

## ABSTRACT

The thesis embodies the results of a detailed geochemical and mineralogical study of the Precambrian, Iron Ore Group of sediments including shales/ argillites, manganese deposits and cherts from the Noamundi basin (Lat  $21^{\circ}$  N to  $22^{\circ}$  N and Long  $85^{\circ}$  E to  $86^{\circ}$  E), eastern India, with a view to determining mainly the chemical environment of deposition and genesis of the manganese ores of the basin. For this purpose, collation and critical examination of extensive data on recent marine and lacustrine ferromanganese deposits and cherts and their comparison with data on their ancient analogues, including those from the eastern Indian shield have been undertaken, in addition to a collection and study of (1) shale/argillite samples from more than six traverses in the Noamundi basin, (2) manganese ores from more than 25 open cut mines distributed throughout the basin, and (3) cherts.

Clay mineralogy of the argillaceous rocks of the Iron Ore Group (IOG) from the Noamundi basin, is represented mainly by kaolinite and  $2M_1$  illite with minor montmorillonite. Paucity of chlorite and potash feldspar, absence of paragonite, pyrophyllite and gibbsite in these assemblages are conspicuous. In general, the kaolinite/illite ratio, the illite crystallinity (IC) and the  $d_{(060)}$  peak position and (002)/(001) peak height ratio of illite change systematically from the stratigraphically higher upper shales to lower shales and suggest diagenetic neoformation of illite in these rocks. Growth of illite during diagenesis and paucity of chlorite indicate that the detrital sediments which accumulated in the basin were rich in kaolinite but poor in smectite group of minerals.

Dominance of  $2M_1$  polytype of illite in the IOG argillites, the range of IC values and the absence of pyrophyllite in the assemblages indicate a maximum of epizone condition of metamorphism ( $\sim 360^{\circ}$  C/2kb) for these sediments. Similar clay mineralogy of the shales/argillites from the marginal and central parts of the basin along with similar crystallinity and polytypism of illites in samples from various parts, including Singhbhum Granite contact around Chaibasa is difficult to reconcile with the idea that Singhbhum Granite phase-III is intrusive into the Iron Ore Group of rocks of the Noamundi basin.

Widespread occurrence of well crystalline kaolinite and authigenic illite and lack of mixed layer clays suggest that these sediments cannot represent recent weathering prod-

ucts. Sporadic montmorillonite is deemed to have resulted from chemical alteration of local tuffaceous material and stabilised in the assemblages through closed system domain type equilibria. Unlike the clay mineral assemblages in Proterozoic shales of the Shield areas of different continents, which are dominated by chlorite and illite, the abundance of kaolinite,  $2M_1$ -illite and persistence of smectite but absence of pyrophyllite and gibbsite in the Noamundi argillites including those associated with BIFs suggest  $\log a_{SiO_2(aq)}$  approximately between -3.35 and -4.25, and the corresponding  $\log(a_{K^+}/a_{H^+})$  between  $\sim 2.0$  and 5.0 in the pore water. These tentative range of activities and their ratios and the associated clay mineral assemblages straddle the average composition of river water between them while the average composition of sea water remain far removed. The existing assemblages of clay minerals, therefore, cannot be reconciled with an initial alkaline sea water composition. A weakly acidic to neutral pH corresponding to river/lake or slightly brackish water composition with low TDS appears to have been the most likely candidate for the basin and pore water, in equilibrium with which the shales/argillites, the BIFs and the associated sediments formed in the Noamundi basin.

The geochemistry of shales from the Noamundi basin exhibit certain unusual features. With respect to Archean, Proterozoic and even Phanerozoic shale averages, these are impoverished in CaO, MgO and Na<sub>2</sub>O but enriched in Fe<sub>2</sub>O<sub>3</sub> (total), Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>. The conspicuously low values of CaO (and partly, MgO) in these shales indicate low carbonate contents in them. The enrichment of Fe<sub>2</sub>O<sub>3</sub>, and in K<sub>2</sub>O relative to MgO and CaO in the Noamundi shales matches with chemical composition of residual fluids derived from late-stage felsic magmatism. The concentration and distribution pattern of Zr, Y, and Ba in these sediments relative to world shale average also favour a granitic source for these elements. A strong positive correlation ( $r=0.87$ ) between Ba and K<sub>2</sub>O in the shales from the southern part of the Noamundi basin, where BIFs occur, and a Sr hike with values close to that of granites in the shales associated with BIFs suggest a felsic magmatic (granitic) source for these components. The distribution pattern of the elements Sc, Co, Ni, Zn and Cu along with Mn and some iron, on the other hand, suggests that underlying basaltic layer is the source for most of these elements in the shales. The distribution of manganese and vanadium in these shales suggest that the redox potential of the Noamundi basin water remained high, in general.

Data on recent lacustrine and marine chemical precipitates reveal that the sediments from these two environments can be distinguished in terms of their composition in the CaO-MgO-Na<sub>2</sub>O-K<sub>2</sub>O system provided carbonates and detrital components associated with them are trivial. It is observed that lacustrine ferro-manganese precipitates display low Na<sub>2</sub>O-K<sub>2</sub>O but high CaO/(CaO+MgO) (>0.70) similar to the world average river water, and ground water composition from certain granitic terrains. In contrast, mature marine ferromanganese precipitates and nodules show a lower (<0.60) lime ratio and variable Na<sub>2</sub>O and K<sub>2</sub>O. Recent pelagic cherts reveal average CaO/(CaO+MgO) ratio comparable to that of ocean water, whereas those affiliated to ocean floor hydrothermal activity span a wide range of composition in the CaO-MgO-Na<sub>2</sub>O-K<sub>2</sub>O space and mostly avoid the lacustrine field. Extension of the observed relations to the ancient deposits reveal that— the majority of the BIFs of the Alogoma and Lake Superior types from USA., Canada, Africa, Australia etc., and a large number of Proterozoic Mn-deposits and cherts display marine signature. However, certain BIFs, Mn-ores and cherts of Proterozoic age from Canada (Rapitan Formation), Africa (Damara Orogen) and India (Sausar Group) reveal fresh to brackish water milieu for their chemical environment of deposition. From a comparison of the CaO/(CaO+MgO) ratio of the present day ferromanganese nodules and cherts from marine and lacustrine environments with those of the Noamundi basin it is observed that these BIFs and cherts appear to have been precipitated in fresh water to brackish water conditions.

Mn-deposits of the Noamundi basin are of two distinct categories viz., primary, sedimentary and secondary, supergene origin. As metamorphism in this basin is of very low intensity, the mineralogy of the primary and secondary ores is more or less similar. Dominant Mn minerals in these deposits, as revealed by XRD, IR and microscopic studies, include pyrolusite, cryptomelane, nsutite, ramsdellite, todorokite, hollandite, coronadite and less commonly lithiophorite, psilomelane, woodruffite, manjiorite, manganite, chalcophanite and hausmannite.

The Mn/Fe ratio of the primary Mn ores ( $0.1 \leq x \leq 20.0$ ) and for the supergene ores  $1.0 \leq x \leq 60.0$  of the Noamundi basin are high and overlaps considerably with fresh water lake and marine deposits. The very low Si/Al ratio, a strong positive correlation between Ti and Al and a strong negative correlation between Si and Fe, unlike ferromanganese

precipitates from hydrothermal exhalatives, suggests that these deposits could not be of typical marine hydrothermal origin. In CaO-MgO-Na<sub>2</sub>O and CaO-MgO-K<sub>2</sub>O diagrams it is observed that the supergene manganese oxide deposits of marine parentage from Pilbara, western Australia, Mary valley deposits from Queensland and Sandur basin, Karnataka, all plot within the marine field, as defined earlier from a compilation of data from all over the world. The majority of the data on the manganese deposits from the Noamundi basin plot in these ternary diagrams in the fresh to brackish water fields, with about ~ 30% data in the marine domain.

In summary, therefore, both clay-mineralogical and geochemical studies of the inter-layered Iron Ore Group of detrital and chemical sediments indicate that the majority of the oxide-type Mn deposits, BIFs, cherts and the argillaceous sediments in the SOIOC formed in dominantly fresh/brackish water lacustrine environment. However, a small percentage of the Mn-ores appear to have formed under saline conditions possibly implying occasional influx of (?) sea water into the basin. Both Mn and Fe, and a number of trace elements in these sediments seem to have been derived from diverse sources, including underlying basalts, felsic magmatism and probably some volcanic/tuffaceous exhalatives. Leaching of upper shales could have provided some Mn for supergene enrichment during lateritization.