Chapter 3

Vizianagram Manganese Ores

3.1. General Introduction

The oldest meta-sedimentary manganese ore deposits have been reported from the Iron Ore Group of India (3200-2950 Ma) and the Raodes Velhas Series, Brazil (>2700 Ma) followed by the Transwal Super Group of Republic of South Africa (2300-1900 Ma), khondalite Group (>2650 Ma), Dharwar Super Group (1500-900 Ma) as per Roy (1981, 2000), the Gangpur Group (946-846 Ma and 1700-2000 Ma) and the Sausar Group (986-846 Ma). The distribution of the sedimentary manganese ores of the phanerozoic age had a broad climatic control, most having been deposited in humid zones, confined to tropical and subtropical moist climatic zones with exceptions of temperate and arid areas never in permafrost regions (Strakhov, 1969). Precambrian meta-sedimentary Mn-ore deposits occur in many countries in formations of variable ages throughout the world (Table 1). Most of the manganese deposits and the enclosing rocks have been metamorphosed were radiometric dating reveals only the age of the latest metamorphic episode and the actual ages of formation of the sedimentary deposits are often uncertain (Roy, 1981). Sedimentary manganese deposits like that of Vizianagram, witness modification by subsequent regional metamorphism were in manganese oxide-carbonate ore bodies and the manganese -silicate-carbonate rocks show an intimate and conformable relationship in a syngenetic sequence, though one may also occur in the absence of the other. The manganese ores of this type are “metamorphosed” rather than metamorphic in the sense that metamorphism means modification only the mineralogy and texture of the ores but has no role in their concentration. Metamorphic events in the region witness their role in concentration of Mn in manganiferous sediments and the term “metamorphosed” manganese ore deposits is of wide usage for continental manganese ore deposits like that of the Vizianagram, deposit. The variations in temperature pressure conditions and the bulk compositions of the system during metamorphic events have led to the development of a range of minerals according to their stability and suitability at the PT conditions. Various models have been proposed to
undermine the genesis of manganese deposits of different types, may be grouped under hydrothermal, sedimentary, metamorphosed, meta-sedimentary and supergene deposits.

Manganese ore deposits show wide variation in the mineralogy in different genetic types like, oceanic manganese nodules, shallow shelf and continental (Land, streams, springs and lacustrine) owing to the differential environmental conditions and source of the elements. The variation in the mineralogy of different genetic types of manganese ores like sedimentary, hydrothermal and metamorphic and supergene deposits can be attributed to a set of factors like source of the elements, basin configuration and other environmental factors. The minerals found in the Vizianagram manganese ore deposits have complex origin involving many stages of their evolution to the present state. The integration of the field observations with that of the laboratory studies like optical and geochemical studies are of vital importance to enhance the blue print of the origin and evolution of the present manganese ores. Sedimentary deposits composed only of manganese oxides, on dynamo thermal or contact metamorphism are thus reconstituted to a high temperature lower oxide assemblage (braunite-bixbyite-hollandite-hausmannite-jacobsite-vredenburgite) as shown by deposits metamorphosed to green schist, to granulite facies and to pyroxene/hornblende hornfels facies in India (Roy, 1962, 1964b, 1964c, 1966, 1968, 1972, 1973; Mitra, 1965; and Lahiri, 1971), Otjosondu, Namibia (De Villiers, 1951) and mount Brandnuten, Norway (Westerville, 1961). In such ore bodies the main changes are the reduction of low temperature higher oxides to the high temperature lower oxides with textural changes to granoblastic texture and granulite fabric. The metamorphosed manganese ore deposits manganese silicate rocks (silicate-oxide, silicate carbonate and mixed assemblages) reflect the initial chemical and mineralogical composition of the sediments and their intensity of metamorphism. With the accumulation of the data on the various aspects of manganese deposits in both terrestrial and oceanic records the unwinding of the mechanism involved in their formation has gained pace during the last few decades. Laboratory studies of the solution and mechanism of the deposition of manganese and other metals in the form of oxides, hydroxides and silicates etc. resulting into modes of formation of manganese deposits of different types are now fairly well understood to a good extent but some problems are yet to be solved.
3.2 Manganese ore bodies of Vizianagram

The Vizianagram manganese ore deposits include bedded oxide ores (Figure 3.2a-c) which are considered primary and syngentic with the enclosing paragneiss (khondalites) and secondary massive botryoidal ores and irregular replacement bodies generally associated with zones of strong structural disturbance (Rao, 1960). The Mn-silicate-carbonate manganese ores in the form of bands and horizons are associated with the oldest geological succession in the region and are very complex due to intricate folding and faulting in the polyphase deformation of the region. The manganese ores of the study area are formed from the manganese silicate oxide and carbonate protore (Rao, 1982). Carbonate remnants are preserved at some deeply weathered mine pits along Perumali and Bangaruvalasa blocks. The manganese oxide ore deposits of Vizianagram occur extensively in the district as a part of meta-sedimentary sequence of the Precambrian khondalite Group (Roy, 1981; Siddiquie, 2004). These manganese ore bodies are conformably interstratified with and enclosed in different members of the khondalites Group and enclosed at different stratigraphic levels with calc-granulite and its contact with garnet-sillimanite-graphite granulite at Koduru, Garividi, Devada, Duvvam, Sadanandapuram and a deposit of about 2 km long east of Chinnaravyam; with garnetiferous quartzite (Garbham) and at contact of quartzite and garnet-sillimanite-graphite gneiss (Avagudem, Gadabavalasa, Ramabhadrapuram) (Roy, 1981; Siddiquie, 2004). The manganese ores occur in a somewhat linear belt in the district Vizianagram, (A.P.) and occur in varied forms with complex structural dispositions. The present study area consists of a dominant rocks Group khondalites, senso stricto-pelitic rocks hosting the manganese deposits (Roy, 1960, 1981; Sivaprakash, 1980; Dasgupta et al., 1993; Siddiquie and Raza, 2008; Siddiquie and Bhat 2008). The manganese ores are largely associated with the calc-granulites along Koduru, Kondapalam and Sadanandapuram (Siddiquie, 2000). The Garividi manganese ore bodies have two associated small pockets of crystalline algal limestone and pockets and lenses of green and red shale (Siddiquie, 2000). The East Garbham quarries are mostly associated with feldspathic and garnetiferous quartzite while as the quarries at central Garbham displays weathered Calc-granulites (Siddiquie, 2000). Siddiquie (2004) reported three main ore horizons in the entire stratigraphic column of the district. The main ore body occurs as a lode and is bifurcated, but it is lenticular at places and occasionally as intercalations with
calc-granulites while as the main ore horizons alternate with the host rocks as distinct bands (Siddiquie, 2000). Manganese mineralization has been structurally presumed as having as synclinal base at Koduru and Garbham with thick sequence and the limbs were severely faulted, disposing the manganese formation in the adjoining areas of Orissa and Northern A. P. (Kasipathi, 2008). These manganese deposits are mined at an extensive scale from last decade due to high demand of medium grade manganese ores throughout world. A number of private, semi-government and government mining companies are actively operating in the district. The mining is done by open cast methods with the latest mechanical equipments and machinery. Siddique and Bhat (2008, 2010), on the basis of association of the manganese ores with the host rocks (Table 5) from Chipurupalle and Garbham blocks of Vizianagram and their field observations, mineralogical and geochemical characteristics classified the ores into metamorphic and secondary ore. On the basis of field studies of the manganese ore deposits, structural and host rock relationship in coordination with the mineralogy the present author has studied and classified the Vizianagram manganese ores into the three categories as;

(i) Stratiform/Primary/Metamorphosed/Syngenetic/Meta-sedimentary Ores
(ii) Secondary/Supergene/Remobilized Ores and
(iii) A miscellaneous or Reworked Ores.

3.2.1 Stratiform/Primary/Metamorphosed/Syngenetic/Meta-sedimentary Ores

The tabular manganese ore bodies which follow the general banding/lamination of the khondalites sequence represent this category of the ores deposits. They have developed in situ and occur conformably with the calc-granulites and quartzite of the khondalite Group (Figures 3.4a-f). These ore horizons are co-folded as open and tight folds and are also faulted at places with the host rocks. These manganese ore horizons have also been encountered in the drill core in operating mines. They primarily found at the contact of calc-granulites and quartzites or as concordant ore bodies with other khondalite members in Vizianagram. Compositions of primary oxides indicate temperatures of peak metamorphism of at least 700°C, Whereas minimum pressure of metamorphism was 6 kb and oxygen fugacity range broadly from 10 (super -2) to 10 (super -12) atm. (Sivaprakash, 1980). The
ore samples of these horizons are laminated, or banded and with gneissic banding (Figure 3.3a-b). These ore horizons are low grade and represent the typical metamorphosed ore mainly consisting of braunite, bixbyite, hausmannite, jacobsite and vredenburgite. These low grade ore samples represent the meta-sedimentary manganese ores of district Vizianagram, (A.P.) which have been under the influence of supergene alteration in the weathering zone.

3.2.2. Secondary/Supergene ore bodies

These types of deposits are found in cross cut (discordant ore bodies) relation with the host rocks and occupy the weak planes like fault planes and fractures. Concordant ones are also found along unconformities and across local lenses and pockets in the form of veinlets. These horizons are mostly characterized by the manganese ores of botryoidal nature with spherical and stalactitic forms and were also found as cavity fillings. The supergene ore comprises of powdery crusts, botryoidal ore pockets and veinlets of sooty black Mn-oxides and hydroxides replacing the upper levels of the syngenetic manganese belt in the terrain almost completely. It is mostly the concentrated and localized supergene Mn-oxides and Mn-hydroxides that are under the mining operations at present. These are dominantly consisting of psilomelane, cryptomelane and pyrolusite, hollandite as the manganese rich minerals. There are clear evidences of leaching in the study area (Figure 3.2f) which is an important part in the mechanism for the formation of the secondary ore.

3.2.3. Miscellaneous/Reworked Ores

These are found as large buried boulders, pockets and concretionary masses (Figure 3.1a and 3.2b) at shallow depths. These ores are mostly found as lateritized and have mixed mineralogy of Fe, Mn, Al minerals. Reworked ores are mostly the remnants of the mined out ores. All the reworked ores have dominant mineralogy of wad, lithiophorite and some pyrolusite.
3.3. Manganese ore mineralization of the study area

Manganese ore deposits have been found to be much complicated in terms of structural disposition with a general strike of NE-SW. On the basis of their areal extent/spread, the area has been divided into seven blocks for the convenience of field observations and sampling. The six blocks of concentrated manganese mineralization hosted by various rock types shown in table 6 and discussed as:

3.3.1. Garividi block

This block of the study area is the central part of the mineralized zone in district Vizianagram, (A.P). The block consists of Garividi, Koduru, Sivaram and Lakshmipuram mines and quarries. The Garividi group of mines exposes most important ore horizon (Ore Horizon III of Siddiquie, 2004) hosted by coarse grained feldspathic quartzites of the khondalite meta-sedimentary sequence with some cahnockites as adjacent outcrops. The ores mineralization is as deep as 100 m below the ground level, becomes lean with depth and disappears with the appearance of basement Garnet-Sillimannite-Gneiss. The ores are in the form of hard lumps and botryoidal. Rare specimens of psilomelane were found in this block during the field work. The quarries and mines of this block represent the potential economic ore deposit of the district with almost entirely medium grade manganese content. The important rock types exposed in the area include calc-silicate granulites, lithomarge and weathered garnet sillimanite gneiss (Siddiquie, 2000). Pegmatite veins are abundant causing the feldspathization of the granulites in the area. The manganese ores especially psilomelane in the area mostly are hard lumps and botryoidal in nature (Figure 3.3d), however specimens of wad are also found in this block. The mineralized zone is spread for about 1.5 km’s in this block. The economically important ore horizons in the area are mostly concordant to the local stratigraphy especially associated with quartzite and calc-granulite. The primary ores are mainly the banded braunite (Figure 3.3f) with supergene pyrolusite in it.

3.3.2 Garbham Block

This block consists of some oldest mines of India in and around the Garbham and Kotakara villages of Vizianagram, district. The main mines and quarries include Pallapgudi, Central Garbham and Kotakara mines. The block is situated around 20 kms NW of Garividi
town with similar geological environment. The ore zone in this block has an aerial extent of about 3 km², consisting of primary/metamorphosed ores hosted by quartzites and calc-granulites as discordant and concordant ore bodies respectively enveloped by garnet biotite gneiss as a major litho unit. The drill core from the operating mining agencies of this block reveals deep mineralization of the manganese. The ore zone is trending E-W having strike of N68°E-S68°W and dip amount of 70°-80°. The average thickness of the ore horizon is about 4 feet however at the end tapers as thin as a few inches in NE of Garbham. Ore stratum is mostly concentrated in the hinge of the fold. The main ores are that of mamilated pyrolusite (Figure 3.3a-b) and psilomelane. The banded manganese within quartzite (Figure 3.4b-c) along Kotakara and Pallapgudi area is very common. However braunite is less abundant in these mines. The main rock out crops includes quartzite and calc-silicate-granulite. The details of the mines and quarries of this block are given in table 6.

### 3.3.3 Chipurupalle block

This block consists of the main mines in Chipurupalle and the surrounding areas of Mangotope, Razam and Aithemvalasa. The mineralized zone in this area is lined by calc-silicate granulites enclaved within feldspathic-quartzite and garnetiferous biotite. The ore zone in this block is of stratiform category and is economically less important with low manganese content as observed in geochemical analysis. Deeper parts of the mines show calc-silicate rocks hosting manganese silicates representing the primary metamorphic ore minerals (braunite, rhodonite, spessartite, vredenburgite and jacobsite). The important specimens collected from these mines are that of pyrolusite with dark steel grey color, hardness of 2-3, with some specimens of braunite and pyrolusite showing steel grey color and secondary or supergene enrichment (Figure 3.3c). The weathered pyrolusite (Figure 3.4d) from mangotope mines is an indicator of weathering and supergene alteration in the area.

### 3.3.4 Salur block

This block of the study area consists of Digva, Medangi, Sarika and Pechipenta manganese mines and quarries. The main ore zone is about one foot thick with an aerial extend of about 3 km’s radius. The ore is of very soft and powdery nature which may be
attributed to the higher level of water table in the area enhancing the supergene enrichment. The main ore horizon is about one and half feet thick and is hosted by quartzite. The host rocks are exposed of calc-granulites and garnetiferous quartzites. The main ores found in these mines are pyrolusite, wad and other Mn-silicates. The important ore specimens of this block include botryoidal psilomelane (Figure 3.3d) and ferruginous manganese ore (Figure 3.3e). The ore is hosted by feldspathic quartzite and lithomarge at places and is characterized by the friable ores of manganese. Biscuit ores are very common with visible garnet content and represent the garnet granulites of the area. While wad from this block are very much fibrous and friable with box work and honeycomb form, dull black in color and very soft and spoils the fingers. The ores has a mixed nature and is economically a low grade ore (Table 6). The ore horizons in deeper strata have a parallelism with the rock types and are categorized under the in situ ore bodies or the primary ores. The ore horizons have a sharp contact with calc-granulite in this area. This block witness deep chemical alteration of the low grade banded manganese silicate carbonate ore.

3.3.5 Bangaruvalasa block

This block comprises of the Avagudem, Rajam and Aithemvalasa villages having an aerial extent of approximately 2 kms. The main ore body of 2m thick is concordant with the entire sequence of laminated quartzite and manganese as foot walls and hanging walls of the prominent fault with some thicker lenses of secondry ores in between them. This block comprises of a stretch of a few quarries with manual mining of the ore. This block exposes deeply weathered calc-granulite overlain by lithomarge, former hosting the secondry ores of cryptomelane and pyrolusite entirely. The outcrops of migmatites and gneisses are seen in and around the manganese bearing strata. The bedded ore bodies and the enclosing rocks have been weathered to a considerable depth in many places, producing supergene pyrolusite and cryptomelane. Most of the lower oxides of manganese show granoblastic fabric hence important from palaeotectonics and genesis point of view. The supergene enrichment of the manganese ores to varied depths in Vizianagram led to the evolution of secondry ores of high manganese content and attracted the attention of exploration geologists and industrialists. The primary manganese ores in the studied terrain are low grade, where as the secondry ores are mostly oxides and
they are medium to almost high grade. The loose and soft wad from Aithemvalasa quarry (Figure 3.4f) suggests the intense weathering and alteration of the primary manganese ores in the area. The supergene ore is mostly kaolinised throughout the studied terrain. The manganese ore mineralization in the present district is summarized in Table 6.

3.3.6. Sadanandapuram Block

These block comprises of Devada, Duvvam and Avagadem mines and represents the potential economic ore deposit of the district with almost entirely medium grade manganese content. The important rock types exposed in the area include crytsalline algal lime stone, lithomarge and weathered garnet Gneiss (Siddiquie, 2000). Pegmatite veins are abundant causing the feldspathization of granulites in this block. The economically important ore horizons in the area are mostly concordant to the local stratigraphy especially associated with quartzite and calc-granulite. The manganese in this area are mostly psilomelane which are hard lumpy and botryoidal in nature as that of the salur block, however specimens of wad are also found in this block. The Mn-silicate-carbonate ore from Duvvam, Sadanandapuram block seen in figure 3.4a indicate the primary ores in the area. The overall mineralized zone is spread for about 1.5 km’s in this block with dominance of the supergene ores.
Table 5  Geology of the manganese Ore deposits and their host rocks of the study area (Siddique, 2004).

<table>
<thead>
<tr>
<th>QUARTZITE ASSOCIATION</th>
<th>CALC-GRANULITE ASSOCIATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Strata bound, co-folded with well defined contacts.</td>
<td>1. Strata bound, co-folded with diffused contacts.</td>
</tr>
<tr>
<td>3. Generally of low grade, 18-28 percent.</td>
<td>3. Higher in Mn content. Generally 30-32 percent Mn with pockets of high grade material.</td>
</tr>
<tr>
<td>4. Consists of manganese silicate and garnet with small band of steel gray and fine-grained material.</td>
<td>4. Consists of mostly pyrolusite, psilomelane, braunite and jacobite with small amounts of garnet and manganese silicate.</td>
</tr>
<tr>
<td>5. The width and thickness of ore zone is generally smaller.</td>
<td>5. The width and thickness of ore zone is greater.</td>
</tr>
<tr>
<td>6. There are a few pockets of garnet, granulite, lithomarge, chert and limonite.</td>
<td>6. Intimately associated with Pockets and bands of lithomarge, chert and limonite.</td>
</tr>
<tr>
<td>7. Coarse quartzfeldspathic rock is invariably present at the foot-wall side and between the underlying rock and manganese ore.</td>
<td></td>
</tr>
</tbody>
</table>

3.4 Mineralogy of manganese ores

Mn has many oxidation states ranging from +2 to +7 but in nature only +2, +3 and +4 states are found. Mn resembles Fe in most of its chemical properties, both having a +2 and +3 vacancies with high spin states for the 3d electrons and with similar ionic radii, hence substitute for each other in small amounts. Manganese has higher valance state of +4 as well which gives rise to a plethora of complex Mn-oxide minerals that do not have Iron counterparts. Higher oxides have manganese in its Mn $^+$4 states. Mn existing in the oxidation states of +3 and +4, it is called as higher oxide and is called as lower oxide if the Mn is in +2 state. Examples of higher oxides are pyrolusite, ramsdellite, psilomelane, cryptomelane and vernadite. Among the higher oxides pyrolusite and ramsdellite are the pure oxides.
Table 6  Distribution and geological details of manganese ore deposits in different blocks of the study area.

<table>
<thead>
<tr>
<th>S. No</th>
<th>Block/ (Toposheet Location Quarry/ Mine)</th>
<th>Rock type</th>
<th>Ore /Minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Garividi block (65 N/11) Garividi, Koduru, Sivaram and Lakshmipuram</td>
<td>Feldspathic-Quartzite, Lithomarge.</td>
<td>Psilomelane, Wad</td>
</tr>
<tr>
<td>2</td>
<td>Garbham block (65 N/7) Kotakara, Pallapgudi Central Garbham,</td>
<td>Quartzites, Calc-Granulites.</td>
<td>Braumite, Bixyite Rhodonite, Pyrolusite Psilomelane</td>
</tr>
<tr>
<td>3</td>
<td>Chipurupalle block (65 N/11) Mangotope, Razam, Aithemvalasa</td>
<td>Feldspathic-Quartzite, Calc-Silicates</td>
<td>Pyrolusite, Spessartite Rhodonite</td>
</tr>
<tr>
<td>4</td>
<td>Salur block (65 N/2) Diguva, Medangi Sarika, Kondalingalavalasa, Pechipenta</td>
<td>Garnetiferous quartzites</td>
<td>Pyrolusite, Wad, Mn-silicates</td>
</tr>
<tr>
<td>5</td>
<td>Bangaruvalasa block Bobilli -Mentada, Ramabhadrapuram, gopalapuram</td>
<td>Quartzites and Calc-granulites</td>
<td>Quartzite/Psilomelane, Wad</td>
</tr>
<tr>
<td>6</td>
<td>Sadanandapuram block (65 N/11) Koduru, Devada, Duvvam, Avagudem</td>
<td>Weathered Garnetiferous Gneiss, Pegmatite.</td>
<td>Psilomelane, Spessartite Rhodonite Wad, Hausmannite</td>
</tr>
</tbody>
</table>
The lower oxides of manganese include its oxides as bixbyte, braunite, Jacobsite, rhodonite, hydroxides like groutite (αMnOOH), feitknechtite (βMnOOH) and manganite. Other manganese minerals include Mn Sulphides like Albandite (Mn²⁺ less common and restricted to reducing environment). Carbonates like Rhodochrosite (MnCO₃), similar to calcite structure and have subsolidus relation with CaCO₃ where 80% of MnCO₃ can be present. Substitution of Mn to dolomite forms kutnahorite [CaMn(CO₃)₂]. The diverse manganese minerals discovered so far can be grouped into Oxides, Hydroxides, Silicates, Carbonates and Phosphates on the basis of the chemistry of manganese minerals. Oxides are further grouped as higher and lower oxides. The mineralogy of the manganese ore depends on the redox potential which is responsible for the concentration of certain minor elements (Barnes, 1967; Calvert and Price, 1970; Scott et al (2002; Summerhayes, 1967; Piper and Williamson, 1977; Calvert and Price, 1977a). The relative enrichment of minor elements in hydrated Mn-oxides or Fe-oxhydroxides is crystallochemically controlled by the oxidation state and stabilization energy of each cation. The predominantly primary ore is compact, microgranular and fine grained material with an inhomogenous composition and structure. The oxide-carbonate-silicate ore has the most diverse mineral composition having varied mineral assemblages as shown in Table 7. The syngenetic/primary ores of Mn-oxide-silicate-carbonate ore is mainly represented by quartz, hausmannite, rhodonite, braunite, rhodochrosite, where as the supergene/secondary/remobilized ores are mostly represented by the main phases of pyrolusite, psilomelane, wad, lithiophorite, magnetite, maghemite, bixbyte, braunite, hausmannite, huebnerite, jacobsite and pyrolusite. Most of them occur predominantly in hydrothermal deposits, whereas chalcophanite, coronadite, delta-MnO₂, groutite, hollandite, lithiophorite, manganite, nsutite, quenselite, ramsdellite, romanchebite, todorokite and woodruffite are generally of supergene origin (Nicholson, 1992). The important minerals of the ores deposits hosted by Archaean paragneisses include pyrolusite, psilomelane, hollandite and cryptomelane, representing alteration products of primary braunite, bixbyte, jacobsite, hausmannite and Vredenburgite (Krishna Rao, 1963). The ores textures and mineral associations support the conclusion that the primary ores were formed by high-grade metamorphism of manganiferous sediments (Rao, 1963) and with the restoration of normal atmospheric conditions, primary oxides and silicates altered to secondary oxides by supergene processes (Sivaprapaksh, 1980). The associated secondary ores
(psilomelane, cryptomelane, lithiophorite, ramsdellite etc.) owe their origin to subsequent alteration of the primary ores followed by secondary enrichment. Rhodochrosite in Koduru and Garbham areas of Vizianagram occurs as primary carbonate (Sivaprakash, 1980). After the peak metamorphism, with cooling, exsolution of hausmannite (second generation) from vredenburgite occurred (Sivaprakash, 1980) while as jacobsite was partly martitized to haematite (Sivaprakash, 1980). Changes in oxygen fugacities in different areas produced local variations in mineralogy and mineral compositions, mainly in jacobsites and garnets (Sivaprakash, 1980). The mineralogy of the phases in which manganese is the major or significant component had not been precisely worked out for a long time and even today many problems are unsolved (Roy, 1981). A wide range of manganese minerals of different groups have been reported from Vizianagram manganese ores by previous workers (Rao, 1960, 1963, 1975; Roy, 1998; Siddiquie and Bhat, 2008, 2010; Dasgupta; 1965 and Dasgupta et al 1993) which belong to different groups as pure oxides, higher oxides, lower oxides, hydroxides carbonate and silicate manganese minerals. Large numbers of manganese minerals have been discovered with the sophisticated methods and techniques till date but many others still wait for confirmation. The various groups of the manganese minerals and their properties reported from Vizianagram, by various workers from time to time are shown in Table 7. Among all these mineral groups the oxides like pyrolusite, psilomelane and cryptomelane are the dominant minerals in Vizianagram manganese ores followed by silicates, carbonates and hydroxides.

The primary ore minerals (bixbyite, braunite, hausmannite, hollandite etc.) are considered to be syngenetic and regionally metamorphosed (Straczek and Krishnaswamy, 1956) and represent primary metamorphosed assemblage in the study area. These ore deposits are found both in continuous and discontinuous bands with variable thickness; width and lengths mostly hosted by calc-granulites and quartzites. The mineralogy of the manganese ore bodies of the Koduru Group metamorphosed to granulite facies include braunite, hollandite, jacobsite, hausmannite, vredenburgite and supergene pyrolusite, cryptomelane and minor Nsutite (Roy 1960). Rao (1963, 1975) reported the same assemblage and reported two new minerals as minor franklinite and bixbyite from Koduru and Garividi mines respectively. In Vizianagram, bixbyite, braunite, hausmannite,
hollandite, jacobsite and vredenburgite formed during peak metamorphism by transformation from syngenetic oxides which existed in the original sediment (Sivaprakash, 1980). Local impersistent beds of Mn-silicate rocks (Spessartite-rhodonite-apatite-quartz) occur within the ores bodies (Roy, 1981). Rhodonite, pyroxmangite, tephroite, manganophyllite, spessartite and spandite are primary silicates and apatite, barytes, K-Ba feldspar, goethite and quartz are primary gangue minerals (Sivaprakash, 1980). Rhodonite resulted by polymorphic inversion from pyroxmangite (Sivaprakash, 1980). The Mn-rich psilomelane and pyrolusite ores are commonly formed in hypergene zone under the influence of meteoric waters (Kuleshov, 2003). The manganese minerals reported from the study area are as;

3.5 Manganese oxides (Pure Oxides)

3.5.1 Pyrolusite

Pyrolusite was named by Haidinger (1831) for the mineral of MnO₂ composition. Ramsdellite is γ-MnO₂ (synthetic) but Dubois (1936) referred it as pyrolusite as α-MnO₂. Pollianite has been used as a synonym for pyrolusite in the literature (Ramdohr, 1956, 1969), however in the present work the name pyrolusite is used to avoid any confusion. Burns and Burns (1978) pointed out the resemblance of single chain of linked (MnO₆) octahedral in pyrolusite to the SiO₄ chains of pyroxenes and considered the pyrolusite as a basis of crystal structures of Mn⁴⁺ oxides. Pyrolusite is thermodynamically the most stable phase among the minerals approaching MnO₂ composition and is almost free of other cations. On heating pyrolusite it transforms to bixbyite (Mn₂O₃) at 650°C (Dressel and Kenworthy, 1961; at 680°C, Hariya, 1961) and to Mn₃O₄ at 1000°C (Dressel and Kenworthy, 1961; Hariya, 1961). The fine pores and shrinkage cracks in pyrolusite encourage the adsorption of (OH)₂ (1-2%) and other elements as impurities (Frenzel, 1980). Being tetragonal in symmetry, pyrolusite may occur as pseudomorph after orthorhombic and groutite. Well developed pure and impure specimens of pyrolusite (Figures 3.3-3.4) from Vizianagram, were mostly found in Garbham block of the study area.
3.5.2 Ramsdellite

An Orthorhombic modification of MnO₂ has a diaspore goethite structure (Bystrom, 1949) and consists of alternating double chains of linked (MnO₆) octahedral similar to that in the amphibole structure (Burns and Burns 1977). Ramsdellite is metastable and rather rare in nature and it easily changes to pyrolusite by exothermic reaction at 500⁰C (Hariya, 1961). Ramsdellite is reported for the first time in the present work in the manganese ores from weathering zone of the study area.

3.5.3 The Nsutite group

Glemser (1939) studied a new synthetic modification of MnO₂ and named it as \( \alpha \)-MnO₂. The natural occurrence of \( \alpha \)-MnO₂ was first of all reported by Schossberger (1940) from West Africa and the name nsutite was given by Zwicker et al. (1962) after the Nsuta deposit of Ghana. This phase of manganese mineral was related to Pyrolusite by McMurdie (1944) while it was considered as poorly crystallized ramsdellite by Cole et al. (1947) and was described as an intergrowth of pyrolusite and ramsdellite by De Wolff (1959). Nsutites in general are pre-dominant in oxidized ores derived from Mn-Carbonate proto ore. Minor amounts of Nsutite have been reported by Roy (1960) from Koduru mines of district Vizianagram, (A.P.).

3.5.4 \( A_1 \text{Mn}_8 \text{O}_{16}.(\text{OH})_2 \) Group

The minerals representing the general formulae \( A_1 \text{Mn}_8 \text{O}_{16}.(\text{OH})_2 \) (\( A = \text{Ba}, \text{K}, \text{Na}, \text{Pb}, \text{Mn as Mn}^{+}, \text{Mn}^{2-} : (\text{OH})_2 \)) may be non essential are hollandite (Ba-analogue), cryptomelane (K-analogue) manjiortite (Na-analogue) and coronadite (Pb-analogue) form an structural series (Frondel and Heinrich, 1942; Fleishcer and Richmond, 1943; Fleishcer, 1964; Burns and Burns, 1977). The structures of these minerals and that of the synthetic like alpha MnO₂ have been shown to be based on that of ramsdellite type (Burns and Burns, 1977). Edge shearing of MnO₆ along the C-axis also shares corners with contiguous double chains. Producing a three dimensional pseudotetragonal framework. In this process a large cavity can accommodate (OH)₂ and cations like Ba²⁺, Pb²⁺, K and Na which are significantly disordered. Butler and Thirsk (1952) showed that substantial amounts of (OH)₂ and large cations are necessary to prevent the collapse of the crystal structure of manganese oxides.
The accommodation of large exchangeable cations like Ba\(^{2+}\), Pb\(^{2+}\), Na and K necessitates the presence of Mn\(^{2+}\) or Mn\(^{3+}\) ions in addition to Mn\(^{4+}\) in the linked MnO\(_6\) tetrahedral to maintain the charge balance.

### 3.5.5 Hollandite

Hollandite is the Ba-analogue of the isostructural series was first described by Fermor (1906, 1908, 1909 and 1917) from Kajlidongri deposit, M. P. India and has been confirmed as a valid species by (Frondel and Heinrich, 1942). The general formulae of the Mn-hydroxide [ (Ba, K)\(_{1.5}\)Mn\(_{3.5}\)O\(_{16.5}\)X\((\text{OH})_2\) ] as quoted in Table 7 for hollandite may be used in the text hereafter in order to avoid the confusion by various formula given by various workers from time to time. Hollandite shows a higher ratio of Mn\(^{4+}\)/Mn\(^{3+}\) than that of psilomelane, the other Ba rich higher oxide of Mn. Hollandite is a widely reported ore from manganese deposits of variable types throughout world and the present manganese ores of Vizianagram (Rao, 1963, 75; Siddiquie and Bhat, 2008). Hollandite also forms in low temperature conditions in the colloform ores (Nambu and Tanida, 1966). Hollandite is formed from psilomelane at 550\(^{0}\)C (Fleishcer and Richmond 1943) and for this reason, hollandite is prevalent in metamorphosed manganese deposits (Roy, 1966, 1968, 1972, 1976b). Hollandite itself transforms to Hausmannite at 1000\(^{0}\)C (Fleishcer, 1964). The stability of hollandite at high temperature has been attributed to the presence of Ba\(^{2+}\) ions in the structure (Burns and Burns, 1977).

### 3.5.6 Cryptomelane

It is a K-analogue of hollandite discovered by Ramsdell (1932). The chemical formulae is K (Mn\(^{4+}\)Mn\(^{3+}\))\(_8\) (O, OH)\(_6\) and is specified by the presence of not only Mn\(^{4+}\) but also Mn\(^{3+}\) and K in its structure. Cryptomelane shows a considerable content of potassium, as 6.6% being the highest and 0.09% (Roy, 1981). Hewett and Olivares (1968) showed the atomic sum of Na + K + Ba + Sr + Ca varies from 0.08 to 1.28 with most of the values near to 1. The Mn\(^{4+}\)/Mn\(^{3+}\) ratio in cryptomelane is higher than that in psilomelane and hence the dominance of cryptomelane over psilomelane in supergene deposits. Cryptomelane is important in supergene environment along with \(\beta\) MnO\(_2\); sometimes people ascribe its formation from ground water. Although these minerals are structural polymorphs they are
not exactly of the same structure. Some of the manganese also occurs in cryptomelane in the form of Mn\(^{\text{IV}}\) to maintain the charge balance necessitated by the inclusion of potassium in the structure. On heating cryptomelane finally changes to hausmannite often through the Mn\(_2\)O\(_3\) phase. The lattice is composed of bands consisting of chains connected by octahedral edges. The bands are connected to form interconnected structural tunnels accommodating minor and trace elements. The mixed valence oxides including cryptomelane are more stable in neutral and alkaline environments than in acidic environments.

3.5.7 Psilomelane

Psilomelane (with 16.6% BaO) was first named by Haidinger (1831) and since then this mineral has been amongst the most described Mn-Oxides. It is casually used in a loose sense for any unidentified hard and compact Mn-Oxide, particularly those with a botryoidal structure (Figure 3.3d). A synonym romanochite for psilomelane is also used in literature by some authors but not hereafter to avoid any confusion in the name psilomelane as proposed by Haidinger (1831) and Fleischcer (1960) for the hydrated Ba-Mn-oxide. Psilomelane (Ba analogue; Monoclinic/Orthorhombic, 16.6% Ba can be accommodated) breaks down to Hollandite at 550°C).

3.5.8 Lithiophorite

It is primarily a hydrous Al-Mn-oxide (Valarelli et al (1968) first of all named by Frenzel (1980) and was confirmed as a valid species by Ramsdell (1932). Wadsley (1952a) suggested that the mineral \([\text{Al, Li (OH)}_2 \text{MnO}_2]\) has a layer structure with alternate sheets of \([\text{MnO}_6]\) octahedral and (Al, Li (OH)) stacked along the C-axis. To maintain charge balance, substitution of Mn\(^{\text{IV}}\) and Mn\(^{\text{III}}\) are necessary to maintain the charge balance in the \([\text{MnO}_6]\) layers is necessary. The chemical formulae of lithiophorite is LiAl\(_2\)(Mn\(^{\text{IV}}\), Mn\(^{\text{III}}\))\(_6\) (OH)\(_6\). In mixed layered lithiophorite, the octahedral layers of various cation compositions are codimensional on plane 001 and have a uniform lattice (Roy, 1981). Trace elements such as Ni, Cu, Co and Zn are concentrated significantly and have been ascribed to accommodation in the gibbsite like sheet of lithiophorite and substitute for Li and Al, while
as Co is incorporated in the edge sharing octahedral of buserite like structure (Marceau et al. (1987, 1990).

3.6 Manganese Hydroxides

Mn hydroxides include α-MnOOH (Grouitite), β-MnOOH (Feitnechtite) and γ-MnOOH (Manganite) minerals occurring in nature as three modifications. Gruner (1947) first described groutite as a new mineral with diasporo-goethite structure. It gets oxidized very slowly to isostructural ramsdellite at 130°C in air and above 300°C transforms topotactically to pyrolusite (Klingsberg and Roy 1969). Manganite (γ-MnOOH) was first of all described by Haidinger (1831). Buerger (1936) determined a monoclinic symmetry (distorted rutile structure) for the mineral. Krishnan and Banerjee (1939a) concluded the manganese occurs as Mn^{3+} and Mn^{4+} in manganite. Dasgupta (1965) reported oriented transformation of manganite, on heating to pyrolusite at 375°C and subsequently to Mn₂O₃ and Mn₃O₄ at 565°C and 950°C respectively. In general manganite is common in low temperature sedimentary and supergene deposits worldwide.

3.7 Lower oxides

This group of manganese ore minerals includes braunite and bixbyite and has been reported from the Vizianagram manganese deposits (Siddiquie, 2004, Siddique and Bhat 2008). The two minerals are discussed in detail as below;

3.7.1 Braunite

It was first of all named by Haidinger (1831). Most workers agree that the mineral has general chemical formulae 3MnO₂. MnSiO₃ corresponding to approximately 10wt% SiO₂ in its structure with the exception of a braunite from Black rock mine, Kalahari, S. Africa which contains only 4.4wt% SiO₂ (De villers, 1975) and the composition agrees with the formulae (Ca. Mn) Mn₁₄SiO₂₄. The former and the widely found variety have been named as Braunite I, while as the later is poor variety as Braunite II. Roy (1981) showed the 2nd highest percentage of manganese in Indian braunite (MnO=37.98%, MnO₂ =40.93%) by Fermor (1909) after that of Långban Sweden bixbyite reported by Mason (1942). Fe may
also be an important but variable substituting element in the braunite structure and so the formula of braunite is also written as $3 \left( \text{Mn}^{3+}, \text{Fe}^{3+} \right)_{2} \text{O}_{5} \cdot \text{Mn}^{2+} \text{SiO}_{3}$ (Hewett and Fleishcer, 1960; Abraham and Schreyer, 1975). Primary braunite is sedimentary in origin although it has metamorphic, hydrothermal and rarely a diagenetic origin. The primary sedimentary braunite occur as accretionary eoliths/pisoliths precipitated as primary sediment within the basins during sedimentation while as the secondary braunite formed by the recrystallization and replacement of the primary braunite by the diagenetic process of the manganese ores as revealed by the mineralogical character and chemical composition of the important phases as well as their textures. Natural braunite is related to $\alpha$-Mn$_2$O$_3$ (cubic structure; Pauling and Shappel, 1930) and revised as orthorhombic by Geller (1971). Maun (1969) emphasized an extremely strong stabilizing effect of silica on Mn$^{3+}$ in braunite structure. The distortion of the Mn$^{3+}$O$_6$ groups as a result of Jahn Teller effect may be instrumental for the stability of braunite and bixbyite type structures (Moore and Araki, 1976). The stability of braunite and bixbyite type structures in manganese deposits affected by the progressive dynamo thermal metamorphism is also well domesrtated (Roy, 1964c, 1964d, 1966, 1972, 1973). Braonite is common mineral in metamorphosed sedimentary manganese oxide ores including the present deposits of Vizianagram. Well developed primary ores with abundant braunite, pyrolusite and psilomelane as massive specimens are found in Vizianagram manganese mines (Figure 3.3 and 3.4). Supergene formation of braunite in the manganese ore deposits is also reported in literature (Hewett and Fleishner, 1960, 1963). Braunite, once formed, remains stable through the entire metamorphic range. Huebner (1967) discussed the possibility of a reaction between braunite and silica to produce rhodonite while Orcel and Pavlovitch (1931) showed that Braunite (8.92% SiO$_2$) on heating to 1400$^\circ$C for 5 h, converted to tephroite and or eutectic intergrowth of tephroite and hausmannite. In natural deposits however, braunite does not transform to or react with other phases rather it is formed as a conversion product of bixbyite (braunite II) in Indian Ore deposits (Roy, 1962, 1966, 1968, 1972, 1973).

### 3.7.2 Bixbyite

It was first named and described by Penfield and Foot (1897) from Thomas Range, Utah, U.S.A. having Mn/Fe ratio as 1. Mason (1946) reported high Fe$_2$O$_3$ (48.84 to 56.66)
fumarolic bixbyites from Argentina. Fermor (1909) discovered sitaparite as a new phase containing lower Fe$_2$O$_3$ (27.60%) and high Ca content (6.145) from regionally metamorphosed sedimentary Mn ores of India. Gruner (1943) showed that this mineral contains 17.25% Fe$_2$O$_3$. Orcel and Pavlovitch (1931) and Dunn (1936) described sitaparite from India. While Mason (1942) showed that the X-ray pattern of sitaparite and bixbyite are identical and therefore rejected the name sitaparite of Fermor (1909). De Villers (1983) recommended that the Mn-Fe sesquioxides should be classified into partridgeite (<10% Fe$_2$O$_3$), sitaparite (10-30% Fe$_2$O$_3$) and bixbyite (>30% Fe$_2$O$_3$). Sitaparite has been assigned to 0-30%Fe$_2$O$_3$ and bixbyite to 30-60% Fe$_2$O$_3$ by Mason (1944), while discussing the phase equilibria of the system Fe$_2$O$_3$-Mn$_2$O$_3$, reluctantly accepted that the phases sitaparite (0-30% Fe$_2$O$_3$) and bixbyite (>30% Fe$_2$O$_3$) may be retained for relatively lower metamorphic and higher fumarolic temperature products but the name partridgeite was rejected by him. All the three names of the system are still in use. However in the present work name bixbyite for the phase (Mn, Fe)$_2$O$_3$ will be used hereafter to avoid any confusion. Bixbyite has been reported from the present study area by many workers (Rao, 1969, 1975; Roy, 1981; Siddique and Bhat, 2008, 2010). There has been a long controversy on the structure and valance states manganese in bixbyite (Pauling and Shappel 1930) and the formula was broadly given as (Mn, Fe)$_2$O$_3$. Moore and Araki (1976) stated that the braunite and bixbyite are not isomorphous as the c-axis of the former is double as that of bixbyite. Depending upon the bulk composition (availability of Si, Fe etc.), temperature and oxygen fugacity, braunite and bixbyite may form together in metamorphosed manganese oxide ore body (Maun, 1959). Gutzmer and Beukes (2006) also described varied Ca content in bixbyite with braunite II as a part of metamorphosed manganese oxide mineral facies from Postmasburg, Republic of S. Africa. The local variations of the metamorphic mineral association of the braunite-bixbyite group reflect variations of the host rock composition instead of the changing P-T conditions of metamorphic alteration (Gutzmer and Beukes, 2006).
3.8 The Fe$_3$O$_4$-Mn$_3$O$_4$ system

The minerals belonging to this system include a solid solution series of magnetite, jacobsite, vredenburgite and hausmannite. Mason (1943a) was the first to determine the phase relations in the system by synthetic experiments covering solid solution members as magnetite, jacobsite, vredenburgite (Intergrowth between jacobsite and hausmannite) and hausmannite. The increase in the manganese content in the system is reflected in the solid solution as the increase in the cell dimensions of the cubic face from right to left in the series (magnetite-jacobsite-vredenburgite-hausmannite). The boundary between magnetite and hausmannite has been drawn arbitrarily at the mid-point of the Fe$_3$O$_4$-MnFe$_2$O$_4$ (manganese ferrite) compositions i.e. 16.7% Mn$_3$O$_4$, that of jacobsite and Vredenburgite at 54%Mn$_3$O$_4$ and that of Vredenburgite and Hausmannite at 91% Mn$_3$O$_4$. Mason (1934b) calculated that for a homogenous metastable Vredenburgite, with 70-80% Mn$_3$O$_4$, a temperature above 700$^\circ$C is required. But all the naturally occurring vredenburgites studied by him contain less than 70% Mn$_3$O$_4$ reflecting the temperature of 500$^\circ$-700$^\circ$C suggesting their origin by regional metamorphism.

3.8.1 Jacobsite

Member of the spinel group usually designated by the formula MnFe$_2$O$_4$ (Deer et al 1963) was first reported from Jackobsberg, Sweden. Though, in nature its composition varies widely in the system Fe$_3$O$_4$-Mn$_3$O$_4$. The compositional limit of Jacobsite was set by Mason (1943a) between 16.7% Mn$_3$O$_4$ (composition half way between Fe$_3$O$_4$ and MnFe$_2$O$_4$) and 54% Mn$_3$O$_4$, by Van and Keith (1958) between 10-54% Mn$_3$O$_4$. All these divisions are arbitrary as the temperature dependent entry of Mn$_3$O$_4$ in Fe$_3$O$_4$ is a continuous process without any structural change demarcating the magnetite jacobsite boundary. The formula of Van and Keith is widely accepted and will be considered in the present work. It has been demonstrated that with rising temperature more and more Mn$_3$O$_4$ can be accommodated in the Fe$_3$O$_4$ structure, expanding the unit cell dimension owing to the larger size of Mn$^{3+}$ (Montoro, 1938; Mason 1943b; Van and Keith, 1958). Jacobsite containing exsolved lamellae of hausmannite show variable cell dimensions and surprisingly most values are lower than those of synthetic or natural jacobsites of manganese ferrite (33%Mn$_3$O$_4$, 67%Fe$_3$O$_4$) composition. Jacobsite is strongly ferromagnetic. Though, the jacobsite has
primarily been described from metamorphosed manganese deposits and much less so form hydrothermal deposits. It has also been reported from superficially formed low temperature deposits, showing colloform texture at Dongri Buzurg, India (Roy 1959b, 1966), Tiaratiene, Morocco (Vinceinie, 1956). Variations in many optical properties and etch tests have been recorded by Roy (1959, 1966).

### 3.8.2 Hausmannite

The spinel structure for hausmannite has been confirmed by Ramdohr (1956). In general Hausmannite contains 5% of Fe$_2$O$_3$ and has Fe and Mn as two ends in its solid solution relation. Hausmannite forms under metamorphic conditions from Mn protoliths of different compositions. 6.85% of ZnO may be present in hausmannite. It occasionally replaces braunite and bixbyite or vice versa. In supergene environments it shows very common replacement along cleavages or irregular fissures of pyrolusite. Hausmannite has been reported from Vizianagram by many workers (Roy, 1981; Rao, 1963 and Siddique and Bhat (2008, 2010).

### 3.8.3 Vredenburgite

This mineral has been a long debate for its name, composition, structure since decades. The name vredenburgite was first given by Fermor (1909) with the chemical formulae $3\text{Mn}_3\text{O}_4.2\text{Fe}_2\text{O}_3$ to a strongly magnetic material, found in association with many other Mn minerals in Madhya Pradesh and Vizagapatnam (Presently Vizianagram, districts of India). Fermor (1909) as a new homogenous phase with the composition $3\text{Mn}_3\text{O}_4.2\text{Fe}_2\text{O}_3$ from metamorphosed manganese ore deposits of India. As cited by Fermor (1938) vredenburgite actually consists of two intergrown phases. Orcel and Pavlovitch (1931) also confirmed that in Vredenburgite one mineral ($\beta$-Constituent) Occurs as lamellae oriented in the crystallographic planes of another ($\alpha$-constituent), which was confirmed by Schneiderhöhn (1931) as the hausmannite lamellae exsolved in jacobsite. The mineral has been undoubtedly proved by many mineralogists, physicists and geologists as an intergrowth of two mineral species rather than an independent mineral species. Vredenburgite forms at high temperature from Fe-Mn rich bulk composition by exsolution of hausmannite in octahedral planes of jacobsite forming what is called as windmanstatten
texture. Fermor (1938), also suggested two new names as ‘Devadite’ and ‘Garividite’ after Devada and Garivi villages of Vizianagram, for the homogeneous phases of different compositions from which Vredenburgite could possibly be formed by exsolution but these names were justifiably rejected by Mason (1947) as superfluous. The field of Vredenburgite in the system Fe$_3$O$_4$-Mn$_3$O$_4$ has been demarcated in between 54-91%Mn$_3$O$_4$ by Mason (1947) and Van and Keith (1958). The homogeneous phase of any composition within this field can occur only at the metastable state in ordinary pressure and temperature. Mason (1943b) described such a phase with a tetragonal structure from Längban deposit Sweden, which was probably formed by reduction of bixbyite during metamorphism at low temperature. Mason (1943b) named this phase α-Vredenburgite. The name Vredenburgite is used only for the windmanstatten exsolution intergrowth of jacobsite and hausmannite only. The mineral serves as a geological thermometer for metamorphic regime of around 600°C (Mason 1947). Roy (1958) has also come across the same Vredenburgites as that of Mason (1947) with jacobsite as host and hausmannite as intergrown lamellae.

### 3.9 Manganese Pyroxenes, Amphiboles and Garnets

These minerals are widespread in the Mn-Silicate and carbonate rocks. Many of these occur in the manganese ore bodies themselves or in rocks closely associated with them. The various manganese pyroxenes and amphiboles of the present interest include diopside, rhodonite, spessartite, pyroxmangite, epidote and peidmontite.

#### 3.9.1 Diopside

The diopside-salite-ferrosalite-hedenburgite (CaMgSi$_2$O$_6$-CaFe$^{2+}$Si$_2$O$_6$ solid solution) series shows some manganese content but according to Deer et al (1963), the average MnO content of diopsides is very low (0.095%) but is still higher as recorded from manganiferous diopsides in manganese ore horizons (Roy, 1971). Also pyroxenes in the diopside-aegirine series which are of aegirine and aegirine-augite composition are often manganiferous. Manganiferous pyroxenoids like bustamite [(Mn, Ca, Fe)SiO$_3$] are much more widely spread in manganese ore bodies and manganiferous rocks. Bustamite occurs in association with hedenburgite or rhodonite and has maximum content of MnSiO$_3$ of 67% implying that Ca occupies one of the three cation positions. Solid solution of bustamite with
Rhodonite appears to be limited but with wollastonite a complete solid solution is possible (Roy 1981).

3.9.2 Pyroxmangite and Rhodonite (Mn, Fe and Ca) SiO₃

Pyroxmangite and rhodonite belong to a group of manganese pyroxenoids having very similar diagnostic properties. Pyroxmangite is predominant in Vizianagram manganese deposits while as rhodonite is a minor mineral and co-occur in some samples with the pyroxmangite. These are ionosilicates close in chemical composition and crystal structure. Rhodonite belongs to triclinic system showing five SiO₄ tetrahedra periodicity. Liebau et al. (1959) suggested that not more than one fifth of the cations linking the [SiO₄] chains can be calcium. Natural rhodonite is never pure MnSiO₃, some substitution of Ca and Fe²⁺ is always there. Klein (1966) described rhodonite with very high magnesium (MgO 14%) with correspondingly low Mn (MnO 25.7 %) content. Glasser (1958) opined that pure MnSiO₃ end member has a rhodonite structure while Peters et al. (1974) considered that only Ca²⁺ can stabilize rhodonite. Rhodonite is well distributed in Vizianagram manganese silicates but less common than spessartite. It is comparatively less in lower metamorphic zones and gradually becomes common as the grade of metamorphism increases from staurolite to Sillimanite zone (Roy and Mitra, 1963). The possibility of these minerals forming depends on the Ca content in the rock. For instance, in the South Urals, rhodonite crystallizes in rocks with no lower than 2.0-2.5 wt % CaO. The amount of this clement in rhodonite varies from 0.5 up to 1 f.c.or, being recalculated to molar fractions \( \chi_{Ca} = Ca/(Ca + Mn + Fe + Mg) \), from 0.1 to 2.0. In contrast, pyroxmangite crystallizes in rocks with low Ca content. The Ca content in pyroxmangite is twice as low (0.10-0.42 f.c, or \( \chi_{Ca} = 0.01-0.6 \)) as in rhodonite. The increase in Ca contribution to pyroxmangite is accompanied by an increasing total amount of iron and manganese. This is not typical of rhodonite. Rhodonite and pyroxmangite are often closely associated with each other. In such cases, the features noted above are especially evident with \( \chi_{Ca} \leq 0.06 \) in pyroxmangite and \( \chi_{Ca} \geq 0.10 \) in rhodonite. Most likely, such compositions correspond to the stability limits of pyroxmangite and rhodonite.
3.9.3 Spessartite (Mn$_3$Al$_2$Si$_3$O$_{12}$)

The spessartite variety of garnet is common in metamorphosed manganese silicate rocks and hydrothermal deposits. Mn-Fe member of the garnet group has been reported from manganiferous rocks associated with iron formation (Klein, 1966). Spessartite has been reported from Vizianagram, khondalites by some workers (Rao, 1963, Siddiquie and Bhat, 2008, 2010). Minerals of the amphibole group are often manganiferous and many vari _et al_, names are in use. Variable replacement of Mg and Fe$^{2+}$ by Mn (maximum 15.62%) has been mentioned by many authors. In tremolite-actinolite-ferroactinolite series, particularly in Mg rich members, replacement by Mn is restricted. However manganactonan, actionolite and manganacton tremolite with 7.38, 5.79% and 4.05-5.42 MnO have been reported from Kaso mine, Japan and Franklin U.S.A. respectively. A name tirodite has shown to correspond to manganacton tremolite-richterite composition (maximum MnO 13.43%; Roy 1974a). Leake (1978) considered tirodite as a monoclinic amphibole with the standard formula Mn$_2$Mg$_5$Si$_8$O$_{22}$ (OH)$_2$ and belong to cummingtonite series.

3.9.4 The Epidote-Piemontite Group

This group is represented by minerals of its isomorphic series. Usually these minerals are subordinate, but when the content of volcanomictic material in the rock is high, the amount of epidote and/or piemontite increases and both become major minerals. The minerals have been reported from the manganiferous rocks of Vizianagram, by many workers (Siddiquie and Bhat, 2008, 2010). An almost complete isomorphic series have been from oxide-carbonate-silicate (braunite) ores from many metamorphosed manganese deposits. Piemontite [Ca$_2$ (Al, Fe, Mn)$_3$ OHSi$_4$O$_{12}$] a manganiferous member of the epidote group is monoclinic commonly found in hydrothermal and metamorphosed sedimentary manganese deposits.
### Table 7

General mineralogical grouping of the manganese ores of district Vizianagram, (A.P).

<table>
<thead>
<tr>
<th>Group</th>
<th>Minerals</th>
<th>Crystal system</th>
<th>Composition</th>
<th>Reference</th>
</tr>
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<tr>
<td><strong>Higher Mn-oxides</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrolusite</td>
<td>Tetragonal/Rutile</td>
<td>MnO₂</td>
<td>Haidinger (1831)</td>
<td></td>
</tr>
<tr>
<td>Ramsdellite</td>
<td>Orthorhombic/Diaspore</td>
<td>MnO₂</td>
<td>Ramsdell (1942)</td>
<td></td>
</tr>
<tr>
<td>Cryptomelane</td>
<td>Tetragonal Mnonoclinic</td>
<td>KAl-Mn₈O₁₆.ₓ (OH)₂</td>
<td>Ramsdell (1942)</td>
<td></td>
</tr>
<tr>
<td>Psilomelane/</td>
<td>Monoclinic Orthorhombic</td>
<td>(Ba, K, Mn, MnₓO₁₀)</td>
<td>Burns and Burns (1977)</td>
<td></td>
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<tr>
<td>Romancheite</td>
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<td></td>
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<tr>
<td>Braunite</td>
<td>Cubic</td>
<td>3Mn₂O₃, MnSiO₃</td>
<td>Orcel and Pavlovic (1931)</td>
<td></td>
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<tr>
<td>Bixbyite</td>
<td>Cubic</td>
<td>(Mn, Fe)₂O₃</td>
<td>Mason (1942)</td>
<td></td>
</tr>
<tr>
<td>Jacobsite</td>
<td>Spinel group</td>
<td>(MnFe₂)O₄</td>
<td>Deer et al (1963)</td>
<td></td>
</tr>
<tr>
<td>Hausmannite</td>
<td>Tetragonal (Deformed)</td>
<td>Mn₃O₄</td>
<td>Burns and Burns (1977)</td>
<td></td>
</tr>
<tr>
<td>Manganite</td>
<td>Monoclinic</td>
<td>γ-MnOOH</td>
<td>Haidinger (1931)</td>
<td></td>
</tr>
<tr>
<td><strong>Mn-Hydroxides</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hollandite</td>
<td>???</td>
<td>[(Ba, K) 1-2 Mn₈O₁₆化合物</td>
<td>Fermor (1908, 1909, 1917 (OH)₂)</td>
<td></td>
</tr>
<tr>
<td>Lithiophorite</td>
<td>???</td>
<td>[(Al, Li) (OH)₂ Mn₃化合物</td>
<td>Wadsley (1952)</td>
<td></td>
</tr>
<tr>
<td>**Mn-silicates/</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn-pyroxenes,</td>
<td>Rhodonite</td>
<td>Triclinic</td>
<td>MnSiO₃</td>
<td>Roy (1981)</td>
</tr>
<tr>
<td>garnets</td>
<td>Peiinontite- Epidote</td>
<td>[Ca₉ (Al, Fe, Mn)₃ OHSi₃O₁₂]</td>
<td>Roy (1981)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Diopside</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Mn-Carbonates</strong></td>
<td>Rhodochrosite</td>
<td>Trigonal</td>
<td>MnCO₃</td>
<td>Deer et al (1963)</td>
</tr>
</tbody>
</table>
In general epidote has Mn\(^{3+}\) < Fe\(^{3+}\) while piemontite has Mn\(^{3+}\) > Fe\(^{3+}\) with similar Al contents. Both these minerals are characteristic of the low grade primary ores or the Mn-silicate Carbonate ores of Vizianagram and reveal their metamorphism and high oxygen fugacity in accordance with their similar counter parts in Mn-silicate-carbonates of South Urals in accordance with Keskinen and Liou (1979, 1984) and Bonazzi and Menchetti (2004).

3.10 Wad

The soft wad like material of the Plancha bedded deposit could not be identified. Wad is a very soft black friable Mn-ore reported from almost all supergene manganese deposits world over. Wad has been reported from Indian manganese deposits especially the Eastern Ghats region like Orissa (Mohapatra et al, 2005 and 2009) and Vizianagram, (Siddiquie, 2004). A hand specimen of wad is shown in Figure 3.4f. The mineral is a secondary ore mineral formed in warm humid tropical climate like that of the present study area.
Figure 3.1  Field photographs showing,

(a) Water logged manganese quarry, Duvvam, Sadanandapuram block;
(b) Manual sieving of low grade manganese ore, Kotakara quarry,
(c) Weathered Mn-Si-carbonate and supergene manganese ore, Devada, Sadanandapuram block, district Vizianagram, (A.P).
Figure 3.2 Filed photographs showing:

(a) Mined out primary manganese ores, Garbham block;
(b) Leeching of Ca in the weathering zone of study area;
(c) Lenses and pockets of manganese within weathered khondalites in Duvvam;
(d) Lumps of Secondary Mn ore in Lithomarge in Salur quarries;
(e) Mn-Si-Carbonate ores at Chipurupalle quarries;
(f) Active open cast mining in the Chipurupalle block, district Vizianagram, (A.P).
Figure 3.3 Well developed hand specimens of,

(a-b) Mammillated pyrolusite from Kotakara quarry, Garbham block;
(c) Secondary pyrolusite with quartzite from Pallapgudi quarry, Garbham block;
(d) Botryoidal psilomelane from Digva mine, Salur block;
(e) Ferrigenous manganese ore with pyrolusite, Digva quarry, Salur block;
(f) Banded braunite with pyrolusite from Pallapgudi quarry, Garividi block, district Vizianagram, (A.P).
Figure 3.4  Well developed hand specimens of,

(a) Mn-silicate-carbonate ore from Duvvam, Sadanandapuram block,
(b-c) Banded manganese within quartzite from Kotakarra quarry, Garbham
(d) Weathered pyrolusite from mangotope mine, Chipurupalle block,
(e) Ferrugenous manganese ore from Perumali block,
(f) Loose and soft wad from Aithemvalasa quarry, Bangaruvalasa block, district Vizianagram,(A.P).