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Geochemical and Petrogenetic Characterization of Ironstone Deposit from Agbaja Formation, Southern Bida Basin, North Central Nigeria

Jubril Izge Hassan

Lecturer, Department of Geology, Federal University Lokoja, Nigeria

Jimoh Abdullateef Onimisi

Lecturer, Department of Geology, Federal University Lokoja, Nigeria

Abstract:

The Campano-Maastrichtian Agbaja Ironstone Formation of the Lokoja district, central Nigeria occur within the Upper Cretaceous sequence of the Bida Basin, central Nigeria, and forms a major part of the enormous iron ore reserve of the Middle Niger Embayment. The Agbaja Ironstone Formation shows some characteristics which are typical of major ironstone deposits of the world. Phanerozoic ironstones from different localities around the world were known to have many features in common; comparable geological setting, similar mineralogy, deposition in a marine environment, the occurrences of ooids in Fe rich strata and intercalation with sandstone, siltstone, mudstone and limestone. These features indicate a similar genesis for all ironstone occurrences, with some local differences and variations. The present study indicates that the Agbaja Ironstone Formation conforms to only a few of these characteristics. In general, the low MgO content, which in most cases falls below the detection limit is good evidence against marine origin for the ooidal and pisoidal ironstones of Agbaja Formation of the Bida Basin and supports reworking of the kaolinitic beds to form ooids possibly as a result of persistent fluvial input and shallowing of the basin and these point to the absence of the favourable conditions necessary for the precipitation of chamosite which was thought to be the precursor mineral for all ironstone deposits. In terms of trace elements, the Agbaja ironstone is similar to ironstone deposits from other parts of the world. Also, the enrichment in Fe_2O_3 and P_2O_5 and depletion in SiO_2 with low Al_2O_3 content does not agree with the insitu laterization process as genesis of the Agbaja ironstones but rather support secondary enrichment as the possible source of the iron and phosphorous enrichment in the deposit and the replacement process which involves removal of silica and alumina as iron is been enriched in the kaolinite precursor.

Keyword: Agbaja, ironstone, silica, alumina, kaolinite

1. Introduction

Iron is an essential ingredient for steel production and despite the anticipated transition into the "silicon age" there is yet to be any satisfactory substitute for steel in any industrialized society. With about 5 wt%, iron is the fourth most abundant element (after Oxygen, Silicon and Aluminum) in earth's crust (Gutzmer and Beukes 1998). Iron is hosted by deposits of various size, grade and origin and is known to occur in sedimentary, hydrothermal and magmatic environments. High-grade ores are usually formed by hydrothermal processes. However, more than 95% of exploited deposits till today are of sedimentary origin (Gutzmer and Beukes, 1998). Iron ores have a wide range of formation in geologic coupled with a wide geographic distribution. They are found in the oldest known rocks of the earth's crust, with an age in excess of 2.5 billion years, as well as in rock units formed in various subsequent ages.

Iron ore deposits occur in various locations in Nigeria, but mainly in the north-central, north-east and south-east regions (KPMG, 2012). The deposits typically occur in form of hematite, magnetite, metasedimentary bands of ferruginous quartzites, sedimentary ores, limonite, maghemite, goethite and siderite. These deposits are grouped into two prominent types; the Banded iron formation occurring in folded bands and lenses associated with the Precambrian metasedimentary schist belts outcropping in the western half of the country which includes the Tajimi, Itakpe, Ajabanoko, Ochokochoko, Toto, Farin Ruwa, Birnin Gwari, Kaura Namoda, % Kakun, Maru, Jama'are, Isanlu, Roni and Ogbomoso areas while the Cretaceous sedimentary deposits occur predominantly around Agbaja, Kotonkarfi, Bassange and Nsude areas respectively (MMSD 2010).

The ironstone deposit of the campano- maestrichtian mid Niger or Nupe basin around Bida and Lokoja districts covers a combined area of about 600km². Ore reserves of over 3billion tones assaying between 40-50% iron have been delineated for these districts (falconer, 1911; Jones, 1955; Adeleye 1976).

These oolitic ironstones formations were first documented by Falconer (1911) as capping to mount patti near Lokoja. Geological survey of Nigeria in 1955 mapped out an extensive ironstone deposit similar to the ones at mount patti around the Lokoja confluence. BRGM (1982) used Samples and lithologies from exploratory wells in these areas to delineate three target areas; Agbaja-mount patti, koton karfe and Basange.

Adeleye, (1971, 1973) suggested that the sediments within these areas were derived from igneous and metamorphic rocks adjacent to the basin. He based this on petrology, heavy mineral analysis and general paleoscope of the middle Niger valley. He suggested a lagoonal subtidal deltaic environment for the deposits.

Several authors have proposed different models as to the origin of the ironstone deposits; Falconer (1911) & Adeleye, (1973) suggested a Syn-sedimentary origin for the ironstones because their depositional characteristics and relationship with other sediments of the basin shows that the ooids were formed within a high energy domain. Du Preez, (1956); Jones, (1955, 1956) and Kogbe, (1978) proposed a lateritic origin based on the absence of fossils in the ironstones bed and presence of Fe-oxide and hydroxide in the ooids. Umoroah, (1987) proposed a diagenetic origin based on petrographic and semi XRD studies, while Abimbola (1994,1997); Mucke (1994); Mucke et al, (1999) and Ladipo et al, (1994) suggested a post-diagenetic iron enrichment origin for the deposit. Elueze, (1999) also describe the deposit as a product of sedimentation and subsequent supergene enrichment.

Jones, (1955, 1965) based on thin section microscopy suggested the ironstones deposits to belong to the European Minnete-type while Mucke et al, (1999) indicated that the deposits are different from the minette-type to which they were previously thought to belong in several ways. They argued that due to the low MgO concentration in the inferred marginal marine depositional environment, a transformation of the sedimentary kaolinitic precursor into chamositic clay minerals during diagenesis failed to occur. Mucke, (1994); Mucke et al, (1999); Ladipo et al (1994), and Abimbola (1997) suggested that the primary matrix material is dominantly kaolinite which was feruginized under post-diagenetic conditions.

Mucke and Farshad (2005) using chemistry, also classified these deposits as kaolinite type.

The present study has the principal objective of providing data on the distribution pattern of major and trace elements in the ironstone deposit which will provide more clues to further understand the genetic characterization and economic potential of these ores for steel production.

1.1. Location and Accessibility

The study area is located to the eastern half of the Nupe Basin, around the Confluence of river Niger and river Benue in central Nigeria (Figure 1). The area falls within the Lokoja district of Abimbola (1994), and lies within latitude 7°54' to 8°00' N and longitude 6°38' and 6°43' E. The Agbaja plateau is one of the three major ironstones deposits isolated as plateau in these area, the other two being Kotonkarfi (North of the Lokoja Confluence) and Basange (South of the Confluence). The plateau is situated west of the confluence, about two kilometers (2Km) west of Okene-Lokoja road and is accessible through Felele-Agbaja road which was paved halfway from Felele to Okpomaba and unpaved from Okpomaba to Agbaja. These and the footpaths were well utilized in the course of the field mapping.

Figure 1: Accessibility Map of the Study Area

1.2. Geology of the Study Area

From the geological mapping, the northern and south eastern part of the study area is covered by the Agbaja plateau which is underlain essentially by ironstones while the southwestern half is dominated by sandstone units and Precambrian basement rocks (Figure 2). The hilly plateau is underlain by ironstones and sandstone lenses in some places capped by lateritic and lithified concretionary materials which supports little or no vegetation and thick bushes and farms can only be seen in places with laterites and where the hard-concretionary crust have been broken down. The margin of the plateau is always steep and sometimes abrupt near the top. There is poor exposure of the ironstone units, the only exposures being at weathered stream channels, edges of the plateau and road-cuts notably along Okpomoba- Agbaja road. At the base of the plateau, the drift is made up of reddish brown to grey lithified sandstone which form small ridges bounded to the plateau with a sharp contact to the ironstones. At some distance away from these ridges and towards the western part of the study area, conglomerates were observed at stream channels and closer to basement rocks. These basal conglomerates which are mostly sub-angular to rounded pebbles are believed to be the contact between the

basement complex rocks and the Lokoja formation which overlies it but the boundary seems to be rather gradational. The western and southern part of the study area is underlain by Precambrian basement rocks which are mostly granites and gneisses.

Figure 2: Sketch Geological Map of Nigeria Showing the Location of Bida Basin (After Obaje 2011), Blocked Area Represents the Location and the Geology of the Study Area

2. Methodology of Geochemical Analysis

Geological field mapping was carried out to ascertain the distribution of various rock units and update the geological map of the study area. Eleven (11) representative samples of the ironstones were selected for geochemical analysis. The samples were pulverized to fine powder form at the Nigerian institute of science and technology laboratory, Samonda, Ibadan using pulverizing machine. Five (5) grams of each sample were collected in a dispensing envelope and labeled. The samples were then sent to Bureau Veritas (Acme) laboratories, Vancouver, Canada for further preparation and analysis. All elemental determination was done using the inductively coupled plasma mass spectrometry (ICP-MS) LF202) package at the Acme Laboratory in Vancouver, Canada.

Geochemical results of major and some trace elements were statistically and graphically treated to show their chemical behavior and characteristics in Agbaja oolitic and pisolitic ironstones.

The correlation coefficients of the major and some trace elements of the Agbaja ironstone samples was also analysed. The following terms were used in this study to explain the type of relationship among different elements in the 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 (after, Murdoch and Barnes, 1985).

3. Results and Discussion

Total whole rock characterization (major and trace elements) was carried out on eleven (11) representative samples. The results are presented in tables with the $\text{Fe}_2\text{O}_{3(\text{t})}$ representing the total iron oxide present in each sample. The results for the major oxides and trace elements with their range and averages are presented in (Tables 1, 2, 4 and 5 respectively). Statistical (correlation analyses) and graphical methods were utilized for analyzing data collected from the bulk chemical analyses.

3.1. Major Elements

Result of the major element (Oxides) concentration is given in tables (1 and 2). The concentration of SiO_2 is lowest in the Oolitic/pisolitic ironstone deposits where its concentration ranges between 2.19-7.63% with an average of 3.74%. The silica content ranges from 21.46-40.08% with an average of 32.93% in the silty concretionary ironstones.

$\text{Fe}_2\text{O}_{3(\text{t})}$ content is higher in the oolitic and pisolitic deposit than the other samples, its concentration ranges from 66.85 – 78.35% with an average value of 74.08% in the oolitic/pisolitic ironstone while it ranges from 48.51-65.37% with an average of 54.68% in the silty concretionary ores. These clearly shows that there is an increase in the concentration of iron

oxide as the silica content reduces which implies that, the marked enrichment of iron in all the ore samples is attributed to the iron-bearing minerals and effective removal of SiO_2 during weathering (Gutzmer *et al.*, 2008).

Alumina ranges from 5.07-10.90% with an average value of 6.97% in the oolitic and pisolitic ironstones while in the silty concretionary ironstones, it ranges from 1.61- 2.27% with an average value of 1.95%. MgO and CaO have concentrations below 0.1% in the oolitic/pisolitic ironstones with values below detection limits of 0.01% in the silty concretionary ironstones while Na_2O , K_2O and TiO_2 have very low concentration values less than 0.05% in most of the sample. MnO ranges from 0.01-0.125% with an average of 0.06% in the oolitic and pisolitic ironstones and lower values in other samples while Cr_2O_3 has concentration values below 0.03% in all the samples analyzed.

Concentration of P_2O_5 ranges from 1.61-3.62% in the oolitic and pisolitic ironstones with an average of 2.63% which is higher than the silty concretionary ironstone where it ranges from 0.37-1.65% with an average of 1.08%. Total carbon concentration ranges from 0.12-0.18% with an average value of 0.16% in the oolitic and pisolitic ironstone samples and lower values for the rest of the samples. However Total sulphur is below the detection limit of 0.02% in most of the samples except in the silty concretionary ironstones where its concentration ranges from 0-0.16% with an average value of 0.09%. Loss of ignition (LOI) value which depicts the content of water in the samples is higher in the oolitic and pisolitic ironstones where it shows concentration value which ranges from 9.1-13.50% with an average concentration value of 11.97%. This value reduces in the concretionary ironstone where it has a range of 8.0-9.8% with an average of 8.80%.

Oxides(Wt%)	L1	L2	L6A2-2	L9	L17	BH1	BH3	Range	Averages
SiO_2	2.44	2.31	2.19	2.71	4.46	4.45	7.63	2.19-7.63	3.74
Al_2O_3	5.43	5.15	5.59	5.07	5.87	10.90	10.75	5.07-10.90	6.97
$\text{Fe}_2\text{O}_3(\text{t})$	78.21	76.43	75.54	74.90	78.35	68.29	66.85	66.85-78.35	74.08
MgO	0.06	Bdl	Bdl	Bdl	0.02	Bdl	Bdl	0-0.06	0.04
CaO	0.06	0.14	0.04	0.07	0.08	0.06	0.09	0.04-0.14	0.08
Na_2O	Bdl	0.01	0.02	Bdl	0.01	Bdl	Bdl	0-0.02	0.01
K_2O	Bdl	0.01	Bdl	Bdl	Bdl	Bdl	Bdl	0-0.01	0.01
TiO_2	0.20	0.15	0.12	0.15	0.15	0.24	0.18	0.12-0.24	0.17
P_2O_5	2.19	2.98	2.71	3.62	1.61	2.86	2.41	1.61-3.62	2.63
MnO	0.09	0.05	0.05	0.02	0.05	0.01	0.12	0.01-0.12	0.06
Cr_2O_3	0.02	0.01	0.01	0.011	0.02	0.02	0.02	0.010-0.02	0.02
TOT/C	0.16	0.13	0.16	0.13	0.22	0.18	0.12	0.12-0.18	0.16
TOT/S	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	0.00	Bdl
LOI	11.00	12.40	13.50	13.10	9.10	13.00	11.70	9.10-13.5	11.97
Total	99.86	99.77	99.93	99.78	99.94	100.01	99.87		

Table 1: Major Elements Concentration in Agbaja Oolitic and Pisolitic Ironstones

*Bdl: Below Detection Limit

Oxides (Wt%)	L3	L5	L6A4	L12	Range	Average
SiO_2	40.08	21.46	37.63	32.56	21.46-40.08	32.93
Al_2O_3	1.89	2.01	2.27	1.61	1.61-2.27	1.95
$\text{Fe}_2\text{O}_3(\text{t})$	48.51	65.37	49.37	55.47	48.51-65.37	54.68
MgO	Bdl	Bdl	Bdl	Bdl	—	—
CaO	Bdl	Bdl	Bdl	0.02	—	0.02
Na_2O	Bdl	0.01	Bdl	Bdl	—	0.01
K_2O	0.02	0.03	Bdl	0.04	0.02-0.04	0.03
TiO_2	0.58	0.72	0.20	0.10	0.10-0.72	0.40
P_2O_5	0.81	0.37	1.50	1.65	0.37-1.65	1.08
MnO	0.01	0.02	0.03	Bdl	0.01-0.03	0.02
Cr_2O_3	0.005	0.006	0.004	0.004	0.004-0.006	0.00
TOT/C	0.08	0.09	0.08	0.06	0.06-0.09	0.08
TOT/S	Bdl	0.16	0.08	0.02	0.00-0.16	0.09
LOI	8.00	9.80	8.90	8.50	8.00-9.80	8.80
Total	100.00	100.00	100.10	100.00		

Table 2: Major Elements Concentration in Silty Concretionary Ironstones

*Bdl: Below Detection Limit

[illegible]

	Zr	Zn	V	U	Th	Sr	Pb	Ni	Cu	Co	As	Cr ₂ O ₃	SiO ₂
	.345	-.635	.379	.489	.566	.045	-.596	-.629	.266	-.067	.065	.827	Fe ₂ O ₃
	-.661	.461	.178	-.036	-.381	-.076	.545	.435	-.056	.423	.439	-.675	Al ₂ O ₃
	.789	-.637	.099	.259	.575	-.149	-.680	-.383	.338	-.213	-.183	.865	LOI
	.194	.390	-.901	-.738	-.394	.160	.093	.207	-.546	-.577	-.806	-.345	MgO
	-.074	-.054	.717	.451	.558	-.364	.458	.456	.229	.835	.308	.116	CaO
	-.220	.235	-.033	-.245	-.095	.746	.038	-.317	-.197	.070	-.123	.003	Na ₂ O
	-.513	.636	-.426	-.538	-.658	-.337	-.274	.481	-.320	.033	.132	-.614	K ₂ O
	-.241	.580	-.353	-.619	-.338	.568	.117	.105	-.374	.078	-.289	-.320	TiO ₂
	.911	-.658	.365	.412	.744	-.179	-.170	-.110	.573	.096	-.061	.778	P ₂ O ₅
	.053	.285	-.781	-.570	-.478	.564	.395	-.123	-.475	-.696	-.685	-.424	MnO
	-.260	.101	.441	.160	.615	-.017	-.022	.103	-.328	.672	-.172	.376	Cr ₂ O ₃
	.704	-.767	.568	.598	.847	-.179	-.520	-.378	.551	.174	.115	1	As
	-.093	-.479	.651	.698	.000	-.344	-.209	-.236	.754	.164	1		Co
	-.189	.195	.614	.188	.564	-.341	.161	.553	-.007	1			Cu
	.571	-.837	.614	.764	.341	-.374	-.364	-.337	1				Ni
	-.124	.634	-.185	-.475	-.019	-.554	.184	1					Pb
	-.438	.353	.010	-.073	-.116	.415	1						Sr
	-.285	.160	-.233	-.210	-.245	1							Th
	.504	-.523	.700	.568	1								U
	.236	-.847	.879	1									V
	.080	-.582	1										Zn
	-.636	1											Zr
	1												

Table 3: Correlation Coefficient for the Major Oxides and Some Trace Elements in Agbaja Oolitic and Pisolitic Ironstones

Wonder *et al.*, (1988) interpreted the chemical composition of ancient and recent metalliferous sediments to reflect contributions from seawater, hydrothermal, biogenic and detrital sources. Proposed methods for distinguishing between these sources are based on differences in their mineralogical, chemical and isotopic composition. Lottermoser and Ashley (1996) illustrated geochemical differences using a series of discrimination diagrams.

The presence or absence of certain elements in the rocks is much helpful and most significant as a pointer to the palaeo-environment and nature of deposition of the sediments in the area. The variations in the major and trace elements abundance also indicates a change in environmental condition of deposition (Mahadevan, 1986). The concentration and kind of element adsorbed or entering into the crystal structure depend on a number of factors which includes the pH, Eh, nature and structure of the adsorbent, availability and concentration of ions (Krauskopf, 1967), the rate of grain growth, rate of sedimentation and other various parameters (Glasby, 1977; Roy, 1981).

Table (3) shows that Fe₂O₃(t) correlates negatively with SiO₂, Al₂O₃, Cr₂O₃, TiO₂, P₂O₅, Zr and some other major oxides and trace elements while it correlates positively with the others.

In the Al₂O₃ – SiO₂ - Fe₂O₃ triangular diagram (Fig. 3), the ironstones plots outside the field of Precambrian BIFs (Govette, 1966) at dwarfed Al₂O₃ levels which is identical to post Precambrian oolitic ironstone deposits of Elueze, (1999), and toward Fe₂O₃ extreme.

Figure 3: $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ (T) Ternary Plot for the Analyzed Samples (After Govett, 1966)

Various factors have been used to determine the abundance of Fe in sedimentary rocks, these includes; provenance, pH & Eh conditions and extent of diagenetic alteration. The Fe content in sedimentary rocks is variable: clay, shale and greywacke (> 6% Fe), arkose (3% Fe), quartz-feldspathic sandstone (0.5% Fe) and carbonate rocks (0.5% Fe) while the iron-rich sedimentary rocks are defined as those containing (15% Fe) or more, and are commonly referred to as ironstones or iron formations (James, 1966).

Higher concentration of $\text{Fe}_2\text{O}_3(\text{t})$ is observed in the oolitic and pisolitic ore where its $\text{Fe}_2\text{O}_3(\text{t})$ contents are found to be higher than the upper concretionary iron units. There is a weak insignificant correlation of $\text{Fe}_2\text{O}_3(\text{t})$ with CaO ($r = 0.04$) and L.O.I ($r = -0.377$), this relationship points towards the absence of calcareous components in iron oxides / hydroxides minerals.

The strong negative correlations of Fe_2O_3 with Al_2O_3 ($r = -0.934$) and SiO_2 ($r = -0.746$) in the ironstone deposit may be due to strong enrichment of immobile Fe_2O_3 due to dominant iron-bearing primary minerals in the deposit. The very strong positive relation between SiO_2 and Al_2O_3 ($r = 0.810$) supported clay mineral (Kaolinite) as being the major contributor of the SiO_2 and Al_2O_3 contents.

The main alumina bearing secondary minerals are kaolinite and gibbsite. Elemental aluminum has the lowest residence time in water. Hence, alumina is relatively less mobile than iron and much less than silica during chemical weathering and therefore undergoes residual enrichment (Ramanaidou *et al.*, 2008). Thus, the relatively higher values of alumina in the Agbaja ironstones are believed to be due to residual enrichment processes. Thus, the slight enrichment of Al in the iron ores samples confirms the supergene origin of the ferruginous ooids and oncoids and argues against a primary marine origin.

Bonatti (1975) suggested that hydrothermal metal – rich deposits could be distinguished from hydrogenous deposits that are formed by diagenetic processes on the basis of the relative abundances of SiO_2 and Al_2O_3 . On the SiO_2 vs Al_2O_3 discriminatory plot (Fig. 4), the oolitic and pisolitic ironstones fall within the diagenetic domain signifying that the original chemical sediments necessary for the formation of the oolitic and pisolitic ironstones were purely diagenetic in origin.

Figure 4: Bivariate Plot of SiO_2 Versus Al_2O_3 for the Ironstones (After, Wonder Et Al., 1988; Crerar Et Al., 1982)

According to Bonatti (1975), pure chemical sediments are enriched in Si, Mn and Fe, but addition of detrital or volcanic material causes their dilution and enrichment of Ti, Al and Zr. The Positive correlation of Al_2O_3 and SiO_2 with Cr_2O_3 and Zr in the oolitic and pisolitic ironstones (Table 3) further indicates that these elements are clearly derived from detrital sources (Lottermoser and Ashley, 2000). Such correlation reflects a common origin for SiO_2 and Al_2O_3 as major oxides with trace elements bearing heavy minerals such as chromite, zircon, rutile and others.

Al_2O_3 and TiO_2 display strong positive correlation ($r = 0.679$) and both correlates negatively with Fe_2O_3 , these relationships are pointing towards an overwhelming component of orthochemical iron. Considering the fact that a typical detrital material has a low iron concentration, a likely source for the iron is definitely secondary enrichment as proposed by previous authors (Abimbola, 1997; Abimbola *et al.*, 1999; and Mucke, *et al.*, 1999). Conversely, the strong positive relationship between Al_2O_3 and TiO_2 implies that much of the Al and Ti may be derived from detrital component.

The Alkali oxides Na_2O and K_2O correlates positively and they both correlates negatively with both Al_2O_3 and SiO_2 which supports the depletion of both oxides in clay minerals (Hirst, 1962). Billings (1978) mentioned that the percentage of (Na) in sediments lesser than its percentage in earth's crust (2.9%, Mason, 1982) could be attributed to great dissolubility of Na through chemical weathering processes. Conversely (Fe) has great separation; therefore, the quantity of (Na) decreases in iron-rich sediments. In general, except for CaO, there is depletion of both the alkali and alkali earth metal oxides (Na_2O , K_2O and MgO) in the ironstones.

The oolitic and pisolitic Agbaja iron ores shows slight enrichment of MnO which shows negative relationship with Fe_2O_3 but relates positively with SiO_2 . Manganese in its 2^+ state is stable to higher oxidizing potential than Fe (Glasby and Schulz, 1999), thus, it may be enriched either during deposition in shallower more oxidizing environment or during diagenetic mobilization of Mn as documented in modern metalliferous sediment (Gurvich, 2006) and the positive relationship between Mn and Silica is in support of detrital materials from detrital source.

The iron ore samples show negative correlation between MgO and SiO_2 & Al_2O_3 suggesting that the MgO content is absent in the silicate phase, its negative correlation with CaO implies that it is unrelated to carbonate minerals while its very low content in the deposits rules out contribution from marine inputs. Its strong positive relation with Fe_2O_3 , V, Th, U, Co, Ni and Pb implies input from probably mafic mineral component.

Table (1) shows strong depletion of CaO in the Ironstones samples and these Strong depletion of CaO in iron-ore indicates the lack of carbonate minerals in the deposit, while the marked enrichment of iron in all the ore samples is attributed to the iron-bearing minerals and effective removal of SiO_2 , TiO_2 and CaO during weathering (Gutzmer *et al.*, 2008).

The weak positive relationship of MnO with CaO ($r = .152$) probably indicates lack of substitution of Ca^{+2} by Mn^{+2} which normally takes place under reducing sea water conditions (Bencini and Allesandro, 1974). The correlation coefficient of MnO with SiO_2 ($r = .492$) and Al_2O_3 ($r = .169$) indicates minimal relation between clay minerals and Manganese in the deposits. The negative correlation of MnO with Fe_2O_3 is attributed to the geochemical similarity in the behavior of Mn and Fe (Krauskopf, 1979) where there is possibility for the replacement of Fe^{+2} by Mn^{+2} in iron oxides containing Fe^{+2} in their structures; therefore, the negative relation of MnO with Fe_2O_3 in the oolitic and pisolitic Agbaja ironstone samples ($r = -.126$) may give an evidence to the replacement of Mn^{+2} by Fe^{+2} in the accessory minerals; rutile and ilmenite.

The low Mn content in the oolitic and pisolitic ironstone samples was probably due to the original low Mn content of source area. Thus, the depletion of MnO and MgO may be related to decomposition of ferromagnesian minerals while the enrichment of MnO exhibits that Mn^{2+} was oxidized to Mn^{4+} and was fixed as insoluble oxide and hydroxide into clay minerals as suggested by (Koppi *et al.*, 1996).

Table (3) clearly shows that there is very weak correlation between CaO and L.O.I ($r = -.172$). Also, there is weak negative correlation of L.O.I. with Fe_2O_3 ($r = -.377$) in addition to other negative relations of L.O.I with SiO_2 ($r = -.291$), TiO_2 ($r = -.027$), weak positive relationship with Al_2O_3 ($r = .108$), Na_2O ($r = .085$), K_2O ($r = .123$) and a very strong positive relationship with P_2O_5 ($r = .858$). This style of relationship above revealed that adsorbed water released through decomposition of carbonate minerals, dehydration or dehydroxylation of goethite and dehydroxylation of clay minerals, especially kaolinite contribute very little to L.O.I content analysed for the oolitic/pisolitic ironstones. Conversely the strong positive relation with P_2O_5 Suggest most of the LOI to be associated with phosphate minerals.

The negative to absence of correlations of CaO with SiO_2 ($r = .098$), Al_2O_3 ($r = -.089$), Ni ($r = -.317$), P_2O_5 ($r = .080$), Co ($r = .070$) and positive correlation with Zn ($r = .235$) also reflects the high effects of diagenetic processes in these deposits. Thus, the ferruginization probably occurred by descending solutions that causes the dissolution, migration and precipitation of various elements based on the Eh/pH conditions prevailing at the time. Such ferruginization phenomenon appeared to be an important phenomenon in the cretaceous, especially in late cretaceous Era in which agbaja ironstone deposits was formed (Mucke and Farshad, 2005).

The lack of significant correlation between P_2O_5 and CaO implies that Ca-P phase mineral such as apatite contributes very little to the phosphorus content of the deposit. Conversely, the inverse correlation of P_2O_5 with silica is possibly owing to the comparable absorption between P and Si into iron Oxy hydroxides (Konhouser, 2007). Thus, the weak negative correlation between P_2O_5 with SiO_2 and Al_2O_3 signifies possible replacement of kaolinite by Phosphorous bearing Mineral (though on a minor scale), indicating that the phosphorus is diagenetic and post diagenetic in origin.

The relatively high P_2O_5 -concentrations (up to 3.62 wt.%), the extremely low CaO-values, which are on average 0.08 wt.% in the ironstones, are in support of P_2O_5 occurring possibly in the form of florencite-(Ce) (Ce, Ca, Ba, Sr) $1.00 \text{ Al}_3 [(\text{OH})_6/(\text{PO}_3\text{OH})/\text{PO}_4]$ and also as strengite $\text{Fe}^{3+}[\text{PO}_4]_2\text{H}_2\text{O}$ as suggested by Mucke *et al.*, (1999). The positive correlation between

pairs of Sr and P_2O_5 ($r = 0.564$) and Sr-CaO ($r = 0.746$) suggest likely hosting of crandallite mineral group for Sr (Calagari *et al*, 2015) while the enrichment of Ba, Sr, Pb Zn, LOI and Ce in the ironstones coupled with the weak to strong positive correlation between P_2O_5 with these elements supports possible contribution of Phosphorous from minerals such as Pyromorphite [$Pb_5(PO_4)_3Cl$], Plumbogummite [$PbAl_3(PO_4)_2(OH)_5 \cdot H_2O$], Aaheylite [$(Fe,Zn)Al_6(PO_4)_4(OH)_8 \cdot 4H_2O$] or Hindsdalite [$(Pb,Sr)Al_3(PO_4)(SO_4)(OH)_6$].

The negative correlation of P_2O_5 with Cr ($r = -0.424$) supports its chemical affinity with V-Ni-Cr-Zn associations in the clay minerals. The mild weathering of ores might have been responsible for their redistribution within the sediment packages. The very high concentrations of iron and phosphate may entrap some Cr. On a minor scale, Cr^{+6} might have been replaced by P^{+5} in the sedimentary basin at the time of diagenesis (Prevot and Lucas, 1980; Saigal and Banerjee, 1987).

P_2O_5 shows negative correlation with Cu ($r = -0.475$). These may be due to leaching or partial weathering of the ore in which part of Cu might have been lost during diagenesis (Saigal and Banerjee, 1987; Singh and Subramanian, 1988).

The relationship of P_2O_5 with V is strongly negative (Table 3) which supports the mutual pentavalent ionic substitution of P_2O_5 by V^{+5} in the phosphorous bearing minerals. The weak positive relation of Zn and P on the other hand may be due to chemical affinity with P_2O_5 and adsorption by clay minerals (Cook, 1972; Banerjee and Saigal, 1988) and their existence on same mineral.

Goldschmidt (1954) reported that under some conditions, TiO_2 is absorbed by clay minerals. The anti-sympathetic relationship shown by 'detrital trace elements' is an inverse correlation with P_2O_5 content and such a relationship is clearly exhibited by TiO_2 (Table 3), which is predominantly in detrital rutile, ilmenite and leucosene (Cook, 1972).

There is a very strong correlation of TiO_2 with Al_2O_3 ($r = 0.679$) and SiO_2 ($r = 0.342$); the later could be attributed to the geochemical similarity between silica and titanium (Spears, 1961) while the earlier is probably from the common association of Ti and Al in clayey materials formed from products of residual weathering since Ti and Al are both hydrolysate elements (Mason, 1966) and are transported together by river to the basin of deposition (Lepp & Goldich, 1964 and Adekoya *et al.*, 2012), indicating that TiO_2 content in the ironstone may be attributed to kaolinite.

3.2. Trace Element

Twenty-Nine (29) trace elements were analyzed. The variations in concentrations of the trace elements in the samples analysed were given in Tables 4 and 5. In general, the trace elements of the ironstone samples are positively related to iron oxides/hydroxides and clay minerals due to their adsorption on the surfaces of these minerals while sometimes, they correlate negatively as could be seen for some selected elements in table (Table 3).

The trace elements analyzed for include: (Sc, Ba, Be, Sn and Zn) with minimum detection limit (MDL) of 1ppm, (Ag, Bi, Cd, Cs, Cu, Hf, Mo, Nb, Ni, Pb, Rb, Sb, Ta, Ti, U, Y, Zr) with minimum detection limit (MDL) of 0.1ppm, (As, Ga, Se, Sr and W) with minimum detection limit (MDL) of 0.5ppm, Co and Th with minimum detection limit (MDL) of 0.2, Hg with minimum detection limit of 0.01ppm and V with minimum detection of 8ppm respectively.

In the oolitic and pisolitic ores analyzed, the trace element concentration varies between 1 – 640.4 ppm. Most individual trace elements show wide concentrations.

Sample No/ Elements (PPM)	L1	L2	L6A62	L9	L17	BH1	BH3	Range	Averages
As	12.20	8.2.00	9.50	10.60	26.40	12.00	7.90	7.90-26.40	12.40
Ba	202.00	546.00	128.00	380.00	181.00	231.00	395	128-546	294.70
Be	11.00	28.00	12.00	20.00	10.00	150	8	8-28	14.90
Bi	1.20	0.90	0.70	0.80	0.90	0.50	0.8	0.5-1.2	0.80
Cd	0.30	0.50	0.20	0.40	0.10	Bdl	Bdl	0-0.5	0.30
Co	36.20	22.00	18.90	8.10	23.30	13.10	21.4	8.1-36.2	20.40
Cs	0.10	0.50	0.50	0.20	Bdl	0.10	Bdl	0-0.5	0.30
Cu	10.00	6.30	5.50	8.20	15.70	15.30	7.7	5.5-15.7	9.80
Ga	14.70	11.50	9.90	9.20	13.80	12.60	14.2	9.2-14.7	12.30
Hf	1.50	1.00	0.80	1.10	1.10	5.00	2.2	0.8-5.0	1.80
Hg	0.03	0.02	0.02	0.04	Bdl	0.05	0.01	0-0.05	0.00
Mo	6.80	4.40	5.30	4.70	8.90	9.20	6.3	4.4-6.8	6.50
Nb	6.50	4.60	3.40	4.00	4.30	6.50	4.5	3.4-6.5	4.80
Ni	23.60	17.40	24.20	10.00	11.70	14.60	10.3	10.0-24.2	16.00
Pb	150.20	101.60	67.00	157.60	56.20	37.90	50.5	37.9-157.6	88.70
Rb	0.20	0.20	0.10	Bdl	0.20	Bdl	0.10	0.00-0.20	0.20
Sc	15.00	11.00	11.00	10.00	9.00	9.00	12.00	9.00-15.00	11.0
Sn	2.00	1.00	1.00	2.00	2.00	2.00	2.00	1.00-2.00	1.70

Sample No/ Elements (PPM)	L1	L2	L6A62	L9	L17	BH1	BH3	Range	Averages
Sr	201.30	640.40	81.60	633.30	231.90	198.00	456.00	81.60-640.40	348.90
Ta	0.30	0.30	0.20	0.20	0.20	0.40	0.30	0.20-0.40	0.30
Th	16.40	11.80	11.10	11.40	13.10	14.60	16.00	11.10-16.40	13.50
U	12.90	7.40	7.80	11.60	15.20	12.00	12.40	7.40-15.20	11.30
V	493.00	304.00	259.00	324.00	508.00	358.00	417.00	259.00-508.00	380.40
W	1.50	0.70	Bdl	4.80	0.70	Bdl	0.90	0.00-4.80	1.70
Y	67.90	62.90	40.20	122.90	44.30	65.80	55.30	40.20-122.90	65.60
Yb	7.75	6.42	4.66	10.37	5.06	8.44	5.050	4.66-10.37	6.80
Zn	302.00	431.00	427.00	270.00	185.00	143.00	224.00	143.00-431.00	283.10
Zr	74.50	44.30	37.40	43.90	45.60	191.50	81.70	37.40-191.50	74.10
Σ(Co+Cu+Ni+Pb+Zn)	522.00	578.30	542.60	453.90	291.90	223.90	313.90	223.90-578.30	418.10

Table 4: Abundance of Trace Elements of the Oolitic and Pisolitic Ironstones

SampleNo/Elements (PPM)	L3	L5	L6A4	L12	Range	Averages
As	5.70	13.70	20.60	3.00	3.00-20.60	10.80
Ba	78.00	11.00	47.00	13.00	11.00-78.00	37.30
Be	11.00	3.00	7.00	2.00	2.00-11.00	5.80
Bi	Bdl	Bdl	Bdl	Bdl	=====	=====
Cd	Bdl	Bdl	0.10	Bdl	=====	0.10
Co	1.40	2.80	6.70	2.00	1.40-6.70	3.20
Cs	0.10	0.90	0.90	Bdl	0.10-0.90	0.60
Cu	4.10	17.50	31.80	7.30	4.10-31.80	15.20
Ga	2.30	3.70	4.50	1.00	1.00-4.50	2.90
Hf	14.30	24.30	3.50	6.00	3.50-24.30	12.00
Hg	Bdl	0.16	0.05	0.02	0.02-0.16	0.10
Mo	0.60	3.30	2.60	1.00	0.60-3.30	1.90
Nb	8.10	11.30	3.10	2.40	2.40-11.30	6.20
Ni	3.40	1.70	8.70	1.90	1.70-8.70	3.90
Pb	3.10	10.40	14.60	3.00	3.00-14.60	7.80
Rb	0.60	0.70	Bdl	0.30	0.30-0.70	0.50
Sc	9.00	37.00	5.00	7.00	5.00-37.00	14.50
Sn	Bdl	Bdl	Bdl	Bdl	=====	=====
Sr	48.20	5.60	25.00	7.00	5.60-48.20	21.50
Ta	0.70	0.80	0.30	0.20	0.20-0.80	0.50
Th	6.60	7.80	2.30	3.20	2.30-7.80	5.00
U	4.10	12.70	28.80	3.90	3.90-12.70	12.40
V	39.00	35.00	118.00	14.00	14.00-118.00	51.50
W	0.70	Bdl	Bdl	0.60	0.60-0.70	0.70
Y	20.60	13.70	16.90	7.70	7.70-20.60	14.70
Yb	2.45	2.58	3.13	0.96	0.96-3.13	2.30
Zn	19.00	57.00	228.00	55.00	19.00-228.00	89.80
Zr	547.70	960.70	138.30	248.50	138.30-960.70	473.80
Σ(Co+Cu+Ni+Pb+Zn)	31.00	89.40	289.80	69.20	31.00-289.80	119.90

Table 5: Abundance of Trace Elements of the Silty Concretionary Ironstones

Arsenic (As) has higher concentration in the oolitic/pisolitic ironstones relative to the silty concretionary iron ores. Normally In acidic environments, the surface of oxides is positively charged causing adsorption of anions (Cornell and Schwertman, 2003). The adsorbed arsenic may be mobilized with phosphate, and these adsorbed anions may be released upon reduction of iron oxides because the available surface area decreases, thus the reduction of iron oxides has been suggested as a mechanism for arsenic oxyanions (AsO_4^{3-}) and phosphates release (Pedersen, 2006).

Ni content ranges between 10.0-24.2ppm with an average of 16ppm in the oolitic and pisolitic ironstones. In oxidate sediments such as, sedimentary iron ores, the concentrations of Ni & Co are generally low, mostly lower than the average of upper lithosphere (Goldschmidt, 1958).

Table (3) Shows a positive relation of Ni with $\text{Fe}_2\text{O}_3(\text{t})$ ($r=.435$), and an inverse relationship with SiO_2 ($r= -.629$) and Al_2O_3 ($r= -.383$). According to (Koppelman and Dillard, 1977), Ni is one of the elements adsorbed on the surface of clay particles like kaolinite and illite and its content may be attributed to the clay minerals (especially kaolinite) and ironoxides/hydroxides (especially goethite). Cobalt also correlates positively with Fe_2O_3 ($r= .423$) and Ni ($r= .553$) and these could be attributed to the similar geochemical behavior of iron, nickel, and cobalt as their radii are close ($\text{Fe}= 1.27\text{\AA}$, $\text{Co}= 1.26\text{\AA}$ and $\text{Ni}= 1.24\text{\AA}$) (Goldschmidt, 1958). Conversely, the negative correlation of both Ni, Co and Fe_2O_3 with both SiO_2 and Al_2O_3 (Table3.) opposes their association with clay minerals/particles as suggested by (Hirst, 1962; Carr and Turekian, 1961; Koppelman and Dillard, 1977.)

The negative correlation coefficients of Zn with Al_2O_3 ($r= -.637$), and SiO_2 ($r= -.635$) give evidence to the lack of relationship of Zinc with clay minerals (Till, 1971), while the close relationship of Zinc with iron minerals is reflected by the positive relations with Fe_2O_3 ($r=.461$), Ni ($r= .634$) and slightly with Co ($r=.195$).

The Zn-Ni-Co triangular diagram (Fig. 5) shows all the samples plotting towards Zn. These may possibly indicate a more alkaline source for the zinc rather than sources from basic or ultra basic rock. Though Choi and Hariya(1992), described samples plotting towards zinc to indicate hydrothermal source. However, Zinc is a chalcophile element and mostly occur as a sulphide in hydrothermal deposit. Consequently, the very low sulphur content in the ironstones which measures below the detection limit of 0.02% has refuted hydrothermal sources for these deposits.

Figure 5: Zn-Co-Ni Ternary Diagram for the Different Rock Types (After Choi and Hariya, 1992)

In ironstones, the elements group (Zn+ Pb + Cu +Ni +Co) has in total a concentration which generally does not exceed 650ppm (Mucke and Farshad, 2005); this case is also evident in the oolitic/pisolitic Agbaja ironstones samples where the total concentration of these elements group ranges between (223.9-578.3ppm) with average of (418.1 ppm). Similarly, ironstones always contain vanadium lying mainly in the range between 150 and 850 ppm (Mucke and Farshad 2005) and these deposits also follow these rules. Thus, the Agbaja oolitic and pisolitic ironstone is similar to ironstone deposits from other parts of the world with respect to these trace elements.

4.Summary and Conclusion

Geochemical analyses indicate that the ironstones are enriched in the highly mobile elements, such as Zn,Mo, U, Th, and depleted in alkali and alkaline earth elements; Mg, Ca, Na, and K, compared to crustal average. Statistical analyses of the concentration of oxides and trace elements indicate that there is a positive correlation between Fe and Mg, Na K, V, Co, Zn, Mo, Pb, As and Ni, and between Mn and the manganophile elements, such as Co, Ba, and Pb. Quartz is present as Si cement, whereas Ti is consistently in low concentrations. The geochemical behavior of the redox-sensitive minor and trace elements, such as V, Cr, Mn, Co, Ni, As, Mo, and U, depends mainly on the recycling of iron and manganese. Zinc is highly mobile element under weathering condition and thus the higher concentration of zinc in the deposit could be attributed to detrital sources from weathered rocks.

There is common agreement that ooidal ironstones can form in both marine and continental sedimentary environments. But the relationship between various oxides and trace elements in the studied oolitic and pisolitic ironstones plotted on discriminant plots points towards diagenetic origin with contribution from detrital sources. In addition, the lower magnesium oxide content in the samples have ruled out the possibility of marine origin.

Given the above, secondary enrichment is ultimately the possible source for the enrichment in iron and phosphorous and the replacement process involves the removal of alumina and dessilification as iron is been enriched in the kaolinite precursor which is in line with the findings of Abimbola, (1997); Abimbola *et al.*, (1999); Mucke *et al.*, (1999); and Elueze, (1999).

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