Geochemical signatures of manganese ores around Barbil, Noamundi-Koira basin, Singhbhum Craton, Eastern India

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ABSTRACT

Palaeoproterozoic Noamundi–Koira Basin (NKB), on the western margin of the >3.0 Ga old Singhbhum Granitoid Complex, forms a horseshoe-shaped synclinorium. Volcanic rocks belonging to Bonai volcanic suite (BVS) occur outside and all-around the NKB that consists of three distinct but conformable stratigraphic units viz; Lower Shale Formation, Middle Banded Hematite Quartzite (BHQ) and/or Banded Hematite Jasper (BHJ) and Upper Shale Formation. The layered, lensoid, lateritoid, and vein type Mn-ore bodies are associated with the Upper Shale Formation. Compositions of the Mn ores widely vary values, SiO$_2$ (1.00%–16.40%), Al$_2$O$_3$ (1.62%–17.20%), Fe$_2$O$_3$ (10.55%–63.28%), MnO (31.75%–75.72%), Ni (25–260 ppm), Co (78–350 ppm), Zn (82–509 ppm) and Cr (13–187 ppm) clearly reflect their submarine hydrothermal source. Litho-stratigraphic considerations also lead to suggest that BHU/BHO and Mn-ore deposits of NKB are genetically related to the BVS. It is suggested that manganese and iron ores were deposited in a (?) Forearc basin associated with the mature island arc or active continental margin setting. FeO and MnO were added to the basin by hydrothermal solutes produced during the Bonai volcanism. BHQ/BHJ precipitation took place under a low redox potential while Mn-ore deposition is a consequence of the high redox potential.

Introduction

In the Singhbhum Craton, extensive development of Palaeoproterozoic Mn-ore deposits and Banded Iron Formation (BIF) has occurred in the Noamundi–Koira Basin (NKB), where large quantities of manganese and iron ores are mined and exported. NKB on the western margin of the 3.0–3.2 Ga old Singhbhum Granitoid Complex (SBGC) forms a NNE plunging horseshoe-shaped synclinorium overturned towards ESE (Saha, 1994). Due to the lack of reliable geochronological and geochemical data on the Mn-ore deposits and associated BIF, divergent views exist on the stratigraphic correlation, age, and tectono-sedimentary evolution of the NKB. Dunn and Dey (1942), Chakraborty and Majumdar (1986), and Saha (1994) considered that the manganese ore bodies and associated BIF of the NKB are stratigraphically equivalent to the >3.1 Ga old BIF of the Gorumahisani–Badampahar Basin. Chakraborty and Majumdar (1986) and Saha (1994) grouped both the sequences in their “Iron Ore Group” and assigned an Archaean age of sedimentation between 2900 Ma and 3200 Ma. However, Prasada Rao, Murthy, and Deekshitulu (1964), Banerji (1974, 1977) and Iyengar and Murthy (1982) are of opinion that the manganese ore deposits and associated BIF in the NKB are much younger to the BIF of Gorumahisani–Badampahar Basin. Proposed genetic models for the BIF and manganese ore deposits of NKB (Fermor, 1909; Dunn, 1935; Banerji, 1977; Chakraborty & Majumdar, 1986; Dasgupta, Sambasiva Rao, & Krishna, 1999b; Roy, 1981, 2000) have remained ambiguous perhaps due to the dual concept on the tectono-stratigraphy of the Singhbhum Craton. As such, the source(s), mechanism and environment of deposition of the manganese (and iron) deposits of NKB are still debated.

It is generally accepted that the deposition of the manganese (and iron) ore is greatly influenced by the changing ocean chemistry, sea level, and climate (Frokes & Bolton, 1984, 1992). Eh-pH-based fractionation of Mn from Fe, in sedimentary basins, has been recognized by several workers (Force & Cannon, 1988; Frokes & Bolton, 1984, 1992; Hem, 1972; Manikyamba & Naqvi, 1997). At higher Eh, stable Mn oxide ores were precipitated during the Palaeoproterozoic. Since Archaean oceans were either anoxic or intermittently and weakly oxic (Kasting, 1987; Walker, 1987; Walker et al., 1983), precipitation of stable manganese oxide ores did not occur, whereas precipitation of iron ores, which required relatively lower Eh were widespread. In Palaeoproterozoic and Phanerozoic basins, a close association between manganese (and iron) deposits and black shale has also been established (Beukes, 1983; Force & Cannon, 1988; Roy, 1992). The occurrence of thick, manganese-rich and iron-rich crusts near active spreading centers of the oceans has also...
confirmed the existence of large-scale juvenile input of manganese and iron to the oceans by sub-marine hydrothermal processes (Toth, 1980). In view of these characteristics, manganese ore deposits (and BIF) of the NKB are important in understanding the complex geological history of Singhbhum Craton. The present paper, concerns with the geochemistry and genesis of the Palaeoproterozoic manganese ore deposits occurring in the Upper Shale Formation around the Barbil area and it deciphers the source of the manganese ores and their depositional setting.

**Geological setting**

The geology of the NKB has been studied extensively by a number of workers including Percival (1931), Jones (1934), Dunn (1940), Banerji (1974, 1977), Murthy and Acharya (1975), Rai, Sarkar, and Paul (1980), Chakraborty and Majumdar (1986), Dasgupta et al. (1999a, 1999b) and Mohapatra, Mishra, and Singh (2009, 2010). NKB trends N-NE and is low plunging synclinorium with an overturned western limb (Chakraborty & Majumdar, 1986) (Figure 1).

The main fold axis has been superposed by a weak WNW-ESE trending cross fold Saha, 1994. The Bonai metavolcanic suite, exhibiting sub-aerial characters in the west (Banerjee, 1982) and submarine in the east (Bose, 1982), perhaps constitutes the basement in NKB. Moreover, the clear separation of iron and manganese into discrete ore bodies in NKB suggests the dawn of an oxidizing atmosphere near the close of Bonai volcanism. All over the world, this transformation is believed to have taken place in the Palaeoproterozoic (Condie & Sloan, 1998). Therefore, it seems reasonable to assign a Palaeoproterozoic age to the BIF and associated manganese ore deposits of the NKB instead of a Mesoproterozoic age as was proposed by Prasada Rao et al. (1964), Banerji (1974, 1977) and Iyengar and Murthy (1982).

Figure 1. Simplified geological map of Barbil, Noamundi-Koira basin.
The metasedimentary rocks of the NKB have been classified into three distinct units. All of these units have conformable contacts. Generally massive or finely laminated, thick bedded, black and dark green shales (phyllites), and tuffites comprise the Lower Shale Formation, that occurs peripheral to the basin and is poorly exposed in the eastern part of the basin, where its thickness does not exceed 30 to 50 m (Banerji, 1977). Towards the top, Lower Shale Formation gradually passes into the 400 to 600-m thick, banded hematite quartzite/jasper (BHQ/BHJ). Stromatolites and microfossils reported from the banded chert are similar to that found in the Lake Superior region (Sarkar, 1984). Chemically, these BHJ/BHQ rocks of the NKB are similar to the Lake Superior type BIF (Majumdar, Chakraborty, & Bhattacharyya, 1982).

The Upper Shale Formation, a mixed chemogenic-clastic facies represented by manganiferous shale, chert, dolomite, and tuff, occurs in the center of the basin. A number of manganese ore bodies occur in the lower part of the Upper Shale Formation in the form of layers and isolated lenses, few associated with chert and few with dolomite beds (Murthy & Ghosh, 1971). Various sedimentary structures like small-scale cross laminations, graded bedding, mud-ball, spastolites of various shapes and sizes and intraclasts have been observed in Upper Shale Formation that indicate a shallow water condition of deposition. Mineralogical and chemical characteristics of the Upper Shale Formation are distinct from typical Archaean, Proterozoic, and Phanerozoic cratonic shales, which commonly contain a considerable amount of chlorite, low Mg and Fe abundances.

The paucity of chlorite and/or abundance of kaolinite and illite in Upper Shale Formation is due to the highest degree of chemical alteration of precursor mafic source and does not indicate its evolution in a freshwater, lacustrine environment (Alvi, Raza, & Khan, 2003). Extensive lateritization of the manganese ore deposits left only a few isolated patches of the outcrops. The manganese ores are ferruginous and alter at the top of the surface into lateritic soil. The manganese ores are usually soft showing distinct lamination of varying thickness and a wide range of colors – grey, pink, brown, and yellowish white. The color bands in the manganese ores vary from few millimeters to several centimeters.

**Sampling and analytical techniques**

Thirty representative manganese ore samples were collected from Barbil, Noamundi-Koira basin, Singhbhum craton. Major elements and selected trace elements, Ni, Cr, Co, V, Cu, Pb, Zn, Sr, and Mo for 30 representative manganese ore samples were determined by a wet chemical method using atomic absorption spectrophotometer (AAS) and X-ray fluorescence technique (XRF). International rock standards IF-G, NDDA-1, NDDA-2 were used for calibrations. Precision better than ± 1% and ± 7% was obtained in major and trace element respectively with comparable accuracies. The analytical results are given in (Table 1).

**Results and discussion**

**Geochemistry**

The average major element compositions of the studied manganese ores differ from the Archaean greenstone belt-hosted Fe+Mn formations (Manikyamba & Naqvi, 1995). Studied manganese ores are characterized by widely variable but relatively higher Fe₂O₃, MnO, Co, Cu, Pb, and Sr concentrations and lower SiO₂, MgO, Na₂O, K₂O, P₂O₅, Ni, Cr, V, Zn, and Mo contents (Table 1)/(Table 2). There appear at least two major mineralogical controls on the absolute abundance of many elements. Widely variable Al₂O₃ (1.62%-17.20%) along with the low CaO (0.04%-0.28%), Na₂O (0.15%-1.05%), and K₂O (0.08%-1.00%) correspond to the observed manganese mineralogy. TiO₂, P₂O₅, Ni, and Cr correlate well with the Fe₂O₃ in these manganese ores indicating their presence in iron oxides (Figures 2 and 3).

**Genesis of manganese ore**

There are four direct sources for material incorporated into sedimentary manganese deposits: hydrothermal, hydrogenous, detrital, and diagenetic. The Si/Al ratio has been used as a simple means of discriminating hydrogenous, hydrothermal, and detrital materials and sources (Crerar, Namson, Chyi, Williams, & Feigenson, 1982) as illustrated in (Figure 4). Si/Al ratio of hydrogenous ferromanganese nodules is about 3, a value typical of marine sediment. The ferromanganese crusts, with a mean Si/Al ratio of 5.1, and iron-rich hydrothermal crusts, with extraordinarily high Si/Al ratio of 600 to 900, indicate that there is an additional source of Si in these deposits. High Si/Al ratios, of 10 to 20 are also founding some of the hydrothermal manganese-rich crusts (Toth, 1980). The Si/Al ratio in the studied manganese ore ranges between 1.90 and 3.90 suggesting that Si and Al were derived mainly from detrital-diagenetic components (Figure 4). The element Ti is essentially immobile in hydrothermal solutions and has long been recognized as an indicator of detrital sedimentation rates (Crerar et al., 1982). The fluctuation in Ti content requires that manganese ore grew faster than the associated manganiferous shale, assuming a constant rate of detrital input. Fe and Mn concentrations of the hydrothermal crusts are typically fractionated, producing Fe-rich
| Sample | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10  | 11  | 12  | 13  | 14  | 15  |
|--------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| SiO₂  | 6.50| 3.86| 10.90| 16.40| 3.60| 3.70| 3.70| 7.20| 2.60| 6.80| 5.85| 1.00| 6.62| 3.70| 3.72 |
| Al₂O₃ | 5.70| 2.85| 8.56| 17.20| 1.89| 3.43| 2.97| 3.35| 1.62| 5.35| 4.78| 2.43| 5.65| 3.65| 2.62 |
| MgO  | 0.18| 0.90| 0.82| 0.18| 0.26| 0.32| 0.26| 0.29| 0.81| 0.28| 0.43| 0.35| 0.16| 0.21|     |
| FeO   | 20.78| 10.55| 41.55| 26.21| 41.92| 16.14| 50.79| 28.28| 26.24| 15.42| 20.28| 32.12| 18.86| 39.75| 63.28 |
| MnO   | 60.29| 75.72| 31.75| 32.85| 46.69| 70.93| 36.46| 53.93| 62.18| 65.41| 62.90| 60.12| 57.30| 59.21| 70.20 |
| CaO   | 0.04| 0.28| 0.28| 0.04| 0.05| 0.06| 0.08| 0.12| 0.14| 0.05| 0.12| 0.11| 0.05| 0.12|     |
| Na₂O  | 0.47| 0.43| 0.48| 0.25| 0.57| 0.39| 0.43| 1.05| 0.49| 0.34| 0.15| 0.23| 0.41| 0.30| 0.75 |
| K₂O  | 0.51| 0.23| 0.03| 0.34| 0.19| 0.22| 0.22| 0.21| 0.56| 0.20| 0.00|     |     |     |     |
| TiO₂  | 0.18| 0.42| 0.83| 0.10| 1.22| 0.14| 0.16| 0.14| 0.15| 0.14| 0.13| 0.17| 0.14| 0.18| 0.16 |
| P₂O₅  | 0.13| 0.13| 0.43| 0.32| 0.40| 0.12| 0.43| 0.31| 0.28| 0.09| 0.11| 0.10| 0.22| 0.12| 0.11 |
| LOI   | 43.55| 41.00| 5.44| 5.18| 4.69| 4.69| 4.80| 4.10| 5.52| 4.30| 4.47| 4.44| 4.42| 4.48| 5.92 |
| Total | 98.40| 99.30| 101.19| 100.18| 100.00| 100.00| 100.01| 97.11| 98.28| 98.88| 98.93| 100.80| 98.51| 98.89| 100.00 |
| Ni    | 30   | 35   | 40   | 40   | 100  | 35   | 55   | 30   | 40   | 35   | 38   | 40   | 30   | 60   |     |
| Cr    | 175  | 50   | 75   | 38   | 25   | 125  | 50   | 13   | 13   | 50   | 100  | 187  | 75   | 125  |     |
| Co    | 110  | 115  | 265  | 330  | 183  | 150  | 120  | 154  | 193  | 95   | 195  | 151  | 195  | 148  |     |
| Cu    | 68   | 35   | 425  | 400  | 140  | 140  | 90   | 125  | 100  | 70   | 145  | 90   | 140  | 110  | 125  |
| V     | 30   | 38   | 25   | 18   | 15   | 17   | 18   | 15   | 15   | 15   | 28   | 25   | 15   | 40   | 22   |
| Pb    | 35   | 20   | 27   | 35   | 16   | 15   | 31   | 16   | 11   | 33   | 21   | 30   | 35   | 33   |     |
| Zn    | 190  | 106  | 109  | 225  | 228  | 232  | 123  | 83   | 124  | 98   | 255  | 181  | 200  | 82   | 283  |
| Sr    | 304  | 54   | 478  | 328  | 42   | 54   | 642  | 83   | 101  | 24   | 464  | 496  | 341  | 173  | 66   |
| Mo    | 5.35 | 7  | 3   | 5   | 6   | 6   | 1   | 4   | 6   | 9   | 9   | 7   | 10   | 8    |     |
| Mn    | 46.69| 8.63| 245.8| 25.44| 36.16| 54.93| 28.23| 41.68| 48.15| 50.65| 46.73| 45.33| 46.98| 35.58| 18.34 |
| Fe    | 11.73| 6.68| 29.06| 18.33| 29.32| 11.29| 35.52| 19.78| 18.35| 10.78| 14.18| 22.46| 13.12| 27.80| 44.26 |
| Mn/Fe | 3.98| 8.78| 0.85| 1.39| 1.23| 48.6| 0.79| 2.11| 2.62| 4.70| 3.30| 2.02| 3.58| 1.28| 0.41 |
| Si/Al | 1.00| 1.19| 1.12| 0.84| 1.68| 0.95| 1.10| 1.89| 1.41| 1.12| 1.08| 0.36| 0.99| 0.89| 1.25 |
| Co/Zn | 0.79| 1.08| 2.43| 1.56| 0.80| 0.65| 0.98| 1.86| 1.56| 0.97| 0.76| 0.76| 2.38|     | 0.52 |

Table 1. Representative chemical composition of manganese ores.
Depositional environment of manganese ores

Submarine hydrothermal activity may occur in a variety of tectonic settings including young (Red Sea-type) and well-established mid-ocean ridges or spreading centers; back-arc marginal basins; intra-plate hot-spots and oceanic islands; and converging plate margins, including island arcs. In order to distinguish the tectonic

Table 2. Correlation coefficient between major oxide and trace elements of Barbil, Noamundi-Koira basin manganese ores, Singhbhum Craton.

| SiO₂ | Al₂O₃ | MgO | Fe₂O₃ | MnO | CaO | Na₂O | K₂O | TiO₂ | P₂O₅ | Ni | Cr | Co | Cu | V | Pb | Zn | Sr | Mo |
|------|-------|-----|-------|-----|-----|------|-----|------|------|----|----|----|----|---|----|----|----|----|
| 1.00 |       |     |       |     |     |      |     |      |      |    |    |    |    |   |    |    |    |    |
| 0.91 | 1.00  |     |       |     |     |      |     |      |      |    |    |    |    |   |    |    |    |    |
| 0.07 | 0.03  | 1.00|       |     |     |      |     |      |      |    |    |    |    |   |    |    |    |    |
| 0.68 | 0.76  | 0.28| 0.16  | 0.33| 0.30| 0.35 | 0.02| 1.00 |      |    |    |    |    |   |    |    |    |    |
| 0.32 | 0.26  | 0.01| 0.24  | 0.70| 0.00| 0.34 | 0.16| 0.33 | 1.00 |    |    |    |    |   |    |    |    |    |
| 0.07 | 0.07  | 0.06| 0.01  | 0.13| 0.10| 0.23 | 0.17| 0.19 | 0.06| 1.00|    |    |    |   |    |    |    |    |
| 0.52 | 0.63  | 0.16| 0.11  | 0.50| 0.08| 0.07 | 0.14| 0.62 | 0.42| 0.14| 0.19| 1.00|   |    |    |    |    |
| 0.53 | 0.51  | 0.15| 0.02  | 0.14| 0.21| 0.03 | 0.20| 0.30 | 0.24| 0.20| 0.08| 0.41| 1.00|   |    |    |    |
| 0.17 | 0.09  | 0.15| 0.01  | 0.09| 0.06| 0.26 | 0.09| 0.17 | 0.22| 0.15| 0.09| 0.04| 0.34| 1.00|   |    |    |
| 0.24 | 0.13  | 0.13| 0.04  | 0.06| 0.02| 0.05 | 0.34 | 0.13 | 0.08| 0.19| 0.35| 0.08| 0.31| 0.06| 1.00|   |    |
| 0.01 | 0.06  | 0.36| 0.05  | 0.05| 0.24| 0.33 | 0.02 | 0.24 | 0.16| 0.62| 0.20| 0.05| 0.10| 0.05| 0.22| 1.00|   |
| 0.16 | 0.26  | 0.06| 0.12  | 0.33| 0.02| 0.29 | 0.49 | 0.22 | 0.29| 0.21| 0.37| 0.28| 0.23| 0.03| 0.35| 0.19| 1.00|
| 0.29 | 0.19  | 0.06| 0.02  | 0.29| 0.09| 0.01 | 0.26 | 0.18 | 0.43| 0.08| 0.47| 0.10| 0.36| 0.42| 0.09| 0.21| 0.23| 1.00|
| **0.19** | 0.12 | 0.21 | 0.16 | 0.35 | 0.08 | 0.31 | 0.05 | 1.00 |   |    |    |    |    |    |    |    |    |    |    |

Figure 2. Relationship of Fe₂O₃ with P₂O₅ in Barbil, Noamundi-Koira basin, Singhbhum Craton.

Figure 3. Relationship of Fe₂O₃ with Ni in Barbil, Noamundi-Koira basin, Singhbhum Craton.

(Fe/Mn >10) or Mn rich (Fe/Mn < 0.1) deposits. In contrast, the Fe/Mn ratio of hydrogenous ferromanganese sediments such as deep-sea manganese nodules averages about unity. Hydrothermal deposits generally contain trace element concentrations (Ni, Co, Cu, Zn, Pb, etc.) well in excess of normal pelagic sediments but in order of magnitude lower than hydrogenous ferromanganese deposits, which are extraordinarily powerful scavengers. These relationships are illustrated in (Figure 5), after Toth (1980). Mn-Fe(Co+Ni+Cu)⁴⁰ diagram (Figure 5) demonstrates that Fe, Mn, and trace element enrichment in the studied manganese ores is similar to those found in hydrothermal deposits.

Co shows little change in concentration and maybe predominantly hydrogenous throughout. Co/Zn ratio is a sensitive indicator of hydrothermal versus an authigenic source of trace elements (Toth, 1980). In general, Co/Zn ratio in hydrothermal crust (both Fe-rich and Mn-rich) is very low averaging at about 0.15 while those of ferromanganese crust and manganese nodules average at 2.5 (Toth, 1980). In the studied manganese ores Co/Zn ratio varies in between 0.28 and 2.43 and averages at 0.75 (Table 1) and shows a weak sympathetic correlation with (Co+Ni+Cu), thus negating a hydrothermal source for their trace element abundance. The low concentrations of the trace elements may be due to the rapid deposition.

The various ternary diagram shows hydrothermal origin. The Fe-Si₂-Mn ternary diagram by Toth (1980) confirmed the hydrothermal diagenetic origin of manganese deposit of the study area (Figure 6). Co, Cu, V, Ni, Zn, and Ba are important trace elements to explain the genesis of manganese ores. On the plotting of discrimination diagram Cu+Ni vs Cu+Pb+V+Zn (Figure 7) (After Nicholson, 1992), all the manganese ore samples are showing hydrothermal origin. The binary plot Co/Zn vs Co+Ni+Cu (After Toth, 1980) also confirmed hydrothermal origin (Figure 8) for the manganese of the study area.

Depositional environment of manganese ores
setting of the depositional site of the studied manganese ore deposits, it seems appropriate to have a critical look at the geological setting of NKB. Recently, it has been suggested on the basis of mineralogical studies that manganese ores and associated argillaceous sediments in NKB accumulated mainly in a freshwater milieu (Dasgupta, Sambasiva Rao, & Krishna, 1999b; Sambasiva Rao & Dasgupta, 1995, 1997). However, this observation does not appear in accordance with the geological scenario. The ternary plot of CaO-Na$_2$O-MgO (after Dasgupta et al., 1999b) distinguishes marine field for the manganese ore samples (Figure 9). In this plot, most of the samples of the study area lie in

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**Figure 4.** Plots of Barbil, Noamundi-Koira basin manganese ore samples at the Si versus Al graph after Crerar et al. (1982).

**Figure 5.** Mn-Fe-(Ni + Co + Cu) X10 ternary discrimination diagram (After Bonatti, Kraemer, & Rydell, 1972; Crerar et al., 1982) for hydrothermal manganese deposits of Barbil, Noamundi-Koira basin, Singhbhum Craton.

**Figure 6.** Plot of Fe-Si$^2$-Mn ternary diagram (After Toth, 1980), showing the manganese ore samples are connected near the hydrothermal field.
the marine field. The lithologic set up of the NKB suggests that Bonai volcanism might have played a dominant role during the precipitation and deposition of the BIF and manganese ores as the Bonai volcanic suite that forms the basement of NKB has a calc-alkaline affinity (Sengupta et al., 1991).

The interaction between seawater and sub-marine basalt leaches Fe, Mn and probably other elements under reducing conditions within the rock mass (Seyfried & Bischoff, 1977, 1981). Further volatile components (HF, H₂S, CH₄, CO₂ etc.) might be added from the volcanic source. All the three stratigraphic units of the NKB, namely Lower Shale Formation, BIF, and Upper Shale Formation have conformable relations with each other. BIF deposition of the basin has been classified as Lake Superior type (Chakraborty & Majumdar, 1986). The shallow marine depositional features recorded in BIF (Ghosh, 1993; Rai et al., 1980) are corroborated by the presence of algal stromatolites (Avasti, 1980; Raha & Moitra, 1992) and both spheroidal and filamentous microfossils (Sarkar, 1984). Grant, Murthy, and Sengupta (1980) have also documented stromatolites from chert and dolomite of the Upper Shale Formation hosting manganese ore bodies. The manganiferous chemical characteristics of the Upper Shale Formation are not comparable with Archaean and Proterozoic cratonic shale compositions. The kaolinite dominated mineralogy and high CIA values (81–97) of the Upper shale indicate a high intensity of chemical weathering in the source region along with precursor sediments derived from the Bonai Volcanic Suite, OMTG, and the para and ortho-amphibolites of Older Metamorphic Group were
deposited in a convergent margin setting (Alvi et al., 2003). Jagannathpur volcanic suite that occurs as faulted outliers within the NKB (Banerjee, 1982) has also been considered as a subduction-related suite (Alvi & Raza, 1991, 2004). Volcanic arc affinity of the Singhbhum Granite Complex that forms the basement and/or intrudes the BIF is also well documented (Saha, 1994).

Hem (1972) has suggested that Eh-pH conditions within the depositional basins control the precipitation of manganese and its fractionation with iron. During the process of deposition at lower Eh, iron solubility is extremely low and therefore iron precipitates first as iron sulphide. At the same time, manganese solubility is high and there is no comparably insoluble manganese sulphide, hence it remains in the solution. Changes of pH and $P_{CO_2}$ are the other influences on iron and manganese solubility Subsequent increase in Eh and/or pH within the basin could produce a manganese-rich and iron-depleted rock. The sols and gels being negatively charged could readily adsorb cations and form different phases like cryptomelane and pisolomelane.

**Conclusions**

The stratigraphic setup of NKB is very different from the Gorumahisani–Badampahar Basin situated in the eastern part of the Singhbhum craton as the later is devoid of Mn-ore deposits. Hence, it is suggested that the stratigraphy of the Singhbhum region should be re-examined considering the modern marker horizons. The studied Mn-ore deposits of NKB are characterized by low Fe/Mn ratios and low trace element concentrations and are similar to those of the present day submarine hydrothermal deposits. The low concentrations of Co, Ni, Cr, Cu, and Pb suggest rapid deposition. The compositional variations in these Mn-ore deposits suggest that they formed by precipitation from submarine hydrothermal solutions with little hydrogenic effects during the Paleoproterozoic era. Geochemical data of manganese ore deposits occurring in the Upper Shale Formation indicate two major mineralogical controls, kaolinite-magnetite, hematite, and ilmenite. The deposition of Mn ores perhaps took place in a mature arc/continental margin setting. Calc alkaline affinity of Bonai Volcanic Suite (Banerjee, 1982), Bonai Granite (Sengupta et al., 1991) and volcanic arc affinity of the Singhbhum Granite that forms the basement and/or intrudes the BIF (Saha, 1994) also support this observation.

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**Disclosure statement**

No potential conflict of interest was reported by the authors.

**References**

Alvi, S. H., & Raza, M. (1991). Nature and magma type of Jagannathpur volcanics, Singhbhum, Eastern India. *Journal Geological Society of India*, 38, 524–531.

Alvi, S. H., & Raza, M. (2004). Geochemistry and tectonic significance of high-Mg andesite, Jagannathpur volcanic suite, Singhbhum craton, Eastern India. *Journal of Applied Geochemistry*, 6(1), 15–24.

Alvi, S. H., Raza, M., & Khan, A. (2003). Geochemistry and tectonic significance of upper shale around Barbil, Singhbhum Craton, Eastern India. *Journal of Applied Geochemistry*, 5, 59–68.

Avasti, P. K. (1980). Stromatolites from iron ore formation of Bonai- Keonjhar district, Orissa, India. *Miscellaneous Publication, Geological Survey of India*, 44, 54–56.

Banerjee, P. K. (1982). Stratigraphy, petrology and geochemistry of some precambrian basic volcanic and associated rocks of Singhbhum district of Bihar and Mayurbhanj and Keonjhar districts, Orissa. *Memoir Geological Survey of India*, 111, 58.

Banerji, A. K. (1974). On the stratigraphy and tectonic history of the iron ore bearing and associated rocks of Singhbhum and adjoining areas of Bihar and Orissa. *Journal Geological Society of India*, 15, 150–157.

Banerji, A. K. (1977). On the precambrian banded iron-formations and the manganese ores of the Singhbhum region, eastern India. *Economic Geology*, 72, 90–98.

Beukes, N. J. (1983). Palaeoenvironmental setting of iron formations in the depositional basin of the transvaal supergroup, South Africa. In A. F. Trendall & R. C. Morris (Eds.), *Iron formations: Facts and problems* (pp. 139–209). Amsterdam: Elsevier.

Bonatti, E., Kraemer, T., & Rydell, H. (1972). Classification and genesis of submarine iron-manganese deposits. In D. R. Horn (Ed.), *Ferromanganese deposits on the Ocean floor* (pp. 149–166). Washington: National Science Foundation.

Bose, M. K. (1982). Precambrian picritic pillow lavas from Nomira, Koenjhar, Eastern India. *Current Science*, 51, 677–684.

Chakraborty, K. L., & Majumdar, T. (1986). Geological aspects of the banded iron formation of Bihar and Orissa. *Journal Geological Society of India*, 28, 109–133.

Condie, K. C., & Sloan, R. E. (1998). *Origin and evolution of Earth* (pp. 497). Printice-Hall.

Crerar, D. A., Namson, J., Chyi, M. S., Williams, L., & Feigenson, M. D. (1982). Manganiferous cherts of the franciscan assemblage: I. general geology, ancient and modern analogues, and implications for hydrothermal convection at oceanic spreading centers. *Economic Geology*, 77, 519–540.

Dasgupta, H. C., Sambasiva Rao, V. V., & Krishna, C. (1999a). Chemical environments of deposition of ancient iron- and manganese-rich sediments and cherts. *Sedimentary Geology*, 125, 83–98.

Dasgupta, H. C., Sambasiva Rao, V. V., & Krishna, C. (1999b). Geology, geochemistry and genesis of the fresh-water precambrian manganese deposits of the iron ore group from Noamundi basin, Eastern India. *Indian Journal of Geology*, 71, 247–264.
Dunn, J. A. (1935). The origin of iron ores in Singhbhum, India. Economic Geology, 30, 643–654.

Dunn, J. A. (1940). Stratigraphy of south Singhbhum. Memoir, Geological Survey of India, 63, 303–369.

Dunn, J. A., & Dey, A. K. (1942). Geology and petrology of eastern Singhbhum and surrounding areas. Memoir, Geological Survey of India, 69(2), 281–456.

Fermor, L. L. (1909). The manganese ore deposits of India. Memoirs of the Geological Survey of India, 37.

Force, E. R., & Cannon, W. F. (1988). Depositional model for shallow-marine manganese deposits around black shale basins. Economic Geology, 83, 93–117.

Frakes, L. A., & Bolton, B. R. (1984). Origin of manganese giants: Sea-level change and anoxic-oxic history. Geology, 12, 83–86.

Frakes, L. A., & Bolton, B. R. (1992). Effects of ocean chemistry, sea level, and climate on the formation of primary sedimentary manganese ore deposits. Economic Geology, 87, 1207–1217.

Ghosh, K. P. (1993). Genesis of the banded iron formation in Jamda-Koira valley—a tentative depositional model. Indian Journal of Earth Science, 20(3–4), 163–172.

Grant, P. R., Murthy, V. N., & Sengupta, S. (1987). The first record of stromatolites from the Koira group (iron ore series), precambrian of Bihar Orissa, India. Miscellaneous Publication, Geological Survey of India, 44, 49–53.

Hem, J. D. (1972). Chemical factors that influence the availability of iron and manganese in aqueous systems. Geological Society of America Bulletin, 83, 443–450.

Iyengar, S. V. P., & Murthy, Y. G. K. (1982). The evolution of archaean-proterozoic crust in parts of Bihar and Orissa, Eastern India. Record, Geological Survey of India, 112(3), 1–5.

Jones, H. C. (1994). The iron ore deposits of Bihar and Orissa. Geological survey of India. Memoir, 63(2), 167–302.

Kasting, J. F. (1987). Theoretical constraints on oxygen and carbon dioxide concentrations in the precambrian atmosphere. Precambrian Research, 34, 205–229.

Majumdar, T., Chakraborty, K. L., & Bhattacharyya, A. (1982). Geochemistry of banded iron formation of Orissa, India. Mineralium Deposita, 17, 107–118.

Manikyamba, C., & Naqvi, S. M. (1995). Geochemistry of Fe-Mn formations of the archaean sandur schist belt, India - mixing of clastic and chemical processes at a shallow shelf. Precambrian Research, 72, 69–95.

Manikyamba, C., & Naqvi, S. M. (1997). Mineralogy and geochemistry of archaean greenstone belt-hosted Mn formations and deposits of Dharwar craton: Redox potential of proto-oceans. Manganese Mineralization: Geochemistry and Mineralogy of Terrestrial and Marine Deposits, 119, 91-103.

Mohapatra, B. K., Mishra, P. P., & Singh, P. P. (2009). Manganese ore deposits in Koira-Noamundi province of iron ore group, north Orissa, India: In the light of geochemical signature. Chemie Der Erde-Geochemistry, 69, 377–394.

Mohapatra, B. K., Singh, S. K., Rao, D. S., Martha, R. K., & Mishra, S. (2010). Characterisation of bog manganese ore associated with bif in iron ore group, north Orissa for its optimum utilization. International seminar on mineral processing MPT-2010, Jamshedpur, pp. 31–38.

Murthy, V. N., & Acharya, S. (1973). Lithostratigraphy of the precambrian rocks around Koira, Sundergarh district, Orissa. Journal Geological Society of India, 16, 55–68.

Murthy, V. N., & Ghosh, B. K. (1971). Manganese ore deposit of Bonai–Koijnhar belt, Orissa. Indian Minerals, 25, 201–210.

Nicholson, K. (1992). Contrasting mineralogical-geochemical signatures of manganese oxides: Guides to metallogenesis. Economic Geology, 87(5), 1253–1264.

Percival, F. G. (1931). The iron ores of Noamundi. Mineral Geology Institute, India. Transactions, 26, 256–261.

Prasada Rao, G. H. S. V., Murthy, Y. G. K., & Deekshitulu, M. N. (1964). Stratigraphic relations of precambrian iron formation and associated sedimentary sequences in parts of Koenjhar, Cuttack, Dhenkanal and Sundergarh districts, Orissa, India. Proceedings, 22nd international geological congress, New Delhi, Section 10, 72–87.

Raha, P. K., & Moitra, A. K. (1992). The first record of stromatolites in banded hematite quartzites (sensu strictu) in the iron ore group of Keonjhar District, Orissa, India—a significant step towards understanding of the depositional environment of the iron ores. 29th International geological congress, Kyoto, Japan, abstract 1–347, 12. 6544.

Rai, K. L., Sarkar, S. N., & Paul, P. R. (1980). Primary depositional and diagenetic features in banded iron formation and associated iron deposits of Noamundi, Singhbhum district, Bihar, India. Mineralium Deposita, 19, 189–200.

Roy, S. (1981). Manganese deposits (pp. 458). London: Academic Press.

Roy, S. (1992). Environments and processes of manganese deposition. Economic Geology, 87, 1218–1236.

Roy, S. (2000). Late archaean initiation of manganese metallogenesis: Its significance and environmental controls. Ore Geology Reviews, 17, 179–198.

Saha, A. K. (1994). Crustal evolution of Singhbhum-north Orissa, eastern India. Memoir Geological Society of India, 27, 341.

Sambasiva Rao, V. V., & Dasgupta, H. C. (1995). Clay mineralogy of the argillites associated with banded iron formations from the Noamundi basin, Eastern India—a clue to its chemical environment of deposition. Indian Minerals, 49(1–2), 31–44.

Sambasiva Rao, V. V., & Dasgupta, H. C. (1997). Clay mineralogy and argillites of the precambrian iron ore group, Naomundi basin, eastern India. Journal Geological Society of India, 49, 179–192.

Sarkar, B. (1984). Microfossils bin the banded iron formation from the Noamundi basin, Eastern India. Quarterly Journal of the Geological, Mining and Metallurgical Society of India, 56, 41–46.

Sengupta, S., Paul, D. K., DeLeter, J. R., McNaughton, N. J., Bandhopadhyay, P. K., & De Smeth, J. B. (1991). Mid-archaean evolution of the eastern Indian craton: Geochemical and isotopic evidence from the Bonai Pluton. Precambrian Research, 49, 23–37.

Seyfried, W. E., & Bischoff, J. L. (1977). Hydrothermal transport of heavy metals by seawater: The role of seawater/basalt ratio. Earth and Planetary Science Letters, 34(1), 71–77.

Seyfried, W. E., & Bischoff, J. L. (1981). Experimental seawater-basalt interaction at 300°C, 500 bars, chemical exchange, secondary mineral formation and implications for the transport of heavy metals. Geochemica et cosmochimica acta, 45(2), 135–147.

Toth, R. J. (1980). Deposition of submarine crusts rich in manganese and iron. Geological Society of America Bulletin, 91, 44–54.

Walker, J. C. G. (1987). Was the archaean biosphere upside down? Nature, 329, 710–712.

Walker, J. C. G., Klein, C., Schidlowski, K., Schopf, J. W., Stevenson, D. J., & Walter, M. R. (1983). Environmental evolution of the archaean-early proterozoic Earth. In J. W. Schopf (Ed.), Earth earliest biosphere:its origin and evolution (pp. 260–290). Princeton, New Jersey: Princeton University Press.