Ore Geology Reviews 78 (2016) 361–370

Contents lists available at ScienceDirect

Ore Geology Reviews

journal homepage: www.elsevier.com/locate/oregeorev

Reworked manganese ore bodies in Bonai-Keonjhar belt, Singhbhum Craton, India: Petrology and genetic study

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ARTICLE INFO

Article history:
Received 5 November 2014
Received in revised form 21 April 2016
Accepted 22 April 2016
Available online 23 April 2016

Keywords:
Manganese ore
Wad
Mangcrete
BIF
Bonai-Keonjhar belt, Odisha
IOG rocks

ABSTRACT

The genetic evolution of three types of reworked manganese ore bodies namely: Detrital, Concretionary (Mangcrete) and Wad in the Precambrian Iron Ore Group occurring in Bonai-Keonjahr belt, Singhbhum Craton, India are reported. All the reworked Mn-ore bodies are developed in a restricted area and have a limited resource. Mangcrete and wad are commonly exposed at the surface and extend to a maximum depth of 10 m while detrital ores are observed below 10–20 m from the surface.

Detrital ore bodies occur as large boulders and are buried under a thick zone of laterite. Mangcrete is concretionary in nature; oolitic, spherulitic and nodular in shape. Broken fragmented of ooloids and pisoloids, often observed in mangcrete, are indications of reworking. Wad exposures are noticed above low to medium-grade bedded manganese ore bodies. Among three reworked ore types, the detrital is of low to medium-grade having Mn:Fe ratio > 5, while wad and mangcrete are of sub-grade (Mn:Fe ~ 1) and off-grade type (Mn:Fe < 1) respectively.

Detrital ore bodies are of allochthonous nature and developed through several stages such as fragmentation of pre-existing ore, leaching and cementation followed by transportation and deep burial. Mangcrete represent chemogenic precipitates at several stages of contemporary Mn-Fe-Al rich fluid under supergene environment. Wad is of bio-chemogenic origin and developed in a swampy region under marine environment due to slow chemical precipitation of Mn-Fe enriched fluid, in several stages nucleating quartz/hematite/cryptomelane detritals.

1. Introduction

In Odisha, manganese ore is found to occur in three stratigraphic horizons and spatially distributed wide apart i.e. Iron Ore Group in Bonai-Keonjhar belt, Gangpur Group in Sundergarh and Eastern Ghats Group in Rayagada-Kalahandi-Balangir belt. Over 90 Mt of manganese ores are reported to occur in Bonai-Keonjhar belt. Compared to the size of the belt, the available literature seems to be limited. Broad geology and geo-economic aspects of this region have been dealt by Former (1909); Spencer (1948); Sen (1951); Ray (1954, 1955); Engineer (1956) and Prasad Rao and Murty (1956). Mookherjee (1966); Basu (1969); Murty and Ghosh (1971); Mishra (1994); Mohapatra et al. (1989, 2009, 2010) and Dasgupta et al. (1999) discussed on the classification, mode of occurrence and genetic aspects of some of the manganese ore deposits of this region. Mineralogical and geochemical studies though reported by Roy (1981), Mohapatra and Bagchi (1961) and Ajmal (1990), are of local significance. Mishra et al. (2006) have classified manganese ore bodies of this region into three broad categories: viz. stratiform, stratabound-replacement and lateritoid types [Mishra et al., 2006 has classified Mn-ore as lateritoid type, not as lateritic type, as suggested by reviewer].

This paper reports another category of ore bodies from the area namely "Reworked Manganese Deposit (RMD)", and discusses on their petrology and genetic evolution. One category of RMD (detrital type) reported in this paper is similar as that of the lateritoid type described by Mishra et al. (2006).

2. Materials and methods

Reworked manganese ore samples were collected from different Mn-ore mines (Detrital type – Belkundi, Mangcrete type – Dalki and Wad – Dubna) located in the Bonai-Keonjhar belt, Odisha, eastern India (Fig. 1). The mineralogical and microstructural studies of these ore samples were carried out using optical, scanning electron microscopy and XRD techniques. Polished sections were made by conventional methods using araldite as mounting adhesive followed by polishing with diamond paste. For SEM study samples were first coated with ultra-thin film of gold by an ion sputter (JFC-1100) and then exposed to electron microscope (JEOL, JSM-35CF, Japan). For this purpose the working height was kept at 15 mm with working voltage ranging between 10 kV to 25 kV. X-ray

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http://dx.doi.org/10.1016/j.oregeorev.2016.04.021
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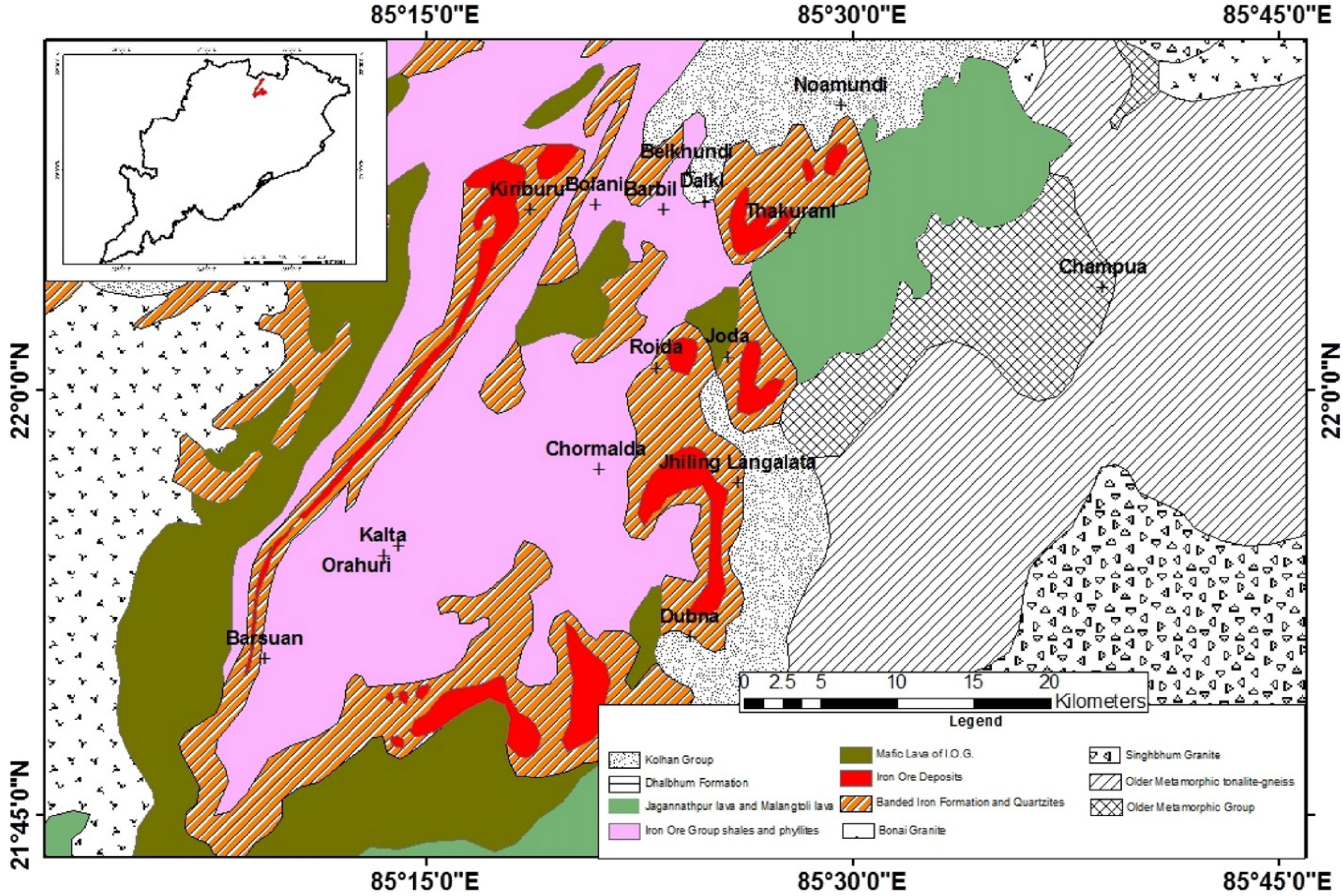

Fig. 1. Location map of the study area.

diffraction technique was used to identify the major mineral phases in each of the three categories of reworked Mn-ores using Philips X-ray Diffractometer (PW-1710,) where Cu K_{α} radiation operating at 40 kV and 20 nA was employed. Major and minor elements in all the ore samples were determined by Philips XRF (PW-1400) using pressed powder pellets.

3. Nature and occurrence of RMD

In general the manganese-ore bodies in the Bonai-Keonjhar belt belong to Precambrian Iron Ore Group of Meso-archean age and are found to be associated with volcano-sedimentary rocks and iron ore. The volcano-sedimentary rocks are comprised mostly of volcanic tuff/volcanic agglomerates and Mn (± Fe) ore bodies. All these have undergone low-grade metamorphism and poly-phase folding resulting in a NNE plunging synclinorium (Jones, 1934) overturned towards south (Sarkar and Saha, 1962). The stratiform type Mn-ore bodies are tabular and show banding, while stratabound ores occur as linear ore bodies and appear botryoidal/nodular. On the basis of field distribution and ore petrology, RMDs (Reworked Manganese Deposits) are grouped in to three categories, viz. Detrital (Reworked-I), Mangcrete (Reworked-II) and Wad (Reworked-III). Generally, each ore body is more or less tabular and is capped by laterite of variable thickness.

Detrital manganese deposits (Reworked-I) have limited depth continuation and are of low-grade types. Field, ore petrology and other geochemical characteristics of a typical detrital deposit for example, Belkundi in the eastern limb of a horse-shoe shaped belt, (Fig. 1) is described in this paper. Mohapatra et al. (2002) have reported similar type of deposits from Orahari on the western limb of the belt, NW of Koira town. Such type of ore deposits occur below a thick lateritic zone (Fig. 2A) and different stages of lateritization are clearly discernible. The ore bodies are usually bouldery in nature and large boulders are seen below 10–20 m depth (Fig. 2B). Small boulders are sometimes welded to form a large one. Occasionally, boulders appear sub-rounded to ovoidal.

Mangcrete deposits (Reworked-II) are located in Dalki, Roida and Chormalda areas of Bonai-Keonjhar belt. However, for the present study mangcrete samples were collected from Dalki mine (Fig. 2C). In the Dalki mine, 2–10 m thick laterite exposures are seen where mangcrete pieces are present in various sizes (Fig. 2D). Small pebbles often show onion like structure. The closer cross sections of some of these concretions show concentric rings. A few pebbles get dislodged from the base and accumulate at the foot hills.

Wad deposits (Reworked-III), occur over low to medium-grade massive/bedded manganese ore bodies of Dubna mine (Fig. 2E). The dimensions of such wad outcrops are 500 m × 100 m with a maximum thickness of about 10 m. These outcrops fan outward, generally thicken down slope and terminate abruptly. The ore bodies are capped by 1–2 m lateritic zone. Volcanic tuff layers/tephra are often observed within the deposit. The tephra appears white, grey and red in colour. Segregation of detritus aggregates are found below 5–6 m depth from the surface (Fig. 2F).

4. Ore petrography

4.1. Detrital (Reworked-I)

In this category of ore deposits, large boulders are found buried under thick lateritic cover. Due to leaching, precipitation followed by

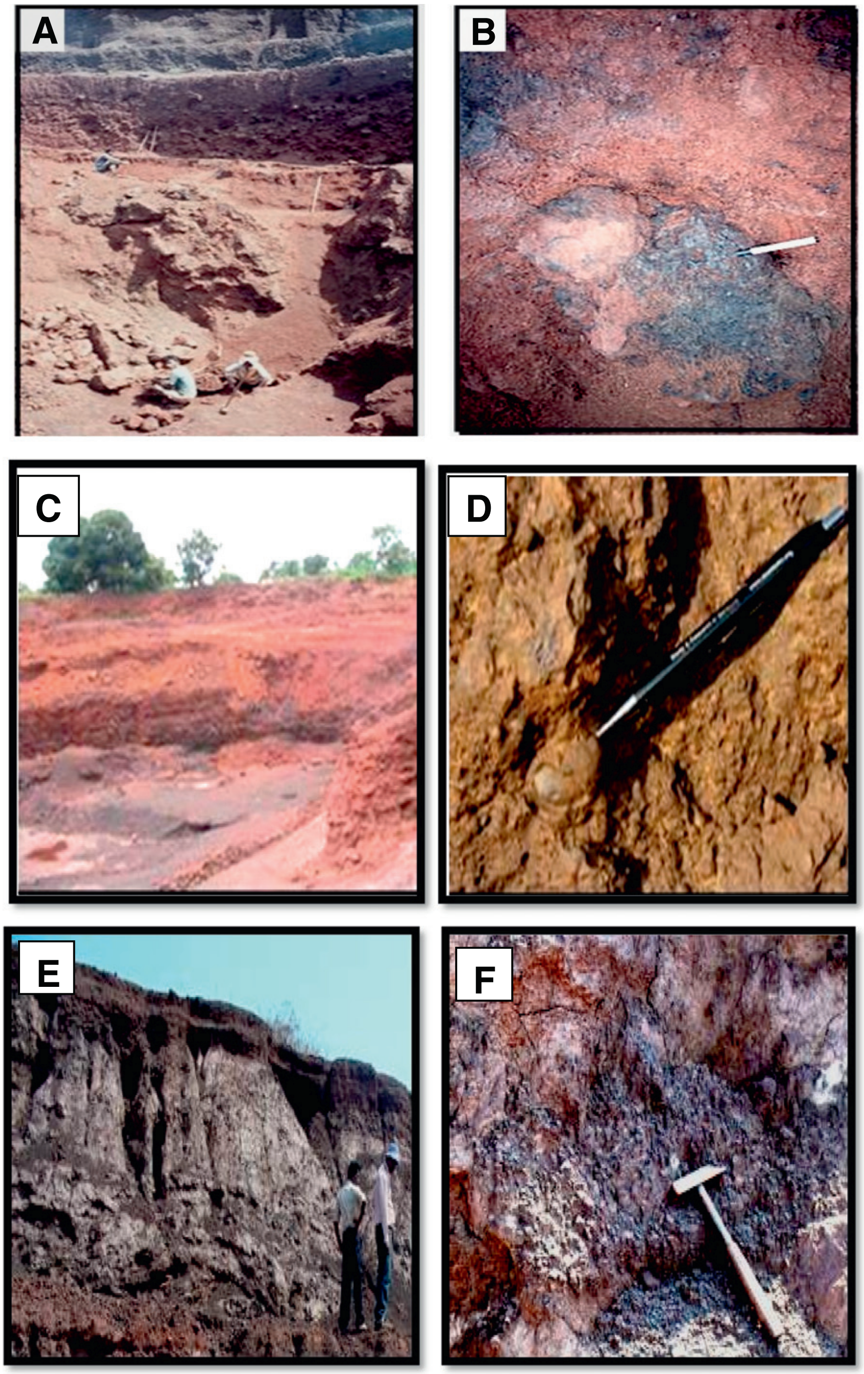

Fig. 2. Mode of occurrence of different types of reworked Mn-ore. A & B: Detrital type, C & D: Mangcrete E& F: Wad. A: Panoramic view of mine showing deep lateritization and bouldery nature of Mn-ore body. B: An enlarged view of an ovoidal boulder at 20 mt depth. C: Occurrence of mangcrete in laterite crust in Dalki Quarry. D: Closer view of a nodular mangcrete. E: Overview of wad outcrop in Dubna. F: Occurrence of detritus aggregates within wad below 3–4 m depth.

lateritization these ores show variation in their morphological and microstructural attributes. While some boulders appear hard and massive due to fragmentation and recementation (Fig. 3A & B), others appear spongy indicating intensive leaching (Fig. 3C & D). Though these morphological types exhibit similar mineralogy, minor variations are observed.

Different minerals recorded in such ore category are cryptomelane, manganite, pyrolusite, lithiophorite, hematite and goethite. In some massive types, isolated grains of martite and cryptomelane are seen enclosed within clay matrices (Fig. 4A). Though cryptomelane occurs as major secondary infillings, it is often oxidized to radiating or mosaic or fan shaped pyrolusite. Manganite fills the inter-granular space of hematite clasts (Fig. 4B). Lithiophorite crystallites grow in the cavities due to precipitation from secondary manganese solution.

Manganese impregnation and cementation occur as colloform, concentric and very fine grained masses while secondary Fe-infillings often grow as tiny specularite (Fig. 4C). The spongy type comprises of pyrolusite, lithiophorite, quartz and kaolinite as the major minerals. The lithiophorite occurs as mosaic grains lining vugs (Fig. 4D).

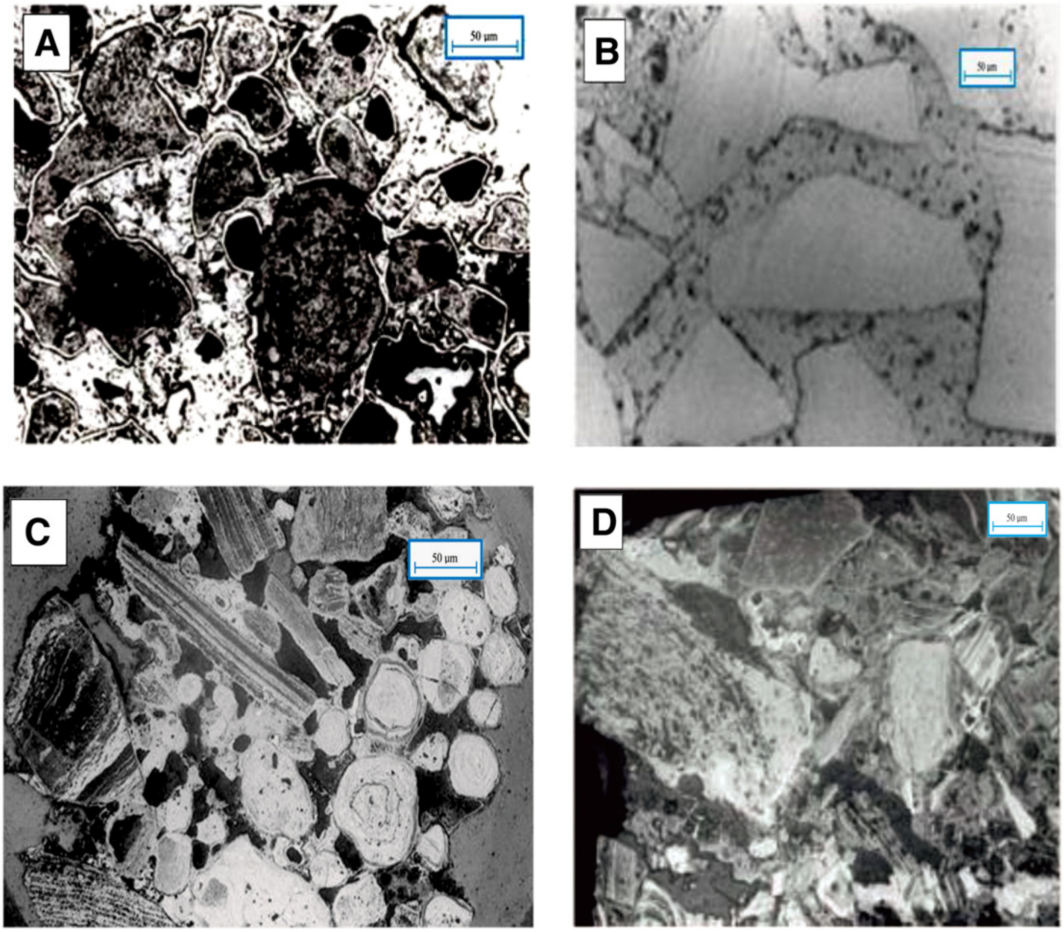

Fig. 3. General microstructure of detrital ore [Point 4. of reviewer's comment complied: recemented changed with detrital and scale bars in figures inserted]. A & B — massive ore C & D — spongy ore. A: A cluster of Mn-ooliths in different shapes and dimension. B: Cryptomelane fragments recemented together by secondary Mn-phase (cryptomenale). C: Primary iron clasts and Mn-pisoliths, in different dimensions and shapes, enclosed by secondary manganese rich phase. D: Primary iron clasts, in different dimensions, enclosed by secondary manganese rich phase.

4.2. Mangcrete (Reworked-II)

Mangcrete occurs as oolitic, pisolitic and nodular pebbles. Some of these ooliths and pisoliths are flattened, round to oval shaped and partially filled by accretionary grains (Fig. 5A). Ooliths are relatively smaller in size (<2 mm) and composed either of cryptomelane or goethite. Mn-ooliths, in varied shape and sizes, occur in clusters and exhibit mamillary texture (Fig. 5B). The pisoliths are relatively larger in size (>2 mm), concentrically banded and show transverse/radial cracks (Fig. 5C).

The pisoliths are found to contain romanechite, cryptomelane and ilmenite grains in the core region with cryptomelane encrustation (Fig. 5D). Two pisoliths are sometimes found welded together forming an eye shaped structure and are further enclosed by cryptomelane of later generation. Manganese ooliths and pisoliths are occasionally traversed by manganese veins of younger generation.

The XRD pattern of mangcrete shows iron (hematite & goethite), manganese (cryptomelane & pyrolusite) and silica (quartz) as major phases. Absence of any X-ray reflection peaks diagnostic of Al-mineral indicates its amorphous state. The close association of cryptomelane and clay (Fig. 6A); cryptomelane and quartz (Fig. 6B) are commonly observed. Mangcrete is almost devoid of any euhedral mineral grains. Pyrolusite, romanechite (Fig. 6C), hematite and ilmenite (Fig. 6D) appear as isolated ill developed grains.

4.3. Wad (Reworked-III)

The major phases of wad are δ-MnO_2 and intricately mixed Mn-Fe. Other subordinate minerals are manganite, romanechite, pyrolusite and lithiophorite along with minor hematite, quartz and kaolinite. Wad is composed of oolitic, pisolitic, sub-rounded, globular, ellipsoidal (Fig. 7) grains nucleating small detritus of quartz, cryptomelane and hematite (Fig. 7A & B). Globular grains are found to be ubiquitous (Fig. 7C). Cross section of a typical wad grain under SEM distinctly shows small detrital grains in its core region (Fig. 7D). The thickness of crust varies and sometimes appear >50 μ. Cryptocrystalline Mn-phase is seen encrusted by mixed limonite-clay phase (Fig. 7B). Mixed limonite-clay and cryptomelane-limonite are commonly observed. Occasionally, manganite, pyrolusite, hematite and romanechite detritus are seen accumulated at the bottom of a wad deposit.

Mineralogical variations between different categories of reworked Mn-ores are given in Table 1.

5. Geochemistry

Remarkable difference in chemical composition is recorded amongst different varieties of reworked manganese ores (Table 2). The detrital type manganese ore is generally of low to medium-grade. The Mn-content varies between different morphological types and also from boulder to boulder within wide limits and so does Fe, Al_2O_3 and SiO_2 content. The mangcretes are usually of marginal-grade (avg, Mn: 16%) and contain appreciable quantities of iron and alumina. The major constituents of wad are iron and manganese. It is composed of around 72% of combined manganese plus iron; 8% of combined alumina plus silica and 20% of water, hence grouped under sub-grade type. The Mn:Fe ratio in the above three categories of manganese ores exhibit wide variation. The detrital types have Mn:Fe ratio of 5 while the value reduces

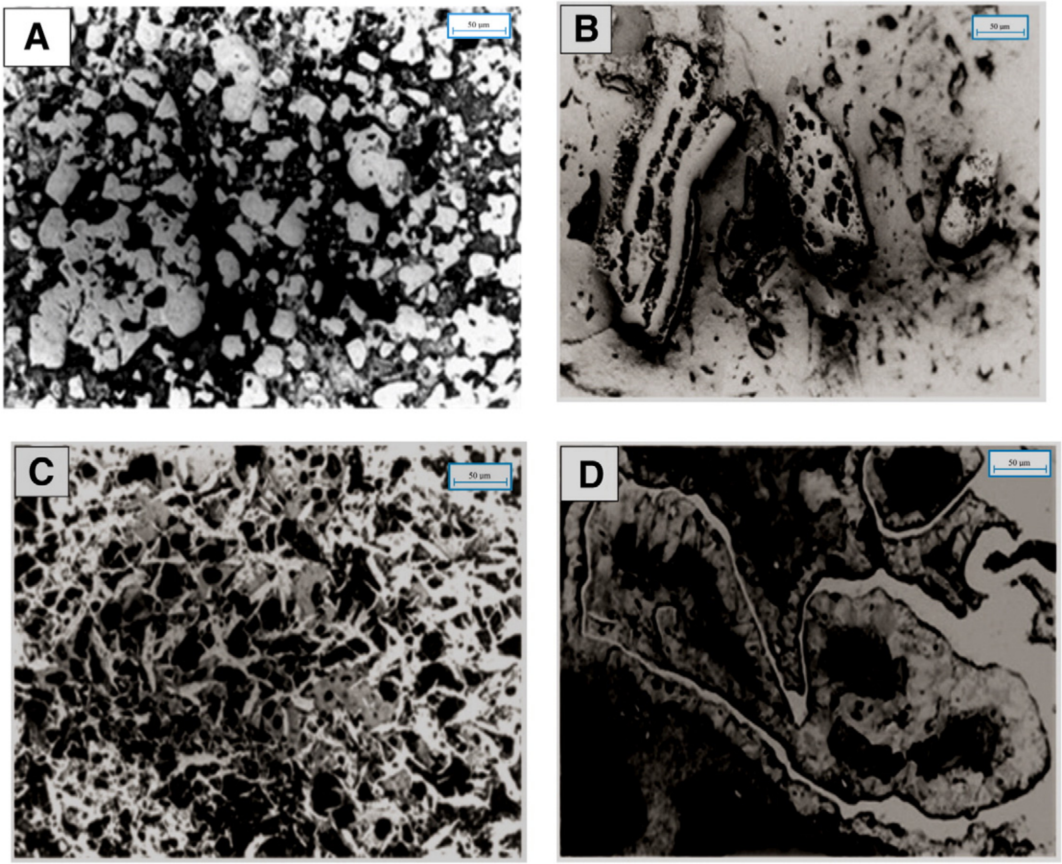

Fig. 4. Optical micrographs showing different minerals in detrital ore [Point 5. of reviewer's comment complied: scale bars inserted in this figure]. A: Cluster of martite and cryptomelane crystals enclosed within clay matrix (black). B: Iron ore clasts (hematite) enclosed within manganite matrix. C: Tiny specularite grains occurring over cryptomelane base. D: Prismatic growth of lithiophorite encrusting a vug.

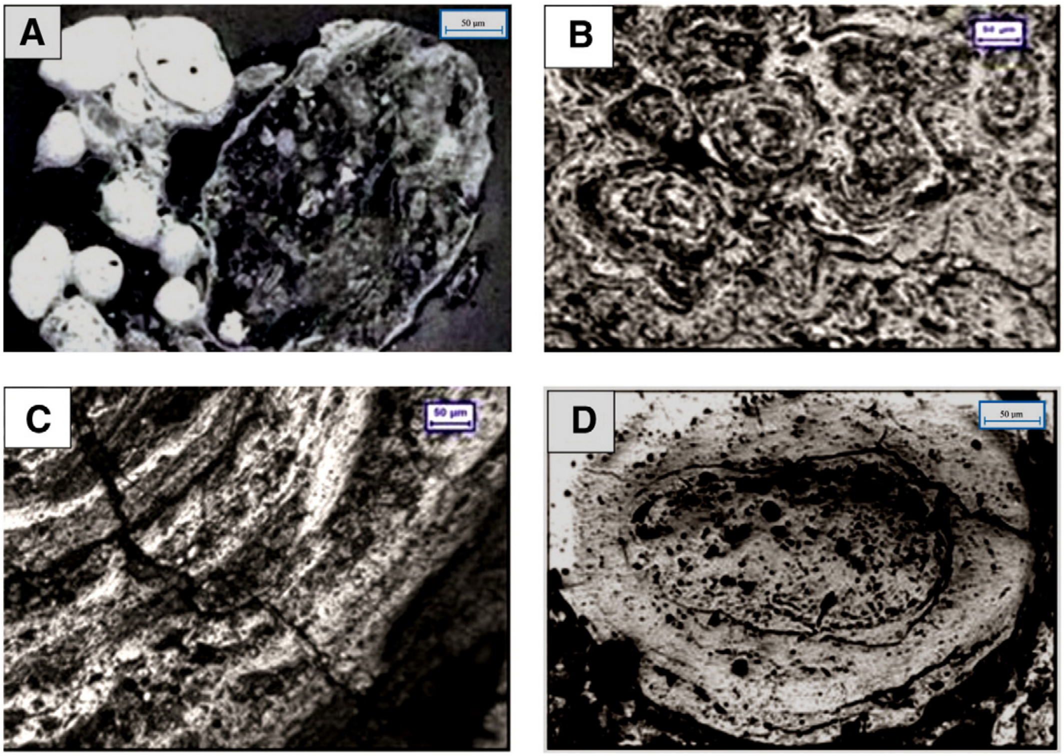

Fig. 5. General microstructure of mangcrete ore. A: Primary Mn-ooliths, in different dimensions, enclosed by secondary manganese rich phase. B: Mamillary texture shown by romanechite. C: Colloform texture shown by cryptomelane. D: A larger pisolith comprising hematite in core encrusted by cryptomelane.

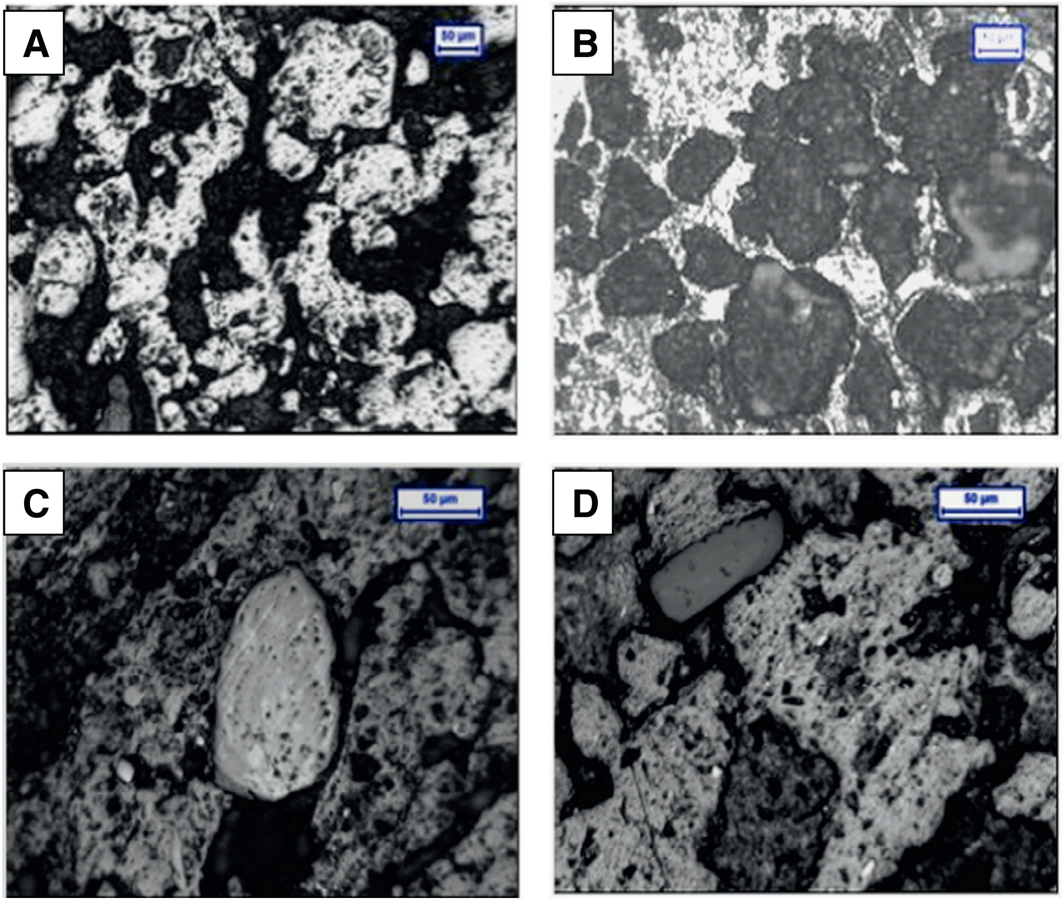

Fig. 6. Optical micrographs showing different minerals in mangcrete ore. A: Irregular shaped cryptomelane associated with clay (black). B: Quartz grains (black) with secondary cryptomelane in inter-granular space. C: A grain of romanechite within a mixed phase of clay and cryptomelane. D: Elongated grain of ilmenite within mixed phase of cryptomelane and romanechite.

to ~1.0 in wad and ~0.64 in mangcrete. The LOI in detrital and mangcrete remains more or less similar (~11) while wad shows very high loss on ignition (>24%).

6. Genetic evolution

The genetic evolution of three reworked Mn-ore types have been interpreted from their field distribution, morphological, microstructural features and mineralogical variations (Table 1).

The reworked-I category of deposits (detrital type) owe their origin to widely different environmental and secondary processes. Different characters of such ore like a) bouldery nature; b) morphological variation and c) compositional dissimilarity between boulder to boulder (some being considerably rich in manganese) are considered while proposing the following sequential developmental stages:

i) Initiation of subsidence of basin consequent to tectonism and folding of Iron Ore Group (IOG) of rocks in this region; ii) mechanical disintegration and erosion of pre-existing crust i.e. manganese ores from higher horizons; iii) intensive leaching of Mn/Fe-bearing rocks/ores; iv) leaching of manganese into solution is described in detail (leaching at low pH, electrochemical reaction between Fe and Mn, reduction under the influence of bacteria etc.) by Pracejus et al. (1988) for Groote Eylandt Mn-ores, Australia. Similar processes might have caused dissolution of manganese in to solution in the study area. The dominant process for the dissolution of Mn-oxides was probably the redox reaction between divalent iron and tetravalent manganese. However, the entire gamut of dissolution and depositional processes continued for a fairly large span of time and over repetitive phases. The Mn-carrying solution percolates, both laterally and vertically through cracks and planes of weakness, in laterite and ores. The Mn-rich solution may precipitate by several processes (Pracejus et al., 1988) but in the present set-up dehydration and subsequent oxidation seems to have influenced the most. During dehydration, shrinkage cracks develop which are often filled with younger Mn-phases; v) precipitation of remobilized Mn/Fe-rich solution followed by cementation of primary and other Mn- and Fe-rich clasts either independently or together depending on their availability; vi) fragmentation of recemented ores into boulders followed by their short-distance lateral and vertical transports, both into adjacent basins during terrain evolution; vii) deep burial of manganese boulders beneath thick sub-recent to recent lateritic cover and development of present topography.

Field distribution, ore petrography and chemistry of reworked-II category of ore bodies (mangcrete) indicate a different genetic evolution. #These are formed from manganiferous laterite, and massive/bedded Mn-ore during post-diagenetic process due to chemical leaching of Mn and Fe followed by slow precipitation of the Mn-bearing descending acid solutions enclosing the detritus in different stages under supergene environment. The leaching of manganese and iron may take place together or one after the other. In the Mn-Fe-Al triad, the solubility of manganese is maximum (and its mobility) and hence, during downward movement of manganese and iron in solution, a change in Eh-pH may lead to precipitation of iron in preference to manganese. Thus, local change in the depositional environment in a restricted area favored the late stage development of mangcrete. The spheroidal type weathering, growth of concentric layers over a nucleus (Fig. 8) indicates chemogenic precipitation during several stages. Where the weathered profile attains sufficient thickness, the upper zone is depleted in manganese which travels deeper and is re-precipitated in the lower zone (Roy,

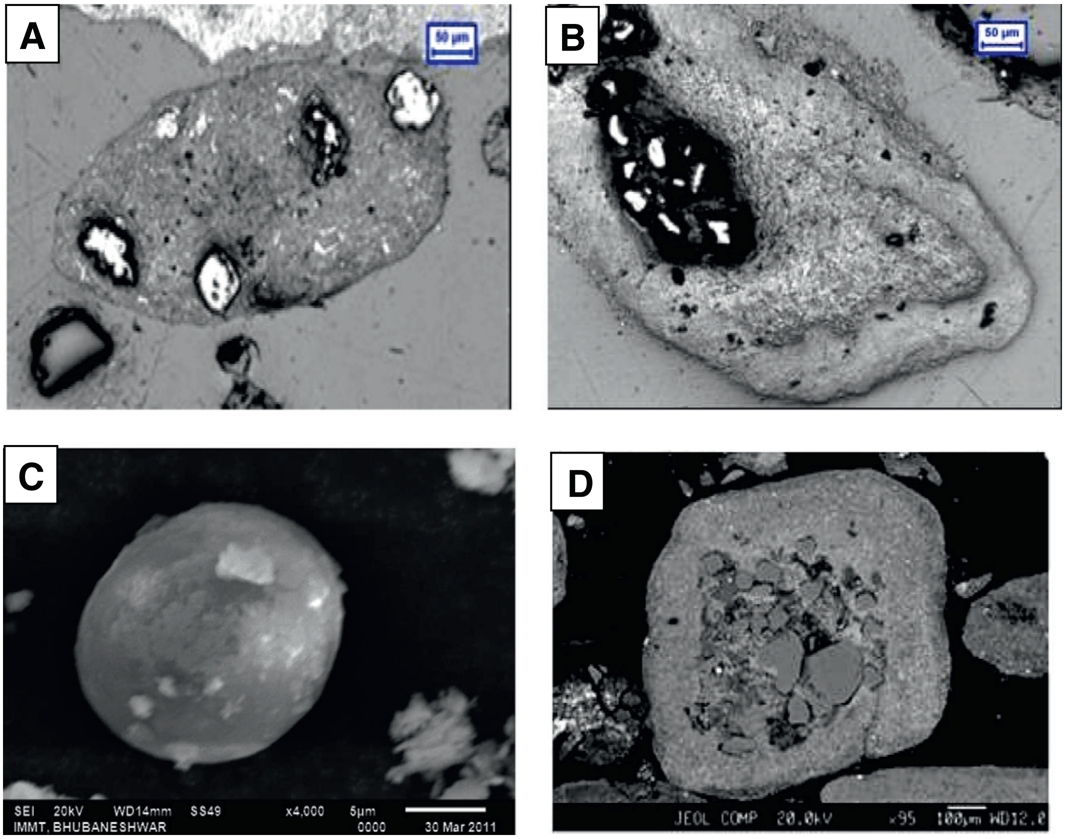

Fig. 7. General microstructure of wad. A: Sub-rounded grain with inclusions of cryptomelane, a small quartz grain is also seen. B: Sub-elliptical grain of mixed facies with inclusions of hematite and cryptomelane. C: A globular grain of wad. D: An equi-dimensional grain containing quartz detritus in the core.

Table 1
Mineralogical variation between different reworked categories of Mn-ore.

	Detrital	Mangcrete	Wad
Major phase	Cryptomelane, lithiophorite, kaolinite, goethite	Cryptomelane, goethite, hematite	δ-MnO_2 mixed Mn-Fe
Minor phase	Pyrolusite, manganite, hematite/martite specularite, quartz	Romanechite, pyrolusite, quartz, ilmenite	Pyrolusite, hematite, goethite, quartz, kaolinite

1981). Pracejus et al. (1988) invoked electrochemical reactions between Fe^{2+}(dissolved in ground water or adsorbed on kaolinite) and Mn^{4+} in the zone of weathering at Groote Eylandt deposit, Australia, and reported that by these reactions, Mn^{4+} in the oxide minerals was reduced and dissolved with consequent deposition of Fe^{3+} phases (goethite, hematite) and clay minerals. On transportation, dissolved Mn^{2+} cemented primary pisolites/oolites and formed mangcrete (Pracejus et al., 1988). Fragmentation of the ooloids and pisoloids was possibly an in-situ process, caused during diagenesis and dehydration. The fragmented ooloids and pisoloids may occur as nuclei in younger pisoloids. These features indicate reworking. The preservation stage of the deposits was accompanied by weathering and lateritization under neutral environmental conditions # [Point 2. of reviewer's comment — complied].

Development of reworked-III deposits (wad) has been reported from low lying marshy lands known as fens (Uglow, 1920; Hanson, 1932; Hariya and Kikuchi, 1964; Greene and Madgwick, 1991; Mita et al., 1994; Usui and Mita, 1995; Pack et al., 2000; Mita and Miura, 2003; Miura et al., 2004; Webb, 2008). Fens form at the base of a slope where the water table intersects the land surface to create a mineral spring. Wad deposits may develop where groundwater enriched in iron and manganese percolates through rock and then emerges as a spring within the confines of a fen. Chemical reaction involving decaying vegetation, bacterial processes, and groundwater causes the manganese and iron to dissolve out as a mixture of manganese-iron oxides and hydroxides. Most of the wad occurrences in the study area appear to have developed in a similar way as in a swampy region. Ooloidal, globular, elliptical nature of grains in wad probably support its shallow basin deposition. The presence of δ-MnO_2 in wad indicates the wetland to have a marine influence. Chemical composition of wad reveals the mineral fluid to be enriched both in Mn and Fe. These elements are released from the existing massive/bedded Mn-ore bodies through microbial activity rather than inorganic chemical processes. Records of fossil remnants like algal filaments, foraminifera, bacteria and diatomite in wad (Fig. 9) confirm that the microorganism (bacteria) catalyze the oxidation of soluble divalent manganese to tetravalent manganese as the

Table 2
Partial chemical analysis results of different reworked types of Mn-ore.

Constituents in wt%	Detrital	Mangcrete	Wad
Mn	40.2	16.6	25.5
Fe	8.2	22.6	24.0
SiO_2	9.8	12.9	5.3
Al_2O_3	5.1	16.6	2.9
LOI	10.5	11.4	24.6
Mn/Fe	5.0	0.64	1.06
	99.6	99.4	98.2

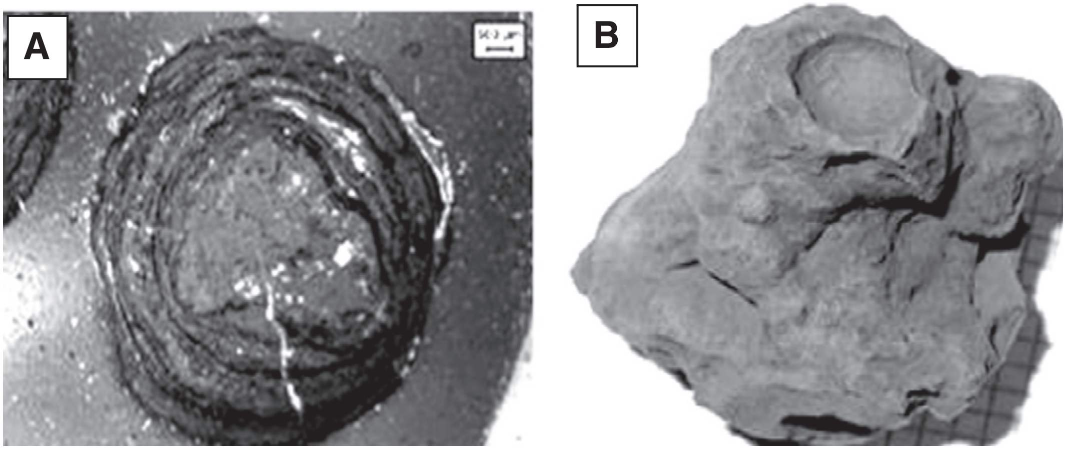

Fig. 8. A: Cross section of a pisolite pebble showing concentric rings. B; A piece of concretion from which oolitic pebble has dislodged.

insoluble oxide (MnO_2) (Nealson and Tebo, 1980). Some of these organisms also cause the oxidation of Fe^{2+} which precipitates as iron oxide (Maithy et al., 1998). The insoluble higher oxides are stable under aerobic condition. Fine to ultra-fine particle size and typical microstructures are indicative of slow precipitation of the mineral rich fluid over the detritus in a low temperature environment. Textural evidence suggest that granule size quartz-hematite-romanechite detritus is probably derived from terrigenous source. Single and multi-stage precipitations of Mn and Fe, nucleating detritus of different minerals (quartz, hematite, cryptomelane etc.) reveal its reworked nature. The concretionary, pisolitic, oolitic and friable nature of wad occurring over a massive/bedded Mn-ore body also indicates reworking # [Point 3. of reviewer's comment — complied].

A schematic diagram showing the evolutionary trend of the three categories of reworked manganese ores in Bonai-Keonjhar belt, Singhbhum Craton, India is given in Fig. 10.

7. Conclusions

Reworked manganese ore bodies in Pre-Cambrian Iron Ore Group, in Bonai-Keonjhar belt, Singhbhum Craton, eastern India have been described in terms of their field distribution, ore-petrology, microstructure and chemistry with a view to find out their genetic evolution.

The detrital manganese ore bodies are of allochthonous type and formed during post lateritization period of terrain evolution. Such ore bodies occur where natural weathering processes have eroded pre-existing manganese ore bodies and deposited the ore fragments within hollows or traps in low lying areas. Secondary processes such as reworking of pre-existing crust, remobilization, solution, precipitation, cementation and transport are responsible for the development and spatial distribution of such type of ore bodies. The lateritization and supergene processes may mask the primary ore (pre-existing crust) to a great extent and it becomes difficult to identify primary structures as

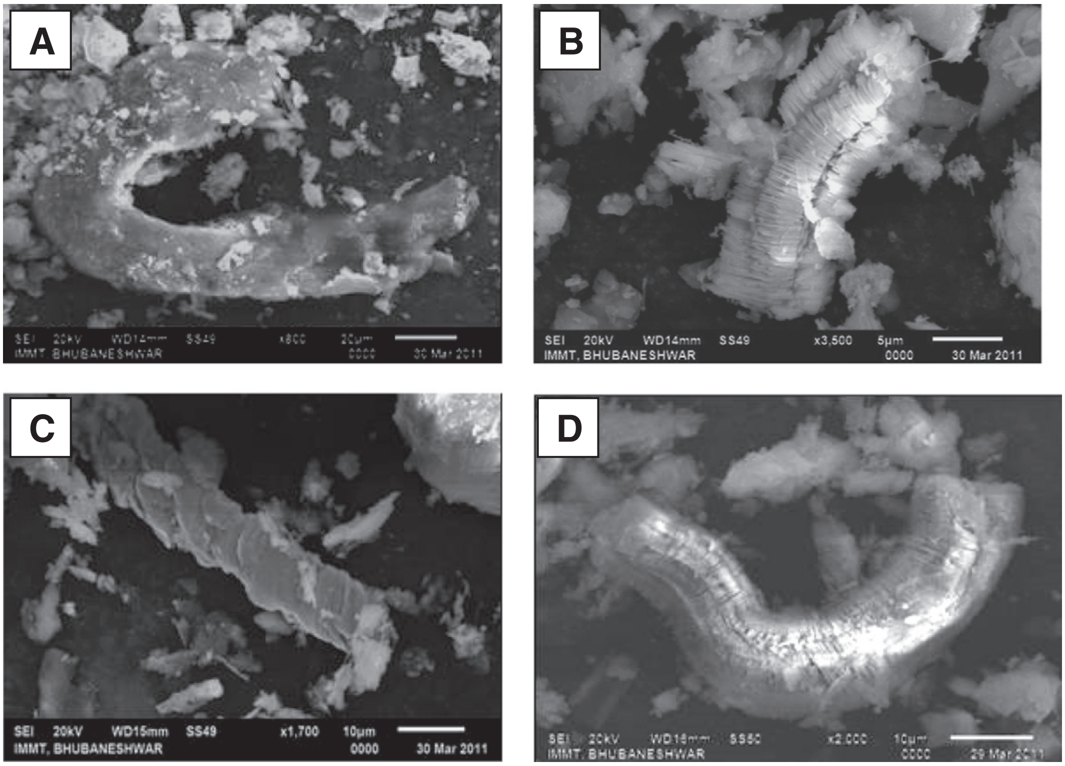

Fig. 9. SEM micrographs of wad from Joda-Barbil region. A: Thick algal filament with concentric rings in the head. B: Elongated foraminifera; C: Spiral bacteria; D: Diatomite.

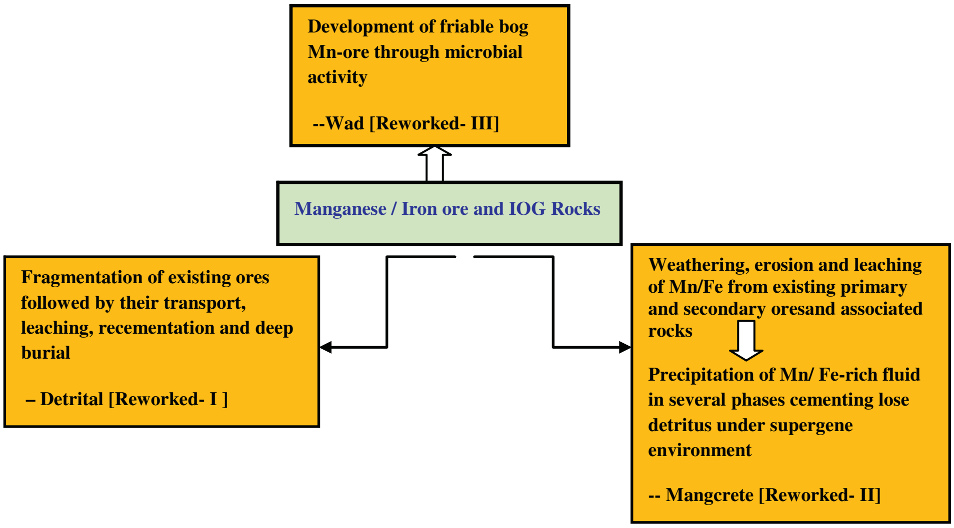

Fig. 10. Schematic diagram showing evolutionary trend of different types of reworked ore.

new morphological varieties develop. Though broad mineralogical composition remains more or less same, some secondary minerals like specularite, manganite and lithiophorite appear in newly formed morphological types. The present day landform is subsequently blanketed by thick sub-recent to recent soil and lateritic cover. Mangcrete is concretionary in nature; rich in iron and alumina and occurs within thick lateritic crust in nodular, spheroidal and pisoloidal shape. Most of the minerals in mangcrete [hematite, goethite, cryptomelane, pyrolusite, quartz and ilmenite] are present as irregular detritus within cryptomelane base of later generation. These concretionary ore bodies are formed during post-diagenetic processes under supergene environment due to solutions and remobilization followed by precipitation embedding the pre-existing detritals. Fragments of ooloids/pisoloids within cryptomelane or romanechite matrix are indications of reworking. Wad zone appears over Mn-ore body up to a thickness of ~10 m. It is soft and powdery in nature and comprises of δ–MnO_2 as major manganese mineral. Hence, wad might have developed in a swampy, wet land region under the influence of marine environment. Micro-organisms play a major role in releasing the Mn and Fe elements from the existing Mn-ore body into solution. Fine oolitic or pisolitic grains in wad are indicative of slow chemical precipitation of Fe-Mn enriched fluid nucleating over quartz or hematite or romanechite grains. Thus, the wad in parts of Bonai-Keonjhar belt has developed over massive and bedded Mn-ore bodies through reworking under a bio-chemogenic process

Conflict of interest

I certify that there is no conflict of interest with any individual or any organization.

Acknowledgements

The authors are highly thankful to the director, CSIR-IMMT, Bhubaneswar for providing infrastructural facilities to carry out the research work. The support extended by the officials of Odisha Mining Corporation, Bhubaneswar during field work is also duly acknowledged

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