

## Geochemical Evidence for the Origin of the Daranna Manganese Deposit, Kebbi State, Nigeria

\*<sup>1</sup>L. M. Adamu, <sup>2</sup>N. G. Obaje, <sup>3</sup>A. A. Sidi, <sup>3</sup>A. K. Aweda, <sup>4</sup>H. M. Liman

<sup>1</sup>Department of Earth Sciences, Kogi State University, Anyigba, Nigeria

<sup>2</sup>Nigerian National Petroleum Corporation Chair in Basinal Studies, Ibrahim Badamasi Babangida University, Lapai, Nigeria

<sup>3</sup>Department of Geology, Ibrahim Badamasi Babangida University Lapai, Nigeria

<sup>4</sup>Department of Geography, Ibrahim Badamasi Babangida University Lapai, Nigeria

[\*Corresponding Author: E-mail: [lukman10musa@yahoo.com](mailto:lukman10musa@yahoo.com)]

### ABSTRACT

Inorganic and organic geochemical and geostatistical studies of manganese ore deposits exposed at Daranna, near Kaoje have been carried out with the aim of characterizing and delineating the origin of the manganese ore deposits. Data were obtained from field observations and chemical analyses of 12 ore samples. Major and trace elements and organic geochemical analyses were conducted with Energy Dispersion X-ray Fluorescence Spectrometer and Rock-Eval pyrolysis method at Geo-data GmbH Garbsen, Germany. Results of the Major and trace elements, total organic carbon content abundances and the correlation among them imply that Daranna mineralizations are mainly of hydrothermal origin with little contribution from contemporaneous volcanic materials and this is confirmed by high Fe/Mn (8.274 to 24.066 wt%) and low Co/Zn ratios and trace element patterns. The significant geochemical characteristics such as high Mn content (22.660 to 62.330 wt%; average 45.919 wt%), low concentration of Fe (2.590 to 3.310 wt%; average 3.008 wt%) reveal a primary distal hydrothermal source for mineralization. The position of samples on Ni–Zn–Co and (Co/Zn)–(Co + Ni + Cu) diagrams and evaluation of these data reveals that hydrothermal activity was the main process with sedimentary influence responsible for mineralization in the Daranna manganese deposit.

**Keywords:** Daranna, Manganese, Trace Element, Major Element, Hydrothermal, Geochemistry

### INTRODUCTION

The 923, 768 km<sup>2</sup> extent area Nigeria is covered in just about uniform ratio by basement and sedimentary rocks terrain (Obaje, 2009). Workers like Odeyemi (1977), Ajibade *et al.* (1987), Caby (1989) reported that the Nigerian Basement Complex is characterized by different grades of metamorphism, orogenies and structural modifications which have been reflected in its complex petrological, structural composition and mineralization potential. Woakes *et al.* (1987), Dada *et al.* (1989), Oyinloye (2006) in their work discussed the younger metasediments in Nigeria to be well known for their mineralization such as Gold, Banded Iron Formation (BIF), lead/zinc ores, tantalite manganese deposits and marble.

Raw Material Research and Development Councils -RMRDC, (2009) reported over 5,000,000 metric tons (MT) of manganese

deposit in Nigeria. Manganese are normally developed as a mineral in the form of silicates, carbonates or oxides of which their origin are hitched to a great many factors: a-few of which are in a scope of tectonic frameworks, with ore deposits being linked with ophiolites as well as continental sedimentary sequences, depositional environment, climate and biogenic conditions (Polgári *et al.*, 2012; Öksüz, 2011; Hein *et al.*, 1997; Bolton *et al.*, 1988). These deposits can be divided into three types based on mineralogy, geochemical composition and tectonic setting: (1) hydrogenous, (2) hydrothermal, and (3) diagenetic/biogenetic-bacterial deposits.

The manganese deposits in this study are located in Daranna village which is situated near Kaoje of Kebbi State (Figure 1). The area lies within the geographical coordinates: 11° 11' N and 4° 7' E. This Daranna manganese occurrence was first

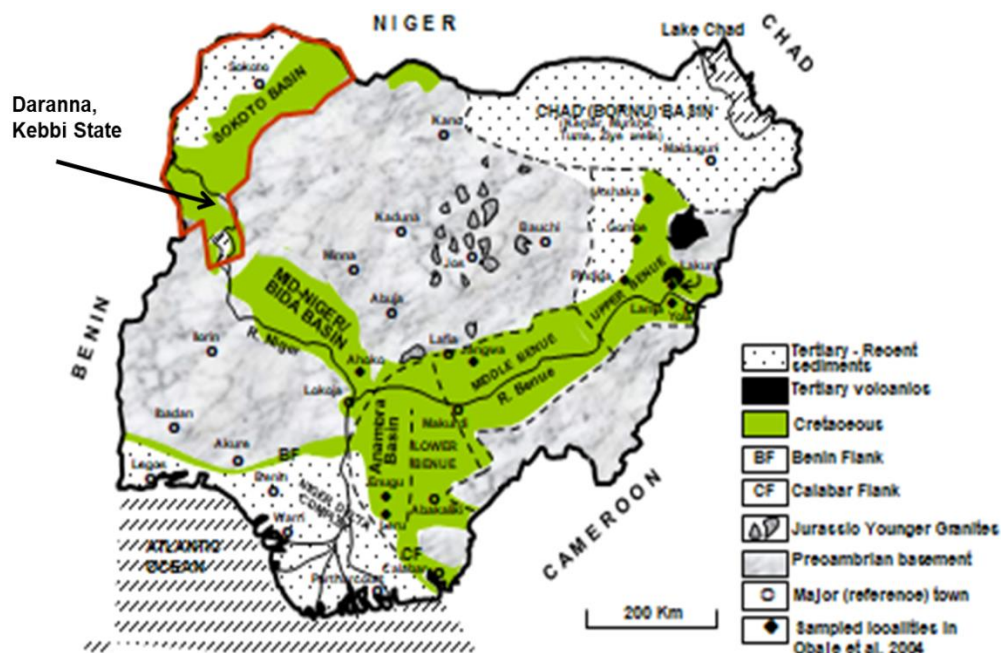
reported by this research based on a tip off by local communities. The study noted that the locality is at the boundary between the Basement Complex and sedimentary rocks of the Sokoto Basin (Figure 1). The Manganese deposits were actually not too distant from an outcropping basement granite-gneiss to the north-west of the deposit but no other rock exposures were mapped again in the vicinity of the manganese deposit to enable a proper deciphering of its modes of occurrence. The Daranna manganese is dark and appears like coal but has more weight when compared with coal (Figure 2). It is being commercially mined by local miners since the deposit is large.

Several works have reported the occurrence of manganese in the northwestern part of Nigeria. Earlier documentation on manganese mineralization appeared in the works of Truswell and Cope (1963), Wright and McCurry (1970), Bar and Mucke (1982), Moneme and Scott (1983), Moneme *et al.* (1982), Mucke and Okujeni (1984), Raeburn (1927) and Bafor and Mucke (1990), Yaro, (1998), Raw Material Research and Development Councils -RMRDC (2009), National Steel Raw Materials Exploration Agency - NSRMEA (2010), Mucke (2005), Muriana *et al.* (2014) and Muriana (2016). Truswell and Cope, (1963) in their work identified pelitic and semi pelitic rocks, banded iron rocks, amphibolites and other minor rocks, like magnesian rich (talcoose rock) and schistose varieties in the Basement Complex. Wright and McCurry, (1970) in their work on the manganese deposits at Mallam Ayuba within the Maru schist belt observed that the manganese mineralization occurs in ridges for over 800 m along a north- south strike and lying near Mallam Ayuba settlement. Bar and Mucke (1982) reported that the ore bodies composed of massives brown- gray-black, jointed or fractured, fine-grained iron manganese mineralization dipping at 850 east with strike direction of 1100,

having according to Moneme and Scott (1983) a conformable beds of quartzite that contains banded iron formation (BIF), gold and amphibolites.

Moneme *et al.* (1982), Mucke and Okujeni (1984) worked on the Tudun Kudu manganese ore and reported that the ore occur within Precambrian Karaukarau schist belt. They according to Moneme *et al.* (1982), Mucke and Okujeni (1984) are Proterozoic rocks, folded into synclinal belts within the crystalline Basement Complex, and metamorphosed to phyllites, quartzites and psammitic schists of low to medium grade. Raeburn (1927) and Bafor and Mucke (1990) in their studies reported small quantities of manganese deposits from Basement rocks in South-eastern and South-western parts of Nigeria (Figure 1). However, they reported that the mineralizations are mostly of poor grade, and thus require some processing to improve quality for industrial uses.

Studies by Yaro, (1998) and Binta *et al.*, (2016) were aimed at upgrading of the manganese ore. These authors worked on decolourization of manganese ore from Maikujeri and Kaoje area using magnetic separation and acid bleaching as route for beneficiation. Binta, (2013) assessed the manganese concentrates in the area with emphasis on its industrial application. Yaro (1996), Binta (2013), Muriana *et al.* (2014), Muriana, (2016) and Binta *et al.* (2016) worked on the beneficiation of Nigeria manganese ores. The investigation carried out by Yaro, (1996) and Muriana *et al.* (2014) concentrated on appraisal of manganese deposits in the study areas with emphasis on its metallurgical features. Muriana, (2016) affirmed the hydrometallurgical extraction of manganese metal by thermal decomposition of the purified manganous nitrate ( $MnN_2O_6$ ) crystals to synthesize the chemical manganese dioxide (CMD) from Madaka area.



**Figure. 1.** Generalized geological map of Nigeria showing location of Daranna within the Sokoto Basin (After Obaje, 2009).

The works of Mücke *et al.* (1999) Mücke (2005), Yaro (1998) and Binta (2013) whose attention channeled to the Banded iron formations (BIFs) which are found to intersperse with manganese ores in the study areas report the association between BIFs and manganese in area around Maru. Mucke (2005) reported that vast majority of manganese deposits are of sedimentary character and emphasized on the importance of additional processes as critical in the development of large accumulation of manganiferous sediments in depositional environment. Available results of geological studies show that in Nigerian, most of the manganese deposits are found in the schist belts in the Basement Complex and are of metamorphic origin (Mucke and Okujeni, 1984). Therefore, this research was conducted with the aim of determining the geochemical compositions

and Petrogenetic characterization of the manganese deposits around Daranna area. Hence, it documents the first geochemical study of the ore deposits in the study area which include descriptions and identification of the deposits in-situ exposures. The study also disclosed the elemental composition of the manganese as well as the organic contents. The findings of this work would help in the understanding of the origin of the Daranna manganese deposits in the study area.

### MATERIALS AND METHODS

Twelve ore samples (300 g each) were systematically collected from the field using grid sampling technique from the Daranna manganese deposit using the materials such as hammer, shovel, sample bags, marker and global positioning system (GPS) (Figure 2)



**Figure 2.** Field photographs of massive manganese deposit at N11°06'51.7" and E004°00'25.1" in Daranna, (a,b,c & d) shows authors doing a macro examination of the deposits insitu.

### Geochemical Methods of Analysis

The Geochemical analysis involved taking the selected samples firstly to the sample preparation laboratory for pulverization in IBBU Lapai CASTER Laboratory, Nigeria. The pulverizing machine ground or milled the rock sample into fine grain form with crystals not more than 60  $\mu\text{m}$ . The pulverized sample was measured and further made into pellets using deionized water. The pellet was then air-dried and introduced into the vacuum chamber of Energy Dispersion X-ray Fluorescence Spectrometer machine and analyzed following the standard procedures (Norrish and Hutton, 1969) at Geo-data GmbH Garbsen, Germany. Major oxide and trace element contents were determined. In addition, in order to strengthen the inorganic geochemical results, six (6) selected manganese field samples from Daranna of the northwestern Kebbi, Nigeria (Table 1) were analyzed for total organic carbon (TOC) using LECO carbon analyzer, and Rock-Eval pyrolysis. The LECO TOC content and Rock-Eval pyrolysis analyses were made in the laboratory of Geo-data GmbH Garbsen, Germany. The Analyses were performed on 80 mg to 102 mg crushed whole rock samples, heated to 600  $^{\circ}\text{C}$  in a helium atmosphere, using a LECO and Rock-Eval 6 unit.

### Geostatistical Analysis of Daranna Manganese Deposit

Multivariate statistical analysis was applied to probe on the relationship between organic and inorganic geochemical study and their instrumentality to unravelling the origin of the Daranna manganese deposit. The results (XRF, LECO and Rock Eval Pyrolysis) obtained for studied samples were statistically analyzed using cluster analysis hierarchical and K-means cluster analysis) and Pearson's correlation by SPSS 15.0 (Zhang *et al.*, 2007). Cluster analysis is based on a matrix measuring the differences between each parameter of each sample. Hierarchical cluster analysis was used to enables the grouping of the samples or parameters without any previous classification (El-Nady and Lotfy, 2016) and these differences were squared. By adding the individual matrices, a summed matrix was obtained. In order that in the final matrix each parameter becomes an equal share, the values of the parameters were preliminarily standardized. Based on the final matrix, dendrograms were constructed following previously described methods (Golobocanin *et al.*, 2004; Adamu *et al.*, 2020). Also Pearson's correlation and Linear regression analyses were performed as described by El-Nady and Lotfy, (2016) and Adamu *et al.*, (2020).

## RESULTS AND DISCUSSION

### Correlation between Major, Trace Elements and Total Organic Carbon (TOC) of the Daranna Manganese Deposits

The correlations among organic contents (Table 1), major and trace element concentrations (Table 2a and b) of ore samples are presented in Table 3, Figure 3 and Figure 4. Elements with similar geochemical behavior are discriminated in the correlation matrix dendrogram (Figure 8). In this respect, three different element groups were determined as (MnO, SiO<sub>2</sub>, LOI, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, CaO, MgO, NiO, ZnO, TiO<sub>2</sub>, CuO, Na<sub>2</sub>O, PbO, V<sub>2</sub>O<sub>3</sub>), (Mn, Pb, Co, Cu) and (Zn-Ni). In the formation of element groups, the similarities of correlation coefficients were taken into account. According to Choi and Hariya, (1992), Bonatti *et al.* (1972), Crerar *et al.*, (1982), Roy *et al.*, (1990) and Nicholson, (1992), positive correlations of Zn and Ni with Mn may give valuable information on the origin of the mineralization under investigation. Al and Ti have detrital characteristics, Mn and Si in association with Pb, Zn and Cu are indicative of hydrothermal activity. The association of Fe<sub>2</sub>O<sub>3</sub> with Pb, which is one of the elements indicating the presence of hydrothermal activity. On the basis of Table 3,

SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> displays same negative correlations mainly with MnO and V<sub>2</sub>O<sub>3</sub> and Ni. Positive correlations of Al<sub>2</sub>O<sub>3</sub> with Zn and Ni may show that these elements have a sedimentary origin. MnO shows negative correlation with SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> that were determined to have a sedimentary origin. This could explain that manganese is derived from a hydrothermal source.

The presence of organic carbon as total organic carbon (TOC) suggest influence of sedimentary processes. The negative correlation of organic carbon (TOC) with all the oxides and trace elements except SiO<sub>2</sub> and Pb suggests influence of sedimentary processes. Major and trace element concentrations of manganese mineralization of various origins from Japan, Turkey and the study area (Nigeria) are compared and results presented in Table 3. In comparison with sedimentary Mn-Fe deposits, it is shown that concentrations of all other trace elements except for Cr and Pb are lower than those of the Daranna mineralization. All these data may imply that the Daranna mineralization might have formed via both hydrothermal and sedimentary processes.

**Table 1:** Total organic carbon content and rock–eval pyrolysis results of Daranna manganese deposit

PARAMETER	KB-1B	KB-1C	KB-2A	KB-3A	KB-4A1	KB-4A2
TOC	2.84	3.13	3.11	4.53	1.96	2.03
S1	0.00	0.00	0.00	0.00	0.00	0.00
S2	0.18	0.05	0.03	0.01	0.01	0.00
S3	0.73	0.78	0.40	0.46	0.31	0.19
HI	6.00	2.00	1.00	0.00	1.00	0.00
OI	26.00	25.00	13.00	10.00	16.00	9.00

S1: mgHC/g rock; S2: mgCO<sub>2</sub>/g rock; HI (hydrogen index): mgHC/g TOC; OI (oxygen index): mgCO<sub>2</sub>/g TOC

Table 2a: Major element content of Daranna manganese ore deposit (major elements in wt %).

MAJOR OXIDE COMPOSITION (%)	KB-1A	KB-1A1	KB-1A2	KB-2B	KB-2B1	KB-2B2	KB-3B	KB-3B1	KB-3B2	KB-4B	KB-4B1	KB-4B2	MIN	MAX	AVERAGE
SiO <sub>2</sub>	14.69	15.20	14.99	29.32	24.53	19.99	6.02	8.020	6.82	41.69	38.99	40.89	6.02	41.69	21.76
TiO <sub>2</sub>	0.09	0.09	0.10	0.12	0.11	0.12	0.07	0.07	0.06	0.15	0.16	0.15	0.06	0.16	0.11
Al <sub>2</sub> O <sub>3</sub>	11.6	12.11	10.80	12.02	11.99	12.12	10.13	10.71	10.61	12.08	12.01	12.07	10.13	12.12	11.51
Fe <sub>2</sub> O <sub>3</sub>	3.02	3.00	3.06	2.98	3.03	3.19	2.59	2.88	2.60	3.21	3.31	3.22	2.59	3.31	3.00
CaO	1.00	0.99	0.89	0.93	1.00	1.00	0.68	0.70	0.60	0.42	0.63	0.38	0.60	1.00	0.77
MgO	0.33	0.40	0.26	0.11	0.22	0.21	0.53	0.41	0.39	0.09	0.13	0.09	0.09	0.53	0.26
Na <sub>2</sub> O	0.04	0.04	0.03	0.02	0.02	0.03	0.03	0.02	0.02	0.03	0.03	0.03	0.02	0.04	0.03
K <sub>2</sub> O	0.92	0.89	0.90	0.68	0.77	0.69	0.91	0.78	0.86	0.34	0.50	0.47	0.34	0.92	0.72
MnO	52.0	54.10	51.94	39.42	41.84	45.63	62.33	60.88	61.67	26.82	27.68	26.66	26.66	62.33	45.91
V <sub>2</sub> O <sub>3</sub>	<0.001	<0.001	<0.001	<0.001	<0.001	0.002	0.002	0.002	0.002	ND	ND	<0.001	<0.001	0.002	0.002
Cr <sub>2</sub> O <sub>3</sub>	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
CuO	0.03	0.05	0.02	0.01	0.02	0.01	0.07	0.06	0.07	0.02	0.02	0.02	0.01	0.07	0.03
ZnO	0.28	0.27	0.19	0.17	0.26	0.20	0.22	0.23	0.22	0.27	0.19	0.28	0.17	0.28	0.23
PbO	0.002	0.002	0.001	ND	ND	ND	0.01	0.008	0.01	ND	ND	ND	0.001	0.01	0.006
NiO	0.24	0.20	0.18	0.08	0.10	0.19	0.21	0.20	0.20	0.18	0.20	0.19	0.18	0.24	0.18
LOI	15.30	12.50	16.40	13.90	15.70	15.98	15.60	14.50	15.40	14.30	15.80	15.20	12.50	16.40	15.04
Summation	99.54	99.88	99.79	99.77	99.61	99.49	99.40	99.50	99.58	99.61	99.69	99.68	99.40	99.88	99.63

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Table 2b: Trace element content of manganese ore deposit

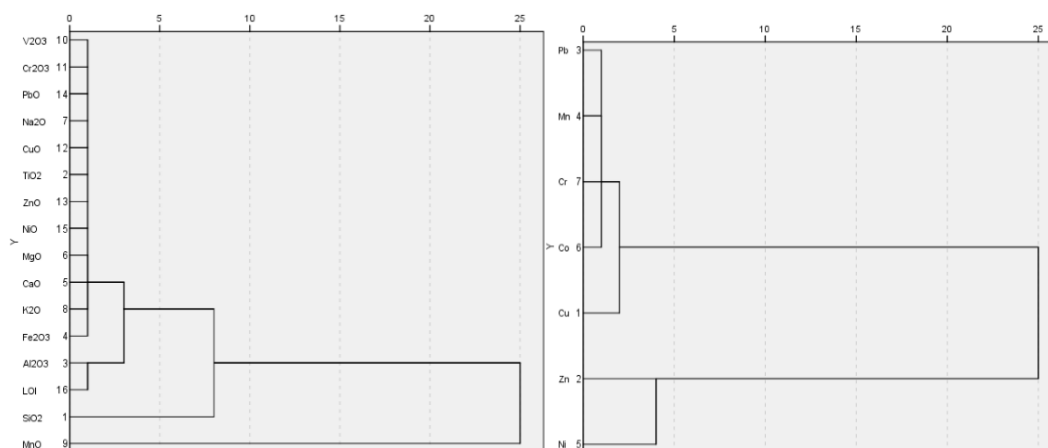
ELEMENTS	KB-1A	KB-1A1	KB-1A2	KB-2B	KB-2B1	KB-2B2	KB-3B	KB-3B1	KB-3B2	KB-4B	KB-4B1	KB-4B2	MIN	MAX	AVERAGE
	249.87	427.19	193.44	73.01	153.32	532.97	581.86	534.03	573.88	167.68	231.55	159.69	73.01	581.86	323.2
	2263.48	2239.40	1597.27	1413.46	2136.25	1662.42	1795.05	1907.74	1835.29	2210.98	1599.94	2251.18	1413.46	2263.48	1909
	18.41	18.41	9.20	ND	ND	ND	74.57	59.65	74.57	ND	ND	ND	9.20	74.57	42.47
	40.28	41.82	40.20	30.51	32.38	35.31	48.24	47.11	47.72	20.76	21.42	20.63	21.42	48.24	35.53
	1920.14	1589.62	1487.32	673.28	845.51	1550.11	1650.42	1595.40	1634.70	1428.14	1577.23	1490.91	673.28	1920.14	1453
	179.04	147.86	159.60	86.70	102.01	98.20	113.61	122.20	116.60	86.69	88.54	87.70	86.70	179.04	115.7
	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Iron	4671.22	4464.31	3487.06	2276.96	3269.48	3878.82	4463.75	4266.16	4282.78	3914.25	3518.70	4010.12	2276.96	4671.22	3875
(Co+Ni)×10	23490.50	21646.81	18403.74	8329.90	11008.45	21812.83	23458.90	22518.40	23251.91	16825.10	18973.29	17383.10	8329.90	23490.50	1892
Co+Ni	2349.05	2164.68	1840.37	832.99	1100.84	2181.28	2345.89	2251.84	2325.19	1682.51	1897.32	1738.31	832.99	2349.05	
	0.07	0.06	0.10	0.06	0.04	0.05	0.06	0.06	0.06	0.03	0.05	0.03	0.03	0.10	0.06
	17.23	18.03	16.97	13.22	13.80	14.27	24.06	21.13	23.71	8.35	8.36	8.27	8.27	24.06	15.62
	0.09	0.09	0.10	0.12	0.11	0.06	0.06	0.07	0.07	0.06	0.05	0.05	0.05	0.12	0.08

**Table 3:** Comparison of Daranna manganese occurrences with manganese ores from other locations

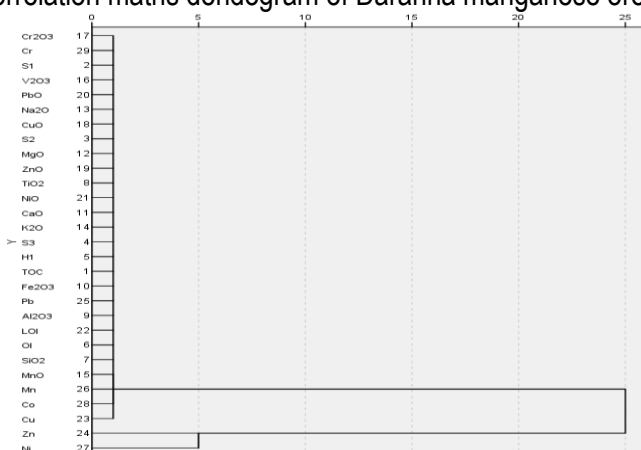
ORE DEPOSIT	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
<b>Origins</b>		A		B		C			AC		A	AB
<b>SiO<sub>2</sub></b>	25.87	63.02	43.69	13.6	10.65	12.67	9.41	16.04	84.39	49.62	44.09	21.76
<b>TiO<sub>2</sub></b>	0.04	0.03	0.32	0.1	0.02	0.04	0.84	0.02	0.06	0.16	0.34	0.111
<b>Al<sub>2</sub>O<sub>3</sub></b>	1.07	0.65	0.73	2.49	2.85	1.27	12.53	0.73	1.29	3.66	0.80	11.52
<b>Fe<sub>2</sub>O<sub>3</sub></b>	2.44	0.68	2.96	3.72	2.46	0.59	20.33	0.26	0.76	6.63	5.75	3.01
<b>MnO</b>	45.59	29.22	45.88	63.78	33.39	67.21	33.78	69.91	8.82	26.79	42.46	45.92
<b>MgO</b>	0.42	0.2	0.6	1.99	1.27	0.08	0.59	0.59	0.3	1.31	0.18	0.27
<b>CaO</b>	5.17	0.24	1.28	4.05	18.96	1.67	6.43	0.24	0.5	2.94	0.69	0.77
<b>Na<sub>2</sub>O</b>	0.12	0.05	0.29	0.24	0.39	0.07	0.07	0.01	0.17	0.18	0.30	0.03
<b>K<sub>2</sub>O</b>	0.21	0.11	0.22	0.05	0.56	0.46	0.88	0.05	0.2	0.67	1.27	0.73
<b>P<sub>2</sub>O<sub>5</sub></b>	0.08	0.04	0.25	0.18	0.31	0.12	3.73	0.07	0.02	0.11	0.13	
<b>Cr</b>	(-)	13.7	45	(-)	26	16	247	(-)	(-)	(-)	29.85	(-)
<b>Co</b>	28.75	25.21	11	13	59	222	404	103.5	85.36	367.4	125.24	115.73
<b>Ni</b>	89.13	69.4	36	10	167	341	305	67.35	86.13	280.4	288.46	1453.57
<b>Cu</b>	62.13	154.9	72	56	26	691	375	80.5	117.74	450.8	28.05	323.21
<b>Zn</b>	77.74	66.6	64	70	49	147	580	62.45	35.62	81.8	230.67	1909.37
<b>Pb</b>	19.68	6.5	49	65	(-)	18	2357	9.33	2.02	25.8	541.6	42.47
<b>Mn/Fe</b>	56.23	97.17	199	18.98	15.03	133.43	2.16	880.33	18.85	6.06	105.37	15.62
<b>Co/Zn</b>	0.38	0.38	0.17	0.19	1.2	1.51	0.7	2.24	2.2	4.49	0.57	0.06
<b>Co/Ni</b>	0.33	0.36	0.31	1.3	0.35	0.65	1.32	1.54	0.99	1.31	0.51	0.08

Key: A = Hydrothermal; B = Sedimentary; C = Hydrogenous; AC =Hydrothermal-Hydrogenous; AB = Hydrothermal-sedimentary  
 Iran (Dehoo (1), Nasirabad (9)); Turkey (Cayirli (2), Ulukent (4), Binkilic (5), Buyukmahal (10)); Pakistan (Waziristan (3), Hazara (7), Zhob (11));  
 Japan (Honde (6)); Nigeria Daranna (12)





**Figure 3.** (a) Major element correlation matrix dendrogram of Daranna manganese ore samples, (b) Trace element correlation matrix dendrogram of Daranna manganese ore samples.



**Figure 4:** Major, trace element and TOC contents correlation matrix dendrogram of Daranna manganese ore samples

### Geochemical Characterization

Chemical compositions of the Daranna Mn deposit are presented in Table 1. MnO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and F<sub>2</sub>O<sub>3</sub> are the most abundant oxides in the Daranna Mn deposit. According to Karakus *et al.* (2010), in the domain with presiding hydrothermal processes, the SiO<sub>2</sub> content is much higher than sedimentary formations. However, in addition to hydrothermal processes, other variables such as diagenetic components, clastic materials and biosilica presence can grow the Si values (Toth, 1980; Polgari *et al.*, 2012). MnO content of ore samples from Daranna is considerably very high (26.660–62.330 wt %). The SiO<sub>2</sub> content ranges from 6.020 to 41.690 wt % in ore samples in Daranna Mn deposit. In the

Daranna Mn deposit, the F<sub>2</sub>O<sub>3</sub> content ranges from 2.590 to 3.310 wt % (Table 1). Mn/Fe ratios according to Hein *et al.*, 1997 is generally controlled by initial ratios in liquid, hydrothermal discharging distance and Eh-pH conditions (Roy, 1992) of the depositional environment, so that the solution of Mn in a wide range of Eh-pH conditions can separate Mn from Fe and cause a variation in Mn/Fe ratios. Consequently, Mn/Fe ratios are anticipated to differ in different environments of deposition. Mn/Fe ratios in the Daranna Mn deposit range from 8.274 to 24.066, which according to Hein *et al.* (1996) and Hein *et al.* (1994), is a leading characteristic of hydrothermal manganese deposits. Submarine exhalative activities (Roy, 1992), are the most

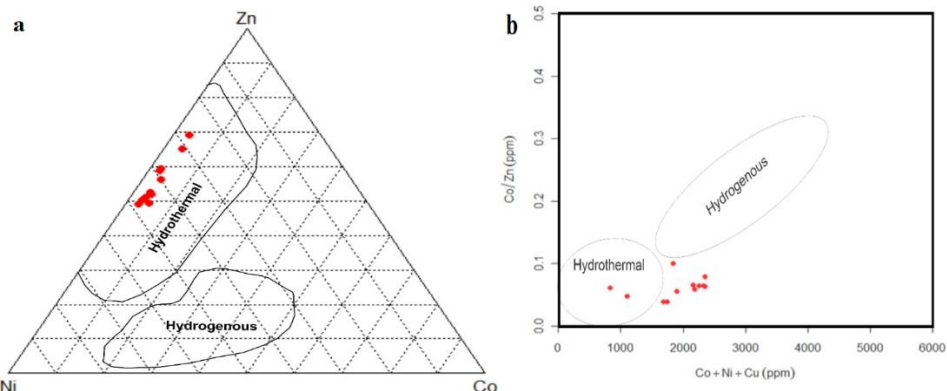
important suppliers of Si that generally precipitate as ferruginous gel. These deposits according to Peters, (1988) are also enriched in Fe relative to Al, whereas detrital sources are more enriched in Al relative to Si of which is tied to the decomposition and destruction of feldspars during transportation. The  $Al_2O_3$  contents of the Daranna Mn deposit present in ore samples varies from 10.130–12.120 wt %, averaging 11.518 wt %. According to the works of Sugisaki *et al.* (1982) and Kato *et al.* (2002); Kato and Nakamura (2003), the  $Al_2O_3$ – $TiO_2$  diagram is widely used to estimate a source of detrital material in sedimentary rocks which Brookins, (1988) attributed to be due to the fact that Ti and Al are generally insoluble in natural waters. Sabatino *et al.* (2011) reported Co to be strongly associated with Mn oxides and concluded that its abundance is reduced on average from hydrogenetic to diagenetic to hydrothermal oxide deposits. Microbial metabolic processes according to Moffett and Ho (1996) and Polgári *et al.* (2012) can increase Co and Mn concentrations in manganese deposits.

According to Toth, (1980), hydrothermal and hydrogenetic manganese deposits have mean Co/Zn ratios of 0.15 and 2.5, respectively. He used Co/Zn ratio to delineate hydrothermal and hydrogenous deposits; hydrothermal and hydrogenous manganese deposits having mean Co/Zn ratio of 0.15 and 2.5, respectively. In the Daranna Mn deposit the average ratio of Co/Zn is 0.061, similar to that of hydrothermal manganese deposits. Behavior of Co is closely related with Ni (Toth, 1980). According to (Toth, 1980), the Co/Ni ratio is an important criterion for determination of sedimentary environment particularly hot water sedimentation on the sea floor which he concluded it to being used to distinguish hydrogenous and hydrothermal deposits. Co/Ni < 1 according to Fernandez and Moro (1998) is indicative of sedimentary origin while Co/Ni > 1 according to Delian, (1994)

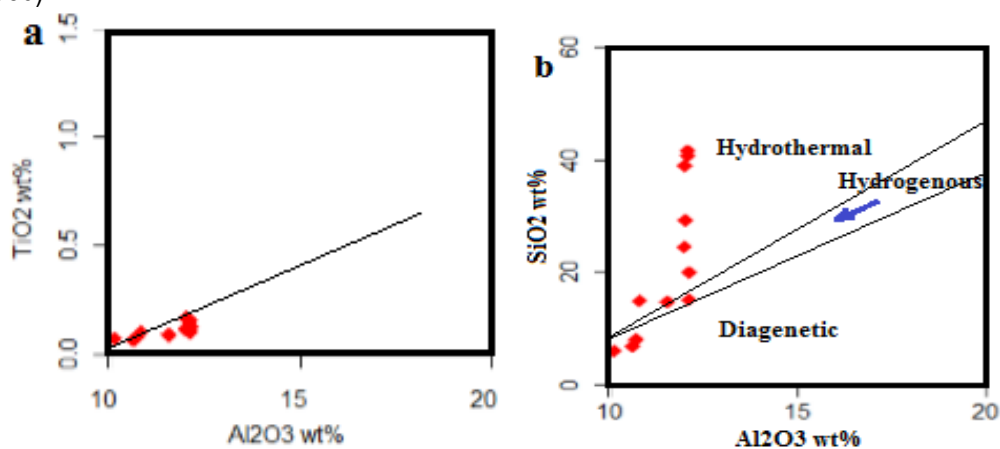
represents for a deep marine environment. A combination of Co/Ni and Co/Zn ratios is proposed as Ni–Zn–Co ternary diagram by Choi and Hariya (1992) in sight to discriminate of dissimilar marine deposits within numerous geneses. In Ni–Zn–Co ternary diagram, the Daranna Mn ore samples overlap the hydrothermal field (Figure 5a). Nicholson, (1992) reveal that hydrothermal veins and their weathered oxide cappings exhibit upraised levels of target and pathfinder elements.

The association Cu–Pb–Zn is consistently enriched where all or most of the elements in the association consistently attain a concentration from the mid-hundreds to thousands of ppm) and is considered to be part of the diagnostic hydrothermal assemblage (Nicholson, 1992). Marine manganese oxides occurring as hydrogenous crusts, coatings and nodules display enrichments in Na–K–Ca–Mg–Sr (all major components of seawater) and those formed in the deep oceanic environment are also enriched in Co–Cu–Ni. Thus, samples from the Daranna Mn deposit are enriched in Co–Cu–Ni hydrothermal area of deep oceanic environment. According to Bonatti *et al.* (1972), hydrothermal Mn oxides exhibit higher depletion in Cu, Ni, Co and Zn than hydrogenetic deposits. This is due to the long presence of hydrogenetic deposits in sea water that causes enrichment of Zn, Co, Ni and Cu by cation adsorption of hydrous iron and manganese oxides (Toth, 1980; Usui and Someta, 1997). The oxidized forms of Mn are very reactive and have a strong adsorption capacity for cationic species (Anschutz *et al.*, 2005); hence, trace metal characteristics of manganese deposits are strongly dependent on the concentration of manganese oxides according to Nicholson, (1992). The Co/Zn vs. Co+Ni+Cu diagram (Toth, 1980), reveals (80%) diagenetic genesis with hydrothermal processes for the Daranna deposits (Figure 5b).

## Adamu *et al*: Geochemical Evidence for the Origin of the Daranna Manganese Deposit...



**Figure 5:** (a) The Daranna Mn deposit on the Ni–Zn–Co ternary diagram (Choi and Hariya, 1992) (b) A plot of (Co/Zn) vs. (Co+Ni+Cu) for the manganese ores of Daranna Mn deposit (after Toth, 1980).



**Figure 6:** (a) TiO<sub>2</sub> vs. Al<sub>2</sub>O<sub>3</sub> diagrams of Daranna manganese ore samples. (b) Bivariate plot of SiO<sub>2</sub> vs. Al<sub>2</sub>O<sub>3</sub> (Choi and Hariya, 1992) in which majority (50%) of the data points of the ore samples fall within the hydrothermal field while 30% and 20% fall within diagenetic and hydrogenous field respectively.

Major element contents of ore samples are given in Table 1. Fe, Mn, Al, Si and Ti concentrations are helpful for evaluations of the origin. Carliss *et al.* (1978), Nicholson (1992), Choi and Hariya (1992) demonstrated that, hydrothermal deposits associated with the active ocean spreading centers display low Fe/Mn ratios. According to Nicholson (1992), Fe-Mn concentrations in exhalative sedimentary deposits vary in a wide range ( $0.1 < \text{Fe/Mn} < 10$ ) reflecting a strong Fe-Mn fractionation and this ratio in hydrogenetic deposits is around 1. Fe/Mn ratios of samples from the study area change in a wide interval (8.274- 24.066). Such a range indicates that mineralization is not hydrogenetic but could be a hydrothermal type. In their detailed geochemical

study on the Tokoro manganese oxide deposits in Japan, Choi and Hariya, (1992) described the deposit as the hydrothermal type and found the Fe/Mn ratio to be 0.017–6.41.

Submarine hydrothermal manganese deposits have low Fe/Mn ratios. In early stages of deposition, Fe/Mn ratios are higher (Bonatti *et al.*, 1972). Fe-Mn deposits are generally formed around the center of active submarine hydrothermal sites while manganese oxide deposits are mostly developed in distal parts of the center (Choi and Hariya, 1992; Lalou, 1983). Like Fe and Mn, Al and Ti contents could also be used to evaluate the origin of mineralization. These two elements are abundantly found in sedimentary formations. High Al and Ti contents

may indicate the sedimentary contribution to mineralization (Nicholson, 1992; Choi and Hariya, 1992; Bonatti *et al.*, 1972; Crerar *et al.*, 1980; Roy *et al.*, 1990). For sedimentary Fe-Mn deposits in Table 3, the average Al and Ti concentrations are taken as 8.82% and 0.91%, respectively. In Daranna mineralizations under investigation, Al concentrations are 10.130 - 12.120% (average is 11.518%) and Ti concentrations are 0.067-0.166% (average is 0.111%) and these values indicate a sedimentary contribution to the mineralization (Table 1 and 4). It was stated in previous works (Crerar *et al.*, 1980; Sugisaki, 1984) that Al and Ti display similar behavior during the mineralization. This relation is clearly shown in Figure 6a. The contents of Al and Ti in the Daranna deposits show a positive correlation (Figure 6a). This high positive correlation, therefore, supports the contribution of detrital material in the formation of the deposits. In Mn mineralization forming in volcanically active regions and in areas where hydrothermal processes are dominant (Table 3), Si content was found to be higher than in sedimentary formations (Nicholson, 1992). Si-Al diagram (Toth, 1980) which was constructed on the basis of Al and Si contents that represent sedimentary and hydrothermal sources, respectively, indicates that mineralization has a sedimentary origin (Figure 6b). Almost all the samples from the Daranna deposits plot within the field of hydrothermal deposits similar to the Waziristan (Pakistan) and Cayirli (Turkey) manganese deposits (Figure 6b). In addition to the hydrothermal processes, other processes and components such as diagenesis, clastic materials, and biosilica can increase the Si concentrations (Polgári *et al.*, 2012; Toth, 1980). The Daranna Mn deposit shows high enrichment in Cu, Zn, Ni and Co by an order of magnitude. Also a distinctive depletion of Cr content occurs in all samples. Average concentrations of Cu, Zn, Ni and Co are 108, 160, 125 and 50 ppm, respectively. These contents of Cu, Ni and Co are relatively low compared with hydrogenetic deposits and are a characteristic of hydrothermal ferromanganese deposits (Heshmatbehzadi and

Shahabpour, 2010). Comparison of some major elements of the Daranna ore samples with various fields given in Table 3 reveals an origin somewhat close to hydrothermal and sedimentary formations. Particularly, SiO<sub>2</sub>, TiO<sub>2</sub>, MgO, CaO, Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O and Fe<sub>2</sub>O<sub>3</sub> values resemble submarine hydrothermal and sedimentary mineralizations in the Dehoo, Ukukent, Hazara, Waziristan, Cayirli, Buyukmahal and Zhob regions classified by Choi and Hariya (1992). The difference between deep marine Mn nodules and submarine hydrothermal deposits was explained by various workers (Nicholson, 1992; Choi and Hariya, 1992; Crerar *et al.*, 1980) with the use of Zn-Co-Ni triangular diagram. Concentrations of Co, Ni, Cu and Zn in hydrothermal Mn-Fe deposits are high than pelagic sediments but lower than those of hydrogenetic deposits (Cronan, 1980). Among these elements, Cu, Ni and Zn are indicative of hydrothermal formations while Co indicates hydrogenetic deposits (Crerar *et al.*, 1980). Results of trace element analyses for the Daranna ore samples are given in Table 3. Zn-Ni-Co triangular diagram for the same samples is shown in Figure 5a. In this respect, since the distribution of samples away from the Co corner, it can be said that mineralization has a hydrothermal origin.

## CONCLUSION

The geochemical and geostatistical studies of the manganese ore deposits in *Daranna*, near *Kaoje* area has been studied and from the results acquired from the analyses, it was concluded that the major and trace element signatures show that hydrothermal processes were responsible for the formation of mineralization at Daranna with a minor contribution from sedimentary detrital materials. Major, trace elements and total organic carbon content abundances and correlation among them imply that Daranna mineralizations are mainly of hydrothermal origin. The high Fe/Mn and low Co/Zn ratios and trace element patterns, the absence of sulfide minerals coupled with relative enrichment of some bioessential elements such as Co, suggest that the Daranna

manganese deposits are hydrothermal in origin with sedimentary influence.

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#### CONFLICT OF INTERESTS

The authors declare that there is no conflict of interests regarding the publication of this paper.

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