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Research Paper

Geochemical and Petrographic Assessment of the Sedimentary Ironstone Exposures of Kaduna-Ife, in the Northern Anambra Basin, Nigeria

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ABSTRACT: *This study presents a comprehensive petrographic and geochemical analysis of ironstone deposits in the Northern Anambra Basin, Nigeria, employing thin-section microscopy and X-ray fluorescence (XRF) spectroscopy. The primary objective was to evaluate these mineralogical composition, textural features, and geochemical characteristics to infer their depositional environment and assess their potential for economic utilisation.Petrographic examination revealed that the ironstones are predominantly composed of iron oxides, notably hematite and goethite, with significant amounts of silica andalumina. Quartz grains exhibited undulose extinction and embayment against the groundmass, indicating minimal alteration and a stable depositional environment. Biotite minerals displayed pleochroism and were associated with alteration products, reflecting diagenetic processes that have contributed to the iron enrichment of the rock. The opaque minerals, likely iron oxides, indicate lateritic weathering under oxidising conditions.Geochemically, the ironstones exhibited high iron content, averaging approximately 49.265%, with low levels of deleterious elements such as sulfur and phosphorus. The silica content was within permissible limits, while the alumina content was relatively high, suggesting the presence of gangue materials. The low levels of calcium oxide and the absence of sulfur oxides point to an oxidising environment during deposition.These findings align with those observed in other ironstone deposits in Nigeria, such as the Agbaja ironstone, which also exhibits high iron content and low levels of sulfur and phosphorus. The integrated petrographic and geochemical analyses indicate that the ironstones of the Northern Anambra Basin formed under conditions conducive to iron enrichment, likely through processes such as lateritic weathering and diagenetic alteration. The high iron content and favourable geochemical characteristics suggest that these ironstones have the potential for economic exploitation, provided that the silica and alumina content are reduced in the beneficiation process. This research contributes to understandingthe mineralogical and geochemical characteristics of ironstone deposits in theMamu Formation of the Northern Anambra Basin by providing valuable insights for future exploration and exploitation endeavours.*

KEYWORDS: *Northern Anambra Basin; Ironstones; Geochemistry; Petrography*

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I. INTRODUCTION

Ironstone deposits within the Northern Anambra Basin have been the subject of considerable geological interest due to their economic significance and implications for basin evolution and paleoenvironmental reconstruction (Akpunonu&Igwebuike, 2024). However, unlike the numerous studies focusing on coal deposits within the Mamu Formation, ironstones within this formation have received limited attention. These ironstones, typically occurring as oolitic, pisolitic, or ferruginous sandstones, are believed to have formed through chemical precipitation and diagenetic processes in a range of depositional environments (Ladipo et al., 1994; Agunleti&Salau, 2015). Petrographic (thin section) and geochemical (X-ray fluorescence, XRF) analyses are essential in understanding the mineralogical composition, diagenetic history, and elemental distribution of these ironstones, providing insights into their provenance, depositional conditions, and post-depositional modifications.

The Anambra Basin, a Cretaceous sedimentary basin in southeastern Nigeria (Alege et al., 2015; Adamu et al., 2018a & b), hosts significant ironstone deposits within formations such as the Mamu, Nsukka, and Enugu Formations.Kaduna-Ife ironstone deposit forms part of the iron ore resource of the Anambra Basin; although not extensively occurring and generally not in substantial quantity, the Kaduna-Ife ironstone deposits are a part of the stretch of ironstone deposits in Mamu Formation, Northern Anambra Basin (Fig.1). The study area, Kaduna-Ife forms a part of the Cretaceous sediments of the Northern Anambra Basin and lies within Longitudes 7^0 44' 00" N to 7^0 45' 00" N and Latitudes 007^0 33' 00" E to 007^o 34' 00" E on sheet 249, Soko SW (Fig. 2). Previous studies (Mucke, 1994; Ladipo et al., 1994) have attributed the formation of these ironstones to a combination of detrital input, marine incursions, and lateritic weathering processes under fluctuating climatic conditions. Lateritic weathering is a process of chemical weathering that occurs in hot and wet tropical areas, leading to the leaching of silica and the concentration of iron oxides, which is likely the reason for the high iron content in these deposits. However, there remains a gap in understanding the geochemical signatures and diagenetic pathways that led to the enrichment and preservation of iron-bearing minerals within these units, particularly within the Mamu Formation in the Northern Anambra Basin.

This study aims to characterise the petrography and geochemistry of ironstone deposits within the Northern Anambra Basin, explicitly focusing on the Mamu Formation, to elucidate their depositional history, diagenetic modifications, and provenance. The specific objectives include: (a). Conducting thin-section petrography to determine the mineralogical composition, texture, and diagenetic features of the ironstones. (b). Utilizing X-ray fluorescence (XRF) analysis to establish the major and trace element geochemistry of the ironstones. (c). Evaluating the paleoenvironmental conditions and diagenetic processes responsible for forming and preserving these ironstones.

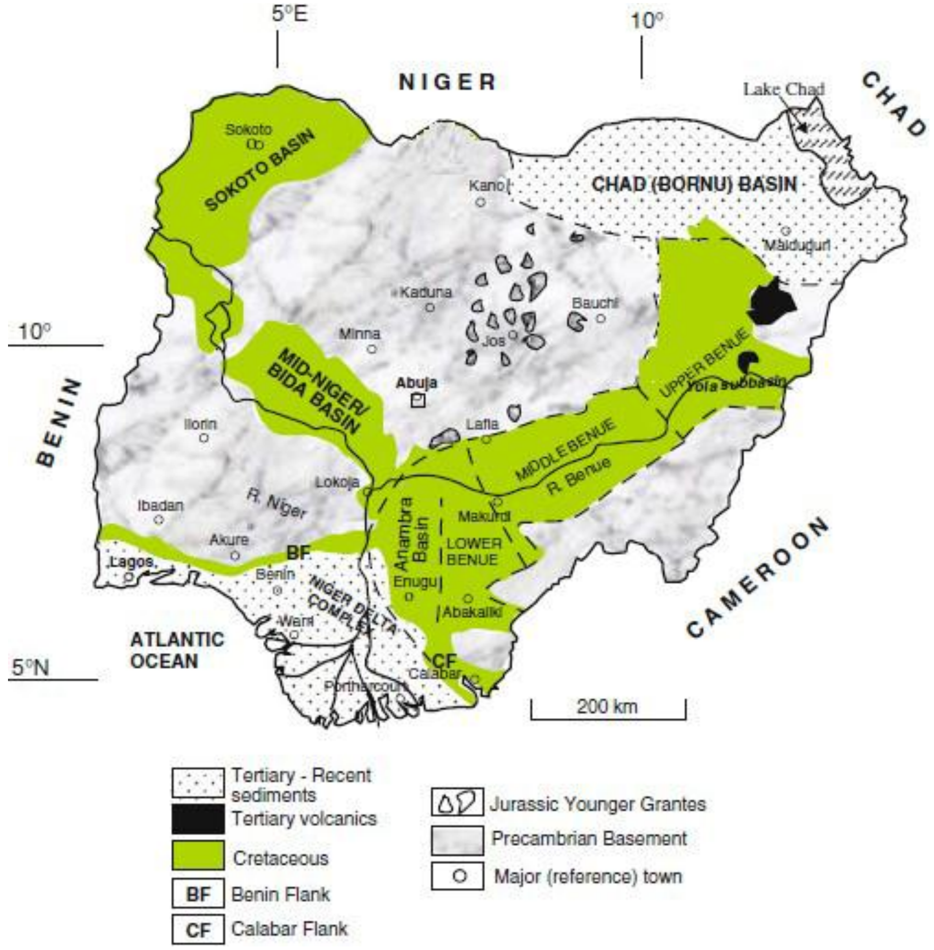

Figure 1: Geological Map of Nigeria showing the various Basins and Basements (after Obaje, 2009)

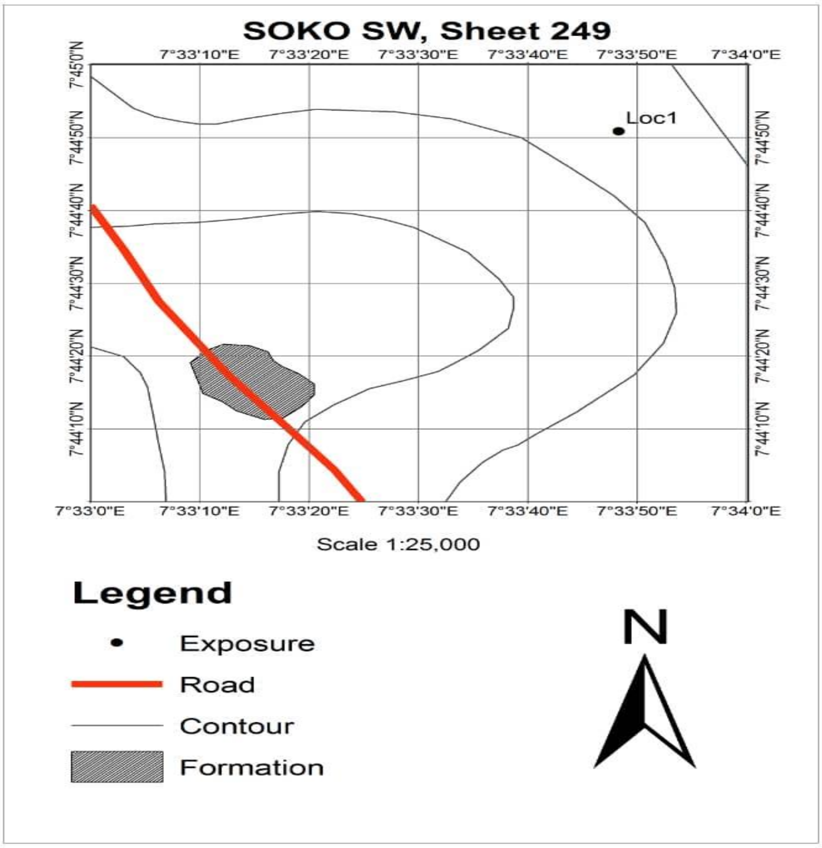

Figure 2: Topographical map of Kaduna-Ife, Soko SW sheet 249 (study area)

II. METHODOLOGY

Fieldwork was conducted in Kaduna-Ife, Ajaja and Abejukolo-Ankpa road in Kogi State within the Northern Anambra Basin, specifically within the Mamu Formation, to identify and document ironstone exposures. A systematic mapping approach was adopted, utilising traverse mapping techniques along accessible outcrops and riverbank sections (Alege et al., 2020; Alege et al., 2023a & b)). The lithological characteristics, bedding structures, and stratigraphic relationships of the outcrops were recorded (Idakwo et al., 2013; William et al., 2024). Fresh ironstone samples were collected using a geological hammer at each sampling point, ensuring minimal contamination. GPS coordinates of sampling locations were recorded, and field observations regarding texture, colour, and mineralogical variations were documented (Izge et al., 2020). Samples were then carefully packaged and taken to the laboratory for further analysis.

The geochemical composition of the ironstones was determined using X-ray fluorescence (XRF) spectrometry, following the standard analytical procedures outlined by prior geochemical studies (Agunleti&Salau, 2015; Okeke et al., 2023; Alege et al., 2024). The samples were first crushed into fine powders and homogenised before being subjected to XRF analysis. The major oxides (SiO_2 , Al_2O_3 , Fe_2O_3 , MgO, CaO, Na_2O, K_2O, TiO_2 , P_2O_5 , and MnO) were quantified to assess the geochemical variability and elemental enrichment trends within the ironstone deposits (Agunleti&Salau, 2015).

Heating powdered samples measured loss on Ignition (LOI) at 1000°C to determine volatile components such as bound water, organic matter, and carbonate phases (Alege & Alege, 2013).The results were used to infer depositional conditions, provenance, and post-depositional modifications affecting the ironstones.

Thin-section analysis was conducted to determine the mineralogical composition and microtextural features of the ironstones. Samples were cut into thin sections (30 µm thickness) using a diamond saw and mounted on glass slides following standard petrographic procedures (Agunlet&Salau, 2015). Thin sections were analysed under a polarising petrographic microscope to identify the primary and secondary mineral phases, grain morphology, and diagenetic features such as cementation, compaction, and replacement (Bonda et al., 2017).The results were used to interpret depositional environments and diagenetic alterations affecting the ironstones (Izge et al., 2020).

III.RESULTS

3.1. Lithology

Within the study area, a large mass of ironstone was encountered; the exposure was located within the coordinate of 7° 44ˈ 52ˈˈN and 7° 33ˈ 48ˈˈE belonging to the Mamu Formation within the Northern Anambra Basin. It was taken with a GPS accuracy of ±3m at 342m. It consists predominantly of fine-grained rocks with dark brown shale of uncertain bed thickness at the base, overlain by an ironstone unit of 1.7m, respectively, covered by a lateritic capping of 0.3m.The shale unit of the study area occurs as thick beds with traces of shells in their matrix. It is dark brown and relatively fine-grained. The shale combines clay and tiny silt materials. Lateritic capping, the topmost layer of the exposure, consists of iron and silica. Like the basal layer of shale, the laterite is weathered with a light brown colouration(Fig.3).

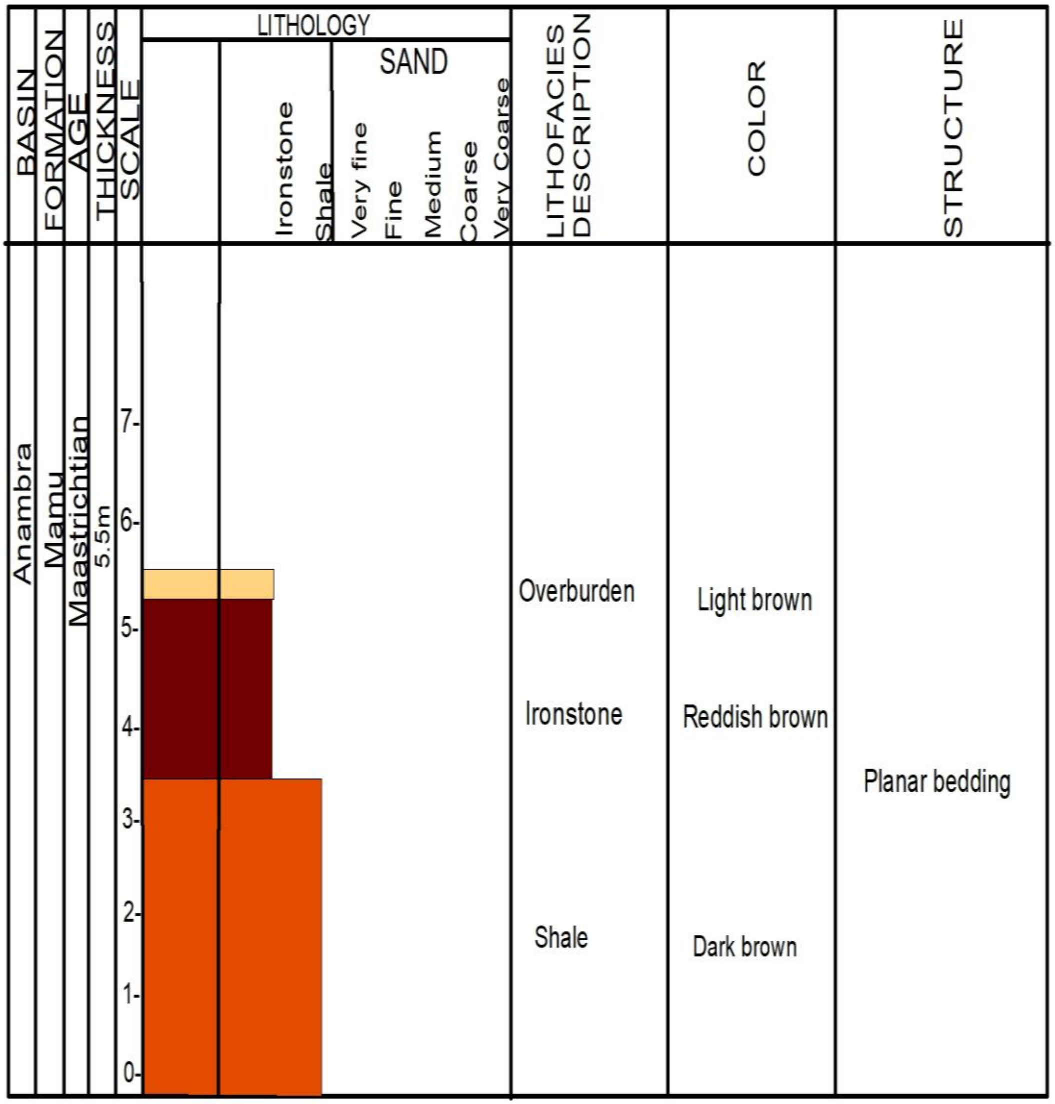

Figure 3: The outcroplog section shows the different lithologies in the study area

3.2. Petrographic analysis

The results of the thin-section analysis of Kaduna-Ife ironstone samples under cross-polarized light and polarised plane light are presented below as Plates 1-3.

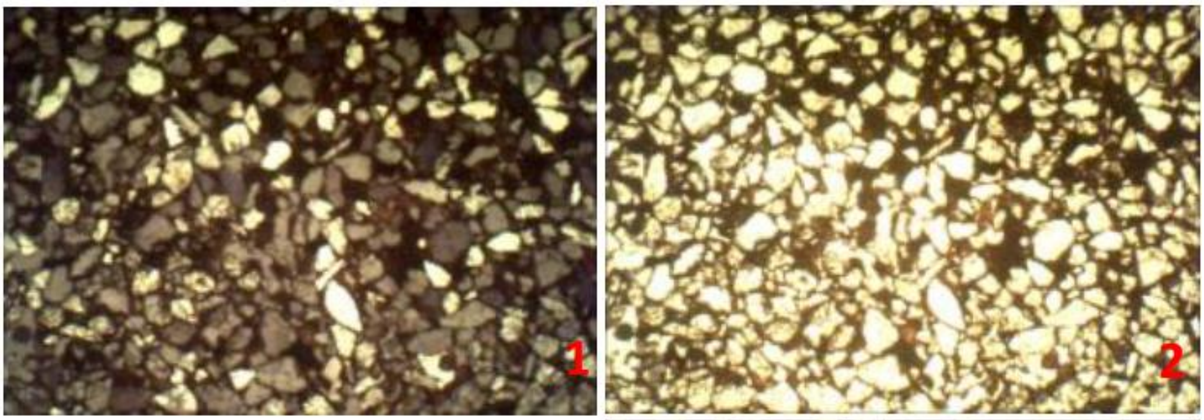

Plate 1: Photomicrographs of sample 1 ironstone under cross-polarized light (1) and polarised plane light (2) (Magnification: x25)

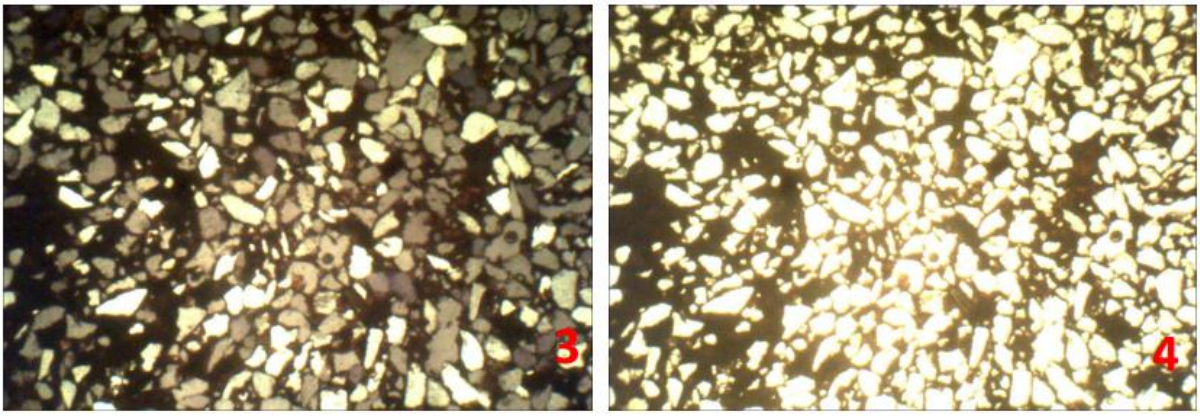

Plate 2. Photomicrographs of sample 2 ironstone under cross-polarized light (3) and polarised plane light (4) (Magnification: x25)

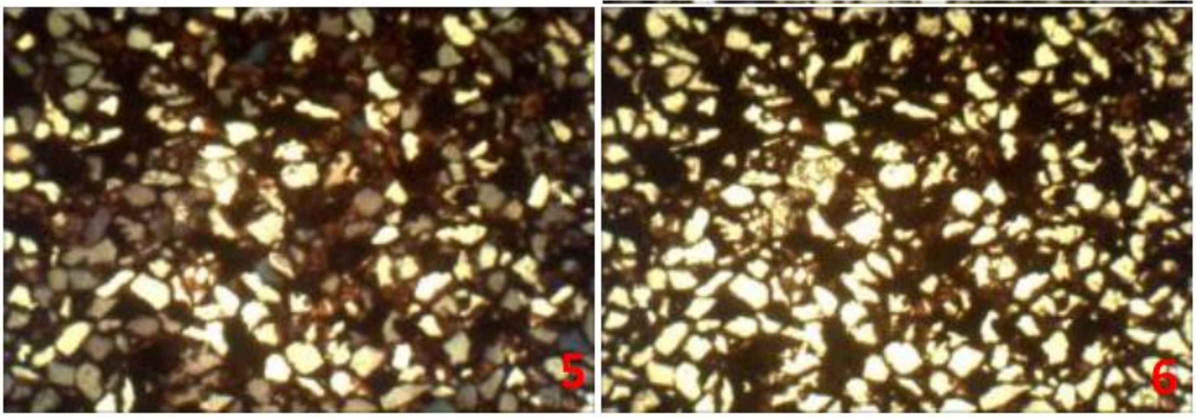

Plate 3: Photomicrographs of sample 3 ironstone under cross-polarized light (5) and polarised plane light (6) (Magnification: x25)

3.3. Geochemistry

Eleven significant elements were identified in the geochemical result and reported as oxide per cent by weight (wt %) for SiO_2, Al_2O_3, FeO_3, MgO, CaO, Na_2O, K_2O, TiO_2, P_2O_5, MnO, and LOI (Table; Figs 4 & 5).

Table 1: Chemical composition (wt. %) of Kaduna-Ife Ironstone

Oxide %	**Sample 1**	**Sample 2**	**Average%**
SiO_2	32.960	32.950	32.955
Al_2O_3	12.540	12.550	12.545
FeO_3	49.280	49.250	49.265
MgO	0.030	0.030	0.030
CaO	0.010	0.010	0.010
Na_2O	0.010	0.010	0.010

K_2O	0.010	0.010	0.010
TiO_2	0.020	0.020	0.020
P_2O_5	0.200	0.210	0.205
MnO	0.300	0.030	0.165
LOI	4.640	4.930	4.785
	100	100	100

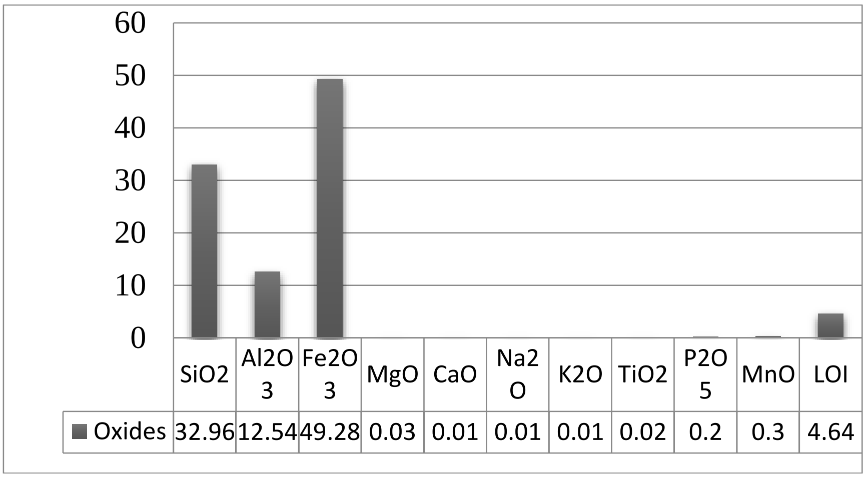

Figure 4: Bar chart showing distribution patterns of the geochemical elements (Wt %) in ironstone in sample 1

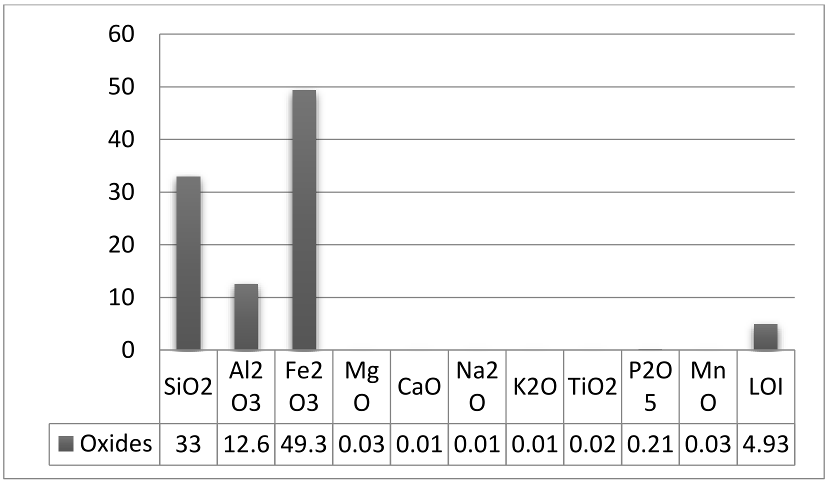

Figure 5: Bar chart showing distribution patterns of the geochemical elements (wt. %) in ironstone in sample 2

IV. DISCUSSION

4.1. Mineralogy and diagenesis

The petrographic analysis revealed that quartz, biotite and opaque minerals are major mineral constituents (Plates 1-3). The quartz mineral was generally unaltered and lacked twinning. It also shows undulose extinction (changes from whitish /milky colour to blue) when the stage is rotated. This suggests some strain within the quartz crystals, often due to tectonic stress or recrystallisation during diagenesis (Tucker, 2001).

Poor cleavage is visible in both cross-polarized and plane-polarised light. Under plane-polarised light, the quartz minerals have embayment against the groundmass of the rock, indicating that the quartz was partially cemented during the later stages of diagenesis (Siehl& Thein, 1989). Under crossed polarised light, the crystals show a white interference colour.The unduloseextinctionsuggests some degree of strain within the quartz crystals, often due to tectonic stress or recrystallisation during diagenesis (Tucker, 2001).

Thebiotite mineral shows brown and green colour. It is pleochroic because of the change from brown to black when rotated. When viewed under plane-polarised light, the grains exhibit numerous dark brown to black pleochroic haloes. On the other hand, the cross-polarized light revealed a mottled appearance characteristic of micaceous minerals exhibited by biotite minerals near extinction. The presence of biotite further indicates that biotite is a primary mineral in the rock that may have been subjected to some alteration, leading to the formation of iron-rich minerals like goethite or hematite (Morad, 1998). Also, its presence suggests that the ironstone could have formed in a depositional environment with moderate to high temperatures, where the biotite was stable before undergoing alteration (Van Houten& Bhattacharyya, 1982).

The opaque mineral was void of extinction and retained black in both plane and cross-polarized light. They were not affected by twinning nor exhibited pleochroism. They do not allow the passage of light.The absence of extinction and pleochroism in the opaque minerals suggests that they are primary iron oxide minerals formed during the later stages of the diagenesis or weathering processes (Van Houten& Bhattacharyya, 1982). Their persistence in the rock points to their role in cementing the matrix and contributing to the ironstone's high iron content, which indicates lateritic weathering processes or ferruginization under oxidising conditions.

Overall, the petrographic features of the study area reflect an ironstone that has undergone significant diagenesis and alteration, with a primary mineralogical composition influenced by iron oxide precipitation in an oxidising environment. The presence of quartz and biotite indicates that the source rock for the ironstone may have been a granitoid or metamorphic rock, which provided the necessary minerals for the formation of ironstone in the basin (Folk, 1980; Morad, 1998).

4.2. Depositional conditions and Diagenesis

The dark brown colouration of Kaduna-Ife ironstone is indicative of extensive weathering, primarily resulting from the leaching of silica minerals. This process occurs due to the chemical alteration and replacement of silica-rich shale by iron compounds through prolonged chemical weathering (Folk, 1980; Siehl& Thein, 1989). The oxidation-reduction reactions involved in this process facilitate the mobilisation and removal of silica while promoting the precipitation of iron-rich minerals such as hematite (Fe_2O_3), goethite (FeO(OH)), and siderite ($FeCO_3$) (Tucker, 2001). This transformation occurs under conditions where fluctuating redox states enhance the dissolution of silicate minerals and the concurrent enrichment of iron oxides and hydroxides, leading to the characteristic colouration and ferruginization of the rock (Berner, 1984; Van Houten& Bhattacharyya, 1982). The light brown colouration of the laterite suggests that the silica content has been leached out (Taylor &Eggleton, 2001).

The dominant oxide in the samples is Fe_2O_3, with an average value of 49.265% (Table 1), confirming the iron-rich nature of the deposits. Such high Fe_2O_3 concentrations are characteristic of ironstone formations that develop through lateritic weathering and chemical precipitation in oxygenated environments (Siehl& Thein, 1989; Morad, 1998). The formation of these deposits is primarily linked to the leaching of silica and alumina in tropical to subtropical climatic conditions (Alege et al., 2024), leading to the concentration of iron oxides such as hematite (Fe_2O_3) and goethite (FeO(OH)) (Van Houten& Bhattacharyya, 1982; Taylor &Eggleton, 2001).The high Fe_2O_3 content (49.265%) suggests that the ironstones are highly ferruginous and formed through iron precipitation in a chemically active environment, possibly linked to marine incursions or lateritic weathering (Agunleti&Salau, 2015).

SiO_2 is the second most abundant oxide in the study, averaging 32.955%, followed by Al_2O_3 at 12.545% (Table 2; Figs 4 & 5). The relatively high silica content suggests incomplete silicate leaching, possibly due to variations in groundwater conditions or post-depositional diagenetic influences (Tucker, 2001). The presence of Al_2O_3 indicates the retention of alumino-silicate minerals such as kaolinite, which is commonly associated with ironstones formed under tropical weathering regimes (Folk, 1980).The moderate SiO_2 (32.955%) and Al_2O_3 (12.545%) indicate the presence of quartz and aluminosilicate minerals, which may be detrital contributions from surrounding basement rocks (Mucke, 1994).

The very low concentrations of MgO (0.03%), CaO (0.01%), Na_2O (0.01%), and K_2O (0.01%) suggest minimal contribution from carbonate or feldspathic materials. This is consistent with ironstone deposits that have extensively leached mobile elements, leaving behind a residual concentration of iron oxides and aluminous clay minerals (Berner, 1984; Siehl& Thein, 1989).

The presence of P_2O_5 (0.205%) and MnO (0.165%) is noteworthy, as phosphorus is often associated with biogenic activity, particularly in shallow marine or lacustrine environments where upwelling promotes phosphatisation (Morad, 1998). The minor manganese content suggests localised reducing conditions, possibly linked to periodic fluctuations in water chemistry that influenced iron and manganese precipitation (Van Houten& Bhattacharyya, 1982).

The loss on ignition (LOI) values (4.785%) reflect volatile components, mainly related to hydroxyl-bearing minerals such as goethite, kaolinite, or organic matter. The moderate LOI suggests partial dehydration of iron oxides and some degree of post-depositional alteration (Taylor &Eggleton, 2001).

Furthermore, the dominance of Fe_2O_3 over FeO(Table 1) suggests that oxidation played a significant role in the ironstone diagenesis, transforming ferrous iron minerals into ferric oxides such as hematite and goethite(Akpunonu&Igwebuike, 2024).The silica and alumina components imply post-depositional silicification and kaolinite formation, supporting lateritic weathering and prolonged exposure to tropical weathering conditions (Obot&Anyakwo, 2012).

The geochemical (XRF) analysis of the Kaduna-Ife ironstoneconfirms that the ironstone deposits in the Northern Anambra Basin are primarily ferruginous with significant silica and alumina components. Iron precipitation influenced their formation under fluctuating redox conditions, detrital influx, and lateritic weathering. The geochemical signature of the studied samples is consistent with ironstones from the Agbaja Formation, suggesting a possible genetic link or similar depositional processes (Hassan &Jimoh, 2019).The results also align with previous studies on Nigerian ironstones and contribute to refining models of their genesis and diagenesis (Ojo, 1995; Okoro &Nwajide, 2008; Hassan &Jimoh, 2019).

V. CONCLUSION

This study provides a comprehensive petrographic and geochemical characterisation of ironstone deposits in the Northern Anambra Basin, utilising thin-section analysis and X-ray fluorescence (XRF) spectroscopy. The findings reveal that the ironstones are predominantly composed of iron oxides, notably hematite and goethite, with significant amounts of silica and alumina. The quartz grains exhibit undulose extinction and embayment against the groundmass, indicating minimal alteration and a stable depositional environment. Biotite minerals display pleochroism and are associated with alteration products, reflecting diagenetic processes that have contributed to the iron enrichment of the rock. The opaque minerals, likely iron oxides, indicate lateritic weathering under oxidising conditions.

Geochemically, the ironstones exhibit high iron content, averaging approximately 49.265%, with low levels of deleterious elements such as sulfur and phosphorus. The silica content is within permissible limits, while the alumina content is relatively high, suggesting the presence of gangue materials. The low levels of calcium oxide and the absence of sulfur oxides point to an oxidising environment during deposition. These geochemical characteristics align with those observed in other ironstone deposits in Nigeria, such as the Agbaja ironstone, which also exhibits high iron content and low levels of sulfur and phosphorus.

In conclusion, the integrated petrographic and geochemical analyses indicate that the ironstones of the Northern Anambra Basin formed under conditions conducive to iron enrichment, likely through processes such as lateritic weathering and diagenetic alteration. The high iron content and favourable geochemical profile suggest that these ironstones have potential for economic exploitation, provided that beneficiation processes are employed to reduce the silica and alumina content. Further studies, including reserve estimation and exploration of beneficiation techniques, are recommended to assess the commercial viability of these ironstone deposits.

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