

Ferromanganese oxide deposits: geochemical and microbiological perspectives of interactions of cobalt and nickel

P.P. Sujith^{a, b, *}, Maria Judith B.D. Gonsalves^a

^aAqua-Geomicrobiology Laboratory, National Institute of Oceanography,
Council of Scientific and Industrial Research, Dona Paula- 403 004, Goa, India

^bSt. Thomas Matriculation Higher Secondary School, Munnanad, Ayyankolly,
The Nilgiris – 643 239, Tamil Nadu, India.

* Corresponding author. Tel.: +91-8300298255, E-mail address: sujith.oceanbio@gmail.com

Abstract

Bacterial participation in the formation of ferromanganese (Fe-Mn) mineral deposits is highly debated, as the precipitation of metals could occur by both chemical and biologically mediated mechanisms. Besides, the enrichment of trace metals like Co and Ni in Fe-Mn deposits is further complicated by the aging process of the crust, scavenging by the Fe-Mn oxide surfaces and co-precipitation by bacterial activity. The concentration of Co in Fe-Mn crusts varies from 0.1 to 1.9% and Ni from 0.2 to 1.1% in individual bulk crusts implying marked heterogeneity in their composition. Several reviews address different aspects like the molecular mechanisms of Co and Ni uptake in bacteria, enzymes containing Ni and Co and their relative toxicity. Nonetheless, only limited data are available on the interactions of Co and Ni with bacteria and how they contribute to the enrichment of these metals in the deep-sea mineral deposits. Hence, this review focuses on the geochemical and microbiological perspective of the interactions of Co and Ni, different modes of their enrichment and requirement for several physiological and biogeochemical processes in bacteria. The detailed survey of the studies indicates that both chemical and biological mechanisms promote the accretion and dissolution of minerals with bacteria accelerating the net oxidation-reduction reactions in their directions. Combined geochemical and microbiological interactions in conjunction with detailed molecular analysis would further confine processes affecting Fe-Mn mineral formation.

Keywords: Extracellular; Intracellular; Cell-surface; Hydrogenetic; Diagenetic; Hydrothermal

1. Introduction

Migration of metal cations like iron and manganese from less oxidizing to more oxidizing conditions in the marine environment contributes to the formation of Fe, Mn and Fe-Mn mineral deposits (Glasby, 2006). The hydrogenetic crusts on seamounts are formed by the precipitation of Fe oxyhydroxide and Mn oxide from cold, ambient ocean water onto rock substrates. Also, the hydrothermal processes can lead to the accumulation of Fe-Mn oxides, sediment fall-out deposits or formation of sub-sediments layers, or impregnations. The strong enrichment of one or the other major element occur near volcanic sites and less commonly at spreading centers as a result of the very different redox potential stability of Fe and Mn (Hein and Koschinsky, 2014). The deposits occurring in the form of nodules and crusts in the marine environment (Figure 1 & 2) cover almost all geomorphologic and tectonic environments of the oceanic basins. However, the process of oxidation of Fe and Mn and their mechanism of precipitation leading to the formation of ferromanganese (Fe-Mn) crusts and nodules in different parts of the oceans are yet unknown (Usui et al., 2020). The physicochemical mechanisms of Fe-Mn deposit formation according to an earlier model by Koschinsky and Halbach (1995) considered intermediate oxygen minimum zone (OMZ) as a major reservoir of reduced manganese (Mn^{2+}) for Fe-Mn crust formation. Nonetheless, model proposed by Usui et al (2017), pointed out that the intermediate OMZ is not a major reservoir of reduced Mn^{2+} rather it is as a place for continuous oxidation and deposition of Mn. The subsequent research findings on manganese cycling in Chesapeake Bay indicate that the redox cycling of Mn is more complex and is intense at the suboxic-anoxic interface with high total Mn and concurrent occurrence of Mn(II), Mn(III) and MnOx species having different redox stability (Oldham et al., 2017). The growth of Fe-Mn crusts are also influenced by ocean currents and erosion with optimum crustal growth occurring at average current magnitude of <0.1 m/s (Yeo et al., 2019). The hydrogenetic crust deposits are found to grow at different parts of the ocean in the depth range of 400 to 7000 meters below sea level (Lusty et al., 2018).

However, differences in opinion existed among the researchers on the biogenic contribution for the formation of Fe-Mn mineral deposits. Some of the geochemists agreed that microorganisms could create suitable niches for mineral formation (Dean and Ghosh, 1981), whereas others proposed that enzymes produced by bacteria are involved in the oxidation and reduction of metals (Callender and Bowser, 1976). Yet, the microbial participation in Fe-Mn mineral formation was difficult to accept among researchers due to the lack of experimental evidences that distinguished the microbial processes from that of abiotic reactions (Callender and Bowser, 1976; Ghiorse, 1984). Since then powerful microscopic techniques, specific metabolic inhibitors, radio isotopes and other available

tools were used in conjunction with experiments to probe the microbial presence and activity in microhabitats (Rosswall, 1973; Emerson et al., 1982). This was followed by several reports that addressed the intimate associations of microorganisms with the natural samples (Ghiorse, 1984; Beveridge et al., 1997; Holden and Adams, 2003; Edwards et al., 2005; Haferburg and Kothe, 2007; Ehrlich and Newman, 2009; Tebo et al., 2010; Dong, 2010). Gradually the bacterial participation in nodule growth gained scientific acceptance (Ehrlich, 1975; Riemann, 1983; Banerjee and Iyer, 1991; Wang and Muller, 2009; Nayak et al., 2013). Yet the microbial role in Fe-Mn crust formation continued to be under scrutiny because of the differences in opinion on processes that drive the accretion process of the hydrogenetic crusts like oxidation, precipitation and growth (Usui et al., 2020).

Mn as a trace metal is important for a number of biogeochemical functions and most importantly as a stabilizing agent and co-factor of multicopper oxidase like enzymes that participate in Mn oxidation (Sujith and Loka Bharathi, 2011 and the references therein). The oxidation of Mn occurs mainly by biotic and abiotic mechanisms (Figure 3) involving microbes, organic matter, light, reactive oxygen species, and mineral surfaces (Godwin et al., 2020). During the oxidation of Mn(II), some microbes could use the reduced Mn(II) species as an energy source through chemolithoautotrophic mode of nutrition (Ehrlich, 1976; Yu and Leadbetter, 2020). Instead, Fe is identified as an integral part of several metalloproteins and enzymes important in metabolism. In oxidized form, Fe(III) serve as an electron acceptor for heterotrophic bacterial growth and in reduced form as Fe(II), the metal serve as an electron donor for chemotrophic and phototropic growth of bacteria and Archaea (Ilbert and Bonnefoy, 2013). The oxidation of Fe by bacteria occurs under acidic and near neutral pH conditions with oxygen as an electron acceptor in aerobic respiration and nitrate, perchlorate or chlorate in anaerobic respiration (Ilbert and Bonnefoy, 2013). On the other hand, the abiotic oxidation of Fe occurs as a function of pH, oxygen and Fe concentrations (Morgan and Lahav, 2007).

Although microorganisms are ascertained to carry out Mn and Fe oxidation at rates greater than abiotic oxidation (Tebo et al., 2007; Melton et al., 2014), the microbial oxidation of these metals under natural settings could also be triggered at a slow rate. For instance, subtle differences in environmental conditions like low temperature, pH and oxygen concentrations, metabolic state of cells, concentration of biomass, absence of an energy source, inhibitors of metabolism, metal resistance and competition between organisms (Gadd, 1990; Pekkonen et al., 2013) affects the active participation of microorganisms in metal enrichment and growth of Fe-Mn oxide deposits. Also, the distribution of microorganisms across the ocean basins shows a widespread occurrence in general with some microbes adapted only to specific niches (D'Hondt et al. 2002). Whilst, the majority of

the microbial population under ambient conditions of the ocean show reduced metabolic rate as opposed to metabolically active microbial population in high-energy rich habitats or at geochemical interfaces (Inagaki and Nakagawa, 2008).

During the mineralization of cobalt rich Fe-Mn crusts on seamounts the biological activities and the organic matter derived as part of their activity could play an important role in diagenesis and mineralization (Zhao et al., 2014). Here, the diagenetic mineralization infers to the production of organic matter rich sediments and minerals in concurrence with the alteration of minerals formed on dead or preserved biological materials. Under suboxic oceanic conditions prevalent in the water column beneath the mid-water interface (Oldham et al., 2017), upper few centimeters of the sediment (Jahnke et al., 1983) and during the phosphatisation episodes of crusts (Josso et al., 2021), bacterial mediation could oxidize metal ions, giving rise to oxides and hydroxides of low crystallinity. Also, the heterogenous population of microorganisms inhabiting the Fe-Mn crust surfaces plays a vital role in controlling the oxidation states of Mn and thereby regulates the supply of biologically mediated metals available for accretion (Kato et al., 2018). However, the oxidation-reduction of metals by microorganisms could be based on activities of redox species at equilibrium in which one process dominates the other depending on the key environmental conditions (Sujith et al., 2014) such as ionic strength, pH, oxygen concentrations, nutrient availability, temperature and pressure (Kato et al., 2018).

Looking at the microbial population inhabiting the crusts and polymetallic nodules revealed differences in diversity and community structure between the hydrogenetic, hydrothermal and diagenetic types of mineral deposits. Studies related to hydrothermal systems reported the dominance of ϵ - and ζ -*Proteobacteria* (Emerson and Moyer, 2010). On the other hand, studies from the seamounts of the northwest Pacific reported the dominance of ammonia oxidizing *Thaumarchaeota*, *Crenarchaeota*, α - and γ -*Proteobacteria* (Nitahara et al., 2011; 2017) and an another study from the Afanasy-Nikitin Seamount, Equatorial Indian Ocean (Sujith et al., 2017a) reported the dominance of Marine group 1 *Crenarchaeota* and Fe-, Mn- and S- oxidizing α - and γ -*Proteobacterial* groups in the hydrogenetic based crusts. Moreover, the bacterial and archaeal groups related to oxidation of nitrogen compounds and methane oxidation were predominantly detected on Fe-Mn crust samples from the Rio Grande Rise, South West Atlantic Ocean (Bergo et al., 2021). Further, observation of microbial population along the mid-ocean ridges showed the occurrence of different bacterial types belonging to *Firmicutes*, *Verrucomicrobia*, *Thermales* and the *Cytophaga–Flexibacter–Bacteroides* groups (Takai et al., 2006). Moreover, the deep low-temperature influenced oceanic crust basalts and sediments along the ridge axis are also home for Mn and S oxidizing bacterial communities

belonging to class α -*Proteobacteria*, β -*Proteobacteria*, γ -*Proteobacteria*, *Actinobacteria* and *Bacilli* (Rathsack et al., 2009). Bacterial members with the capability to oxidize and/or reduce Mn belonging to *Alteromonas*, *Pseudoalteromonas*, *Shewanella* and *Colwellia* are identified and proposed as key members in the formation of polymetallic nodules (Wu et al., 2013; Blothe et al., 2015). However, the above results are not conclusive as the diversity of microbial communities of diagenetic nodules show pronounced spatial variability as well based on sampling sites (Shiraishi et al., 2016; Wu et al., 2013; Blothe et al., 2015; Molari et al., 2020). The aforementioned studies show that the diversity of microorganisms occurs everywhere regardless of the type of samples. Nonetheless, the environmental settings of a geographical region directly affect the abundance and the taxonomic and functional composition of a microbial community (Pinheiro et al., 2019) and thereby the whole ecosystem.

Fe and Mn oxides are amid the strongest oxidants and sorbents in the marine environment. They control the transport and speciation of metals, geochemical cycling of carbon, and flow of electrons within different soils and sediments (Learman et al., 2011). However, the factors contributing to the formation of Fe-Mn oxide deposits has been highly debated. The biotic vs abiotic model or mixed contribution models have been a source of active discussion in the community with some strong arguments on both sides. The following sections propose a review of a long-lasting debate on the participation and impact of biological activity in the formation and metal enrichment of Fe-Mn oxide deposits. The review compares and contrasts the geochemistry, mineralogy and microbial ecology of hydrogenetic, hydrothermal and diagenetic types of mineral deposits. The geochemical and biological control on the oxidation and reduction of Co and Ni on Fe-Mn oxide surfaces are also discussed with respect to nodules and crusts.

2. Types of bacterial interactions with metals

2.1. Extracellular interactions

Among the different mechanisms that bacteria follow in interacting with metals (Figure 4), extracellular interactions play a prominent role. The extracellular interactions function through the elaboration of detoxifying agents which then reacts with the metals outside the cell, rendering them harmless. Mostly, the extracellular material acts as a resistant barrier for the metal entering into the cell. Such interactions may be important, especially in slime-producing organisms or those organisms that grow in an extracellular matrix composed of proteins and polysaccharides (Dugan et al., 1970; Kurek et al., 1991). It permits the organisms to grow and survive in the presence of high metal concentrations which gets adsorbed and precipitated within the extracellular matrix (Ford and

Ryan, 1995). Further, they could also help in the binding of metal ions and serve as nucleation sites (Dong, 2010). Apart from these functions, extracellular polysaccharides (EPS) and other surface appendages help the bacterial cells in attaching to the surfaces, serve as anchors to solid surfaces and participate in the dissolution of solid mineral phases (Welch and Vandevivere, 1994; Welch et al., 1999). The extracellular interactions could vary from the ability to leach metals from rocky substrate by the production of acidic metabolites to the formation of colloidal-sized EPS metal complexes. This occurs as a direct consequence of negatively charged functional groups like pyruvyl, phosphoryl, hydroxyl, succinyl, carbonyl or carboxyl, and uronyl groups on the exopolymer (Ford and Ryan, 1995).

2.2. Cell-surface interactions

The uptake and accumulation of metal ions by the bacterial cells from any environment are primarily adsorbed on the cell walls or other components located outside the protoplast. Such an uptake of the metal may or may not have an essential cell function but it governs the distribution of metals in natural waters (Schultze-Lam et al., 1996). The different components encountered at the cell surface which may be involved in such adsorption phenomena consists of slime layers, capsules, sheaths, stalks, flagella and fimbriae (Kaltwasser and Frings, 1980). For bacteria with negative reaction for Gram's stain (Gram negative), it is the phosphoryl group that act as potential sites for metal binding (Ferris, 1989; Schultze-Lam et al., 1996). On the other hand, in Gram-positive bacteria, carboxyl and phosphoryl groups serve as electronegative sites for metal binding (Doyle, 1989). The bacterial interactions with metals lead to the nucleation and the formation of fine-grained minerals with anions from the external milieu acting as counter-ions for additional metal complexation (Schultze-Lam et al., 1996). Therefore, metal binding to cell-surface functional groups is considered to be an important step prior to intracellular accumulation and utilization in different cellular functions. The binding of metal cations to cell-surface functional groups are also affected by pH. With a decrease in pH, the negative cell surface charge undergo neutralization by the excess of protons (H^+) in the surrounding environment and vice versa occurs with an increase in pH (Ayala-Torres et al., 2014). The variation in pH affects the solubility of metals and consequently their binding to the negatively charged cell surfaces.

2.3. Intracellular interactions

The uptake of metal ions in excess exerts toxic effect on bacterial cells (Nies, 1999). The toxicity is overcome through trafficking systems that comprise uptake systems, efflux systems, metallochaperones and metal-storage proteins (Komeda et al., 1997; Eitinger et al., 2005). Also,

bacteria counterbalance the intracellular concentration of toxic metals by a concerted increase in inorganic sulfide and phosphate contents (Aiking et al., 1984). Nevertheless, in some instances bacteria concentrate metals intracellularly in substantial amounts (Sar et al., 2001; Glasauer et al., 2004). This occurs as an adaptive strategy wherein bacterial cells avoid metal toxicity through vacuolar compartmentalization, sequestration in polyphosphate bodies and polyhydroxybutyrate production (Keasling, 1997; Sujith et al., 2010) (Figure 5 & 6). This helps the bacterial cells in regulating the cytosolic metal ion concentration (Keasling, 1997; Gonzalez and Jensen, 1998). The metal ions which get bound to polyphosphates undergo hydrolysis at the expense of adenosine triphosphate (ATP). The inorganic metal phosphates so released are transported outside the bacterial cell through inorganic phosphate transport system.

3. Major forms of marine mineral deposits

The formation of mineral deposits could occur by biogenic or abiogenic processes. These deposits of minerals in the form of nodules and crusts (Figure 2) are formed biologically by the precipitation of inorganic substances surrounding an organic matrix (Verlaan, 1992; Wang et al., 2009) or abiologically by the hydrothermal deposition of economically important metals in region with active volcanic/heat anomalies such as on mid-oceanic ridges, hotspots, back-arc and fore-arc basins, etc (Josso et al., 2017; Lusty et al., 2018). The common mineral deposits on seamounts comprise of the 1) hydrogenetic Fe-Mn crusts, 2) hydrogenetic Fe-Mn nodules on sediment-covered seamount surfaces and 3) phosphorite deposits (Hein et al., 2010). Apart from the aforementioned seamount deposits, the other major Mn deposits found widely distributed on abyssal plains are the polymetallic nodules. The nodules are formed either by direct precipitation from ambient bottom seawater (hydrogenetic) and pore water (diagenesis) or a mix of both the processes in various quantities with changing contributions through time (Klinkhammer et al., 1982). Here we focus on more abundant and potentially economic types of mineral deposits such as the hydrogenetic, hydrothermal and diagenetic types of deposits of Fe and Mn.

3.1. Hydrogenetic crusts

Mineral deposits formed on the summit and flanks of seamounts by hydrogenetic processes have Fe and Mn as the major oxide sink with relatively high concentrations of Co (Hein et al., 1992). The hydrogenetic precipitation involves an inorganic colloidal-chemical and surface-chemical process (Usui et al., 1989; Halbach et al., 2008; Glasby et al., 2010). The colloidal precipitation entails the inorganic speciation and the partitioning of hydrated dissolved elements from seawater between Mn oxide and Fe oxyhydroxide phases based on their surface charge. The cations with

positive charge bind strongly to negatively charged MnO₂ surfaces by coulombic electrostatic interactions (Koschinsky and Hein, 2003). On the other hand, negatively charged ions and those ions with neutral and low charge density interact with FeOOH phase by forming specific covalent bonds (Koschinsky and Hein, 2003). The resulting hydrogenetic crusts formed from such an interaction have chemical composition resembling a hydrogenetic group (Mn, Co, Ni), a hydrogenetic/detrital group (Al, Si), and a hydrogenetic/biogenic/detrital group (Ba, Zn, Cu, Ca, P) (Wen et al., 1997; Koschinsky and Hein, 2003). The hydrogenetic crusts occur in topographic heights of open-ocean seamount where the supply of terrigenous, volcanogenic and biogenic components is very low (Usui and Someya, 1997) and also in high bioproductivity or detrital areas along the continental margins (Conrad et al., 2017). Irrespective of the samples tested, the hydrogenetic Fe-Mn crust composition of samples from different geographical locations were found to reflect the ambient seawater composition (Mizell et al., 2020).

The hydrogenetic crusts are characterized by very high porosity (60%), high specific surface area (300 m² g⁻¹) and extremely slow growth rate (1-6 mm/Ma) (Cowen et al., 1993; Koschinsky and Hein, 2003). They occur on any exposed indurated surfaces kept clean of sediments (ridges, hills, plateaus, boulders and seamounts) and have a mean Fe/Mn ratio of 0.7 for open-ocean seamount crusts and 1.2 for continental margin seamount crusts (Hein et al., 1997). The concentration of elements in the Fe-Mn crusts are governed by the metal concentration in seawater, colloid surface charge, degree of oxidation, types of complexing agents, physical properties and growth rates (Li, 1981). The more recent investigations demonstrate that the age of deposits and growth rate are the more fundamental variables that govern the thickness of the crust (Josso et al., 2020). Also, the recent investigations using remotely operated vehicles at tropic seamount demonstrate that thicker crusts are not restricted to a particular depth of the ocean rather occur at almost all depths (Josso et al., 2017; Lusty et al., 2018).

Fe-Mn crusts (and nodules) are dominantly X-ray amorphous. The crystalline phase weight percentage of these minerals accounts for 5-20%. The dominant crystalline mineralogy of hydrogenetic crusts contain the minerals vernadite (δ MnO₂), birnessite (Na₄Mn₁₄O₂₇·9H₂O), ferroxhyte (δ -FeOOH) and todorokite [(Na,Ca,Mn)₂Mn₅O₁₂·3H₂O] wherein ferroxhyte and todorokite are considered as a marker of suboxic alteration/diagenesis associated with phosphatisation (Cronan, 1975; Nath, 2007). Concentrations of Ni and Cu increases with depth in seawater and are more enriched in diagenetically influenced crusts with todorokite as the dominant mineral phase. The mineralogical structure of todorokite favours the incorporation of Ni and Cu when released from partial dissolution of preexisting oxides under suboxic conditions. On the other

hand, Co is more enriched in encrustations on exposed rock surfaces from a shallower depth with δMnO_2 as the dominant mineral phase (Cronan, 1975; Glasby et al., 2010 and the references therein). The higher concentration of Co in shallow seawater, as is Mn which is its main scavenger allows the precipitation of Co in elevated regions. Therefore the shallow crusts are richer in Mn and Co and the deeper ones are richer in Ni and Cu (Mizell et al., 2020). The Co enriched crusts are also found where water masses are most isolated from continental-coastal and where hydrothermal sources of metals are poor (Manheim and Lane-Bostwick, 1988). The hydrothermal vent waters are enriched in Fe and Mn but the ratio of Co: Mn and Co: Mn+Fe in vent fluids and marine hydrothermal oxides are lesser than that of normal ocean waters by a magnitude of two (Manheim and Lane-Bostwick, 1988). Whilst, the hydrothermal fluids are Co-poor as dilution of vent fluid in seawater is extremely rapid and crusts forming close to continental margins have lower Co because of its larger component of detrital material compared to open ocean deposits. The hydrogenetic crusts are therefore found to have higher enrichment of Co and slower growth rate in contrast to hydrothermal crusts having faster growth rate and lesser enrichment of Co.

3.2. *Hydrothermal crusts*

The seafloor hydrothermal activities along the mid-ocean ridges produce plumes with turbidity anomalies for excess suspended particles and high concentrations of dissolved metals (Ray et al., 2020). The massive release of hydrothermal fluid associated with venting may have major implications for chemical flux into the ocean and serve as nutrients for enhanced biological activity (Dick et al., 2013; Dick, 2019; Baumberger et al., 2020). The metal ions derived from active submarine volcanoes precipitate chemically to form metalliferous sediments (Koschinsky and Hein, 2003). Likewise, the hydrothermal deposits formed by the precipitation of elements from hydrothermal fluids are mineral precipitates of Mn-Fe-Si with varying compositions containing pure Mn oxides to almost pure Fe oxides with highly variable concentrations of amorphous silica and/or nontronite (Pelleter et al., 2017). These hydrothermal oxide deposits of Fe or Mn are depleted in REE (Rare Earth Elements), Yttrium and HFSE (High Field Strength Elements) owing to the faster growth rate and higher content of either Fe or Mn oxides (Josso et al., 2017). Besides, the enrichment of transition metals like Ni, Co and Cu could also occur on hydrothermal deposits due to the lack of precipitation of high-temperature metal sulfides, isolation of the hydrothermal system and scavenging ability of birnessite and busserite/todorokite from the aqueous phase (Pelleter et al., 2017). The hydrothermal crustal deposits are formed under conditions of high temperature, depleted salinity, reducing conditions at low pH and elevated Mn and Fe concentrations (Juniper and Tebo, 1995; Murton et al., 2006). They occur in areas with high heat flow such as mid-ocean ridges, mid-

plate submarine rift zones, back-arc basins, hotspot volcanoes, island arcs, inactive ridges and spreading centers (Shterenberg et al., 1990; Hein et al., 1996; Eckhardt et al., 1997; Glasby, 2006). The growth rate of hydrothermal manganese deposits are characterized by high to extremely high growth rates ($>1000 \text{ mm Ma}^{-1}$) and very high Mn/Fe ratio of 10 to 4670 (Usui et al., 1989; Glasby, 2006). The mineral phases are composed of pyrolusite, braunite, bementite, hematite, chlorite, smectite, quartz, anhydrite and todorokite minerals (Mottl, 1983; Jones, 1985). The dominant minerals observed near hydrothermal vents are Fe-oxides (rich in Si and Mn) and Fe-sulfides, together with some sulfates, silicates, and carbonates (Juniper and Tebo, 1995; Glasby, 2006).

3.3. Polymetallic nodules of hydrogenetic and diagenetic origin

The Fe-Mn nodules of hydrogenetic type are formed by the precipitation of elements from near-bottom seawater. They are predominantly found in areas with oxygen-rich waters and low sedimentation. On the other hand, nodules of diagenetic type are formed by oxic and -suboxic diagenesis with elements supplied from sediment pore water (Verlaan and Cronan, 2021 and the references therein). The nodule type formed by oxic process occur in sediments with oxygen $> 5 \mu\text{mol l}^{-1}$ (Hein and Koschinsky, 2014) and sufficient concentrations of labile organic matter (Takematsu et al., 1989). Whereas, the latter type of nodule formed by suboxic diagenesis have Mn/Fe ratio > 30 and occurs in regions with high bioproductivity in surface waters and poor ventilation (ie.) during glacial period in deep waters (Wegorzewski and Kuhn, 2014). Yet the most common type of nodules is the mixed type with hydrogenetic layer exposed to the water column and diagenetic layer buried in the sediments (Halbach and Puteanus, 1988; Verlaan and Cronan, 2021). The nodules of hydrogenetic and diagenetic types differ in their chemical composition and mineralogy (Baturin, 1988; Kuhn et al., 2017). The nodules formed via diagenetic route have relatively higher concentrations of Mn and Cu. On the other hand, nodules of “high grade” from fields between the Clarion and Clipperton fracture zones with an average Fe and Mn content have relatively higher concentrations of Ni (up to 2%) compared to Co (0.5%) (McMurtry, 2001). For a more detailed review on the mean composition of polymetallic nodules from different nodule fields the readers are referred to Hein et al., (2020). Co is known to positively correlate with Fe in diagenetic nodules and with Mn in hydrogenetic nodules (Halbach et al., 1982). The enrichment of Co in nodules inversely relates to the growth rate (Halbach et al., 1983). The diagenetic nodules at times grow at an extreme rate of 168 mm Myr^{-1} (Reyss et al., 1982) in comparison to its usual growth rate of $10\text{-}100 \text{ mm Myr}^{-1}$ frequently reported from the deep-sea (Glasby, 2006). While the hydrogenetic nodules grow at a very slow rate of $1\text{-}5 \text{ mm Myr}^{-1}$ with bottom seawater as the source of metals (Krishnaswami et al., 1982). Diagenetic nodules are porous, light and have an average

specific gravity of about 2.4. Their colour varies from earthy black to brown depending upon the relative Mn and Fe content. On an average, nodules contain 32% Mn-dioxide, 22% Fe-oxides, 19% silicon dioxide and 14% water by weight while other elements like aluminum oxides, calcium and magnesium carbonates, metals like Ni, Co, Cu, Zn and Mo are present in smaller quantities (Mero, 1960). The concentrations of Co of 1.5, 0.91 and 0.56% occur in nodules from the Pacific, Indian and Atlantic Oceans respectively (Hamilton, 1994). The dominant mineral phases of Mn and Fe in nodules are todorokite, vernadite and hydrous iron (Thijssen et al., 1985). Depending on the modes of formation, the diagenetic nodules have high enrichment of Ni in contrast to the higher enrichment of Co in hydrogenetic crust and Mn in hydrothermal crust (Table 1).

4. Formation of metal rich mineral deposits

4.1. Abiogenic mineralization

Abiogenic mineralization involves only inorganic reactions. The chemical and physical forces drive the accumulation of new inorganic ions required for abiogenic mineralization (Wang and Muller, 2010). The circulation pattern of different water masses in regions of influence affect the composition of nutrients and metals required for the formation of crusts on seamount (Schott and McCreary Jr, 2001). Moreover, the continental run-off and aeolian input function as the major contributor of metals to the ocean. This is followed by utilization of metals in different biogeochemical processes. The use of nutrients and its regeneration from localized biological production in the water column supply metals to crusts (Benites et al., 2020). In addition, the elements derived from volcanic activity guide the formation of fall-out deposits proximal to the fluid source. On the other hand, seawater being the sole source of metals for the formation of hydrogenetic crusts precipitates chemically to form oxides of Fe and Mn (Mizell et al., 2020). The mineralization of Fe-Mn crusts could occur depending on the initiation of growth, the magnitude of availability of the inorganic elements and temperature (Persson et al., 1995).

The diagenetic mineralization which represents the abiogenic form of metal precipitation from pore-water occurs by the relatively sudden change in oxidizing conditions in the sedimentary environments (Wilson et al., 1986). This could occur by the progressive burial of newly oxidized deposits of metals formed at the sediment-seawater interface. The continuous biological activity within the sediment consumes oxygen which would lead to suboxic pore-water conditions (Thamdrup, 2000). The suboxic conditions of the pore water then destabilize/reduce the metal oxides leading to the partial or total dissolution and release of reduced metals in pore waters (Tostevin and Poulton, 2019). The upward migration of the pore water by progressive compaction and fluid escape

mechanism on meeting the shallower redox barrier (either as a front, or at surface of pre-existing mineral, e.g. nodules) reprecipitate the reduced cations in the form of oxides (Benites et al., 2020; Versteegh et al., 2021). The regeneration of metals in pore water by the aforementioned mechanisms plays a key role in regulating the chemical composition of the diagenetic crusts and nodules. The oxidation of metals like Fe(II) and Mn(II) at the redox fronts could be affected by pH, redox potential, molecular oxygen and the availability of nitrate (Zhang et al., 2014).

4.2. Biogenic mineralization

Deep sea minerals like Fe-Mn crusts and polymetallic nodules are not only formed by abiogenic (mineralization) routes but also by biogenic mineralization (biomineralization) involving microorganisms (Tebo et al., 1997; Wang and Muller, 2009). Biogenic mineralization develops and proceeds in close association with organic molecules and matrices (Lowenstam and Weiner, 1989). The biogenic mineralization process occur widely and involves the participation of both prokaryotic (bacteria) and eukaryotic (plants, protozoa and metazoa) organisms (Verlaan, 1992; Gilbert et al., 2005). Among the eukaryotes, certain yeasts and yeast-like fungi are found associated with the cold hydrothermal samples and basalt surfaces. Of the different fungal isolates studied by Connell et al., 2009, few isolates were found to produce siderophores and one of the isolates could oxidize manganese. Study of the manganese oxide with fossilized fungal communities on sub-seafloor basalts by electron paramagnetic resonance spectroscopic analyses suggests the biological origin of the botryoidal Mn oxides (Ivarsson et al., 2015). Within the nodules, bacteria with surface S-layers arranged on biofilm like structures initiates Mn deposition (Wang and Muller, 2010). The microbial interactions that aids the formation of mineral aggregates/deposits occurs as an induced (Frankel and Bazylinski, 2003) or a controlled (Bazylinski and Frankel, 2003) process. In the induced mechanism, reactions occur at the interface between organic membranes and their inorganic environment (eg. nodules and crusts). The organic matrix functions as the nucleation platform for the deposition of the mineral followed by physical or chemical forces (Wang and Muller, 2009; Chu et al., 2012). In the controlled mechanism, the biomolecules such as proteins, polysaccharides or glycoproteins control the initiation and growth of the mineral (Konhauser, 2007; Wang and Muller, 2009).

5. Cobalt an essential nutrient and a trace metal

5.1. Sources of cobalt

The sources of Co for human use are primarily obtained from mining and processing of cobalt-bearing ores and secondarily from the recycling of Co-containing materials (Smith and Carson, 1981; Barceloux, 1999). The natural contributor of Co in geologic environment are from

erosion (wind-blown continental dusts), weathering of rocks and soil, seawater spray, volcanoes, forest fires and continental and marine biogenic emissions. Presently, the Co exploited for commercial use is obtained from terrestrial deposits formed primarily by direct crystallization in vein deposits by hydrothermal processes. The important ores of cobalt are cobaltite (CoAsS), linnaeite (Co₃S₄), safflorite (CoAs₂), and skutterudite (CoAs_{3-x}) (Hazen et al., 2017). Significant resources of cobalt that needs further investigation for exploitation and use include the nodules and crusts. Certain encrustation deposits (“cobalt-rich crusts”) in shallow waters contain Co concentrations up to 2.5% (Kim et al., 2006).

5.2. Bacterial requirement of cobalt

Co is typically found in association with Ni in nature and is present in low abundance with respect to Fe. It is required as an essential element in prokaryotes with requirement at higher levels in anaerobes than in aerobes (Santander et al., 1997). The largest groups of enzymes that require Co are the B₁₂ enzymes (Kobayashi and Shimizu, 1999). Besides, eight non-corrin Co containing enzymes have been isolated and characterized. They include methionine aminopeptidase, prolidase, nitrile hydratase, glucose isomerase, methylmalonyl-CoA carboxytransferase, aldehyde decarboxylase, lysine-2,3-aminomutase and bromoperoxidase (Kobayashi and Shimizu, 1999). It is required as an essential part of vitamin B₁₂ or cobalamin synthesis in ruminal microorganisms (McDowell, 2000; Blust, 2012; Eitinger, 2013a) and is also required as an essential element for phytoplankton productivity. Co could substitute for zinc in enzymes required for phytoplankton productivity and forms an essential part of primary production (Maret and Vallee, 1993; Price and Morel, 1990; Intwala et al., 2008). The metal acts as an inducer of nitrate reductase enzyme in organisms growing with nitrate as the sole source of nitrogen (Nicholas et al., 1962). Besides, it plays an important role in the metabolism of *Rhizobia* and its symbiotic relationship with leguminous host (Lowe and Evans, 1962). Thus, the limitation of Co in the natural environment affects not only the biological function of organisms but also the associated processes that drive the key biogeochemical cycles.

5.3. Bacterial oxidation and reduction of cobalt

The geochemical cycling of Co is in part mediated by microbial action (Tebo et al., 1984; Lee and Fischer, 1993; Moffett and Ho, 1996; Taillefert et al., 2002). The direct oxidation of Co(II) to Co(III) by Mn oxidizing microorganisms occur owing to the similarity in redox potential between Co and Mn (Tebo and Lee, 1993; Lee and Tebo, 1994). On the other hand, the indirect oxidation of Co(II) occurs by Mn oxidizing microorganisms through biogenic Mn oxide formation (Murray et al., 2007). The enrichment of Co gets strengthened by adsorption of Co(II) to the vacant sites of the

biogenic Mn oxides (Murray and Dillard, 1979; Hem et al., 1985). Subsequent to adsorption, the fixation of Co takes place through oxidation of Co(II) by Mn(IV). The Co(III) replaces the displaced Mn in the surface of marine manganates (Burns, 1976). On the other hand, several prokaryotes have been shown to couple the oxidation of organic and inorganic molecules to the reduction of Co(III) to Co(II) (Witschel et al., 1999; Blessing et al., 2001; Liu et al., 2002; Roh et al., 2002). The bacterial reduction of $\text{Co}^{\text{III}}\text{EDTA}^-$ has been proposed to couple with the chemical oxidation of $\text{Co}^{\text{II}}\text{EDTA}^{2-}$ by the Mn(IV) oxide mineral pyrolusite resulting in biotic-abiotic cycling between $\text{Co}^{\text{II}}\text{EDTA}^{2-}$ and $\text{Co}^{\text{III}}\text{EDTA}^-$ (Gorby et al., 1998). Studies by Caccavo et al. (1994) and Gorby et al. (1998) state that $\text{Co}^{\text{III}}\text{EDTA}^-$ could serve as terminal electron acceptor for anaerobic respiration in *Shewanella alga* strain BrY and in dissimilatory Fe(III)-reducing bacterium *Geobacter sulfurreducens*. The *Shewanella alga* strain BrY could reduce $\text{Co}^{\text{III}}\text{EDTA}^-$ to $\text{Co}^{\text{II}}\text{EDTA}^{2-}$ enzymatically with a 1:1 stoichiometry (Gorby et al., 1998). The redox potential for $\text{Co}^{\text{III}}\text{EDTA}^- / \text{Co}^{\text{II}}\text{EDTA}^{2-}$ ($E^0 = 129\text{mV}$) is estimated to be great enough to provide energy to support microbial growth with acetate, lactate or H_2 as an electron donor. It is also suggested that soluble CoEDTA complexes could serve as electron shuttles between metal reducing bacteria and Mn(IV) minerals (Gorby et al., 1998). This would diminish the requirement of direct cell contact with the mineral surface in dissimilatory metal reducing bacteria that grows with Mn(IV) oxide as a terminal electron acceptor.

6. Nickel an essential element for few important reactions

6.1. Sources of nickel

Natural weathering of rocks, volcanic activity, forest fires, vegetation and wind-blown dust contributes to Ni distribution in geologic environment which includes rocks, sediment, water, air, soil and life (Iyaka, 2011; Schaumloffel, 2012). Ni is concentrated in the ultramafic and mafic rocks in concentrations of 2000 and 200 mg kg^{-1} respectively (Krauskopf, 1967; Savage, 1995). In igneous rocks, Ni is partitioned into Mg and Fe rich minerals such as olivine, pyroxene, amphibole and spinel. At low temperatures, Ni gets incorporated into a variety of silicates and hydroxides such as smectite clay, sepiolite, talc and brucite (Decarreau, 1985; Savage, 1995). Economically exploitable ore deposits of Ni are the laterites and sulfides containing 1-3% Ni (Mukherjee, 1998). Elevated concentrations of Ni in surface waters may also result from a variety of anthropogenic sources. They include mining, smelting and refining, metal plating and manufacturing, Ni-cadmium battery disposal, and fossil fuel refining and combustion (Stokes, 1981; Nriagu and Pacyna, 1988; Doig and Liber, 2007).

6.2. Bacterial requirement of nickel

Ni is an important trace element required for many prokaryotic microorganisms, certain fungi, algae and plants (Sawers, 2013; Eitinger, 2013b). It is an essential co-factor for a group of metalloenzymes that are primarily involved in energy and nitrogen metabolism, detoxification processes, hydrolysis of urea, uptake and production of hydrogen, methanogenesis, and acetogenesis (Hausinger, 1987; Macomber and Hausinger, 2011; Eitinger, 2013b). The different enzymes that contain Ni are urease, [NiFe] hydrogenase, Ni-superoxide dismutase, carbon monoxide dehydrogenase, acetyl CoA synthase/decarbonylase, acireductone dioxygenase and methyl coenzyme M reductase (Macomber and Hausinger, 2011). The other proteins specifically involved in Ni metabolism are either required for transport of Ni or for its insertion into the prosthetic groups of Ni containing enzymes (Sawers, 2013).

6.3. Bacterial oxidation and reduction of nickel

Studies on the interactions between bacteria and Ni have mostly dealt with the inhibition of microbial activities by divalent nickel ions and the nickel-dependent stimulation of growth and metabolism in microbes (Kaltwasser and Frings, 1980). Biological oxidation of Ni(II) to Ni(III) has not yet been documented. This has been mainly because of the unstable nature of Ni(III) in aqueous medium (Nies, 1999). However, bacteria are found to immobilize soluble Ni [Ni(II)] by intracellular accumulation and precipitation (Hitchcock et al., 2009; Sujith et al., 2010). Intracellular sequestration of Ni into polyphosphate bodies and its compartmentalization at high concentration has also been reported to occur with selected bacterial strains (Sar et al., 2001; Tripathi and Srivastava, 2007). Subsequent to uptake and accumulation of Ni in the cell envelope by bacteria, Ni(II) was precipitated as nickel phosphide and nickel carbide crystals in *Pseudomonas aeruginosa* (Sar et al., 2001). A bacterial isolate oxidizing Mn belonging to *Halomonas* sp also immobilized Ni as nickel phosphide and nickel sulphide (Sujith et al., 2010). Further, studies carried out with *Escherichia coli* expressing an alkaline phosphatase enzyme revealed that nickel is immobilized as a complex with hydrogen uranyl phosphate (Basnakova et al., 1998). Nevertheless, it has been shown recently that bacterial genera belonging to *Pseudomonas* are capable of reducing Ni(II) to elemental Ni under aerobic conditions (Zhan et al., 2012). The bacterium utilized several substrates as electron donors during the bioreduction of divalent Ni. In this organism, Ni(II) has been proposed to serve as an electron acceptor (Zhan et al., 2012). In general the heterotrophic bacteria and others belonging to *Thiobacillus* group of organisms are also known to participate in the reductive leaching of Ni from nickeliferous lateritic ore, natural pentlandite and nickel bearing-pyrrhotite (Sukla and Panchanadikar, 1993; Cwalina et al., 2000; Ke and Li, 2006).

7. *Participation of microbes to the generation of Fe-Mn crusts*

The microbial interactions could be considered vital for the formation of Fe-Mn crusts as microbes are known to interact with the metals by both active and passive mechanisms (Ehrlich and Newmann, 2009). The microbial interactions with metals occur in different metabolic types of bacteria. Among them, the chemolithoautotrophs represent organisms that use CO₂ as the source of carbon and reduced inorganic compounds (H₂, S²⁻, Fe²⁺, NO²⁻, NH⁴⁺ etc.) as the source of energy. The chemolithotrophy can be both aerobic and anaerobic depending on the electron acceptor (Gomez and Amils, 2002). The aerobic chemolithoautotrophs function as primary producers in hydrothermal vent ecosystems and are found either as symbionts or free-living species (Nakamura and Takai, 2014). The chemoautotrophic oxidation of Fe and Mn though not an abundant process compared to sulfur oxidation, occurs widely under aerobic conditions in deep-sea hydrothermal systems. The microbes in that process of metal oxidation use Fe and Mn for the production of biomass (Nakamura and Takai, 2014). Also, the potential energy yield for aerobic oxidation of Fe dictates a direct relationship with Fe(II) concentrations in the hydrothermal fluid. On the other hand, chemoautotrophic bacteria belonging to sulfur-oxidizers use nitrate instead of oxygen as an electron acceptor under anaerobic conditions (Gottschal and Kuenen, 1981) which help different microbes thrive under conditions of alternating supply of substrates.

In addition, a study from the Black Sea reports autotrophic H₂S oxidation coupled to the reduction of MnO₂ by *Sulfurimonas*. The Mn(II) formed from the reduction of MnO₂ were found to precipitate as Ca-rich Mn(II) carbonate [Mn(Ca)CO₃] (Henkel et al., 2019). Despite several studies (Ehrlich, 1976; 1987; Thauer et al., 1977; Myers and Nealson, 1988; Ehrlich and Salerno, 1990) addressed that Mn(II) oxidation could be coupled to energy conservation, more recent experimental investigation with a bacterial isolate *Candidatus Manganitrophus noduliformans* demonstrate that bacteria derive energy from extracellular Mn(II) oxidation and fix CO₂ into cellular biomass (Yu and Leadbetter, 2020). Also, evidences from fossil records identified certain Fe-oxidizing chemoautotrophs with the potential to accumulate intracellular polyphosphate in the process of conserving energy under aerobic conditions and form phosphatic mineral deposits (Crosby et al., 2014). This would help the bacteria adapt to the varying redox conditions in their distinct habitats. Whereas, the chemolithoautotrophic members of ammonia-oxidizing archaea and nitrite-oxidizing bacteria has been found to inhabit the Fe-Mn crust substrates of Rio Grande Rise, south-west Atlantic Ocean (Bergo et al., 2021). Based on the availability of reduced substrates, the microbes associated with the crustal deposits are stated to function as primary producers. In an another study on the weathering of Fe(II) silicate minerals by chemolithotrophic Fe(II) oxidizing bacteria,

Napieralski et al., (2019) pointed out that mineral-derived Fe(II) serve as the primary energy source for microbial growth. Also, an interesting observation on the occurrence of novel chemoautotrophic Fe(II) oxidizing bacterium *Mariprofundus ferrooxydans* on metalliferous deposits at Loihi Seamount (Emerson et al., 2007) evoke the importance of chemoautotrophy in the cycling of iron and carbon in the seamount crusts (Bach and Edwards, 2003). Further, it was observed from our study that the immobilization of metals (Sujith et al., 2011) and autotrophic fixation of carbon could occur at the expense of metals in deep-sea sediments from Central Indian Ocean Basin (Das et al., 2011). The results indicate that chemosynthetic activity could be more widespread in microbial communities and that bacteria could act as bio-seeds in the initiation and growth of polymetallic nodules (Wang and Muller, 2009).

Recent studies also show that distinct microbial communities inhabit different rock coatings with varied composition and mineralogy (Marnocha and Dixon 2014). Geochemical analysis of the crustal composition revealed the occurrence of carbon, nitrogen, sulfur and phosphorous that is microbially derived (Dilek et al., 2008). In concurrence with the geochemical results, culture-independent studies of the cobalt-rich crusts indicated the occurrence of α - and γ -*Proteobacteria* which are ecologically important in Fe and Mn oxidation, sulfur oxidation, marine methane oxidation and utilization of buried organic matter or dissolved inorganic carbon (Nitahara et al. 2011; Sujith et al., 2017a). Besides, ammonia oxidizing archaeal group were also found to dominate the microbial population on crusts (Nitahara et al. 2011).

Cross section of manganese crusts and nodules showed internal microstructures and features resembling microbial entities and coccolithophores (Iyer, 1991; Banakar and Tarkian, 1991; Wang and Muller 2009). The latter has been found to act as bio-seeds for the growth of hydrogenetic crusts and bacteria as bio-seeds for the growth of polymetallic nodules (Wang et al., 2009). Further, evidences based on biomarkers like n-alkanes (n-C₁₈) and nitrogen compounds by GC-MS analysis could relate the occurrence of bacterial mineralization on crusts (Gonzalez et al., 2011). Recent studies by Zhao et al. (2014) also provide supportive evidence for microbial participation wherein the activities of organisms and their derivative organic matter were found to influence the mineralization of cobalt-rich Fe-Mn crusts on seamounts. Intimate association of microbial biofilms with freshly formed Fe(III) and Mn(IV) oxides on basalt surfaces in a hydrothermally influenced setting also provide evidence for microbial initiation of Fe-Mn crust formation (Templeton et al., 2009). The mineralogical characterization of the crusts indicated poorly crystalline and amorphous oxides of Mn with resemblance to oxides produced typically by bacteria (Lowenstam, 1981; Hein et al., 2000). EDS in conjunction with SEM analysis of laboratory incubated Fe-Mn crust samples

showed the exchange of ions, numerous bacterial cells, exopolysaccharides and structures resembling secondary minerals formed by bacteria (Sujith et al., 2014; 2017b). The volcanic hosted hybrid Mn–oxide deposits and Fe-Mn deposits in Lechuguilla and Spider caves also show evidences to support biogenic process in the formation of crusts (Northup et al., 2003; Kiliyas et al., 2007). In the process of interactions the epilithic, endolithic and chemosynthetic members of the crusts benefit from minerals with oxides serving as electron source and reduced metals as energy source (Shock, 2009).

The microbial ability to interact with charged surfaces, ability to carry out reactions at cellular, sub-cellular and molecular levels, participate in oxidation-reduction reactions, potential to facilitate the exchange of ions and their capacity to modify the pH and Eh conditions mediate changes in available reactive chemical species (Silverman and Ehrlich, 1964; Gadd 2009). Also, the larger surface area-volume ratio, potential to tolerate higher concentrations of metals and metabolic flexibility give microbes the ability to survive under wide nutrient regimes (Douglas and Beveridge, 1998). One such example could be the facultative chemolitho(auto)trophs or mixotrophs. They usually grow aerobically, use both organic and inorganic substrates for growth and fix CO₂. They coexist in nature with obligate chemolithoautotrophic bacteria and occasionally oxidize reduced inorganic compounds without conserving energy (Gottschal and Kuenen, 1981). However, the facultative members may have competitive advantage over obligate chemolithoautotrophs in utilizing alternate substrates under nutrient limited growth conditions unlike obligate chemoautotrophic bacteria that grow only on specific substrate.

Metagenomic studies on north-west Pacific seamount Fe-Mn crusts identified the putative genes involved in dissolution and precipitation of Mn besides other genes that are important in C, N and S cycling which implies the role of microbes in the growth of Fe-Mn crusts (Kato et al., 2019). Another studies based on 16S rRNA gene sequencing showed significant difference in microbial community structure between Fe-Mn crusts and seawater (Nitahara et al. 2017) which suggests spatial variability in environmental parameters and difference in sample properties shape the microbial community population structure of different environmental samples. Culturing of bacteria from Fe-Mn crusts in Co amended seawater media showed high tolerance to Co and the capacity to immobilize the metal (Krishnan et al., 2006; Antony et al., 2011). Also, experiments conducted under laboratory conditions with whole crust fragments harboring microbial communities and metals solubilized from crusts in seawater, incubated at ambient temperature and pressure conditions showed that microbes associated with the Fe-Mn crust promote the immobilization of metals compared to that by abiotic processes (Sujith et al., 2017b). In addition, our studies with pure

cultures of Mn oxidizing bacteria from the Carlsberg Ridge in Co (Antony et al., 2011) and Ni (Sujith et al., 2010) amended seawater media showed that immobilization of Co and Ni could be achieved even in the absence of Mn. The results thus re-examines the accepted paradigm that Mn oxidation govern the fate of other elements on Fe-Mn crust surfaces.

Besides, ongoing research evidences indicate that mineral deposits other than Fe-Mn crusts with an abiogenic history also involve the participation of microorganisms. The periodic massive encrustation of microbial biofilms in banded iron formation is evident from the data on well-preserved microbial fossils and chemical analysis (Chi Fru et al., 2013; 2015). Also, experimental approaches to understand the microbial role in Fe-Mn mineral formation could be deduced when evidences similar to Mn precipitation by *Candidatus Manganitrophus noduliformans* (Yu and Leadbetter, 2020), silicate precipitation by *Bacillus subtilis* and calcium phosphate precipitation by *Ramlibacter tataouinensis* are carried out (Urrutia and Beveridge, 1994; Benzerara et al., 2004). Thus the understanding of microbial activity contributing to crust formation could be evident under circumstances when predominant microbial activities are assessed by experiments, tools and techniques that differentiate the chemical from the biological processes (Table 2).

8. Geochemical characteristics of cobalt and nickel

8.1. Cobalt

The name cobalt refers to the German word *kobold*, meaning 'goblin' or 'evil sprite' (Lindsay and Kerr, 2011). It is the 30th most abundant element (Kim et al., 2006; Lindsay and Kerr, 2011) and exists in the oxidation states of +1 to +4. The Co^{2+} has an ionic radius of 0.72Å and an atomic radius of 1.32Å (Young, 1957; Hamilton, 1994). The concentrations of Co have been found to vary with different samples of nodules and crusts (Table 1). Co is precipitated in association with the oxide phases of Fe and Mn and crystalline sediments such as aluminosilicates (Blust, 2012). In most of the sulfide rich marine systems the formation of FeS is kinetically favored since the solubility of FeS is greater than that of CoS (Saito et al., 2003) with hydrothermal fluid concentrations of 14 - 2272 $\mu\text{mol Fe}$ and 0.03 - 0.18 $\mu\text{mol Co}$ (Seyfried Jr et al., 2003). The Co thus incorporates partly within other sulfide phases such as FeS rather than precipitating as CoS (Morse and Arakaki, 1993). In shallow waters, up to 98% of Co are bound to the sediments and suspended particulate matter (Robertson et al., 1973). The Co in its reduced form as Co(II) occurs in different solid phases such as chloro-, sulfato- and carbonato-complexes, whereas Co(III) occurs as hydroxide or oxyhydroxide mineral phases (Ahrland, 1975; Manheim, 1986). The oxidized form of Co includes asbolite ($\text{CoO}\cdot 2\text{MnO}_2\cdot 4\text{H}_2\text{O}$), heterogenite ($\text{CoO}\cdot 2\text{Co}_2\text{O}_3\cdot 6\text{H}_2\text{O}$), sphaerocobaltite (CoCO_3) and

erythrite ($3\text{CoO} \cdot \text{As}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$) (Young, 1957). Being a less siderophilic element the metal shows high affinity for sulfur (Zajic, 1969). Also, because of its strong oxidizing properties, $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ decomposes rapidly in aqueous solution to yield oxygen from the oxidation of water by CoIII (Greenwood and Earnshaw, 1997; Kim et al., 2006).

8.2. Nickel

Ni represents the 7th most abundant transition metal in the Earth's crust (Adriano, 2001). It is closely related to Co in its chemical and biochemical properties and is depleted in surface ocean waters and enriched at depth (Twining et al., 2012). Both Ni and Co show nutrient-like depth profile with minimum concentration at the surface and enriched concentrations at deeper depths due to the biological uptake of metals as micronutrients by phytoplankton at the surface (Saito et al., 2010; Twining et al., 2012). The transition metal Ni typically exists in the Ni(0) and Ni(II) oxidation states although the +I and +III oxidation states could exist under certain conditions. The ionic radius of Ni(II) is 0.69Å and atomic radius is 1.39Å. Ni occurs in its reduced form as Ni^{2+} all through the pH and Eh ranges in most natural waters. Under low pH conditions, more of H^+ ions compete with Ni^{2+} species for adsorption sites on hydrous iron oxides which then leads to the decreased adsorption of Ni. At the same time, with higher pH values between 5 and 6, less number of H^+ ions competes with Ni^{2+} species for adsorption sites on hydrous iron oxides which then leads to the increased adsorption of Ni (Green-Pedersen et al., 1997). Nonetheless, Ni prefers Mn over Fe in adsorption due to the favourable electrochemical interactions and balance (Richter and Theis, 1980; Green-Pedersen et al., 1997). Ni is capable of forming strong complexes with organic ligands and Fe (oxy)hydroxides (Nimmo et al., 1989; Donat et al., 1994; Nieminen et al., 2007; Doig and Liber, 2007) and therefore the bioavailability of Ni may be limited in the natural environment. Depending on oxygen concentrations, Ni exist either as free aqueous species under oxic conditions or as insoluble NiS under anoxic conditions. The metal also exist as stable NiHCO_3^+ , NiCO_3^0 and $\text{Ni}(\text{OH})_2^0$ in alkaline/calcareous waters. In most soils Ni is bound to ion exchange sites or is coprecipitated with aluminium and Fe (oxy)hydroxides (Nieminen et al., 2007).

9. Industrial uses of cobalt and nickel

Co is an economically and environmentally important metal as it forms dense and strong alloys with certain metals and metalloids (Tebo and Lee, 1993). In industries, Co-60 is used as source of gamma radiation for the sterilization of foods and medical materials (Blust, 2012). In chemical form, Co is used as pigments in glass, ceramics and paint industries. It is also used as a catalyst in petroleum refinery and as trace metal additives for agricultural use (Habashi, 2013).

Nickel's economic importance lies in its unique physicochemical characteristics, the most important of which include its strength, high temperature stability, corrosion resistance, malleability, ductility, heat and electrical conductive properties and aesthetic properties (Mukherjee, 1998; Reck et al., 2008; Pyle and Couture, 2012). Metallic nickel and nickel compounds are used in industrial and different commercial applications (Nieminen et al., 2007; Reck et al., 2008; Schaumloffel, 2012; Pyle and Couture, 2012). Besides, they are also used in the preparation of chemicals and several allied products, petroleum refining, metal products, aerospace applications, machinery and many others (Mukherjee, 1998).

10. Summary

The study highlights that microorganisms intrinsic to the Fe-Mn oxide surfaces partake in the accretion process of crusts and nodules not only by serving as catalysts but also by directly participating in the processes of metal enrichment. However, the number of studies in the field that support the claim is very limited and more detailed studies is required to establish the active participation of microbes in the biogenic accretion process. Use of advanced molecular methods, sophisticated analytical tools and interdisciplinary studies would improve our understanding of the geomicrobial processes governing Fe-Mn mineral formation.

Acknowledgements

We thank the Director, National Institute of Oceanography, Goa for the support and facilities. The work is based on the Ph.D thesis entitled "Ecology of metal-microbe interactions in ferromanganese crusts of the Afanasy-Nikitin Seamount" by Sujith P.P. The study was carried out as part of the project "Preliminary exploration of cobalt-rich seamount crusts in the northern Indian Ocean" funded by the Ministry of Earth Sciences (Government of India). SPP acknowledges the Council of Scientific and Industrial Research, New Delhi-India, for the award of Senior Research Fellowship. This manuscript has NIO contribution No xxxx.

References

- Adriano, D.C., 2001. Trace Elements in Terrestrial Environments. Springer, New York.
- Ahrland, S., 1975. Metal complexes in seawater. In: Goldberg, E. D. (Ed.), Dahlem workshop on the nature of seawater. Dahlem Konferenzen, Abakon Verlagsgesellschaft, Berlin, pp. 219-244.
- Aiking, H., Stijnman, A., Garderen, C.V., Heerikhuizen, H.V., Riet, J.V., 1984. Inorganic phosphate accumulation and cadmium detoxification in *Klebsiella aerogenes* NCTC 418 growing in continuous culture. Appl. Environ. Microbiol. 47, 374-377.

- Antony, R., Sujith P.P., Fernandes, S.O., Verma, P., Khedekar, V.D., LokaBharathi, P.A., 2011. Cobalt Immobilization by Manganese Oxidizing Bacteria from the Indian Ridge System. *Curr. Microbiol.* 62: 840-849.
- Ayala-Torres, C., Hernandez, N., Galeano, A., Novoa-Aponte, L., Soto, C-Y., 2014. Zeta potential as a measure of the surface charge of mycobacterial cells. *Ann. Microbiol.* 64, 1189-1195.
- Bach, W., Edwards, K., 2003. Iron and sulphide oxidation within the basaltic ocean crust: implications for chemolithoautotrophic microbial biomass production. *Geochim. Cosmochim. Acta* 67, 3871-3887.
- Banakar, V.K., Hein, J.R., Rajani, R.P., Chodankar, A.R., 2007. Platinum group elements and gold in ferromanganese crusts from Afanasiy–Nikitin seamount, equatorial Indian Ocean: Sources and fractionation. *J. Earth Syst. Sci.* 116, 3-13.
- Banakar, V.K., Tarkian, M., 1991. Genesis and growth of internal microstructures of manganese nodule. *Indian J. Mar. Sci.* 20, 20-24.
- Banerjee, R., Iyer, S.D., 1991. Biogenic influence on the growth of ferromanganese micronodules in the Central Indian Basin. *Mar. Geol.* 97, 413-421.
- Barceloux, D.G. 1999. Cobalt. *Clin. Toxicol.* 37: 201-216.
- Basnakova, G., Finlay, J.A., Macaskie, L.E., 1998. Nickel accumulation by immobilized biofilm of *Citrobacter* sp. containing cell-bound polycrystalline hydrogen uranyl phosphate. *Biotechnol. Lett.* 20, 949-952.
- Baturin, G. N ., 1988. *Geochemistry of manganese and manganese nodules in the Ocean.* Springer, Netherlands, 356p.
- Baumberger, T., Lilley, M.D., Lupton, J.E., Baker, E.T., Resing, J.A., Buck, N.J., Walker, S.L., Fruh-Green, G.L., 2020. Dissolved Gas and Metal Composition of Hydrothermal Plumes from a 2008 Submarine Eruption on the Northeast Lau Spreading Center. *Front. Mar. Sci.* <https://doi.org/10.3389/fmars.2020.00171>.
- Bazylinski, D.A., Frankel, R.B., 2003. Biologically controlled mineralization in Prokaryotes. *Rev. Mineral. Geochem.* 54, 217-247.
- Benites, M., Hein, J.R., Mizell, K., Blackburn, T., Jovane, L., 2020. Genesis and Evolution of Ferromanganese Crusts from the Summit of Rio Grande Rise, Southwest Atlantic Ocean. *Minerals* 10, 349; doi:10.3390/min10040349.
- Benzerara, K., Menguy, N., Guyot, F., Skouri, F., de Luca, G., Barakat, M., Heulin, T., 2004. Biologically controlled precipitation of calcium phosphate by *Ramlibacter tataouinensis*. *Earth Planet. Sci. Lett.* 228, 439-449.
- Bergo, N.M., Bendia, A.G., Ferreira, J.C.N., Murton, B.J., Brandini, F.P., Pellizari, V.H., 2021. Microbial Diversity of Deep-Sea Ferromanganese Crust Field in the Rio Grande Rise, Southwestern Atlantic Ocean. *Microb. Ecol.* <https://doi.org/10.1007/s00248-020-01670-y>.

- Beveridge, T.J., Hughes, M.N., Lee, H., Leung, K.T., Poole, R.K., Savvaidis, I., Silver, S., Trevors, J.T., 1997. Metal-microbe interactions: contemporary approaches. *Adv. Microb. Physiol.* 38, 198-243.
- Blessing, T.C., Wielinga, B.W., Morra, M.J., Fendorf, S., 2001. $\text{Co}^{\text{III}}\text{EDTA}^-$ reduction by *Desulfovibrio vulgaris* and propagation of reactions involving dissolved sulfide and polysulfides. *Environ. Sci. Technol.* 35, 1599-1603.
- Blothe, M., Wegorzewski, A., Müller, C., Simon, F., Kuhn, T., Schippers, A., 2015. Manganese-Cycling Microbial Communities Inside Deep-Sea Manganese Nodules. *Environ. Sci. Technol.* 49, 7692–7700.
- Blust, R., 2012. Cobalt. In: Wood, C.M., Farrell, A.P., Brauner, C.J. (Eds.), *Fish Physiology: Homeostasis and toxicology of essential metals*. Elsevier Inc, pp. 291-326.
- Burns, R.G., 1976. The uptake of cobalt into Fe-Mn nodules, soils, and synthetic manganese (IV) oxides. *Geochim. Cosmochim. Acta.* 40, 95-102.
- Caccavo, F., Lonergan, D.J., Lovley, D.R., Davis, M., Stolz, J.F., McInerney, M.J., 1994. *Geobacter sulfurreducens* sp.-nov., a hydrogen and acetate-oxidizing dissimilatory metal-reducing microorganism. *Appl. Environ. Microbiol.* 60, 3752-3759.
- Callender, E., Bowser, C.J., 1976. Freshwater ferromanganese deposits. In: Wolf, K.H. (Ed.), *Handbook of Strata-Bound and Stratiform ore deposits*. Amsterdam, Elsevier, pp. 341-394.
- Chi Fru, E., Ivarsson, M., Kiliyas, S. P., Bengtson, S., Belivanova V., Marone F., Fortin D., Broman, C., Stampanoni, M., 2013. Fossilized iron bacteria reveal a pathway to the biological origin of banded iron formation. *Nat. Commun.* 4, 2050.
- Chi Fru, E., Ivarsson, M., Kiliyas, S. P., Frings, P. J., Hemmingsson, C., Broman, C., Bengtson, S., Chatzitheodoridis, E., 2015. Biogenicity of an Early Quaternary iron formation, Milos Island, Greece. *Geobiology* 13, 225–244.
- Chu, J., Stabnikov, V., Ivanov, V., 2012. Microbially induced calcium carbonate precipitation on surface or in the bulk of soil. *Geomicrobiol. J.* 29, 544-549.
- Connell, L., Barrett, A., Templeton, A., Staudigel, H., 2009. Fungal diversity associated with an active deep sea volcano: Vailulu'u Seamount, Samoa. *Geomicrobiol. J.* 26, 597-605.
- Conrad, T., Hein, J.R., Paytan, A., Clague, D.A., 2017. Formation of Fe-Mn crusts within a continental margin environment. *Ore Geol. Rev.* 87, 25-40.
- Cowen, J.P., de Carlo, E.H., McGee, D.L., 1993. Calcareous nannofossil biostratigraphic dating of a Fe-Mn crust from Schumann Seamount. *Mar. Geol.* 115, 289-306.
- Cronan, D.S., 1975. Manganese nodules and other Fe-Mn oxide deposits from the Atlantic Ocean. *J. Geophys. Res.* 80, 3831-3837.
- Crosby, C.H., Bailey, J.V., Sharma, M., 2014. Fossil evidence of iron-oxidizing chemolithotrophy linked to phosphogenesis in the wake of the Great Oxidation Event. *Geology* 42, 1015–1018.

- Cwalina, B., Fischer, H., Ledakowicz, S., 2000. Bacterial leaching of nickel and cobalt from pentlandite. *Physicochem. Probl. Miner. Process.* 34, 17-24.
- Das, A., Sujith, P.P., Mourya, B.S., Biche, S.U., Loka Bharathi, P.A., 2011. Chemosynthetic activity prevails in deep-sea sediments of Central Indian Basin. *Extremophiles* 15, 177-189.
- Dean, W.E., Ghosh, S.K., 1981. Geochemistry of freshwater ferromanganese deposits in North America. In: Varentsov, I.M., Grasselly, G.Y. (Eds.), *Geology and Geochemistry of Manganese*. Hungarian Academy of Sciences, Budapest, pp. 256-277.
- Decarreau, A., 1985. Partitioning of divalent transition elements between octahedral sheets of trioctahedral smectites and water. *Geochim. Cosmochim. Acta* 49, 1537-1544.
- Krauskopf, K.B., 1967. *Introduction to Geochemistry*. McGraw-Hill Book Co., New York, 721 p.
- D'Hondt, S., Rutherford, S., Spivack, A.J., 2002. Metabolic activity of subsurface life in deep-sea sediments. *Science* 295, 2067-2070.
- Dick, G. J., 2019. The microbiomes of deep-sea hydrothermal vents: distributed globally, shaped locally. *Nat. Rev. Microbiol.* 17, 271–283.
- Dick, G. J., Anantharaman, K., Baker, B. J., Li, M., Reed, D. C., and Sheik, C. S. 2013. The microbiology of deep-sea hydrothermal vent plumes: ecological and biogeographic linkages to seafloor and water column habitats. *Front. Microbiol.* 4:124. doi: 10.3389/fmicb.2013.00124.
- Dilek, Y., Furnes, Y., Muehlenbachs, K., 2008. *Links Between Geological Processes, Microbial Activities & Evolution of Life*. Springer, 337p.
- Doig, L.E., Liber, K., 2007. Nickel speciation in the presence of different sources and fractions of dissolved organic matter. *Ecotoxicol. Environ. Saf.* 66, 169-177.
- Donat, J.R., Lao, K.A., Bruland, K.W., 1994. Speciation of dissolved copper and nickel in South San Francisco Bay: a multi-method approach. *Anal. Chim. Acta.* 284, 547-571.
- Dong, H., 2010. Mineral-microbe interactions: a review. *Front. Earth Sci. China* 4, 127-147.
- Douglas, S., Beveridge, T.J., 1998. Mineral formation by bacteria in natural microbial communities. *FEMS Microbiol. Ecol.* 26, 79-88.
- Doyle, R.J., 1989. How cell walls of gram-positive bacteria interact with metal ions. In: Beveridge, T.J., Doyle, R.J. (Eds.), *Metal Ions and Bacteria*. Wiley, New York, pp. 275-293.
- Dugan, P.R., Macmillan, C.B., Pfister, R.M., 1970. Aerobic heterotrophic bacteria indigenous to pH 2.8 acid mine water: predominant slime-producing bacteria in acid streamers. *J. Bacteriol.* 101, 982-988.
- Eckhardt, J.D., Glasby, G.P., Puchelt, H., Berner, Z., 1997. Hydrothermal manganese crusts from Enareta and Palinuro seamounts in the Tyrrhenian Sea. *Mar. Georesour. Geotechnol.* 15, 175-209.
- Edwards, K.J., Bach, W., McCollom, T.M., 2005. Geomicrobiology in oceanography: microbe-mineral interactions at and below the seafloor. *Trends Microbiol.* 13, 449-456.

- Ehrlich, H.L., 1975. The formation of ores in the sedimentary environment of the deep-sea with microbial participation: the case for ferromanganese concretions. *Soil Sci.* 119, 36-41.
- Ehrlich, H.L., 1976. Manganese as an energy source for bacteria. In: Nriagu, J.O. (Ed.), *Environmental biogeochemistry*. Ann Arbor Science, Michigan, pp. 633–644.
- Ehrlich, H.L., 1987. Manganese oxide reduction as a form of anaerobic respiration. *Geomicrobiol. J.* 5, 423–431.
- Ehrlich, H.L., Newman, D.K., 2009. *Geomicrobiology*. Taylor and Francis Group, CRC Press, Boca Raton, USA.
- Ehrlich, H.L., Salerno, J.C., 1990. Energy coupling in Mn²⁺ oxidation by a marine bacterium. *Arch. Microbiol.* 154, 12–17.
- Eitinger, T., 2013a. Cobalt transporters. In: Uversky, V.N., Kretsinger, R.H., Permyakov, E.A. (Eds.), *Encyclopedia of Metalloproteins*. Springer, pp. 678-682.
- Eitinger, T., 2013b. Nickel transporters. In: Uversky, V.N., Kretsinger, R.H., Permyakov, E.A. (Eds.), *Encyclopedia of Metalloproteins*. Springer, pp. 1515-1519.
- Eitinger, T., Suhr, J., Moore, L., Smith, J.A.C., 2005. Secondary transporters for nickel and cobalt ions: Theme and variations. *BioMetals* 18, 399-405.
- Emerson, D., Moyer, C.L., 2010. Microbiology of seamounts: Common patterns observed in community structure. *Oceanography* 23, 148-163.
- Emerson, D., Rentz, J.A., Lilburn, T.G., Davis, R.E., Aldrich, H., Chan, C., Moyer, C.L., 2007. A novel lineage of Proteobacteria involved in formation of marine Fe-oxidizing microbial mat communities. *PLoS ONE* 2, e667.
- Emerson, S., Kalthorn, S., Jacobs, L., Tebo, B.M., Nealson, K.H., Rosson, R.A., 1982. Environmental oxidation rate of manganese(II): bacterial catalysis. *Geochim. Cosmochim. Acta* 46, 1073-1079.
- Ferris, F.G., 1989. Metallic ion interactions with the outer membrane of gram-negative bacteria. In: Beveridge, T.J., Doyle, R.J. (Eds.), *Metal Ions and Bacteria*. Wiley, New York, pp. 295-323.
- Ford, T., Ryan, D., 1995. Toxic metals in aquatic ecosystems: A microbiological perspective. *Environ. Health. Persp.* 103, 25-28.
- Frankel, R.B., Bazylinski, D.A., 2003. Biologically induced mineralization by bacteria. *Rev. Mineral. Geochem.* 54, 95-114.
- Gadd, G.M., 1990. Heavy metal accumulation by bacteria and other microorganisms. *Experientia* 46, 834-840.
- Gadd, G.M., 2009. Heavy Metal Pollutants: Environmental and Biotechnological Aspects. In: Schaechter, M. (Ed.), *Encyclopedia of Microbiology*. Elsevier Inc., pp. 321-334.
- Ghiorse, W.C., 1984. Biology of iron- and manganese-depositing bacteria. *Ann. Rev. Microbiol.* 38, 515-550.

- Gilbert, P.U.P.A., Abrecht, M., Frazer, B.H., 2005. The organic–mineral interface in biominerals. *Rev. Mineral. Geochem.* 59, 157-85.
- Glasauer, S., Langley, S., Beveridge, T.J., 2004. Intracellular manganese granules formed by a subsurface bacterium. *Environ. Microbiol.* 6, 1042-1048.
- Glasby, G.P., 2006. Manganese: predominant role of nodules and crusts. In: Schulz, H.D., Zabel, M. (Eds.), *Marine Geochemistry*. Springer, Berlin-Heidelberg, pp. 371-427.
- Glasby, G.P., Mountain, B., Vineesh, T.C., Banakar, V.K., Rajani, R., Ren, X., 2010. Role of hydrology in the formation of Co-rich Mn crusts from the Equatorial N Pacific, Equatorial S Indian Ocean and the NE Atlantic Ocean. *Resour. Geol.* 60, 165-177.
- Godwin, C.M., Zehnpfennig, J.R., Learman, D.R., 2020. Biotic and Abiotic Mechanisms of Manganese (II) Oxidation in Lake Erie. *Front. Environ. Sci.* 8, 57. doi: 10.3389/fenvs.2020.00057.
- Gomez, F., Amils, R. 2002. Evolution of microbial energy conservation: from chemolithotrophy to photosynthesis. In: Montesinos, B., Gimenez, A., Guinan, E.F. (Eds.), *The evolving Sun and its influence on planetary environments*, Astronomical society of the Pacific 269, 217-225.
- Gonzalez, F. J., Somoza, L., Maldonado, A., Torres, T., Ortiz, J. E., 2011. Microbial induced mineralization in Co-rich ferromanganese crusts from the Scotia Sea. *Mineralogical Magazine* 75, 933.
- Gonzalez, H., Jensen, T.E., 1998. Nickel sequestering by polyphosphate bodies in *Staphylococcus aureus*. *Microbios* 93, 179-85.
- Gorby, Y., Caccavo, F.J.R., Bolton, H.J.R., 1998. Microbial Reduction of Cobalt^{III}EDTA- in the Presence and Absence of Manganese(IV) Oxide. *Environ. Sci. Technol.* 32, 244-250.
- Gottschal, J.C, Kuenen, J.G.1981.Physiological and ecological significance of facultative chemolithotrophy and mixotrophy in chemolithotrophic bacteria. In: *Microbial growth on C1 compounds; proceedings of the third international symposium*, Sheffield, pp. 92-104.
- Green-Pedersen, H., Jensen, B.T., Pind, N., 1997. Nickel adsorption on MnO₂, Fe(OH)₃, montmorillonite, humic acid and calcite: a comparative study. *Environ. Technol.* 18, 807-815.
- Greenwood, N.N., Earnshaw, A., 1997. *Chemistry of the elements*, Elsevier Ltd.
- Habashi, F., 2013. Cobalt: Physical and Chemical Properties. In: Uversky, V.N., Kretsinger, R.H., Permyakov, E.A. (Eds.), *Encyclopedia of Metalloproteins*, Springer, New York; doi: 10.1007/978-1-4614-1533-6.
- Haferburg, G., Kothe, E., 2007. Microbes and metals: interactions in the environment. *J. Basic Microbiol.* 47, 453-467.
- Halbach, P., Giovanoli, R., von Borstel, D., 1982. Geochemical processes controlling the relationship between Co, Mn, and Fe in early diagenetic deep-sea nodules. *Earth Planet. Sci. Lett.* 60, 226-236.

- Halbach, P., Puteanus, D., 1988. The Manganese Nodule Belt of the Pacific, Geochemical trends of different genetic types of nodules and crusts, In: Halbach P., Friedrich G., von Stackelberg U. (Eds.), (Enke, Stuttgart), pp 61–69.
- Halbach, P., Schwarz-Schampera, U., Marbler, H., 2008. Platinum and some other trace metals in ferromanganese crusts- geochemical models to explain contradictions. In: *Marine Minerals: Technological Solutions and Environmental Challenges*. University of Mississippi, Oxford, USA, p. 1-6.
- Halbach, P., Segl, M., Puteanus, D., Mangini, A., 1983. Co-fluxes and growth rates in Fe-Mn deposits from central Pacific seamount areas. *Nature* 304, 716-719.
- Hamilton, E.I., 1994. The geobiochemistry of cobalt. *Sci. Total. Environ.* 150, 7-39.
- Hausinger, R.P., 1987. Nickel utilization by microorganisms. *Microbiol. Rev.* 51, 22-42.
- Hazen, R.M., Hystad, G., Golden, J.J., Hummer, D.R., Liu, C., Downs, R.T., Morrison, S.M., Ralph, J., Grew, E.S., 2017. Cobalt mineral ecology. *Am. Mineral.* 102, 108-116.
- Hein, J.R., Conrad, T.A., Staudigel, H., 2010. Seamount mineral deposits: a source of rare metals for high-technology industries. *Oceanography* 23, 184-189.
- Hein, J.R., Gibbs, A.E., Clague, D.A., Torresan, M., 1996. Hydrothermal mineralization along submarine rift zones, Hawaii. *Mar. Georesour. Geotechnol.* 14, 177-203.
- Hein, J.R., Koschinsky, A., 2014. Deep Ocean Ferromanganese Crusts and Nodules. In: Scott, S (Ed.), *Treatise on Geochemistry*. Elsevier Ltd, pp. 273-291.
- Hein, J.R., Koschinsky, A., Bau, M., Manheim, F.T., Kang, J.K., Roberts, L., 2000. Cobalt-rich ferromanganese crusts in the Pacific. In: Cronan, D.S. (Ed.), *Handbook of marine mineral deposits*. CRC Press, New York, pp. 239–280.
- Hein, J.R., Koschinsky, A., Halbach, P., Manheim, F.T., Bau, M., Kang, J.K., Lubick, N., 1997. Iron and manganese oxide mineralization in the Pacific. *Geol. Soc. London Spl. Pub.* 119, 123-138.
- Hein, J.R., Koschinsky, A., Kuhn, T., 2020. Deep-ocean polymetallic nodules as a resource for critical materials. *Nat. Rev. Earth Environ.* 1, 158–169.
- Hein, J.R., Schulz, M.S., Gein, L.M., 1992. Central Pacific cobalt rich Fe-Mn crusts: historical perspective and regional variability. In: Keating, B.H., Bolton, B.R. (Eds.), *Geology and Offshore Mineral Resources of the Central Pacific Basin*, Circum-Pacific Council for Energy and Mineral Resources. Springer, New York, pp. 261-283.
- Hem, J.D., Robertson, C.E., Lind, C.J., 1985. Thermodynamic stability of CoOOH and its coprecipitation with manganese. *Geochim. Cosmochim. Acta.* 49, 801-810.
- Henkel, J.V., Dellwig, O., Pollehne, F., Herlemann, D.P.R., Leipe, T., Schulz-Vogt, H.N., 2019. A bacterial isolate from the Black Sea oxidizes sulfide with manganese(IV) oxide. *Proc. Natl. Acad. Sci.* 116, 12153-12155.

- Hitchcock, A.P., Dynes, J.J., Lawrence, J.R., Obst, M., Swerhone, G.D., Korber, D.R., Leppard, G.G., 2009. Soft X-ray spectromicroscopy of nickel sorption in a natural river biofilm. *Geobiology* 7, 432-453.
- Holden, J.F., Adams, M.W.W., 2003. Microbe–metal interactions in marine hydrothermal environments. *Curr. Opin. Chem. Biol.* 7, 160-165.
- Iibert, M., Bonnefoy, V., 2013. Insight into the evolution of the iron oxidation pathways. *Biochim. Biophys. Acta* 1827: 161-175.
- Inagaki, F., Nakagawa, S., 2008. Spatial distribution of the seafloor life: diversity and biogeography. In: Dilek, Y., Furnes, H., Muehlenbachs, K. (Eds.), *Links between geological processes, microbial activities and evolution of life*. Springer Publications, UK, pp. 135-158.
- Intwala, A., Patey, T.D., Polet, D.M., Twiss, M.R., 2008. Nutritive Substitution of Zinc by Cadmium and Cobalt in Phytoplankton Isolated from the Lower Great Lakes. *J. Great Lakes Res.* 34, 1-11.
- Ivarsson, M., Broman, C., Gustafsson, H., Holm, N.G., 2015. Biogenic Mn-Oxides in Seafloor Basalts. *PLoS One* 10: e0128863.
- Iyaka, Y.A., 2011. Nickel in soils: A review of its distribution and impacts. *Sci. Res. Essays* 6, 6774-6777.
- Iyer, S. D., 1991. Comparison of internal features and microchemistry of ferromanganese crusts from the Central Indian Basin. *Geo-Mar. Lett.* 11, 44-50.
- Jahnke, R.A., Emerson, S.R., Roe, K.K., Burnett, W.C., 1983. The present day formation of apatite in Mexican continental margin sediments. *Geochim. Cosmochim. Acta* 47, 259-266.
- Jones, T.S., 1985. Manganese. In: *Mineral facts and problems*. Bureau of Mines Bull 675, US Department of the Interior, Washington, DC, pp. 483-497.
- Josso, P., Lusty, P., Chenery, S., Murton, B., 2021. Controls on metal enrichment in ferromanganese crusts: temporal changes in oceanic metal flux or phosphatisation? *Geochim. Cosmochim. Acta* doi: <https://doi.org/10.1016/j.gca.2021.06.002>
- Josso, P., Pelleter, E., Pourret, O., Fouquet, Y., Etoubleau, J., Cheron, S., Bollinger, C., 2017. A New Discrimination Scheme for Oceanic Ferromanganese Deposits using High Field Strength and Rare Earth Elements. *Ore Geol. Rev.* 87, 3-15.
- Juniper, S.K., Tebo, B.M., 1995. Microbe-metal interactions and mineral deposition at hydrothermal vents. In: Karl, D.M. (Ed.), *The Microbiology of Deep-Sea Hydrothermal Vents*. CRC Press, New York, p. 219–253.
- Kaltwasser, H., Frings, W., 1980. Transport and metabolism of nickel in microorganisms. In: Nriagu, J.O. (Ed.), *Nickel in the Environment*. Wiley, New York, p. 463-491.
- Kato, S., Hirai, M., Ohkuma, M., Suzuki, K., 2019. Microbial metabolisms in an abyssal ferromanganese crust from the Takuyo-Daigo Seamount as revealed by metagenomics. *PLoS One* 14, e0224888.

- Kato, S., Okumura, T., Uematsu, K., Hirai, M., Iijima, K., Usui, A., Suzuki, K. 2018. Heterogeneity of Microbial Communities on Deep-Sea Ferromanganese Crusts in the Takuyo-Daigo Seamount. *Microbes Environ.* 33, 366-377.
- Ke, J., Li, H., 2006. Bacterial leaching of nickel-bearing pyrrhotite. *Hydrometallurgy* 82, 172-175.
- Keasling, J.D., 1997. Regulation of intracellular toxic metals and other cations by hydrolysis of polyphosphate. *Ann. NY. Acad. Sci.* 829, 242-249.
- Kiliyas, S. P., Detsi, K., Godelitsas, A., Typas, M., Naden, J., Marantos, Y., 2007. Evidence of Mn-oxide biomineralization, Vani Mn deposit, Milos, Greece. In: Andrew, C.J. (Ed.), *Digging deeper: proceedings of the ninth biennial Meeting of the Society for Geology Applied to Mineral Deposits*. Irish Association of Economic Geologists, Dublin, Ireland, pp. 1069–1072.
- Kim, J.H., Gibb, H.J., Howe, P.D., 2006. Cobalt and inorganic cobalt compounds. In: *Concise International Chemical Assessment Document 69*. The International Labour Organization and the World Health Organization, 94 p.
- Klinkhammer, G., Heggie, D. T., Graham, D. W., 1982. Metal diagenesis in oxic marine sediments. *Earth Planet Sci. Lett.* 61, 211-219.
- Kobayashi, M., Shimizu, S., 1999. Cobalt proteins. *Eur. J. Biochem.* 261, 1-9.
- Komeda, H., Kobayashi, M., Shimizu, S., 1997. A novel transporter involved in cobalt uptake. *Proc. Natl. Acad. Sci. USA.* 94, 36-41.
- Konhauser, K., 2007. Biomineralization. In: *Introduction to geomicrobiology*. Blackwell Science Ltd, USA, pp. 139-191.
- Koschinsky, A., Halbach, P., 1995. Sequential leaching of marine ferromanganese precipitates: Genetic implications. *Geochim. Cosmochim. Acta* 59, 5113-5132.
- Koschinsky, A., Hein, J.R., 2003. Uptake of elements from seawater by Fe-Mn crusts: solid-phase associations and seawater speciation. *Mar. Geol.* 198, 331-351.
- Krishnan, K.P., Fernandes, C.E.G., Fernandes, S.O., Loka Bharathi, P.A., 2006. Tolerance and immobilization of cobalt by some bacteria from ferromanganese crusts of the Afanasiy Nikitin Seamounts. *Geomicrobiol. J.* 23, 31-36.
- Krishnaswami, S., Mangini, A., Thomas, J.H., Sharma, P., Cochran, J.K., Turekian, K.K., Parker, P.D., 1982. ¹⁰Be and Th isotopes in manganese nodules and adjacent sediments: nodule growth histories and nuclide behaviour. *Earth Planet Sci. Lett.* 59, 217-234.
- Kuhn T., Wegorzewski A., Rühlemann C., Vink A., 2017. Composition, Formation, and Occurrence of Polymetallic Nodules. In: Sharma, R. (Eds.), *Deep-Sea Mining*. Springer, Cham. https://doi.org/10.1007/978-3-319-52557-0_2.
- Kurek, E., Francis, A.J., Bollag, J-M., 1991. Immobilization of cadmium by microbial extracellular products. *Arch. Environ. Contam. Toxicol.* 20, 106-111.

- Learman, D.R., Wankel, S.D., Webb, S.M., Martinez, N., Madden, A.S., Hansel, C.M., 2011. Coupled biotic-abiotic Mn(II) oxidation path way mediates the formation and structural evolution of biogenic Mn oxides. *Geochim. Cosmochim. Acta* 75, 6048–6063.
- Lee, B.-G., Fisher, N.S., 1993. Microbially mediated cobalt oxidation in seawater revealed by radiotracer experiments. *Limnol. Oceanogr.* 38,1593-1602.
- Lee, Y., Tebo, B.M., 1994. Cobalt(II) oxidation by the marine manganese(II)-oxidizing *Bacillus* sp. strain SG-1. *Appl. Environ. Microbiol.* 60, 2949-2957.
- Li, Y.-H., 1981. Ultimate removal mechanisms of elements from the ocean. *Geochim. Cosmochim. Acta.* 45, 1659-1664.
- Lindsay, D., Kerr, W., 2011. Cobalt close-up. *Nature Chem.* 3, 494.
- Liu, C., Gorby, Y.A., Zachara, J.M., Fredrickson, J.K., Brown, C.F., 2002. Reduction kinetics of Fe(III), Co(III), U(VI), Cr(VI), and Tc(VII) in cultures of dissimilatory metal-reducing bacteria. *Biotechnol. Bioeng.* 80, 637-649.
- Lowe, R.H., Evans, H.J., 1962. Cobalt requirement for the growth of *Rhizobia*. *J. Bacteriol.* 83, 210-212.
- Lowenstam, H. A., 1981. Minerals formed by organisms. *Science* 211, 1126-1131.
- Lowenstam, H.A., Weiner, S., 1989. *On Biomineralization*. Oxford University Press, New York.
- Lusty, P.A., Hein, J.R., Josso, P., 2018. Formation and Occurrence of Ferromanganese Crusts: Earth's Storehouse for Critical Metals. *Elements* 14, 313–318.
- Macomber, L., Hausinger, R.P., 2011. Mechanisms of nickel toxicity in microorganisms. *Metallomics* 3, 1153-1162.
- Manheim, F.T., 1986. Marine cobalt resources. *Science* 232, 600-608.
- Manheim, F.T., Lane-Bostwick, C.M., 1988. Cobalt in ferromanganese crusts as a monitor of hydrothermal discharge on the Pacific sea floor. *Nature* 335, 59-62.
- Maret, W., Vallee, B.L., 1993. Cobalt as probe and label of proteins. *Methods Enzymol.* 226, 52-71.
- Marnocha, C. L., Dixon, J. C., 2014. Endolithic bacterial communities in rock coatings from Karkevagge, Swedish Lapland. *FEMS. Microbiol. Ecol.* 90, 533-542.
- Mascarenhas-Pereira, M.B.L., Nath, B.N., Borole, D.V., Gupta, S.M., 2006. Nature, source and composition of volcanic ash in sediments from a fracture zone trace of Rodriguez Triple Junction in the Central Indian Basin. *Mar. Geol.* 229, 79-90.
- McDowell, L.R., 2000. Vitamin B12. In: *Vitamins in Animal and Human Nutrition*. Iowa State Press, Ames, pp. 523-563.
- McMurtry, G. M., 2001. Authigenic deposits. In: Steele, J.H., Thorpe, S.A., Turekian, K.K. (Eds.), *Marine Chemistry and Geochemistry*. Academic Press, London, UK, pp. 325-335.

- Melton, E., Swanner, E., Behrens, S., Schmidt C., Kappler, A., 2014. The interplay of microbially mediated and abiotic reactions in the biogeochemical Fe cycle. *Nat. Rev. Microbiol.* 12, 797–808.
- Mero, J.L., 1960. Minerals on the ocean floor. *Sci. Am.* 203, 64-72.
- Mizell, K., Hein, J.R., Lam, P.J., Koppers, A.A.P., Staudigel, H., 2020. Geographic and oceanographic influences on ferromanganese crust composition along a Pacific Ocean meridional transect, 14 N to 14S. *Geochemistry, Geophysics, Geosystems*, 21, e2019GC008716.
- Moffett, J.W., Ho, J., 1996. Oxidation of cobalt and manganese in seawater via a common microbially catalyzed pathway. *Geochim. Cosmochim. Acta*, 60: 3415-3424.
- Molari, M., Janssen, F., Vonnahme, T.R., Wenzhöfer, F., Boetius, A., 2020. The contribution of microbial communities in polymetallic nodules to the diversity of the deep-sea microbiome of the Peru Basin (4130–4198 m depth). *Biogeosciences* 17, 3203–3222.
- Morgan, B., Lahav, O., 2007. The effect of pH on the kinetics of spontaneous Fe(II) oxidation by O₂ in aqueous solution—basic principles and a simple heuristic description. *Chemosphere* 68(11), 2080–2084.
- Morse, J.W., Arakaki, T., 1993. Adsorption and coprecipitation of divalent metals with mackinawite (FeS). *Geochim. Cosmochim. Acta* 57, 3635-3640.
- Mottl, M.J., 1983. Metabasalts, axial hot springs, and the structure of hydrothermal systems at mid-ocean ridges. *Geol. Soc. Am. Bull.* 94, 161-180.
- Mukherjee, A.B., 1998. Nickel: a review of occurrence, uses, emissions, and concentration in the environment in Finland. *Environ. Rev.* 6, 1-15.
- Murray, J.W., Dillard, J.G., 1979. The oxidation of cobalt(II) adsorbed on manganese dioxide. *Geochim. Cosmochim. Acta.* 43, 781-787.
- Murray, K.J., Webb, S.M., Bargar, J.R., Tebo, B.M., 2007. Indirect oxidation of Co(II) in the presence of the marine Mn(II)-oxidizing bacterium *Bacillus* sp. strain SG-1. *Appl. Environ. Microbiol.* 73, 6905-6909.
- Murton, B.J., Baker, E.T., Sands, C.M., German, C.R., 2006. Detection of an unusually large hydrothermal event plume above the slow-spreading Carlsberg Ridge: NW Indian Ocean. *Geophys. Res. Lett.* 33, 1-5.
- Myers, C.R., Nealson, K.H., 1988. Bacterial manganese reduction and growth with manganese oxide as the sole electron acceptor. *Science* 240, 1319–1321.
- Nakamura, K., Takai, K., 2014. Theoretical constraints of physical and chemical properties of hydrothermal fluids on variations in chemolithotrophic microbial communities in seafloor hydrothermal systems. *Prog. Earth Planet. Sci.* 1, 5.
- Napieralski, S.A., Buss, H.L., Brantley, S.L., Lee, S., Xu, H., Roden, E.E., 2019. Microbial chemolithotrophy mediates oxidative weathering of granitic bedrock. *Proc. Natl. Acad. Sci.* 116, 26394–26401.

- Nath, B.N., 2007. Processes of formation of Fe-Mn manganese nodules and crusts. In: Refresher course on marine geology and geophysics. October to November 2007, Lecture notes. pp. 63-69.
- Nayak, B., Das, S.K., Munda, P., 2013. Biogenic signature and ultra microfossils in ferromanganese nodules of the Central Indian Ocean Basin. *J. Asian Earth Sci.* 73, 296-305.
- Nicholas, D.J.D., Kobayashi, M., Wilson, P.W., 1962. Cobalt requirement for inorganic nitrogen metabolism in microorganisms. *Proc. Natl. Acad. Sci.* 48, 1537-1542.
- Nieminen, T.M., Ukonmaanaho, L., Rausch, N., Shotyk, W., 2007. Biogeochemistry of nickel and its release into the environment. *Met. Ions. Life. Sci.* 2, 1-30.
- Nies, D.H., 1999. Microbial heavy-metal resistance. *Appl. Microbiol. Biotechnol.* 51, 730-750.
- Nimmo, M., Van Den Berg, C.M.G., Brown, J., 1989. The chemical speciation of dissolved nickel, copper, vanadium, and iron in Liverpool Bay, Irish Sea. *Estuar. Coast. Shelf. Sci.* 29, 57-74.
- Nitahara, S., Kato, S., Urabe, T., Usui, A., Yamagishi, A., 2011. Molecular characterization of the microbial community in hydrogenetic ferromanganese crusts of the Takuyo-Daigo Seamount, northwest Pacific. *FEMS. Microbiol. Lett.* 321, 121-129.
- Nitahara, S., Kato, S., Usui, A., Urabe, T., Suzuki, K., Yamagishi, A., 2017. Archaeal and bacterial communities in deep-sea hydrogenetic ferromanganese crusts on old seamounts of the northwestern Pacific. *PLoS One* 12, e0173071.
- Northup, D. E., Barns, S. M., Yu, L. E., Spilde, M. N., Schelble, R. T., Dano, K. E., Crossey, L. J., Connolly, C. A., Boston, P. J., Natvig, D. O. and Dahm, C. N., 2003. Diverse microbial communities inhabiting ferromanganese deposits in Lechuguilla and Spider Caves. *Environ. Microbiol.* 5, 1071–1086.
- Nriagu, J.O., Pacyna, J.M., 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature* 333, 134-139.
- Oldham, V.E., Jones, M.R., Tebo, B.M., Luther, G.W., 2017. Oxidative and reductive processes contributing to manganese cycling at oxic-anoxic interfaces. *Mar. Chem.* 195, 122-128.
- Pekkonen, M., Ketola, T., Laakso, J.T., 2013. Resource Availability and Competition Shape the Evolution of Survival and Growth Ability in a Bacterial Community. *PLoS ONE* 8(9), e76471. doi:10.1371/journal.pone.0076471.
- Pelleter, E., Fouquet, Y., Etoubleau, J., Cheron, S., Labanieh, S., Josso, P., Langlade, J., 2017. Ni-Cu-Co-rich hydrothermal manganese mineralization in the Wallis and Futuna back-arc environment (SW Pacific). *Ore Geol. Rev.* 87, 126-146.
- Persson, A.E., Schoeman, B.J., Sterte, J., Otterstedt, J.-E., 1995. Synthesis of stable suspensions of discrete colloidal zeolite (Na, TPA) ZSM-5 crystals. *Zeolites* 15, 611-619.
- Pinheiro, J.C., dos Santos, L.T., Henriques, I., Silva, A., Barauna, R.A., 2019. Linking the environmental microbial diversity and antibiotic resistance. In: Das, S., Dash, H.R (Eds.), *Microbial diversity in the genomic era*. Academic Press, USA, pp. 451-457.

- Price, N.M., Morel, F. M. M., 1990. Cadmium and cobalt substitution for zinc in a marine diatom. *Nature* 344, 658-660.
- Pyle, G., Couture, P., 2012. Nickel. In: Wood, C.M., Farrell, A.P., Brauner, C.J. (Eds.), *Fish Physiology: Homeostasis and Toxicology of Essential Metals*. Elsevier Inc, pp. 253-289.
- Rathsack, K., Stackebrandt, E., Reitner, J., Schumann, G., 2009. Microorganisms isolated from deep sea low-temperature influenced oceanic crust basalts and sediment samples collected along the Mid-Atlantic Ridge. *Geomicrobiol. J.* 26, 264-274.
- Ray, D., KameshRaju, K.A., Srinivas Rao, A., SuryaPrakash, L., Mudholkar, A.V., Yatheesh, V., Samudrala, K., Kota, D., 2020. Elevated turbidity and dissolved manganese in deep water column near 10°47'S Central Indian Ridge: studies on hydrothermal activities. *Geo-Mar. Lett.* 40, 619–628.
- Reck, B.K., Muller, D.B., Rostkowski, K., Graedel, T.E., 2008. Anthropogenic nickel cycle: insights into use, trade, and recycling. *Environ. Sci. Technol.* 42, 3394-3400.
- Reyss, J.L., Marchig, V., Ku, T.L., 1982. Rapid growth of a deep-sea manganese nodule. *Nature* 295, 401- 403.
- Richter, R.O., Theis, T.L., 1980. Nickel speciation in a soil/water system. In: Nriagu, J.O. (Ed.), *Nickel in the Environment*. John Wiley and Sons, New York, pp. 189–202.
- Riemann, F., 1983. Biological aspects of deep-sea manganese nodule formation. *Oceanol. Acta.* 6, 303-311.
- Robertson, D.E., Silker, W.B., Langford, J.C., Petersen, M.R., Perkins, R.W., 1973. Transport and depletion of radionuclides in the Columbia River. In: *Radioactive contamination of the marine environment*. IAEA, Vienna, pp.141-158.
- Roh, Y., Liu, S.V., Li, G., Huang, H., Phelps, T.J., Zhou, J., 2002. Isolation and characterization of metal-reducing *Thermoanaerobacter* strains from deep subsurface environments of the Piceance Basin, Colorado. *Appl. Environ. Microbiol.* 68, 6013-6020.
- Rosswall, T., 1973. Modern methods in the study of microbial ecology. *Ecological Bulletin* 17, 511p.
- Saito, M.A., Goepfer, T.J., Noble, A.E., Bertrand, E.M., Sedwick, P.N., DiTullio, G.R., 2010. A seasonal study of dissolved cobalt in the Ross Sea, Antarctica: micronutrient behavior, absence of scavenging, and relationships with Zn, Cd, and P. *Biogeosciences* 7, 4059-4082.
- Saito, M.A., Sigman, D.M., Morel, F.M.M., 2003. The bioinorganic chemistry of the ancient ocean: the co-evolution of the cyanobacterial metal requirements and biogeochemical cycles at the Archean-Paleoproterozoic boundary? *Inorganica Chim. Acta* 356, 308-318.
- Santander, P.J., Roessner, C.A., Stolowich, N.J., Holderman, M.T., Scott, A.I., 1997. How corrinoids are synthesized without oxygen: nature's first pathway to vitamin B12. *Chem. Biol.* 4, 659-666.
- Sar, P., Kazy, S.K., Singh, S.P., 2001. Intracellular nickel accumulation by *Pseudomonas aeruginosa* and its chemical nature. *Lett. Appl. Microbiol.* 32, 257-261.

- Savage, D., 1995. The geochemical behavior of nickel in the repository environment. *Mat. Res. Soc. Symp. Proc.* 353, 1159-1166.
- Sawers, R.G., 2013. Nickel in Bacteria and Archaea. In: Uversky, V.N., Kretsinger, R.H., Permyakov, E.A. (Eds.), *Encyclopedia of Metalloproteins*. Springer, pp. 1490-1496.
- Schaumloffel, D., 2012. Nickel species: analysis and toxic effects. *J. Trace Elem. Med. Biol.* 26, 1–6.
- Schott, F.A., McCreary Jr, J.P., 2001. The monsoon circulation of the Indian Ocean. *Prog. Oceanogr.* 51, 1-123.
- Schultze-Lam, S., Fortin, D., Davis, B.S., Beveridge, T.J., 1996. Mineralization of bacterial surfaces. *Chem. Geol.* 132, 171-181.
- Seyfried Jr, W.E., Seewald, J.S., Berndt, M.E., Ding, K., Foustoukos, D.I., 2003. Chemistry of hydrothermal vent fluids from the Main Endeavour Field, northern Juan de Fuca Ridge: Geochemical controls in the aftermath of June 1999 seismic events. *J. Geophys. Res.* 108, 2429, doi:10.1029/2002JB001957.
- Shiraishi, F., Mitsunobu, S., Suzuki, K., Hoshino, T., Morono, Y., Inagaki, F., 2016. Dense microbial community on a ferromanganese nodule from the ultra-oligotrophic South Pacific gyre: Implications for biogeochemical cycles. *Earth Planet. Sci. Lett.* 447,10-20.
- Shock, E.L., 2009. Minerals as energy source for microorganisms. *Econ. Geol.* 104, 1235–1248.
- Shterenberg, L.E., Aleksandrova, V.A., Gablina, I.F., Lelikov, E.P., Sivtsov, A.V., Stepanetx, M.I., 1990. Composition and structure of manganese crusts from the Sea of Japan. *Geol. Pac. Ocean.* 5, 232-237.
- Silverman, M. P., Ehrlich, H. L., 1964. Microbial formation and degradation of minerals. *Adv. Appl. Microbiol.* 6, 153-206.
- Smith, I.C., Carson, B.L., 1981. Trace metals in the environment. Ann Arbor, MI, Ann Arbor Science Publishers.
- Stokes, P.M., 1981. Nickel in aquatic systems. In: Effects of nickel in the Canadian environment. National Research Council of Canada, Ottawa, pp. 77-117.
- Sujith, P.P., Das, A., Mourya, B.S., Loka Bharathi, P.A., 2011. Immobilization of manganese, cobalt and nickel by deep-sea-sediment microbial communities. *Chem. Ecol.* 27, 189-206.
- Sujith, P.P., Gonsalves, M.J.B.D., Bhonsle, S., Shaikh, S., Loka Bharathi, P.A., 2017a. Bacterial activity in hydrogenetic ferromanganese crust from the Indian Ocean: a combined geochemical, experimental and pyrosequencing study. *Environ. Earth Sci.* 76, 191.
- Sujith, P.P., Khedekar, V.D., Girish, A.P., Loka Bharathi, P.A., 2010. Immobilization of nickel by bacterial isolates from the Indian Ridge System and the chemical nature of the accumulated metal. *Geomicrobiol. J.* 27, 424-434.
- Sujith, P.P., Loka Bharathi, P.A., 2011. Manganese oxidation by bacteria biogeochemical aspects. *Prog. Mol. Subcell. Biol.* 52, 49–76.

- Sujith, P.P., Mourya, B.S., Krishnamurthi, S., Meena, R.M., Loka Bharathi, P.A., 2014b. Mobilization of manganese by basalt associated Mn(II) oxidizing bacteria from the Indian Ridge System. *Chemosphere* 95, 486-495.
- Sujith, P.P., Ramanan, D., Gonsalves, M.J.B.D., Loka Bharathi, P.A., 2017b. Microbial activity promotes the enrichment of cobalt over nickel on hydrogenetic ferromanganese crusts. *Mar. Georesour. Geotechnol.* 35, 1158-1167.
- Sukla, L.B., Panchanadikar, V., 1993. Bioleaching of lateritic nickel ore using a heterotrophic micro-organism. *Hydrometallurgy* 32, 373-379.
- Taillefert, M., MacGregor, B.J., Gaillard, J.F., Lienemann, C.P., Perret, D., Stahl, D.A., 2002. Evidence for a dynamic cycle between Mn and Co in the water column of a stratified lake. *Environ. Sci. Technol.* 36, 468-476.
- Takai, K., Nakagawa, S., Reysenbach, A.L., Hoek, J., 2006. Microbial ecology of Mid-Ocean Ridges and Back-Arc Basins. In: Christie, D.M., Fisher, C.R., Lee, S.M., Givens, S. (Eds.), *Back-Arc spreading systems: geological, biological, chemical and physical interactions*. Geophysical Monograph Series, American Geophysical Union, pp.185-213.
- Takematsu, N., Sato, Y., Okabe, S., 1989. Factors controlling the chemical composition of marine manganese nodules and crusts. *Mar. Chem.* 26, 41–56.
- Tebo, B.M., Clement, B.G., Dick, G.J., 2007. Biotransformations of manganese. In: Hurst, C.J., Crawford, R.L., Garland, J.L., Lipson, D.A., Mills, A.L., Stetzenbach, L.D. (Eds.), *Manual of environmental microbiology*. ASM Press, Washington, pp. 1223-1238.
- Tebo, B.M., Geszvain, K., Lee, S.-W., 2010. The molecular geomicrobiology of bacterial Manganese(II) oxidation. In: Loy A, Mandl M, Barton, L. (Eds.), *Geomicrobiology: Molecular and Environmental Perspective*. Springer, pp. 285-308.
- Tebo, B.M., Ghiorse, W.C., van Waasbergen, L.G., Siering, P.L., Caspi, R., 1997. Bacterially mediated mineral formation: insights into manganese(II) oxidation from molecular genetic and biochemical studies. In: Banfield, J.F., Nealson, K.H. (eds) *Geomicrobiology: interactions between microbes and minerals*. Mineral Soc Am, Washington, DC, pp 225–266.
- Tebo, B.M., Lee, Y., 1993. Microbial oxidation of cobalt. In: Torma, A.E., Wey, J.E., Lakshmanan, V.L. (Eds.), *Biohydrometallurgical Technologies*. The Minerals, Metals and Materials Society, Warrendale, Pennsylvania, pp. 695-704.
- Tebo, B.M., Nealson, K.H., Emerson, S., Jacobs, L., 1984. Microbial mediation of Mn(II) and Co(II) precipitation at the O₂/H₂S interfaces in two anoxic fjords. *Limnol. Oceanogr.* 29, 1247-1258.
- Templeton, A.S., Knowles, E.J., Eldridge, D.L., Arey, B.W., 2009. A seafloor microbial biome hosted with incipient ferromanganese crusts. *Nat. Geosci.* 2, 872-876.
- Thamdrup, B., 2000. Microbial manganese and iron reduction in aquatic sediments. *Adv. Microb. Ecol.* 16, 41-84.
- Thauer, R. K., Jungermann, K., Decker, K., 1977. Energy conservation in chemotrophic anaerobic bacteria. *Bacteriol. Rev.* 41, 100–180.

- Thijssen, T., Glasby, G.P., Friedrich, G., Stoffers, P., Sioulas, A., 1985. Manganese nodules in the Central Peru Basin. *Chemie. Der. Erde.* 44, 1-12.
- Tostevin, R., Poulton, S.W., 2019. Suboxic sediments. In: Gargaud, M., Irvine, W.M., Amils, R., Cleaves, H.J., Pinti, D., Quintanilla, J.C., Viso, M. (Eds.), *Encyclopedia of Astrobiology*, Springer-Verlag GmbH Germany, pp. 1-4.
- Tripathi, P., Srivastava, S., 2007. Mechanism to combat cobalt toxicity in cobalt resistant mutants of *Aspergillus nidulans*. *Indian J. Microbiol.* 47, 336-344.
- Twining, B.S., Baines, S.B., Vogt, S., Nelson, D.M., 2012. Role of diatoms in nickel biogeochemistry in the ocean. *Global Biogeochem. Cy.* 26, GB4001.
- Urrutia, M.M., Beveridge, T.J., 1994. Formation of fine-grained metal and silicate precipitates on a bacterial surface (*Bacillus subtilis*). *Chem. Geol.* 116, 261-280.
- Usui, A., Hino, H., Suzushima, D., Tomioka, N., Suzuki, Y., Sunamura, M., Kato, S., Kashiwabara, T., Kikuchi, S., Uramoto, G.-I., Suzuki, K., Yamaoka, K., 2020. Modern precipitation of hydrogenetic ferromanganese minerals during on-site 15-year exposure tests. *Sci. Rep.* 10, 3558.
- Usui, A., Mellin, T.A., Nohara, M., Yuasa, M., 1989. Structural stability of marine 10Å manganates from the Ogasawara (Bonin) Arc: implication for low-temperature hydrothermal activity. *Mar. Geol.* 86, 41-56.
- Usui, A., Nishi, K., Sato, H., Nakasato, Y., Thornton, B., Kashiwabara, T., Tokumaru, A., Sakaguchi, A., Yamaoka, K., Kato, S., Nitahara, S., Suzuki, K., Iijima, K., Urabe, T., 2017. Continuous growth of hydrogenetic ferromanganese crusts since 17 Myr ago on Takuyo-Daigo Seamount, NW Pacific, at water depths of 800 – 5500 m. *Ore Geol. Rev.* 87, 71-87.
- Usui, A., Someya, M., 1997. Distribution and composition of marine hydrogenetic and hydrothermal manganese deposits in the northwest Pacific. *Geol. Soc. London Spl. Pub.* 119, 177-198.
- Verlaan, P.A., 1992. Benthic recruitment and manganese crust formation on seamounts. *Mar. Biol.* 113, 171-174.
- Verlaan, P.A., Cronan, D.S., 2021. Origin and variability of resource-grade marine ferromanganese nodules and crusts in the Pacific Ocean: A review of biogeochemical and physical controls. *Geochem.* <https://doi.org/10.1016/j.chemer.2021.125741>.
- Versteegh, G.J.M., Koschinsky, A., Kuhn, T., Preuss, I., Kasten, S., 2021. Geochemical consequences of oxygen diffusion from the oceanic crust into overlying sediments and its significance for biogeochemical cycles based on sediments of the NE Pacific. *Biogeosci. Discuss* <https://doi.org/10.5194/bg-2021-112>.
- Wang, X., Muller, W.E.G., 2009. Marine biominerals: perspectives and challenges for polymetallic nodules and crusts. *Trends. Biotechnol.* 27, 375–383.
- Wang, X., Muller, W.E.G., 2010. Are Polymetallic Nodules, Crusts and Vents Biominerals? *J. Sci. Hal. Aquat.* 2, 5-20.

- Wang, X., Schloßmacher, U., Natalio, F., Schroder, H.C., Wolf, S.E., Tremel, W., Muller, W.E.G., 2009. Evidence for biogenic processes during formation of ferromanganese crusts from the Pacific Ocean: Implications of biologically induced mineralization. *Micron* 40, 526-535.
- Wegorzewski, A.V., Kuhn, T., 2014. The influence of suboxic diagenesis on the formation of manganese nodules in the Clarion Clipperton nodule belt of the Pacific Ocean. *Mar. Geol.* 357, 123–138.
- Welch, S.A., Barker, W.W., Banfield, J.F., 1999. Microbial extracellular polysaccharides and plagioclase dissolution. *Geochim. Cosmochim. Acta.* 63, 1405-1419.
- Welch, S.A., Vandevivere, P., 1994. Effect of microbial and other naturally occurring polymers on mineral dissolution. *Geomicrobiol. J.* 12, 227-238.
- Wen, X., DeCarlo, E.H., Li, Y.H., 1997. Inter element relationship in Fe-Mn crusts from the central Pacific Ocean: Their implications for crust genesis. *Mar. Geol.* 136, 277-297.
- Wilson, T.R.S., Thomson, J., Hydes, D.J., Colley, S., Culkin, F., Sørensen, J., 1986. Oxidation fronts in pelagic sediments: diagenetic formation of metal-rich layers. *Science* 232, 972-975.
- Witschel, M., Egli, T., Zehnder, A.J.B., Wehrli, E., Spycher, M., 1999. Transport of EDTA into cells of the EDTA degrading bacterial strain DSM 9103. *Microbiology* 145, 973-983.
- Wu, Y.H., Liao, L., Wang, C.S., Ma, W.L., Meng, F.X., Wu, M., Xu, X.W., 2013. A comparison of microbial communities in deep-sea polymetallic nodules and the surrounding sediments in the Pacific Ocean. *Deep-Sea Res I Oceanogr. Res. Pap.* 79, 40-49.
- Yeo, I.A., Howarth, S.A., Spearman, J., Cooper, A., Crossouard, N., Taylor, J., Turnbull, M., Murton, B.J., 2019. Distribution of and hydrographic controls on ferromanganese crusts: Tropic Seamount, Atlantic. *Ore Geol. Rev.* 114, doi: <https://doi.org/10.1016/j.oregeorev.2019.103131>.
- Young, R.S., 1957. The geochemistry of Cobalt. *Geochim. Cosmochim. Acta.* 13, 28-41.
- Yu, H., Leadbetter, J.R., 2020. Bacterial chemolithoautotrophy via manganese oxidation. *Nature* 583, 453 doi: 10.1038/s41586-020-2468-5.
- Zajic, J.E., 1969. Microbes and cobalt. In: *Microbial biogeochemistry*. Academic press, New York, pp. 169-178.
- Zhan, G., Li, D., Zhang, L., 2012. Aerobic bioreduction of nickel(II) to elemental nickel with concomitant biomineralization. *Appl. Microbiol. Biotechnol.* 96, 273-281.
- Zhang, C., Yu, Z.-G., Zeng, G.-M., Jiang, M., Yang, Z.-Z., Cui, F., Zhu, M.-Y., Shen, L.-Q., Hu, L., 2014. Effects of sediment geochemical properties on heavy metal bioavailability. *Environ. Int.* 73, 270–281.
- Zhao, J., Zhang, H., Wu, G., Lu, B., Pulyaeva, I. A., Zhang, H., Pang, X., 2014. Biomineralization of organic matter in cobalt-rich crusts from the Marcus–Wake Seamounts of the western Pacific Ocean. *Acta. Oceanol. Sin.* 33, 67–74.

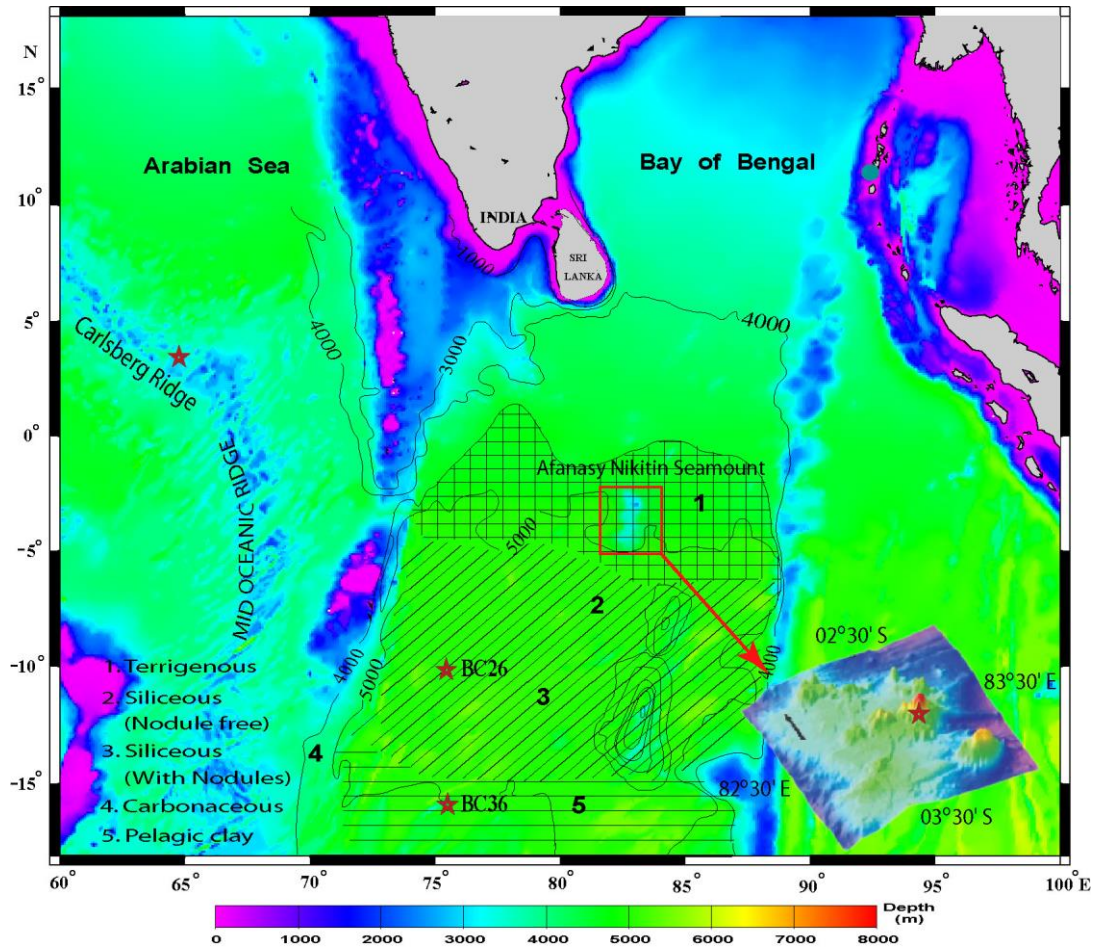


Figure 1. Map show different sampling locations, sediment types of Central Indian Ocean Basin (CIOB) and 3D inset of bathymetry data of the Afanasy Nikitin Seamount (ANS). The symbol star represents the stations from where the box core and crust samples were collected. The inset map of ANS has been sourced from Banakar et al., (2007) and sediment types of CIOB after Mascarenhas-Pereira et al., (2006).

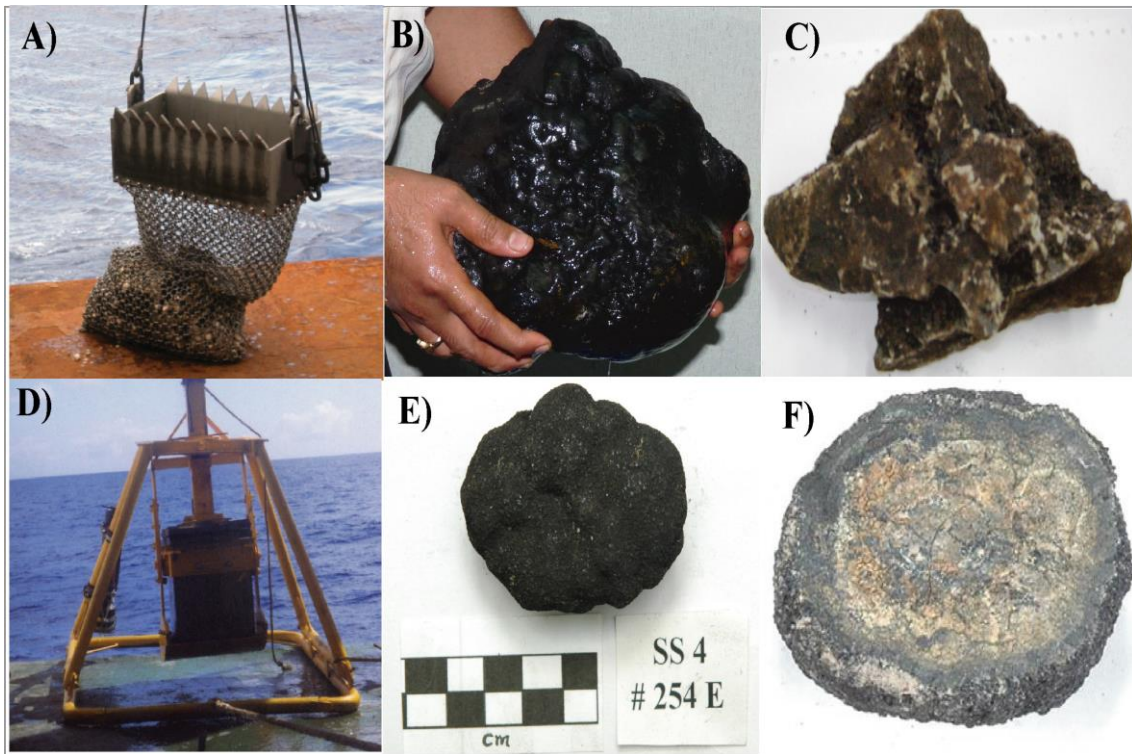


Figure 2. Photographs of Fe-Mn crusts and manganese nodules collected from different geographical locations of the Indian Ocean region. A) Chain bag dredge on-board with samples of Fe-Mn crust from the Afanasy Nikitin Seamount (ANS), B) sample of Fe-Mn crust from the ANS, C) sample of basalt dredged from the Carlsberg Ridge, D) box core (BC) sampler on-board with deep-sea sediment and manganese nodule from the Central Indian Ocean Basin (CIOB), E) sample of manganese nodule from CIOB (1cm slip and voyage number is shown) and F) internal structure of a manganese nodule (Mn nodule images- photo courtesy of Vineesh T.C, CSIR-NIO, Goa).

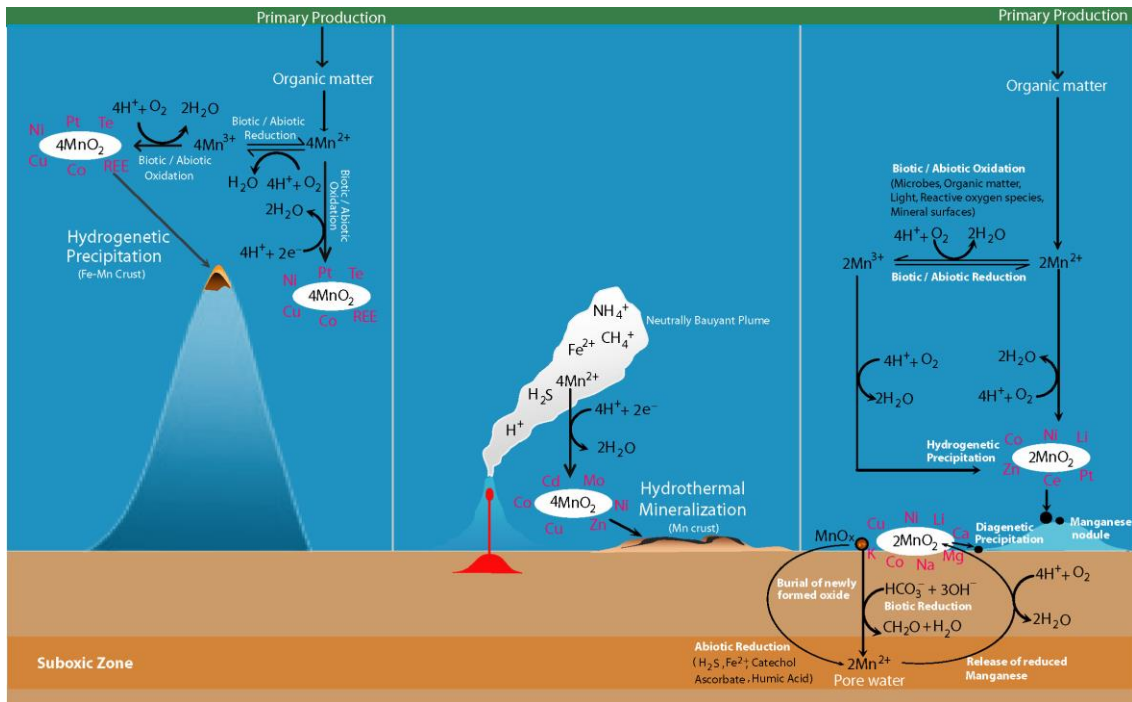


Figure 3. Schematic illustration of the biotic and abiotic processes proposed to control the oxidation and reduction of Mn in a hydrogenetic, hydrothermal and diagenetic types of mineral deposits.

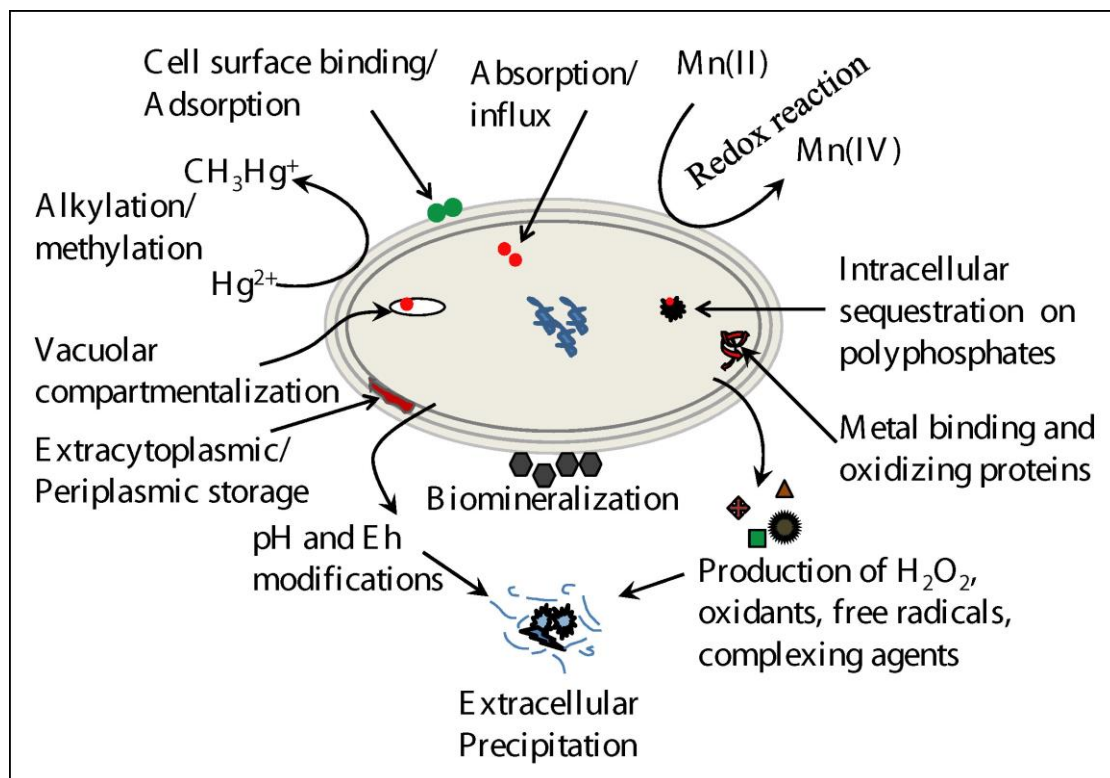


Figure 4. Mechanisms of interactions between bacteria and metals.

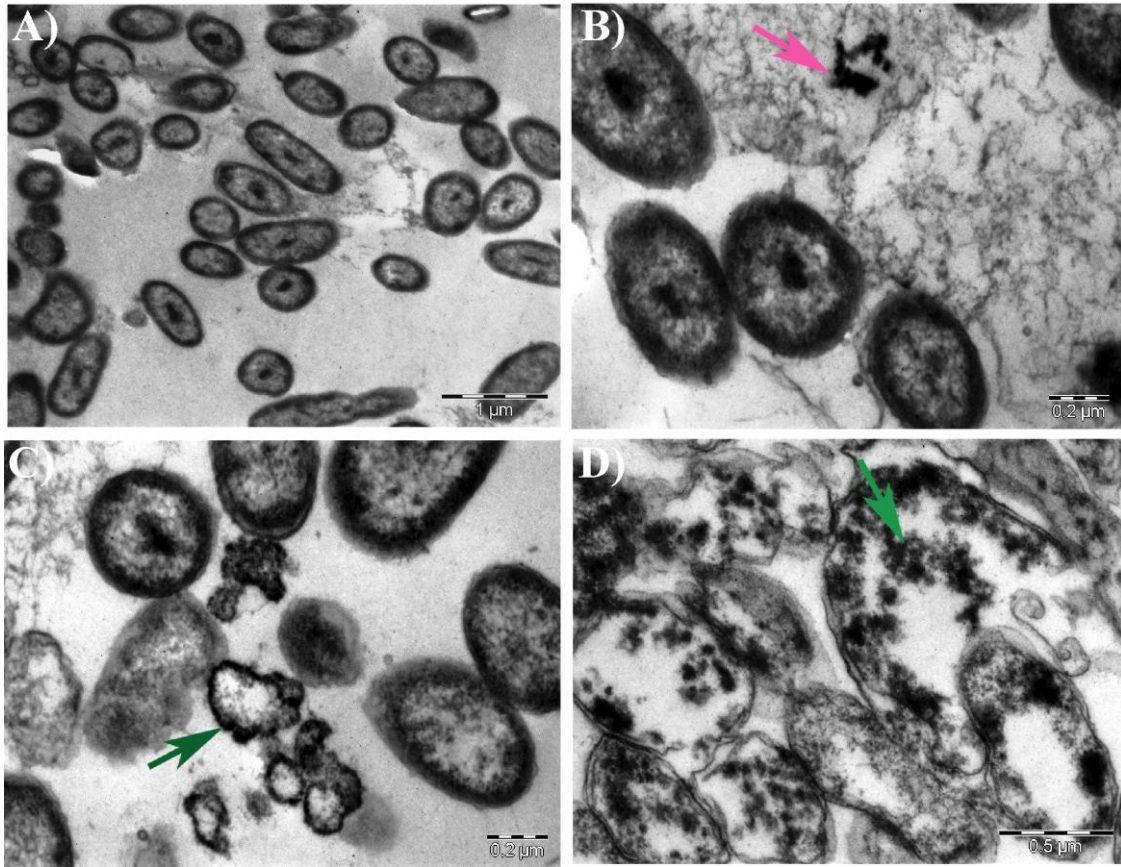


Figure 5. Horizontal and vertical cross sections of bacteria show electron dense precipitates of metals. TEM of A) Controls lacking metals, B) extracellular cobalt (pink arrow), C) periplasmic nickel and D) cytoplasmic nickel (green arrows).

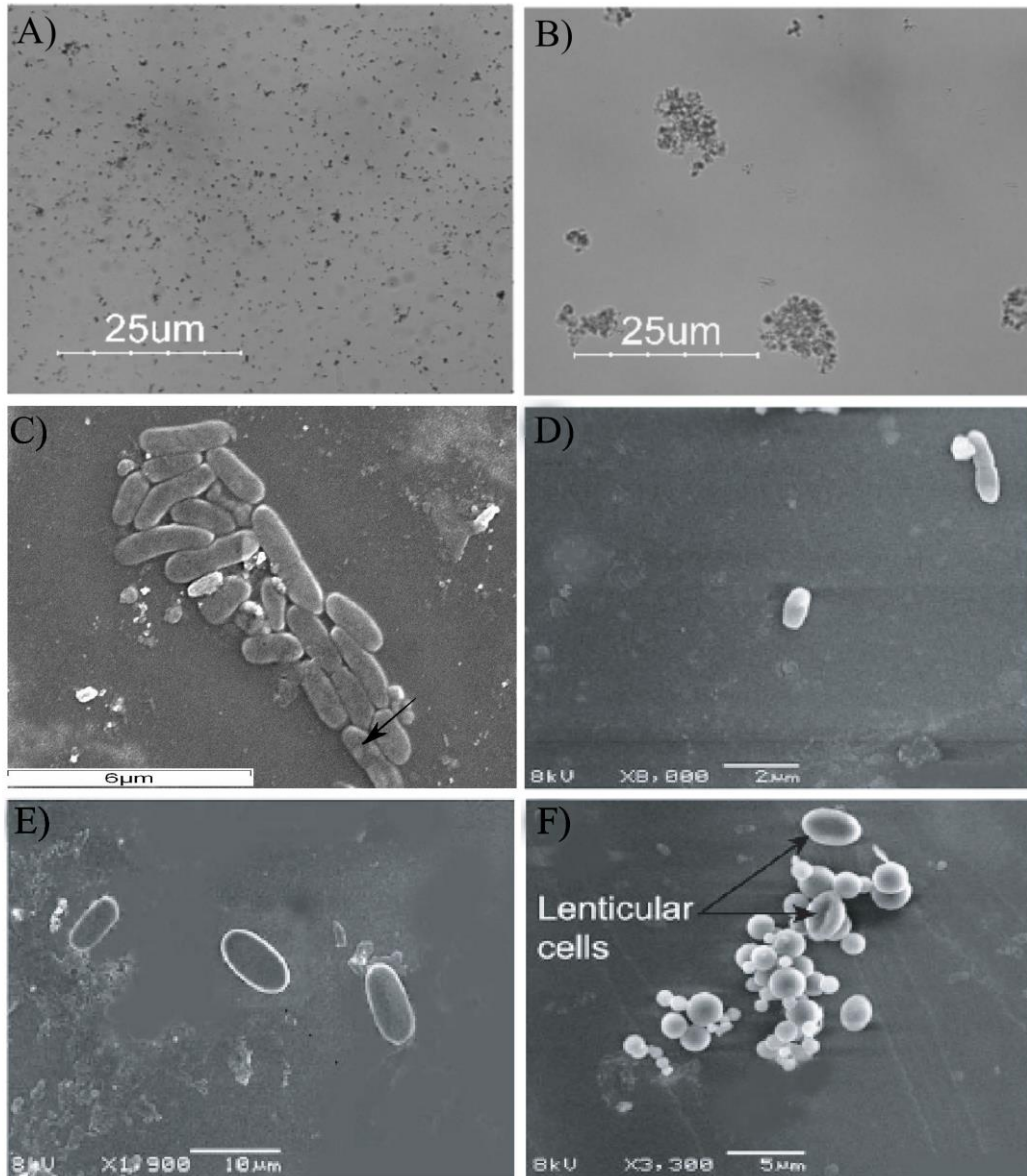


Figure 6. Adaptive strategies and mechanisms in bacteria to counteract metal toxicity on exposure to nickel and cobalt. A) Bacterial cells unexposed to metals, B) bacterial cell aggregation, C) cell encrustation (Sujith et al., 2010), D) reduction in cell surface to volume ratio, E) intracellular storage of Ni as granules and F) change in cell morphology (Antony et al., 2011).

Table 1. Summary of details on ferromanganese crusts and manganese nodules from the world ocean.

Characteristics	Parameters	Fe-Mn Crust	Manganese Nodules	Reference
Authigenic deposits	Types	Hydrogenetic, hydrothermal, mixed type.	Diagenetic, hydrogenetic, mixed type.	Bostrom and Kunzendorf (1986) McMurtry (2001)
	Occurrence	Seamounts, oceanic islands, terraces and submerged platforms.	Near-shore, lacustrine, marginal seas, lake environments and deep ocean.	
	Substrate or nucleus	Limestone, basalt, breccia, phosphorite, iron stone.	Clay, pumice, red clay, rock fragments, nodule fragments, shark tooth or ear bone of a whale.	Mero (1960) Bostrom and Kunzendorf (1986) Hein et al (2000)
	Water depth (m)	~ 400 to 4000	~ 3000 to 6000	
Physical properties	Mean bulk density (g cm ⁻³)	1.3	1.35	Jauhari and Pattan (2000) Koschinsky and Hein (2014)
	Mean porosity (%)	60	60	
	Specific surface area (m ² g ⁻¹)	325	~ 150	
	Growth rate (mm My ⁻¹)			Krishnaswami et al (1982) Reyss et al (1982)
	<ul style="list-style-type: none"> • Hydrogenetic type • Diagenetic type 	1 to 5 -	1 to 5 Up to 168	
Thickness and size	5 to 136 mm	2.5 to 10 cm	Hein et al (2012)	
Mineralogy	Manganese minerals	Vernadite, Todorokite	Vernadite, Birnessite, Buserite, Todorokite, Asbolan	Koschinsky et al (1997) Usui and Someya (1997) Hein et al (2000)
	Iron minerals	Feroxyhyte, Goethite	Feroxyhyte, Ferrihydrite, Goethite	Baturin (1988) Koschinsky and Hein (2014)
	Detrital minerals	Quartz, Feldspar, Carbonate Fluorapatite	Aluminosilicate Phillipsite, Quartz, Feldspar,	Piper (1974) Hein et al (2000)

Table 1. Summary of details on ferromanganese crusts and manganese nodules from the world ocean (Continued).

Characteristics	Parameters	Fe-Mn Crust	Manganese Nodules	Reference
Chemical composition	Water content	Up to 35 %	Up to 20%	Koschinsky and Hein (2014)
	Iron (%)	17.8 to 18.1	6.96 to 9.5	Baturin (1988) Jauhari and Pattan (2000)
	Manganese (%)	14.5 to 17.0	22.4 to 25.6	Clark et al (2013)
	Cobalt (%)	0.1 to 1.9	0.12 to 0.15	Koschinsky and Hein (2014)
	Nickel (%)	0.2 to 1.1	0.66 to 1.14	Kodagali and Sudhakar (1993) Novikov et al (2013)
	Fe/Mn ratio:			
	• Hydrogenetic type	0.4 to 1.2 (0.7±0.2)	-	Koschinsky and Hein (2014)
	• Mixed type, hydrothermal & continental margin hydrogenetic crusts	1.0 to 3.0	-	
	Mn/Fe ratio:			
	• Hydrogenetic type	-	Up to 2.5	Jauhari and Pattan (2000)
• Diagenetic type	-	> 5.0		
• Mixed type	-	0.96 to 8.76		
Biom mineralization	Bio-seeds	Coccolithophores	Bacteria	Wang et al (2009)

Table 2. Methods to determine the microbial diversity and activity, elemental composition and analyses of chemical and biological properties of Fe-Mn minerals.

Sl.no	Techniques	Uses
1	High-throughput 454 sequencing and metagenomics Microarray –based genomic technology (GeoChip) Fluorescence in situ hybridization (FISH) 16S rDNA analysis	Molecular genetic methods for analyzing microbial community composition, structure and function of culturable and non-culturable microbes inhabiting Fe-Mn mineral surfaces.
2	Isotope labeling and microautoradiography	Tracers for the study of metabolic activity and elemental distribution in different environmental samples.
3	X-ray fluorescence spectroscopy (XRF) X-ray photoelectron spectroscopy (XPS) Inductively coupled plasma mass spectrometry (ICP-MS) Atomic absorption spectroscopy (AAS) Atomic emission spectroscopy (AES) Energy dispersive X-ray (EDX)	Elemental composition and surface analysis of natural and synthetic oxides of iron, manganese etc.
4	Fourier transform infrared spectroscopy (FTIR) Nuclear magnetic resonance spectroscopy (NMR) Electron paramagnetic resonance (EPR)	Determination of functional groups and properties of organic molecules for the identification of organic materials.
5	Extended X-ray absorption fine structure (EXAFS) X-ray absorption near edge structure (XANES) Mössbauer spectroscopy Voltammetry /Polarography	Determination of elemental oxidation states or metal species.
6	X-ray diffraction (XRD) Selected area electron diffraction (SAED) Raman spectroscopy	Structural characterization and identification of Fe-Mn minerals.
7	Atomic force microscopy (AFM) Scanning transmission electron microscope (STEM) Scanning electron microscope (SEM) Transmission electron microscope (TEM) Confocal laser scanning microscopy (CLSM)	High resolution and sub-micron scale imaging for understanding the finer details of microbial cells and their role in metal sequestration and precipitation.
8	Metabolic poisons	Experimental differentiation of biological from abiological processes to deduce the role of microorganisms in the formation of Fe-Mn minerals.