Chapter 4
Ore microscopy and Petrography

4.1 General Introduction

Ore mineralogy serves as a tool in the genetic interpretation of the manganese ore (Nicholson, 1992, Calendar and Bower, 1976). It also serves as an economic aspect in the mining and exploration of the ores deposits. The mineralogy of some continental manganese ore like the Vizianagram, has been hampered by the metamorphism and weathering of the original manganese ores. The ores mineralogical correspondence between the manganese ores of different blocks and horizons of the study area reveals some variation in mineral assemblages of the primary and secondary manganese ores throughout the study area. Manganese ore minerals of the study area were specifically also discussed by Krishna Rao (1963a, 1963b and 1967), Dasgupta (1993), Roy (1981), Siddique and Bhat (2010).

Detailed optical studies of the manganese ores from deeper parts of the mines of Vizianagram are dominantly the primary ores (concordant/meta-sedimentary). The dominant minerals in the samples of the primary ores are the manganese carbonates and silicates which are dominantly the diagenetic to metamorphose ore from the deeper unaltered or least altered parts of the study area. However ore samples from oxidation zone and the discordant ore bodies, local pockets and veins, being supergene ores are characterized by the dominance of minerals like psilomelane, cryptomelane and pyrolusite. Important micro textures and structures confirmed by scanning electron microscope (SEM) reveal sequential phases in the paragenesis of the manganese ores from sedimentary, metamorphosed to supergene phases in the study area. The various types of mineral assemblages and micro textures carried out in the present piece of research work from the manganese ores of Vizianagram are presented in table 8. The important samples from the different stratigraphic levels and blocks studied for optical and XRD tests are detailed as follows;
4.2 Mineralogy of selected ore samples

The ore microscopy and XRD of a number of samples from the Vizianagram, district, A.P reveals members of almost all groups of manganese ore minerals like Mn-silicates, Mn-carbonates and Mn-oxides and hydroxides. The ore minerals identified under reflected light and XRD tests include rhodochrosite (rhc), braunite (brn), hausmannite (hsm), jacobsite (jcb), spessartite (sps) rhodonite (rhd) pyrolusite (pyr), cryptomelane (crp), psilomelane (psi), ramsdellite (rms) and magnetite (mgt) as seen in Figures (4.1 - 4.7). The gangue minerals found throughout the study area include quartz (qtz), apatite (apt) and calcite (cal), etc. The present study shows that the deeper ore horizons in the major mines are less altered by weathering and are characterized by the presence of different set of minerals representing the metamorphosed assemblages with some remnants of the original carbonate material while that of the near surface zones are the result of oxidation and supergene enrichment. A brief mineralogy of the selected samples of both primary and secondary manganese ores of the different blocks of the study area is as follows;

4.2.1 Garbham block samples

The samples collected from this block are mainly the Mn-silicate-carbonate ores. The ore microscopy and XRD of the ore samples from this block confirms the presence of rhodochrosite, pyrolusite, calcite and quartz, spessartite, rhodonite and pyromelane (Figure 4.1 and 4.3a-b). The sample KTK2 collected from the deeper level of Kotakara quarry is massive, hard and compact nature and fine grained in nature with jet black color. The ores microscopic studies of the sample confirm the presence of alternate lamellae of psilomelane with rhodochrosite (Figure 4.1a). The sample CGBl from hinge zone of the fold near Central Garbham quarry, Garbham block, district Vizianagram, (A.P). The sample is hard and compact in nature with SG of about 3-3.5, greenish streak and hardness is 6. The microscopic study of the polished section confirms the presence of spherulites of rhodochrosite with pyrolusite where as the XRD of the sample also confirms the presence of rhodochrosite, pyrolusite and psilomelane (Figures 4.1b and 4.3a). The presence of rhodonite and spessartite and other Mn-silicates such as spessartite and rhodonite with abundant pyrolusite and psilomelane in sample PLD1 from Pallapgudi quarry is also clear (Figure 4.1c and 4.3b) in this block. The polished ore blocks of Garbham mine show a variety of minerals that are
characteristic of metamorphosed manganese deposits. The minerals include spessartite, rhodonite, pyroxmangite with some apatite and feldspar. The texture is granoblastic in these ores. Spessartite occurs as small isometric, often euhedral grains mainly related to segregations of pyroxmangite and rhodonite. Generally spessartite contains appreciable amounts of Ca and Fe, the etch test behaviour is +ve with H$_2$O$_2$ + H$_2$SO$_4$ in which it shows scratches with saturated SnCl$_2$ and blackens quickly. Etching is -ve with the HCl, HNO$_3$, KCN, HgCl$_2$, H$_2$SO$_4$ and FeCl$_3$ etc. The presence of rhodonite may be attributed to the breakdown of braunite. Depending upon the bulk composition (availability of Si, Fe etc.), temperature and oxygen fugacity, braunite and bixbyite may form together in metamorphosed manganese ore deposits (Muan, 1959a). Rhodonite is observed as colorless mineral under microscope but is seen in yellow to pinkish under PPL. One set of cleavage is common with occasional two sets at almost right angles. It is non pleochroic with an extension angle of around $20^\circ$-$22^\circ$ and 2V angle of $75^\circ$ under X-Nichols. The granoblastic texture of rhodonite bearing samples are commonly seen in the primary ores under microscope (Figure 4.1c) and occasional poikiloblastic texture with spessartite. Spessartite is usually fine grained with occasional large idioblasts of spessartite with rhodonite. Almost similar association of metamorphic minerals overlaps sedimentary diagenetic manganese accumulation formed in reduction environments. Relics of rhodochrosite can be locally seen in samples least affected by the metamorphism. Metamorphosed manganese ores have been reported to contain rhodonite, tephorite, spessartite, rhodochrosite and Mn-rich magnetite in Spain (Jimenez-millán and Velilla, 1998), in the Eastern Carpathians of Romania (Hirtopanu and Scott, 1999), in Urals, Russia (Gerasimov et al, 1999) and in China (Zeng and Liu, 1999).

4.2.2 Sadanandapuram block samples

This block is represented by the both metamorphic and supergene mineral assemblages along Devada, Duvvam and Sadanandapuram quarries. The specimen SDP1 is characterized by dark black color with metallic lustre, hard and compact nature, S. G is 4 and hardness is 6. The specimen has a black streak with shiny pyrolusite. The minerals detected in the microscopic studies and XRD test of the sample include pyrolusite, jacobsite, psilomelane, magnetite, hausmannite, with some gangue minerals (Figures 4.2 and 4.3c). Presence of jacobsite in the studied sample SDP1 was felt by its
attraction by simple magnet which is not felt in the jacobsite lacking samples. The samples bearing jacobsite were also understood by heating up of the sample during the polishing process and may be attributed to the high Fe content of the samples. The jacobsite and hausmannite strands form a windmanstatten texture (Figure 4.2b) which is a typical vredenburgite characteristic of the metamorphosed manganese of the many continental manganese ores. Jacobsite shows diffuse boundaries with hausmannite with small remnants of magnetite (Figure 4.2c) and jacobsite as seen in Figure 4.13. The observed mineralogy of the sample suggests clear paragenetic evolution of the assemblage. Jacobsite is a Mn rich spinel and belongs to cubic system behaves isotropic. Laminae of hausmannite are seen as intergrowth with the host jacobsite in many other samples from the mines of this block typical windmanstatten texture (Figure 4.2b). Under microscope first of all, the mode of occurrence and morphology of hausmannite lamellae attract attention. This mineral occurs as elongated strands irregular in shape and actively corroded by pyrolusite (Figure 4.2b). Such aggregates are likely the metamorphosed manganese ore minerals partly replaced with secondary pyrolusite of the supegene origin. The present jacobsite in vredenburgite under chemical tests show +ve etch reactions with saturated SnCl₂ where grains shows etch marks after five minutes. It also shows positive etch test with H₂O⁻²⁻H₂SO₄. However it shows negative tests with all other standard reagents. Pyrolusite was seen as secondary replacement product through out the field under observation. Orcel and Pavlovitch (1931), detected weak anisotropism in the host mineral of the intergrowth in Vredenburgite and called them a constituent (hausmannite). Jacobsite was also found -ve with etch tests as compared to the host a constituent. Finally Dunn (1936) declared vredenburgite as an intergrowth of jacobsite and hausmannite. The first Optical, X-Ray and magnetic observations by Deb (1943) showed the jacobsite is host mineral in Vredenburgite.

4.2.3 Garividi block samples

This block is dominated by manganese oxides like pyrolusite and psilomelane with some minor rhodochrosite. The ore sample GRV1 collected from Garividi mine of the study area and is characterized by the botryoidal form (Figure 4.3f). The polished section of the sample GRV1 is dominantly consisting of psilomelane with minor gangue when observed under reflected light. Psilomelane is occupied in the joint
loops of the colloform pyrolusite and rhodochrosite (Figure 4.4a). Psilomelane and pyrolusite shows vein replacement with rhodochrosite in the sample GRV2 (Figure 4.4b). Psilomelane is seen as wavy strands of black color through the view in a matrix of pyrolusite with minor gangue minerals. Pyrolusite in these polished sections was identified as white to yellowish minerals of fine to coarse grains. High reflectance and distinct pleochroism from white to yellow. It also shows strong anisotropism in the shades of grey to yellow. It also appears as a ground mass in most of the samples indicating the samples of the oxidation zone of the study area. The ore is also characterized by hard and massive nature with 4.5 S. G and hardness is 6.5. The dominant ore minerals confirmed from this block include psilomelane and pyrolusite and rhodochrosite (Figure 4.4a-c).

### 4.2.4 Chipurupalle block samples

This block is characterized by the predominance of braunite and bixbyite with some rhodochrosite. The primary ore samples are layered, hard and massive in character and are characterized by dull lustre. The S. G is approximately 4 while hardness of 4.5 with a white streak. Dull lustre and greasy feci is very clear. The sample MGT 1 is also hard and massive with hardness of 6. The ore microscopy and XRD test of these samples confirms the presence of braunite, bixbyite and pyrolusite (Figure 4.5b). under microscope some grains of braunite and bixbyite with traces of quartz and apatite are also observed. The bixbyite grains seem to be co-genetic with braunite and have overall granoblastic texture in the field under view. Rhodochrosite is associated as accessory phase with the main braunite phase in as seen in (Figure 4.5a-c). The XRD image of the sample MGT2 confirms the presence of braunite and rhodochrosite (Figure 4.7b).

### 4.2.5 Salur block samples

This block is dominated by the secondary ores with supergene ore minerals like pyrolusite, psilomelane, cryptomelane and ramsdellite, quartz, apatite and other gangue minerals. Cryptomelane, psilomelane and pyrolusite like manganese oxide mineral phases are concentrated in the supergene enriched zone but also occur as microscopic veinlets that crosscut other manganese minerals. The sample DGV1 from diguva quarry is very hard and compact, black streak with approximate S. G is 4-5 and hardness is 6
and is characterized by the presence of abundant psilomelane with steel grey color shiny crystals of pyrolusite oriented randomly along with the psilomelane and gangue. Under PPL the psilomelane shows dark grey color, isotropic nature and pleochroism in the shades of steel grey to blue grey (Figure 4.6a). The refractive index of psilomelane is higher than other minerals and Canadabalsm. The polished ore block of the sample shows blades as well as anhedral grains of psilomelane. Grains of psilomelane ranging in size from 0.5-0.8 mm are surrounded by minute rims of pyrolusite and quartz (Figure 4.6a).

4.2.6 Bangaruvalasa block samples

This manganese ore samples from Bangaruvalasa block of the study area dominantly consists of braunite, rhodochrosite and psilomelane. Cryptomelane occasionally embays and cross-cuts rhodochrosite and braunite while as the pyrolusite is seen as a vein filling secondory ores material (Figure 4.6b). Braunite shows typical anisotropies under X- Nichols and exhibits definite grain boundary relations with the adjacent minerals like jacobsite and hausmannites from the study area when observed under PPL. It also shows the diffuse boundaries with paragenetic counterparts (Figures 4.6b). The dominance of braunite and pyrolusite in the sample is clear from the higher weight percentage of Mn in the sample (Table 8). Ramsdellite (β-MnO₂) a crystallographic form (polymorph) of pyrolusite has been confirmed in the sample BGR1. Under chemical tests the mineral was confirmed by etch reactions with many reagents. It shows positive effects with H₂O₂ as effervescence and no effect on surface, turns slightly dark lightly with FeCl₃ in HCl, H₂O₂ + H₂SO₄ were it stains black rapidly and black with SnCl₂ (saturated). Negative effects were seen with that of HCl, HNO₃, KOH, HgCl₂ etc. The X-ray powder pattern of the sample BGR1 (Figure 4.7c) also confirms the optically observed pyrolusite, cryptomelane, ramsdellite, pyrolusite and quartz.

4.3 Mineral assemblages and paragenesis

The ores microscopic and XRD data supported by the geochemical data of the respective samples from the manganese mines of the study area have shown a well developed ore mineral paragenesis and assemblages with respect to the environmental conditions. The mineral assemblages are neither uniform for all the operating mines and
quarries nor they are uniform from horizon to horizon with depth. However there is a
great variation in mineral assemblages within the district. The previous mineralogical
details of the study area as reported by many workers (Fermor, 1908; Krishna Rao, 1954,
Sivapraksh, 1981; Siddiquie and Bhat, 2008) were taken into due consideration for
unveiling the possible mineral paragenesis.

4.3.1 Rhodochrosite- hausmannite – rhodonite-pyroxmangite-spessartite
4.3.2 Braunite - jacobsite – hausmannite -vredenburgite
4.3.3 Braunite- bixbyite – rhodonite
4.4.4 Pyrolusite-cryptomelane-ramsdellite-maghemite

4.3.1 Rhodochrosite- hausmannite – rhodonite-pyroxmangite-spessartite

This assemblage is the characteristic of primary ores of the Vizianagram, district.
The diagenetic origin of rhodochrosite is evident in its morphology. It is common in
metamorphosed manganese ores of India, Bulgaria and Urals. Rhodochrosite is rarely
reported as an intermediate oxidation product of Mn-carbonate in supergene oxidation.
The bulk of this mineral is represented by minute spherulites of threadlike crystals that
grew in a fine-grained carbonate or silicate matrix. Such spherulites are most likely
postdated the ores matter sedimentation. The spherulites of rhodochrosite in
Vizianagram manganese ore deposits resembles the rhodochrosites of Bulgaria and
Southern Urals which are completely diagenetic as worked out by Aleksiev (1960).
Admixtures of Mn-carbonate, aluminous sediments and silica and manganiferous sheet
silicates in volcanogenic sediments may also lead to the formation of spessartite in a
rising temperature (Hsu, 1968). The presence of rhodochrosite with or without quartz in
some lenses of manganese ores of district Vizianagram, (A.P.) represents the products of
the original carbonate-silicate-oxide rock that escaped later metamorphism.
Rhodochrosite and quartz co-exist only at very low grades of metamorphism (Huebner,
1967 and , 1969; Peters et al (1974), which is in accordance with the presence of quartz
with rhodochrosite in the ore samples from the hinge zones of the folds, where they had
been least affected by the metamorphism. Rhodochrosite often replaces Mn-oxides
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<tr>
<th>Sample/ID</th>
<th>Main Mineral(s)</th>
<th>Associated Mineral(s)</th>
<th>Accessory Mineral(s)</th>
<th>Microtexture</th>
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<td>Rhodochrosite, psilomelane,</td>
<td>Pyrolusite</td>
<td>Quartz, Apatite</td>
<td>Banded and Replacement</td>
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<td>Rhodochrosite</td>
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<td>Mn-silicates</td>
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<td>Quartz, Calcite</td>
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<td>Magnetite</td>
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<td>Gangues</td>
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<td>Pyrolusite</td>
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completely. However, where the entire resource of carbon dioxide was consumed in the course of carbonation, an excess of manganese could have been retained in the oxide form as hausmannite where rhodochrosite has a high content of FeCO$_3$, jacobsite may also form from decarbonation product at high temperature (Huebner, 1967). The primary ores enriched in Si, Al, Mn and Fe are largely composed of quartz, pyroxmangite and rhodonite. Some samples are mostly composed of rhodonite or pyroxmangite and quartz with small to negligible amounts of rhodochrosite, calcite, peidmontite and epidote are
sporadic. The relationships between these minerals are equivocal. In many places, fine intergrowths of rhodochrosite with quartz are observed; however, elsewhere, quartz and rhodochrosite do not make up a stable assemblage but react with each other to crystallize pyroxmangite or rhodonite as:

\[ \text{MnCO}_3 + \text{SiO}_2 = \text{Mn(SiO}_3 \text{)} + \text{CO}_2 \quad (\text{Reaction-1}) \]

(Rhodochrosite) (Quartz) (Rhodonite)

The replacement of carbonate with pyroxenoid is especially evident in the banded ore (Figure 4.1c). Rhodochrosite is locally retained therein only within the beds of newly formed pyroxmangite as isometric or irregularly shaped relics isolated from quartz. The pyroxmangite and rhodonite crystals themselves contain numerous inclusions of both rhodochrosite and quartz. Pyroxmangite and rhodonite could have formed not only as products of reaction of quartz with rhodochrosite (Reaction-1) but also as a result of other processes, for example, by interaction of quartz with caryopilite (Reaction 2) or Mn-oxides. At an excess of SiO₂, the quartz-pyroxmangite (rhodonite) assemblage was formed in ore in all cases. The Mn-rich hausmannite-tephroite, rhodochrosite-tephroite rocks close in composition due to silica gain (Hsu, 1968). Schematically this process can be ascribed as the following reaction (for the particular case of rhodonite formation):

\[ \text{Mn}_2(\text{SiO}_4) + (\text{SiO}_2)_{aq} \rightarrow 2\text{Mn(SiO}_3 \text{)} \quad (\text{Reaction-2}) \]

Tephroite Solution Rhodonite

In accordance with Hsu (1968), the temperature of spessartite formation at a pressure of 2.5 kbar should not be lower than 410°C as possible pressure and temperature for metamorphism of Vizianagram manganese ores. At the same time, spessartite is one of the most abundant primary ore minerals at the deposit. Spessartite crystallization at high temperature was also suggested by researchers on manganese deposits from Belgium, Ghana, California and other regions (Flohr and Huebner, 1992; Theye et al. 1996; Nyamt, 2001). The primary ores that occur throughout the banded stratiform ore horizons are largely of pyroxmangite (rhodonite), rhodochrosite and
quartz; with spessartite. With regard to mineral assemblages, quartz, hausmannite, rhodochrosite, pyroxmangite are possibly important minerals formed in the main ore layer in the course of burial metamorphism at a maximum temperature and pressure of 250°C and 2.5 Kb respectively. The formation of pyroxmangite and rhodonite depended on the Ca distribution in ore minerals at constant temperature and pressure. It is possible that pyroxmangite was formed in ore depleted in Ca, whereas enrichment in Ca led to the appearance of rhodonite. The manganese content in jacobsite increases with the grade of metamorphism from low greenschist to amphibolite facies. Oxidation of FeSiO3-rich and hence rhodonite or pyroxmangite may result in micrographic intergrowth of jacobsite and rhodonite. The textural relationship of rhodonite and spessartite reveals overlapping or cogenetic growth. Spessartite idioblasts are seen embedded in secondary pyrolusite and quartz matrix throughout in the primary ores (Figure 4.1c).

4.3.2. **Braunite- bixbyite – rhodonite-cryptomelane**

This assemblage is typical in the most continental metasedimentary and metamorphosed manganese ores. The assemblage is characteristic of the primary ores of deeper levels in some mines of the study area representing the metamorphosed manganese beds of the district. Braunite a lower oxide of manganese on heating gives rise to hausmannite was shown by laboratory experiments conducted by Orcel and Pavlovitch (1931) supporting the paragenesis of the assemblage through metamorphism in the present research work. Vredenburgite the intergrown hausmannite (Mn rich member) and jacobsite (Fe rich member) in the primary ore samples are frequently observed in the studied ore. Hausmannite, MnO4 is Mn rich mineral with Zn and Mg as main substitutes, which accounts for higher Mg and Zn concentrations of the respective samples. The composition is close to MnO4 with only minor substitution by other elements. The formation of hausmannite in metamorphosed manganese deposits is a function of high temperature and concomitant reduction and its presence, in the absence of jacobsite, reflects a low iron composition. The formation of jacobsite depends on the iron content in the original bulk composition, temperature and oxygen fugacity. The higher jacobsite content in the primary ore samples are reflected as high iron content of the primary ore samples (1-6) as shown in table 8. A maximum of 6.91% FeO has so far been recorded from iron rich hausmannites of Kangban deposits of Sweden however;
Mason (1943) considered this as close to limiting value in the structure of hausmannite at room temperature. The hausmannite lamellae also show pleochroism and anisotropies in shades of dark grey to green. The individual grains often show a well developed lamellar twinning. The present observations support the results of Deb (1939) and Roy, S. (1958) where there is no homogeneity in Vredenburgite. According to Fermor (1938), the excess oxygen over the simple (Fe, Mn)₃O₄ shown by Indian Vredenburgites suggests that the original material was not a spindled and that on unmixing it broke down not to jacobsite and hausmannite alone but also gave rise to some free MnO₂ in the form of pyrolusite and psilomelane. Mason (1943) also reported homogenous Vredenburgite in a metastable state from Långban and was named as γ-Vredenburgite. Mason (1947) contradicted Fermor by stating that the MnO₂ in the form of pyrolusite or psilomelane, found in association with Vredenburgite, is only a secondary replacement product, replacing selectively the hausmannites only. Mason studied the system Fe₂O₄-Mn₃O₄-ZnFe₂O₄ and found that the variation of iron and manganese in Vredenburgite is continuous and hence no differentiation into different species based on the relative content of Fe and Mn. It has been clearly shown that in the Fe₂O₄-Mn₃O₄ system, the compositional field assigned to hausmannite at room temperature is 91-100% Mn₃O₄ (Mason, 1943; Van and Keith, 1958) and the Fe content decreases in higher temperature so that at 1160⁰ C hausmannite is iron free. Hausmannite lamellae in jacobsite or the windmanstatten texture and a diffused boundary contact (Figure 4.2b-c) indicate their oogenesis and the definite paragenesis suggests transformation of pyrolusite and braunite into hausmannite at higher temperatures in the case of Vizianagram ores, some of the segregated hausmannite lamellae show unique morphology of irregular shape actively corroded by pyrolusite (Figure 4.2b) indicating the metamorphosed relics of primary sedimentary manganese oxides and or hydroxides partly replaced by manganese oxides.

4.3.3. Braunite- bixbyite-rhodonite

Braunite (Mn₃SiO₁₂) is an important lower oxide of manganese which takes up manganese during the increasing grade of metamorphism from bixbyite. Braunite has about 10-Wt% of SiO₂ and is not a pure oxide. It is rather a silicate but conventionally called as lower oxide of Mn. It breaks down as per the following process;

\[
\text{Mn}_3\text{SiO}_{12} = 3 \text{Mn}_2\text{O}_3 + \text{MnSiO}_3 \quad (\text{Reaction-3})
\]
In principle, the above pair can serve as an application in geochronology. Braunite commonly found in all metamorphosed manganese deposits ranging from the diagenetic to granulite facies (800°-900°C) with varied composition due to Mn\(^{2+}\), Fe\(^{3+}\) exchange with bixbyite. Braunite is not found in polymetallic oceanic nodules because they have not been subjected to temperature at least 100°C and if found may be due to biogenic reduction. Braunite is present in Archaean and Proterozoic manganese deposits of Kalahari, S. Africa and India containing around 4.5% of SiO\(_2\) and 4.5% of CuO (Wt %) as suggested by (Roy, 1981). 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 (Muan, 1959a, 1959b). Pyrolusite in this assemblage is of secondary replacement origin and indicates the enrichment of manganese by supergene enrichment process in the zone of weathering. In metamorphosed manganese ore deposits of the Vizianagram, the manganese silicate ore (silicate-oxide, silicate-carbonate and mixed assemblages) reflect the initial chemical and mineralogical composition of the sediments and their intensity of metamorphism. The crystal structure of the metamorphic braunite is not identical to that of the normal braunite. The c-axis of the metamorphic one is double to that of normal braunite and has been named as Braunite II as a distinction from normal Braunite (Braunite I). Braunite II is the only one of its kind in the world believed to be formed due to hydrothermal activity. Due to the fact of crystallographic differences the difference in optical behaviour and XRD patterns (Figure 4.5b-c, 4.7b) of the present braunite from sedimentary braunite is very obvious.

4.3.4. Pyrolusite-cryptomelane-ramsdellite-maghemite

Cryptomelane is mostly found in low temperature metamorphic and weathering environments. Cryptomelane containing samples are soft, black, velvety ground mass but in some samples consist of numerous, very thin, closely spaced needles of cryptomelane or hollandite oriented with their long axes perpendicular to the velvety surface. Cryptomelane, a low temperature mineral converts into bixbyite at 600°C. However the dominance of cryptomelane in some samples indicates least conversion. The presence of the higher oides of manganese in secondary ore sample is a function of
high chemical activity in the system. For cryptomelane, the sum of Na + K + Ba + Sr + Ca of the geochemical data goes around 1 (Hewett, 1963). The accommodations of large cations depend upon the temperature of the environment of formation and hence the origin of these minerals becomes distinct. The abundance of pyrolusite in the Vizianagram manganese ore is in close association with cryptomelane in most of the samples. Pyrolusite and cryptomelane are also seen in the cracks and boundaries of other minerals and appears to have developed at the expense of later, presumably by the Mn ions changing positions (Bystrom and Bystrom, 1950). Ramsdellite mostly observed as tabular to blocky crystals in this assemblage follows either hollandite or psilomelane in the paragenetic sequence. One possible explanation of this sequence is that in the absence of the large cations present in the hollandite structure the double strings composed of oxygen octahedra around manganese ions may be knitted together to form a ramsdellite-like arrangement (Bystrom and Bystrom, 1950). The appreciable strontium content and the sympathetic variation of strontium with barium in cryptomelane and psilomelane indicate that the strontium is probably present in the structure of these minerals and perhaps substitutes in barium or water molecule sites in cryptomelane. The presence of strontium in these sites may be responsible for some of the differences between XRD powder patterns of cryptomelane as well as the optical properties. The assemblage suggests supergene alteration and enrichment of higher oxides from the high temperature earlier mineral of metamorphosed nature. The association of magnetite and maghemite suggest supergene alteration of the Mn-Fe component of the primary ores of the study area. Occurrence of globular, colloform, concentrically zoned and other structures typical of gel crystallization is characteristic of the studied ores from different blocks of district Vizianagram, (A.P.).

4.4 Ore textures and microstructures

The microscopic examinations of the Vizianagram manganese ores revealed the presence of open space filling, colloform, pseudocolloform, banded and replacement textures. Manganese oxides mostly show micro-banding, while as Mn-carbonate and Mn-Silicate ore have a monotonous microscopic pattern and are mostly characterized by grey brown color with occasional micro wavy banding and common spherulites or pelitomorphic/micro lumpy aggregates. The manganese oxides like psilomelane and
pyrolusite show colloform/ pseudo colloform or botryoidal and mammillated and acicular textures (Figures 4.1a-b, 4.2a and 4.3). Primary ores generally show granoblastic and banded texture while the secondary ores typically possess acicular and colloform texture.

4.4.1 **Open space filling texture**

The texture is seen as the deposition of younger and secondary material along the vugs, fractures and cracks of the older ones, the later being friable in nature (Figures 4.5, 4.6). It is indicated by the presence of pyrolusite and cryptomelane in most of the samples. The higher frequency of the texture reveals the shearing as a result of tectonic disturbances as well as the chemical alteration in the weathering zone of the ores deposits. Fissure replacement and honeycomb texture is better seen in case of the banded ore (Figure 4.8c, 4.9c), suggesting a highly operative chemical alteration and supergene process.

4.4.2 **Colloform texture**

This texture is indicated by concentric rhythmic bands concavo-convex surfaces in which curvature is always convex towards the younger surface. Sometimes it is observed in spheroid, mammillary or botryoidal forms (Pettijohn, 1975). This type of texture always results from precipitation from hot colloidal aqueous solutions coming from deeper levels. The collofrom texture is displayed by many polished specimens as seen in figures 4.1 and 4.4.

4.4.3 **Banded texture**

This texture is used to describe the nearly parallel arrangement of bands or lamellae which generally differ in the color and composition. The texture is a representation of alternate compositional banding of lamellae in case of the present ore (Figures 4.1a and 4.5b). The ore samples display this feature best in polished specimen as well as under PPL.
4.4.4 Rim replacement texture

This typical texture is the characteristic of the supergene ores from weathering zone in which a mineral grain is surrounded by a rim of the reaction product formed between it and the invading solution (Figure 4.4b and 4.6a). The reaction product formed may be complete or incomplete ring depending on the rate of material supply.

4.4.5 Vein replacement texture

This kind of texture has been observed in most of the polished specimens of the Vizianagram, Mn ores (Figure 4.5c). The cracks and fissures in the dominant mineral phase of the studied ores are invaded by the circulating fluids with some specific elements transforming the host mineral into new minerals. Examples are secondary pyrolusite, psiolomelane and crytomelanac.

4.4.6 Crystallographic intergrowth

The only crystallographic growth found in the present Mn ores of district Vizianagram, (A.P) is that of hausmannite and Jacobsite. The intergrowth as a whole has been named as Vredenburgite by Fermor in, 1909. However there had been a long debate over the nomenclature of the mineral but the name Vredenburgite is still used for the intergrown Jacobsite and hausmannite, wherein the hausmannite lamellae are oriented in the (III) direction of jacobsite and is called as Windmanstetten texture (Fig 4.2b). The hausmannite lamellae are straight extending upto the boundary of the host. Three sets of such lamellae in some polished specimens. The same texture has been reported by Roy, (1958) from the Tirodi mines of Balaghat district (M.P), India. The intergrowth has been first of all reported by Schneiderhöhn (1931) and Orcel and Pavlovitch (1931) as exsolution. Similar microstructures have been observed between braunite and hausmannite (Fig… but the hausmannite lamellae are oriented at an angle to braunite. Such Intergrowths have evidently formed due to exsolution and are similar to that reported by Roy (1960) from Tirodi, M. P.

4.4.7 Mutual boundary relations

The present manganese ores from the district Vizianagram, (A.P) reveal diffuse mineral boundary contacts between jacobsite and hausmannite, pyrolusite and
psilomelane, rhodochrosite and bixbyite and braunite and bixbyite (Figures 4.2c, 4.5a, 4.5c). In most cases such a contact is perfectly smooth. The microstructures suggest co-crystallization or simultaneous crystallization but cannot be regarded as equivocal evidence (Edwads, 1954). However, in the absence of any evidence contrary to this and the intimate association of these two minerals, a more or less same age relation is suggested for both. Grain boundary replacement texture (Figure 4.8b) and Intergrowth texture (Figure 4.8b) are also seen in the studied ore (Figure 4.8a).

4.4.8 Colloform texture

The most important texture from the paragenetic sequence point of view is replacement and colloform textures and is well seen in the polished sections and SEM images of the Vizianagram manganese ores (Figures 4.4a and 4.9a). The texture is best seen in the rhodochrosite, psilomelane and pyrolusite bearing ore samples specimens mostly. The replacement process is widely suggested as the mechanism for the origin of the texture. Primary minerals are mostly enveloped by second generation minerals along grain boundaries and fracture walls. Vredenburgite is mostly replaced by psilomelane while as pyrolusite replaces psilomelane. Braunite replaces cryptomelane in sample while bixbyite surrounds pyrolusite in some samples. Bixbyite also surrounds hausmannite in some cases. Pyrolusite shows an endotherm at 650\(^0\)–700\(^0\)c (Neumann, 1977), owing to bixbyite (Mn\(_2\)O\(_3\)) formation and at 920\(^0\)–970\(^0\)c gives beta hausmannite.
Figure 4.1 Photomicrographs showing,

(a) Alternate compositional lamellae of rhodochrosite and supergene psilomelane and Pyrolusite in primary Mn ore Central Garbham mine;
(b) Distorted spherulites of rhodochrosite with secondry pyrolusite in the Primary Mn ore, Kotakara quarry;
(c) Idioblasts of Mn-silicates-spessartite and rhodonite in the matrix of secondry pyrolusite and psilomelane, in primary Mn ore, Pallagudi quarry district Vizianagram, (A.P).
Figure 4.2 Photomicrographs showing,

(a) Etched jacobsite with supergene pyrolusite in secondary ore from Devada quarry;
(b) Lamellae of hausmannite and jacobsite with pyrolusite in primary Mn ore Duvvam quarry;
(c) Diffused boundaries of jacobsite and hausmannite in the primary Mn ore Sadanandapuram quarry; district Vizianagram, (A.P).
Figure 4.3 XRD images showing,

(a) Pyrolusite, rhodochrosite, apatite, quartz, psilomelane in primary Mn ore Central Garbham quarry;
(b) Spessartite, pyrolusite, rhodonite, pyroxmangite and quartz in secondary Mn ore, Pallapgudi quarry;
(c) Quartz, jacobsite, hausmannite, magnetite and pyrolusite in the primary Mn ore, Duvvam quarry, district Vizianagram, (A.P).
Figure 4.4 Photomicrographs showing,

(a) Pyrolusite, Psilomelane and gangue in secondary Mn ore, Devada;
(b) Replacement texture of pyrolusite and rhodochrosite in secondary ore, Garividi block;
(c) Colloform of psilomelane with pyrolusite and gangue in secondary Mn ore Garividi, district Vizianagram, (A.P).
Figure 4.5 Photomicrographs showing,

(a) Etched rhodochrosite, bixbyite with supergene pyrolusite in the secondary Mn ore Mangotope quarry;
(b) Alternate compositional lamellae of rhodochrosite and braunite in primary ore Mangotope quarry, and
(c) Granoblastic braunite and bixbyite with a vein of cryptomelane in ore Mangotope quarry, district Vizianagram, (A.P).
Figure 4.6 Photomicrographs showing,

(a) Supergene psilomelane, pyrolusite and gangue in secondary Mn ore, Perumali quarry;
(b) Vein of secondary pyrolusite and cryptomelane in braunite and rhodochrosite in secondary Mn ore, Bangaruvalasa block;
(c) Well-developed ramsdellite, psilomelane, cryptomelane and quartz with gangue in secondary Mn ore, Avagudem, district Vizianagram (A.P).
Figure 4.7 XRD image showing,

(a) Supergene psilomelane, pyrolusite, apatite and quartz in secondary Mn ore Garividi mine;
(b) Braunite, bixbyite cryptomelane and rhodochrosite in Primary Mn ore from Mangotope quarry;
(c) Psilomelane, pyrolusite, ramsdellite and quartz in secondary Mn ore Avagudem, Vizianagram (A.P).
Figure 4.8 SEM images showing,

(a) Grain boundary replacement texture of spessartite (black) with pyrolusite (white) in primary Mn ore, Pallapgudi quarry;
(b) Intergrowth texture in Vredenburgite in primary Mn ore from Duvvam quarry;
(c) Fissure replacement and layered structure of Mn-Silciate carbonate ore from Garbham, district Vizianagram, (A.P).
Figure 4.9 SEM images showing,

(a) Closely folded lamellae of colloformic pyrolusite in the secondary Mn ore, Garividi block;
(b) Patches of carbonate remnant in the primary braunite bearing ore, Mangotope quarry, Chipurupalle block;
(c) Honeycomb structure of secondary Mn ore, from Perumali quarry, Vizianagram.