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**The genesis of manganese deposits in the Ali Khanzai Block
from the Zhob Ophiolite, Pakistan: Inferences from
geochemistry and mineralogy**

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3 1 **The genesis of manganese deposits in the Ali Khanzai block of the Zhob Ophiolite,**
4 **Pakistan: Inferences from geochemistry and mineralogy**
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40
41 19 **Abstract**

42
43 20 The Zhob Ophiolite comprises the Naweoba, Omzha and Ali Khanzai blocks, which
44
45 21 are surrounded by the sediments of the Alozai Group and Loralai Formation. The Ali Khanzai
46
47 22 block contains metamorphic, ultramafic, gabbroic, volcanic and volcanoclastic rocks with
48
49 23 associated chert. The Zhob manganese deposits found in the Ali Khanzai block, occur in
50
51 24 banded, lenticular and massive forms within red to brown coloured metachert. Braunite and
52
53 25 pyrolusite are the main constituent manganese-bearing minerals with minor hausmannite,
54
55 26 hematite and barite while quartz is the major gangue mineral with some carbonate minerals.
56
57 27 Geochemical evidence from the major oxides indicates that the manganese mineralization and
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28 associated metachert at Zhob were formed by hydrothermal activity with little contribution
29 from contemporaneous volcanic materials and this is confirmed by high Fe/Mn and low Co/Zn
30 ratios and trace element patterns. These deposits formed along with seafloor spreading centres
31 and were later obducted as part of Ali Khanzai block of Zhob Ophiolite.

32
33 **Key Words:** Zhob Ophiolite, Manganese ore, Hydrothermal, Genesis

34 35 **1. Introduction**

36 Manganese deposits occur in a range of tectonic settings, with ore deposits being
37 associated with ophiolites as well as continental sedimentary sequences. These deposits can be
38 divided into three types based on mineralogy, geochemical composition and tectonic setting:
39 1) hydrogenous, 2) hydrothermal, and 3) diagenetic/biogenetic-bacterial deposits (Polgari et
40 al., 2012; Oksuz, 2011; Hein et al., 1997; Bolton et al., 1988). Hydrogenous deposits occur as
41 ferromanganese crusts which are slowly precipitated (2–10 mm/Ma) from seawater on the
42 seafloor usually via microbial mediation and are usually depleted in Mn minerals and rich in
43 amorphous iron compounds (Oksuz, 2011; Jach and Dudek, 2005; Usui and Someya, 1997;
44 Toth, 1980). Hydrogenous deposits are characterized by a low Mn/Fe ratio (~1) and high trace
45 element concentrations, particularly Ni and Cu (Usui and Someya, 1997; Hein et al., 1996,
46 1997; Usui and Nishimura, 1992; Ingram et al., 1990; Toth, 1980;).

47 In contrast, hydrothermal deposits precipitate directly from low-temperature
48 hydrothermal solutions (Hein et al., 1997; Ingram et al., 1990) and are commonly stratabound
49 and laminated or occur as irregular bodies and epithermal veins. They are found in modern and
50 ancient environments in marine settings adjacent to either spreading centres or intraplate
51 seamounts, or subduction-related island arc settings (Roy, 1992, 1997). Diagenetic or bacterial
52 deposits are mainly found as nodules and precipitate from hydrothermal solutions or pore

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3 53 waters. These manganese deposits are generally related to oxidation of organic matter and
4
5 54 formation of Mn-carbonate mineralization (Oksuz, 2011; Polgári et al., 1991, 2012), however,
6
7 55 they can also form by a combination of these processes. Unlike hydrogenous deposits,
8
9 56 hydrothermal and diagenetic deposits have high Mn/Fe ratios and low trace metal contents
10
11 57 (Hein et al., 1994, 1996). Although diagenetic and hydrothermal deposits are similar in some
12
13 58 ways, these two types can be distinguished on the basis of their morphology, tectonic setting
14
15 59 and growth rates (Kuhn et al., 1998).

19 60 In Pakistan, manganese deposits are reported mainly from North Waziristan, Lasbela,
20
21 61 Kurram, Bajaur, Mohmand, and Mansehra. All the manganese deposits are associated with
22
23 62 ophiolitic rocks except that of Mansehra, which is hosted by a continental sedimentary
24
25 63 sequence (Asif, 2014; Shah and Moon, 2004; Shah and Khan, 1999; Naseem et al., 1997;
26
27 64 Ahmed, 1992). Among these deposits, the North Waziristan (45 wt. % MnO), Lasbela (40 wt.
28
29 65 % MnO) and Bajaur manganese (55.39 wt. % MnO) deposits are economically significant due
30
31 66 to their grade and accessibility (Asif, 2014; Shah and Khan, 1999; Naseem et al., 1997).

35 67 The Zhob Ophiolite, in the Zhob valley, is located north-northeast of the Muslim Bagh
36
37 68 Ophiolite (Fig.1b) and hosts several types of economic deposits including manganese ores
38
39 69 (Ahmed, 1969, 1975; Bilgrami, 1964a, b; Jones, 1961; Heron and Crookshank, 1954). The
40
41 70 manganese deposits in this study are located in the Ali Khanzai block of the ophiolite which is
42
43 71 situated 16 km south of Zhob city (Fig.1c). This Zhob manganese occurrence was first reported
44
45 72 by Ahmed (1975), who described the manganese occurring in the form of veins and layers,
46
47 73 associated with basalt and chert. The Zhob manganese is being commercially mined since the
48
49 74 deposits contain an average 42.5 wt. % MnO. In the current study, we present the first
50
51 75 petrographic descriptions, mineralogy, and geochemistry of the Zhob manganese ores found
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53 76 associated with the Ali Khanzai block of the Zhob Ophiolite and propose a model for its
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55 77 paragenesis.
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78 2. Regional Geology and Zhob Ophiolite

79 The Zhob Ophiolite is exposed in northwestern Pakistan and is part of the suture zone
80 marked by the Bela, Muslim Bagh and Waziristan ophiolite complexes (Sengor, 1987; Fig.
81 1a). In the south, the rocks of the suture zone are thrust over the Calcareous zone, which is
82 comprised of a marine succession (Triassic-Jurassic) of the Sulaiman Fold-Thrust Belt. In
83 contrast, in the north, the rocks of the suture zone are overlain by the Pishin-Katawaz flysch
84 succession, comprising the Nisai (Eocene) and Khojak Formations (Oligocene) (Fig. 1b). The
85 rock units in immediate contact with the Zhob Ophiolite include the Jurassic Alozai Group
86 (Durrani, 2012) at the base, and the Nisai Formation (Eocene-Oligocene; Bukhari et al., 2016)
87 at the top.

88 The Zhob Ophiolite consists of three separate blocks; the Naweoba, Omzha and Ali
89 Khanzai blocks. These blocks contain metamorphic rock, serpentinized peridotite, mafic
90 oceanic crustal rocks, basaltic volcanic rocks and sedimentary rocks such as chert and
91 mudstone. These blocks contain a few narrow elongated bodies of diorite parallel to peridotite
92 and volcanic rocks.

94 3. Geology of the Ali Khanzai block and manganese ore deposits

95 The Ali Khanzai block is approximately 12 km long and up to 3 km wide, and is located
96 about 16 km to the south of Zhob city (Fig. 1c). The Ali Khanzai block consists of metamorphic
97 rocks, a mantle section, mafic oceanic crustal rocks and a basalt-chert unit (Fig. 1c; Rehman,
98 2019). The contacts between various rock units of the Ali Khanzai block are sharp and
99 sometimes irregular because it is tectonically disturbed (Rehman, 2019). Sub-ophiolitic
100 metamorphic rocks found beneath the mantle section are mostly amphibolites, greenschists and
101 mica schist. The mantle section is fragmented and distributed across the base of this block and
102 is composed of dunite and harzburgite which are highly serpentinized. The crustal section

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3 103 contains mainly layered and massive gabbros and some doleritic dykes which are quite
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5 104 deformed and tectonically disturbed. The volcanic-chert-unit is the largest unit of Ali Khanzai
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8 105 block and comprises volcanic rocks, volcanoclastic rocks and metachert. Basalt is a significant
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10 106 volcanic rock and occurs commonly in pillow and sheet forms. These units cannot be
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12 107 stratigraphically correlated across the Ali Khanzai block due to intense folding, faulting and
13
14 108 the exotic nature of the rocks in the block.

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17 109 Chert in the volcanic-chert-unit is highly folded, fractured and metamorphosed, and
18
19 110 hosts manganese mineralization. These metacherts are fine-grained and crystalline and are thin
20
21 111 to medium-bedded. They have gradational contacts with underlying volcanic rocks and are
22
23 112 interbedded with volcanic rocks in some localities. The metacherts of the Ali Khanzai block
24
25 113 are cryptocrystalline and comprise fine-grained quartz along with minor clay minerals and
26
27 114 mainly consist of non-detrital free silica. Occasionally the metachert contains radiolarian tests
28
29 115 that are filled with detrital quartz and clay minerals.

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32
33 116 Manganese mineralization in the Ali Khanzai block is identified by its black colour in
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35 117 the field (Fig. 2). Manganese deposits are scattered (50 to 100 meters apart) and occur as small
36
37 118 deposits associated with reddish-to-brown metachert of the basalt-chert-unit of the Ali Khanzai
38
39 119 block (Fig. 1c). These deposits are collectively described here as the Zhob manganese deposits
40
41 120 and are currently being explored and mined, however the actual size of these manganese
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43 121 deposits remains unknown.

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47 122 The ore deposits in the investigated area are scattered and irregular but conformable
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49 123 with their host rocks. They lie above the volcanic rock-chert unit and are associated with
50
51 124 reddish-to-brown metachert. The ore deposits occur at a variable distance from the boundaries
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53 125 between metachert and volcanic rocks. The thickness of the ore bodies varies from 1 cm to 200
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55 126 cm, they are separated by layers of reddish-to-brown metachert. The general trend of the
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57 127 mineralization is SW-NE and is consistent with the bedding of the host rock. Manganese ores
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3 128 and host rocks are folded, faulted and fragmented, indicating that considerable deformation
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5 129 occurred after the formation of the deposits. These ore deposits occur in layered, banded,
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7 130 lenticular and massive forms (Fig.2). The lenticular and layered ore bodies are surrounded by
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9 131 metacherts (Fig. 2a-b). The banded form of manganese, containing Mn-rich phases, are thin to
10
11 132 medium in size and are clearly visible and alternate with bands of the host the metachert (Fig.
12
13 133 2c). Massive manganese is very thick and irregular (Fig. 2d) and has sharp contacts with the
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15 134 host metacherts. The pockets of manganese ore are enveloped by the surrounding host rock
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17 135 and are disconnected and rounded to subrounded.
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23 24 137 **4. Samples and analytical methods**

25
26 138 Around 60 samples of massive, layered and banded ores and metachert (host rocks)
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28 139 were collected in the field. These samples of ores and metachert were studied petrographically.
29
30 140 The least-altered 13 samples of ores and 7 samples of metachert were selected for major and
31
32 141 trace element analysis. Fe_2O_3 , MnO , MgO , CaO , Na_2O , TiO_2 and K_2O were determined by
33
34 142 atomic absorption spectrometry (Perkin Elmer 3300, equipped with graphite furnace), while
35
36 143 SiO_2 , P_2O_5 and Al_2O_3 were analysed by a Pye Unicam UV/visible spectrophotometer (detailed
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38 144 methodology and standards are in Appendix; supplementary material). The trace elements such
39
40 145 as Cu, Pb, Zn, Ni, Cr, and Co were also determined by the Atomic Absorption Spectrometry
41
42 146 (detailed methodology and standards are in Appendix; supplementary material). The loss on
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44 147 ignition (L.O.I.) was determined by heating the samples at 1000 °C in a muffle furnace.
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49 148 Petrographical and mineralogical studies were carried out using both polarized and
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51 149 reflected light microscopy of polished thin sections. All of the above studies were carried out
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53 150 at the Geochemistry Laboratory of the National Centre of Excellence in Geology, University
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55 151 of Peshawar, Pakistan.
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3 152 The mineralogical studies of ore and gangue minerals are based on a combination of
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5 153 X-ray powder diffraction analysis (XRD Bruker D-8 Advance with Cu anode operating at a
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8 154 generator voltage of 40 kV) and ore microscopy at Center of Excellence in Mineralogy,
9
10 155 University of Balochistan, Quetta, Pakistan.

11
12 156 The qualitative phase composition of the ore and gangue minerals were analysed by
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14 157 Micro X-ray fluorescence spectroscopy (μ -XRF) using polished blocks of the representative
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17 158 samples. The X-ray fluorescence analysis was conducted on a Bruker M4 Tornado X-ray
18
19 159 machine at the Institute of Geoscience at Aarhus University, Denmark. The source used was a
20
21 160 single rhodium target X-ray tube. All samples were scanned using the same parameters. The
22
23 161 spot size was 20 μ m and the distance between measured points was 25 μ m. Two spectrometers
24
25 162 were operated at a range of 40 keV / 130 kcps. The X-ray tube was run at 50kV electron voltage
26
27 163 and the current was set to 600 μ A. All analyses were carried out in a vacuum.

28
29 164 Quantitative mineral chemistry of manganese minerals was analyzed at the Department
30
31 165 of Geoscience, Aarhus University, Denmark, using a JEOL JXA-8600 electron microprobe
32
33 166 equipped with EDS (energy dispersive x-ray spectroscopy) with an acceleration voltage set to
34
35 167 15KeV and a current beam of 10nA. The beam diameter was 5 μ m with a counting time of 20
36
37 168 seconds. For the calibration of the microprobe natural mineral standards were used. The
38
39 169 analysis quality was monitored with two in-house standards; clinopyroxene BB1 and
40
41 170 labradorite (Oslo plagioclase). These standards were measured intermittently and compared
42
43 171 with the known composition to check the quality of the analysis. Carbon-coated polished thin
44
45 172 sections were used for this analysis.

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47 173

48 174 **5. Mineralogy and petrography of manganese ore**

49 175 X-Ray diffraction has determined that braunite and pyrolusite are the most dominant
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51 176 Mn-minerals with associated minor hausmannite, hematite and barite while quartz is most the
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3 177 common gangue mineral. Braunite is the principle manganese mineral and it ranges in shape
4
5 178 from microcrystalline to coarse-grained and anhedral to subhedral. Microcrystalline braunite
6
7 179 is intermixed with microcrystalline to cryptocrystalline quartz while the coarse-grained
8
9 180 braunite grains are interlocked with each other and are occasionally cross-cut by veinlets of
10
11 181 quartz (Fig. 3a). Coarse-grained braunite usually occurs as a homogeneous mass but is also
12
13 182 found as a rim around pyrolusite (Fig. 3b). Pyrolusite occurs as massive anhedral to subhedral
14
15 183 grains as well as disseminated grains in Mn minerals and gangue minerals and it can also fill
16
17 184 cracks and spaces between minerals. It is also found in micro-veins formed by filling of
18
19 185 fractures and cracks in braunite and gangue minerals particularly cryptocrystalline quartz (Fig.
20
21 186 3c). Massive pyrolusite grains show needle, flake and fibrous shapes (Fig. 3d). Breccia-like
22
23 187 textures between pyrolusite and quartz are also common.

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27
28 188 Hematite is associated with Mn minerals and occurs as a fine-grained matrix (Fig. 3b)
29
30 189 enclosing Mn minerals and forms veins along with gangue minerals. Hematite also occurs as
31
32 190 finely disseminated grains together with microcrystalline Mn minerals and cryptocrystalline
33
34 191 quartz. Gangue minerals are predominantly quartz and carbonate with minor barite. Quartz is
35
36 192 usually crushed due to deformation and is cryptocrystalline to microcrystalline. It occurs as
37
38 193 veinlets and well-developed crystals, filling vugs or interstitial spaces of manganese and iron
39
40 194 minerals (Fig. 3e). Carbonate is mainly calcite that commonly forms irregular or sometimes
41
42 195 oval patches and fills the veins and cracks within manganese and iron oxide matrix. Barite is
43
44 196 very rare and fills cavities in manganese-rich phases (Fig. 3f).

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49 197 Hence, three stages of mineralization are recognized in Zhob manganese
50
51 198 mineralization including; early, middle, and late stages. The early stage is represented by
52
53 199 massive pyrolusite minerals, while the middle stage is characterized by braunite with
54
55 200 replacement textures and enclosing pyrolusite. Late-stage supergene mineralization

201 comprising pyrolusite, hematite and barite minerals are found infilling fractures and
202 fissures (Fig. 4).

203

204 **6. Geochemistry**

205 **6.1. Mineral chemistry**

206 Compositions of the main minerals identified in the Zhob manganese ore are given in
207 Table 1. Braunite is one of the most significant manganese ore minerals and it normally
208 contains up to 10 wt. % SiO_2 (Roy, 1981). However, in silicate-rich braunite SiO_2 contents can
209 be up to 40%, depending on temperature and partial oxygen pressure during formation (Maun,
210 1959; Naseem, 1996). The studied ore from the Ali Khanzai block contains both normal
211 braunite and silicate-rich braunite. The average composition of normal braunite is SiO_2 (13.0
212 wt. %), Al_2O_3 (1.5 wt. %), Fe_2O_3 (1.1 wt. %), Mn_2O_3 (82.9 wt. %), MgO (0.3 wt. %) and CaO
213 (1.45 wt. %) while silicate-rich braunite contains SiO_2 (28.4 wt. %), Al_2O_3 (1.2 wt. %) and
214 MnO (67.5 wt. %).

215 Pyrolusite is also a dominant mineral in the Zhob deposits with a typical composition
216 of 98.3 wt. % MnO_2 and 0.90 wt. % Fe_2O_3 . The low totals indicate the presence of some
217 absorbed water in the pyrolusite (Gutzmer and Beukes, 1997; Frenzel, 1980).

218 Hematite is an accessory mineral and its composition averages 89.7 wt. % Fe_2O_3 , 9.1
219 wt. % Mn_2O_3 and 1.6 wt. % TiO_2 . However, the high contents of Mn_2O_3 suggest that hematite
220 may have incorporated Mn into its structure from the coexisting Mn-phases during
221 metamorphism (Shah and Moon, 2004).

222 The few grains of barite that have been observed have an average composition of 70.0
223 wt. % BaO , 27.1 wt. % SO_3 and 0.9 wt. % SrO . Small amounts of FeO , CaO and MnO in the
224 barite composition may have been substituted for BaO .

225

226 **6.2. Whole Rock Geochemistry**

227 The whole-rock composition of manganese ores and host rocks of the studied deposits
228 are given in Tables 2 and 3, respectively. Manganese ore samples have been divided into Mn-
229 rich and Fe-rich manganese ores. Average major elements contents (wt. %) of Mn-rich and Fe-
230 rich manganese ore samples and their host rocks are compared in Fig. 5a. Mn-rich ores are
231 higher in MnO and lower in Al₂O₃, Fe₂O₃ and SiO₂ than Fe-rich ores. Host rocks are much
232 higher in SiO₂ than manganese ores while almost similar in the other major elements to the
233 manganese ores.

234 Trace element concentrations (ppm) of Mn-rich and Fe-rich manganese ores and their
235 host rocks are compared in Fig. 5b. Fe-rich manganese ores are higher in Pb, Co, Ni, Zn and
236 Cu and more depleted in Cr than the Mn rich ores. Trace element contents in the host rocks are
237 much lower than in the manganese ores except for Cu and Cr which are broadly the same. The
238 samples of Fe and Mn-rich ores will be discussed together in the following section because
239 they have been sampled from the same deposits.

240

241 **7. Discussion**

242 The common veining, brecciation, mesh textures and crushed grains of ore and gangue
243 minerals of Zhob manganese deposits reveal that after their formation, the rocks of the studied
244 area may have undergone regional metamorphism (see Gutzmer and Beukes, 1997; Ostwald
245 and Nayak, 1993; Roy et al., 1990; Abs-Wurmbach et al., 1983; Dasgupta and
246 Manickavasagam, 1981; Roy, 1981). The mesh texture, in which pyrolusite is surrounded by
247 braunite, indicates the replacement of pyrolusite by braunite and suggests that braunite was
248 formed due to the reaction between pyrolusite (early formed phase) and iron-oxide (hematite)
249 and subsequent recrystallization and remobilization caused incorporation and readjustment of
250 Mn, Fe, Si, P, Al and Pb from pyrolusite, hematite, quartz, and barite (Shah and Moon, 2004).

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3 251 The occurrence of pyrolusite as relics within braunite confirms this inference. However, the
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5 252 presence of pyrolusite as fracture-filled micro-veins could also be related to supergene
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8 253 enrichment (Shah and Moon, 2004). Braunite is a characteristic mineral of greenschist to
9
10 254 granulite facies conditions (Gutzmer and Beukes, 1997; Abs-Wurmbach et al., 1983; Roy,
11
12 255 1981). Hence, the mineralogy and texture of the minerals found in the Zhub manganese ores
13
14
15 256 support the idea that rocks of the area have been locally subjected to greenschist facies
16
17 257 metamorphism.

18
19 258 The major oxides SiO_2 , Fe_2O_3 , MnO , Al_2O_3 and TiO_2 and trace element contents as well
20
21 259 as ratios of major and trace elements are useful in assessing the paragenesis of manganese ore
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23
24 260 deposits (Zarasvandi et al., 2013; Polgari et al., 2012; Karakus et al., 2010; Shah and Khan,
25
26 261 1999; Crerar et al., 1982).

27
28 262 The Si vs. Al binary discrimination diagram proposed by Toth (1980) and Peters
29
30 263 (1988), is widely used to assess the hydrothermal, sedimentary or hydrogenous (i.e., from
31
32
33 264 seawater deposition) origins of manganese mineralization (Oksuz, 2011; Karakus et al., 2010;
34
35 265 Mücke et al., 1999; Nicholson, 1992). SiO_2 concentration is typically high in hydrothermally-
36
37 266 formed sediments as compared with hydrogenous deposits (Karakus et al., 2010). Almost all
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39
40 267 the samples from the Zhub deposits plot within the field of hydrothermal deposits similar to
41
42 268 the Waziristan (Pakistan) and Dehoo (Turkey) manganese deposits (Fig. 6a). In addition to the
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44
45 269 hydrothermal processes, other processes and components such as diagenesis, clastic materials,
46
47 270 and biosilica can increase the Si concentrations (e.g., Polgari et al., 2012; Toth, 1980).

48
49 271 The triangular plot of $\text{Mn-Fe}-(\text{Co}+\text{Ni}+\text{Cu}) \times 10$ (Hein et al., 1992; Crerar et al., 1982;
50
51 272 Toth, 1980; Bonatti, 1972) has also been successfully used to help distinguish manganese
52
53
54 273 mineralization of various origins. The Zhub ores again plot in the hydrothermal field (Fig. 6b)
55
56 274 almost identical to Waziristan (Pakistan) and Dehoo (Turkey) manganese deposits. The Zn-
57
58 275 Ni-Co triangular diagram (Choi and Hariya, 1992) also shows the hydrothermal origin of Zhub
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3 276 deposits (Fig. 7a) and illustrates that they are compositionally similar to other hydrothermal
4
5 277 manganese deposits like those in Waziristan (Pakistan) and Dehoo (Iran). The Co/Zn vs.
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7 278 Co+Ni+Cu diagram (Toth, 1980), once again reveals the hydrothermal genesis of the Zhob
8
9 279 deposits (Fig. 7b).

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11
12 280 Mn/Fe ratio is used to delineate the origin of manganese deposits; for example, for
13
14 281 lacustrine deposits ($Mn/Fe < 1$), hydrogenous deposits ($Mn/Fe = 1$), SEDEX deposits (0.1
15
16 282 $< Mn/Fe < 10$) (Nicholson et al., 1997) while a high Mn/Fe ratio is characteristic of
17
18 283 hydrothermal deposits (Jach and Dudek, 2005). The Mn/Fe ratios of the Zhob manganese
19
20 284 deposits range from 1.7 to 561 (mean 106). The available average Mn/Fe ratios of world
21
22 285 manganese deposits are as follows: Waziristan - 199 (Shah and Khan, 1999), Cayirli - 97
23
24 286 (Karakus et al., 2010), Dehoo - 80 (Lotfi, 2017), Hazara - 2 (Shah and Moon, 2004), Eymir -
25
26 287 880 (Oksuz, 2011), Nasirabad – 19 (Zarasvandi et al., 2013), Buyukmahal - 48 (Oskuz and
27
28 288 Okuyucu, 2014), Binkilic - 15 (Gultekin, 1997), Ulukent - 19, (Ozturk,1993) and Hinode - 133
29
30 289 (Choi and Hariya,1992). The comparison of the world manganese deposits is shown in Table
31
32 290 4. Among these deposits Waziristan, Cayirli and Dahoo are hydrothermal exhalative
33
34 291 manganese deposits associated with ophiolites. The Hazara, Nasirabad, Buyukmahal, and
35
36 292 Eymir deposits are of hydrothermal- hydrogenous origin while Binkilic, Ulukent, and Hinode
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38 293 deposits are formed in hydrogenous environments. Thus, the range of Mn/Fe ratio (1.7 to 561;
39
40 294 avg. 106) of the Zhob manganese ore deposit is consistent with those of hydrothermal
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42 295 exhalative manganese deposits.

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45 296 The behavior of Co and Ni are closely related to each other and are also closely
46
47 297 associated with Mn oxides. On average, cobalt abundances decrease from hydrogenous to
48
49 298 diagenetic and to hydrothermal manganese deposits (Zarasvandi et al., 2013; Sabatino et al.,
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51 299 2011). Deposits with $Co/Ni < 1$ are characteristic of sediments deposited in hot water
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53 300 (Fernandez and Moro, 1998) whereas $Co/Ni > 1$ indicates a deep marine environment of
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3 301 formation (Toth, 1980). Apart from one sample, Co/Ni ratios in the Zhob manganese ore
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5 302 deposit are lower than 1 suggesting a sedimentary contribution to the mineralization (Table 2).
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8 303 Co/Zn ratios of ~0.15 are characteristic of hydrothermal manganese ore deposits while a ratio
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10 304 of ~2.5 indicates a hydrogenous origin for a manganese ore deposit (Toth, 1980). Co/Zn ratio
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12 305 for the Zhob manganese deposits ranges from 0.13 to 0.9 and indicates a hydrothermal origin
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14 306 for the manganese mineralization. These values are similar to the Waziristan manganese
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16 307 deposit and Dehoo ore deposit (Table 4). Although Co/Zn ratios suggest a hydrothermal origin
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18 308 for the Zhob ore deposits, Co/Ni ratios indicate a small contribution from a sedimentary
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20 309 component during the formation of the manganese deposits.
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24 310 Like Fe and Mn values, concentrations of Ti and Al are also useful for the assessment
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26 311 of the genesis of Mn ore deposits. Al and Ti contents are high in the sedimentary environment
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28 312 and they have the same behavior during the formation of an ore deposit (Sugisaki, 1984; Crerar
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30 313 et al., 1982). Detrital materials are an important source of Al in the chemical precipitates of
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32 314 manganese ores (Zarasvandi et al., 2013; Polgari et al., 2012; Maynard, 2010), while titanium
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34 315 is essentially constant in hydrothermal solutions and is thus a measure of clastic (detrital) input
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36 316 (Şaşmaz et al., 2014; Shah and Khan, 1999; Sugisaki, 1984). The contents of Al and Ti in the
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38 317 Zhob deposits show a positive correlation (Fig. 7c) except for one sample which has markedly
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40 318 high Al₂O₃, probably due to alteration. This broad positive correlation, therefore, supports the
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42 319 contribution of detrital material in the formation of the deposits.
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48 49 321 **7.1. Genetic model of Zhob manganese deposits**

50
51 322 The Zhob Ophiolite is part of the Bela-Zhob-Waziristan ophiolitic belt (Sengor, 1987).
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53 323 Ophiolites of this belt were obducted on the western margin of the Indian continental plate as
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55 324 the oceanic crust of Neo-Tethys Ocean and formed in a supra-subduction zone environment in
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57 325 Late Cretaceous (Kakar et al., 2014; Mahmood et al., 1995; Sawada et al., 1995). The Ali
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3 326 Khanzai block of Zhob Ophiolite was the part of the crust Neo-Tethys ocean that contains
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5 327 manganese mineralization associated with metachert. By considering the models of Bonatti et
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7 328 al. (1976), Canon and Force (1983) and Buhn et al. (1992), a simple genetic model can be
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9 329 proposed for the origin of the Zhob manganese deposits (Fig. 8). The downward circulation of
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11 330 seawater into the fractured oceanic crust and interaction of the seawater with hot oceanic crust
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13 331 caused progressive warming and reduction and increase in the acidity that generated
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15 332 hydrothermal solutions (Roy, 1992). These solutions were able to leach Mn, Fe and other
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17 333 metals from the basaltic oceanic crust. Finally, the metal-enriched hydrothermal solutions
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19 334 convected upward to the seafloor lead the deposition of manganese and ferromanganese
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21 335 deposits.
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26 336 The precipitation of different metals from the hydrothermal solutions are the result of
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28 337 decreasing pressure and temperature and increasing Eh and/or pH in the solution. Cooling of
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30 338 the hydrothermal solution may occur during circulation through cooler rocks and/ or by
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32 339 subsurface mixing with seawater. The origin of the Zhob manganese deposits similar to those
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34 340 of present-day hydrothermal systems within mid-oceanic spreading centers (Shah and Khan
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36 341 1999; Roy, 1992). The formation of these deposits can be related to the Neo-Tethys Ocean
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38 342 where these deposits originated along with sea-floor-spreading centres and were later obducted
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40 343 as part of Zhob Ophiolite. During obduction, the Zhob Ophiolite has undergone metamorphism
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42 344 which may have caused alteration of the manganese deposits.
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46 345 It is now understood that Fe compounds are less stable compared to Mn and so
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48 346 precipitate close to hydrothermal vents. Conversely, Mn is more stable in aqueous solution and
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50 347 so precipitates further away from hydrothermal vents at sea floor spreading centers (Roy, 1992;
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52 348 Panagos, 1984). The precipitation of Mn and Fe and their compounds are controlled by Eh
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54 349 and/or pH of the hydrothermal solution (Frakes and Bolton, 1992; Panagos, 1984). In low Eh
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56 350 and/or pH conditions Mn is more mobile relative to Fe. The fractionation of Mn compounds
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3 351 from Fe compounds suggests a spatial variation in Eh and/or pH (Panagos, 1984). Considering
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5 352 Fe and Mn concentrations of mineralization in the study area, it is likely that the Zhob deposits
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8 353 were formed from a hydrothermal source and the high Fe contents, indicate that mineralization
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10 354 was probably proximal to a hydrothermal vent at a sea floor spreading center.

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12 355 It is clear from the geochemical data in Figs. 6 and 7, and low Mn/Fe ratios (Table 3)
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14 356 of the host rocks (metachert) that metachert was formed by hydrothermal processes with a
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16 357 limited contribution from sedimentary (contemporaneous volcanic) components. The
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18 358 conformable nature of the Zhob manganese deposits and host metachert indicate that Mn and
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20 359 Si were probably both derived from the same hydrothermal source. Metachert contains
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22 360 radiolarian tests and this suggests that the metachert is formed from a mixture of biogenic and
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24 361 hydrothermal sediments.
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30 363 **8. Conclusions**

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33 364 The Zhob manganese ore deposits are hosted by red to brown metachert in the Ali
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35 365 Khanzai block of the Zhob Ophiolite. Braunite and pyrolusite are the main manganese minerals
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37 366 that occur together with minor hematite and barite. Gangue minerals are mainly quartz and
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39 367 carbonate minerals. Major and trace element signatures show that hydrothermal processes were
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41 368 responsible for the formation of mineralization at Zhob with a minor contribution from detrital
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43 369 (contemporaneous volcanic) materials. Therefore, it is concluded that the Zhob manganese
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45 370 deposits are hydrothermal in origin.
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For Review Only

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Tables and Figures Captions

Table 1. Mineral chemistry of manganese minerals from Zhob manganese deposits.

Table 2. Whole rock major oxide (wt. %) and trace element (ppm) geochemical composition of manganese ore of the Zhob Ophiolite.

Table 3. Whole rock major oxide (wt. %) and trace element (ppm) geochemical composition of the host rocks of Zhob manganese deposits.

Table 4. Comparison between some major and trace element composition of the Zhob manganese occurrences and different types of manganese ores in the world.

Fig.1. Geological map showing (a) The study area, (b) Map of the Western Sulaiman Belt showing occurrences of the Zhob Valley Ophiolites and its surrounding rock units and (c) Map of Ali Khanzai block of the Zhob Ophiolite with the occurrences of manganese deposits (modified after Rehman, 2019; Siddiqi et al., 2016; Kakar et al., 2013; Bannert et al., 1992; HSC, 1960). BO; Bela Ophiolite, KO; Khanozai Ophiolite, MO; Muslim Bagh Ophiolite, WO; Waziristan Ophiolite, DO; Dargai Ophiolite, CO; Chilas Ophiolite, CF; Chaman Fault, PS; Penjwai Suture, HF; Herat Ophiolite, KB; Karakorum Block, MMT; Main Mantle Thrust, MBT; Main Boundary Thrust.

Fig.2. Field photographs showing (a) lenticular shape of manganese deposit surrounded by metachert, (b) layers of manganese surrounded by metacherts, (c) Mn-rich phases forming alternate bands with host metachert, and (d) massive manganese ore. Mn=manganese, Ch=metachert

Fig.3. Photomicrographs and micro-XRF scans showing (a) Braunite grains cross-cut by veinlets of quartz, (b) braunite enclosing pyrolusite forming a relic texture, (c) Pyrolusite microveins formed by filling of fractures and cracks in braunite and gangue minerals, (d) Massive pyrolusite grains showing fibrous sections, (e) Quartz in veinlets and well-developed crystals, filling vugs or interstitial spaces of manganese and iron minerals and (f) Barite filling cavities in manganese-rich phases. Note Fig (b) and (f) are micro-XRF images. Bra=Braunite, Pyr=pyrolusite, Hem=Hematite, Qz=Quartz.

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3 **Fig.4.** Diagram of the ore paragenetic succession of the Zhob manganese deposits.
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5 **Fig.5.** Diagrams showing comparison of **(a)** major oxides and **(b)** trace elements in Mn-rich, Fe-
6 rich ores and host rocks.
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8 **Fig.6. (a)** Bivariate plot of Si versus Al (Choi and Hariya, 1992) in which data points of the ore
9 samples fall within the hydrothermal field. **(b)** Ternary plot of Fe-Mn-(Ni + Co + Cu) ×
10 10 (Bonatti et al., 1972, modified by Toth, 1980) with the plotted data points within the
11 hydrothermal field.
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15 **Fig.7. (a)** Zn–Co–Ni diagram showing data for the manganese ores of Zhob, with fields for
16 hydrothermal and hydrogenous deposits (after Choi and Hariya, 1992). **(b)** A plot of Co/Zn
17 vs. Co+Ni+Cu for the manganese ores of Zhob (after Toth, 1980) and **(c)** TiO₂ vs Al₂O₃
18 diagrams of manganese ore samples.
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22 **Fig.8.** Hypothetical model showing the geological environment of formation of the Zhob
23 manganese deposits.
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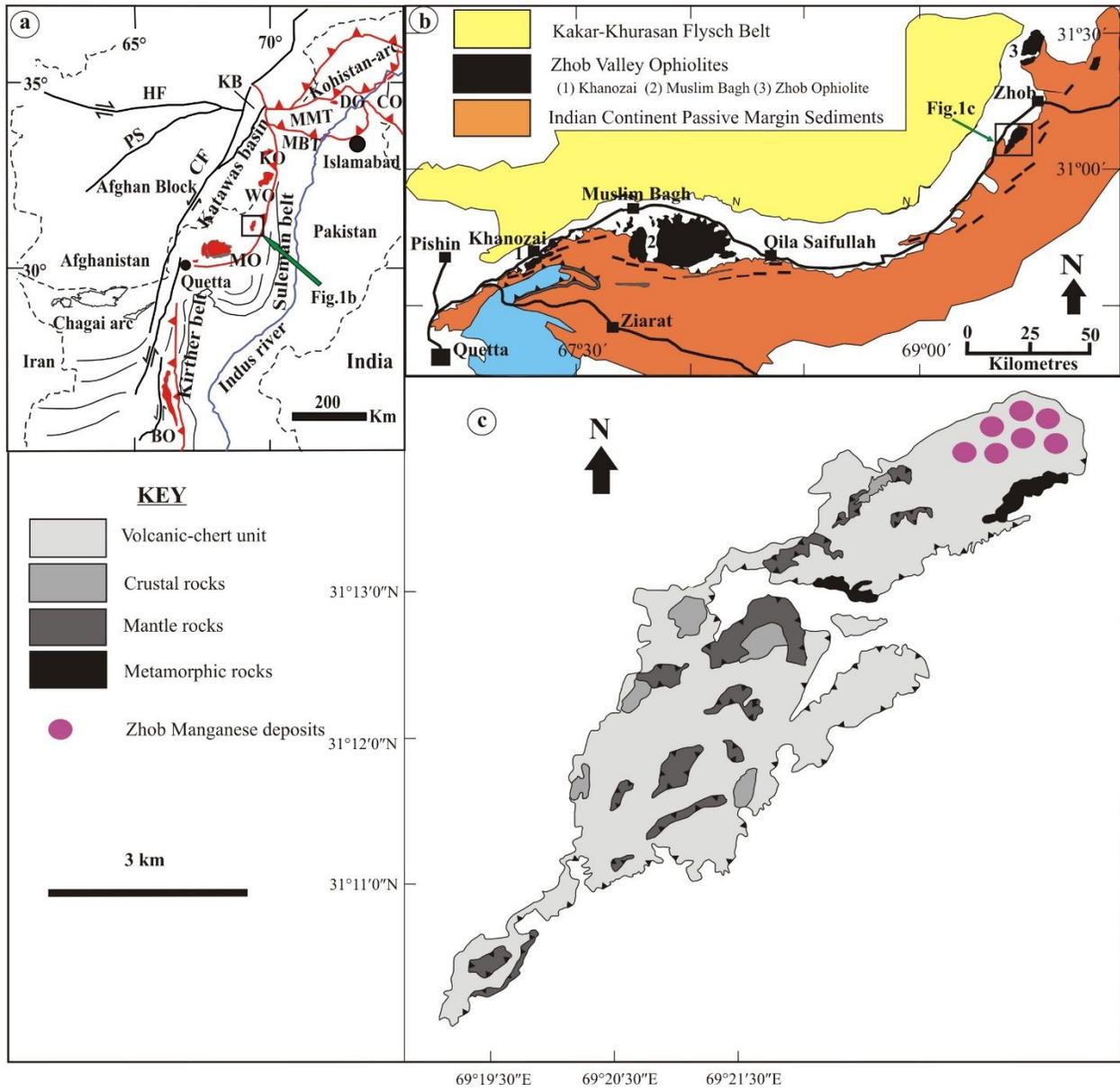


Fig.1

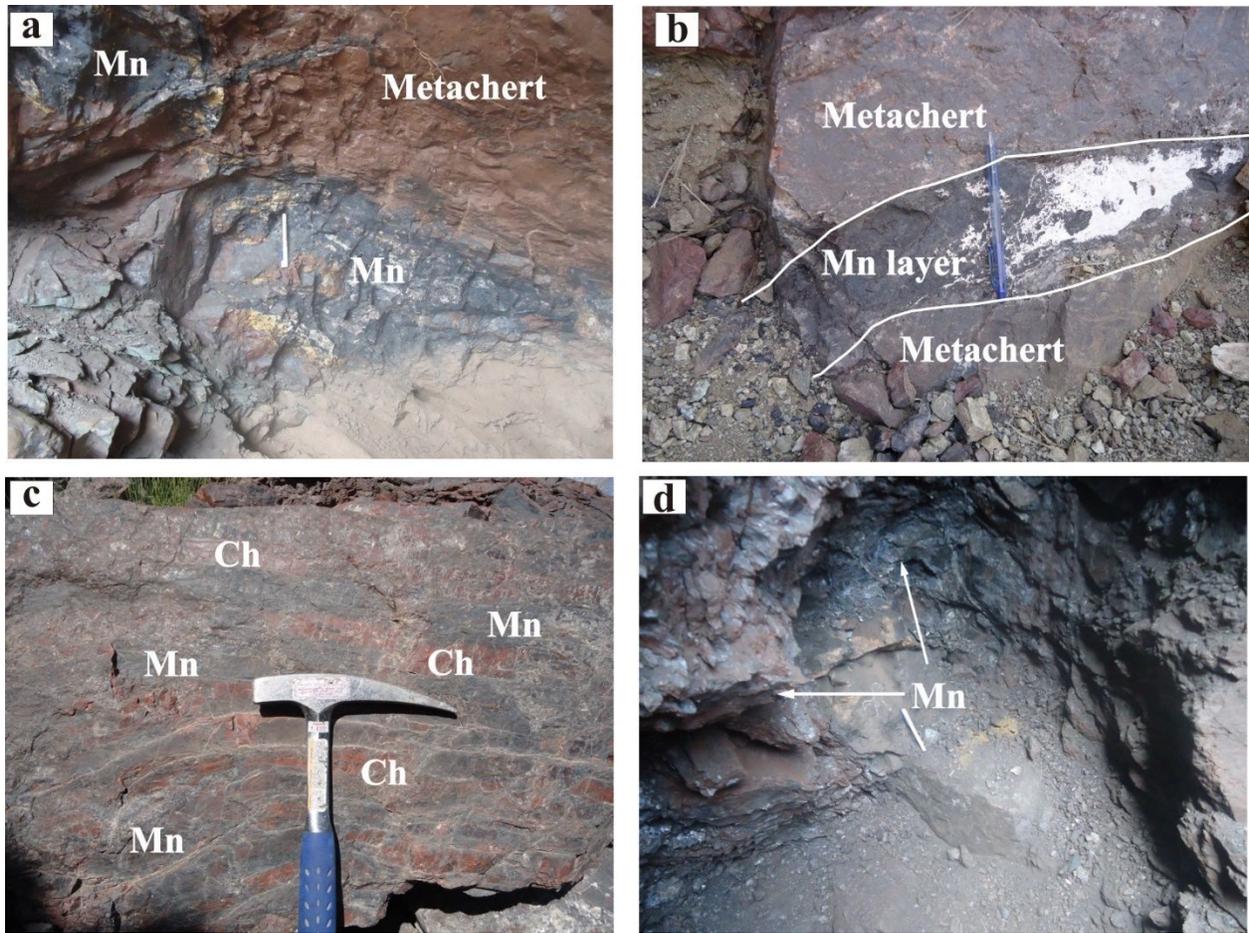


Fig. 2

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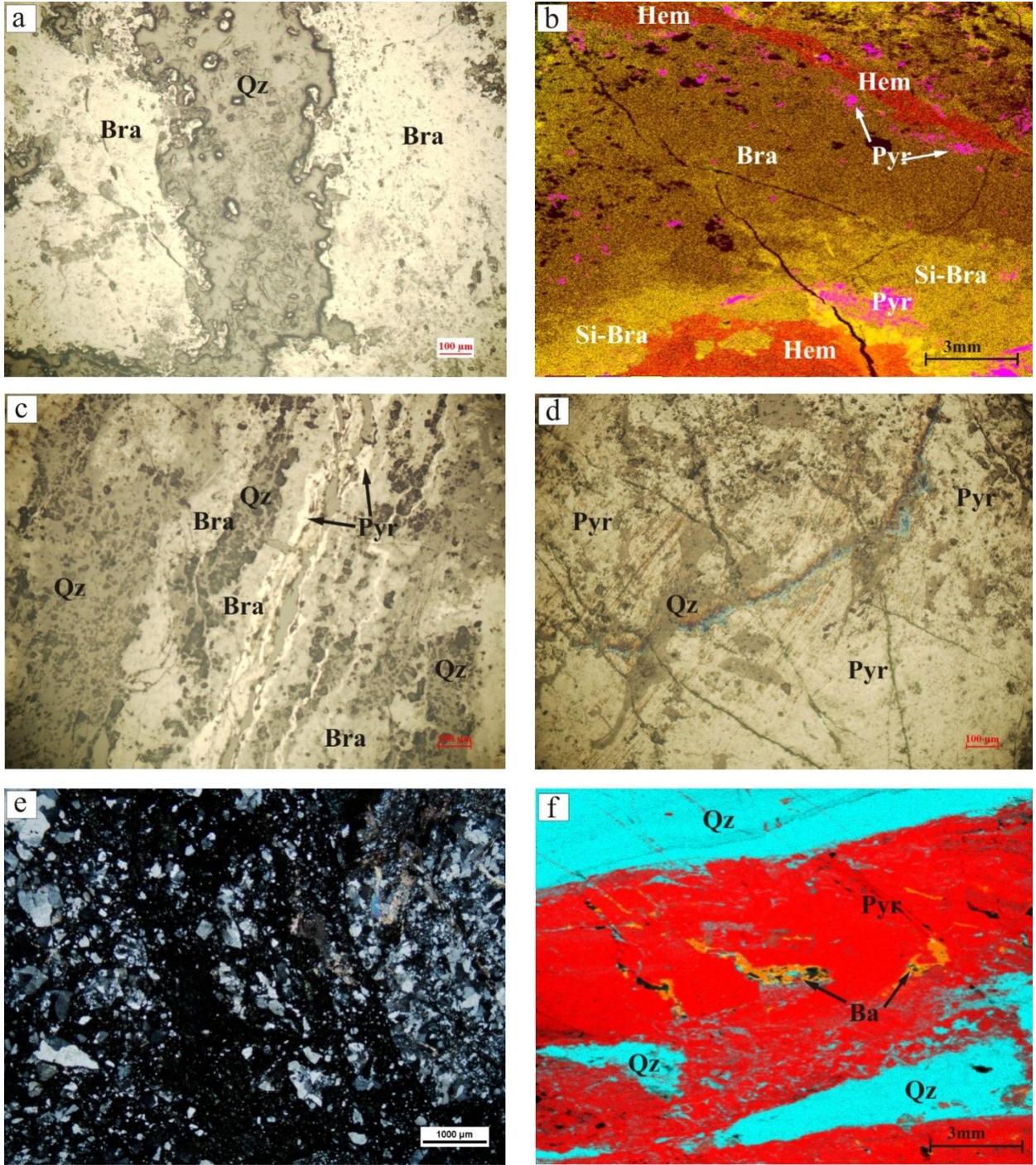


Fig. 3

Ore minerals	Stages of ore mineralization		
	Early	Middle	Late
Pyrolusite	-----		-----
Braunite		-----	
Hausmannite			-----
Hematite			-----
Barite			-----
Silica gangue	-----	-----	-----

Fig. 4

Or Review Only

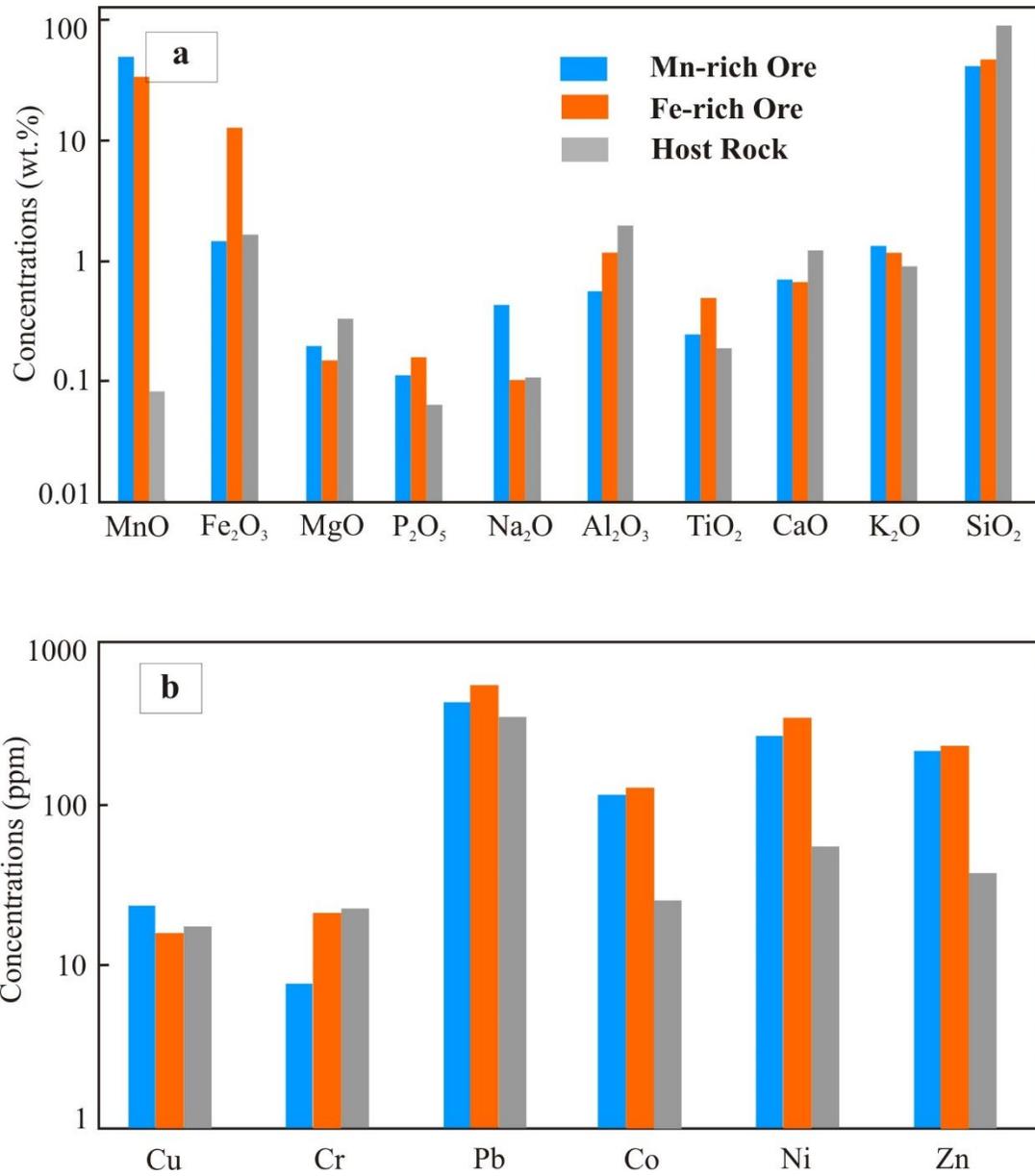


Fig.5

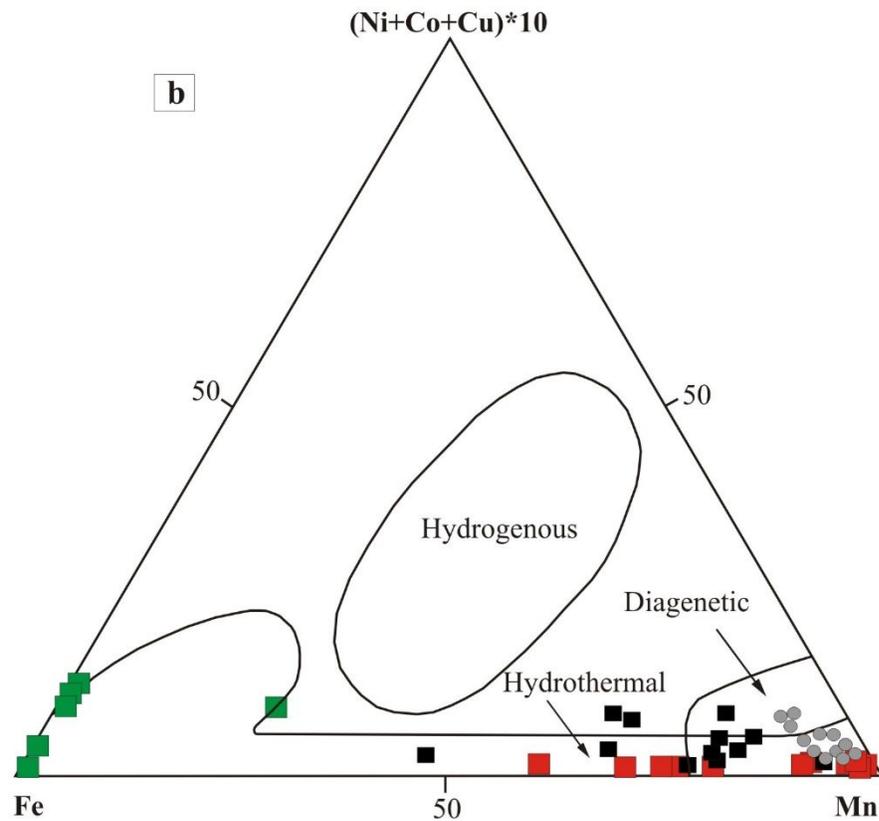
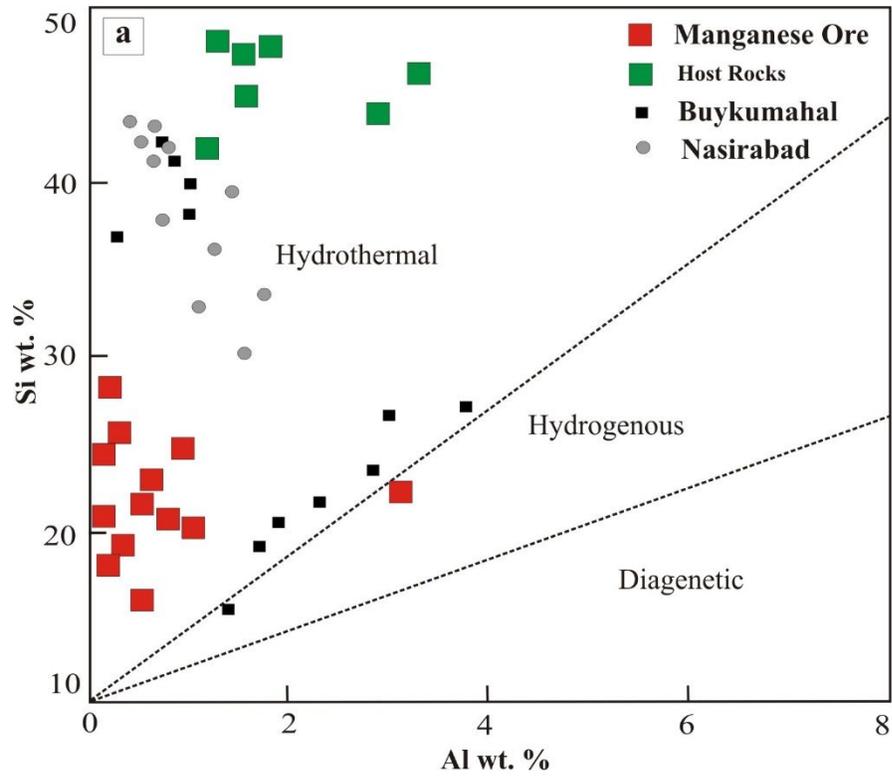


Fig.6

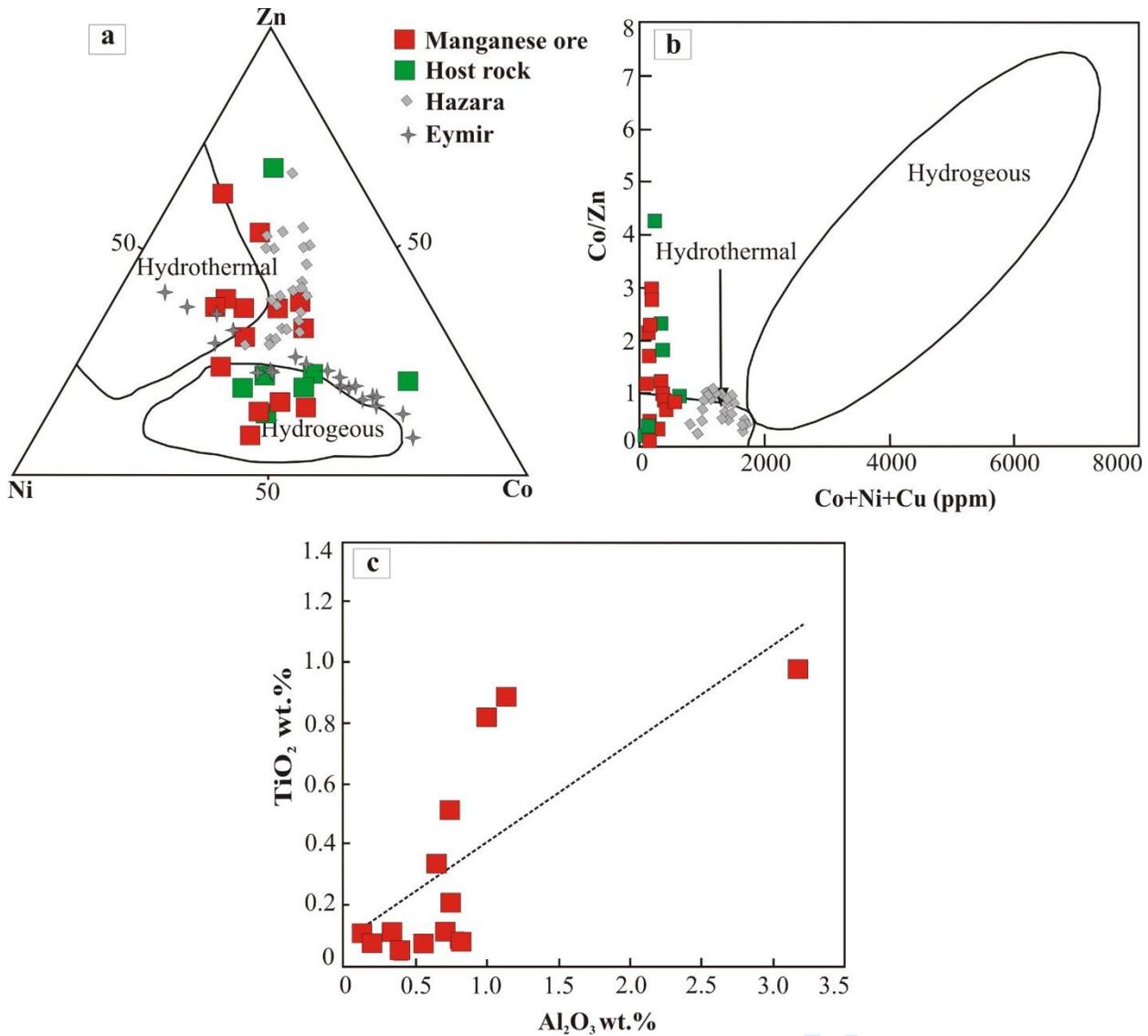


Fig.7

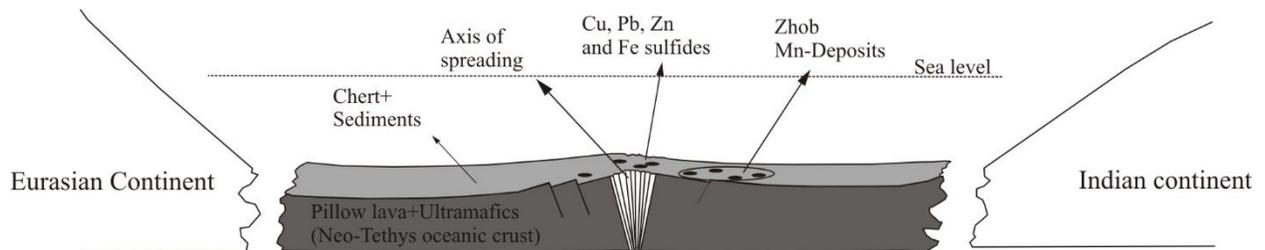


Fig.8

Table 1. Mineral chemistry of manganese minerals of Zhob manganese deposits

	Normal Braunite		Si-rich Braunite		Pyrolusite		Hematite		Barite		Detection Limit	
SiO ₂	13.02		SiO ₂	28.41	SiO ₂	bdl	SiO ₂	bdl	CaO	2.98	SiO ₃	0.06
Al ₂ O ₃	1.46		Al ₂ O ₃	1.18	Al ₂ O ₃	dbl	TiO ₂	1.62	SrO	0.85	Al ₂ O ₃	0.05
Fe ₂ O ₃	1.09		Fe ₂ O ₃	0.85	Fe ₂ O ₃	0.90	Al ₂ O ₃	bdl	BaO	69.98	Fe ₂ O ₃	0.10
Mn ₂ O ₃	82.19		Mn ₂ O ₃	67.52	MnO ₂	98.31	Fe ₂ O ₃	89.27	MgO	bdl	Mn ₂ O ₃	0.08
MgO	0.29		MgO	0.43	MgO	0.00	Mn ₂ O ₃	9.11	FeO	0.87	MgO	0.07
CaO	1.45		CaO	0.24	CaO	bdl	MgO	bdl	MnO	0.12	CaO	0.05
Na ₂ O	0.20		Na ₂ O	0.27	Na ₂ O	bdl	CaO	bdl	SO ₃	25.05	Na ₂ O	0.04
K ₂ O	bdl		K ₂ O	bdl	K ₂ O	bdl	Na ₂ O	bdl	Total	99.85	K ₂ O	0.05
Cr ₂ O ₃	bdl		Cr ₂ O ₃	bdl	Cr ₂ O ₃	bdl	K ₂ O	bdl			Cr ₂ O ₃	0.09
Total	99.75		Total	98.93	Total	99.24	Cr ₂ O ₃	bdl			TiO ₂	0.04
							Total	100			SrO	0.03
											SO	0.08

	Ions calculation based on 12 (O)				based on 2 (O)		based on 3 (O)		based on 4 (O)	
Si	1.54	Si	2.88	Si	0.00	Si	0.00	Ca	0.00	
Al	0.20	Al	0.14	Al	0.00	Ti	0.04	Sr	0.01	
Fe ³⁺	0.10	Fe ³⁺	0.06	Fe ³⁺	0.02	Al	0.00	Ba	1.03	
Mn	8.21	Mn	5.80	Mn ⁴⁺	1.97	Fe ³⁺	1.89	Mg	0.00	
Mg	0.05	Mg	0.07	Mg	0.00	Mn ³⁺	0.10	Fe	0.00	
Ca	0.18	Ca	0.03	Ca	0.00	Mg	0.00	Mn	0.00	
Na	0.05	Na	0.05	Na	0.00	Ca	0.00	S	0.99	
K	0.00	K	0.00	K	0.00	Na	0.00			
Cr	0.00	Cr	0.00	Cr	0.00	K	0.00			

bdl=below detection limit

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Table 2. Whole rock major oxides (wt. %) and trace elements (ppm) geochemical composition of manganese ore of Zhob manganese deposits

Sample	Mn-Rich							Fe-Rich						Detection Limit
	Z97b	ZA101	ZA102	Z103a	ZA104a	ZA104b	Z105b	Z106a	Z97a	Z105a	Z105M	Z108	ZA108b	
MnO	49.21	48.18	33.07	54.80	51.36	51.02	51.46	46.08	25.47	36.71	33.23	32.01	39.38	0.005
Fe ₂ O ₃	0.31	4.36	3.19	1.16	1.76	0.13	0.83	0.09	16.83	8.95	13.98	10.7	12.5	0.005
MgO	0.3	0.44	0.09	0.11	0.26	0.12	0.08	0.16	0.15	0.05	0.14	0.24	0.19	0.005
P ₂ O ₅	0.01	0.05	0.6	0.1	0.06	0.01	0.02	0.04	0.14	0.16	0.36	0.07	0.05	0.005
N ₂ O	0.07	0.18	0.1	2.72	0.09	0.06	0.09	0.08	0.13	0.06	0.09	0.1	0.14	0.005
Al ₂ O ₃	0.63	0.16	0.16	0.56	0.33	0.8	1.08	0.71	0.37	0.73	3.21	1.01	0.63	0.005
TiO ₂	0.53	0.07	0.1	0.08	0.12	0.07	0.91	0.11	0.07	0.21	0.97	0.84	0.34	0.005
CaO	0.06	1.44	0.05	0.52	1.81	0.26	bdl	1.44	0.02	0.01	1.39	0.35	1.59	0.005
K ₂ O	1.38	1.72	1.23	1.83	0.85	1.08	1.23	1.31	1.08	1.08	1.23	1.38	1.08	0.005
SiO ₂	43.21	36.5	55.11	32.37	39.19	41.84	41.01	47.44	49.6	51.2	43.95	49.68	42.05	0.005
LOI	4.35	6.20	5.30	5.50	3.30	4.40	3.50	2.55	5.50	0.90	3.15	3.80	1.20	
Total	100.06	99.30	99.00	99.75	99.13	99.79	100.21	100.01	99.36	100.06	101.70	100.18	99.15	
Mg	38.11	37.31	25.61	42.43	39.77	39.51	39.85	35.68	19.72	28.43	25.73	24.79	30.50	
Fe	0.22	3.05	2.23	0.81	1.23	0.09	0.58	0.06	11.77	6.26	9.78	7.48	8.74	
Mn/Fe	176	12.24	11.48	52.30	32.31	435	69	567	1.68	4.54	2.63	3.31	3.49	
Cu	43	17.2	5.2	39	8	45	3.6	25	36.4	10	23.2	3.2	7	0.05
Co	bdl	29.8	bdl	8.4	3.2	9.6	8	3	41.2	16	4	18.8	26	0.05
Pb	305	706	558.2	29	410	212.4	687	484.4	378	687.4	647	546.2	390.2	0.05
Co	85.2	21	105	179	168.2	185	124	90	80.2	140	231	131	90.4	0.05
Ni	313.4	132.2	314.6	198.6	379.4	344.4	147	219.6	333.6	403	437.4	287	239.8	0.05
Zn	175	163.2	250	305	184.2	240	320	145	161	394.2	408.2	141	115.4	0.05
Co/Zn	0.49	0.13	0.42	0.59	0.91	0.77	0.39	0.62	0.50	0.36	0.56	0.93	0.78	
Co/Ni	0.27	0.16	0.33	0.90	0.44	0.54	0.51	1.59	0.24	0.35	0.53	0.46	0.38	

LOI=Loss of Ignition, bdl=below detection limit

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Table 3. Whole rock major oxides (wt. %) and trace elements (ppm) geochemical composition of host rocks of Zhob manganese deposits

Sample	Z97H	Z97aH	Z104H	ZA106	Z111H	ZA112	Z113H	Detection Limit
MnO	0.01	0.51	0.01	0.01	0.01	0.01	0.01	0.005
Fe ₂ O ₃	1.33	1.30	2.34	1.13	2.02	2.13	1.11	0.005
MgO	0.11	0.08	0.12	0.14	1.42	0.22	0.23	0.005
P ₂ O ₅	0.03	0.01	0.34	0.01	0.02	0.01	0.02	0.005
Na ₂ O	0.08	0.14	0.04	0.05	0.15	0.15	0.14	0.005
Al ₂ O ₃	1.58	1.75	1.23	1.54	1.39	3.29	2.91	0.005
TiO ₂	0.09	0.08	0.08	0.50	0.07	0.27	0.24	0.005
CaO	0.62	0.46	4.11	0.06	0.20	1.65	1.52	0.005
K ₂ O	0.64	0.51	1.23	1.31	0.77	0.93	0.94	0.005
SiO ₂	88.43	93.11	84.18	93.83	93.40	91.03	87.63	0.005
LOI	7.25	1.90	5.90	1.95	0.60	0.95	5.90	
Total	100.17	99.85	99.58	100.53	100.05	100.64	100.65	
Mn	0.01	0.39	0.01	0.01	0.01	0.01	0.01	
Fe	0.93	0.91	1.64	0.79	1.41	1.49	0.78	
Mn/Fe	0.01	0.43	0.01	0.01	0.00	0.01	0.01	
Cu	46	21.20	26.20	6.40	5	7	13.00	0.05
Cr	34.00	16	5.20	12.00	41.40	33.40	15	0.05
Pb	193	397	302.40	390.40	322.20	316	435.20	0.05
Co	19.20	26.40	45	24.40	37.20	6	23.40	0.05
Ni	18.40	88.20	74	83.40	39	6	66.40	0.05
Zn	30	27	60	38	47	27	40	0.05
Co/Zn	0.64	0.98	0.75	0.64	0.79	0.21	0.59	
Co/Ni	1.04	0.30	0.61	0.29	0.95	0.97	0.35	

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Table 4. Comparison between some major and trace element composition of the Zhob manganese occurrences and different type of manganese ores in the world

Country	Iran	Turkey	Pakistan	Turkey	Turkey	Japan
Ore deposit	Dehoo (1)	Cayirli (2)	Wazirstan (3)	Ulukent (4)	Binkilic (5)	Honde (6)
Origins	hydrothermal	Hydrothermal	Hydrothermal	Sedimentary	Sedimentary	Hydrogenous
SiO ₂	25.87	63.02	43.69	13.6	10.65	12.67
TiO ₂	0.04	0.03	0.32	0.1	0.02	0.04
Al ₂ O ₃	1.07	0.65	0.73	2.49	2.85	1.27
Fe ₂ O ₃	2.44	0.68	2.96	3.72	2.46	0.59
MnO	45.59	29.22	45.88	63.78	33.39	67.21
MgO	0.42	0.2	0.6	1.99	1.27	0.08
CaO	5.17	0.24	1.28	4.05	18.96	1.67
Na ₂ O	0.12	0.05	0.29	0.24	0.39	0.07
K ₂ O	0.21	0.11	0.22	0.05	0.56	0.46
P ₂ O ₅	0.08	0.04	0.25	0.18	0.31	0.12
Cr	(-)	13.7	45	(-)	26	16
Co	28.75	25.21	11	13	59	222
Ni	89.13	69.4	36	10	167	341
Cu	62.13	154.9	72	56	26	691
Zn	77.74	66.6	64	70	49	147
Pb	19.68	6.5	49	65	(-)	18
Mn/Fe	56.23	97.17	199	18.98	15.03	133.43
Co/Zn	0.38	0.38	0.17	0.19	1.2	1.51
Co/Ni	0.33	0.36	0.31	1.3	0.35	0.65

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38Table 4 *continue*

Pakistan	Turkey	Iran	Turkey	Pakistan
Hazara (7)	Eymir (8)	Nasirabad (9)	Buyukmahal (10)	Zhob (This Study)
Hydrothermal- Hydrogenous	Hydrothermal- Hydrogenous	Hydrothermal- Hydrogenous	Hydrothermal- Hydrogenous	Hydrothermal
9.41	16.04	84.39	49.62	44.09
0.84	0.02	0.06	0.16	0.34
12.53	0.73	1.29	3.66	0.80
20.33	0.26	0.76	6.63	5.75
33.78	69.91	8.82	26.79	42.46
0.59	0.59	0.3	1.31	0.18
6.43	0.24	0.5	2.94	0.69
0.07	0.01	0.17	0.18	0.30
0.88	0.05	0.2	0.67	1.27
5.73	0.07	0.02	0.11	0.13
247	(-)	(-)	(-)	29.85
404	103.5	85.36	367.4	125.24
905	67.35	86.13	280.4	288.46
375	80.5	117.74	450.8	28.05
580	62.45	35.62	81.8	230.67
3357	9.33	2.02	25.8	541.6
4.16	880.33	18.85	6.06	105.37
0.7	2.24	2.2	4.49	0.57
1.32	1.54	0.99	1.31	0.51

39 Analysis after (1) =Lofti et al. (2017), (2) =Karakus et al. (2010), (3) =Shah and Khan (1999), (4) =Ozturk (1993), (5) =Gultekin
40 (1998), (6) =Choi and Hariya (1992), (7) =Shah and Moon (2004), (8) =Oksuz (2011), (9) =Zarasvandi et al. (2013), (10) =Oksuz
41 and Okuyucu (2014)

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