



Geochemistry and origin of Fe-Mn oxide mineralization in Kaoje-Derena and their environs, northwestern Nigeria

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Abstract

The mineralogy and origin of the schist hosted manganite and sandstone hosted goethite mineralizations west of Zuru schist belt Nigeria was investigated. A total of five goethite and ten manganite samples were selected. Half of each samples were pulverized and subjected to geochemical analysis for the major oxides, trace and rare earth elemental compositions using X-ray fluorescence while the other halves were polished for their mineralogical analyses through Raman spectroscopy. The result of the Raman spectroscopy showed that the manganites were made up essentially of psilomelane, todorokite and brookite, while the goethites were dominantly goethite, rutile and ilmenite. The result of the elemental analysis was subjected to Principal Component Analysis (PCA) using SPSS 22 software and discriminating plots using TriPlot software. The results of the discriminating plots showed that the goethites were related to hydrothermal processes whereas the manganite ores related to detrital-diagenetic processes. The conclusion drawn from the integration of field evidences, geochemical results, mineralogy, cluster analysis and discriminating plots was that the manganite ores were products of supergene enrichment, while in contrast, the goethites were formed primarily from hydrothermal processes but have been remobilized to its present position as a result of changing Eh-pH conditions in Kaoje and its environs.

Keywords Geochemistry · Goethite · Manganite · Supergene enrichment · Hydrothermal field

Introduction

Mineralization is a relatively complex process of concentrating valuable metals above norms within the earth crust. Several attempts to explain the phenomena of concentrating these metals have been based on geologic settings, types of mineralizing fluid, ore mineralogy, geochemistry, stratigraphy, ore structure or combination of two or more of these (Fillie 2014a and b; Beura et al. 2016; Prochaska 2016). The Nigerian terrain is enriched with both metallic and non-metallic minerals which occur in three main metallogenic

provinces namely the Precambrian Basement Complex, the Jurassic Younger Granite and the Cretaceous-Tertiary sedimentary basins (Akanke and Kinnaird 1992). These provinces are characterized by mineralizing fluids whose origin vary between metamorphic, magmatic and connate water (Barton and Johnson 2000). The type and style of concentrating the valuable metals in these provinces also differ. In view of the differences in the host rock, mineral associations and continuous search for mineral deposits to meet the rising demand for minerals across the world, there is need for investigation and evaluation of reported origin, mineralogy and geochemistry of the mineralization across the globe. This work is aimed at determining the geochemistry and origin of Fe-Mn oxide mineralizations in Kaoje and its environs.

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Methodology

The geological mapping of the area was carried out in both dry and wet seasons between July 2011 and December 2012. The laboratory works carried out include geochemical analysis and

Raman spectroscopy. The result of the geochemical analysis was subjected to statistical analysis. Half of the selected goethite and manganite ore samples were polished by cutting the selected ores into 1.5 cm diameter and about 0.5 cm thickness. The surface to be polished was smoothened by rubbing it against carborandum of different grades until the desired smoothness was achieved. The smooth surface was thereafter polished with magnesium oxide for Raman spectroscopic analysis. Part of these samples was also pulverized using pulverizing machine for major oxides, trace and rare earth element analysis. In the laboratory, 5 g of the Fe and Mn ores was weighed and roasted to determine loss on ignition (LOI). The roasted sample was fused in a platinum-gold crucible with a commercial lithium tetraborate flux. The molten material was cast in a platinum mold. The fused discs were analysed by XRF. The result from the geochemical analyses was thereafter subjected to Principal Component Analysis. The discriminating plots were done using TriPlot software.

Geology of the area

The study area, Kaoje and its environs, lies in the contact zone of extreme western part of the Zuru schist belt, northwestern Nigeria with the Sokoto sedimentary basin. The Zuru schist belt is believed to be the largest and the least understood schist belt in northwestern Nigeria (Danbatta and Garba 2007). It is also considered to be relatively unmineralized. This study area is bounded by longitude 3° 55' E and 4° 10' E, and latitude 11°00' N and 11°15' N, covering an approximate area of 676 km².

The geology of the area can be grossly divided into the Basement Complex rock and the sedimentary rocks (Fig. 1). The Basement Complex rocks are migmatite, banded gneiss, granite gneiss, quartz-mica schist, granite and pegmatite. The migmatite rock occurs about 1.5 km southeast of Barkin-Ruwa. This rock is also exposed along Barkin-Ruwa-Buya road. On the field, the general trend of the rock is NW-SE. It is highly fractured, conical in shape and associated with pegmatites.

The banded gneiss occurs as elongated rock body within the schist about 2 km southwest of Buya and midway between Idowa and Derena. The banded gneisses are rich in quartz with pervasive jointing. Some of the joints have been filled by quartz and quartzo-feldsparitic veins in most cases. The granite gneisses are poorly banded and occur as boulders of rock in some places. Associated features such as joint have different trends between 184° to 240° essentially. Quartz veins that are associated with the gneisses strike within the range of 300° to 312°.

The schist cover about one-fifth of the study area and is extensively weathered. The schist is also characterized by various joints and fractures and occurs as low-lying exposures composed essentially of quartz and mica, with minor presence of biotite and feldspar. The schist also occurs as xenoliths

within a pegmatitic body close to Barkin-Ruwa, along Barkin-Ruwa-Buya traverse. The joints within the schist have been filled by pegmatitic and quartz intrusion of varying dimension. Other intrusions associated with the schists are quartzo-feldsparitic in composition. The granitic bodies occur towards the southern part of the study area. The granitic rocks occur as boulders and cobbles of rocks and are closely associated with weathered schist in the southern-most part of the study area. In some of the rocks, the minerals are weakly aligned. Mineralogically, the granites are composed of quartz, biotite and sodic feldspar mainly.

Other rocks in this area are essentially pegmatites and quartzolites. The pegmatitic rocks in this area are seen associated with the schist and migmatite mainly. Mineralogically, the pegmatites are made up of quartz, biotite, K-feldspar, tourmaline (in the southeastern part) and chalcedony (in the northwestern part). Most of the pegmatites which are associated with the schist have been extensively weathered with some of them occurring as residual hill of weathered rock close to Barkin-Ruwa. The quartzolites occur as veins and veinlet exploiting the fractures within the rocks and ores in the study area.

Sedimentary rocks in this area occupy more than 60% of the area studied. These rocks belong to the Sokoto/Lullemmeden Basin. This Basin is a cratonic basin believed to have been formed by tectonic epirogenic movement or stretching and rifting of tectonically stable crust during the Paleozoic (Ajibade et al. 1987). The age of the sediments in this basin reduces towards the SW from the north (Bassey and Eminue 2014).

The sedimentary rocks in the study area belong to the Taloka Formation. These rocks form most of the elevated features in the area. These features include the Biongbé, Morongba and Koremi hills. In the northeastern part of Kaoje, the sedimentary rocks occur as remnant of gully eroded rock. These rocks are finely laminated with characteristic trace fossils. Other characteristic of these rocks is their semi-consolidated nature. The rocks in this area include fine laminated silty sandstones and massive silty sandstones. Other sedimentary rock types seen are kaolinitic mudstone, finely laminated siltstones and kaolinitic claystone. All these are exposed along Kaoje-Idowa road and towards the edge of the area studied in the northeastern part of Kaoje.

Iron (goethite) occurs as vein, boulders and sedimentary capping in the northeast of Kaoje and southeast along Kaoje-Taka-Lafia axis mainly. The iron ore shows conspicuous alternating bands (1–2 cm thick) of iron and chert-rich layers in most of the locations while few are massive iron ore with little or no cherty contents (Fig. 2a). The iron ore is characterized mainly by the brownish colouration of goethite. This ore is also seen among the beds of the sedimentary rocks along Kaoje-Idowa road.

The manganese ores occur in form of boudins in almost NE-SW direction from Buya through Derena to eastern part of

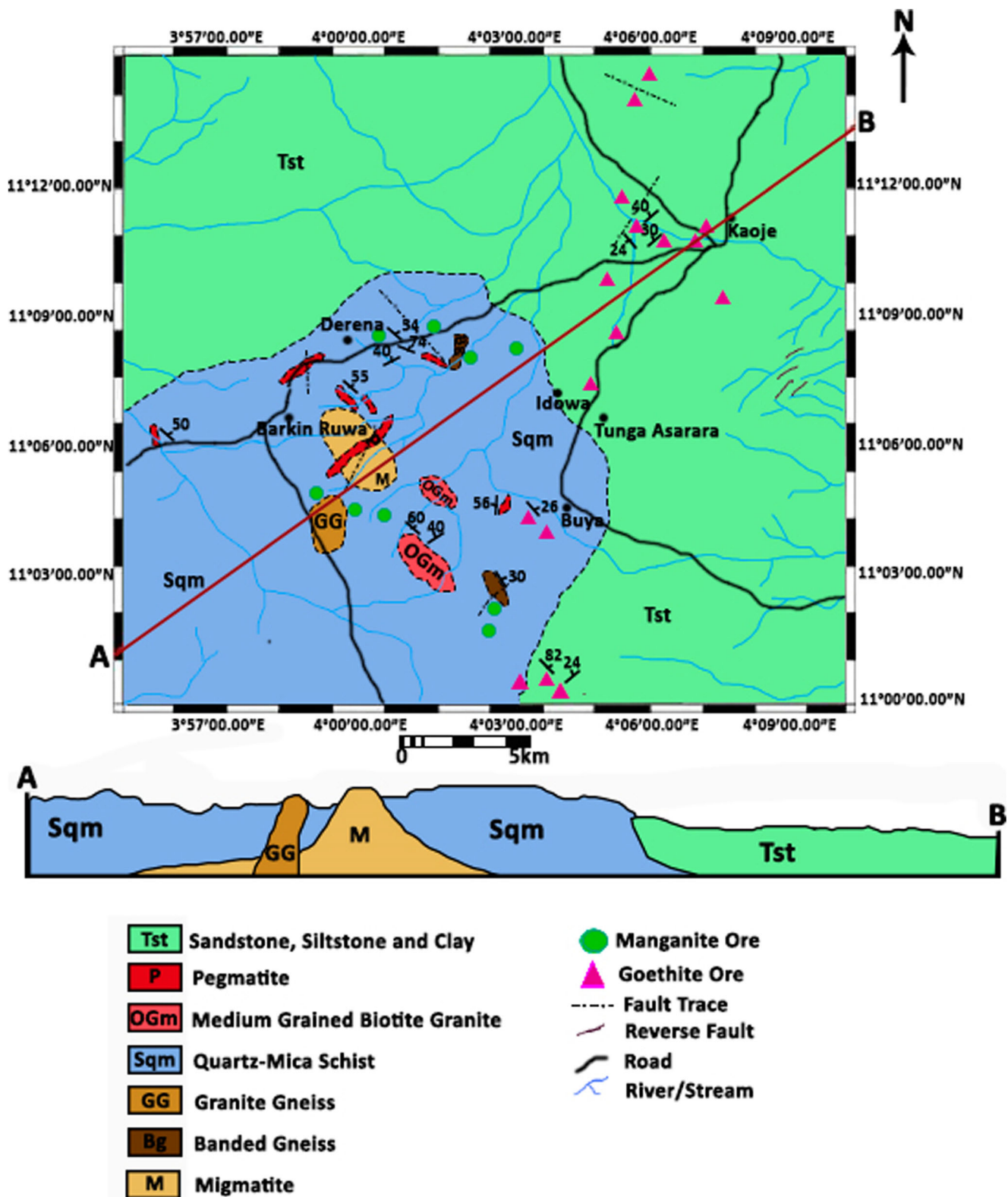


Fig. 1 Geological map of Kaoje and its environs (part of Kaoje sheet 94SE and Bani sheet 95SW)

Barkin-Ruwa. These ores occur as black and sometimes black laminated, non-fissile exposures mainly around Buya-Derena axis essentially. The Mn ore is associated with quartz veins

(Fig. 2b). These quartz veins get reduced towards Buya and are seen as quartzite body with a length traceable for more than 50 m and a width of 17 m. This occurs in-between the

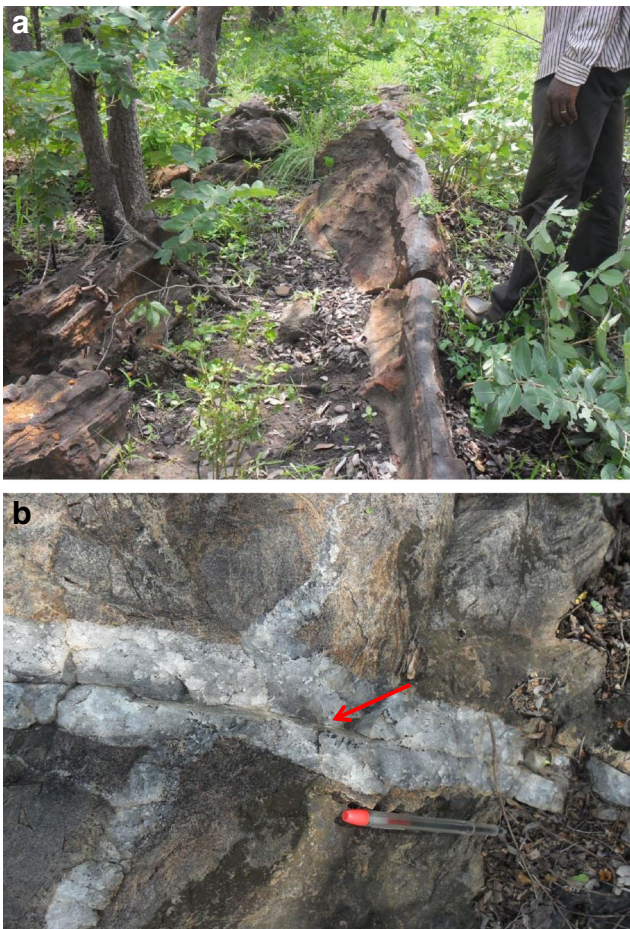


Fig. 2 **a** Field photograph showing iron ore band in Kaoje area along Kaoje-Dukamaje road. **b** Quartzofeldspatic vein in manganite ore. The thicker vein cut the thinner one and it has been fractured. Red arrow points to the fracture

manganese outcrops about 3 km northeast of Buya. The manganese itself occurs as boulders and cobbles of rock body forming a conically shaped hill.

Results

The geochemical results of concentration of major elements and that of trace and rare earth elements of 15 ore samples are shown in Tables 1 and 2, respectively. The results of the correlation analysis of major oxides in the goethite and manganite ores are shown in Tables 3 and 4, respectively. Those that are statistically significant at $p < 0.05$ and $p < 0.01$ are shown by single asterisk (*) and double asterisk (**) respectively in the correlation tables.

The high correlation coefficient recorded between Al_2O_3 and TiO_2 in the goethite ores implies mixing of the detrital material during ore precipitation (Öksüz and Okuyucu 2014). The good correlation between the Al_2O_3 and Fe_2O_3 in the manganite ores is enhanced by the similarities in the

geochemical behaviour of Fe and Al especially in gradually replacing each other in solution. The negative correlation coefficient between MnO and Fe_2O_3 ($r = -0.0666$ in goethite and $r = -0.1222$ in manganites) implies that these oxides have been precipitated under different environmental conditions or have different sources (Ibrahim and Rehab 2014). The negative correlation coefficient could as well show clearly relative high mobility of Mn compared to Fe in sedimentary environment despite their close similarities in geochemical behaviour. The differences in their mobility also might have influenced their differentiation and segregation in fluid containing them (Simmonds and Ghasemi 2007) causing Mn to precipitate later than Fe (Ibrahim and Rehab 2014). Most of the correlated elements have positive correlation coefficients with Fe in the goethite ores correlation result (Table 5) compared to Mn but converse is true in the manganite ores correlation result (Table 6). These differences in the notation of the correlation coefficients showed that the elements had selectively adsorbed on the Mn and Fe in their respective ores.

The negative correlation coefficient of SiO_2 with Fe_2O_3 ($r = -0.9457$ in goethites) and the negative correlation coefficient between SiO_2 and MnO ($r = -0.7627$) shows that it is not likely that detrital quartz grain was added to Fe and Mn mineralization processes (Saad et al. 1994). The positive correlation coefficient between the following pairs of elements: Ni-Co ($r = 0.788$ in Mn and $r = 0.966$ in goethite), Co-Pb ($r = 0.700$ in manganite), Co-Zn ($r = 0.739$ in manganites and $r = 0.902$ in goethite), Ni-Pb ($r = 0.742$ in manganite), Ni-Zn ($r = 0.761$ in goethite and $r = 0.861$ in manganite) and Zn-Pb ($r = 0.638$ in manganite) (Tables 5 and 6) is interpreted to depict contribution of hydrothermal solution to the mineralization processes because they are enriched in hydrothermal fluid (Ibrahim and Rehab 2014) that affected Kaoje and its environ. The negative coefficient of correlation between MnO-MgO ($r = -0.4658$ in manganite and $r = -0.3536$ in goethite) and MnO-CaO ($r = -0.5323$ in manganite and $r = -0.0318$ in goethite) (Tables 3 and 4) is interpreted to be an indication of non syn-precipitation of carbonate mineral with neither goethite nor manganese ores. The positive coefficients of correlation between these pairs, $\text{Al}_2\text{O}_3\text{-K}_2\text{O}$ ($r = 0.8812$ in goethite and $r = 0.3102$ in manganite), $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5$ ($r = 0.3426$ in goethite and $r = 0.2501$ in manganite), and the negative coefficient of correlation between $\text{P}_2\text{O}_5\text{-K}_2\text{O}$ ($r = -0.2283$ in manganite) show that these oxides were not sourced from a single source (sedimentary formation) (Ibrahim and Rehab 2014).

PCA analysis of 49 trace and rare earth elements from the ore samples except for elements with constant value such as B (< 20 ppm), Se (< 0.1 ppm), Ta (< 0.05 ppm) and Pd (10 ppm) was carried out. Component values of ≤ 0.3 were not outputted during the analysis to reduce the bulkiness of the result and since in most cases, they are not significant.

From the analysis, 10 factor groups are distinct (Table 7). Factor 1 accounts for 33.352% of the elements while factor 2

Table 1 Concentration of the analysed major oxide in selected ore samples (manganites and goethite ores). G, goethite; M, manganite; I, ironstone (non-banded goethite)

Ore type	Element/sample no.	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	CaO (%)	MgO (%)	Na ₂ O (%)	K ₂ O (%)	MnO (%)	TiO ₂ (%)	P ₂ O ₅ (%)	Cr ₂ O ₃ (%)	BaO (%)
G	7	46.87	1.77	44.92	0.01	<0.01	<0.01	0.02	0.05	0.07	0.17	0.003	<0.01
G	8	60.91	1.29	33.31	0.02	<0.01	<0.01	0.01	0.07	0.07	0.21	0.003	0.01
I	49	51.19	3.00	40.42	0.01	<0.01	<0.01	0.02	0.03	0.06	0.04	0.007	<0.01
G	75e	53.27	1.45	39.94	0.03	<0.01	<0.01	<0.01	0.11	0.13	0.02	0.012	<0.01
I	81	54.45	3.51	35.34	0.07	0.03	<0.01	0.04	0.04	0.18	0.32	0.008	0.01
M	19	16.99	19.24	8.57	0.86	0.23	<0.01	0.46	30.36	0.52	0.12	0.002	0.11
M	20	49.47	14.33	6.58	2.90	0.35	0.01	0.18	19.38	0.54	0.03	0.012	0.03
M	21	50.82	15.10	7.22	5.84	0.97	<0.01	0.02	17.97	0.48	0.09	0.011	0.08
M	22	41.61	17.65	8.91	7.10	1.40	<0.01	0.08	20.60	0.35	0.38	0.011	0.02
M	23	46.79	13.82	6.51	5.70	1.87	<0.01	0.03	21.15	0.68	0.20	0.015	0.11
M	40	53.01	13.56	6.42	2.49	0.63	<0.01	0.01	19.41	0.81	0.11	0.014	0.02
M	40b	35.46	18.66	8.34	4.06	0.71	<0.01	0.08	27.43	0.49	0.12	0.007	0.02
M	154	38.12	19.31	13.33	6.44	2.55	<0.01	0.04	17.33	1.07	0.57	0.016	0.03
M	156	36.81	20.16	8.86	8.47	1.69	<0.01	0.03	19.50	0.16	0.05	0.003	0.05
M	217b	41.86	15.56	7.56	6.24	1.78	<0.01	0.02	23.71	0.38	0.32	0.010	0.13

accounts for 15.293%. Factor 3 accounts for 11.989%. These first three factor groups account for more than 50% of the whole elements and are therefore important. Factor 4 is next to factor 3 with percentage variance of 6.291 while factor 5 has percentage variance of 6.032. Factor 6 accounts for 5.752% while factor 7 accounts for 4.991%. Factors 8, 9 and 10 have percentage variance of 4.987, 3.820 and 3.712%, respectively. Cumulatively, the percentage accounted for by the 10 factor groups is 96.219%. This implies that either there is a leakage in the system or that the system is not a closed system, if not, the cumulative variance accounted for by the 10 factor groups should sum up to 100%.

Factor 1 of the principal component analysis has K, Al, Rb, Ga, S, V, Ti, Cs, Sc, Cd, Cu, Co, Sr, Mo, Y, Pt, Sn, Li, Zn and Ni. This factor group relates to evaporites settings that are rich in Fe-Mn minerals or sediments generated from weathering of ferromagnesian rocks with detrital incursion in lower oxidizing environments (Krauskopf and Bird 1995; Levinson 1981). The association of incompatible elements in this factor group is typical of the odd geochemical association in sedimentary manganese (Krauskopf and Bird 1995). Factor 2 with Ag, Bi, Au, Na, Te, Be, Ba and Nb represents hydrothermal incursion during the formation diagenetic/detrital components of the Fe-Mn ores (Levinson 1981). Factor 3 has Th, Ce, La, As, In and Hg. This group is related to cherty magnetite. Factor 4 has P and Ca with P having slightly higher loading than Ca. This group implies that the limited CaO in the absence of carbonate is hosted essentially in a phosphate mineral phase, e.g. apatite, and relates to marine sedimentary Banded Iron Formation (BIF). Factor 5 (Ge, Pb, Re, U) is related to hydrothermal intrusion with selective wall rock leaching (Levinson 1981).

Factor 6 has Zr and Hf. It is a phase of adding some terrigenous material into the ore formational processes. Factor 7 with Mg and Sb suggests secondary dolomitic carbonate as the main carbonate phase (Lucilia et al. 2015) while factor 8 has high negative loadings for Cr and Fe but positive loadings for the Mn. This factor group shows the inclusion of Cr being trapped in the crystal structure of the Fe-Mn ore especially in the Fe phase during their crystallization probably because of the favourable condition that generally favours the first transition metal elements (Lucilia et al. 2015).

Factors 9 (W) and 10 (Tl) are related to leaching of elements from the fluid of granitic composition that exploited the available fracture spaces after deformation of the mineralization (Levinson 1981).

Two of the results of the Raman spectroscopy are shown in Fig. 3a, b while Tables 8 and 9 show the interpretation of the Raman peaks in the goethites and manganites, respectively. From the result, the ores are enriched essentially in manganite, quartz, goethite and akaganeite.

The discriminating plot done to unravel the origin of the ore deposits vary from the ternary plot of Fe, Mn and combined Ni, Co and Cu as shown in Fig. 4 through binary plot of Co and Ni against As, Cu, Mo, Pb, V and Zn (Fig. 5) and the plot of Si against the Al (Fig. 6). From the ternary plot (Fig. 4), the Fe ores are associated with the hydrothermal fluid while the Mn ores are essentially hydrogenous. The binary plot of Co + Ni against As + Cu + Mo + Pb + V + Zn (Fig. 5) also supports the ternary diagram (Fig. 4) that the Fe ores are essentially related to hydrothermal condition but the Mn ores are product of supergene ambient condition at the earth surface. Si plot against Al (Fig. 6) is in line with the earlier two diagrams

Table 2 Concentration of trace and rare earth elements in the selected ore samples

Ore type	Element	sample no.	Mo (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)	Ag (ppb)	Ni (ppm)	Co (ppm)	Mn (ppm)	Fe (%)	As (ppm)	U (ppm)	Au (ppb)
G	7		0.65	16.24	1.46	55.1	10	14.8	2.5	236	5.51	0.7	0.71	12.3
G	8		0.78	88.52	5.33	110.3	33	15.3	5.7	414	14.50	2.3	5.44	12.2
I	49		0.36	47.74	21.66	91.2	17	10.5	2.5	198	14.63	<0.1	3.18	13.0
G	75e		0.66	16.01	2.17	241.4	27	27.9	17.3	439	20.38	0.2	1.28	10.8
I	81		1.19	10.46	5.24	250.2	15	84.2	34.2	239	16.14	7.7	1.72	0.9
M	19		11.79	230.73	16.22	1120.6	51	1416.4	460.9	>10,000	4.30	152.9	2.28	2.1
M	20		2.31	33.48	4.09	221.9	59	241.6	47.7	>10,000	2.51	195.7	1.07	10.2
M	21		1.29	13.82	2.24	273.2	60	468.9	97.3	7636	1.16	158.2	0.83	18.5
M	22		9.92	53.27	4.86	938.6	27	568.7	94.0	8892	1.51	111.2	0.76	6.5
M	23		0.94	72.85	4.42	1077.1	48	1214.8	181.5	>10,000	1.34	246.2	1.58	3.0
M	40		0.94	11.82	4.08	47.6	15	73.5	11.8	4209	1.43	61.3	1.72	6.1
M	40b		0.86	24.41	2.93	366.9	44	885.4	147.1	>10,000	2.28	97.0	0.88	8.3
M	154		1.42	21.23	2.66	51.2	22	173.6	44.3	>10,000	1.53	95.6	2.74	1.4
M	156		0.44	4.30	0.78	14.2	46	124.0	11.9	>10,000	0.76	9.9	1.28	4.0
M	217b		0.40	29.16	13.65	667.9	263	1169.1	79.0	>10,000	1.78	1.8	2.40	55.0
Ore type	Element	sample no.	Th (ppm)	Sr (ppm)	Cd (ppm)	Sb (ppm)	Bi (ppm)	V (ppm)	Ca (%)	P (%)	La (ppm)	Cr (ppm)	Mg (%)	Ba (ppm)
G	7		0.8	1.2	0.01	0.09	0.03	5	<0.01	0.015	0.7	9.3	<0.01	13.5
G	8		1.2	1.2	0.02	0.09	0.03	17	<0.01	0.056	1.3	13.4	<0.01	58.2
I	49		2.9	1.4	0.02	0.06	<0.02	5	0.01	0.008	1.5	23.1	<0.01	7.3
G	75e		0.7	1.1	0.02	0.12	0.03	19	0.01	0.004	1.0	38.6	<0.01	14.1
I	81		3.4	2.8	0.06	0.06	<0.02	6	0.05	0.090	4.2	13.8	0.02	35.1
M	19		7.0	230.3	5.20	0.03	0.98	180	0.17	0.040	32.0	3.1	0.08	864.7
M	20		3.2	31.4	0.90	0.07	1.65	83	0.06	0.009	20.8	16.5	0.01	235.8
M	21		7.3	35.8	0.66	0.17	0.56	13	0.12	0.034	67.3	8.6	0.05	700.0
M	22		2.1	112.5	1.63	0.16	1.43	15	0.49	0.165	36.9	11.6	0.41	166.6
M	23		13.7	54.4	2.43	0.16	1.17	9	0.36	0.096	59.4	6.2	0.19	995.5
M	40		8.2	21.9	0.18	0.11	2.17	22	0.05	0.036	18.8	10.8	0.01	151.6
M	40b		1.9	60.6	0.91	0.11	14.83	45	0.07	0.051	17.0	4.4	0.03	148.7
M	154		11.5	54.9	0.16	0.08	1.09	20	0.57	0.257	33.3	15.3	0.06	132.3
M	156		1.0	18.9	0.17	<0.02	3.34	14	0.08	0.019	10.1	2.2	0.02	497.8
M	217b		3.5	95.6	1.06	0.07	44.88	9	0.42	0.156	24.2	4.1	0.11	1477.3
Ore type	Element	sample no.	Ti (%)	B (ppm)	Al (%)	Na (%)	K (%)	W(ppm)	Sc (ppm)	Tl (ppm)	S (%)	Hg (ppb)	Se (ppm)	Te (ppm)
G	7		0.003	<20	0.14	0.001	<0.01	<0.05	1.1	<0.02	<0.02	<5	<0.1	<0.02
G	8		0.003	<20	0.18	0.001	<0.01	<0.05	2.8	0.12	<0.02	<5	<0.1	<0.02
I	49		0.003	<20	0.30	0.001	<0.01	<0.05	3.1	<0.02	<0.02	<5	<0.1	<0.02
G	75e		0.008	<20	0.17	0.001	<0.01	0.19	3.6	<0.02	<0.02	<5	<0.1	<0.02

Table 2 (continued)

I	81	0.005	<20	0.33	0.001	<0.01	<0.05	2.1	<0.02	<0.02	15	<0.1	<0.02
M	19	0.073	<20	4.80	0.010	0.32	0.18	16.6	<0.02	0.03	20	<0.1	1.22
M	20	0.030	<20	1.15	0.003	0.12	0.38	7.7	0.11	<0.02	<5	<0.1	0.56
M	21	0.012	<20	0.27	0.001	0.02	<0.05	4.5	<0.02	<0.02	9	<0.1	0.41
M	22	0.021	<20	0.59	<0.001	0.06	0.07	5.5	<0.02	<0.02	7	<0.1	0.24
M	23	0.023	<20	0.19	0.002	0.02	0.10	6.7	<0.02	<0.02	31	<0.1	0.59
M	40	0.012	<20	0.17	<0.001	0.01	0.05	4.4	0.05	<0.02	<5	<0.1	0.18
M	40b	0.020	<20	1.02	0.002	0.07	0.82	5.7	<0.02	<0.02	21	<0.1	1.78
M	154	0.019	<20	0.58	0.012	<0.01	<0.05	2.8	<0.02	<0.02	7	<0.1	0.35
M	156	0.005	<20	0.49	0.011	0.01	0.14	1.2	0.05	<0.02	19	<0.1	0.11
M	217b	0.015	<20	0.14	0.086	0.02	0.23	7.0	0.07	<0.02	20	<0.1	2.99
Ore type	Element sample no.	Ga (ppm)	Cs (ppm)	Ge (ppm)	Hf (ppm)	Nb (ppm)	Rb (ppm)	Sn (ppm)	Ta (ppm)	Zr (ppm)	Y (ppm)	Ce (ppm)	In (ppm)
G	7	0.7	0.05	0.2	0.06	0.07	0.6	0.4	<0.05	2.5	1.15	2.9	0.03
G	8	0.6	<0.02	0.3	0.06	0.07	0.3	0.4	<0.05	1.7	8.23	10.3	<0.02
I	49	0.7	0.03	0.7	0.18	0.04	0.4	0.4	<0.05	6.8	1.23	6.6	<0.02
G	75e	0.8	<0.02	0.2	0.08	0.16	0.1	0.8	<0.05	2.4	1.63	2.3	<0.02
I	81	0.8	0.04	0.6	0.18	0.06	0.4	0.3	<0.05	7.0	7.68	19.8	<0.02
M	19	22.5	0.20	0.2	0.18	0.04	7.8	2.8	<0.05	4.9	21.55	112.1	0.14
M	20	6.8	0.12	0.2	0.22	0.06	2.8	1.5	<0.05	5.5	8.76	71.9	0.04
M	21	3.2	0.03	0.1	0.19	0.03	1.0	0.6	<0.05	6.3	11.16	138.5	0.15
M	22	7.8	0.11	0.2	0.17	0.05	2.9	3.5	<0.05	6.7	9.05	60.2	<0.02
M	23	2.1	0.03	<0.1	0.12	0.17	1.8	0.8	<0.05	3.2	2.44	121.3	0.11
M	40	2.6	0.02	0.2	0.19	0.03	0.4	0.9	<0.05	5.7	2.15	45.0	0.08
M	40b	8.2	0.03	0.3	0.21	0.03	2.0	1.2	<0.05	6.3	5.01	45.1	0.09
M	154	2.4	0.02	0.1	0.08	0.07	0.3	1.1	<0.05	5.0	4.86	100.1	0.04
M	156	2.6	0.03	0.1	0.02	0.05	0.6	0.7	<0.05	0.8	6.28	22.1	<0.02
M	217b	2.5	0.04	0.2	0.06	0.21	1.5	1.2	<0.05	2.0	6.41	33.9	0.10
Ore type	Element sample no.	Re (ppm)	Be (ppm)	Li (ppm)	Pd (ppm)	Pt (ppm)	Fe/Mn	Mn/Fe	MnO/Fe ₂ O ₃	CaO/CaO + MgO	Co/Ni	Co/Zn	Al/(Al + Fe + Mn)
G	7	<1	1.2	<0.1	<10	<2	233.47	0.0042	0.001	0.53	0.17	0.05	0.02
G	8	<1	6.9	<0.1	<10	<2	350.24	0.0029	0.002	0.69	0.37	0.05	0.1
I	49	2	1.4	<0.1	<10	<2	738.89	0.0014	0.0007	0.53	0.24	0.03	0.02
G	75e	2	1.2	0.1	<10	2	464.24	0.0022	0.003	0.77	0.62	0.07	0.01
I	81	<1	1.2	0.2	<10	4	675.31	0.0015	0.001	0.07	0.41	0.14	0.02
M	19	<1	1.6	12.0	<10	73	<4.3	>0.2326	3.543	0.79	0.33	0.41	0.47
M	20	<1	0.9	8.7	<10	25	<2.51	>0.3984	2.945	0.89	0.20	0.21	0.24
M	21	2	0.8	4.8	<10	35	1.52	0.6579	2.489	0.86	0.21	0.36	0.12
M	22	<1	0.8	1.9	<10	8	1.70	0.5882	2.312	0.84	0.17	0.10	0.2
M	23	<1	3.6	1.7	<10	46	1.34	0.7463	3.249	0.75	0.15	0.17	0.07
M	40	<1	0.7	0.2	<10	3	3.40	0.2941	3.023	0.89	0.16	0.25	0.08
M	40b	1	3.0	2.7	<10	28	<2.28	>0.4386	3.289	0.85	0.17	0.40	0.23
M	154	<1	0.7	4.6	<10	26	<1.53	>0.6536	1.300	0.72	0.26	0.87	0.25
M	156	<1	0.7	9.1	<10	3	<0.76	>1.3158	2.201	0.83	0.10	0.84	0.21
M	217b	2	10.2	1.2	<10	9	<1.78	>0.5618	3.136	0.78	0.07	0.12	0.05

G goethite, M manganite, I ironstone (non-banded goethite)

Table 3 Result of correlation analysis of major oxides in Fe ores

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	MnO	TiO ₂	P ₂ O ₅	Cr ₂ O ₃	BaO
SiO ₂	1										
Al ₂ O ₃	−0.2126	1									
Fe ₂ O ₃	−0.9457**	−0.0953	1								
CaO	0.2764	0.5483	−0.5240	1							
MgO	0.1213	0.7364	−0.4217	0.9429**	1						
K ₂ O	−0.2103	0.8812*	−0.1148	0.7378	0.9129*	1					
MnO	0.2765	−0.7376	−0.0666	−0.0318	−0.3536	−0.6455	1				
TiO ₂	0.1319	0.4415	−0.3454	0.9560**	0.8438*	0.6321	0.1683	1			
P ₂ O ₅	0.2978	0.3426	−0.4934	0.6474	0.7551	0.6729	−0.3941	0.4543	1		
Cr ₂ O ₃	−0.0470	0.1953	−0.0045	0.4142	0.2070	0.0540	0.4808	0.6064	−0.4231	1	
BaO	0.7735	0.1805	−0.8914*	0.6233	0.6124	0.3727	−0.1443	0.4063	0.8294*	−0.2655	1

(Figs. 4 and 5). This plot also suggests detrital-diagenetic process as the likely origin of the Mn as against the hydrothermal condition of the Fe ores.

Discussion

Manganese (Mn) has similar chemistry with iron (Fe) although manganese minerals are rarer compared to those of iron. Unlike Mn, Fe is considered to be the second most abundant metal in the earth (Jensen and Bateman 1981) and occurs in different forms such as oxide, sulphide and aluminosilicate, e.g. chamosite. Fe may exist alone in an environment but Mn rarely exists alone or far from Fe ore deposit.

These minerals, under suitable pH and Eh conditions usually exist together as divalent ions (Krauskopf and Bird 1995). The manganite and goethite ores in the study area occur almost in a linear manner in the NE-SW direction. This style of mineralization is considered to be controlled by the fault system mapped in the eastern part of the area. This claim is made

because some signatures of the faulting process are preserved in the ores. From microscopic study of the ores, it was evident that the ores have been subjected to series of deformation after their formation. Some of the deformational features include fracture, striation, intergranular cleavages and cavity associated with ores. It is also evident that the ores are not monomineralic. From the Raman spectroscopy, most of the minerals in the ore are not primary. They are essentially pseudomorph minerals produced as a result of changing environmental conditions (Zwicker et al. 1962; McHardy and Thompson 1971). The presence of pyrolusite in some of the ore minerals assemblage is of secondary replacement and indicates the enrichment of manganese by supergene enrichment process in the zone of weathering (Siddiquie et al. 2015).

Factor 1 of the ore is made up essentially of the lithophile elements while the chalcophile and siderophile elements constitute some minor percentage of the factor group. The presence of these various groups of elements in a single phase of mineralization implies varying environmental conditions or the presence of material sourced from different environments

Table 4 Result of correlation analysis of major oxides in Mn ores

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	MnO	TiO ₂	P ₂ O ₅	Cr ₂ O ₃	BaO
SiO ₂	1											
Al ₂ O ₃	−0.7765**	1										
Fe ₂ O ₃	−0.4274	0.7354**	1									
CaO	0.2378	0.2513	0.3369	1								
MgO	0.1158	0.2063	0.5805*	0.7934**	1							
Na ₂ O	0.2820	−0.3346	−0.2843	−0.3146	−0.4026	1						
K ₂ O	−0.7525**	0.3102	0.0167	−0.6843*	−0.5848*	0.2168	1					
MnO	−0.7627**	0.3223	−0.1222	−0.5323	−0.4658	−0.1909	0.6916*	1				
TiO ₂	0.1681	−0.2130	0.3761	−0.3057	0.2270	−0.0110	−0.0749	−0.2592	1			
P ₂ O ₅	−0.0901	0.2501	0.7429**	0.3923	0.7390**	−0.3441	−0.2283	−0.2101	0.4738	1		
Cr ₂ O ₃	0.7253*	−0.6181*	0.0419	0.1233	0.4064	0.1399	−0.5637	−0.6516*	0.7005*	0.4751	1	
BaO	−0.2605	−0.1631	−0.2571	−0.0318	0.1198	−0.2425	0.2338	0.3621	−0.1975	−0.0400	−0.2036	1

Table 5 Result of correlation analysis for selected trace and rare earth elements in Fe ores

	Mo	Cu	Pb	Zn	Ni	Co	Mn	Fe	As	Th	Sr	Cd	Bi	V	Ca
Mo	1														
Cu	-0.265	1													
Pb	-0.555	0.307	1												
Zn	0.619	-0.446	-0.297	1											
Ni	0.887*	-0.505	-0.258	0.761	1										
Co	0.843*	-0.517	-0.313	0.902*	0.966**	1									
Mn	0.080	0.327	-0.511	0.350	-0.169	0.038	1								
Fe	0.155	0.027	0.115	0.792	0.317	0.516	0.528	1							
As	0.928*	-0.214	-0.215	0.547	0.929*	0.834*	-0.202	0.151	1						
Th	0.301	-0.107	0.603	0.251	0.593	0.475	-0.649	0.194	0.628	1					
Sr	0.784	-0.385	0.013	0.545	0.938**	0.834*	-0.440	0.163	0.941**	0.805	1				
Cd	0.821*	-0.318	-0.031	0.708	0.963**	0.914*	-0.223	0.387	0.942**	0.754	0.968**	1			
Bi	-0.143	0.186	-0.692	-0.214	-0.500	-0.397	0.705	-0.194	-0.484	-0.979	-0.717	-0.656	1		
V	0.016	0.359	-0.406	0.363	-0.194	0.023	0.992**	0.602	-0.238	-0.597	-0.451	-0.224	0.640	1	
Ca	0.848*	-0.438	-0.116	0.637	0.979**	0.900*	-0.330	0.216	0.955**	0.719	0.989**	0.978**	-0.625	-0.350	1
P	0.894*	0.081	-0.216	0.397	0.780	0.677	-0.073	0.103	0.951**	0.532	0.813*	0.830*	-0.353	-0.112	0.820*
Cr	-0.338	-0.202	0.095	0.514	-0.121	0.118	0.491	0.767	-0.416	-0.208	-0.315	-0.142	0.093	0.563	-0.255
Mg	0.858*	-0.430	-0.130	0.624	0.977**	0.894*	-0.330	0.197	0.961**	0.710	0.988**	0.975**	-0.612	-0.352	0.999**
Ba	0.575	0.623	-0.311	0.110	0.233	0.204	0.443	0.119	0.503	0.002	0.211	0.305	0.193	0.406	0.235
Al	0.283	-0.124	0.613	0.357	0.604	0.523	-0.560	0.337	0.599	0.988	0.785	0.766	-0.977**	-0.496	0.709
Sc	-0.304	0.303	0.354	0.418	-0.159	0.049	0.548	0.879*	-0.284	0.006	-0.252	-0.042	-0.056	0.646	-0.233
Cs	0.199	-0.566	-0.130	-0.301	0.252	0.054	-0.778	-0.771	0.266	0.216	0.374	0.144	-0.230	-0.846*	0.337
Nb	0.005	-0.309	-0.563	0.539	-0.030	0.205	0.765	0.519	-0.289	-0.634	-0.363	-0.194	0.591	0.756	-0.232
Rb	-0.002	-0.136	0.090	-0.650	-0.037	-0.280	-0.795	-0.917*	0.125	0.208	0.189	-0.056	-0.201	-0.851*	0.108
Sr	-0.313	-0.210	-0.280	0.380	-0.268	-0.022	0.687	0.536	-0.541	-0.611	-0.543	-0.382	0.515	0.712	-0.445
Zr	0.148	-0.301	0.646	0.239	0.527	0.426	-0.738	0.168	0.476	0.959	0.728	0.656	-0.993**	-0.678	0.642
Ce	0.799	0.019	0.044	0.442	0.822*	0.715	-0.246	0.206	0.953	0.759**	0.909*	0.918*	-0.616	-0.254	0.889*
In	-0.145	-0.332	-0.385	-0.587	-0.287	-0.408	-0.345	-0.899*	-0.262	-0.444	-0.267	-0.459	0.408	-0.432	-0.265
Be	0.073	0.910*	-0.091	-0.259	-0.293	-0.294	0.527	0.029	0.005	-0.251	-0.273	-0.180	0.390	0.517	-0.276
Li	0.863	-0.469	-0.164	0.689*	0.992**	0.930**	-0.274	0.259	0.947	0.679	0.975*	0.978*	-0.586	-0.295	0.997*
P															
Mo															
Cu															
Pb															
Zn															
Ni															
Co															
Mn															
Fe															
As															

Table 5 (continued)

[illegible]

Table 6 Result of correlation analysis for selected trace and rare earth elements in Mn ores.

Mo	Cu	Pb	Zn	Ni	Co	Mn	Fe	As	Th	Sr	Cd	Bi	V	Ca	P
Mo	1														
Cu	0.790**	1													
Pb	0.533	0.749**	1												
Zn	0.645*	0.728**	0.638*	1											
Ni	0.372	0.686*	0.742**	0.861**	1										
Co	0.691*	0.958**	0.700*	0.739**	0.788**	1									
Mn	0.121	0.264	0.203	0.333	0.436	0.306	1								
Fe	0.650*	0.849**	0.728**	0.470	0.556*	0.269	0.148	1							
As	0.222	0.367	-0.066	0.432	0.270	0.399	0.148	0.279	1						
Th	-0.120	0.187	-0.002	0.171	0.144	0.187	-0.165	0.512	0.109	0.512					
Sr	0.848**	0.915**	0.843**	0.748**	0.717**	0.882**	0.305	0.806**	0.438	0.180	0.895**	1			
Cd	0.763**	0.979**	0.741**	0.837**	0.786**	0.964**	0.305	0.796**	0.438	0.180	0.895**	0.739**	1		
Bi	-0.289	-0.166	0.475	0.098	0.397	-0.103	0.218	-0.003	-0.550*	-0.322	0.090	-0.112	0.780**	1	
V	0.662*	0.856**	0.613*	0.360	0.402	0.804**	0.225	0.953**	0.296	-0.057	0.739**	-0.210	0.204	-0.306	1
Ca	0.182	0.032	0.174	0.357	0.198	-0.027	0.324	-0.162	0.343	0.343	0.049	0.204	-0.349	0.953**	1
P	0.053	-0.106	0.076	0.125	0.042	-0.149	0.238	-0.192	0.318	0.128	-0.129	0.234	-0.128	0.233	0.309
Cr	-0.031	-0.310	-0.371	-0.340	-0.585*	-0.437	-0.220	-0.122	0.309	0.222	-0.374	-0.378	-0.128	0.233	0.467
Mg	0.542	0.170	0.117	0.660*	0.283	0.118	0.129	-0.107	0.169	0.222	0.338	-0.034	-0.201	0.642*	0.467
Ba	-0.045	0.310	0.645*	0.515	0.702*	0.354	0.289	0.117	-0.031	0.151	0.400	0.605*	0.038	0.187	0.021
Al	0.745**	0.920**	0.650*	0.451	0.482	0.882**	0.272	0.922**	0.226	-0.032	0.843**	-0.205	0.968**	-0.184	-0.240
K	0.769**	0.912**	0.672*	0.511	0.509	0.867**	0.270	0.953**	0.313	-0.092	0.834**	-0.176	0.980**	-0.214	-0.297
Sc	0.694*	0.928**	0.832**	0.697*	0.725**	0.905**	0.218	0.931**	0.385	0.080	0.865**	0.028	0.881**	-0.088	-0.211
Cs	0.874**	0.829**	0.627*	0.562*	0.396	0.717**	0.269	0.835**	0.323	-0.203	0.798**	-0.203	0.868**	-0.068	-0.205
Nb	-0.285	-0.027	0.385	0.400	0.503	-0.029	0.360	-0.151	-0.029	0.253	0.077	0.665*	-0.309	0.514	0.393
Rb	0.840**	0.946**	0.726**	0.691*	0.637*	0.907**	0.313	0.910**	0.348	-0.086	0.901**	-0.119	0.909**	-0.088	-0.223
Sn	0.931**	0.594*	0.465	0.608*	0.305	0.483	0.169	0.538	0.109	-0.285	0.743**	-0.121	0.486	0.312	0.204
Zr	0.353	0.070	-0.151	0.023	-0.131	0.115	-0.367	0.259	0.404	0.054	0.051	-0.402	0.192	-0.071	0.005
Ce	0.230	0.408	0.063	0.344	0.276	0.469	0.059	0.217	0.774**	0.703*	0.428	-0.476	0.246	0.169	0.069
In	0.054	0.443	0.464	0.385	0.626*	0.601*	-0.135	0.373	0.328	0.390	0.493	0.145	0.311	-0.216	-0.273
Be	-0.249	-0.015	0.557*	0.329	0.593*	0.050	0.289	0.035	-0.313	-0.085	0.074	0.943**	-0.180	0.299	0.256
Li	0.399	0.531	0.218	0.004	0.029	0.463	0.429	0.546	-0.204	0.380	0.443	-0.352	0.738**	-0.346	-0.400

Cr	Mg	Ba	Al	K	Sc	Cs	Nb	Rb	Zr	Ce	In	Be	Li
Mo													
Cu													
Pb													
Zn													
Ni													
Co													
Mn													
Fe													

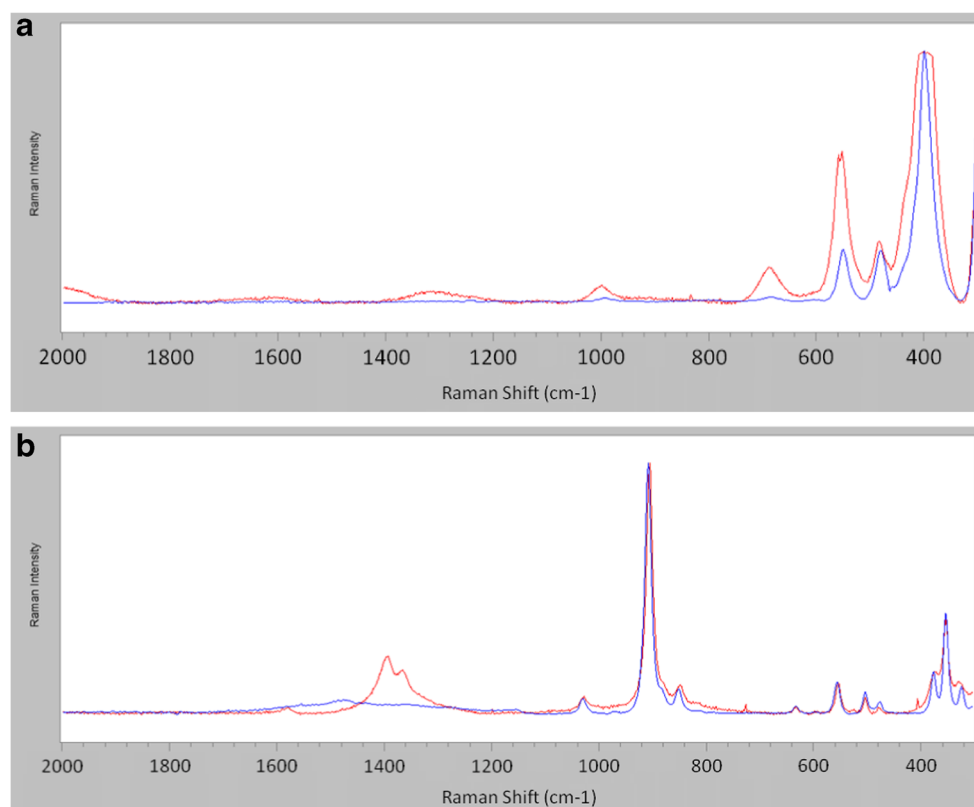
Table 7 Rotated Component Matrix of the Ore factor analysis

	Component									
	1	2	3	4	5	6	7	8	9	10
K	0.981									
Al	0.970									
Rb	0.966									
Ga	0.958									
S	0.945									
V	0.943									
Ti	0.935									
Cs	0.925									
Sc	0.904									
Cd	0.893		0.318							
Cu	0.888				0.321					
Co	0.880		0.353							
Sr	0.876									
Mo	0.855						0.324			
Y	0.846									
Pt	0.720		0.646							
Sn	0.711			0.460			0.391			
Li	0.698				−0.303		−0.401	0.323		
Zn	0.626		0.313				0.580			
Ni	0.586	0.483	0.429							
Ag		0.968								
Bi		0.951								
Au		0.939								
Na		0.936							0.351	
Te		0.860								
Be		0.798				−0.308				−0.338
Ba	0.300	0.719	0.447							
Nb		0.599				−0.539		−0.398		
Th			0.886	0.316						
Ce	0.375		0.841							
La			0.820							
As	0.369		0.744							
In	0.400	0.390	0.710							
Hg		0.302	0.403			−0.395		0.362	0.402	0.344
P				0.897						
Ca			0.315	0.871						
Ge			−0.351		0.753	0.387				
Pb	0.409	0.362			0.685					
Re		0.538			−0.666					
U					0.649					−0.556
Zr						0.884				
Hf						0.828				
Mg				0.556			0.759			
Sb	−0.315		0.464		−0.311		0.679			
Cr								−0.871		
Fe			−0.390	−0.309	0.369			−0.692		
Mn	0.368		0.407	0.424	−0.328			0.434	0.340	
W									0.881	
Tl										−0.923

but is present in or around the mineralization domain. The condition prevailing may vary from neutral-slightly alkaline or reducing environment. This factor group also has its

elements in neutral to alkaline environment, with the exception of Mo that is very mobile and Cd with medium mobility (Andrew-Jones 1968), as immobile or has low mobility. Al

Fig. 3 **a** Raman spectra of goethite in location 7. **b** Raman spectra of manganite in location 55



with the smallest ionic radius ($0.61 \text{ \AA}$) (Levinson 1981) in the group is believed to have been trapped early in the crystal structure of the mineral formed while other smaller ionic radius elements especially from the Pt to Ni are latter introduced into the mineralization. Like factor 1, Na in factor 2 has the highest mobility relative to the rest of the elements in this factor group but the chemical affinities of the elements in the group vary. With Au being the only siderophile element, lithophile elements also dominate while chalcophile elements are slightly less populated in this group. The association of the elements could have been enhanced because the ionic radii of

these elements that are closely related with the exception of Te ($2.21 \text{ \AA}$) and Be ($0.35 \text{ \AA}$) (Levinson 1981). This implies partial substitution or replacement of one element by the other as the environmental condition fluctuates. Most noteworthy is the Bi and Na, chalcophile and lithophile element but with the same ionic radius. It can also be said that the size of the elements aided the association depicted by this factor.

Factor 3 has two groups of elements: the chalcophile and the lithophile. From the factor analysis, the lithophile elements

Table 8 Raman peaks in goethite and their interpretation

Mineral	Raman peak value in goethite
Akaganeite	~ 390
Bayerite	~ 550
Ferroxyhyle	~ 680
Gibbsite	~ 400
Goethite	~ 390, ~ 995, ~ 680, ~ 550, ~ 480, ~ 385
Maghemite	~ 680, ~ 685
Nordstrandite	~ 390, ~ 595
Magnetite	~ 670, ~ 666, ~ 540–550, ~ 490,
Quartz	~ 460, ~ 464
Hematite	~ 610, ~ 500, ~ 410,
Manganite	~ 600

Table 9 Raman peaks in manganite and their interpretation

Mineral	Raman peak value
Akaganeite	~ 390
Bayerite	~ 550, ~ 900.5
Boehmite	~ 500, ~ 499.5
Ferrihydrite	~ 1375,
Ferroxyhyle	~ 1325, ~ 1350, ~ 680
Gibbsite	~ 400
Goethite	~ 995, ~ 680, ~ 550, ~ 480, ~ 390
Maghemite	~ 680, ~ 1400
Nordstrandite	~ 350, ~ 390, ~ 595
Magnetite	~ 540–550, ~ 490
Quartz	~ 464
Hematite	~ 610, ~ 500, ~ 410
Manganite	~ 600

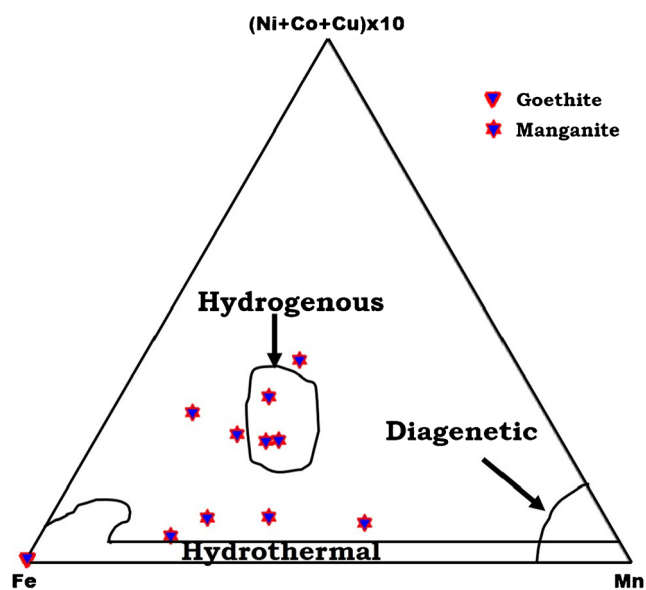


Fig. 4 Fe-(Ni + Co + Cu) $\times$ 10-Mn discriminating ternary diagram plot (plotted after Bonatti et al. 1972, Crerar et al. 1982 and Hein et al. 1992). Note the iron that plotted in the extreme Fe axis in hydrothermal field

are the first set of elements to have been precipitated before the introduction of the chalcophile elements. This scenario contradicts the picture painted by factors 1 and 2 where the environmental condition seemed to be fluctuating and become fairly stable towards the end of the phase represented by factor 2 as interpreted. This condition persisted until a change in the condition to condition that favours precipitation or deposition of lithophile elements. The ionic radius of the precipitated groups also increases down the factor in their respective geochemical class of element. This is completely different from the other two factors, i.e. factors 1 and 2.

Factor 4 with two elements P and Ca is also relatively unique. P, a siderophile element with comparatively very small ionic radius (0.25 Å) to Ca (ionic radius of 1.08 Å),

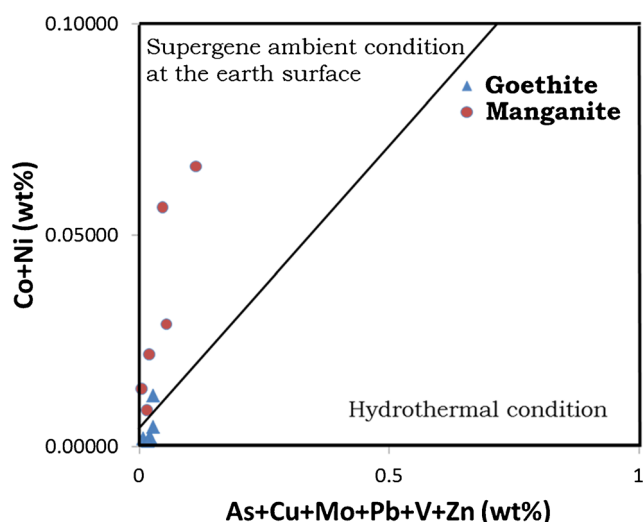


Fig. 5 Trace element discrimination binary diagram for deposits of supergene and hydrothermal origin (plotted after Nicholson 1992)

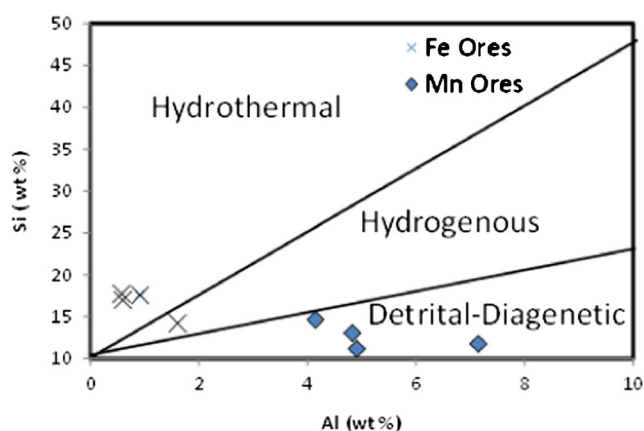


Fig. 6 Si-Al discriminating binary diagram (plotted after Peters 1988)

is grouped together with the lithophile element. This may justify the interpretation of P being trapped within the Ca by occupying the available spaces within the Ca-rich minerals in the area. Other explanation that can be given is related to the organophilic nature of these elements (Curtis 2008). This implies that, they might be related in the precursor material that is yet to be completely broken down or get transformed into another. The period between the phase or mineralization stage typified by factors 3 and 4 also show clearly a sharp shift from the environmental conditions that favour the chalcophile elements to siderophile elements and then become rhythmic. The condition existed throughout the remaining phases of mineralization coupled with the introduction of terrigenous and/or foreign bodies into the mineralization process thereby accounting for the association of elements with varying chemical affinities in the same factor group. The introductions of the foreign bodies most likely took place in the earlier, middle and later parts of the factor groups. This is because of the inconsistency in the chemical affinity of the elements, the variations in ionic radius of the elements down the groups also attest to this. While elements in factor 6 have almost the same ionic radius (range of 0.01 Å) and belong to the lithophile group of Goldschmidt classification of elements (Goldschmidt 1937), other factor group, e.g. factor 7, with close relationship in their ionic radius does not belong to the same class of elements. Fe and Mn in factor 9 are described as minor organophile elements. This justifies their associations even though they belong to different groups in Goldschmidt classification.

According to Rona (1978), the Mn/Fe ratio in hydrothermal Fe-Mn deposits is higher than 10 or lower than 0.1. The hydrogenous deposits have an approximate ratio that equals 1. The average of Mn/Fe ratio of the manganite ores from Kaoje and its environs is approximately 0.59 (Table 10). This value is higher than 0.1 and less than 10 proposed by Rona (1978). It is however approximately equal to 1. In contrast, the Fe ores have an average Mn/Fe value of 0.0024. This value is less than 0.1 as suggested for hydrothermal ore deposits. Furthermore, higher or lower Mn/Fe ratio suggests hydrothermal deposits. It

Table 10 Comparison of Fe-Mn deposits across the world (Ibrahim and Rehab 2014) with Fe-Mn ores from Kaoje and its environs, NW, Nigeria

No of samples	22	9	14	7	13	20	9	5	10
Regions	Hazara Pakistan	Baby Bare, Northeast Pacific Ocean	Wakata, Japan	Ulukenn, Turkey	Binkilic, Turkey	Eymir, Turkey	Um Bogma, Sinai, Egypt	Kaoje (goethite)	Kaoje (manganite)
Origin	Hydrothermal-hydrogenous	Hydrothermal	Hydrothermal	Sedimentary	Sedimentary/diagenetic	Volcano-sedimentary	Hydrothermal	?	?
SiO ₂ (%)	9.41	2.02	58.16	13.68	10.65	16.04	1.81	53.34	41.09
TiO ₂ (%)	0.84	0.04	0.04	0.1	0.02	0.02	0.05	0.10	0.55
Al ₂ O ₃ (%)	12.53	0.27	0.55	2.49	2.85	0.73	0.93	2.20	16.74
Fe ₂ O ₃ (%)	20.33	2.30	0.92	3.72	2.46	0.26	19.51	38.79	8.23
MnO (%)	33.78	48.52	32.5	63.78	33.39	69.91	57.26	0.06	21.68
MgO (%)	0.59	1.58	0.19	1.99	1.27	0.59	0.71	0.01	1.22
CaO (%)	6.43	0.97	4.15	4.05	18.96	2.4	3.38	0.03	5.01
Na ₂ O (%)	0.07	0.64	0.04	0.24	0.39	0.01	0.66	0.01	0.01
K ₂ O (%)	0.88	0.22	0.1	0.05	0.56	0.05	0.34	0.02	0.10
P ₂ O ₅ (%)	3.73	0.04	0.1	0.18	0.31	0.07	0.12	0.15	0.20
Ba (ppm)	6304	7091.67	13.79	427	6892	2364.7	1762	25.6	537
V (ppm)	573	172.33	258	—	106	132	260	10	41
Cr (ppm)	247	8.89	10	—	26	—	293	19.6	8.3
Co (ppm)	404	135.33	2	13	59	103.5	127	12.4	117.6
Ni (ppm)	305	300.67	28	10	167	67.35	133	30.5	633.6
Cu (ppm)	375	226	50	56	26	80.5	1138	35.79	49.51
Zn (ppm)	580	123.22	26	70	49	62.45	1211	149.6	477.9
Pb (ppm)	2357	—	112	65	—	9.33	125	7.17	5.59
Rb (ppm)	24	14.22	2	—	—	0.77	10	0.4	2.1
Sr (ppm)	—	877.44	85	185	2100	116.47	674	1.5	71.6
Y (ppm)	—	10	5	—	15	8.45	36	3.98	7.77
Nb (ppm)	—	1.5	3	—	—	0.15	1	0.08	0.07
Zr (ppm)	—	9.22	12	—	32	8.46	98	4.1	4.6
Co/Ni	1.32	0.45	0.07	1.3	0.35	1.54	0.88	0.36	0.18
Co/Zn	0.7	1.1	0.08	0.19	1.2	2.24	0.11	0.07	0.37
Mn/Fe	2.16	26.89	39	18.98	15.03	880.33	23.27	0.0024	0.5887

also implies high segregation and/or differentiation of Mn and Fe in sedimentary environment (Ibrahim and Rehab 2014). The Mn/Fe ratio value for the manganite ore in Kaoje and its environs is from > 1.3158 to 0.2326 while that of goethite is from 0.0042 to 0.0014 . Although the average of the Mn/Fe ratio of both the goethite and manganite in the study area is not close to any of the values in Table 10, their average values suggest that the manganite is hydrogenous while the goethite is related to hydrothermal condition.

Similar to Mn/Fe ratio, Toth (1980) proposed that Co/Zn ratio of 0.15 is indicative of hydrothermal Fe-Mn deposits while ratio of 2.5 implies hydrogenous settings. Average of the ratio of Co to Zn of manganite ores from Kaoje and its environs is 0.37 while the goethite has an average value of 0.07. The ratio of 0.07 of the goethite in the study area is approximately equal to the average of the Co/Zn ratio of Um Bogma deposit (0.11) when rounded to 1 decimal place and almost the same with that of Wakata, Japan (0.08) (Table 10). These two deposits are hydrothermal in origin; hence, it suggests that the goethites from Kaoje and its environs are of hydrothermal origin. The average of the ratio of Co to Zn in the manganite ore is not close to any of the compared deposits. It lies between the value of Ulukun, Turkey (0.19) and Hazara, Pakistan (0.7) (Table 10). The Fe-Mn deposits of Ulukun, Turkey and Hazara, Pakistan are sedimentary and hydrothermal-hydrogenous in origin, respectively. The average ratio value of 0.37 recorded for the manganite in Kaoje area implies therefore, that the manganite is not hydrothermal in origin but hydrogenous or diagenetic in origin. The highest and lowest values in manganite ores are 0.87 and 0.10 while that of goethite are 0.14 and 0.03, respectively. Olobaniyi (1997), in an attempt to quantify the extent of hydrothermal contribution to the protolith of Isanlu BIF, stated that ores with low $Al/(Al + Fe + Mn)$ values have more hydrothermally derived materials compared to those with higher values. The goethite from this study area has relatively lower ratio of $Al/(Al + Fe + Mn)$ (0.0155) compared to the manganite (0.2535). These relatively lower values suggest that the goethite mineralization is more influenced by hydrothermal fluid than the manganite.

Conclusion

From the integration of the field data, geochemical and statistical analysis and discriminating plots, it is concluded that there are two types of mineralization in this area and two host rocks. These mineralizations are the manganite mineralization that is hosted by the quartz-mica schists, while the second mineralization is the goethite mineralization that is hosted essentially in the clastic sedimentary rocks (sandstones, siltstone and sandstiltstones) in the study area. The goethite mineralizations are in the northeastern part of the area (Sire Yamayamusa-Kaoje axis) and occur mostly as sedimentary

cappings. Other goethite enrichment is in the northwestern part of the area along Taka Lafia-Derena axis and in the southern part of the area (south of Barkin-Ruwa). The manganite mineralizations are nucleated around Derena-Buya axis and south of Barkin-Ruwa. They trend in NE-SW direction with Buya settlement having the northern boundary while Barkin-Ruwa has the southern boundary of the mineralization. This trend coincides with the trend of the faults and the fault trace that were mapped in the northeastern part of the area, thereby implying that the mineralization is structurally controlled.

The goethites in this area are product of hydrothermal mineralization (Fig. 6) followed by remobilization while the manganites are products of supergene enrichments. The mineralization systems in this area are not closed-type thereby giving room for some materials, for example, fresh water and terrigenous materials to enter the system while volatile and mobile elements left the system with changing environmental conditions.

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