-Ako area. The diagrams show systematic geochemical trends characteristic of highly differentiated felsic magmas. The Omu sample, with the lowest SiO_2 content, contains the highest concentrations of MgO, CaO, TiO_2 , and FeOt, indicating a relatively less evolved composition. In contrast, the Aba Farm Itapaji sample, with the highest SiO_2 content, is depleted in these oxides, reflecting advanced fractional crystallization (Rahaman, 1988; Oyinloye, 2011).

The general decrease in MgO, CaO, TiO_2 , and FeOt with increasing SiO_2 indicates progressive removal of ferromagnesian minerals, calcic plagioclase, and Fe–Ti oxides during magma evolution. Al_2O_3 and Na_2O also show slight decreases, whereas K_2O remains consistently high, reflecting the abundance of K-feldspar and the highly evolved nature of the pegmatitic melt (Frost et al., 2001; Frost & Frost, 2011).

Overall, the Harker variation patterns indicate that the pegmatites represent highly evolved felsic melts produced through advanced fractional crystallization, consistent with the late-stage magmatic evolution of the Pan-African Basement Complex (Peccerillo & Taylor, 1976; Rahaman, 1988).

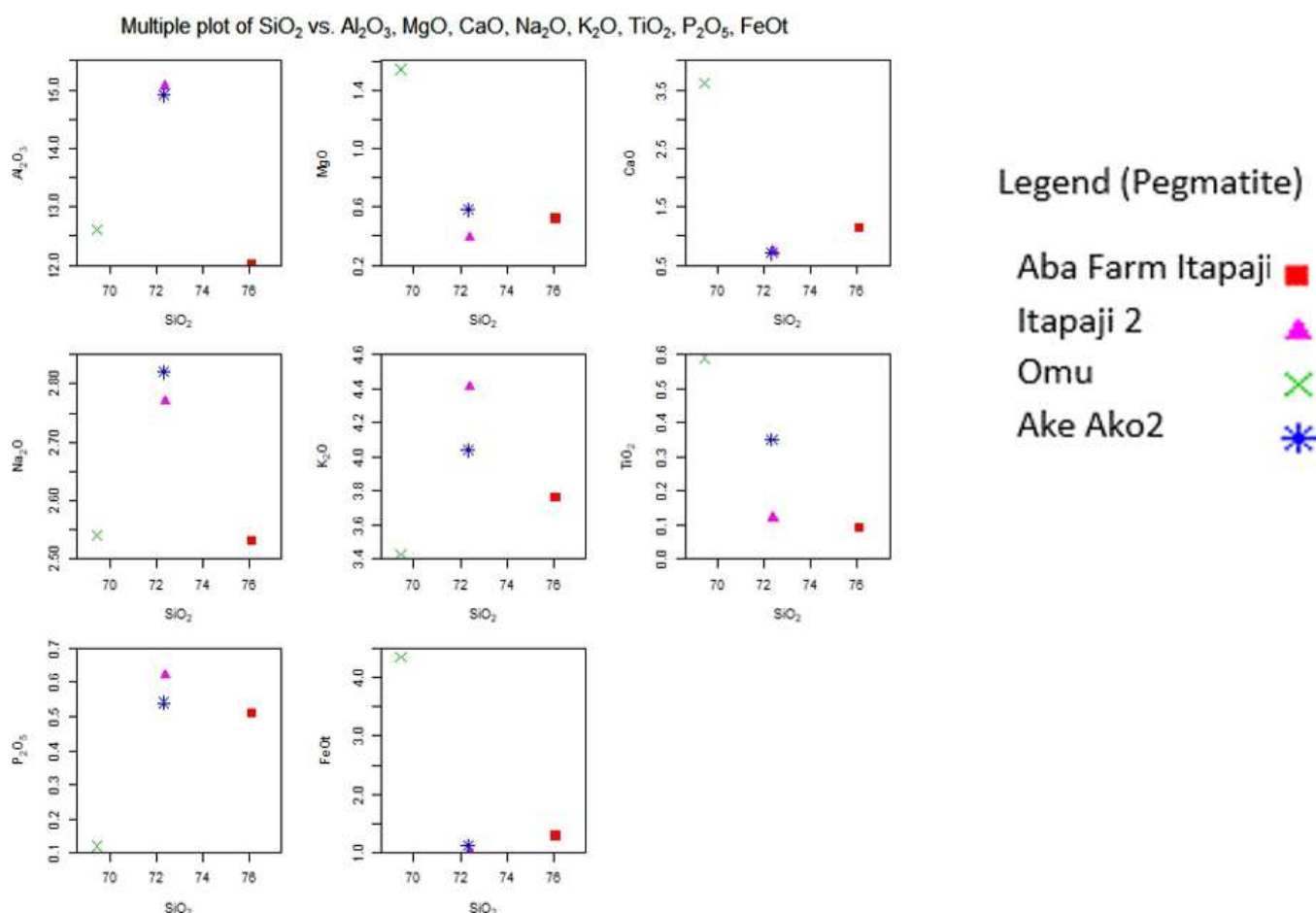


Fig. 26. Harker variation diagrams showing the relationships between SiO_2 and the major oxides (Al_2O_3 , MgO , CaO , Na_2O , K_2O , TiO_2 , P_2O_5 , and FeO) for the pegmatites from the Ikole–Itapaji–Ake-Ako area. The geochemical trends indicate advanced fractional crystallization and the evolution of highly differentiated felsic magmas (after Peccerillo & Taylor, 1976).

The A/CNK–A/NK diagram (Figure 27), after Shand (1943), classifies the pegmatite samples according to their alumina saturation characteristics. The samples are predominantly peraluminous, with only the Omu sample plotting within the metaluminous field. The metaluminous composition of Omu ($\text{A/CNK} < 1.0$) suggests crystallization from a relatively less evolved felsic magma, whereas the other samples ($\text{A/CNK} > 1.0$) indicate increasing aluminium enrichment during magma evolution (Shand, 1943; Frost et al., 2001).

The Aba Farm Itapaji, Itapaji 2, and Ake Ako 2 samples exhibit weakly to strongly peraluminous compositions,

reflecting advanced fractional crystallization and the evolution of highly differentiated pegmatitic melts. The higher A/CNK value of the Ake Ako 2 sample suggests the greatest degree of aluminium saturation within the suite (Rahaman, 1988; Oyinloye, 2011).

Overall, the predominance of peraluminous compositions and the absence of peralkaline samples indicate that the pegmatites evolved from highly fractionated calc-alkaline granitic magmas emplaced during the late stages of the Pan-African tectono-magmatic evolution of the Nigerian Basement Complex (Frost & Frost, 2011; Peccerillo & Taylor, 1976).

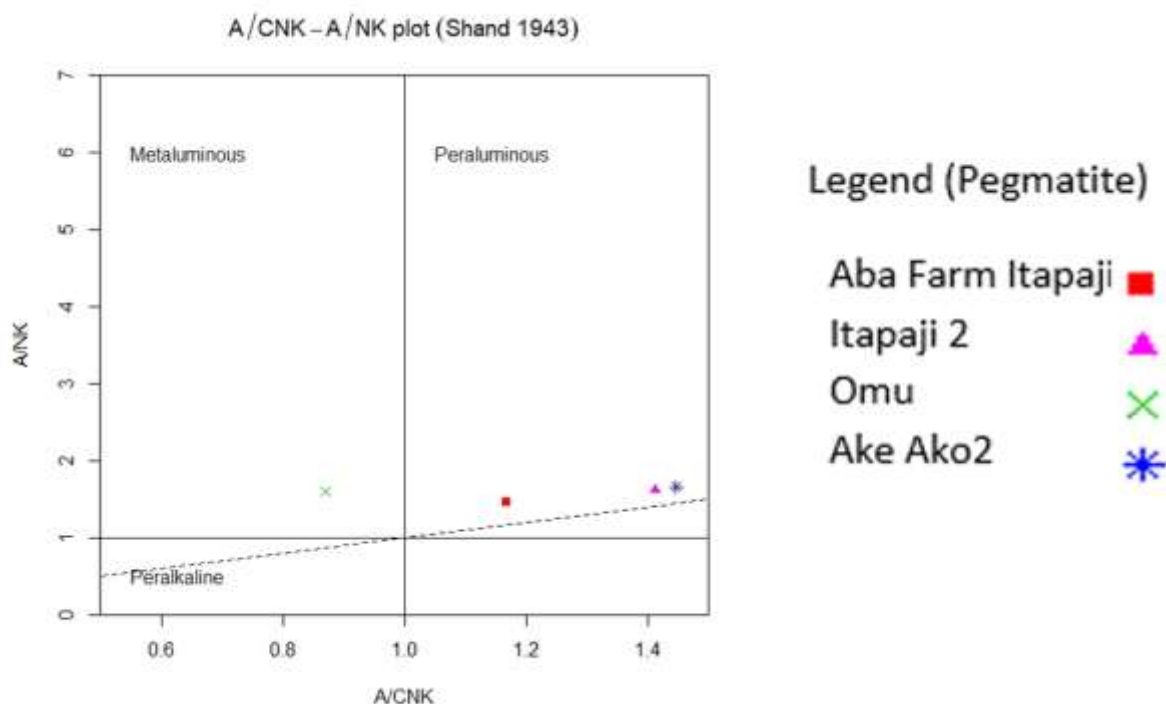


Fig. 27. A/CNK–A/NK alumina saturation diagram showing that the pegmatites from the Ikole–Itapaji–Ake-Ako area are predominantly peraluminous, with one metaluminous sample, indicating derivation from highly evolved felsic magmas through extensive fractional crystallization and crustal interaction (after Shand, 1943).

4.9 Integrated Major Oxide Geochemistry, Contamination Factor and Pollution Load Index

The integration of the major oxide geochemistry with the Contamination Factor (CF) and Pollution Load Index (PLI) demonstrates that the geochemical characteristics of the Ikole–Itapaji area are controlled predominantly by the composition of the Precambrian Basement Complex rather than widespread anthropogenic contamination. The major oxide classification diagrams indicate that the crystalline rocks evolved mainly through fractional crystallization, producing predominantly calc-alkaline, magnesian, and metaluminous to weakly peraluminous granitoids that constitute the principal source of the major and trace elements observed in the soils (Rahaman, 1988; Oyinloye, 2011).

The sequential extraction results further show that most trace metals occur within the Fe–Mn oxide, sulfide/strongly bound, and residual fractions, indicating strong mineralogical control inherited from the parent rocks. This interpretation is consistent with the residual phase, where Fe and Mn dominate the geochemical composition, confirming that weathering of ferromagnesian and silicate minerals is the principal source of these elements. The relatively low concentrations observed in the water-soluble and exchangeable fractions

indicate limited metal mobility under present environmental conditions.

The Contamination Factor results, however, reveal localized enrichment of Cd and Pb at a few sampling locations, while most other metals exhibit low to moderate contamination levels. Although the elevated Cd and Pb values may partly reflect localized anthropogenic inputs, their distribution does not alter the overall lithogenic signature established by the major oxide geochemistry. Similarly, the Pollution Load Index indicates that most sampling locations remain within acceptable to moderately polluted conditions, suggesting that natural geological processes exert a stronger influence on soil chemistry than human activities.

Overall, the integrated geochemical evidence indicates that the elemental composition of the study area is largely controlled by the evolution and weathering of calc-alkaline Pan-African granitoids, with only localized enrichment of environmentally sensitive metals. The combined application of major oxide geochemistry, sequential extraction, Contamination Factor, and Pollution Load Index therefore provides a comprehensive framework for distinguishing natural geogenic signatures from localized environmental contamination within the Ikole–Itapaji

Basement Complex (Peccerillo & Taylor, 1976; Frost et al., 2001).

4.10 Study Limitation

The present study provides a comprehensive assessment of the geochemical characteristics of the Ikole–Itapaji area; however, certain limitations should be acknowledged. The major oxide geochemical interpretation was based on a limited number of representative rock samples for each lithological unit, which, although adequate for lithological characterization, may not fully capture the complete geochemical variability of the entire Basement Complex.

The sequential extraction and pollution assessment were restricted to selected soil samples collected from representative locations within the study area. Consequently, localized variations in trace metal distribution associated with seasonal changes, land-use practices, or small-scale anthropogenic activities may not have been fully represented. In addition, the Contamination Factor (CF) and Pollution Load Index (PLI) were calculated using average shale values as background concentrations, which may differ slightly from the natural local geochemical background of the study area.

Furthermore, this study focused primarily on major oxide geochemistry and trace metal partitioning without incorporating isotopic analyses or geochronological investigations that could provide additional constraints on magma sources, timing of emplacement, and crustal evolution. Future studies integrating isotopic techniques, mineral chemistry, and a larger geochemical dataset would provide a more detailed understanding of the petrogenesis, tectonic evolution, and environmental geochemistry of the Ikole–Itapaji Basement Complex.

V. CONCLUSION

This study integrated geological mapping, major oxide geochemistry, sequential extraction, Contamination Factor (CF), and Pollution Load Index (PLI) to evaluate the petrogenesis of the crystalline basement rocks and the environmental status of soils within the Ikole–Itapaji area, Southwestern Nigeria. Geological mapping revealed that the area is underlain predominantly by migmatite, granite gneiss, granite, pegmatite, and charnockite, reflecting a complex Precambrian geological history involving high-grade metamorphism, partial melting, granitoid emplacement, and Pan-African tectonic reworking.

Major oxide geochemistry indicates that the granitoids evolved mainly through fractional crystallization, producing calc-alkaline, predominantly magnesian, and metaluminous to weakly peraluminous compositions. The

Harker variation diagrams, A/CNK–A/NK plots, and Fe-number classifications collectively suggest that the rocks were derived from genetically related magmas with only minor crustal contamination, consistent with Pan-African granitoid evolution within the Nigerian Basement Complex.

Sequential extraction demonstrates that most trace metals are concentrated in the Fe–Mn oxide, sulfide/strongly bound, and residual fractions, indicating strong lithogenic control and limited mobility under present environmental conditions. The low proportions of metals in the water-soluble and exchangeable fractions further suggest that the majority of trace metals remain strongly retained within the soil matrix and are not readily available for migration or biological uptake.

The Contamination Factor and Pollution Load Index reveal that, although the overall geochemical signature is dominated by natural weathering of the basement rocks, localized enrichment of cadmium (Cd) and lead (Pb) occurs at some sampling locations. These elevated values indicate moderate to considerable contamination in specific areas and suggest that localized anthropogenic activities may have contributed to metal accumulation. While the present environmental risk is generally low because most metals are retained within relatively stable geochemical fractions, changes in soil pH, redox conditions, or prolonged weathering could enhance the release and mobility of Cd and Pb. Such mobilization may result in soil and groundwater contamination, uptake by food crops, bioaccumulation through the food chain, and ecotoxicological impacts on soil microorganisms and vegetation. Prolonged human exposure, particularly to cadmium and lead, may increase the risk of kidney dysfunction, neurological disorders, developmental impairment in children, skeletal damage, and other chronic health effects, underscoring the need for continuous environmental monitoring and sustainable land-use management.

Overall, the study establishes that the geochemistry of the Ikole–Itapaji area is controlled primarily by the composition and evolution of the underlying Precambrian Basement Complex. Nevertheless, the localized enrichment of potentially toxic metals highlights the need for periodic environmental monitoring, particularly in agricultural and residential areas, to prevent future ecological degradation and possible human exposure. The integrated approach adopted in this study provides a reliable framework for understanding basement rock petrogenesis, evaluating trace metal behaviour, and supporting sustainable environmental management and future mineral exploration within the study area.

5.1 Recommendations

Based on the findings of this study, the following recommendations are made:

1. Periodic environmental monitoring of soils within the Ikole–Itapaji area should be undertaken to track changes in trace metal concentrations, particularly cadmium (Cd) and lead (Pb), which exhibited localized enrichment in the Contamination Factor analysis.
2. Agricultural activities should be accompanied by routine soil quality assessments to ensure that trace metal concentrations remain within acceptable limits for sustainable crop production and to minimize the potential transfer of toxic metals into the food chain.
3. Anthropogenic activities capable of introducing heavy metals into the environment, such as indiscriminate waste disposal, excessive agrochemical application, and poorly managed artisanal activities, should be properly regulated to prevent further metal accumulation in soils.
4. Public awareness programmes should be implemented to educate local communities on the potential environmental and health implications of heavy metal contamination and the importance of adopting environmentally sustainable land-use practices.
5. Future studies should incorporate larger sample populations, seasonal sampling, groundwater and surface water analyses, and biological assessments to provide a more comprehensive evaluation of trace metal mobility, bioavailability, and ecological risk within the study area.
6. Advanced geochemical techniques, including isotope geochemistry, mineral chemistry, and geochronological analyses, are recommended to further constrain the petrogenesis, magma sources, and tectonic evolution of the granitoids within the Ikole–Itapaji Basement Complex.
7. The integrated geological and geochemical information generated in this study should be utilized as baseline data for future mineral exploration, environmental impact assessments, and land-use planning within the Ikole–Itapaji–Ake-Ako area and other parts of the Nigerian Basement Complex.

Declaration of competing interests

Ethical Approval

This study did not involve human participants, animals, or any form of clinical or ethical experimentation. Therefore, formal ethical approval was **not required**.

Declaration of generative AI and AI-assisted technologies in the manuscript preparation process

During the preparation of this work, the authors used ChatGPT (GPT-5-mini) to assist with language editing and content organization. After using this tool, the authors reviewed, revised, and verified all content to ensure accuracy, originality, and authenticity, and take full responsibility for the content of the published article.

Consent to Participate

As no human participants were involved in this research, obtaining consent for participation was **not applicable**. All research activities adhered to standard field and laboratory protocols without the involvement of people.

Consent to Publish

This study does not include any personal, sensitive, or identifiable information. Consequently, consent to publish was **not applicable**. All data presented are **scientific observations and analyses**, fully anonymized, and pose no ethical concerns.

Availability of Data and Materials:

The datasets used and analyzed during this study are available from the corresponding author upon reasonable request.

Authors' Contributions

Adeleke Ojo conceived and designed the study, conducted the geological field investigations, collected the rock and soil samples, carried out the laboratory investigations, performed the major oxide geochemical, sequential extraction, and environmental risk analyses, interpreted the results, prepared the figures and tables, and wrote, revised, and approved the final manuscript.

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