CHAPTER 4
ORE MICROSCOPY AND PETROGRAPHY

4.1 GENERAL STATEMENT

The mineralogical studies of the manganese ores with the associated country rocks were carried out to elaborate the mineralogical composition, texture, genesis, diagenetic changes, process of chemical weathering and alterations in different tectonic processes. The objective of this study was to investigate the mineralogical correspondence between the manganese minerals and the associated country rocks. Special emphasis was given to the study of samples collected from the contact between the ore body and the host rocks, to facilitate the study of mineral formation or intermixing between them if they were deposited in the same cycle of deposition with some degree of fluctuations in the depositional basin. The mineralogical characteristic between the manganese ores of different location and horizons from the three mines of the study area reveals some variation in the mineral assemblages of the primary and secondary manganese ores throughout the study area. The mineralogy of manganese ores of the study area were in detailed discussed by Fermor (1909); Dunn & Roy (1939); Babu and Nayak (1961); Narayanasmwami et al. (1963); Roy (1958, 1962, 1964a & b); Shukla & Anandalwar (1973); Vemban & Nagarajaiah (1974); Jain et al. 1990; Dasgupta et al. (1993); Shau et al. (1993); Banerjee et al. (2007); Gupta et al. (2009); Kanungo et al. (2003, 2007, 2008 & 2014); Kanungo & Sutaone (2013); Roy, 1964(a & b) and Siddiquie et al. 2015 b&c point out that the paragenesis of manganese minerals is associated with the gondites rock of Tirodi.

Detailed optical studies of the manganese ores which were collected from the study area are dominantly the primary ores. The manganese rich formation consists of three Mn ore minerals types, viz. (i) Mn oxide ores, (ii) Mn silicate-oxide ore and (iii) Mn silicate-carbonate-oxide ore type found in the study area (Roy et al. 1986) and (Siddiquie et al. 2015 b&c). Braunitite, bixbyite, hollandite, pyrolusite, psilomelane and hausmannite are observed as predominance manganese mineral of these mines. The authors are trying to establish the mineralogy of manganese ores of Bharweli, Tirodi and Ukwa area of Balaghat district, Madhya Pradesh of Sausar group with the help of present works. Geological traverses were taken in these blocks to identify the different litho units, their disposition and to observe variation of lithology. Special
emphasis was laid to observe variation if any, in the host rocks across both sides of manganese ore horizons. The mineralogical characteristics between the manganese ores of different location from the study area reveal some variation in mineral assemblages of the primary and secondary manganese ores. The mineral chemistry of study area is necessary to establish the paragenesis and textural relation which will be helpful to delineate the phase equilibrium condition of the manganese ore and associated host rock of the study area. The important manganese samples collected from three mines at different levels and channels studied for optical and XRD are detailed as follows:

4.2 MINERALOGY OF STUDY AREA

The ore microscopy and XRD of selected samples of manganese ores from the Balaghat district, M.P. reveals three types of manganese ore minerals like Mn oxide ores, Mn silicate-oxide ore and Mn silicate-carbonate-oxide ore. The minerals identified under reflected light and XRD analysis include braunite, pyrolusite, psilomelane, bixbyite, hollandite, hausmannite, magnetite, cryptomelane, jacobsite, rhodonite as seen in the Figure 4.1-4.3. The gangue minerals found throughout the study area include haematite, quartz and calcite etc. The present study shows that the deeper ore horizons in the mines characterized by weathering and the presence of different sets of minerals representing the metamorphosed assemblages. A detailed mineralogy of the selected samples of both primary and secondary manganese ores of the three mines of the study area is discussed well in this chapter. The paragenesis of manganese is also concluded on the basis of optical properties of polished blocks of manganese ore samples.

4.3 ORE MINERALOGY

Manganese ores exhibit varied micro-structural and textural features due to multistage deformation and recrystallization. The mineralogical and petrographical studies include identification of these minerals, their forms, nature of occurrence and their textural relationships. A range of techniques were applied to the mineralogical and chemical characterization using optical microscopy. These tools provide important physico-chemical properties of the main ore minerals.

The microscopic study of the polished sections of the manganese ores of the
Balaghat area reveals the following mineral assemblages: Braunite, Hollandite, Bixbyite, Manganite, Hausmannite, Pyrolusite, and Psilomelane.

4.3.1 BRAUNITE: $3(MnFe)_2O_3 MnSiO_3$

Braunite was first named after the Wilhelm von Braun (1790-1872) of Gotha, Thuringia, Germany. The composition of Braunite is $3(MnFe)_2O_3 MnSiO_3$ and the crystal system is tetragonal. It is usually forms compact or fine granular masses and the grain size increasing with the higher grade of metamorphism. It is found as the most abundant in all the ore bodies of Balaghat manganese deposit. The braunite shows wide variation in grain size, from fine to very coarse grain (Figure 4.1a, b, d-f; 4.2a, f; 4.3a-f). Braunite shows local alteration to Hausmannite (Figure 4.1c). Well developed primary ore with abundant braunite, pyrolusite and psilomelane as massive specimens are found in manganese mines of Balaghat (Figure 4.1a and 4.3a).

Two generations of braunite have been detected in these deposits (Figure 4.1a). The first generation braunite formed earlier in the paragenetic sequence. In the lower grades of metamorphism, it is deformed, elongated and dimensionally oriented parallel to the banding. Braunite is generally dark grey in colour. The second generation braunite is light grey in colour and is undeformed due to metamorphism (Figure 4.1a).

1) Optical properties

Under ore microscope in oil immersion, it gives dark grey and the cleavage is absent. Under crossed nicols, it shows weak anisotropism. Twinning and internal reflection are absent in braunite. Under the microscope in air, it gives light grey with brownish tint and internal reflection is rare. It has weak pleochroism, low reflectivity and weak anisotropic in oil immersion.

2) Etch reaction

On etching of braunite with HNO$_3$ (Con.) HCL (Con.), KCN, KOH and H$_2$SO$_4$ (Con.) gives negative result but with SnCl$_2$ (Sat.) shows strong etching. When it is etched with H$_2$O$_2$ (dil. 20%) show very slow effervescence along fractures but there is no stain on surfaces. When it is etched with H$_2$O$_2$ + H$_2$SO$_4$ show slightly darkness.
4.3.2 Hollandite: $\text{Ba(MnFe)}_8\text{O}_{16}$

The composition of hollandite is $\text{Ba(MnFe)}_8\text{O}_{16}$. The mineral was described for the first time from Indian deposits by Fermor (1909). Hollandite has been widely present in ore bodies metamorphosed to different grades, apparently derived from low temperature oxides. Under the microscope the mineral is white in colour with a yellowish tint and is strongly pleochroic from white to grayish white with the cleavage direction giving the brightest colour. Cleavage is well developed, and is parallel to (110). It is strongly anisotropic having shades of blue, gray and yellow (Figure 4.1 e-f, 4.2d, f; 4.3a, c, e).

1) Optical properties

Hollandite crystallizes in tetragonal system. Hollandite is strongly pleochroic mineral and show dark greyish to white colour with a precipitated yellow tint. On the observation between cross nicols, hollandite show strong anisotropism but basal sections are isotropic.

2) Etch reaction

On etching of hollandite with $\text{H}_2\text{SO}_4$ acid and $\text{H}_2\text{O}_2$ gives positive result. As a result the present twining feature will be more prominent and clear. Hollandite gives negative results on etching with $\text{HCl}$ acid, $\text{HNO}_3$ acid and hydrogen peroxides.

4.3.3 BIXBYITE: $(\text{MnFe})_2\text{O}_3$

Bixbyite forms in isometric system with chemical composition of $(\text{MnFe})_2\text{O}_3$. It is very fine grained and cannot be identified megascopically. Under microscope it is non-pleochroic. Reflectivity is slightly higher than Braunite. Cleavage is not distinct. Under cross nicols, it is completely isotropic with absence of internal reflection (Figure 4.1 c-f, 4.2d, 4.3b-d).

1) Optical properties

Under microscope bixbyite is non-pleochroic and isotropic mineral. Bixbyite is biscuit coloured with a tinge of green in oil and yellowish grey in air. The reflectivity of bixbyite is higher than braunite. The grains of bixbyite are rounded and oval in shape. Some grains of Bixbyite contain lamellar twinning. Part of the iron oxide is coarse grained and recrystallised and such hematite exhibits lamellar twinning.
4.3.4 HAUSMANNITE: Mn$_3$O$_4$

Chemical composition is Mn$_3$O$_4$ and the crystal system is tetragonal. Hausmannite shows dark grey to greyish white colour, with a distinct pleochroism. It is nearly euhedral. Hausmannite is coarse grained aggregates crystals associated with braunite and bixbyite (Figure 4.1d). It is also associated with bixbyite and manganosite (Figure 4.1c). It is also observed associated with manganite (Figure 4.2b) and also associated with vredenburgite, jacobsite and cryptomelane (Figure 4.2e). It is also seen associated with hollandite, braunite and cryptomelane (Figure 4.3c).

1) Optical properties

It shows irregular twinning and lamellae often intersecting each other. It shows strong pleochroic in shades of dark grey. It is also strongly anisotropic mineral with moderate reflectivity. But reflectivity of hausmannite enhance in the presence of immersion oil.

2) Etch reaction

On etching of hausmannite with H$_2$O$_2$ and H$_2$SO$_4$ acid give positive results with dark black tarnishing. On etching with SnCl$_2$ it gives black tarnishing. On etching with HCl acid, HNO$_3$ acid and FeCl$_2$ gives negative results.

4.3.5 MANGANITE: MnO(OH)

Manganite is in the form of prismatic crystals with radiated texture. Its chemical composition is MnO(OH) and the crystal system is monoclinic. It is very fine grained. Under microscope it is dark greyish, strongly pleochroic from light to dark grey. It is observed as dark grey associated with braunite, psilomelane and pyrolusite (Figure 4.1a, b and 4.3a). It is observed with hausmannite in Figure 4.2b.

Optical properties

Under crossed nicols, it is strongly anisotropic in shades of bluish grey and violet grey showing straight extinction. It forms prismatic as well as lamellar crystal in aggregate, radiating from a common center. It shows weaker bireflectance and anisotropic.

4.3.6 PYROLUSITE: MnO$_2$

The composition of pyrolusite is MnO$_2$ having tetragonal crystal system. It is strongly anisotropic in nature with yellowish to brownish blue colour. It is fine to coarse grained euhedral tabular to prismatic crystals. Pyrolusite is observed associated with braunite and psilomelane (Figure 4.1a-b, 4.2c, e; 4.3a).
4.3.7 PSILOMELANE: (Ba, H₂O)₂ Mn₅O₁₀

Psilomelane is a name assigned to a group of manganese minerals having composition of (Ba, H₂O)₂ Mn₅O₁₀. It shows bluish grey to greyish white colour and strong anisotropism. It shows deformation texture with pyrolusite and exhibits it's alteration from pyrolusite. Psilomelane is observed associated with pyrolusite and braunite (Figure 4.1a-b, 4.3a).

4.3.8 JACOBSITE: MnFe₂O₄

Jacobsite occur in isometric system. Jacobsite occur as a free grain with cryptomelane and hausmannite (Figure 4.2e) and also with braunite and hollandite (Figure 4.2e).

1) Optical properties

Under microscope jacobsite is non-pleochroic and isotropic mineral. It is dark brownish grey and sometimes with a faint yellow tint in air and dark green tint observable in oil. Some varieties are isotropic and others feebly anisotropic. In all polished block jacobsite occur as a idiomorphic grains.

4.3.9 VREDENBURGITE: (Mn₆Fe)₂O₄

Vredenburgite is a homogenous tetragonal in metastable phase. It is occurs as irregular masses, commonly as definite pseudomorphs after bixbyite. It is observed as lamellar marked parting results of orientated replacement of bixbyite. It has colour of shades of grey in oil immersion. Vredenburgite is observed in the study area associated with braunite, cryptomelane, pyrolusite and jacobsite (Figure 4.2a, c, & e).

4.3.10 CRYPTOMELANE: K(Mn⁴⁺,Mn²⁺)₆O₁₆

Cryptomelane is a potassium manganese oxide mineral with chemical formula K(Mn⁴⁺,Mn²⁺)₆O₁₆. It is crystalline material with fairly strong shades of grey in colour. It has occurs as well developed fibrous or acicular crystals. It is usually found as fine to coarse grained masses. It is found with pyrolusite as common mineral. In the area under study, it is found associated with pyrolusite, vredenburgite, hausmannite, jacobsite and braunite (Figure 4.2a, c, e-f). It is also associated with spessartite, hollandite, hausmannite and rhodochrosite (Figure 4.3d, e-f)

4.4 PARAGENESIS OF MANGANESE ORES

Mineralogical, textural and paragenetic studies of the manganese ore bodies from different metamorphic zones of the Sausar Group (Madhya Pradesh-Maharashtra
manganese belt) have been carried out by the present author and other previous workers (Roy, 1958, 1959, 1961, 1962, 1963; Roy and Mitra, 1962; Roy and Nandy, 1962; Roy and Purkait, 1965; etc.). The metamorphic zones of the Sausar Group have been delineated by the study of the pelitic rocks (phyllites and mica schists) with chlorite, biotite, almandine, staurolite, kyanite and sillimanite. Since the manganese ore bodies are intimately interbanded and co-folded with these rocks, they have been assumed to have undergone the same intensity of metamorphism (Siddiquie et al. 2015b &c). The mineralogical constituents and their paragenesis in these individual ore deposits of study areas have been given in Table 4.1.

It may be seen that in all ore bodies of low temperature formation (mainly of colloidal derivation), pyrolusite, cryptomelane etc., are commonly present, which reflects the stability of the minerals closely approximating MnO₂ in composition, with mainly Mn⁴⁺ in the low temperature condition. Therefore, in the original syngenetic manganiferous sediments as well, in an oxidising condition, there is a strong possibility of the presence of these minerals in stable assemblage (Siddiquie et al. 2015b &c).

When the sedimentary manganese formations are regionally metamorphosed, braunite is the earliest mineral to crystallize in most metamorphic deposits. In most cases, this early braunite is considerably deformed, showing that the deformational forces continued to act beyond its crystallisation period. Bixbyite generally follows this braunite though in some cases the relation is unclear in Tirodi area. According to Schneiderhohn (1931), bixbyite was formed by reaction between braunite and hematite as represented in the following equation:

$$\text{Mn. MnO}_3 + \text{Fe}_2\text{O}_3 \rightarrow (\text{Mn. Fe}) \text{MnO}_3$$

Braunite    Hematite    Bixbyite

A second generation braunite has formed replacing bixbyite along crystallographic directions and grain boundaries and such replacement is understandable considering the similarity in structure of the two minerals. Braunite, however, never yields bixbyite by replacement, primarily due to the fact that the silica, in its structure, is very well screened and it imparts a great stability to the Mn³⁺ in the structure of the mineral. In increasing temperature condition, generally the formation of bixbyite takes
place later than early braunite, indicating its higher temperature of formation and
everywhere it is apparent that bixbyite crystallised independent of braunite. Here the
bixbyite follows the first generation braunite in the sequence of crystallisation, though
is itself converted to a second generation undeformed braunite later in the waning
stage. The same assemblage of manganese oxide phases continues with increasing
intensity of metamorphism even after the appearance of almandine in the pelitic
schists, as at Bharweli-Ukwa area (almandine zone). In almandine zone, at Bharweli-
Ukwa area, bixbyite formed at the peak of metamorphism with its crystallisation
outlasting deformation. In spite of considerable iron in the bulk composition, jacobsite
or vredenburgite did not form. It may be noted, however, that in Bharweli-Ukwa area,
the metamorphism had, apparently, just reached almandine zone as shown by the very
minute size of the garnets and the relative fine grained nature of the phyllitic schists.
Jacobsite and vredenburgite, however, definitely appear in stable assemblage in
sillimanite zone in the Tirodi area. In the sillimanite zone, bixbyite continues to be
stable with jacobsite, vredenburgite and free hausmannite at the peak of
metamorphism. Thus the assemblages of the manganese oxide minerals can be plotted
against different metamorphic zones of study areas as shown in the below Table 4.2.


Table 4.1 Paragenesis of the ore minerals in deposits of Balaghat Manganese Belts (M.P.)

<table>
<thead>
<tr>
<th></th>
<th>METAMORPHIC</th>
<th>COLLOIDAL</th>
<th>SECONDARY</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>I</td>
<td>II</td>
</tr>
<tr>
<td><strong>Bharweli area, (Roy, 1962)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Almandine zone</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Braunite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bixbyite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hollandite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manganite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hematite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyroilanite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cryptomelane</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

|         |             |           |           |
| **Tirodi area, (Roy, 1958 & 1962)** |             |           |           |
| Sillimanite zone |             |           |           |
| Braunite  |             |           |           |
| Bixbyite  |             |           |           |
| Vredenburgite |           |           |           |
| (Metastable)|             |           |           |
| Hausmannite|             |           |           |
| Jacobsite |             |           |           |
| Hollandite|             |           |           |
| Manganite |             |           |           |
| Pyroilanite |           |           |           |
| Cryptomelane |             |           |           |
| Hematite  |             |           |           |

|         |             | I         | II        |
| **Ukwa area, (Roy, 1962)** |             |           |           |
| Almandine zone |             |           |           |
| Braunite  |             |           |           |
| Bixbyite  |             |           |           |
| Hollandite|             |           |           |
| Manganite |             |           |           |
| Hematite  |             |           |           |
| Pyroilanite |           |           |           |
| Cryptomelane |             |           |           |
Table 4.2 Specific assemblages of manganese oxide minerals in different metamorphic zones (Roy, 1964b).

<table>
<thead>
<tr>
<th>Low temperature 'gel' formation</th>
<th>Area</th>
<th>Manganese oxide mineral assemblages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorite zone</td>
<td>Shivrajpur, Gujarat</td>
<td>Braunite- (pyrolusite-cryptomelane)</td>
</tr>
<tr>
<td>Biotite zone</td>
<td>Kajlidongri, Jhabua District, M.P.</td>
<td>Braunite-bixbyite-hollandite- (pyrolusite-cryptomelane-hematite)</td>
</tr>
<tr>
<td>Almandine zone</td>
<td>Bharweli-Ukwa area, Balaghat District, M.P.</td>
<td>Braunite-bixbyite-hollandite-manganite- (pyrolusite-cryptomelane)</td>
</tr>
<tr>
<td></td>
<td>Dongri Buzurg (west)- Kurnura area, Bhandara District, Maharashtra</td>
<td>Braunite-hollandite-manganite- (pyrolusite-cryptomelane)</td>
</tr>
<tr>
<td>Stauroilite-Kyanite zone</td>
<td>Chikla-Sitasaongi area, Bhandara District Maharashtra</td>
<td>Braunite-bixbyite-hollandite-manganite- (pyrolusite-cryptomelane)</td>
</tr>
<tr>
<td></td>
<td>Gowahari Wadhona area, Chhindwara District, Madhya Pradesh</td>
<td>Braunite-bixbyite-hollandite-manganite- (pyrolusite-cryptomelane)</td>
</tr>
<tr>
<td>Sillimanite zone</td>
<td>Ramdongri-Gumgaon area, Nagpur District, Maharashtra</td>
<td>Braunite-bixbyite-hollandite-manganite- (pyrolusite-cryptomelane)</td>
</tr>
<tr>
<td></td>
<td>Tirodi-Sitapathore area, Balaghat District, Madhya Pradesh</td>
<td>Braunite-bixbyite-hollandite-manganite- (pyrolusite-cryptomelane)</td>
</tr>
</tbody>
</table>
4.5 ORE MINERAL ASSEMBLAGES

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 in different levels with depth. However there is some variation in mineral assemblages within the study area. Though the number of manganese minerals found in nature is considerably large, only a few are particularly important, in representing different pressure-temperature conditions during geological processes. This study will only be confined to the consideration of these minerals. They are pyrolusite (MnO₂), psilomelane [(Ba,H₂O)₃Mn₃O₁₀, Wadsley, 1952, 1953], cryptomelane (K₂Mn₂O₂₈, Richmond and Fleischer, 1942), braunite (3Mn₂O₄, MnSiO₃), bixbyite ((Mn, Fe)₂O₅), vredenburgite (Mn,Fe)₂O₄) jacobsite (MnFe₂O₄) and hausmannite (Mn₃O₄). Similar mineralogical details of the study area are also reported by many workers (Fermor, 1909; Roy, 1964 a & b; Banerjee et al. 2007, Siddique, 2004, Siddiquie & Bhat, 2008, Siddiquie et al. 2015 b&c) and were taken into due consideration for unveiling the possible mineral paragenesis.

4.5.1 Primary ore minerals assemblages and mineral paragenesis

The dominant Mn-minerals found in these ores include rhodochrosite, braunite, bixbyite, vredenburgite, hausmannite and jacobsite, spessartite and rhodonite. The important assemblages and paragenesis are detailed as follows:

Rhodochrosite-braunite-bixbyite-rhodonite

Jacobsite-hausmannite-vredenburgite

Hausmannite-rhodonite-pyroxmangite-spessartite

Rhodochrosite-braunite-bixbyite-rhodonite

This assemblage is the characteristic of primary ores of Balaghat district. The diagenetic origin of rhodochrosite (MnCo₃) is evident in its morphology Figure 4.3 e, f) in many samples from hinge zone of folds. 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. The spherulites of rhodochrosite in Balaghat manganese ore deposits resemble rhodochrosites of Bulgaria and Southern Urals which are completely diagenetic as worked out by Aleksiev (1960). The ore samples contains rhodochrosite with quartz are specifically from the hinge zones of the folds, where they were least affected by the metamorphism. In many places, fine intergrowths of rhodochrosite with quartz are observed and these two react with each other to crystallize rhodonite as;

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

(Rhodochrosite) (Quartz) (Rhodonite)

The rhodochrosite crystals themselves contain numerous inclusions of both rhodochrosite and quartz (Figure 4.3f).

Braunite (Mn$_3$SiO$_{12}$) is an important lower oxide of manganese and takes up manganese during the increasing grade of metamorphism from bixbyite. Braunite has about 10-Wt% of SiO$_2$ and is not a pure oxide. It is rather a silicate but conventionally called as lower oxide of manganese. It breaks down as per the following process;

\[ \text{Mn}_3\text{SiO}_{12} = 3 \text{Mn}_2\text{O}_3 + \text{MnSiO}_3 \quad \text{(Reaction-2)} \]

(Braunite) (Bixbyite) (Rhodonite)

In principle, the above pair can serve as an application in geochronology. Braunite commonly found in all metamorphosed deposits from the diagenetic to granulite facies (800$^0$-900$^0$c) with varied composition due to Mn$^{3+}$, Fe$^{3+}$ exchange with bixbyite. Braunite is present in Archaean and Proterozoic manganese deposits of Kalahari, S. Africa and India containing around 4.5% of SiO$_2$ Wt% and 4.5% of CaO Wt% (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). Pyrolusite in this assemblage is of secondary replacement origin and indicates the enrichment of manganese by supergene enrichment process in the zone of weathering (Figure 4.1a-b). In metamorphosed manganese ore deposits of the Balaghat, 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 4.4-4.9) of the present braunite from sedimentary braunite is very obvious.

**Jacobsite-Hausmannite-Vredenburgite**

This assemblage is typical in the most continental meta-sedimentary 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. The hausmannite lamellae also show pleochroism and anisotropies in shades of dark to green (Figure 4.c-d, 4.2b, e, 4.3c). Vredenburgite is intergrown in the hausmannite (Mn-rich member) and jacobsite (Fe-rich member) of the primary ore samples which are frequently observed in the ore blocks (Figure 4.2e). The individual grains often show a well-developed lamellar twinning (Figure 4.1c-d, 4.2b, e). The present observations support the results of Deb (1939) and Roy, (1958) where there is no homogeneity in Vredenburgite.

The formation of hausmannite in metamorphosed manganese oxide ore is a function of high temperature and concomitant reduction and its presence, in the absence of jacobsite, reflects a bulk composition low in iron (Figure 4.2e). The formation of jacobsite depends on the iron content in the original bulk composition, temperature and oxygen fugacity. 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.

**Hausmannite-rhodonite-pyroxmangite-spessartite**

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 Balaghat district, (M.P.), represents the products of the original carbonate-silicate-oxide rock that escaped latter metamorphism. Rhodochrosite often replaces Mn-oxides 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.

The primary ores enriched in silica, 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, peimontite and epidote are sporadic (Figure 4.3e, f). 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 the above reaction-1.

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 tephroite (reaction 3) 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 and rocks close in composition due to silica gain. Schematically this process can be ascribed as the following reaction (for the particular case of rhodonite formation);

\[ \text{Mn}_2 (\text{SiO}_4) + (\text{SiO}_2)_{aq} \rightarrow 2\text{Mn (SiO}_3) \quad \text{(Reaction-3)} \]

In accordance with Hsu (1968), the temperature of spessartite formation at a pressure of 2.5 kbar should be not lower than 410°C as possible pressure and temperature for metamorphism of Balaghat manganese ores. At the same time, spessartite is also observed as primary ore minerals at this deposit. Spessartite crystallization at high temperature was also suggested by researchers of manganese
deposits in Belgium, Ghana, California and other regions (Flohr and Huebner, 1992; Theye et al. 1996; Nyame, 2001). The primary ores that occur throughout the banded stratiform ore horizons are largely of pyroxmangite (rhodonite), rhodochrosite and quartz; with spessartite (Figure 4.3e-f). 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 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 green schist 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 4.3e-f).

4.5.2 Secondary ore mineral assemblages and mineral paragenesis

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 holländite 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 (Hewett et al. 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 Balaghat manganese ore is in close association with cryptomelane in most of the samples (Figure 4.2c, e). Pyrolusite and cryptomelane are also seen in the
cracks and boundaries of other minerals and appears to have developed at the expense of latter, 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 magnesite 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 ore from different blocks of the study area.

4.6 TEXTURES

The manganese minerals of my study area show different textures due to presence of different mineral association. The different texture observed in polished block of manganese ore under the reflected light of microscope which have been observed are given below:

(1) Granular texture
(2) Replacement texture
(3) Veined texture
(4) Colloform texture
(5) Framboidal texture
(6) Crystallographic intergrowth
4.6.1 Granular Texture:

It is texture resulting from the aggregation of mineral grains of more or less equal size of grains, which is shown by all the ore minerals found in the form of fine anhedral to course euhedral grains of ore minerals. Braunite is most common showing granular texture with pyrolusite and psilomelane (Figure 4.1a). Hollandite also shows granular texture with braunite, pyrolusite and psilomelane (Figure 4.3a).

4.6.2 Replacement Texture:

It is a texture which exhibits one mineral replaced the other mineral. It is observed among the most of the manganese mineral of the study area. These replacement textures are occurred along the cleavage, fracture and grain boundary. Various types of replacement texture observed are as follows:

- Cryptomelane occurs as veins in hollandite and braunite along the mineral boundary, transecting several grains of the latter (Figure 4.2f). Veins wall are irregular, crenulated and do not match each other.
- Braunite is replaced by pyrolusite and psilomelane in Figure 4.1b. Hausmannite is replaced by bixbyite and manganosite as in irregular pattern (Figure 4.1c). Bixbyite replacing the hollandite and jacobsite in Figure 4.2d.
- Network replacement texture is observed in the Figure 4.2b, manganite mineral is replaced by hausmannite.
- Cleavage rim replacement texture is observed in Bharweli mine, hollandite is replaced by braunite and bixbyite (Figure 4.1f).

4.6.3 Veined Texture:

Some veins are observed megascopically along and across the bedding planes in manganese ores of the study area. Hollandite forms irregular veins in the braunite and jacobsite matrix along the cracks and fillings and also across bedding planes (Figure 4.1e).

4.6.4 Colloform Texture:

It is a texture where crystals have grown in a radiating and concentric manner which may reflect underlying geochemical controls. This texture is often found in manganese mineral of the study area. Colloform texture is formed by cryptomelane in braunite and bixbyite (Figure 4.3b).
4.6.5 Framboidal texture:

These textures are aggregates of spherical grains or minerals. Framboidal texture is observed as spherical mineral by braunite and hollandite in hausmannite and cryptomelane from the area under study (Figure 4.3c).

4.6.6 Crystallographic intergrowth:

It is the intimate union of two or other mineral grains, often in parallel position, produced by simultaneous crystallization. Crystallographic intergrowth is observed between braunite, cryptomelane and bixbyite. Crystallographic emulsion texture is observed between the rhodochrosite, cryptomelane and braunite in spessartite and hollandite (Figure 4.3c). This emulsion texture is similar to spherical replacement texture and occurs at grain boundaries and as discrete grains. This texture is also observed between hollandite, cryptomelane, rhodochrosite and braunite in spessartite (Figure 4.3f).

4.7 RESULT OF ANALYTICAL TECHNIQUE

X-Ray Diffraction analysis of selected samples confirmed the presence of bixbyite, pyrolusite, hollandite, vredenburgite and rhodochrosite in the polished ore blocks of manganese of study area. Some associated minerals are also clearly recognized on the XRD spectrum. The position of lowest and highest peak of bixbyite (d = 4.67330 - 1.65538, Figure 4.4), hollandite (d = 3.46983 - 1.65638, Figure 4.4), vredenburgite (d = 4.87131-1.49796, Figure 4.6), rhodochrosite (d = 6.92679-1.91700, Figure 4.8), pyrolusite (d = 3.09925-1.42967) and hausmannite (d = 4.87131 - 1.36842, Figure 4.6). The observed peak positions of these minerals showed that they are virtually indistinguishable. Gangue mineral such as quartz is also observed on XRD spectrum which is represented by peaks (Figure 4.4 & 4.7).
Figure 4.1 Photomicrograph of manganese ore showing a) granular texture shown by pyrolusite (Pyr), psilomelane (Psi), manganite (Mng) and braunite (Brn) of two generation, b) replacement texture of braunite (Brn) by pyrolusite (Pyr) and psilomelane (Psi), c) replacement texture shown by hausmannite (Hsm) in bixbyte (Bxy) and manganosite (Mns) intergrowth in hausmannite (Hsm), d) mutual boundary texture between braunite (Brn) and bixbyte (Bxy) associated with hausmannite (Hsm) and manganosite (Mns), e) vein replacement texture shown by hollandite (Hol) in braunite (Brn) and f) cleavage rim replacement texture shown by hollandite (Hol) in braunite (Brn) and bixbyte (Bxy) from Bharweli mine, Balaghat district, M.P., India.
Figure 4.2 Photomicrograph of manganese ore showing a) mutual boundary texture shown by vredenburgite (Vrd), braunite (Brn), jacobsite (Jcb) and cryptomelane (Crp), b) network replacement texture between hausmannite (Hsm) and manganite (Mng), c) mutual boundary texture shown by vredenburgite (Vrd), pyrolusite (Pyr) and cryptomelane (Crp), d) replacement texture in bixbyte (Bxy) by hollandite (Hol), e) sharp contacts between hausmannite (Hsm), jacobsite (Jcb), pyrolusite(Py) and cryptomelane (Crp) in the metamorphosed ores and f) vein replacement texture shown by cryptomelane (Crp) in hollandite and braunite from Tirodi mine, Balaghat district, M.P., India.
Figure 4.3 Photomicrograph of manganese ore showing a) granular texture shown by hollandite (Hol), braunite (Brn), psilomelane (Psi), Pyrolusite (Pyr) and manganite (Mng) b) colloform texture shown by cryptomelane (Crp) in braunite (Brn) and bixbyite (Bxy), c) framboidal texture shown by braunite (Brn) and hollandite (Hol) with hausmannite (Hsm) and cryptomelane (Crp), d) crystallographic intergrowth texture shown by cryptomelane (Crp) in braunite (Brn) and bixbyite (Bxy), e) crystallographic emulsion texture shown by spessartite (Spt), rhodochrosite (Rhc), hollandite (Hol), braunite (Brn) and cryptomelane (Crp), and f) crystallographic emulsion texture shown by cryptomelane (Crp), braunite (Brn), hollandite (Hol) and rhodochrosite (Rhc) in spessartite (Spt) from Ukwa mine, Balaghat district, M.P., India.
Figure 4.7: Showing 26 position of bixbyite, and quartz (Trodal mine, Malgathar)

Figure 4.6: Showing 26 position of hausmannite, proustite and vredenbourgite