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Biogenic Wad in Iron Ore Group of Rocks of Bonai- Keonjhar Belt, Orissa

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Abstract: Outcrop of wad, about 3-5 m thick, associated with low to medium-grade manganese ore deposits in Iron Ore Group (IOG), is present in large quantum in Bonai-Keonjhar belt, Orissa. It is often inter-bedded with volcanic ash layers. Wad is powdery, fine grained, black to blackish-brown in colour, very soft, readily soils the fingers and its hardness on the Mohs' hardness scale is 1-3. The wad zone is capped by a thin lateritic zone and overlies manganese ore beds of variable thickness in Dalki, Guruda and Dubna mines. Wad constitutes two mineral phases, viz. manganese oxides (δ-MnO_2, manganite, romanechite with minor pyrolusite) and iron oxides (goethite/limonite and hematite) with minor clay and free quartz. Mixed limonite-clay and cryptomelane-limonite are commonly observed. Under microscope the ore appears oolitic, pisolitic, elipsoidal to globular in shape having small detritus of quartz, pyrolusite / romanechite and hematite at the core. The ore contains around 23% Mn and 28% Fe with ~7% of combined alumina and silica. Wad might have developed in a swampy region due to slow chemical precipitation of Fe-Mn-Co enriched fluid, nucleating over quartz/hematite grains. Influence of a marine environment is indicated from δ-MnO_2 phase. Remnants of some microfossils, like algal filament, bacteria, foraminifera and diatomite are observed in wad sample under SEM. These microorganisms might have been responsible for the oxidation of dissolved Mn^{2+} and Fe^{2+} precipitates. These findings suggest bio-chemogenic origin of wad in Bonai-Keonjhar belt of Orissa.

Keywords: Ferromanganese Oxide, Microbial Formation, Iron Ore Group, Orissa.

INTRODUCTION

Wad, variously named as bog manganese ore, black ochre, earthy manganese, wetland manganese, morass etc., is known all over the world (Mohapatra et al. 2006; Canterford, 1984; Mita and Miura, 2003). Wad, often poorly crystalline, constitutes manganese oxides/ hydroxides containing significant amounts of oxides/ hydroxides of other metals and adsorbed metals (iron and other transitional metals, alkali elements etc.). Based on type of metal adsorption, it is termed as cobaltian wad, cuprian wad, ferrian wad etc. Recovery of cobalt from cobaltian wad is reported (Canterford, 1984). Miura et al. (2004) described the tephrochronology and diagenesis of the manganese wad deposit at the Akan Yunotaki hot spring, Hokkaido, Japan. Wad has unique physical properties and may be directly used as adsorbant (Pack et al. 2000).

Recent studies have shown that most of these deposits are formed as a result of microbial activity (Hariya and Kikuchi, 1964; Greene and Madgwick, 1991; Mita et al. 1994; Usui and Mita, 1995; Mita and Miura, 2003; Miura et al. 2004). However, data on characteristics and depositional processes of wad from Bonai-Keonjhar region are scanty. This is the first report of microbial activity in manganese precipitation and formation of wad deposits in the Iron Ore Group of rocks, Orissa. However, biological remains and organo-sedimentary structures from Iron Ore Group, Barbil area, Orissa have been earlier reported by Maithy et al. (1998).

This paper describes the mode of occurrence, mineralogy and chemistry of wad from Dalki-Siljora-Dubna mines with a view to establish its genetic evolution in Iron Ore Group of rocks.

NATURE OF WAD DEPOSITS

Wad outcrops, located in the mine profile of Dalki (N 22°05' 11.6": E 85°23' 36.5") Siljora (N 21°53' 42.1" : E 85° 22'45.3"), Dubna (N 21°51' 19.8 ": E 85°23' 27.1") of Barbil-Joda region, are seen overlying low to medium-grade manganese ore bodies. The manganese ore forms a part of Banded Iron Formation (BIF) in Iron Ore Group of rocks of Bonai-Keonjhar belt, Orissa (Fig.1). The dimensions of such

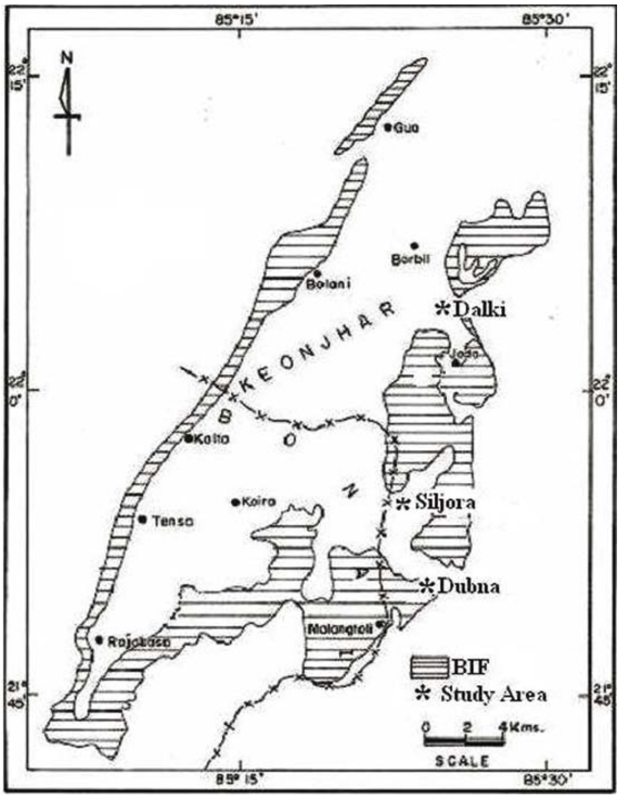

Fig.1. Map showing BIF and wad occurrence in Dalki-Siljora-Dubna, in parts of Bonai-Keonjhar Belt, Orissa.

wad outcrops are 500 m x 100 m with a maximum thickness of about 10 m.

These outcrops fan outward (Fig.2A), generally thicken down slope and terminate abruptly. The deposits seldom contain more than several hundred tonnes of ore. In most instances, they are too small, discontinuous and low grade for economic consideration. The ore bodies are capped by 1-3meter lateritic zone (Fig. 2 B and C). Slump structure in form of open folds is seen in Fig.2B. Several volcanic tuff layers and layers of manganese-iron oxide are observed within the deposit (Fig. 2 C). Sometimes, tephra is seen mixed with manganese oxide through out the profile (Fig.2B). The tephra appears white, grey and red in colour. Below 3-4 m from the top, the profile contains detritus aggregates (Fig. 2D).

MINERALOGICAL CHARACTERISTICS

Wad is black, bluish black to brownish black in colour and shows dull to earthy lusture. It is very soft, powdery, fine grained (avg. 30μm), soils the hand with black, brownish black, reddish brown streak. Its hardness on the Mohs' hardness scale is 1-3.

The XRD pattern illustrated in Fig.3 indicates the presence of δ-MnO_2 as major manganese phase. The X-Ray

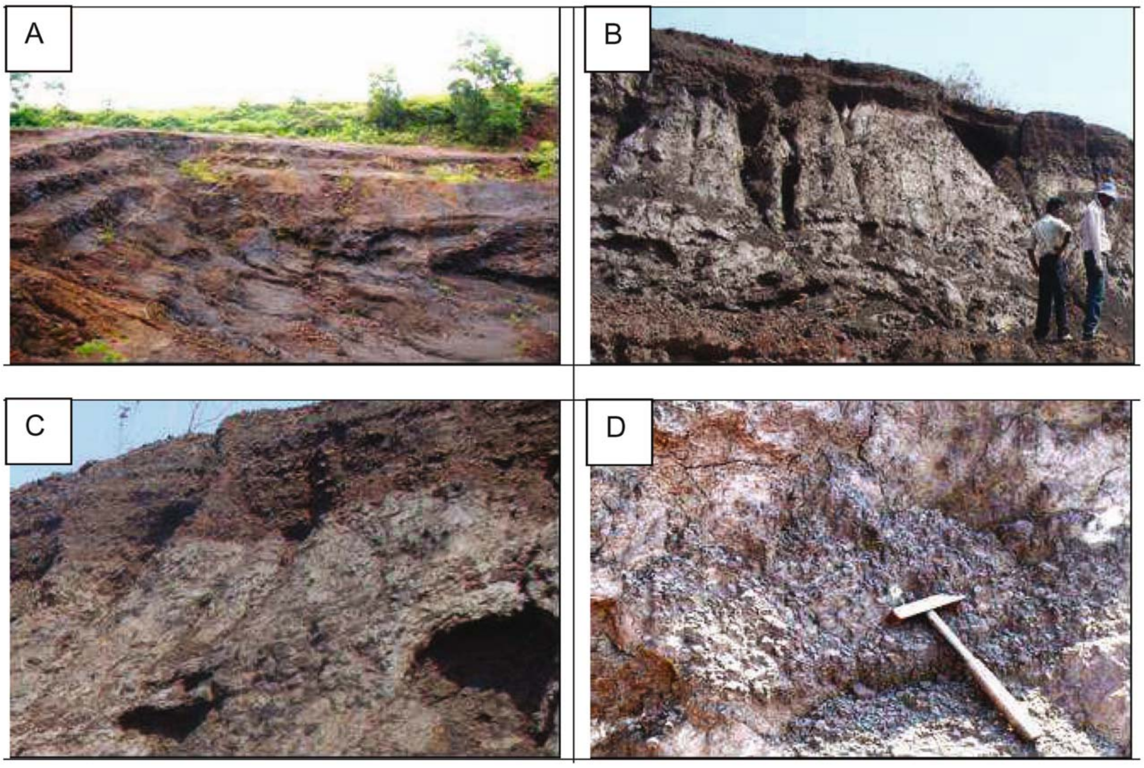

Fig.2. Overview of wad outcrops in **A.** Dalki mine **B.** Siljora mine **C.** Dubna mine **D.** Detritals in the bottom part of a wad outcrop, in Joda-Barbil region, Orissa

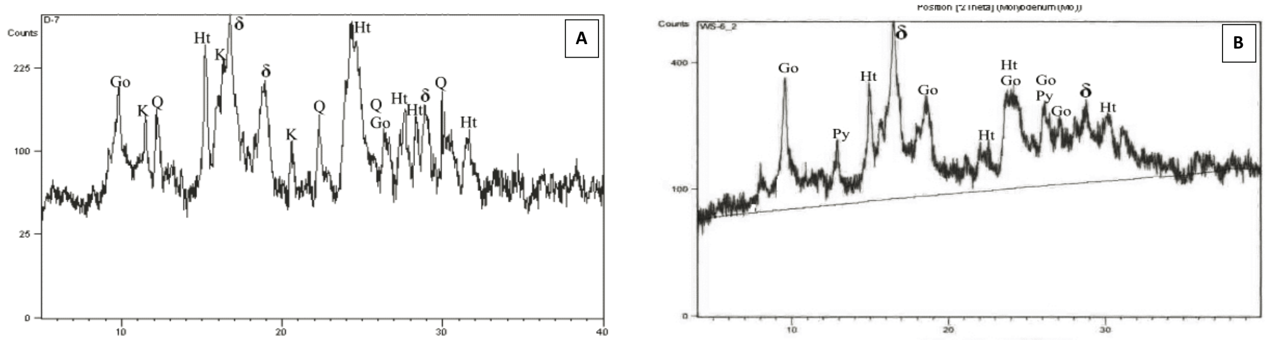

Fig.3: XRD pattern of wad sample from two mines **A.** Dubna Mine; **B.** Dalki Mine {Py: Pyrolusite; Go: Goethite; Ht: Hematite; δ: δ-MnO_2; K: Kaolinite, Q: Quartz}

reflection peaks between 2.42 - 2.45 **Å** and 1.40-1.41 **Å** are due to poorly crystalline δ-MnO_2 phase. Marine manganese minerals (todorokite and birnessite) in wad have also been reported elsewhere (Miura et al. 2004). Minor variation in XRD pattern between Dubna and Dalki sample is noticed (Fig. 3A & B). Other subordinate minerals in the present sample are hematite, goethite, quartz, kaolinite, manganite, romanechite, pyrolusite and lithiophorite. The micro-morphology of wad grains was examined under both optical (Fig. 4 A-C) and scanning electron microscope (Fig.4 D-F). The grains appear in varied shape such as: oolitic, pisolitic, sub-rounded, globular (Fig.4D), ellipsoidal (Fig 4E) etc. having small detritus of quartz and hematite in the core (Fig.4B). Cross section of a wad grain under SEM distinctly shows detrital grains in the core region (Figs. 4E and F). Crust may be single or multi-layered (Figs. 4 E and B). The thickness of crust varies and sometimes appears <50μ. Manganite is fibrous, while romanechite is anhedral and occasionally oxidized to pyrolusite. Sometimes intergrowth of hematite and clay exhibits spongy texture (Fig. 4C).

Cryptocrystalline Mn-phase is often seen encrusted by mixed limonite-clay phase (Fig. 4 B). Mixed limonite-clay and cryptomelane-limonite are commonly observed. Occasionally, manganite, pyrolusite, hematite and romanechite detritus are found to be accumulated in a wad profile.

CHEMICAL CHARACTERISTICS

The major constituents of wad are iron and manganese. It is composed of 76-82 wt % Fe_2O_3+MnO with Al_2O_3 + SiO_2

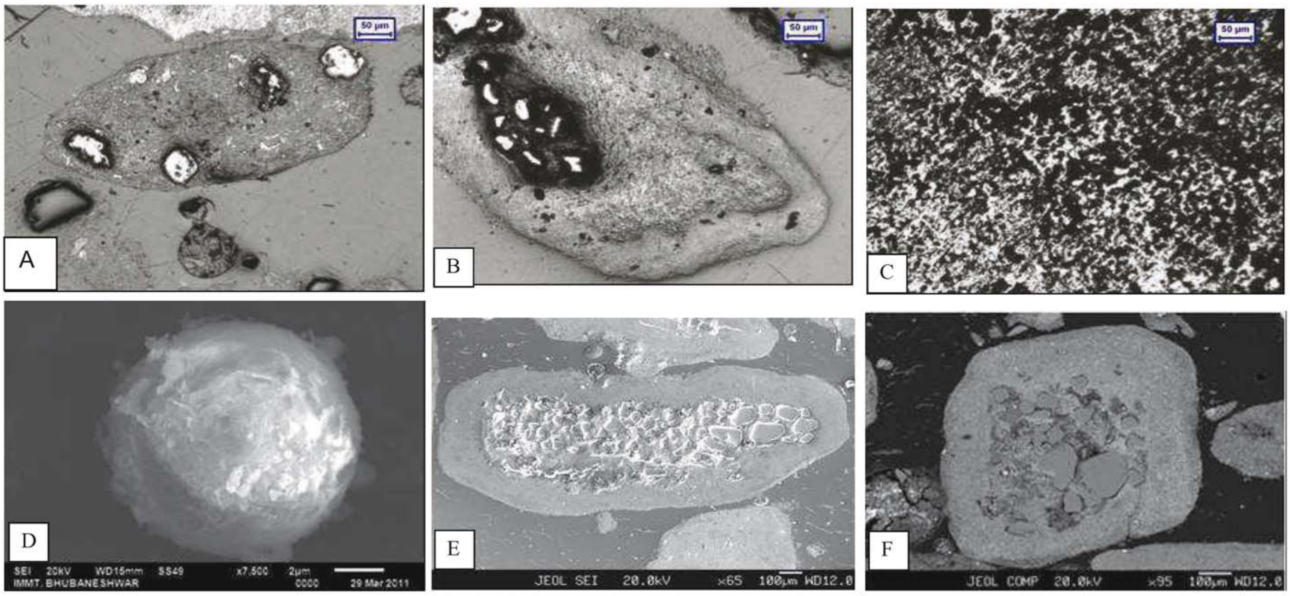

Fig.4. Optical (A,B,C) and electron micrographs (D,E,F) of wad. **(A)** Sub-rounded grain with inclusions of cryptomelane, a small quartz grain is also seen. **(B)** Sub-eliptical grain of mixed facies with inclusions of hematite and cryptomelane. **(C)** Intricately intergrown fine hematite and clay showing spongy texture. **(D)** A globular grain of wad; **(E)** An elliptical grain with a large core containing quartz grains. **(F)** An equi-dimensional grain containing quartz detritus in the core.

Fig.5. DTA and TGA graph of Wad sample.

content ranging between 6 and 10 wt percent. The chemical analysis of three wad samples collected from Dalki, Siljora and Dubna deposits are given in Table 1. Because of high iron content the wad from this region may be termed as ferrian wad.

The ore shows very high loss on ignition (18-22%). Very high TG loss (~22%) is also revealed from thermograph shown in Fig. 5. The average concentrations of K_2O and BaO are 0.7% and 0.12% respectively. P_2O_5 content in the wad is remarkably low i.e. 0.18% (Table 1).

Table 1. Chemical analysis results (in %) of wad from three different localities

Loc.	Mn	Fe	SiO_2	Al_2O_3	P_2O_5	BaO	K_2O	LOI
Dalki	23.06	28.65	5.34	2.94	0.18	0.12	0.70	20.65
Siljora	25.51	30.73	4.75	2.05	0.13	0.10	0.59	21.95
Dubna	21.86	26.08	6.69	4.06	0.23	0.14	0.81	18.77

Compositional map (Fig. 6) of polished surface of wad grains brought out through X-ray imaging under EPMA shows very fine dispersion of Mn, Fe and Co embodying fairly large detritus quartz grains at the core region. The micrograph clearly demonstrates the amorphous to cryptocrystalline phases of intricately associated manganese and iron. The grain shows very poor dispersion of Al. Cobalt is also seen adsorbed with Mn/Fe-phases.

MICROFOSSIL RECORD

Wad samples were examined under SEM and features that resemble microfossils were documented. These microfossils possibly indicate some level of bacterial activity during formations of wad.

In the SEM image, the wad sample shows small individual to large coiled filament (Figs. 7A) structure of algal origin. Similar species have been reported by Miura et al. (2004) in Yunotaki wad, Hokkaido, Japan. Individual filaments in the present case may be of half circle shape (Fig. 7B) or show coiled habit (Fig. 7C). The former filament has a hood showing concentric rings (Fig. 7 B). Some sample contains fossils looking like tubular micro foraminifera (Fig. 7D) and spiral bacteria (Fig. 7E). Diatomite or diatomaceous earth is seen in many samples (Fig.7F). Diatoms are unicellular or colonial algae with silicified cell walls which are left behind as skeletons when they die. The study indicates that manganese might have been formed either intra-or extra cellular.

GENESIS

Development of wad/bog manganese ore have been reported elsewhere in low lying marshy lands known as fens (Uglow, 1920; Hanson, 1932; 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 precipitate out as a mixture of manganese-iron oxides and hydroxides. Most of the wad occurrences in Dalki-Siljora-Dubna mine in parts of Bonai-Keonjhar belt, Orissa are seemingly developed in a similar way in a swampy region.

Ooloidal, globular, elliptical nature of particles in wad probably support its shallow basinal deposition. The

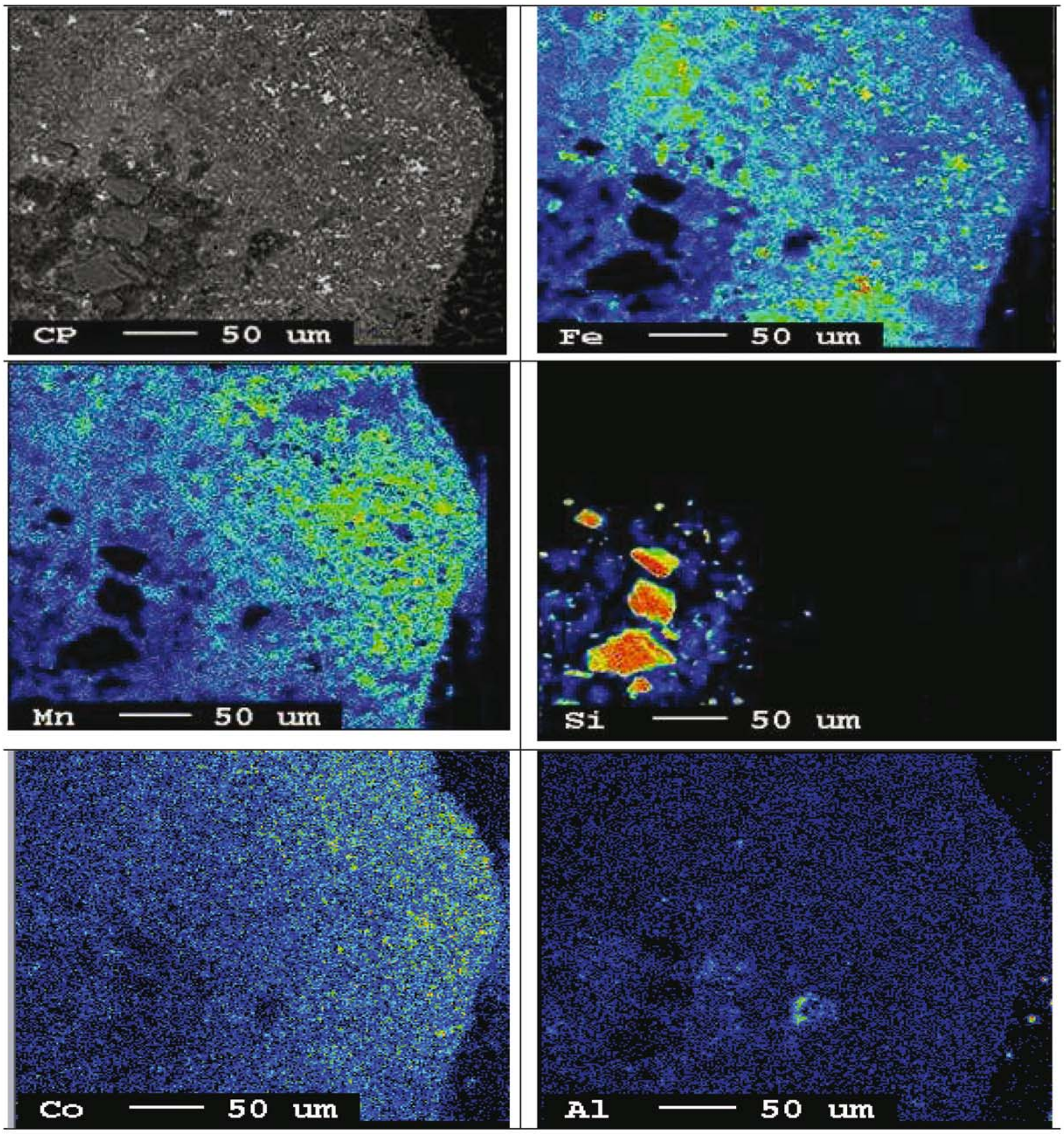

Fig.6. Electron micrographs of wad sample showing back scattered image (CP) and distribution of Fe, Mn, Si, Co and Al elements.

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 in Mn, Fe with trace of cobalt. Fine to ultra fine particle size and typical microstructure are indicative of slow precipitation of the mineral rich fluid, in several successive stages, over the detritus nucleus in a low temperature condition. Textural evidences suggest that granule size quartz/hematite grains are detritus probably from terrigenous source. Presence of tephra layers in wad profile reveal that manganese precipitation was intervened by volcanic exhalation.

Record of fossil remnants in wad indicates that the microorganism (bacteria) catalyze the oxidation of soluble divalent manganese to tetravalent manganese as the insoluble oxide (MnO_2) (Nealson and Tebo, 1980). Some of these organisms also cause the oxidation of Fe^{2+} which precipitates as iron oxide. The insoluble higher oxides are stable minerals under aerobic condition. The above findings suggest that the development of wad in parts of Bonai-Keonjhar belt is caused by microbial activity of chemical precipitates rather than inorganic chemical process alone.

CONCLUSIONS

Wad/bog manganese ore is exposed below thin latertic blanket in Dalki- Siljora - Dubna mines overlying the

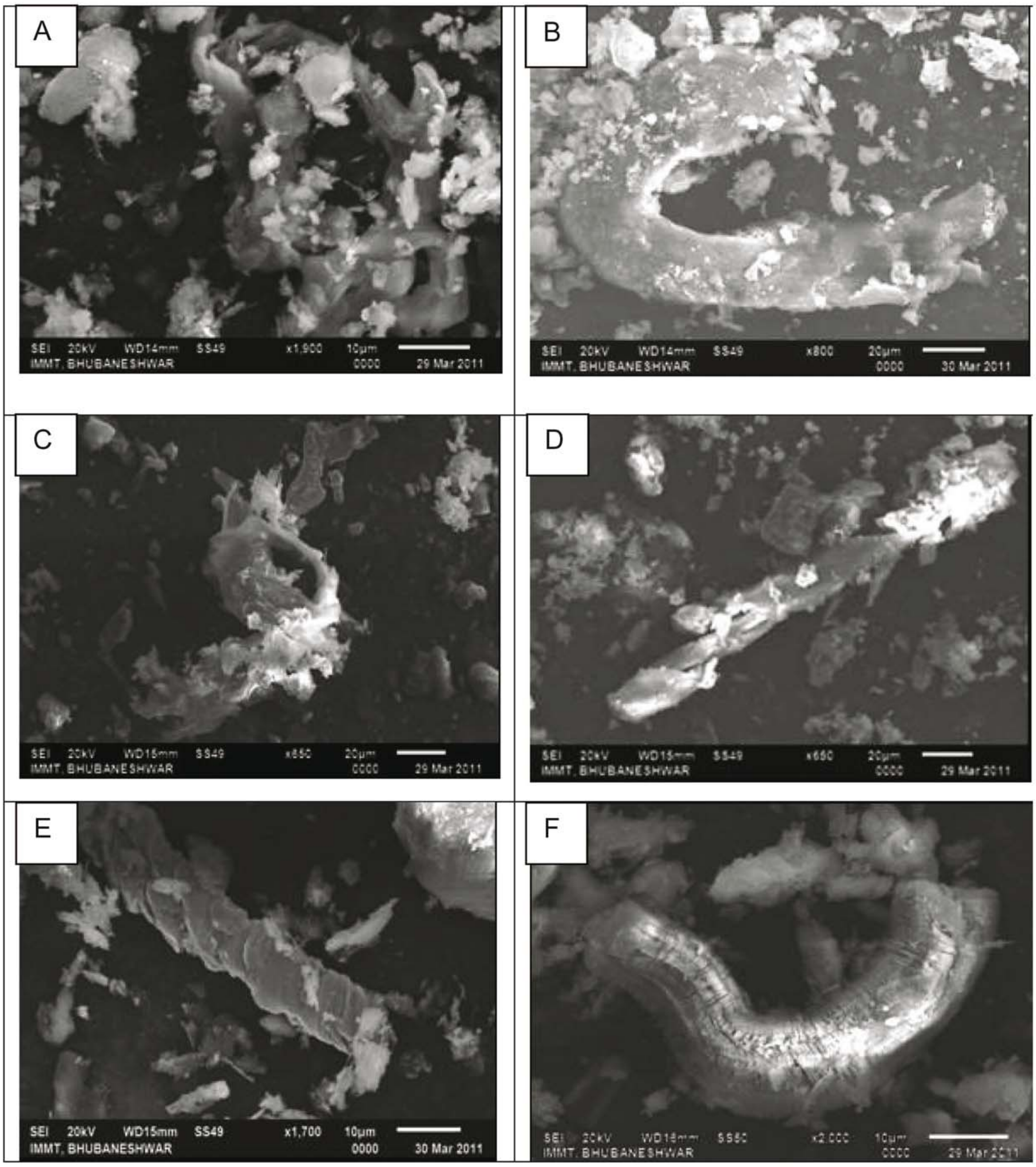

Fig.7. SEM micrographs of wad from Joda-Barbil region. **A.** Coiled filament structure of algal origin; **B.** Thick algal filament with concentric rings in the head; **C.** Coiled filament; **D.** Elongated foraminifera; **E.** Spiral bacteria; **F.** Diatomite

manganese ore bands in parts of Bonai- Keonjhar belt, Orissa. It is soft and powdery in nature and comprises of small oolitic/pisolitic grains. Quartz/hematite detritus appear in the core region of oolities which are encrusted by one to two Fe-Mn layers having minor Co. The major manganese mineral in wad is δ–MnO_2. Thin bands of volcanic ash are sometimes seen inter-bedded with wad. The wad contains in average 23% Mn, 20% Fe with 7% combined alumina-silica and around 0.2% of cobalt. Remnants of micro-fossils like filament of algal origin, bacteria, foraminifera, and diatomite are recorded in wad.

Wad might have developed in a swampy, wet land region as reported elsewhere by some workers. However, its formation in the present study area was getting intervened by inflow of tephra from a volcanic source. Marine influence in formation of wad is suggested from dominating δ–MnO_2 phase. Fine oolitic/pisolitic grains in wad are indicative of slow chemical precipitation of Fe-Mn-Co enriched fluid nucleating over quartz/hematite grains. Such detrital grains occurring either as nucleus or accumulated at the foothill of wad profile are terriginous input into the swampy region. Oxidation of Mn and Fe precipitates was probably possible through biogenic activity. Thus, the wad in parts of Bonai-Keonjhar belt has developed through a bio-chemogenic process.

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