Chapter 7
Discussion and Genesis

The manganese ore deposit and the associated khondalite members in district Vizianagram, (A.P) are a part of Indian metasedimentary manganese ore deposits distributed mostly in the Precambrian gneiss and khondalites in the Eastern Ghats Mobile Belt. The metasedimentary manganese deposits of small to moderate size hosted by the khondalites and charnockites are spread in the Eastern Ghats Granulite Belt that covers a large sector of the East Coast of India (Figures 1.1 and 1.2). The present manganese ore bodies are concentrated in the district Vizianagram, (A.P) and lies between the 18° 12'- 18° 30' N latitude and 83° 20'- 83° 45' E longitudes. The study area falls in Dharwar system of India which is synonym for the Archaean and represents the oldest Supergroup of Geological Formations of India (Fermor, 1909). It constitutes the most metamorphosed sector of the Precambrian Indian shield hosting several mineral deposits. The entire region is also included under East Gondwana along with Antarctica and Srilanka where reassembly of East Gondwana has juxtaposed the EGB against the parts of East Antarctica between 40° and 70° East Latitude (Yoshida, 1995). The entire EGB is cut by the NW-SE trending linear rift zones, the Mahanadi and the Godavari Grabens in the north and south respectively, representing the Palaeozoic-Mesozoic sedimentation locales (Rao, G.V. 2001). The EGMB is an important polymetamorphic granulite belt which has importance in reconstructing past continental configuration and the geological processes in the region (Dasgupta and Sengupta, 1995). The entire Belt has undergone polyphase deformation (Bhattacharya, 1997) and three episodes of regional metamorphic events whose imprints are not preserved uniformly in all phases. A significant proportion of the granulite terrain is occupied by the metasedimentary rocks mainly (khondalites) which attained deep burial upto 35 kms indicated by the barometric estimates of ca 10 kbar in the region (Rickers et al, 2001). The field observation of the study area shows a complex structural figure of folds, faults and fractures of diverse types (Figures 2.3a, b, d and f) indicating the complex regional tectonics. The foliation of the khondalites follows the regional bedding planes and is also maintaining the parallelism with the compositional banding intruded by some secondary pegmatite intrusions (2.3b). Geologically, the region represents one of the few documented high
grade terrains in the world, metamorphosed at ultra-high temperature (~1000°c) and 9-10 Kbar (Dasgupta and Sengupta, 1995; Harley, 1998). On the basis of isotopic geochemical studies of Rickers et al. (2001), the EGB has been divided into North Eastern Ghat Belt (NEGB) and South Eastern Ghat Belt (SEGB) with Vizianagram, falling in Late Archaean SEGB of 3900 – 2500 Ma. The study area, Vizianagram is an integral part of Eastern Ghats Granulite Belt (EGB) and represents a part of the eastern coastal strip of India. The Vizianagram manganese ores and host rocks as investigated in the light of different tectonic environments and the global manganese mineralization in hydrogenous, sedimentary, diagenetic and hydrothermal environments. Several issues pertaining to conditions and mechanisms of district Vizianagram, (A.P), manganese ore deposit formation remained debatable so far, however the present author attempted to unearth the genesis of the ores with respect to geological, mineralogical and geochemical aspects and made some important and simplified conclusions. Manganese ores have evolved in a few important phases of metallogenesis in the region and the manganese ores in district Vizianagram, (A.P) are co-genetic as evident from the collective field evidence and the geochemistry and mineralogical modules of the ores and host rocks. The manganese ore genesis in the study area is believed to be of metasedimentary nature (Rao, G.V, 1969; Siddiquie 2004; Siddique and Bhat 2010). The occurrence of the extensive manganese ore deposits, Iron oxides and laterites and bauxites along with the pockets of graphite in the EGB support rapid changes both in the physico chemical environmental conditions, during and after the formation of khondalites (Raju and Rao, 2001). The lithological assemblage of gametiferous quartzites, garnet-sillimanite gneisses (khondalites), garnet-biotite gneisses, cordierite-bearing gneisses, marbles and calc-silicate gneisses imply shallow-water deposition in a shelf-like environment or intracratonic, basins or troughs, respectively (Katz, 1989).

The primary manganese ores in the present piece of research work are observed as metasedimentary in the general opinion (Sivaprakash, 1980; Krishna Rao, 1963a, 193b and 1966; Siddiquie, 2004; Siddiquie and Bhat, 2008 and 2010) as seen in their mineral assemblages and the geochemistry while as the secondary ores are the supergene ores formed from the primary ores by supergene enrichment. The primary ores are the sedimentary equivalents of bedded type sedimentary manganese ore deposits which have undergone metamorphism as evident in the figures 3.4a-c. These metasedimentary ore deposits underwent a vigorous weathering and supergene
alterations that led to the formation of the present economic ore deposit. The complete knowledge on the mechanism involved and the origin of the manganese ores of district Vizianagram, (A.P) ore is scarce. The available literature on the study area shows varied opinions on the origin of this complex mineralogy. However, the present author correlates this diverse manganese ore mineralogy with the complex regional tectonics and the associated metamorphism and later supergene alteration. In this study, the author has compiled a detailed geochemical and mineralogical picture of the ores and their host rock to present a possible mode of formation of the manganese ores of district Vizianagram, (A.P). The present study of major and trace element geochemistry, ore microscopic, petrographic and XRF results reveal a very intrusting sequential evolution from the sedimentation and co-precipitation to diagenetic stage followed by regional metamorphism and post metamorphic supergene enrichment.

7.1 Mineralogical signatures

The mineralogy of the primary manganese ores of the study area is of utmost importance to unravel the original manganese rich protolith and the possible conditions associated with the formation of these ores within in the bulk geochemical system. The primary ore mineral assemblages and that of the host rocks at this stage represent the metamorphism of granulites in the region. The mineral assemblages in both the primary manganese ores and host rocks are found in response to the declared metamorphism in the region which in itself reveals the existence sedimentary protolith in the palaeo basin. The coexistence of both the banded primary metamorphosed manganese ores and the khondalite-charnockite terrain witness the co-metamorphism of the earlier sedimentary sequence with some compositional heterogeneity as evident in the studied mineral assemblages (Table 8) and the bulk geochemistry (Tables 9 and 17). The primary ores of district Vizianagram, (A.P) along with the calc-granulites and other khondalite members have preserved important mineralogical trails in support of the initial sedimentary protolith and the later metamorphism. The occasional blasto bedding structures and metamorphic rhythmic succession of the supracrustal rocks are well preserved in the terrain suggesting the isochemical metamorphism of the khondalites. Sapphirine present in some areas of the terrain also suggests HPT metamorphism (Kamineni and Rao,
1988). The layered and occasionally folded nature of the khondalite Group of rocks and the original sedimentary layering in the primary ores are apparent in the primary ores (Figures 2.3a, f and 3.4a-d respectively). The ores microscopic and XRD studies of the ore samples confirm the presence of ore minerals of Mn-Silicates, Mn-Carbonates and Mn-Oxides as detailed in figures 4.1-4.9 and tables 7 and 8. The secondary ores are dominated by the Mn-oxides especially pyrlosite and psilomelane and cryptomelane. The secondary manganese ores of the study area are formed from the primary manganese silicate oxide and carbonate protore (Krishna Rao, 1954, 1956a, 1956b, 1963a, 1963b, 1964, 1967; Krishna Rao and Dhana Raju, 1966; Mukhopadhyay et al., 2005 and Siddiquie and Bhat, 2008, 2010). Mn-silicates, Mn-carbonates and Mn-oxides are well preserved in the manganese ore quarries of Perumali and Bangaravvalasa arcs of the study area (Tables 6 and 8). The present mineralogical studies makes full agreement with the previous workers (Mahadevan and Rao, 1956); Starczek and Krishnaswamy (1956); Siddiquie (2004) and Siddiquie and Bhat (2010) who declared that the primary ore deposits are metamorphosed and are conformable with the host rocks. The presence of secondary ore minerals showing the enhancement in manganese oxide formation and the overall weight percentage of the manganese and dearth of the lower oxides associated with complete disappearance of the low Mn ore minerals. The host rocks possess metamorphic mineral assemblages (Grt-Opx-Biot-Qtz) in garniferous quartzo-felspathic gneiss and calc-silicate. The stratigraphic association and the mineral assemblages of the primary ores and their host rocks clearly suggest that they are co-metamorphosed under ultra high temperature. The primary ore horizons dominantly comprise of metamorphic ore minerals such as braunite, rhodochrosite, jacobsite, hausmannite, vredenburgite and spessartite, pyroxmangite and rhodonite as detailed in table 8. The primary manganese ores with variable silicate-carbonate admixtures represent the metamorphosed ores of the study area and have discussed in detail by Siddiquie (2004) and Siddiquie and Bhat (2008). The ores mineralogical constitution and the textural relationship at both suggest the syn-metamorphic origin of the primary ores. Among the primary manganese oxide minerals braunite enjoys the full swing at all the stages of metamorphism and deformation. The primary or metasedimentary manganese ores of district Vizianagram, (A.P) contain the rhodochrosite-quartz - hausmannite – rhodonite - spessartite with associated pyrolusite and psilomelane. Metamorphism can be accounted as responsible for the crystallization of the major
silicates such as rhodonite and pyroxmangite. The mineral assemblage of spessartite + rhodochrosite + quartz represents the low metamorphic assemblage as a remanent protore for the high grade carbonate lacking assemblages such as that of hausmannite and jacobsite. The exsolution of Jacobsite and hausmannite among the primary minerals evolved as Vrcbenburgite with windmanstatten texture (Figure 4.2b) suggests the lowering of pressure and temperature after the peak regional metamorphism. The presence of spessartite in manganese ores suggests decarbonation reaction during prograde metamorphism (Roy, 1981). According to Glasby and Schultz (1999) neither rhodochrosite (MnCO₃) nor siderite (FeCO₃) can form in the marine environment in equilibrium with sea water. However, as shown by Berner et al (1970), rhodochrosite does occur in both anoxic sulphidic and non-sulphidic environments whereas siderite is restricted to marine and non-marine anoxic non-sulphidic methaneic environments. The mode of origin of spessartite in metamorphosed manganese ores derived from the sedimentary protoliths continues to be a matter of considerable debate (Schreyer et al, 1992; Thyee et al, 1996).

Spessartite garnet pervasively developed in manganese silicates and carbonates rich rocks and is seen to possess minor inclusions of quartz and rhodochrosite. Such a texture reveals the formation of the spessartite through the metamorphic reaction between rhodochrosite and quartz in accordance with Nyame (2001). Spessartite was experimentally synthesized from Mn Chlorite by Hsu (1968) which made various investigators (Abrech, 1989) to believe that the same reactants may have stabilized spessartite bearing assemblages in some rocks, however the opinion was criticized by Dasgupta et al (1993), who pointed out that spessartite formation from Mn chlorite and quartz had not been clearly documented in naturally occurring Mn Silicate rocks. Kramm (1976) suggested a Mn-Montmorillonite precursor for spessartite, but was subsequently disputed by Schreyer et al (1992) who rather presented evidence in favour of a rhodochrosite precursor. According to Roy (1966, 1981), spessartite in some metamorphosed occurrences may have been formed from a variety of manganese oxides or oxihydroxides and/or Mn-carbonates admixed with siliceous and argillaceous sediments. The opinion of Roy (1973, 1981) that spessartite in manganiferous rocks was derived from metamorphism of manganese oxides, alumina and silica is also suggested by later workers (Siddiquie and Bhat, 2008) and Siddiquie and Raza (2008). Also there is no zoning of core and rim in the case of primary ore minerals suggesting that the conditions during the porphyroblastic growth
were uniform. Nyame (2001) suggested three possibilities of spessartite formation in the Mn ores of metamorphic origin could be attributed to the following reactions;

1. Rhodochrosite + quartz + Aluminous Phase (?) = spessartite + H$_2$O + CO$_2$
2. Mg-Kutnahorite + Quartz + Aluminous Phase (?) = spessartite + H$_2$O + CO$_2$.
3. Mg-Kutnahorite + Quartz + Aluminous Phase (?) = Ca – Rhodochrosite + spessartite + H$_2$O + CO$_2$.

Till date no Kutnahorite was reported by any author from the study area and so the rhodochrosite is understood as the only mineral phase to be acclaimed as the precursor mineral phase. The metamorphic P-T conditions suitable for the formation of spessartite was experimentally investigated by Hsu (1968) who reported growth of spessartite from Mn-Chlorite and quartz at around 370-490°C and 0.5 to 3 kb water pressure. However based on the observations in natural assemblages and on the fact that no reversals were obtained in the equilibrium experiments, some authors have suggested that spessartite may be stable at much higher temperatures (Roy, 1981; Flohr and Heubner, 1992). Almost similar opinion of high temperature formation of spessartite was given by theye et al (1996) and Nyme (2001). The other associated mineral counter parts were spessartite forming mineral reactions may occur during very low grade regional metamorphism possibly well below ≈ 300°C, in response to relatively low temperatures within manganese rich sediments of appropriate bulk composition (Nyme, 2001). The presence of spessartite with rhodochrosite and quartz within the Mn-silicate carbonate rocks of district Vizianagram, (A.P) provide useful information on the stability of spessartite in the precursor impure carbonate protolith. Temperature, pressure, bulk composition, fluid phase and fugacity of oxygen are important factors known to influence the stability of Mn-rich phases during metamorphism (Peters et al, 1974; Dasgupta, et al, 1993; Jimenez-Millan and Velilla, 1998). Flohr and Huebner (1992) documented the mineral assemblage Hausmannite-rhodochrosite-tephorite-spessartite-rhodonite-jacobsite from a possible carbonate precursor in metamorphosed sedimentary deposits of Sirra Nevada, California. Thus the formation of these phases is not a function appropriate bulk composition with suitable O$_2$, CO$_2$ and H$_2$O fugacity only but other factors such as Eh, pH. Acidity etc. Inclusions of rhodochrosite and quartz in porphyroblastic spessartite indicate the former minerals stabilize under appropriate Eh pH conditions probably in the diagenetic environment (Dasgupta et al, 1993). The
opinion is in agreement with the observed rhodochrosite (Figure 4.5b). The joint presence of spessartite with other carbonate materials in spessartite bearing manganese silicates (Figure 4.1c, 4.8a) suggest miscibility gap and temperatures below the crest of solvus (<500°C) in the conformity with the CaCO3 -MnCO3 binary plots of several authors (Goldsmith and Graf, 1957). According to Peters (1988) and Winter et al. (1982), the persistence of rhodochrosite + quartz + spessartite assemblage and absence of Mn-silicates such as rhodonite and pyroxmangite in the Mn bearing rocks suggest lower temperature and pressure of 475°C and 2 Kbar, respectively, for XCO2 < 1. Experiments of Goldsmith (1983) show that the temperatures of >500°C are required for the spessartite growth in the spessartite carbonate system (MnCO3-CaCO3) which supports the development of present mineral paragenesis in the primary ore. According to the qualitative phase diagrams provided by Abs-Warmbuch and Peters (1999) as seen in Fig 1), rhodochrosite may not coexist with spessartite and quartz in the absence of additional phases such as rhodonite, braunite, hausmannite, pyroxmangite, bixbyite, galaxite and tephroite irrespective of O2 fugacity and metamorphic conditions in the manganese bearing rocks. However, because only small amounts of Ca and Mg can be incorporated during spessartite growth, the components of interest in spessartite formation approximate the system SiO2 -Al2O3 -MnO-CO2 -H2O. The dominant Mn-carbonate + Quartz ± spessartite assemblage suggest that higher amounts of Mn compared with Si, Al and other major oxides prevailed in the protolith at the time of spessartite growth. The Si-Al-Mn bar chart shown in Figure 5.5a, further supports the fact that there was sufficient MnO and in some cases SiO2 but much less Al2O3 in the original Mn rich sedimentary protolith. Hence it is obvious that the Al phase largely determined spessartite crystallization in the metamorphosed protolith. The nature and composition of the fluid phase during metamorphism also influence the appearance of some minerals. Spessartite formation from Mn carbonates is essentially a decarbonation-dehydration process (Roy, 1981), a mixed H2O-CO2 fluid may have been in contact with both reactants and products under closed system conditions. This mixed fluid, however, may not have significantly influenced the equilibrium reactions described above because of the dominant reactant carbonate-quartz assemblage and the low grade nature of metamorphism in the rocks. Abs-Warmbach and Peters (1999) investigated the relationship between oxygen fugacity and metamorphic grade
in aluminous manganese rich rocks (i.e., the system Mn-Al-Si-O) and suggested that oxygen fugacity could be a critical parameter in the mineral reactions.

The presence of rhodochrosite in the primary ores are the precursor carbonates ore minerals in the district Vizianagram, (A.P) manganese ores is most probably of diagenetic origin. Mn carbonate ore minerals observed in the present ores are most probably formed by early diagenetic reaction of dissolved Mn^{2+} in reducing environments and diagenetically derived from manganese oxides by reaction with HCO_3 after the precipitation of MnO_2. Similarly, some carbonate relics transformed by diagenetic reactions to Mn carbonate. There is strong evidence for primary Mn oxides transformed to Mn carbonates from the mineralogical manifestations of the primary and secondary ores. In the microscopic studies, small euhedral rhodochrosite crystals observed within large Mn oxides referred to diagenetic origin. These are apparently associated with a diagenetic reaction of Mn oxides to dominant Mn-Silicate-Carbonates and generated by pore water-mineral interacting. On the other hand, both stratiform ores show some continuity along strike and absence of the lenticular, anatomizing structure of the manganese-ore horizon on the gross scale suggest that the manganese oxide deposit is primary in origin. The presence of the thin Mn-Silicate-Carbonate ore bands co-folded with the khondalites shows that there is a restricted stratigraphic transition between the formation Mn rich horizons (Figures 3.2c and e). When considered these evidences and the results of diagnostic diagrams together, it can be said easily that the Vizianagram, Mn oxides represent a primary sedimentary origin but, the Mn-silicate-carbonate ore formation occurred during post-depositional reactions. The main ore body follows the regional strike of the khondalites sequence and extends upto many kms within the khondalites and does not extend beyond khondalites. According to Golovenko and Starikova (2007), relatively large (a few meters along the strike) ore lodes can be formed beyond an immediate contact with the stratificated ore bodies only with the participation of hydrothermal solutions and thus the confinement of the present manganese ores with the khondalites prevent the author to not to understand the ores deposit as a typical hydrothermal deposit. However, Vizianagram, type of ore mineralogy and geochemistry is predominantly related to shallow water hydrogenous environment with metasedimentary or metamorphosed mineral assemblages. The mineralogical features coupled geochemical characters of the studied district
Vizianagram, (A.P) manganese ores provide substantial evidences for the mixed source of manganese in a shallow shelf environment and are significant for the construction of the possible genetic model for manganese ores however the mineralogical data alone may lead to an erroneous genetic assessment. Only integrated investigations can achieve the total perspective.

7.2 Geochemical signatures

The present ores are chemically characterized as inhomogeneous, siliceous, ferruginous and carbonaceous with minor exceptions of some purer samples. The bulk ore and host rock geochemistry (Tables 8 and 24) and the discrimination diagrams (Figures 5.10-5.14 and 5.31-5.33) for the analyzed primary and secondary manganese ore samples from the district Vizianagram, (A.P) has shown many evidences in support of mixed contribution from the hydrothermal and terrigenous components in a shallow shelf hydrogenous environment. Manganese seems to be the principal constituent of the manganese ores in the study area and has attained its high concentration as a result of fractionation and separation during diagenesis from the other rock forming elements during process of weathering, transport, deposition, diagenesis and metamorphism and the later supergene process. The bulk composition of the ores could effectively be described in terms of the system SiO\textsubscript{2} - Al\textsubscript{2}O\textsubscript{3} - MnO-FeT, CaO-MgO-CO\textsubscript{2}-H\textsubscript{2}O. The present manganese ores show significant variation in chemical composition especially with respect to Si, Mn, Fe and Al among major elements. The Ti, Al and Mg contents are comparable with the respective values in the khondalites as deciphered from the various important correlations of the major and trace elements. The present ore mineral assemblages as discussed in section 4.3 in the study area have developed as a result of varying bulk compositions particularly Mn, Al, Si, Fe, Ca and Mn and the formation of these minerals is controlled by the ratio of mineral forming elements (mainly Mn, O, Fe, Al, Ca and Si). The Ti, Al, Fe, Ca and Mg contents are comparable with the respective values in the background khondalites. The values of the ore forming elements in the khondalites are much lower than that of the primary and secondary ores. The khondalites are characterized by the higher Wt% age of Si, Al, Fe and Ca but lower concentration of Fe and Mn. The understanding of the presence of these elements in the system demands more justification in terms of the state of the
constituents and the then environmental conditions and the post depositional
diagenesis, metamorphism and supergene alteration. The interesting part of this part
of the research work is to understand the source and delivery of the constituents of the
ores material and their state (either solution or solid state) that lead to the formation
of the initial sedimentary protolith.

The detailed geochemical analysis in the light of mineralogical
manifestations reveals the enrichment of some Mn, Si, Al, Fe, Cu, Ni, Pb and Zn
indicating an intense delivery of hydrothermal and terrigenous matter to the
sedimentation environment. Evidences of endogenic as well as exogenic source of ore
elements can be evident in the studied ores (Figures 5.10-5.14 and 5.31-5.33).
Precipitation of the exogenic matter in the rock association demonstrated by the
concentration of characteristic assemblage of ore elements like Mn, Fe, Cu, Ni, Pb
and Zn (Figure 5.16-5.17 and tables 9-10) as well as the pyroclastic mixture recorded
by the presence of feldspars and spessartite etc in some ore samples and the host
rocks of district Vizianagram, (A.P). Higher silica content in primary ores can be
ascribed to abundant braunite content as a result of syngenetic ore formation prior to
the metamorphism. Relatively high amounts of Si, Al, and Ti as well as good
correlations between SiO₂ and Al₂O₃ and TiO₂ (Tables 9-10) in the manganese ores
of district Vizianagram, (A.P) may be due to the admixture of detrital material during
precipitation as depicted from the Fe-Al-Mn ternary plot (Figure 5.11, After; Choi
and Hariya, 1992) and the discrimination diagram of Si/Al (Figure 5.13, After; Peters
1998). The high Al concentration in both the host rocks and manganese ores are
indicative of sedimentary contribution (Crerar et al., 1982). Higher vaules of Si and Al
in the primary ores, but higher Mn is observed in the secondary ores (Figure 5.5)
suggests clear supergene enrichment. Generally in hydrous conditions Al-Fe-Mn
triad, the solubility of manganese is maximum (as is its mobility) and hence, during
downward movement of iron and manganese in solution, a change in Eh-pH may lead
to precipitation of iron in preference to manganese and an effective separation
between the two may take place. In Si-Al discrimination diagram of Peters (1988),
Vizianagram manganese ores fall as hydrogenous-detrital deposits as shown in Figure
5.13. Moreover, as the Mn/Al ratio increase contemporaneously from the host rocks to
secondary ore, the Al/(Al + Fe) ratio in the primary ores virtually remains the same.
The combined Al-Fe-Mn diagram (Figure 5.11; After, Choi and Hariya, 1992) of the
thirty manganese ore samples illustrates the geochemical specialization of the ore (Al and Fe concentration in primary ores while as the Mn concentration in the secondary ores. When plotted on Si-Fe-Mn ternary plot (Figure 5.10) of Toth (1980) the ores indicate Fe-Si poor and Mn rich tendency of the secondary ores with the higher content of Si and Fe in the primary ore and all the ore samples fall close to hydrogenous–diagenetic fields. Similar genetic nomination of detrital-hydrogenous is seen in the ternary diagram of Fe-Mn-(Ni+Cu+Co) shown in figure 5.12. In addition to these diagrams the Si/Al and Mn/FeT ratios (Table 14) agrees with the compositional trend of the general Precambrian manganese ore deposits as compiled by Maynard (2007 and 2010). Almost all the analyzed samples show wide variation in SiO₂, MnO₂ Al₂O₃ and Fe₂O₃ values (Table 11-13). Drastic difference in the Mn weight percentage in the manganese ores and their host rocks reveals changes in the physico-chemical conditions of the basin that favoured the Mn mineralization with the decreased terrigenous supply. The dearth of the Si, Al and Ti was counter balanced by the formation of manganiferous protolith with the supply of manganese being higher than other ore forming elements.

The oceanic waters have enormous dissolved Mn²⁺ ions in oxygen minimum zone and Mn²⁺ in the upper zone where Mn²⁺ gets precipitated as MnO₂ at the redoxcline (Figure 7.1). However the ferruginous nature of the primary ores is still a debate. According to Canfield et al (1993) adsorption of Mn²⁺ and Fe²⁺ onto Mn and Fe oxides can significantly reduce the concentration of Mn²⁺ and Fe²⁺ especially in bioturbated sediments where adsorbed species become oxidized in contact with oxygen and recycled iron oxides with free adsorption sites are rapidly re-available. This mechanism could be possible for the flocculation of Fe-Mn hydroxides and Mn-oxides leading to the formation of the manganiferous sedimentary protoliths which later resulted into the formation of primary ore. General trend of variation in the Mn/Fe ratio from the SEDEX, hydrothermal to hydrogenous, sedimentary and lacustarine supergene manganese ore is a common fact. Hydrothermal deposits are characterized by high Mn/Fe ratio and low trace metal Concentrations (Hein et al, 1993) than the sedimentary and supergene manganese ores. The approximate Mn-Fe relations are defined as Mn/Fe <1 for lacustarine environment, Mn/Fe =1 for hydrogenous origin and Mn/Fe = 0.1-10 for SEDEX deposits (Nicholson et al, 1997; Oksuz, 2011). The Mn/Fe ratio of manganese ores of the study area are Mn/Fe = 1.27
and 4.14 in the primary and secondary manganese ores secondary ores. The values are neither consistent with the hydrothermal exhalative manganese ore deposits of ophiolitic and submarine spreading centers (Crerar et al, 1982) nor with the marine and SEDEX deposits (Nicholson et al, 1997). The average Mn/Fe ratios of sedimentary manganese ores of Ulukent (Turkey) have been reported as 2.16 -18.98 (Gultekin, 1998) which is somewhat close to the present manganese ores of district Vizianagram, (A.P) and can be understood as an original sedimentary ore deposit with a due contrast in the primary and secondary ore. The contrast and Mn enrichment in the values can be ascribed to fractionation of Fe and Mn and the post depositional metamorphism and supergene alteration primary and secondary manganese ores respectively. The present Mn/Fe values are slightly higher than typical lacustrine and hydrogenous environment but the Mn rich and Fe poor compositional similarity of the Vizianagram manganese ores to some shallow sea/shelf deposits (Harris and Troup, 1969; Thomas and Cronan, 1972; Callender and Bower, 1976) is clearly diagnostic. The moderately elevated Mn/Fe ratios of the present Mn ores are lower than deep marine manganese nodules suggesting that hydrogenous and diagenetic mechanisms, together or separately might have acted in the Mn enrichment as well as the manganophyllic trace elements in accordance with Roy (1992). According to Mita et al (1994), hydrous Fe free manganese minerals precipitate as manganese (Mn⁴⁺) mineral after the oxidation of dissolved Mn²⁺ from the interstitial water of unconsolidated surface sediments in the course of early diagenesis of the sediments and the minor essential elements (Cu, Ni, Zn are subsequently incorporated between the sheet structure by Ion exchange. Negative correlation of Mn with Fe can be ascribed to the fractionation and the supergene enrichment of the studied ores. Manganese due to its high solubility stays longer in solution is transported farther than low soluble Fe counterpart indicating the remote hydrothermal source of Mn with continental Fe from the Archaean mafic province (Figure 7.1). According to (Nicholson, 1990) emission of hydrothermal solution in shallow continental basins has also produced strata bound manganese ore deposits. Higher Mn/Fe ratios of both the primary and secondary manganese ores reveals fractionation of Fe and Mn. Nicholson (1992) summarized some potentially diagnostic positive correlations of Mn from different genetic types of the manganese ores, namely Mn-Ba for fresh water oxides; Mn-Pb for dubhites (oxides formed by the weathering of a mineralized sequence) and Mn-As for hydrothermal deposits.
According to the author, geochemical associations are related to a given deposit type and normalization of the oxide chemistry against manganese content can be employed as a discriminatory in defining element pattern. In case of district Vizianagram, (A.P), manganese shows positive correlation with Cu, Ba, Ni and Pb (Figures 5.18 e-f and 5.19a) suggesting a fresh water and supergene alteration in accordance with Nicholson (1992). The negative correlation of Mn with Si-Al-Fe and Cu (Tables 9-10) dominantly reflects the clastic contribution of these elements excluding Mn itself during the manganese mineralization. The results of these correlations showed that Mn shows positive correlation of Fe with Co and V in the present manganese ores but negative correlation with the element group Zr Zn, Mo and Pb (Tables 9-10) pointing to the ferrophilic nature of V and Pb rather than their manganophilic. Burns and Brown (1972) suggested similar tendencies in hydrogenous manganese minerals as observed in the Vizianagram manganese ores indicating the hydrogenous origin of the present manganese ores of Vizianagram. These results provide indirect evidence that different mechanisms are responsible for the elevated contents of Mn and the groups of trace elements in the primary and secondary ore.

In addition to Mn, the manganese ores are enriched by several factors relative to the regional background of the host rocks in the terrain and include the trace elements like Ni-Cu-Co and Li. Interestingly, increase in the Mn/Fe value during diagenesis of the most Mn ore deposits and later supergene enrichment promotes increase in the contents of microelements like Ni, Cu, Co and Li of the manganese group and decrease in contents of elements of the iron group as evident by the inter-elemental correlation. This feature is related to the primary sedimentary accumulation of the trace elements of the Precambrian and the diagenesis of the initial protolith. Early diagenetic migration of Mn, Ni, Cu, Mo, V and Co from the manganiferrous sediments can also be accounted for the primary ores genesis. The Mn- Ba-Co-Ni-Zn geochemical association also suggests a freshwater origin (Bruland, 1983 and Nicholson, 1992). The inter-elemental correlations between the constituents of the primary ores of the study area indicate a partial contribution of the dissolved Mn with Fe and other terrigenous material towards a common basin. The conditions of the precipitation of the manganese in the shelf zone are a complex mechanism and needs more justification. Generally the Archaean Mn deposits are all high Fe, whereas younger deposits. The present manganese ore is generally Mn rich and Fe poor with high values of Mn/FeT (Maynard, 2010) which corresponds to the general
characteristics of the older sedimentary ore deposits of the Archaean Period having higher values of Mn/Fe indicating the efficient mechanism of separation of Mn and Fe. According to Sapozhnikov (1967) the depositional behaviour of Mn is governed by the hydro geochemical regime of the basin. For Mn, the role of MnOOH and MnO₂ in formation of Mn oxides has long been known. Bricker (1965) showed that MnOOH was precipitated first on oxidation of Mn₂C and then immediately oxidized giving the appearance of direct precipitation to the more highly oxidized phase. The MnOOH present in the marine environment is is widely accepted (Hem et al, 1989). However, the reaction pathway proposed by Giovanoli (1980) does not show MnOOH as an intermediate in the formation of marine manganese ores as does that of Bricker (1965). Crerar et al (1980) pointed out that Mn³⁺ is unstable with respect to Mn⁵⁺ and Mn⁷⁺ and therefore considered that Mn is as Mn²⁺ and Mn⁴⁺ in equal amounts (Gramm-Osipov et al, 1997). Mn is accumulated from the sea water by chemical adsorption of Mn²⁺ on Fe hydroxides with the subsequent oxidation during exchange redox process. According to Hem (1972), Brookins (1988), Gramm-Osipov et al (1990) and Gammons and Seward (1996), Mn²⁺ is the principal aquatic species of Mn in sea water. However, Mn⁴⁺ is confined to reduced waters while as Mn²⁺ to the oxidized waters in accordance with Maynard (2010). Precipitation of Mn may be due to the dilution of stagnant bottom waters by the oceanic water loaded with Mn⁴⁺, resulting in the development of oxidizing physicochemical conditions that promote the precipitation of Mn²⁺ from the oxidation zone. The upwelling and expansion of the Oxygen Minimum Zone (OMZ) as declared by Jenkins et al (1991). The expansion of reducing conditions on the seafloor, possibly due to the enhanced surface-water productivity, caused mobilization of Mn oxides from deep water sediments into the mid-water column and transfer to shallow water sediments (Maynard, 2010). This oceanic Mn in combination with the fresh Mn of the oceanic hydrothermal sources lead to the higher concentration of dissolved Mn⁴⁺ in the OMZ. The upper boundary of the OMZ forms the redoxcline (contact plane between the oxidized surface waters and reduced bottom waters) as seen in Figure 7.1. Precipitation of Mn²⁺ is controlled by reducing conditions and the concentration of Mn⁴⁺ in the reduced waters below the oxidized waters in the shelf zone. The cyclic precipitation of Mn²⁺ from the oxidized surface waters into the dissolved Mn⁴⁺ terminates at the point of contact with the sediment surface. At this contact position, Mn²⁺ can be re-oxidized to insoluble MnO₂ which falls to the bottom where it is
converted to Mn-carbonate during early diagenetic reaction with organic matter (Calvert and Pederson, 1996). At the same time by oxidizing environment's effect Ni, Pb and Zn could also form compounds with oxides of Mn together, such as \( \text{Zn}_2\text{Mn}_3\text{O}_8 \), \( \text{Ni}_2\text{Mn}_3\text{O}_8 \) and \( \text{Pb}_3\text{Mn}_3\text{O}_8 \) and so on. These formative oxides made Mn more oxidized and concentrated. Thus Ni, Pb and Zn accordingly are enriched along with Mn elementary ceaseless concentration. \( \text{Pb}^{2+}, \text{Zn}^{2+}, \text{Ni}^{2+} \) and \( \text{Mn}^{2+} \) may also form isomorphous compounds with Mn and Fe. When these isomorphous compounds entered zone of oxidation from native zone, manganese could convert from \( \text{Mn}^{4+} \), to \( \text{Mn}^{2+} \) and \( \text{Mn}^{3+} \), associated with rise in Eh value (Jiang et al, 2006). Along the suggested redoxcline the precipitated accumulation of large amounts Mn-oxides and hydroxides with the sedimentary admixture was followed by diagenetic carbonate formation place in the shelf zone. This model of the manganese ore genesis in the present study area is the most possible mechanism of precipitation of manganese ores as shown in Figure 7.1. Concentration of this material in the sedimentation zone was fostered by the stagnant reducing environment of bottom water. Ore deposition was promoted by the periodic delivery of fresh portions of ocean water that created oxidizing conditions favourable for the precipitation of Mn. According to Usui et al (1986), hydrous Fe free manganese minerals precipitate as manganese (Mn\(^{4+}\)) mineral after the oxidation of dissolved Mn\(^{2+}\) from the interstitial water of unconsolidated surface sediments in the course of early diagenesis of the sediments and the minor essential elements (Cu, Ni, Zn are subsequently incorporated between the sheet structure by ion exchange. According to Canfield et al (1993) adsorption of Mn\(^{2+}\) and Fe\(^{2+}\) onto Mn and Fe oxides can significantly reduce the concentration of Mn\(^{2+}\) and Fe\(^{2+}\) especially in bioturbated sediments where adsorbed species become oxidized in contact with oxygen and recycled iron oxides with free adsorption sites are rapidly re-available. This mechanism may be accounted for the flocculation of Fe-Mn hydroxides leading to the formation of the manganiferous sedimentary protoliths for the primary ore. High phosphorus in the manganese ores of the study area may be attributed to its strong positive correlation with Fe\(^{2+}\) instead of Mn. Fe shows positive correlation with P\(_2\)O\(_5\) in the present manganese ores just like most other sedimentary manganese ores. A high degree of correlation of P with Fe has been shown for the first time by Calvert and Price (1977b) from the shallower parts of pacific which points to the shallow shelf environment of the present ores. There are substantial evidences in support of the shallow water-hydrogenous origin of the present
manganese ore such as high Ba, P and K as compared to the typical deep marine hydrothermal manganese ores. The enrichment of variable valence and other biophile elements (such as P, Fe, Mn, Co, Cu, Sr, Ba, Ni and Zn) is also a characteristic of bacterial activity sediments. Fe in the manganese ores of district Vizianagram, (A.P) shows positive correlation with Al, Co, Mo, Zn and Zr (Tables 14-15 and Figures 5.19-20). Mn is negatively correlated with Si and insignificant relation with P2O5 and V suggests varied sources of Fe and Mn rather than a common source. The direct hydrothermal influx of Fe seems less significant as compared to terrigenous supply from the ferruginous host rocks as evident in the elemental correlations of Fe with Mn and the Mn:Fe ratio. The dominant iron species in sea water include Fe (OH)3, Fe (OH)2 and Fe (HS)O3 as stable aqueous species under reducing conditions while as goethite (FeO(OH)), maghemite (Fe2O3) and magnetite (Fe3O4) appear to be the stable solid phases in marine conditions (Bruland, 1983).

Bruland et al (1994) suggested that goethite is the stable phase at the redox conditions of sea water and that Fe is present in sea water in both particulate and soluble form and might have been formed with the manganiferous sedimentary protolith with the manganese in the initial stages. These species of Fe are the probable source of Fe for the studied manganese ores in the present terrain. In addition, it is concentrated in the detrital material formed at the expense of destruction of ferruginous rocks. Iron is also a characteristic element of the hydrothermal influx in the marine sources and its major portion in the sediments of marginal seas occurs in terrigenous clay minerals (smectites, chlorites and Fe-hydromicas) which can also be accounted as the source of Fe for the studied ore. Rozenson and Heller-Kallai (1976a, 1976b) showed that the potential of repeated reduction and oxidation of Fe within silicates with the aid of chemical agents which could be the possible reason of the highly variable content of Fe in the present manganese ores and their host rocks. Varied forms of Fe in the manganese ores of almost all samples in the form of maghemite, magnetite, vredenburgite and jacobsite, haematite etc can be attributed to the reactive character of Fe. According to Canfield et al (1992) sedimentary iron can be regarded as reactive from two perspectives, the bio-available fraction consisting of iron oxy-hydroxide (FeOOH H2O: poorly crystallized, easily reducible) and iron oxides (goethite, haematite, magnetite: well crystallized, only soluble by strong
reducing agents). Iron phases like iron oxy-hydroxide, iron oxides and iron-containing silicates are too reactive (Canfield et al., 1992; Kostka et al., 1996) discovered experimentally the microbial Fe (III) reduction within terruginous clay minerals which was postulated before by Lyle (1983) and can be accounted as the iron components of original sedimentary protolith and the resulting mineral phases in the present ore rather than the biogenous fraction. The difference in stability fields of FeOOH is less readily mobilized but more readily precipitated than MnOOH in the marine environment (Crerar and Barnes, 1974; Davison, 1993). This means that Mn is more mobile than Fe in both submarine hydrothermal (Hannington and Jonasson, 1992; Lilley et al., 1995) and shallow marine (Glasby, 1977) environments. Due to this fact the present manganese ores have high Mn than Fe in both primary and secondary ores. Barium content of the present manganese ore is high as compared to the hydrothermal or deep marine manganese ores as detailed in tables 15-16. Higher content of Ba is indicative of sedimentary origin in accordance with Gültekin (1998) and Oksuz (2011). In general the Ba content of fresh water deposits is higher than the marine because the low concentration of sulphides present in the fresh water prevents precipitation of barite, leaving Ba free for substitution in Mn-minerals principally psilomelane. When the fresh water and sea water mix up barium precipitates easily as BaSO₄ and therefore in freshwater sedimentation Sr/Ba <1 while as in marine deposits it is >1 (Fan, 1994). According to Nicholson (1992), the positive correlation of Mn with Ba-Co-Ni-Zn is a characteristic of fresh water manganese ores. Similar positive correlations of Mn with Ba-Co-Ni-Zn in the present manganese ores (Figures 5.10 to 5.13) suggests shallow-fresh water genesis of the ore. Higher wt% Ba in the secondary manganese ores of Vizianagram also agrees well with their supergene alteration similar to the findings of Nicholson (1992). Some of the ore samples are characterized by the virtual lack of indicator elements of the terrigenous Source (Al, Ti and Mg) and the low Ca content, while silica and Mn contents are high. This fact suggests high rates of the accumulation of ore bearing sediments in some sectors of the seafloor. Under these conditions, the chemogenic and terrigenous sedimentation was suppressed by the input of hydrothermal material. During the diagenesis of such sediments, the reducing species of Mn reacted with the siliceous gel to form silicate compounds, while the excess metal was fixed in rhodochrosite as the result of reaction with carbon dioxide in interstitial waters. Presence of moderate Ca also suggests a carbonate precursor which in general is confined to shelf zones. With
respect to Na and K, the former has lower concentration in the manganese ores of the study area (Table 9 and Figure 5.6). Most of the manganese mineral phases are the carriers of Na and other alkalis and include cryptomelane, psilomelane and hollandite (Siddiquie, 2005 and Siddiquie and Raza, 2008). With respect to Na and K, the manganese ores of district Vizianagram, (A.P) have higher K than Na values in both primary ores and secondary ores as seen throughout the district (Table 8). Higher weight percentage of Ca in the sedimentary-diagenetic and shallow marine manganese ores than hydrothermal and deep marine manganese ores (Table 15) is a clear with minor exceptions. According to Cretar et al (1982) the positive correlation of Mn with Ca but negative correlation with Fe suggests early diagenesis and the carbonate replacement of hausmannite and rhodochrosite. Generally the MnCO$_3$ becomes the predominant aqueous species at pH values > 9.1. Suggesting increase in Eh and pH in the geochemical system after the precipitation of the initial Mn phases from the water. Higher concentration of Na$^+$, K$^+$, Ba$^{2+}$ and Ca$^{2+}$ as observed in the manganese ores of Vizianagram suggests high redox potential in accordance with Burns and Burns (1977) pointing to the existence of the redoxcline of Maynard (2010) as a result of the mixing of the fresh and saline water at the time of precipitation of the manganiferous protolith on the shelf zone. The Na-Mg discrimination diagram of Nicholson (1988) as seen in (Figure 5.15) shows that the present manganese ores fall close to the fresh water-shallow water environment instead of the marine field.

The trace element geochemical characteristics show that the formation of the manganese deposits in district Vizianagram, (A.P) is not determined by single element, but results from interactions of many elements. Although content of some elements are low in concentration but they have played an important role in manganese concentration process. The trace element data of the primary and secondary manganese ores from district Vizianagram, (A.P) shows three distinct groups of trace elements as Ni-Cu-Co, Pb-Zn-Zr and Sr-Cr-V-Li in the order of declining concentration as can be seen in the variation diagram (Figures 6.7a-b). The comparison shows much similarity in Ni and many other trace elements of the secondary ores with that of Orissa, India (Mohapatra and Nayak, 2005a and 2005b). The ores show close similarity of Cu contents with the manganese ores of Koryu, Japan (Table 15-16). The concentration of Co and Cr content is again higher than the other manganese ores like that of Turkey, China and Pacific Ocean but lower than
that of Orissa as detailed in Table 15-16. The average Sr values of 115.49 and 254.06 ppm recorded in the primary ores and secondary ores respectively and are far lower than that of the reported values from Orissa, Turkey, Pacific, China and U. S. A (Table 15-16). The average V content shows insignificant values while as Pb shows slightly elevated values. Zr is higher in the primary ores than in the secondary ores and in the overall ore it shows higher peaks than that of the reported values from Pacific manganese ores and that of Orissa (Table 15-16). All the similarities suggest a mixed source of the hydrothermal, biogenous and terrigenous and volcano-clastic sources. In general, Mn and Fe are considered as two main elements that adsorb the trace elements irrespective of any surface charge and were also concluded from the experimental studies of Krauskopf (1956). Trace elements like Ni and Cu show positive correlation with Mn as they are all gradually gathered followed by the increase of Mn content, which was determined by element’s nature. It was also shown by Murray and Brewer (1977) that Mn oxides and Fe oxides are extremely efficient scavengers of cations and anions alike, irrespective of surface charge and so the higher values of the manganophyllic and ferrophyllic trace elements with the former as more efficient due to the higher values of Wt% of Mn in the ores. Most of the trace elements are very close to the values of that of the manganese ores of Orissa (Mohapatra and Nayak, 2005a and 2005b), metasedimentary Garividi and Chipurupalle (Siddique, 2004) and Barbil (sedimentary) manganese deposits (Table 15-16). Fe- (Co+Ni+Cu) -Mn discrimination diagram of (Bonatti et al (1972), Ni-Zn-Co discrimination diagram of (Choi and Hariya, 1992) and Co/Zn vs Co+Ni+Cu of discrimination diagram (Toth, 1980) were also used to probe the Vizianagram manganese ore genesis and were found very conclusive in the present piece of research work.

The concentration of cobalt is 530.80 and 866.38 ppm in the primary and secondary manganese ores of district Vizianagram, (A.P). The highest concentration of Co in the manganese ores recorded so far in the available literature is 1.79 wt% (Hewett. et al (1963) from Western supergene oxides of Cherry Geek, Montana. The levels of Co found in the current study area are far higher than the range of the typical hydrothermal deposits \( (i. e < 300 \text{ ppm}) \). The values of Co being highest in the sea mounts and other deposits of elevated areas (up to 1 Wt% on Kelvin sea mount) and lowest in the topographically depressed basins suggests that different mechanisms were involved in the formation of these ores. Higher contents of Co and Fe in the
high redox potential areas of topographic highs has been attributed their accommodation by δ-MnO₂ (Barnes, 1967; Goldberg, 1961; Burns (1965, 1976), Cronan and Thooms (1969) which can be accounted as the mechanism of incorporation in the ferro-manganese oxide minerals of the study area. CO₂⁻ in sea water is initially adsorbed on the surface of δ-MnO₂ near vacancies in the edgesheared MnO₆ octahedral and is then oxidized; low spin CO₃⁺, then enters the δ-MnO₂ lattice (Burns, 1976). Also, the ionic radius of CO₃⁻ is similar to that of Mn⁴⁺ (0.54Å) and can be considered as the substitute during the formation of the oxyhydroxides of manganese and iron during their formation from the shallow shelf waters in the oxic environment. Good correlation between Fe and Co suggests absorption of Co by Fe phase (Banerjee and Miura, 2001; Halbatch et al (1981) and due to this fact the samples with high FeT wt% values are seen to contain higher values of Co in the present study (Tables 9 and 17). The Co/Ni ratio is an important criterion for determination of sedimentary environment and is used to distinguish hydrogenous and hydrothermal deposits (Toth, 1980). Co/Ni values in both the primary and secondary manganese ore is 0.60 hence indicates the sedimentary environment. The Co/Zn vs Co+Ni+Cu of discrimination diagram of Toth (1980) suggested hydrothermal diagenetic fields and on the basis of present interpretation the author suggest the hydrothermal/diagenetic field nominations (Figure 6.12). The lower values of Co/Ni than the ores associated with marine topographic highs also indicate that precipitation of the ores was not hot water sedimentation and the depth of the basin was almost alike throughout the study area in accordance of Fan (1994) and Nicholson (1992). Thus Co/Ni ratios also support that both sedimentary and shallow marine environments were effective for the formation of Vizianagram manganese deposit which are basically hydrogenous compounds of manganese. The Co/Zn ratios are low as compared to deep marine, typical volcanogenic and hydrothermal manganese ores. The average Co/Zn values of 0.97 in the primary ores are high but is as high as 4.63 in the supergene or secondary ores of the study area indicating gain in the Co contents with supergene enrichment of the ores and agrees well with the finding of Nicholson (1986, 1992). Manganese ore minerals also adsorb Cu and other trace metals from sediments during the process of diagenesis as per the findings of Volkov and Sternberg (1981), Bazilevskaya (1985). Higher concentration of trace elements such as Cu and Ni are also known to be the products of early diagenetic (Halbatch et al (1981b; Calvert and Price, 1972). Preferential uptake of
Ni, Co and Cu is seen in Vizianagram manganese ores as compared to the manganese ores of other genetic types as seen in Table 15-16. The positive Mn-Ni-Cu correlation generally observed has also been explained by the mechanism of formation of todorokite by the recrystallization of δ-MnO₂ in the presence of Ni²⁺ and Cu²⁺ ions (Burns and Burns, 1978). Generally the secondary ores contain higher concentrations of total base metals (Co+Cu+Ni+Zn) than secondary ores. Cu, Ni, Zn, Mo, K and Ba can preferably enter the todorokite lattice in the areas of relatively low redox potential in deep sea and continental margins in low and high cation concentration respectively, incorporation of trace elements occurs in diffuse outer part of the electrical-double layer substrate and into the disordered inner layer todorokite structure (Murray et al, 1968). The relative concentration of base metals in the primary ores are Ni>Co>Cu, while as in secondary ores it is Cu > Ni > Co indicating the dominance of hydrothermal contribution for the primary ores and the supergene addition of Cu in the secondary ores. In continental margin areas the manganese ore deposits have trace metals Ni, Co, Cu as they may form stable chelates within the sediments. The variable concentrations of Ni, Co, Cu and Zn within the ores of the study area also reveal fluctuations in the trace element supply towards the depositional environment. The concentration of Ni, Co, Cu in the manganese ore is also determined by the Mn/Fe ratio. Hydrothermal and volcanogenic-sedimentary deposits of varying composition have been reported from the flank of the East Pacific Rise (Mn/FeO = 0.06, Low content of Ni, Co, Cu by Bonatti et al, 1972, 1976) and from Hess Deep the Mn/Fe is 0.77 with content of Ni, Co and Cu relatively enriched (Burnett and Piper, 1977), while as the Galapagos spreading center having Mn/Fe of 555-5000 with Ni, Co, Cu content very low (Moore and Vogt, 1976). The average concentration of Cu, Pb and Ni of the studied samples shows much similarity with the Precambrian manganese ores of Orissa and Vizianagram, (Acharya et al, 1996; Siddiquie and Raza, 1990) Bhandara, Maharashtra (Rai et al, 1979) and Barbil, Orissa (Ajmal, 1990); Vizianagram, (A.P), (Siddiquie and Bhat, 2010). When plotted on a ternary diagram incorporating the diagnostic marine elemental assemblage Co-Cu-Ni, the Vizianagram ores lie distinctly away from the position of ferromanganese nodules of the Pacific and Indian oceans; the Arndilly (hydrothermal) and San Francisco (volcanogenic) manganese ore deposits. Ni and Cu are taken up dominantly in the divalent state but Cu is of particular interest because of its known depletion in Co-rich manganese crusts taken below the oxygen minimum zone. Compositional
data plotted on Fe-Mn- (Co+Ni+Cu) x 10 ternary diagrams of Bonatti et al (1972) shows that all the samples fall within the detrital-hydrogenous field. According to Banerjee and Miura (1998) and Banerjee and Miura (2001), mobility of Mn is higher compared to Ni, Cu and Co under suboxic conditions. Therefore, higher Mn/Fe ratios as compared to the marine ferromanganese ores could indicate oxic conditions overlying suboxic sediments or the high redox potential in the palaeo basin of the present manganese ores in accordance with the finding of Banerjee and Miura (2001).

Also the variable Sr/Ba values are the same as the Sr anomaly, the Sr/Ba values of the Mn ores and khondalites are low reflecting the shelf facies sedimentary environment with low salinity conditions. The apparent contrast in the bulk ore geochemistry of the primary and secondary manganese ores (Figures 5.6 and 6.7) reveals the channelization of the ore forming elements especially the Mn and the manganophylic trace elements from the primary and secondary manganese ores. In Mn-Fe-(Co+Ni+Cu) x 10 ternary diagram (Figure 5.13) after Bonatti et al (1972) and Crerar et al (1982), all samples fall in detrital-hydrogenous field. Since Mn is also negatively correlated with the trace elements like Zr, Zn, Mo and Pb but there is positive correlation of Fe with Co and V (Tables 14-15) pointing to the ferrophilic nature of V and Pb rather than their manganophilic. Burns and Brown (1972) suggested similar tendencies in hydrogenous manganese minerals as observed in the Vizianagram manganese ores indicating the hydrogenous origin of the present manganese ores of Vizianagram. Pb and Zn values are comparatively low in the present ores. Laboratory results of Gadde and Laitinen (1974) showed that over the pH range 2–8 the extent of adsorption of Zn is always high. The higher concentration of Pb and Zn in the primary ores can be considered as the diagnostic hydrothermal and volcanogenic input in accordance with the result of researchers on the manganese ores (Zantop, 1981; Nicholson, 1986 and, 1988; Ajmal, 1990). Results of the geochemical study of manganese ores from the district Vizianagram, (A.P) made it possible to refine the genesis of the ores in the study area and some peculiarities of the geochemistry of manganese ore forming processes. Affiliation of the manganiferrous association to the volcanogenic (hydrothermal) sedimentary type is proven by several indicators such as the facies genetic interpretation of the ores hosting section, the petrochemical and mineral composition of rocks in the ores bearing rock association, the presence of coeval volcanic formations. But the slightly lower concentration of Pb and Zn in Vizianagram ores distinguishes them from the typical hydrothermal-volcanogenic
manganese ores (Table 5.4) pointing to the supergene alteration and mixed sources of contribution. The average Co/Zn ratio of the thirty ore samples from Vizianagram is 4.41 and being greater than 1 suggests the hydrogenous origin in accordance with Toth (1980). Source Cr in the present manganese ores has been attributed to the mafic rocks of the region by Rao (1983) and Siddiquie (2004). Moderate contents of Li can either be associated in high temperature manganese minerals or with Al and may be accounted as the cause of their higher concentration in the primary ores as compared to the secondary ores. The possible source of Li was most probably the hydrothermal discharge into the depositional basin. Additional input may be due to the terrigenous supply through weathering of alkali pyroxenes during the manganese mineralization in the study area. The major and trace element diagnostic diagrams and the absence or below determination limit concentration of As and Ag etc indicate that the Vizianagram manganese ore deposit is not hydrothermal type. On the basis of accumulation of manganese mineralization in the oxic zone, the possible association with sea-level fluctuation, associated rocks and occurrence in a sequence of rocks containing shallow-shelf sedimentary facies. The concept of “colloidal gel” of Roy (1981) suggests solution rich in the elements like Ba, K and Pb seems to have invaded the ores after the primary consolidation metamorphism because the present samples from primary ore horizons are devoid or least associated with these elements. In the light of major and trace element studies, the present research work concludes that the manganese ores of district Vizianagram, (A.P) are the result of a set of geological process that have operated in the Precambrian followed by diagensis and the latest supergene alteration which operates at present as well metasediments, including manganese ores of district Vizianagram, (A.P) were formed during diagensis by the intervention of sulfur reducing bacteria reflecting the sedimentary origin of these host rocks. The ores was formed primarily in the oxic system followed by anoxic treatment as evident in the presence of pockets of shale as detailed by Siddiquie (2004) and Siddiquie and Bhat (2010).

The Precambrian transgression is mostly responsible for large input of dissolved Mn and organic matter to sea water. As a result of this, a oxygen minimum zone (OMZ) or the anoxic zone with restricted change with the basin led to the accumulation of dissolved Mn and Fe with low Eh values (Eh<0) in the shelf water column. During this period, the continued hydrothermal fluids rich in manganese
were released into the anoxic sea from some remote location where they remained in solution till they reached the favourable site of deposition in the shelf were they were trapped and preserved with organic matter. In the stage of peak transgression, both oxygen depletion and dissolved Mn reached to a maximum level in the reducing waters. The present manganese ores are largely associated with the early stages of marine regression leading to relative deepening of the oxidation-reduction interface. In this stage, the sea water becomes more oxic and anoxic deep sea water enriched in Mn$^{2+}$ has transgressed to a self region containing abundant oxygen. So, manganese ores are deposited within restricted basinal areas reflecting an estuary or lagoon, as a function of gradually raising the Eh and pH. Sedimentation in the late stages of transgression was most probably dominated by the deposition of lime stone shale and sand stones. As a function of increasing thickness of sedimentation and the presence of HCO$_3$ in sea water, some primary manganese oxides transformed to manganese carbonates and dissolved manganese again led to diagenetic reactions in the protolith and most probably some calcite pisoliths also transformed to manganese carbonates in this stage. All these evidences suggest that the ores were initially deposited in the shallow-water zone of continental shelf in an oxic environment followed by anoxic treatment. The suggested depositional model for the Vizianagram manganese deposit is given in Figure 7. Moreover, the present ore can in no way be considered as aquagene (found in alluvial sands and on sediment water interface on ocean floors in the form of crusts instead as hydrogenous being the syngenetic intrastate ore deposits as depicted by their field characteristics and the mineralogy. In case of the solid phase, various MnO$_2$ phases and MnOOH appear to be stable but according to Brookins (1988) the main solid phases are MnO$_2$, MnO and MnO$_x$\(\delta\)MnO$_2$, one of the principal minerals occurring in manganese ores , has a standard free energy of -108.9 kcal/mole (Bricker, 1965). It can be shown that the stability boundary for $\delta$ MnO$_2$ has the same gradient as the boundaries for pyrolusite and lies between these two lines. Nonetheless, these solid Mn Oxy-hydroxide phases are not thermodynamically stable under deep sea conditions. The latest stages of ore formation appear as secondary ore minerals like pyrolusite, cryptomelane, psilomelane and ramsdellite are represented by supergene alterations leading to the transformation of primary manganese silicate-carbonate ore into oxide phases (pyrolusite and cryptomelane). These ore minerals are observed widely in the secondary ores along weakest zones-bedding planes of ore beds and cross cutting
fissures. When comparing oxide mineralization in stratified or primary ore horizons and the discordant manganese oxide ore confined to the khondalite sequence of the study area the different stages and the involved mechanisms are clear in their formation. During the post-metamorphic period, prolonged exposure of the deposit to atmospheric oxygen and meteoritic waters has caused the primary minerals to undergo supergene alteration. Most of the primary manganese oxide minerals are totally obliterated by weathering and supergene processes. The manganese silicates like spessartite are also affected. Under supergene conditions, due to strong oxidation effects, the manganese oxides of lower valency states (primary minerals) were transformed into manganese oxides of higher valency states e.g. pyrolusite, cryptomelane and romanechite. Development of cryptomelane/romanechite and goethite from garnet can be cited as an example. During this supergene process, elements such as Mn, Fe, P, Al and Ti are enriched and Mg, Ca and Si are leached from primary manganese minerals. The colloform manganese ores in the study area suggests the colloidal deposition of the secondary ores which is a universally accepted fact and consists of pyrolusite, psilomelane and cryptomelane at the most. The formation of the colloformic ores seems to be similar to that of the botryoidal ores of Visakhapatnam and Srikakulam as described by Rao (1960), “which are formed by the alteration and concentration of the manganese in bedded deposits”. However the colloformic ores may be formed either by transportation of the constituents in true solution and their precipitation as colloids at the site of deposition or transportation of the constituents in a colloidal solution and their flocculation at the site of deposition (Roy, 1981; Nicholson, 1997). But the views did not satisfy the experimentalists to a good extent as it was not clearly understood that in what state the solution was and the mode of transport. The continued research work by Straczek et al (1956) opined that the secondary Mn ores were formed in situ as a result of supergene oxidation of the gondites and associated braunite even at a depth of 400 ft or more from the surface in Dongari Buzurg mines. This opinion was strongly argued by Roy (1965) which according to him cannot account for the existence of cavernous and colloform ores. Roy (1965) introduced the concept of “colloidal gel” as an invading material rather the in situ supergene oxidation or weathering. On the other hand Boydell (1925) concluded that the ores showing various colloformic structures are of colloidal origin and the colloform bandings in them are likely to have been formed at ordinary temperatures and pressures under geological conditions. The
abundance of the colloform structures in the secondary Mn ores indicate that they were derived largely by dissolution and deposition by ground water through supergene alteration and enrichment whereby the primary ore minerals have been altered and or changed to the secondary minerals mentioned above. The altered primary and newly formed secondary ore minerals have been deposited as the secondary ore deposits as discordant bodies along fractures, bedding places and fault planes within the preexisting ores bodies and host rocks.

Figure 7.1  Hypothetical genetic models showing the genesis of the manganese ores of district, Vizianagram (A.P).