



Geochemistry and origin of Mn deposits in the Bela ophiolite complex, Balochistan, Pakistan

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Abstract

We have studied geochemical characteristics, mineralogy and origin of the manganese deposits in Bela ophiolitic complex. Geochemical investigation was conducted in order to discuss the elemental correlations and to infer the probable origin of manganese deposits in Bela ophiolites. Ore microscopy was conducted to identify different manganese minerals and their paragenesis. Psilomelane and braunite were found to be the major ore minerals. Mineral paragenesis sequence as observed was braunite forming first. Psilomelane formed in later stages because it has been found that psilomelane is altering the braunite. Magnetite was observed as a secondary mineral as vein filling and cutting through both the braunite and psilomelane, therefore, younger than the psilomelane and braunite. The gangue minerals observed in the studied samples were quartz, cryptocrystalline silica and calcite. The correlations among different major and trace elements showed diversity of relations. MnO showed negative correlation with Fe₂O₃ (−0.73), Si₂O (−0.27), positive correlation with Al₂O₃ (0.54), TiO₂ (0.36), MgO (0.22), Pb (0.23), Ni (0.07), Cr (0.12), and no correlation was established with Zn, Cu, Co. Binary diagram of Si versus Al and ternary discrimination diagrams of Fe–(Ni + Co + Cu) × 10–Mn and Ni–Zn–Co showed hydrothermal-diagenetic-type deposits. Furthermore, the present study suggests that the enriched manganiferous fluid during its upward movement within the Tethys oceanic crust near spreading center started precipitating Mn along with Fe on the sea floor. Later on, these manganese minerals were obducted on land between Indian plate and Helmond block of Eurasian plate in existing position accompanying pillow basalt and pelagic sediments.

Keywords Manganese ore · Bela ophiolite · Hydrothermal · Ore microscopy · Geochemistry

Introduction

Manganese metal and its alloys play a significant role in various industrial sectors including, metallurgical, non-metallurgical and steel industries; however, there is considerable controversy about its origin (e.g., Magaritz and Brenner 1979; Shah and Moon 2007; Oksuz 2011; Öksüz and Okuyucu 2014). Manganese addition enhances the forging qualities of steel, the steel strength, durability, stiffness, hardness; it also improves the wearing resistance and hardenability of

the steel structures. The steel industry has massive demand of manganese mineral in order to make or give appropriate shape to the steel structures by adding required amount of manganese. It is estimated that about 90 percent of the total manganese ore is ultimately consumed in the production of and steel. Manganese ore can be deposited in various forms based on their origin. The form of manganese deposition includes the hydrothermal, sedimentary, volcanic-sedimentary, seas, shallow and deep marines, hydrothermally modified and hydrothermal (e.g., Fan and Yang 1999; Fan et al. 1999; Liu et al. 2019). Generally, the manganese deposits occur in various grades, size and origin including different oxides manganese ores (e.g., El-Hasan et al. 2008, Heshmatbehzadi and Shahabpour 2010). Manganese deposits on industrial scale are discovered in various parts around the globe: (e.g., Nikopol of Ukraine, Georgia, Groote Eylandt deposit of Northern Australia (Varentsov 1982; Frakes and Bolton 1992), manganese deposits of Japan (e.g., Miura and Hariya 1997), manganese deposits of Turkey (Öztürk and

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Frakes 1995) and also the manganese deposits are found in India (Nicholson et al. 1997). In addition to aforementioned manganese deposits, the industrial-scale giant manganese ore deposits are also found in various parts of the world such as Kalahari (Republic of South Africa), sets of Oligocene deposits of the Paratethys (Ukraine, Georgia, Kazakhstan, and Bulgaria), the northern Urals (Russia) and the Gulf of Carpentaria (e.g., Oksuz 2011) although the manganese deposits in Pakistan mainly occur in Federally Administered Tribal Areas (FATA) in NW, Kurram and Bajaur Agencies, in Mansehra (KP), Mohmand Agency, Hazara, Waziristan, Khuzdar and Lasbela, Baluchistan area. The manganese ores of Hazara area occur in the continental sedimentary sequences, while rest of the manganese ores are generally found in the ophiolitic sequences (e.g., Ahmed 1992; Naseem et al. 1997; Shah and Khan 1999; Shah and Moon 2007). The Bela ophiolite belt is interesting from an economic perspective because of the occurrences of iron ores, copper sulfides, extensive manganese deposits and associated minerals (e.g., Naseem et al. 1997, 2012). Manganese minerals found within Bela ophiolites of Aptian–Maastriichtian age are in association with Jurassic–cretaceous sediments (e.g., Naseem et al. 2012). Geologically, the Bela ophiolitic belt offers favorable environment, depositional criteria for discovering promising manganese deposition. The manganese-bearing rocks extend in a 380-km-long narrow belt from south of Lasbela to Khuzdar in the north (Zaigham and Mallick 2000; Xiong et al. 2011). In this belt, the manganese deposits occur usually as lensoidal body interbedded with metachert in pillow basalt as a host rock (e.g., Ahmed 1992; Shah and Khan 1999; Naseem et al. 2012). The Lasbela district of Balochistan province of Pakistan has manganese deposits that are associated with meta-pelagic sediments accompanying pillow basalts in ophiolite complex. As per the author's knowledge, there are not many studies that have performed detailed investigation on the origin of manganese ore deposits of Bela ophiolite of Balochistan, Pakistan, except Naseem et al. (1997, 2012) and Ali (1971), who had conducted mainly mineralogical studies of manganese ores and relatively tried to understand its origin. Although a vast array of data on the geology of manganese deposits and particularly pertaining to the chemical composition of manganese host rocks and ores is accumulated, many questions of manganese ore-genesis remain only partially answered. The main aim of this study is to provide the detailed information on the geochemical and mineralogical characteristics in order to understand the origin, provenance and deposition of manganese ore in the Bela ophiolite complex. Further, the present study assessed the existence of major oxide, selected trace elements and mineralogy of the manganese deposits of Bela ophiolite. The results are then presented, and their implications are discussed. Finally, the conclusions drawn from present study are offered.

Regional geological setting and study area

Ophiolites are exposed in different localities in Pakistan, from the Karakoram–Himalaya thrust to Lasbela district at the south (e.g., Zaigham 1991). Among them, the Bela ophiolite complex is the largest exposure (e.g., Zaigham 1991; Gnos et al. 1998). Ophiolites were obducted on the western and northern part before the Indian and Eurasian continental–continental collision at the Cretaceous–Tertiary boundary (Gnos et al. 1997, 1998; Mahmood et al. 1995; Burg and Chen 1984; Searle 1983). The counter-clockwise separation of Madagascar and Indian–Seychelles may have caused the emplacement of Bela ophiolite rocks as a result of crustal shortening and ingestion of oceanic lithosphere between African–Arabian and Indian–Seychelles Plates (e.g., Gnos et al. 1998). Bela ophiolite belt is bounded to the east by Jurassic age Mor Range, Jurassic-to-Cretaceous age Pab range and Kirthar range of Tertiary age (Sarwar 1992; Zaigham and Mallick 2000). Western boundary of Bela ophiolite is bounded by Ornach-Nal-Chaman fault system (Gansser 1966; Kazmi 1979; Farah et al. 1984; Sarwar 1992). Generally, the sedimentary rocks ranging in age from Jurassic–Cretaceous (Naseem et al. 1997) to early Tertiary (e.g., Sarwar 1992) are associated with Bela ophiolite. 3–5 km-thick sequence of Bela ophiolites consists of ultramafics, serpentinites, diabase-gabbro sills and dykes, basaltic pillow lavas, pelagic limestones and metapelites (e.g., Sarwar 1992). Gnos et al. (1998) divided Bela oceanic lithosphere into two sequences: (1) an ophiolitic upper unit forming single thrust sheet which is exposed mainly in northern exposure of Bela ophiolite and (2) lower accretionary wedge and trench sediments comprising tholeiitic MORB lavas, late Cretaceous hot spot-related magmatic rocks, and Aptian-to-early Eocene sedimentary rocks. Gnos et al. (1998) divided these two units because of their distinct structural style, age and paragenesis. The manganese deposits are almost exclusively associated with mafic lavas and jasperitic chert-type pelagic sediments. The sample collection location of the different stations is shown in Fig. 1a; however, the outcrop from where samples of Mn ore deposits are obtained is shown in Fig. 2. However, Fig. 3 shows the outcrop exposure of another station Mn deposits displayed by different colors, and samples from this location were also collected for analysis.

Materials and methods

The Bela ophiolitic belt offers favorable environment, depositional criteria for discovering promising manganese deposition. In order to investigate the geochemical

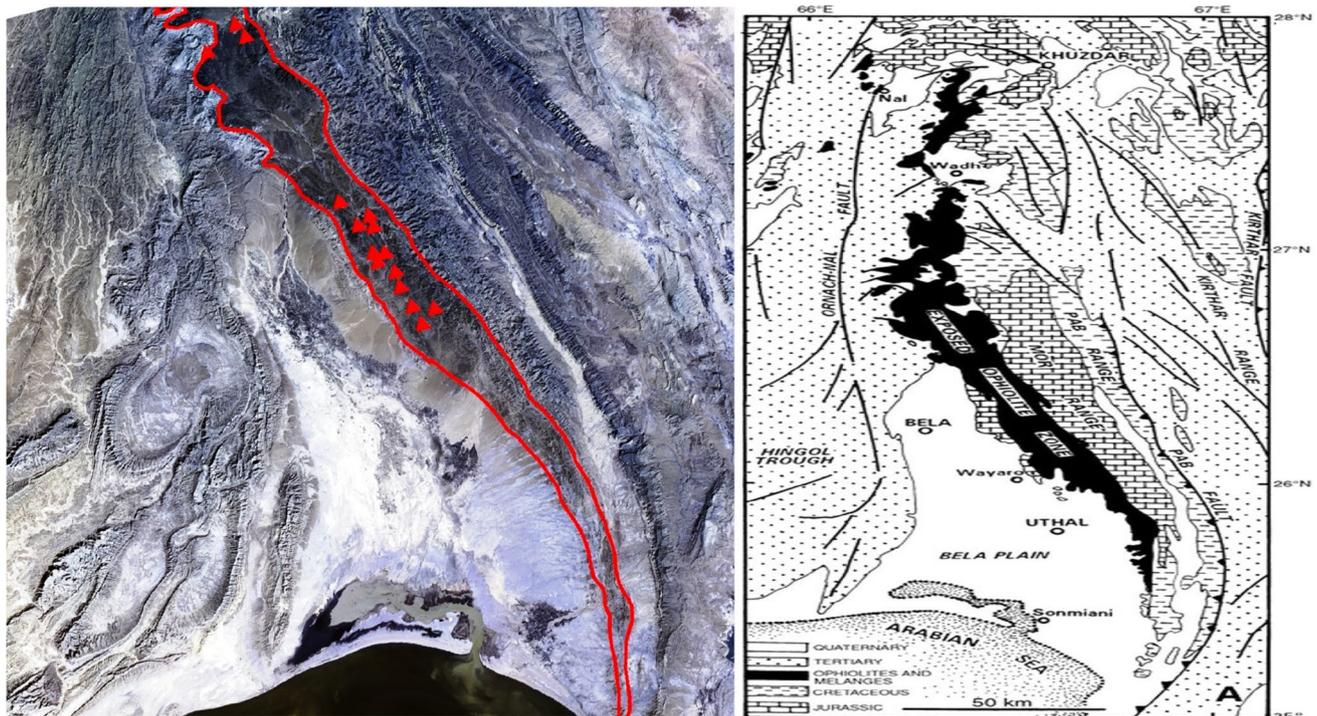


Fig. 1 a Illustration shows the Mn sample locations falling in the Ophiolite of Bela Zone on Landsat image. b Regional Geological Map showing Bela ophiolite and surrounding area (after Zaigham and Mallick 2000)

characteristics and origin, several fresh samples from Bela ophiolite complex manganese deposits were collected. Fieldwork of 7 days was conducted in different stream cuts through ophiolites rocks. In total, 26 samples were taken from various places including the Siro Dhora, Sukkan Nala, Gajri Nai, Khariri Nai, Saanp dhoro and other different exposures of manganese deposits in the part of Bela ophiolites sequence (Fig. 3), extending from south to north near Karachi metropolis. Some of them were mining sites, and some were taken from small showings of the manganese ore. Then the selected 15 samples were analyzed for major and trace elements geochemistry. The major elements and selected trace elements were analyzed using Panalytical Axios Wavelength-Dispersive X-ray Fluorescence (WD-XRF), Model PW-4440. Prior to XRF geochemical analysis, the samples were grinded in grinding mill. The grinded material was passed through 200 mesh in order to homogenize the sample size. Afterward, 1 g of dried samples was fired in oven at 1000 °C for 2 h to find out their Loss on Ignition (LOI) so that any organic and carbonate material, if present in the samples, may be removed and calculated. After LOI, 0.5 g of remaining samples was mixed with 5 g of dilithium tetraborate in a platinum crucible and put it in the bead sampler for 20 min to form beads and was analyzed for major elements. The selected trace elements were analyzed by using dry powdered pellets. Prior to making the

correlations of geochemical data, the major and trace elements were recalculated as an anhydrous (LOI-free) mass and adjusted them to 100%. In addition to this, these 15 samples were used to conduct their ore microscopy. Prior to ore microscopic analysis, the polished sections of collected Mn samples were prepared. The surfaces of samples were polished with alumina to make the surface even and fresh. Later on, these polished sections were analyzed using Leitz reflected microscope. Furthermore, manganese ores were quantitatively ciphered using geochemical and mineralogical data in order to discuss and evaluate possible degrees of geochemical correlation among different elemental concentrations and use them to interpret their origin and deposition. Furthermore, an attempt was made to generate the binary and ternary relationships in order to assess the petrogenesis and origin.

Results and discussion

Geochemical analysis

Major elements

In order to assess the quality of manganese ore deposits and to determine the origin (e.g., hydrothermal, hydrogenous, and diagenetic processes), the geochemical analysis

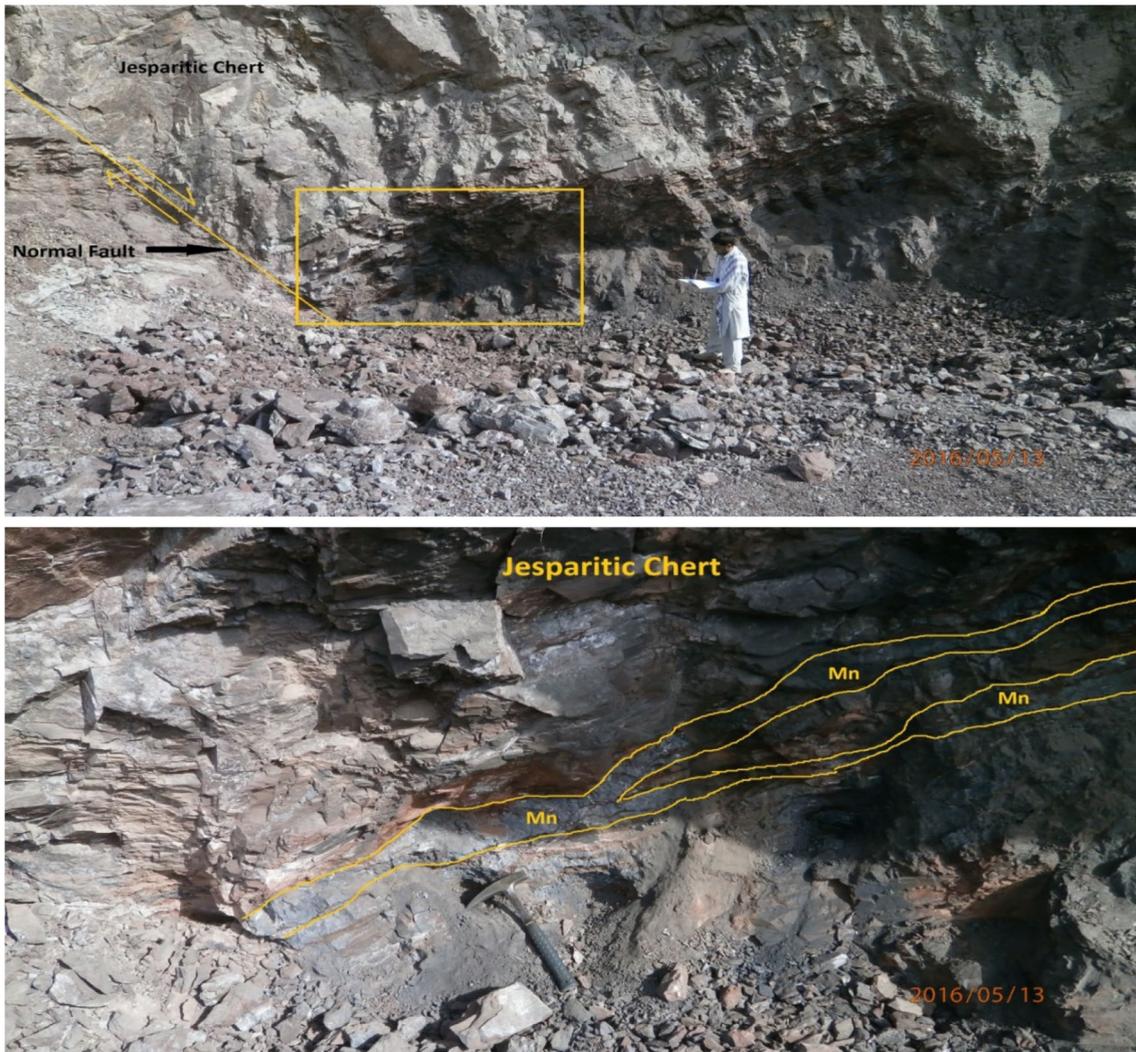


Fig. 2 Illustration shows the photograph of one location from where Mn ore samples were collected for analysis. The close capture of the area selected with rectangle is also shown

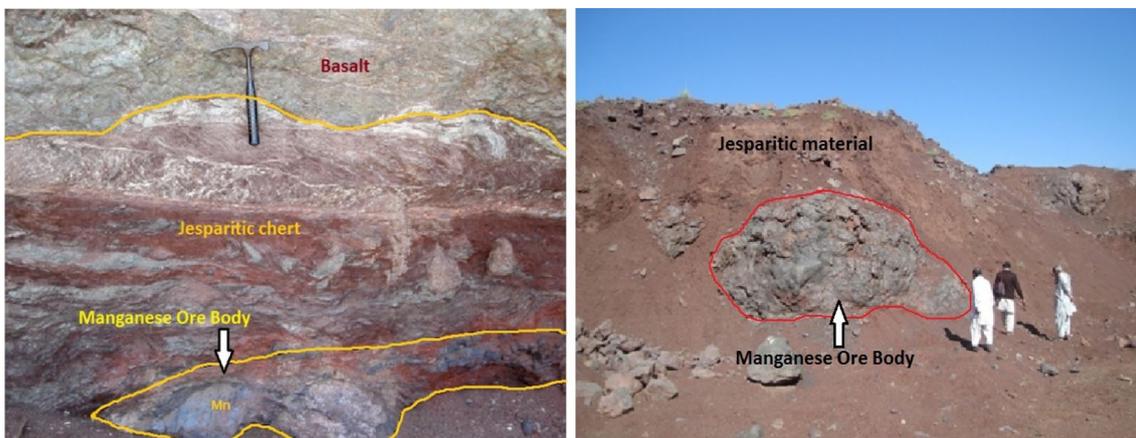


Fig. 3 Field photographs of exposed Mn ore bodies **a** manganese ore body in a vein form hosted by jespertic chert. **b** Exposed Mn ore deposits ore in unconsolidated jespertic material in the Bela ophiolite

Table 1 Major elemental composition of Mn deposits of Lasbela area

Major elements (%)												
S. no.	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	MgO	TiO ₂	MnO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	L.O.I	Total
BM02	47.1	5.72	1.8	0.67	0.72	36.92	2.1	0.91	1.09	0.16	1.98	100.1
BM06	45.34	7.51	1.72	0.72	1.01	37.46	0.9	0.41	0.67	0.3	3.01	101.0
BM09	50.24	11.03	0.25	0.18	0.34	29.98	1.94	0.73	0.73	0.28	2.32	101.0
BM13	46.01	8.63	1.2	0.69	0.93	32.56	1.85	0.56	0.92	0.4	2.31	100.0
BM13	44.85	7.78	1.04	1.4	0.79	35.01	1.55	0.61	0.09	0.05	2.03	100.2
BM15	43.09	10.73	1.05	1.8	0.81	28.91	0.99	0.31	0.88	0.08	5.34	100.0
BM16	41.86	10.3	1.9	0.27	0.56	32.83	0.73	0.03	0.67	0.19	3.67	100.0
BM17	41.31	8.47	0.65	0.34	0.3	34.55	1.71	0.37	0.18	0.36	4.89	101.1
BM18	47.41	10.32	1.75	1.21	0.71	34.69	0.45	0.57	0.47	0.42	2.04	100.0
BM19	49.03	11.86	1.5	0.54	0.49	30.02	2.3	0.76	0.73	0.09	2.89	100.2
BM25	46.19	13.63	1.6	0.49	0.18	31.33	2.06	0.08	1.01	0.37	3.05	100.0
BM26	45.09	10.07	9.7	0.31	0.25	30.84	0.7	0.11	0.21	0.04	2.69	100.0
BM27	48.52	9.59	1.79	0.56	0.36	34.1	0.94	0.2	0.54	0.27	4.03	100.9
BM30	51.3	11.37	0.5	0.21	0.29	29.41	1.89	0.09	0.38	0.37	4.28	100.1
BM32	45.8	10.7	1.5	1.43	0.26	36.21	1.51	0.32	0.09	0.07	2.94	100.8

is essential. The chemical composition of samples obtained from manganese deposits of Lasbela is presented in Table 1. The major elements, Si, Ti, Al, Fe, Mn, Ca, Mg, Na, K, P, along with selected trace elements (Cu, Pb, Zn, Ni, Cr, Co) were analyzed. Table 1 shows that Lasbela Mn deposits have SiO₂ ranging from 41.31 to 51.3 wt%, Fe₂O₃ from 5.72 to 13.86 wt%, MnO from 28.91 to 37.46 wt%, MgO from 0.18 to 1.8 wt%, CaO from 0.45 to 2.3 wt% Al₂O₃ from 0.25 to 1.9 wt%, Na₂O from 0.03 to 0.91 wt%, K₂O from 0.09 to 1.09 wt%, TiO₂ from 0.18 to 1.01 wt% and P₂O₅ from 0.05 to 0.42 wt%. These samples also have high LOI (up to 5.34%) which may be due to higher percentage of secondary carbonates in the samples. These deposits do not show high-grade MnO (28.91–37.46 wt%), and it is relatively higher in Fe₂O₃ (5.72–13.86 wt%). These deposits are more or less similar to that of other deposits of the world as shown in Table 1. All major elements oxides are plotted against MnO in order to understand their mutual correlation. The correlation was

fitted on the data (Table 2) and found that there is a negative correlation between Fe₂O₃ versus MnO ($r=0.73$) as shown in Fig. 4. Al₂O₃ and MnO regression coefficient resulted in $r=0.54$. The correlation for the rest of the major oxides is SiO₂–Fe₂O₃ ($r=0.48$), Al₂O₃–MgO ($r=0.24$), Al₂O₃–TiO₂ ($r=0.33$), Al₂O₃–MnO ($r=0.54$) and CaO–Fe₂O₃ ($r=0.78$), and negative correlation between Al₂O₃–CaO ($r=-0.27$), MnO–CaO ($r=-0.19$), MnO–SiO₂ ($r=-0.27$), Fe₂O₃–Na₂O ($r=-0.39$), Fe₂O₃–K₂O ($r=-0.12$) and P₂O₅–MgO ($r=-0.38$) (Table 2). The relation between SiO₂ and CaO against MnO showed the vaguely defined negative correlation. Furthermore, we plotted, TiO₂, Na₂O and MgO that have also resulted into vaguely defined positive correlation against MnO. Moreover, the correlation between Al₂O₃ and P₂O₅ data shows scattered relation and therefore, exhibit no correlation with MnO. The binary plot between elements Si versus Al strongly indicated the hydrothermal origin of studied manganese samples Fig. 7c.

Table 2 The correlation coefficient for the major oxides

Oxides	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	MgO	TiO ₂	MnO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅
SiO ₂	1.00	0.48	-0.17	-0.27	-0.22	-0.27	0.38	0.27	0.15	0.22
Fe ₂ O ₃		1.00	0.03	0.14	-0.47	-0.73	-0.02	-0.39	-0.12	0.00
Al ₂ O ₃			1.00	0.24	0.33	0.54	-0.27	0.01	0.34	0.00
MgO				1	0.46	0.22	-0.26	0.18	-0.12	-0.38
TiO ₂					1	0.36	-0.22	0.45	0.32	0.01
MnO						1	-0.19	0.26	-0.20	0.04
CaO							1	0.43	0.29	0.06
Na ₂ O								1	0.26	-0.9
K ₂ O									1	0.13
P ₂ O ₅										1

Trace elements

The trace elements analyzed from present study of the Bela manganese deposits have greater variations. Pb is ranging from 8 to 87 ppm, Zn from 29 to 121 ppm, Cu from 67 to 137 ppm, Ni from 5 to 31 ppm, Cr from 21 to 56 ppm and Co from 9 to 33 ppm (Table 3). All the trace elements were plotted against MnO and other major oxides in order to define their mutual relation with source and the origin of Bela Mn deposits. The correlations coefficients of some major oxides with selected trace elements produced positive relations among the data reported as shown in Table 4, as

K_2O-Cu ($r=0.78$), Fe_2O_3-Zn ($r=0.35$), $CaO-Pb$ ($r=0.35$), $CaO-Ni$ ($r=0.07$), SiO_2-Ni ($r=0.43$) and Al_2O_3-Ni ($r=0.26$), Al_2O_3-Co ($r=0.40$) and $MnO-Cr$ ($r=0.12$) and the majority of the plots have resulted into negative correlation. The negative correlation between some selected major oxides and trace elements is reported here as $MgO-Zn$ ($r=-0.44$), SiO_2-Ni ($r=-0.35$), Al_2O_3-Cu ($r=-0.38$), TiO_2-Cu ($r=-0.53$), Na_2O-Cu ($r=-0.56$), TiO_2-Zn ($r=-0.52$), TiO_2-Zn ($r=-0.52$), P_2O_5-Ni ($r=-0.29$), P_2O_5-Zn ($r=-0.13$), Al_2O_3-Cr ($r=-0.05$), and all other major elements and their correlation coefficients with trace elements are provided in Table 4. Most of the plotted

Fig. 4 Selected plots of major oxides showing the correlation between Al_2O_3 versus MnO and Fe_2O_3 versus MnO

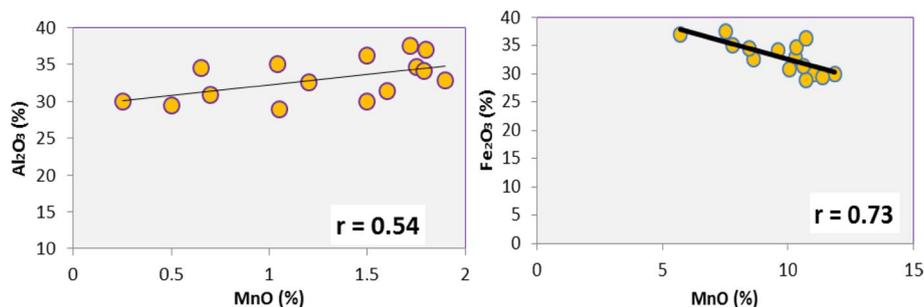


Table 3 Trace chemical elements composition of Mn deposits of Lasbela area, Balochistan

Sample ID	Trace elements (ppm)						
	Pb	Zn	Cu	Co	Ni	Cr	Fe/Mn
BM02	46	33	76	9	7	21	0.14
BM06	87	74	95	31	19	38	0.18
BM09	35	61	87	24	31	43	0.33
BM13	64	54	67	16	12	41	0.24
BM13	77	32	121	32	24	28	0.2
BM15	41	29	89	19	13	34	0.33
BM16	32	121	107	12	29	21	0.28
BM17	79	53	134	25	31	49	0.22
BM18	8	69	93	33	9	42	0.27
BM19	78	31	85	17	21	25	0.36
BM25	41	98	105	21	15	56	0.39
BM26	59	121	137	27	18	39	0.29
BM27	37	107	96	12	6	48	0.25
BM30	51	89	115	26	5	23	0.34
BM32	65	94	108	14	29	51	0.27

Table 4 Correlation coefficients among major oxides and some selected trace elements

Oxides	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	MgO	TiO ₂	MnO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅
Pb	-0.21	-0.32	-0.18	0.00	0.15	0.23	0.35	0.14	-0.3	-0.28
Zn	0.00	0.35	0.14	-0.44	-0.52	0.00	-0.46	-0.80	-0.24	-0.13
Cu	-0.35	0.11	-0.38	-0.16	-0.53	0.00	-0.25	-0.56	-0.78	-0.2
Co	0.00	0.20	0.4	0.09	0.13	0.00	-0.27	0.00	-0.45	0.21
Ni	0.43	0.07	0.26	-0.08	-0.21	0.07	0.07	0.00	-0.38	-0.29
Cr	0.09	0.3	-0.05	0.07	-0.38	0.12	-0.02	0.24	-0.15	0.34

relations between major oxides with trace elements were vague, though few of them were reasonably well-fitted correlations and are shown in Fig. 5. The trace elements Zn and Co plotted have weakly defined negative correlation against MnO, Pb and Cr, indicating weakly induced positive correlation against MnO (Table 4). However, Cu and Ni indicate scattered correlations when plotted against manganese (Mn). These findings suggest that the hydrothermal fluid containing elements of from different sources with dominating mafic source contributed to the formation of manganese deposit in Bela ophiolite complex. The trace elements (Cu, Pb, Zn, Ni, Cr, Co) are very low in the Mn ore bodies, therefore, similar to submarine hydrothermal deposits (Bonatti et al. 1972; Crerar et al. 1982; Nicholson 1992; Choi and Hariya 1992) in most cases such as in Mn-oxide deposits of East Pacific Rise and the Galapagos areas that reported with higher trace elements (Cu, Zn, Ni and Co) as compared to that of pelagic sediments. However, the deposits of Mn-oxide deposits of East Pacific Rise and the Galapagos areas have higher trace elements and are much lower than that of the hydrogenous manganese iron (Mn–Fe deposits) of Cronan and Moorby (1981) and Choi and Hariya (1992) and have distinguished the hydrogenous deposits of deep-sea Mn-nodules and submarine hydrothermal Mn deposits as observed from their ternary diagrams. The Ternary plots of Mn ore deposits of present study data show that the majority of plotted samples lie near the Ni–Zn intersection, where the submarine hydrothermal Mn-deposits. The hydrogenous Mn deposits, having relatively high Co contents, however, occupy the field closer to Co apex in this diagram.

Mineralogy

The ore microscopic observations revealed that the two manganese minerals are present within the samples obtained from Bela ophiolite (1) psilomelane, and other is (2) braunite along with magnetite as an accessory mineral. In addition to that, the gangue minerals in the samples observed includes the quartz, cryptocrystalline silica and calcite as shown in Fig. 6. Minerals observed under ore microscopy were confirmed from the chemical data by showing the presence of manganese minerals braunite and psilomelane containing

accessory mineral of Fe ore magnetite. Magnetite may be responsible for slightly higher elemental iron (Fe) content determined by chemical analysis. Detected Si element percentage is the part of both cryptocrystalline and quartz forms. Further, the characteristics of main minerals observed within these deposits of manganese are described separately.

Psilomelane

Psilomelane is the major mineral in most of the samples, showing granular look and sometime botryoidal. It shows moderate reflectance. Color varies from light gray, grayish white to yellowish gray. Psilomelane is seen to replace the braunite mineral in many thin-section studies. The psilomelane is believed to be precipitated in moderate-temperature hydrothermal environment and also forms as an alteration of pre-existing manganese minerals.

Braunite

Braunite occurs second in abundance to psilomelane in many studied samples that shows it is the primary mineral in many samples which is being altered at many places into psilomelane forming alteration rims at boundaries (Fig. 6e). It is usually present in grayish white color. Its texture observed is mainly botryoidal. It shows high reflectance than psilomelane as observed from Fig. 6e in this manuscript.

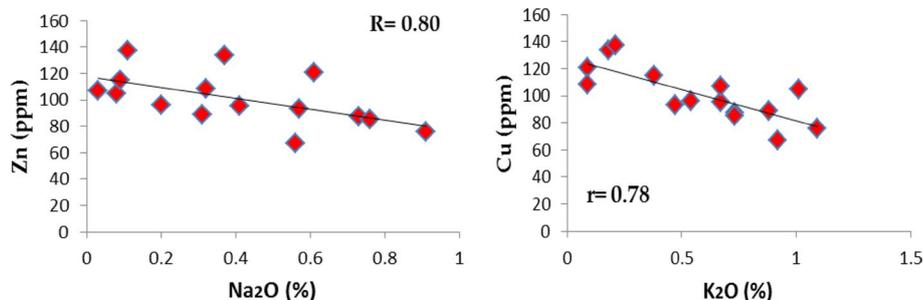
Magnetite

Magnetite is present as secondary filled mineral as shown in Fig. 6a. At some places, it forms a veinlet in the samples cutting through the braunite or psilomelane; and it also occurs in subhedral-shaped crystals in the matrix of Mn minerals, as shown in Fig. 6f.

Mineral paragenesis

In mineral formation sequence, it is shown by ore microscopy that braunite was the first mineral to form in the studied samples; the character of this is shown in Fig. 6e. Later on, braunite was replaced by psilomelane mineral as shown in

Fig. 5 Plot of some selected trace elements Cu, Zn, versus Na_2O and K_2O for the Mn deposits of Lasbela area



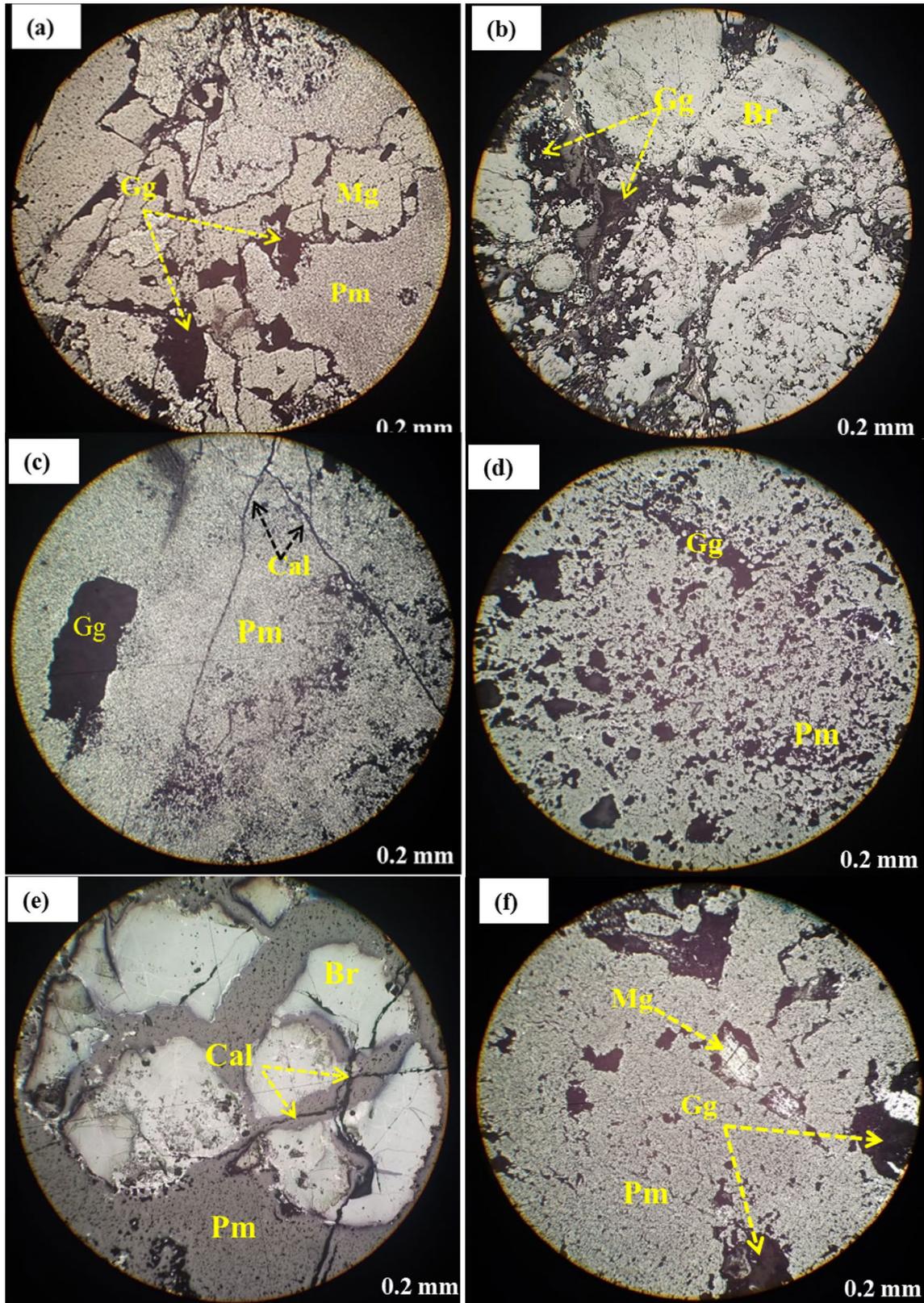


Fig. 6 Polished-section photomicrographs illustrating the of manganese ore samples captured under reflected light ore microscope

Fig. 6e. Magnetite is also a secondary mineral in the studied samples, which has formed the secondary veinlets in the Mn minerals. Therefore, the sequence of minerals formation from older to younger could follow the sequence given as follows,

Braunite → Psilomelane → Magnetite

In Figure 6a–f, the mineralogical characteristics of manganese ore deposits from Bela ophiolite complex are described: (a) It is shown in photomicrograph, the magnetite (Mg), as a secondary vein cuts the psilomelane (Pm) groundmass along with gangue (Gg) minerals. (b) Photomicrograph shows that there is braunite (Br) mineral along with gangue (Gg) minerals and some section pits. (c) Photomicrograph shows the psilomelane (Pm) as a main manganese mineral along with gangue (Gg) and two small secondary calcite (Cal) veins. (d) The psilomelane (Pm) is the main mineral along with the scattered gangue (Gg) as it could be seen in the photomicrograph. (e) There are two manganese minerals: One is braunite (Br) which is altered by psilomelane (Pm) as alteration rims could be seen around braunite (Br) grains; calcite (Cal) also cuts the braunite (Br) as secondary veins. (f) Psilomelane (Pm) is the main manganese mineral in the matrix that hosts the secondary magnetite (Mg) grains along with gangue (Gg) minerals.

Discussion

Geochemical analysis shows that the hydrothermal activity was responsible in forming the manganese deposits in Bela ophiolite complex. In this ophiolite sequence, both banded- and lenticular-type manganese deposits are found in close association with jasperitic cherts and basalts, in a highly deformed tectonic setting. Bela manganese deposits geochemical characteristics are similar to most of the other Pakistani manganese minerals such as Waziristan and Hazara (e.g., Shah and Moon 2007), and also have similarity with the Baby Bare, Baft Ophiolitic melange Kerman (Iran) Wakasa deposits. Comprehensive analyses of the selected Mn deposits found around the world were compared with the present study data and are provided in Table 5.

Based on the geochemical data and from ternary and binary relations, ophiolite Bela complex manganese deposit belongs to the submarine hydrothermal and diagenetic-type deposits (Fig. 7a–d). Generally, the hydrothermal solutions form by the percolating seawater deep into the oceanic crust, making the water warmer with depth and its acidity also increases with increasing depth. These aforementioned conditions are suitably offered by the seafloor spreading centers accompanying the oceanic crust (e.g., Bonatti et al. 1972; Crerar et al. 1982; Peter and

Scott 1988). These solutions are typically formed near the sea floor spreading center as it provides much deeper and interconnected fractures along with it. When these hydrothermal solutions are hot enough to extract metals from country rocks and deposit those metals when these solutions reach at relatively cooler surroundings. Ophiolites are upper mantle to oceanic crustal rocks in combination with the above-deposited pelagic sediments; the hydrothermal deposits associated with them are exposed when these rocks are obducted on land by tectonic forces as in the case of Bela ophiolites. These Bela ophiolites rocks were part of Tethys oceanic crust and they were obducted when the southeastern part of Eurasian and western part of Indian plate closed the then-present Tethys sea and formed continental–continental convergent plate boundary (e.g., Sarwar 1992; Gnos et al. 1998; Zaigham and Mallick 2000; Xiong et al. 2011). Generally, iron (Fe) is accompanied with hydrothermal environment-type manganese deposits in a significant amount. While Fe compounds are less stable in hydrothermal solutions as compared to manganese, they deposit first; and manganese compounds are much stable and get deposited much later than Fe by hydrothermal solutions (e.g., Panagos and Varnavas 1984; Roy 1981, 1992). In the end, it could be summarized that the manganese ores in Bela ophiolites were probably formed by hydrothermal solutions along sea floor spreading center that was the floor of Tethys Sea. Later on, these deposits were obducted and exposed by collision between Indian and Eurasian continental plates in the current position as a part of Bela ophiolites accompanying pillow lavas and jasperitic chert.

The trace elements concentrations in hydrothermal-type deposits are much less than hydrogenous-type deposits (e.g., Cronan and Moorby 1981; Choi and Hariya 1992). The binary plots of manganese ore deposits of Bela ophiolite data reveal that most of the plotted samples fall under the category of submarine hydrothermal environment (Fig. 7a–d).

The ternary diagram of Mn–Fe–(Co + Ni + Cu) × 10 after Bonatti et al. 1972; Crerar et al. 1982; Hein et al. 1992) data has occupied the hydrothermal and diagenetic fields as shown in Fig. 7a. In Ni–Zn–Co diagram (Choi and Hariya 1992), all samples occupied space close to the hydrothermal field (Fig. 7b). A binary relation was developed as Si–Al diagram after (Peters 1988) the data from all samples fell in the hydrothermal area as shown in Fig. 7c. The ternary plot among Fe–Si × 2–Mn triangular diagram of Toth (1980) samples does not occupy particular field but is close to the diagenetic and hydrogenous fields (Fig. 7d). From the analysis of the results of major and selected trace elements, it was observed that the hydrothermal–diagenetic processes played an important role in the formation of Bela ophiolitic complex.

Table 5 Comparisons and classifications of Bela Mn deposits with other Mn deposits discovered in different regions of modern geological settings around the world (after Oksuz 2011)

No. of Samples	7	28	22	9	14	7	13	23	10	20	27
Countries	China	Pakistan	Hazara	Northeast Pacific Ocean	Japan	Turkey					Pakistan
Regions	Guichi	Waziristan	Hazara	Baby Bare	Wakasas	UluKent	Binkilic	Cayirli	Kasimaga	Eymir	Bela, Mn deposits
Origin	Sedimentary	Volcano-sedimentary	Hydrothermal-hydrogenous	Hydrothermal	Hydrothermal	Sedimentary	Sedimentary-diatogenic	Volcano-Sedimentary	Volcano-sedimentary	Hydrothermal-sedimentary	This study
SiO ₂ %	(-)	43.69	9.41	2.02 ^a	58.16	13.68	10.65	63.02	13.43	16.04	46.21
TiO ₂ %	(-)	0.32	0.84	0.04 ^a	0.04	0.1	0.02	0.03	0.10	0.02	0.53
Al ₂ O ₃ %	(-)	0.73	12.53	0.27 ^a	0.55	2.49	2.85	0.65	2.95	0.73	1.86
Fe ₂ O ₃ %	(-)	2.96	20.33	2.30 ^a	0.92	3.72	2.46	0.68	14.33	0.26	9.85
MnO %	(-)	45.88	33.78	48.52 ^a	32.5	63.78	33.39	29.22	40.43	69.91	32.99
MgO %	(-)	0.6	0.59	1.58 ^a	0.19	1.99	1.27	0.20	12.72	0.59	0.72
CaO %	(-)	1.28	6.43	0.97 ^a	4.15	4.05	18.96	0.24	6.82	2.40	1.44
Na ₂ O %	(-)	0.29	0.07	0.64 ^a	0.04	0.24	0.39	0.05	0.06	0.01	0.40
K ₂ O %	(-)	0.22	0.88	0.22 ^a	0.1	0.05	0.56	0.11	0.19	0.05	0.58
P ₂ O ₅ %	(-)	0.25	3.73	0.04 ^a	0.1	0.18	0.31	0.04	0.08	0.07	0.23
Ba (ppm)	212.56	415	6304	7091.67	13.79	427	6892.00	1229.40	2719.40	2364.70	(-)
V (ppm)	167.86	144	573	172.33	258	(-)	106.00	143.70	106.10	132.00	(-)
Cr (ppm)	107.21	46	247	8.89	10	(-)	26.00	13.70	10.00	(-)	37.27
Co (ppm)	4.77	11	404	135.33	2	13.00	59.00	25.21	49.50	103.50	21.20
Ni (ppm)	89.39	36	305	300.67	28	10.00	167.00	69.40	23.00	67.35	17.93
Cu (ppm)	31.03	72	375	226	50	56.00	26.00	154.90	126.80	80.50	101.00
Zn (ppm)	137.36	64	580	123.22	26	70.00	49.00	66.70	63.50	62.45	71.07
Pb (ppm)	16.49	49	2357	(-)	112	65.00	(-)	6.50	53.50	9.33	53.33
Thy (ppm)	(-)	2	31	1	2	(-)	(-)	0.40	433.20	0.57	(-)
Rb (ppm)	37.8+9	2	24	14.22	2	(-)	(-)	2.90	5.00	0.77	(-)
Sr (ppm)	741.34	(-)	(-)	877.44	85	185.00	2100.00	243.40	255.00	116.47	(-)
Y (ppm)	21.75	(-)	(-)	10	5	(-)	15.00	33.00	22.20	8.45	(-)
Nb (ppm)	6.76	(-)	(-)	1.5	3	(-)	(-)	0.70	11.10	0.15	(-)
Zr (ppm)	(-)	(-)	(-)	9.22	12	(-)	32.00	4.00	26.90	8.46	(-)
Co/Ni	0.05	0.31	1.32	0.45	0.07	1.30	0.35	0.36	2.15	1.54	1.61
Co/Zn	0.03	0.17	0.7	1.1	0.08	0.19	1.20	0.38	0.78	2.24	0.37
Mn/Fe	(-)	199	2.16	26.89	39	18.98	15.03	97.17	12.02	880.33	4.48

(-), there is no analysis

^aThe values are from element type

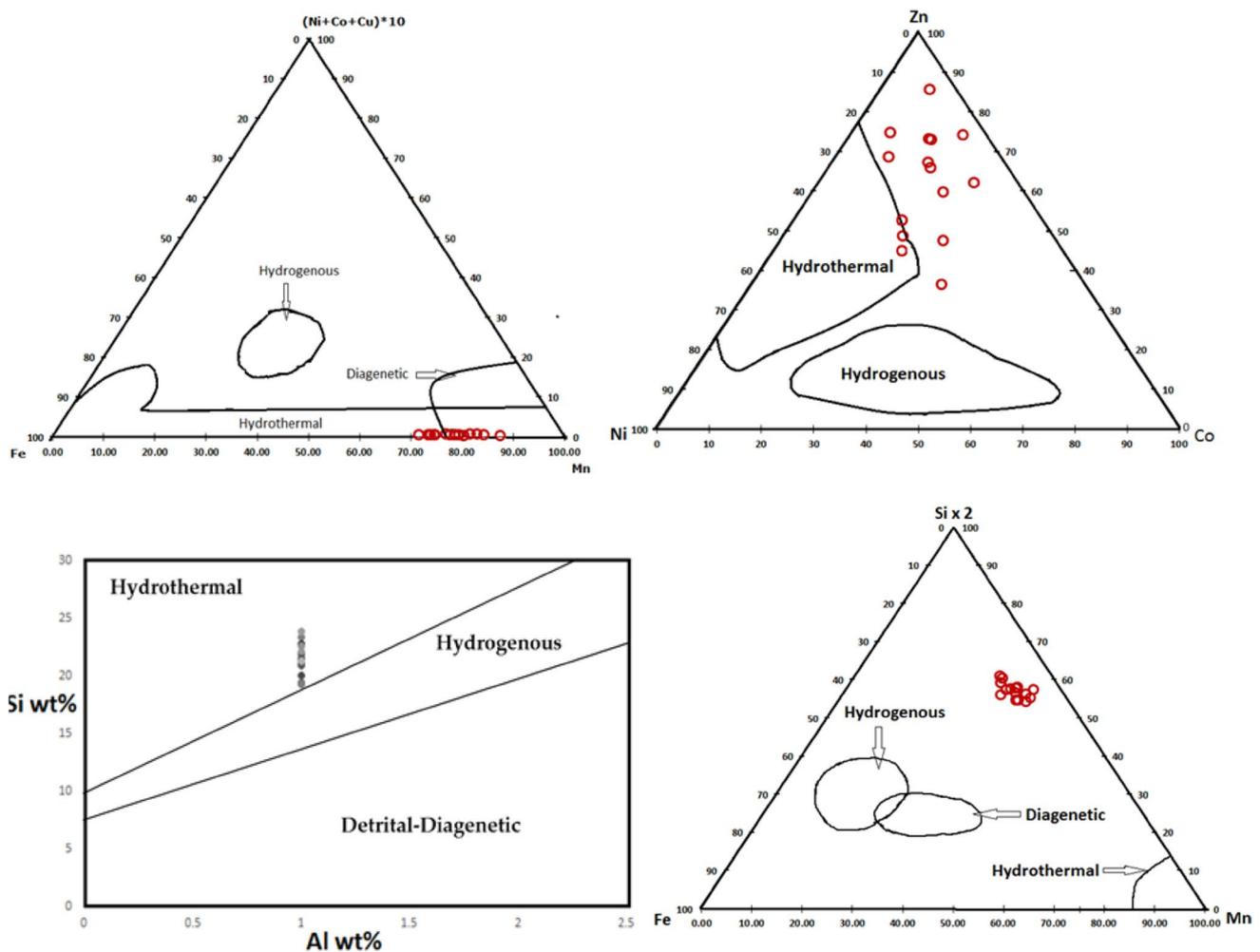


Fig. 7 a–d Fe–(Ni + Co + Cu) × 10–Mn discrimination diagram (Bonatti et al. 1972; Crerar et al. 1982; Hein et al. 1992), b Ni–Zn–Co diagram (Choi and Hariya 1992), c Si/Al diagram (Peters 1988), d Fe–Si × 2–Mn diagram (Toth 1980)

Conclusions

An extensive work was conducted in order to assess the origin, composition and geochemical characteristics of the Bela ophiolites found in Balochistan, Pakistan. From this study, the following conclusions were drawn,

The ore bodies of Bela ophiolites were banded massive to lenticular in appearance. The major and trace element data suggest hydrothermal-diagenetic-type origin for these Mn deposits.

Braunite and psilomelane manganese minerals and gangue minerals of cryptocrystalline silica, quartz and calcite are the main constituents along with minor magnetite.

Lasbela Mn deposits are formed by the submarine hydrothermal solution in an ocean floor spreading center environment within the Paleo–Tethys Ocean.

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