Abstract

Manganese ore deposits are widely distributed both in time and space extending greater part of the earth (Roy, 1981, 2000) and are extensively distributed on continents (Table 1) in the form of oxides, carbonates and silicates. Sedimentary manganese deposits are the largest deposits followed by volcanic hosted ones. The deposition of manganese was initiated from Late Archaean period probably with the development of oxygen oases in the otherwise reducing hydrosphere (Nicholson, 1997). The various parameters of palaeoclimate and tectonics played major role in manganese metallogenesis with space and time since the initiation in Archaean (Roy, 2000). The major global manganese ore deposits of the Proterozoic age can be grouped as Palaeo-proterozoic, Neoproterozoic and Cenozoic showing contrasts in bulk ore geochemistry and mineralogical manifestations recording the Earth’s past environment (Maynard, 2010). The largest volume of Palaeo-Proterozoic manganese deposits are in Kalahari region of South Africa while as the largest Neo-proterozoic deposit is in Brazil with many smaller deposits occurring in China and India. Indian manganese ore deposits are dominantly meta-sedimentary and supergene in nature distributed mostly in the Precambrian gneisses and Khondalites concentrated in the states of Andhra Pradesh, Bihar, Goa, Gujarat, Karnataka, Madhya Pradesh, Maharashtra, Orissa, Rajasthan and Tamil Nadu. The meta-sedimentary manganese deposits of small to moderate in 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 (Figure 1.1). The manganese ore deposits of district Vizianagram, (A.P) hosted by the Khondalite-Charnockite terrain in Eastern Ghats Mobile Belt is about 60 km distant from the Visakhapatnam city of A.P, India. The manganese ore bodies are mainly concentrated between the 18°12’N-18°30’N latitude and 83°20’E-83°45’E longitudes in the study area along Garividi, Garbham, Chipurupalle, Bangararuvalasa, Avgudem and Sadanandapuram blocks (Figures 1.2 and 2.2) as detailed in table 4. The lithology in the present study area is dominantly mixed meptapelites with clear mapable bands of quartzites and Calc-granulites and the 2nd group as charnockites mainly the massif types. The present Mn-silicate, Mn-carbonate and Mn-oxide ores located in the high grade, pelitic and calc-silicate granulites and garnetiferous quartzites (Roy, 1960, 1981; Sivaprakash, 1980; Dasgupta et al, 1993, Siddiuiiqe, 2010). The Calc silicate granulites and Quartzo-feldspathic gneisses host the
Mn-silicate carbonate rocks in Kotakara-Garbham area of Vizianagram (Mukhopadhyay, et al 2002). The Calc silicate granulites and Quartzo-feldspathic gneisses host the Mn-silicate carbonate rocks in Kotakara-Garbham area of Vizianagram (Roy, 1981; Mukhopadhyay et al., 2005). Present field work also made it clear that the manganese ores in the area occur primarily in association with Calc-Granulites, less often with other garnet sillimanite gneiss and quartzite members of the Khondalite group.

The present piece of research work includes both field and laboratory experiments. The present research work will stress upon the bulk geochemistry including the major, minor and trace elements of the manganese ores and the host rocks of the studied terrain with emphasis on the various other aspects like metamorphic transformations of mineral phases and the resultant geochemistry to project the desired geochemical picture of the studied ore deposits. The present work aims at a critical assessment of the parameters that controlled the chemical composition of the Vizianagram manganese ores through changes in physical and chemical environments from the Early Archaean triggering the inauguration of sedimentary manganese metallogenesis and the later metamorphism and mineralogical changes to the recent supergene enrichment. The Vizianagram manganese ore deposits were studied in both field with reference to the tectonic, lithological and structural controls of ore deposition and in laboratory for their geochemical and mineralogical aspects to probe the possible conditions associated with their formation and the later transformations. The hand specimens of the variety of manganese ore samples collected from different mines and quarries of the study area are detailed in chapters 2 and 3. The ore mineralogical studies coupled with their field disposition in the study area indicate clear distinction of primary or metamorphosed manganese ores and secondary or supergene manganese ores (Figures 3.3 and 3.4) altogether hosted in the khondalite group of the terrain. 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 followed by supergene enrichment. The primary manganese ores (metamorphosed or meta-sedimentary ores) consisting mainly of manganese silicates and minor manganese oxides occur conformably enclosed in the pelitic khondalites, calc-silicate granulite and weathered quartzite. While as the secondary ores bodies of supergene nature are discordant with the host rocks through the terrain and are mammillary and botryoidal in form (Figures 3.3 and 3.4).
The granulites grade metamorphism declared in the region is evident in both the field and hand specimens of the host rocks (Figures 2.3-2.4) as well as in the ore samples (Figure 3.4). The Metamorphosed manganese deposits from Koduru and Garbham areas consisting of manganese silicates like bixbyite, braunite, hausmannite, rhodonite, spessartite, hollandite, jacobsite and vredenburgite as primary manganese oxides and silicates. The secondary ore minerals like pyrolusite, cryptomelane, psilomelane, ramsdellite, lithiophorite were also detailed by previous workers Sivaprakash, 1980; Krishna Rao, 1954, 1956a, 1956b, 1963a, 1963b; Krishna Rao and Dhana Rajju, 1966; Siddique, 2004; Siddique and Bhat, 2008) and are shown in figures 4.1-4.9.

The geochemical analysis of thirty ore samples from the six blocks of district Vizianagram, (A.P) shows higher values of Si, Al, Fe, P, Na, Mg and K in the primary ores while as the higher values of Mn, P, Ca, Ti and Ba are seen in the secondary ores as shown in table 8 and figures 5.1-5.5. The distribution pattern of minor elements like K₂O, Na₂O, MgO, CaO, BaO, TiO₂ and P₂O₅ in Vizianagram manganese ores vary in their concentration within limited range (Tables 11-13). The overall ore shows higher concentration of potassium, but average Na₂O, CaO, MgO, BaO and TiO₂ goes around 1% as seen in tables 11-13. The ores have a mixed source of hydrothermal, oceanic and terrigenous components as evident in the discrimination plots and ternary plots of Si-Al-Mn, Mn-Al-Fe, Mn-Al-F, Al-Ti Fe-Mn-Si (Figures 5.10-5.14). The discrimination diagrams of Ni + Co + Cu Vs Ni + Cu and ternary plots of Ni-Zn-Co (After; Choi and Hariya), Ni + Co + Cu Vs Co/Zn, (Toth, 1980 and Choi and Hariya, 1992) shown in figure 5.30-5.33 along with the positive correlations of Mn-Ni-Cu-Zn (Figure 5.17) indicate the hydrogenous, shallow-shelf sedimentary-diagenetic genesis of the present manganese ores. The ores show sedimentary hydrogenous nature with respect to high Mn and Ba values, positive correlation of Mn with Ba-Co-Ni-Zn (Figure 5.16 and tables 9-10) in accordance with Nicholson (1992). Ba/Sr values also indicate sedimentary nature in accordance with Fan (1994). The dissolved oceanic Mn was dominantly contributed by remote marine hydrothermal sources and was carried to the shelf zone due to its high solubility and longer transportation as compared to its co-generated Fe counterpart which gets deposited near the vent. The Mn remained in the dissolved state as Mn²⁺ in the oxygenated surface waters of the ocean and in Mn⁴⁺ in the reduced deep water. The two water columns are demarcated by the redoxcline across which the Mn alternates as Mn²⁺ and Mn⁴⁺ across the redoxcline for most of its life span till it reaches
the sediment surface in the shelf zone where the Mn$^{2+}$ is deposited as MnO$_2$ over the shelf carbonate platform as shown in the hypothetical genetic model in Figure 7.1. The influx of elision, gas and water fluids along a fault zone from the sedimentary sequences of the sedimentary basin, which resulted in specific physicochemical conditions in the bottom and silt waters; this, in turn, provided conditions for the accumulation of the elements of anoxic environments and retention in the sediments of Mn and trace elements precipitating from hydrothermal plumes. The precipitated MnO$_2$ reacted with the available Si, Ca, Al and Fe in the system of Mn-rich sediments leading to the formation of earlier Mn-silicate and carbonate protolith. During this stage of Mn mineralization the Si, Al, Ca, Fe, Ba, P and Ti from the terrigenous sources was consumed in the formation of the manganese silicates and carbonates.

The primary manganese ores are enriched in Si, Fe, Ba, P, Ni, Cu, Co and V in comparison to other manganese ores (Tables 8, 15 and 16) and are considered as primary metamorphosed ores while as the manganese enriched ores of higher oxides are secondary in nature and are of supergene nature formed from the pre-existing primary or metamorphosed ores were also worked out by previous workers (Krishna Rao, 1963a, 1963b; Krishna Rao and Dhana Raju, 1966, 1964, 1967; Roy, 2000; Siddiquie and Raza, 2008; Siddiquie and Bhat, 2010). The original sediments probably contained some amount of phosphorous (Sivaprakash, 1980; Bhattacharya et al, 1984; Siddiquie and Raza, 2008; Siddiquie and Bhat, 2010) and more phosphorous in the form of apatite appears to have been introduced into the manganese ores through granitic and pegmatitic activities (Rao.S.V.G. et al, 1981; Acharya et al, 1994a, 1994b, 1997; Siddiquie and Bhat, 2010). 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 ore and host rocks. The manganese ores of district Vizianagram, (A.P) seems to have evolved in a few important phases of co-precipitation and sedimentation as Mn-rich sediments followed by their diagenesis, regional metamorphism and later supergene enrichment (Figure 3.3). The primary ore mineral assemblages in the study area include the diagenetic Mn-carbonate like rhodochrosite to high grade ore minerals like spessartite, rhodonite, vredenburgite, hausmannite and jacobsite. The abundance of garnet, sillimanite, quartz and apatite and in the host rocks also suggests the high grade metamorphism. The development of the metamorphic ore minerals like vredenburgite, jacobsite and hausmannite (Figure 4.2) confirms the high grade metamorphism. These
phases are evident in the studied mineralogical assemblages of all the types of ores in the study area and the bulk geochemistry and the stratigraphic, structural and tectono-metamorphic evidences in the field. The initial manganiferous sedimentary protolith was deposited in a stable shelf environment with a mixed source of Mn dominantly from hydrothermal sources with sub ordinate contribution from terrigenous source as shown in the hypothetical genetic model (Figure 7.1). Some deep and remotely generated marine hydrothermal plumes were enriched in Mn, Cu, Ni, Pb and Zn. These elements were carried in solution state by the oceanic water and were delivered to the shelf zone during favorable conditions of their precipitation and deposition. The presence of remote hydrothermal springs supplying Mn and some other elements and generating plumes with elevated contents of these elements in deep waters is obvious in some ternary plots and discrimination diagrams (Figures 5.10-514) in accordance with Toth, 1980; Choi and Hariya, 1992; Bonatti, et al, 1972; Peters, 1988. Metasedimentary deposits occur in high grade granulite terrains in shallow-water shelf regimes (Roy, 1981) which in accordance with the present mineralogical findings in the light of geochemistry are conclusive for the genesis of the manganese ores of district Vizianagram, (A.P). From the mineral-chemical attributes of the manganese deposits, the author proposed that the oxide ores were formed when anoxic bottom water enriched in Mn$^{4+}$ was up welled on the continental margin and mixed with oxygenated surface water (Figure 7.1). The process initiated most probably in the late Proterozoic in the light of geochronology of the region coupled with the present evidences. The geochronological data on the rocks of Eastern Ghats belt are meager and show a wide scatter. The wide range of ages has been attributed to superposed granulite and amphibolites facies events and the accompanying structural re-working (Mezger and Cosca, 1999; Sengupta et al, 1999). Nevertheless, the available geochronological data (Mezger and Cosca, 1999) clearly point to an Archaean event during 2.8 and 2.6 Ga, which can be taken as the minimum age of sedimentation of the Khondalite Group.

Manganese carbonates were diagenetically derived from these initial Mn-oxides by reaction with calcareous material in the shelf zone probably under evaporative conditions. Continental weathering acted as a part of possible source for manganese and iron, supplied through acidic surface water and ground water to the depositional palaeo-basin. Relatively high amounts of Si, Al and Ti as well as good correlations between SiO$_2$ vs Al$_2$O$_3$ and Al$_2$O$_3$ vs TiO$_2$ in the Vizianagram manganese ores may be due to the admixture of detrital material during precipitation as depicted from the discrimination
The elevated contents of Si, Al, Fe and Ti are evident. Featured and elevated concentration of Mn against the background host rocks indicates the formation of manganese-rich ore minerals in specific bands within the earlier combined system of manganiferous sedimentary protolith. The ores have attained the concentration of Mn with the development of the metamorphosed mineral assemblages. It is during this stage of ore formation that Mn-silicates were formed at a higher rate instead of the earlier Mn-Carbonates of diagenetic stage which was consumed in the decarbonation process and subsequent genesis of Mn-silicates. During the post-metamorphic period, prolonged exposure of the deposit to atmospheric oxygen and meteoric 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 the 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 economically important Vizianagram manganese ore deposits were formed by oxidation of pre-existing metamorphosed Mn-oxide (with Mn$^{2+}$ and Mn$^{3+}$) and Mn-silicate rocks (Roy, 1981). The evidence in favour of the weathering and alterations in the studied manganese ore deposit are the laterites which are characteristically concentrated in the upper zone of the weathered profile (Figures 2.3f and 3.1-3.2). The rocks most amenable to supergene concentration of manganese in the...
weathering zone are Mn-rich carbonates followed closely by Mn-silicate-carbonates. Manganese silicate carbonate admixtures were produced as a consequence of influx of detritus and hydrogenous constituents during sedimentation. Mn oxides are either formed in situ by oxidation of the carbonates ore through dissolution, limited vertical and lateral migration and re-precipitation (Roy, 1988 and 1991).

The mineralogical and chemical characteristics observed in the host rocks reflect heterogeneity in the metapelite composition dominantly meta-aluminous and indicate more than one source for the parent sediments. The mineralogical observation of the host rocks suggests clear metamorphism in the present area (Figure 2.5). The source rocks are predominantly ferromagnesian especially shale-greywacke sequence in PCM type of environment with some igneous intrusions adding some granitic-trondhjemitic component as evident in the discrimination diagrams and ternary plots of the khondalites and chamcokites (Figures 6.8-6.21). Geochemical characteristics of the host rocks suggest that the provenance for these rocks was a mixed source of shale-greywacke sequence and tonalite/trondhjemite probably the Archaean crust in accordance with Raju and Rao (2001), Siddique and Bhat (2010) and Bhattacharya et, al (2012). However, the premetamorphic sedimentary protolith package of shale-greywacke is indicative of their formation in a stable shelf milieu and PCM type of environment as depicted from figures 6.12-6.17 which supports the formation of the shallow shelf manganese ores in the study area.