Geochemical and Mineralogical Investigation of Iron Mineralization in Ardogu and its Environment, Central Nigeria: Implications for Origin and Resource Potential

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Abstract

Geochemical and mineralogical studies of iron ores in Ardogu and its environments, in central Nigeria were done to characterize it for iron mineralization and resource potential. Thirty core ironstone samples were selected from ten drilled boreholes for geochemical and mineralogical analyses. Geochemical results of selected samples reveal higher concentrations of Fe_2O_3 with low contents of SiO_2, Al_2O_3, P_2O_5, CaO and MnO. The geochemical based ternary plot classified the iron ores as ironstone. A petrographical investigation of 10 selected samples reveals the composition of oolites and pisolites with the presence of few quartz grains within the iron rich mineral grains. Qualitative and quantitative mineralogical study using x-ray diffraction shows mineral assemblages including; iron oxides, silicates and carbonates. Mineralogical compositions and textural characteristics of the ironstones suggest genesis related to syngenetic and diagenetic processes. The paleoenvironment during deposition of the Fe-rich sediments is suggested to be an anoxic, organic rich and reducing condition during early diagenesis but with the development of the oolitic and pisolitic textures, there were prevalent oxidizing and dehydrating conditions. The similarity between the chemical data of the studied ironstones with some published data within Bida Basin shows economically viable market values.

Keywords: core samples, oolitic iron ore, geochemical, Ardogu, Bida Basin.

1. Introduction

Iron whose estimates have been put at about 4.7% of the earth's crust; occurs in high percentages in almost all sedimentary rocks [1]. Researchers like [2, 3] among others have concluded that iron concentrations in most of the sedimentary rocks are in few percentages, but less commonly occur in form of ironstones or iron formations where its content is more than 15% corresponding to 19.3 and 21.4 wt.% FeO and Fe_2O_3 respectively. Generally, the sedimentary rocks that are rich in iron are defined as those containing 15% Fe or more, these rocks are commonly described as ironstones or iron formations. The mobilization and fixation of the iron are determined by the environmental conditions such as oxidizing and alkalinity conditions, thereby aiding the precipitation of insoluble iron (Fe^{3+}oxides/hydroxides); conversely, acidic and reducing environmental conditions aid the dissolution of ferrous compounds. The released irons precipitate easily as oxides or hydroxides as well as substitutes for Mg and Al in many iron bearing minerals based on prevailing environmental conditions [4]. The behavior of iron and its precipitated minerals are governed by the low temperature geochemistry of the earth's surface and/or diagenetic environment [5]. Iron may precipitate as ferric oxide or hydrate (e.g. maghemite, goethite, hematite, lepidocrocite), as a ferrous-ferric oxide (magnetite), as a ferric-ferrous silicate (glauconite), as ferrous-ferric silicate (e.g. chamosite, greenalite), as a carbonate (siderite), or as a sulfide (pyrite, marcasite, or less stable precursors) [6]. The physico-chemical properties of iron-rich rocks vary greatly, as they may or may not contain >50% ooids, pisoids, peloids and oncoids. Sedimentary iron ores are found in three main classes which are bog iron ores, ironstones and banded iron formations [7]. Banded iron formations are Precambrian in age, whereas ironstones are formed in Phanerozoic age [1]. Those irons in Phanerozoic occur essentially as thin sequences deposited in non- marine or shallow marine environments [8].

The study area of this research is located at Ardogu within the southern Bida Basin, central Nigeria (Figure 1). Generally, ironstone deposits in the Bida Basin (e.g. Agbaja, Patti, Bassange, Ate, Sakpe, Batati, Koton Karfi, Okofi) had been studied by various authors including [9, 10, 11, 12, 13, 14 and 15]. The ironstone deposits in Bida Basin have been estimated to be about 2 billion tons [13]. However, there had been no report on the investigation and characterization of iron ore in Ardogu and its environs unlike those mentioned above. This study therefore, aimed at evaluating the mineralogical characterization of the iron deposit in Ardogu and its suitability for exploitation. To achieve these aims, geochemical and mineralogical studies which are paramount in iron-ore characterization were employed to investigate and evaluate the ore potential for resource development. This will also guide future exploration for associated minerals. This is important now, due to the recent clamour by the new government of Federal Republic of Nigeria for other resources as a substitute for the Oil and Gas.

2. Geological setting

The Bida Basin is an embayment whose trend is in NW-SE and perpendicular to the main axis of the Benue Trough and Niger-Delta Basin of Nigeria [16, 17]. It is a rift bounded tensional structure resulting from faulting that is associated with the Benue Trough system separating the African and Brazilian plates [18]. However, a wrench fault tectonic model was suggested by [10]. It is a two-fold sedimentary basin comprising the Northern and Southern Bida sub-basins (Figure 2). The Northern Bida sub-basin consists of Bida Sandstone Formation (Doko and Jima member), Sakpe Ironstone Formation, Enagi Siltstone Formation and Batati Ironstone Formation. The southern Bida sub-basin consists of the Lokoja Formation, the Patti Formation and Agbaja Ironstone Formation.

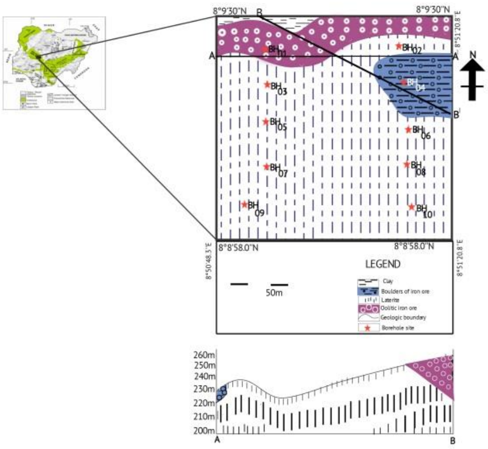

Figure 1: Map showing the geology of area study and the borehole points

AGE	NORTHERN BIDA BASIN		SOUTHERN BIDA BASIN		DEPOSITIONAL ENVIRONMENT
Maastrichtian	Batati Formation		Agbaja Formation		Continental-Shallow marine
	Enagi Formation		Patti Formation		Brackish-Shallow marine
	Sakpe Formation				
Campanian	Bida Formation	Jima Member	Lokoja Formation	Claystone (member) Sandstone (member)	Continental Fluvial Deposits
		Doko Member		Basal Conglomerate (member)	
					Unconformity
Pre-Cambrian - Paleozoic					Basement Complex

Figure 2: Generalized stratigraphic sequence of the Bida Basin (Adapted from [17]).

3. Analytical methodology

Samples from ten (10) diamond core drilled boreholes were collected at regular interval per borehole and at points of good core recovery. The samples were then subjected to series of analytical methods including; petrographic, mineralogical and geochemical analysis. A total of 30 samples (3 from each borehole) were collected for the laboratory analysis. These samples were pulverized to a size of ~200 μm for chemical analysis. The selected representative samples were analyzed for major elements using X-ray fluorescence spectrometry at the National Steel Raw Materials Exploration Agency Laboratory, Kaduna, Nigeria while the generated data were processed with statistical analysis for further interpretations. The qualitative and quantitative mineralogical composition of 10 selected samples was determined by X-ray diffraction (XRD) at the Geology laboratory, University of Pretoria, South Africa. Preparation and petrographic studies of thin and polished sections for mineralogy, texture and microstructural characterization were conducted at the Department of Geology, Kwara State University, Malete, Kwara State.

4. Result presentation

4.1. Geochemistry

The result of the geochemical analysis is shown in Table 1 while their mean values are presented in Table 2. The mean result revealed higher iron-oxide (Fe_2O_3) content with values ranging from 50.70 to 70.79% (average=62.91%). Other oxides have relatively low concentrations compared to the iron-oxide (e.g. Al_2O_3 9.13-15.67%; SiO_2 5.63-11.27%; P_2O_5 1.75-2.63%; CaO 0.11-0.91% and MnO 0.10-0.39%). According to [19], the anomalous

Table 1. Geochemical result showing oxide compositions of iron ore from Ardogu

BH	Sampling Depth (m)	SiO_2	Al_2O_3	P_2O_5	CaO	Fe_2O_3	MnO	TiO_2
01	2.5	7.64	13.04	2.05	0.18	76.86	0.004	0.23
	5.0	9.75	13.09	2.67	0.28	73.64	0.57	ND
	7.5	3.56	8.55	1.52	ND	86.17	0.02	0.17
02	2.0	12.32	18.15	3.24	0.23	65.31	0.51	0.23
	4.0	10.14	16.01	2.54	0.28	70.39	0.64	ND
	6.0	8.71	16.86	4.92	0.27	68.82	0.42	ND
03	3.0	12.00	16.00	2.20	0.13	67.42	0.18	0.25
	6.0	8.80	13.00	2.20	0.24	73.48	0.13	ND
	9.0	13.00	18.00	2.40	0.23	63.30	0.15	0.29
04	2.0	9.70	13.00	2.20	0.20	72.60	0.13	0.24
	4.0	13.00	18.00	2.00	0.17	64.52	0.18	0.26
	6.0	8.90	12.00	2.00	0.25	75.25	0.059	0.002
05	2.0	9.48	10.86	2.13	0.27	76.42	0.84	0.002
	4.0	13.07	18.29	2.35	0.24	65.45	0.24	0.37
	6.0	7.90	11.00	2.30	0.22	76.20	0.19	ND
06	2.0	8.03	11.29	2.99	1.04	76.41	0.23	ND
	4.0	11.00	13.00	2.30	1.61	69.91	0.25	ND
	6.0	15.93	19.61	3.55	0.41	59.62	0.85	0.04
07	3.0	11.00	16.00	2.60	0.327	67.55	0.38	ND
	6.0	7.70	10.00	2.30	0.28	76.67	0.46	ND
	9.0	12.00	16.00	1.80	0.21	67.81	0.052	0.004
08	3.0	8.00	12.00	2.20	0.124	75.65	0.30	ND
	6.0	3.27	7.21	1.40	ND	87.39	0.61	0.12
	9.0	8.12	12.58	2.43	0.28	76.30	0.28	ND
09	2.0	11.09	17.17	3.57	0.20	67.75	0.22	ND
	4.0	15.51	20.68	2.84	0.14	60.44	0.06	0.31
	6.0	8.80	12.00	2.30	0.19	74.78	0.093	ND
10	2.0	13.00	17.00	2.00	0.19	66.57	0.003	0.24
	4.0	6.26	10.97	2.29	1.17	78.69	0.59	ND
	6.0	10.00	15.00	2.60	0.383	69.62	0.10	0.29

Table 2. Average oxides composition values of iron ore from Ardogu

Sample	Al_2O_3	SiO_2	P_2O_5	CaO	Fe_2O_3
BH01	11.84	7.15	2.10	0.16	78.75
BH02	17.86	10.95	3.71	0.27	71.45
BH03	15.67	11.27	2.27	0.20	68.07
BH04	14.30	10.20	2.07	0.21	70.79
BH05	13.19	10.04	2.28	0.25	74.24
BH06	14.82	11.55	2.95	1.09	69.59
BH07	14.00	10.23	2.13	0.27	70.68
BH08	10.56	6.51	2.02	0.13	80.80
BH09	16.36	11.64	2.87	0.18	68.94
BH10	18.35	12.51	2.95	0.74	65.45
Average	14.70	10.21	4.34	0.35	71.88

concentration of iron in all ore samples (Table 2) is caused by the removal of SiO_2, MgO and CaO while Al_2O_3 concentrations in the iron ore might be sourced from the alumina contents.

Goethite is the main iron oxide mineral with subordinate amounts of hematite and magnetite with maghemite as a trace. Kaolinite and quartz were identified as gangue minerals. Trace amounts of siderite present as the only iron sulphide phase. Stability of hematite in an oxidizing environment is higher but, it is low in reducing environment. It is formed by the dehydration of goethite through the removal of hydroxyl sheets and some of the oxygen in strips parallel to the c-axis to form water. In the studied samples, hematite increases upward and does confirm field observations but goethite is more abundant in the samples IL01 - IL07. Magnetite (Fe_3O_4) is also present as one of the ferromagnetic minerals, and this might have yielded maghemite by oxidation process according to [20].

4.2 Mineralogical Compositions

4.2.1 Petrographic Study

Petrographic studies of the ten (10) samples reveal that iron ore is composed of variable ooids consisting primarily of iron oxides, broken pieces of older ooids and pisolites while most of the quartz grains are present as inclusions within the iron rich mineral grains. It is generally noted that the deposit is composed of more ooidal ironstones varieties than quartz types (Figure 3).

4.2.2 X-Ray Diffraction

The relative abundance of minerals for bulk samples was determined through the X-Ray Diffraction technique (Figure 4). Generally, bulk mineralogical studies reveal mineral assemblages as follows; iron oxides/hydroxides (hematite, goethite, magnetite and maghemite) which have low solubility, hence, high stability, obvious coloration and high surface area are very effective sorbents for dissolved species. Kaolinite and quartz are the most common silicate minerals in samples IL01 and IL07– IL11, whereas siderite ($FeCO_3$) was identified in samples IL08, IL09 and IL10 as the only carbonate mineral present (Table 3). The result indicates that the source of iron (Fe^{2+}) is from goethite, hematite, magnetite and/or siderite because these minerals are found in all the analyzed samples.

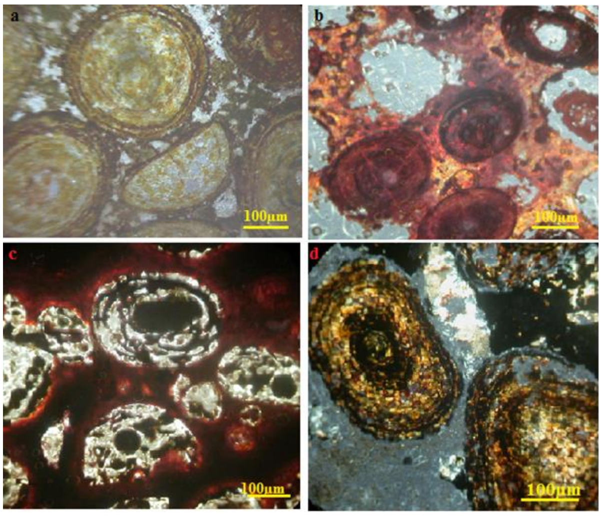

Figure 3: Thin-section photomicrographs of the ironstone of Ardogu: (a) Ooids consisting of kaolinite in a slightly ferruginized groundmass (IL08; PPL), (b) Ferruginized and redeposited pisoids in a goethite groundmass (IL02; CPL), (c) Ooids consisting of goethite partially replace by kaolinite consisting of goethite groundmass (IL01; CPL) and (d) Partially altered ooids replaced by siderite embedded in a groundmass consisting of kaolinite (IL10; CPL).

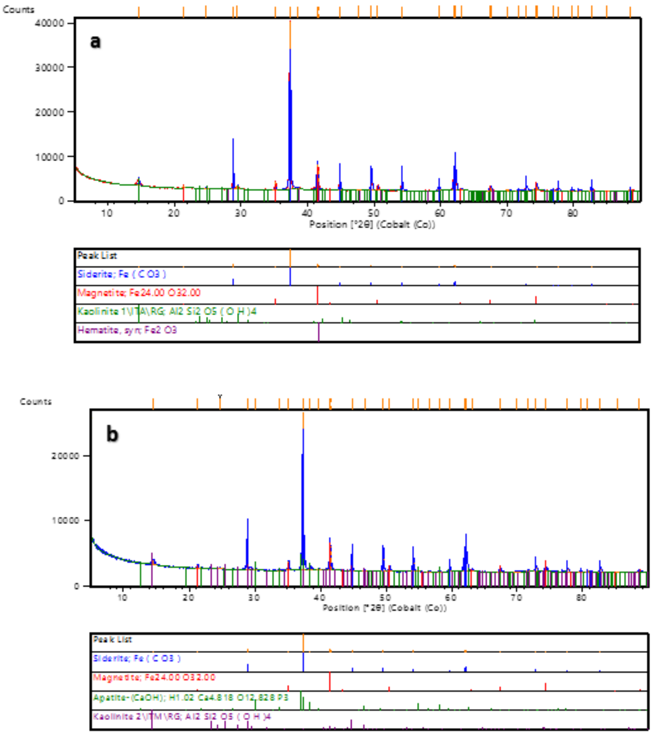

Figure 4: XRD result of analyzed ironstones (a) IL09 and (b) IL 10) showing the mineralogical composition presented in table 1 based on their peaks.

Table 3:
Bulk quantitative and qualitative results of the ironstone from XRD analysis

Minerals	IL01	IL02	IL03	IL04	IL05	IL06	IL07	IL08	IL09	IL10
Goethite	88.71	85.69	100.0	85.87	76.22	69.09	51.48	-	-	-
Hematite	4.84	3.65	-	1.6	8.05	3.03	5.75	-	4.80	-
Magnetite	-	10.67	-	12.53	15.74	-	-	4.22	16.45	18.04
Maghemite	-	-	-	-	-	27.87	42.77	-	-	-
Kaolinite	5.22	-	-	-	-	-	-	6.91	19.40	5.07
Quartz	1.24	-	-	-	-	-	-	-	-	-
Siderite	-	-	-	-	-	-	-	88.87	59.35	67.91
Apatite	-	-	-		-	-	-	-	-	8.98

4.4 Statistical analysis

Statistical methods employed in this study include correlation; factor and cluster analyses and they were utilized for further confirmation of the data collected from the bulk chemical analyses.

4.4.1 Correlation coefficient

Geochemical results of the oxides composition of iron ores presented in table 1 were subjected to statistical analysis to reveal their geochemical behavior and attributes. Correlation analysis is a statistical test that determines the linear association between the pairs of data. [21] stated that the coefficient of correlation 'r' has its value range from -1.0 to +1.0 and indicates the linear relationship between the pairs of data. The negative sign shows negative correlation while the positive sign indicates positive correlation and zero indicates no correlation. The following terms after [22] were adopted in this study to explain the type of relationship among different oxides in the studied iron ore samples.

Very strong: where (r) between (±0.99 to ±0.75).
Strong: where (r) between (±0.74 to ±0.50).
Moderate: where (r) between (±0.49 to ±0.38).
Weak: where (r) between (±0.37 to ±0.0).
Where significant value of (r) = 0.38.

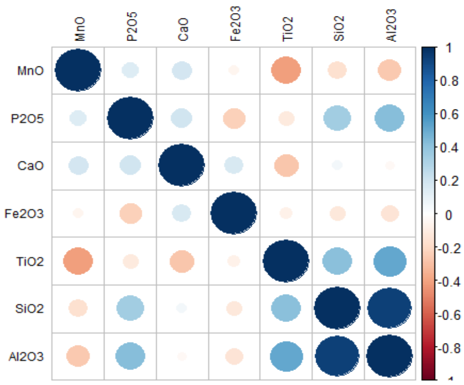

Figure 5: Graphical representation of the correlation analysis.

4.4.2 Factor analysis

The factor analysis (Principal Components Analysis) was also employed to clarify and determine the important factors affecting the oxide distribution and their predominant associations within the group of geochemical variables [23]. This Principal Component Analysis (PCA) was carried out based on chemical analyses of thirty samples. The significant value (p=0.0034) has been adopted in the interpretation, and any value less than 0.05 is significant. In this set of samples (Fe_2O_3, SiO_2, Al_2O_3, P_2O_5, CaO, MnO and TiO_2), two distinct geochemical groups (factors) with contribution of 80.00% were delineated among the oxide compositions. Factor 1 is composed of oxides SiO_2, Al_2O_3 and P_2O_5 whereas Factor 2 is composed of CaO, and MnO. These factors are further interpreted as follows:

Factor 1 (F1)

Factor 1 relates positively with Al_2O_3, SiO_2 and P_2O_5 but negatively with Fe_2O_3, MnO and TiO_2. This factor contributes 31.1% of the total cumulative variance. The oxides in this group represent the replacement and silicification processes of iron oxides/hydroxides. This factor also expresses clay minerals occurrences in the iron ore of Ardogu.

Factor 2 (F2)

Factor 2 accounts for 48.7% of the cumulative variance and relates positively with P_2O_5, MnO and CaO but negatively with SiO_2, Al_2O_3 and TiO_2. The relationship among these oxides is interpreted to account dominantly for the presence of clay minerals.

5. Discussions

5.1 Genesis and Paleoenvironment

The relationship of iron oxides mineral assemblages (hematite, magnetite and goethite), silicates (kaolinite, quartz) and carbonates (siderite) throws some light on the diagenetic history. Mineralogical studies also reveal the presence of Fe-rich materials (e.g. hematite and goethite) which were probably formed by secondary diagenetic processes such as intense chemical weathering of the pre-existing claystones and later conversion of Fe-rich materials initially contained in unconsolidated ooids in abundance. This suggestion aligns with the submission of [24] that hematite in sedimentary rocks is formed primarily by diagenesis of a hydrated ferric oxide precursor, e.g. goethite. The ternary geochemical field classification using SiO_2–Fe_2O_3–(FeO+MnO) diagram classified the iron ore in Ardogu and its environments to be sedimentary in origin as expected, therefore referred to as ironstones (Figure 5). The mineralogical compositions (e.g. goethite and hematite) and textural characteristics (i.e. Fe-oxyhydroxides, ooids and peloids) of the studied ironstones may suggest composition from both intra-basinal components and diagenetic components formed by the hematitization of the precursor amorphous Fe-oxyhydroxides as well as clay mineral (Kaolinite) which might probably due to the loss of carbonate that took place during the oxidation of ferrous iron to ferric. It can be suggested that initial Fe-rich material, probably amorphous hydroxides or goethite, was likely to have been produced by intense chemical weathering, lateritization, in a humid tropical climate.

The high abundance of iron (Fe_2O_3) concentrations in the geochemical result might be a good indicator that shows changes in oxygen fugacity that resulted in the precipitation of iron oxides under oxidizing conditions. Meanwhile, hematite which is identified in abundance in the studied samples is suggested by [25] and [24] to be a stable mineral under moderate to strongly oxidizing conditions. Also, siderite ($FeCO_3$) as identified in few oolitic ironstone samples is suggested to have precipitated at negative Eh, i.e., under reducing conditions, with high carbonate activity and low sulfide activity in sediment pore-waters [25, 24 and 26], because low sulfide activity is rarely attained in marine sediments because of abundant dissolved sulfate. Therefore, based on the above, it can be deduced that there was a change in paleoenvironmental conditions from strongly reducing conditions to relatively oxidizing conditions. Generally, abundant of oolitic ironstones in the deposit might be due to the reworking process by the large amounts of iron supplied to the marine environment during the reworking of terrestrial weathering products. This is because most of the ooids in the samples are not broken and have smooth outlines, which possibly indicate the in situ origin of these ooids. The sediments, which make up the initial iron oolite, probably represent an anoxic, organic rich, reducing situation in a shallow-marine environment. The anoxic conditions that accommodate siderite precipitation may have also developed through bacterial decomposition of organic matter. After the formation and consolidation of the initial ooids, the material was converted to hematite ooids during diagenesis. Statistically, it is interesting to note that the distribution style of SiO_2 as revealed in the geochemical data indicates two sources within the environment. The strong positive correlation between SiO_2 and Al_2O_3 (r=0.94) is attributed to the source of SiO_2 from quartz whereas strong correlation of TiO_2 with Al_2O_3 (r=0.51), moderate correlations of TiO_2 with SiO_2 (r=0.41) and TiO_2 with MnO (r=-0.41) may be attributed to the source from aluminosilicate which is indicated by the presence of kaolinite which is present as the only clay mineral. Low distribution of CaO contents in the chemical data supported by low siderite composition and weak correlation of CaO with Fe_2O_3 (r= 0.16) may suggest non-carbonate environment. Also, low correlation of CaO with SiO_2, P_2O_5 (0.05 and 0.20 respectively) might be attributed to the low silicification and phosphatization process.

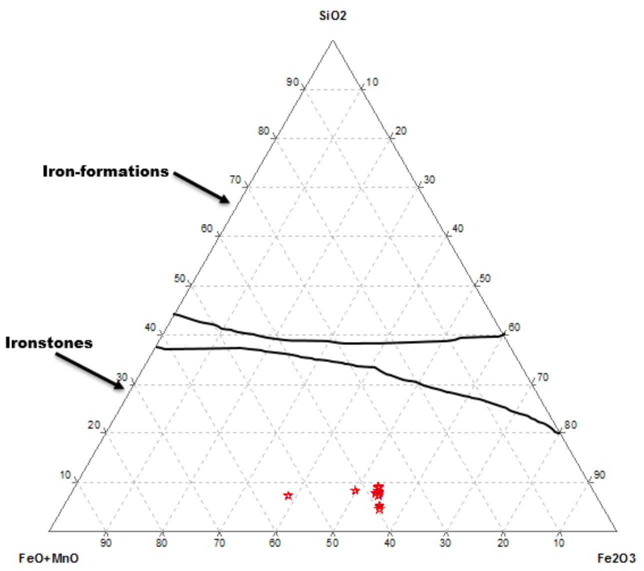

Figure 5: Ternary (FeO+MnO)-Fe_2O_3-SiO_2 diagram of Ardogu samples plotted within ironstones samples [27].

5.2 Ore Mineralization and Resource Potential

The geochemical result of the ironstones is closely related with the mineralogical investigation and the results compare well with typical iron deposits in Nigeria (Table 4). According to [28], silica is one of the principal deoxidizers used in the making of steels to improve soundness i.e. to be free from decay or defects which increases the strength and hardness of steel, therefore, the silica in form of SiO_2 is low in this result and this compare favourably with other published data as presented in table 3. Low phosphorus content supports increases resistance to corrosion and improves machinability in free cutting steels; therefore, sufficient phosphorous removal may be only possible by pyrometallurgical or hydrometallurgical processes.

Table 4
Average Chemical Composition of Ironstone from Ardogu compared with other deposits in Bida Basin, Nigeria

Element	Present Study	Okofi Ore (%) [29]	Agbaja Ore (%) [30]	Koton-Karfe (%) [31]	Patti (%) [31]
Fe_2O_3	48.52	57.35	42.80	47.10	52.16
Al_2O_3	12.78	7.56	9.60	5.75	1.00
SiO_2	8.92	7.90	5.29	3.84	8.55
P_2O_5	2.18	1.00	2.20	2.20	4.20
MnO	0.26	0.07	0.01	0.17	-
CaO	0.30	0.18	0.42	0.30	-

6. Conclusions

The mineralogical, petrographical and geochemical studies of the ironstone in Ardogu, southern Bida Basin Nigeria were studied to characterize it for industrial development and usage. Higher concentrations of Fe_2O_3 with low CaO, P_2O_5, MgO, TiO_2, Al_2O_3 and SiO_2 contents in the studied samples are well compared with iron deposits data from other parts of Bida Basin, Nigeria. The discrimination diagram based on major elements SiO_2-Fe_2O_3-(FeO+MnO) reveals the sedimentary origin of the ironstone. Mineralogical data showed that the ironstone is oolitic and pisolitic type and are composed mainly of iron mineral assemblages (hematite, goethite, magnetite and maghemite) with little carbonates (siderite) and silicates (kaolinite, quartz). The mineral assemblages are essentially related to diagenetic processes such as iron oxides replacements, silicification and goethitization in addition to mechanical and chemical compaction in an anoxic condition. Correlation and factor analysis also reveal signature to support diagenetic processes. It can therefore be concluded that integrated geochemical petrographical and mineralogical study deemed this deposit as economical. By incorporating the additional value of so-products and the application of the current metallurgical processing technologies, this deposit shows the potential to be economically viable in the present market.

Conflicts of Interest

The authors of this paper hereby state that we do not have any conflicting interest

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