Manganese Ore Minerals Assemblages and Mineral Paragenesis with the Help of Ore Petrography and XRD Studies of Balaghat District, (M.P.) India

By F. N. Siddiquie, Kh. Burhamuddin, Mohd. Shaif & Juned Alam

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Abstract- The regionally metamorphosed syngenetic sedimentary bodies of manganese ores in the Sausar Group of Balaghat district, Madhya Pradesh exhibit a definite trend in the formation and transformation of manganese oxide phases with progressive metamorphism. A regional trend is clearly noticeable from the paragenesis of Ore minerals in the manganese ore bodies from different metamorphic zones. Braunite forms at a very low temperature, appearing in the chlorite zone of regional metamorphism, and it continues in stable form right up to the sillimanite zone. Bixbyite as a high temperature mineral appears first in biotite zone and also appears in the sillimanite and almandine zone in the Balaghat. It shows evidences, at places, of conversion to hausmannite, and a second generation of this mineral is also found to have been formed as conversion product in the cleavages of the latter in ore bodies of sillimanite zone in Tirodi areas. Free hausmannite is characteristic of only the sillimanite zone. Bixbyite is accompanied by hollandite which is also a transformation product of psilomelane formed in elevated temperature condition. The association of braunite, bixbyite and hollandite (in the absence of jacobsite, hausmannite and vredenburgite) continues to the almandine zone (Bharweli-Ukwa area).

Keywords: manganese ore, sausar group, balaghat district, metamorphism, paragenesis, metamorphic zones, manganese oxide minerals.

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Abstract- The regionally metamorphosed syngenetic sedimentary bodies of manganese ores in the Sausar Group of Balaghat district, Madhya Pradesh, exhibit a definite trend in the formation and transformation of manganese oxide phases with progressive metamorphism. A regional trend is clearly noticeable from the paragenesis of ore minerals in the manganese ore bodies from different metamorphic zones. Braunite forms at a very low temperature, appearing in the chlorite zone of regional metamorphism, and it continues in stable form right up to the sillimanite zone. Bixbyite as a high temperature mineral appears first in biotite zone and also appears in the sillimanite and almandine zone in the Balaghat. It shows evidences, at places, of conversion to hausmannite, and a second generation of this mineral is also found to have been formed as conversion product in the cleavages of the latter in ore bodies of sillimanite zone in Tirodi areas. Free hausmannite is characteristic of only the sillimanite zone. Bixbyite is accompanied by hollandite which is also a transformation product of psilomelane formed in elevated temperature condition. The association of braunite, bixbyite and hollandite (in the absence of jacobsite, hausmannite and vredenburgite) continues to the almandine zone (Bharweli-Ukwa area).

The trend of formation and transformation of manganese oxide minerals with increasing of temperature in metamorphic condition has been indicated. The absolute temperature of formation of the individual phases and the mineralogical trend found in the manganese ore bodies could be correlated to the results from phase equilibrium studies including manganese, iron and silica.

Keywords: manganese ore, sausar group, balaghat district, metamorphism, paragenesis, metamorphic zones, manganese oxide minerals.

I. Introduction

Balaghat district is placed at the Madhya Pradesh-Maharashtra manganese belt of central India extending from 21°19’ to 22°24’ North latitude and 79°31’ to 81°3’ East longitude. These manganese belts make an arcuate belt of about 150 kms long and 25 to 30 meters wide in NE-SW direction and extend in the East-West direction from Chhindwara district in the West through Nagpur and Northern Bhandara District in the middle of the Balaghat (Fermor, 1909, 1936; and Narayanaswami, et. al. 1963). The manganese deposit of the Balaghat district, M.P., founds as NNE-SSW to ENE-WSW trending conformable bands in the form of lenses of varying sizes, enclosed within the meta-sedimentary sequence of Sausar Group of rocks of Precambrian age shown in Fig. 1 (Banerjee, et. al. 2007). The Madhya Pradesh-Maharashtra manganese belt is the largest manganese ore deposits of India which are intensely deformed and metamorphosed varies from green schist facies to upper amphibolite facies with gradual increase in the grade of metamorphism from East to West (Gupta, et. al. 2009).

Three manganese mines viz. Bharweli mine, Tirodi mine and Ukwa mine are selected for mineragraphic studies in Balaghat district. These are working manganese mines operated under the Manganese ore India limited (MOIL) in which Bharweli mine (largest underground manganese mine in the Asia), Tirodi mine (open cast mine) and Ukwa mine (both open cast and underground mine). Braunite, bixbyite, hollandite, jacobsite, pyrolusite, psilomelane, vredenburgite and hausmannite are observed as predominance manganese mineral of these mines. The study area was studied in detailed by (Fermor, 1909) in his classic memoirs and Dunn & Roy (1939); Roy, (1958, 1962, 1964(a), & 1964(b), 1966; Babu and Nayak (1961); Narayanaswami, et. al. (1963); Shukla and Anandalwar (1973);Vemban and Nagarajaiah (1974); Jain, et. al. 1990; Dasgupta, et. al. (1993); Banerjee, et. al. (2007); Gupta, et. al. 2009;Kanungo, et. al. 2003, 2007, 2008, & 2014) and Kanungo and Sutaone (2013) were carried out detailed mineralogy of the study area and proposed their views. Systematic mineragraphic study of manganese ore of my study area was not carried out by earlier workers. Banerjee, et. al. (2007), Roy, (1964, a & b) and Roy, et. al. 1986, carried out the mineralogy, paragenesis and genesis of manganese ore and associated host rocks of the study area. Roy, 1964(a & b) point out that the paragenesis of manganese minerals is associated with the gondites rock of Tirodi.
The authors are trying to establish the paragenetic trend of the manganese ores from different metamorphic zones and have tried to correlate the mineral assemblages and mineral paragenesis of manganese ores of Bharweli, Tirodi and Ukwa area of Balaghat district, Madhya Pradesh of Sausar group with the help of these works. 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.

II. GEOLGY OF THE BALAGHAT MANGANESE ORES

The manganese ore bodies of the study areas occur conformably with the metasedimentary sequence of the Sausar Group (Fermor, 1909; Pascoe, 1950; Straczek et al., 1956; Narayanaswami, et al., 1963; Vemban and Nagarajaiah, 1974). The Sausar Group hosts the largest productive manganese ore deposits of India, contributing about 80% of the total production of the country. Rocks of Sausar Group consists of a sequence of regionally metamorphosed cross bedded quartzite, pelite, carbonate and manganese ores deposited on a stable platform (Bandyopadhyay et al. 1995). The meta-sedimentary manganese ore deposits of large size are hosted by the gneiss and quartzites in the Balaghat district of M.P. The important mines with better exposure of the ore bodies and host rocks include Bharweli, Tirodi and Ukwa mines. The manganese deposits are importantly available within the pelitic Mansar Formation as pointed out by Roy, 1966. Older and younger gneisses, migmatites, ortho-gneisses, late and post-tectonic granite plutons, pegmatites and vein quartz, all of apparent Precambrian age have been partly mixed up with and emplaced in the Sausar rocks (Narayanaswami, et al. 1963). Rocks of Sausar group are intruded by amphibolites appear to have a calcareous parentage (Subramanyam, 1972). Detailed geochronologic studies are lacking within this belt; however, Roy et al. (2006) on the basis of Rb-Sr and Sm–Nd geochronological studies, argue that the main phase of metamorphism (amphibolite-grade) took place between 800 and 900 Ma.

Folding is the major structural control and foliation planes are a minor structural control for the concentration of manganese due to tectonism and metamorphism. The drag folding, foliation planes, kink bands, pressure shadow zones, strain slip cleavages and the joints as reported by Siddique (2004) are zones along which supergene enrichment of the manganese ores have been carried out by meteoric waters. Jain, et. al. (1990) proposed that the rocks of Bharwell-Ukwa manganese belt of Balaghat may be admitted an independent stratigraphic status of ‘Bharwell Group’. younger to the Sausar Group. The stratigraphic succession proposed by Narayanaswami, et. al., (1963) is given in the Table.1.

III. FIELD WORK AND SAMPLING

About forty seven Manganese ore samples and fifteen host rocks were collected systematically from the study area. Out of this, 30 Mn Ore samples were selected for mineragraphic and geochemical studies. The manganese ores of the Balaghat mines were studied in the field with reference to the tectonic and structural controls of ore deposition. The present sampling and field data with photographic documentation was carried out in standard order. Preferential and careful selection of both primary and secondary ores was carried out for the present piece of research work. The selected samples were coded and packed as per their respective locations for laboratory use. The primary ore samples like braunite ores show typical metamorphic banding as seen in fig. 2. (a-d). The secondary ore samples especially pyrolusite and psilomelane (Fig. 3).
IV. Materials and Methods

Out of 47 Mn Ore samples collected from the study areas, 30 Mn Ore samples were selected for mineragraphic studies. These mineragraphic microscopic studies of Mn Ore samples were conducted by polished blocks; examined the minerals of this polished blocks under the reflected light of microscope with the help of air and oil immersions lenses. 13 manganese ore samples were selected for XRD analysis to confirm the ore minerals present in the manganese ore samples. XRD analysis was conducted by XPERT-PRO PHILIPS at Geological Sciences Department, Jadavpur University, Kolkata. Analytical XRD techniques were used on operating current 40KV-30ma and results were obtained on 2θ positions in the form of peaks of count time of 30 minutes.

Table 1: Stratigraphic succession of Sausar Group (Bandopadhyay, et. al., 1995, modified from Narayanaswami, et. al., 1963)

<table>
<thead>
<tr>
<th>FORMATION</th>
<th>LITHOLOGY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bichua Formation</td>
<td>Dolomite, Marble, Calc silicate gneiss schist.</td>
</tr>
<tr>
<td>Junewani Formation</td>
<td>Metapelite (Mica Schist), Quartzite, granulite, biotite-Gneiss (Reworked basement).</td>
</tr>
<tr>
<td>Charboli Formation</td>
<td>Quartzite, feldspathic Schists, Gneisses, Autoclastic Quartz, Conglomerate.</td>
</tr>
<tr>
<td>Mansar Formation</td>
<td>Metapelite (mica-schists and gneisses), graphitic Schists, Phyllite quartzite, major manganese deposits and gondite.</td>
</tr>
<tr>
<td>Lohangi Formation</td>
<td>Calc-Silicate Schists and gneisses, marble, Manganese deposits.</td>
</tr>
<tr>
<td>Sitasaongi Formation</td>
<td>Quartz mica Schists, Feldspathic Schists, mica gneiss, Quartzite, Conglomerate.</td>
</tr>
<tr>
<td>Tirodi Gneiss</td>
<td>Biotite gneiss, Amphibolite, Calc-Silicate Gneiss (Tirodi Gneiss), Granulites, Mica Feldspathic Schists.</td>
</tr>
<tr>
<td>Older Metamorphics</td>
<td>Charnockite, Orthogneisses and Granite Biotite Gneisses, hornblende Gneisses, Amphibolites and calclgranulites</td>
</tr>
</tbody>
</table>

Figure 2: Hard, soft massive and banded manganese ore sample collected from a) Bharweli underground mine b) Tirodi open cast mine, c) Tirodi underground mine and d) Ukwa underground mine, Balaghat district, M.P.

V. Paragenetic Trends and Regional Metamorphism of Manganese Ores

Mineralogical, textural and paragenetic studies of the manganese ore bodies from different metamorphic zones of the Sausar Group (Madhya Pradesh-Maharashtra) have been carried out by the author and his associates (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. The mineralogical constituents and their paragenesis in these individual ore deposits of study areas have been given in Table 2.
### Table 2: Paragenesis of the ore minerals in deposits of Balaghat Manganese Belts (M.P.)

<table>
<thead>
<tr>
<th>METAMORPHIC</th>
<th>COLLOIDAL</th>
<th>SECONDARY</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Almandine zone</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bharweli, (Roy, 1962)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>II</td>
<td></td>
</tr>
<tr>
<td>Braunite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bixbyite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hollandite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manganite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hematite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrolusite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cryptomelane</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Sillimanite zone</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tirodi area, (Roy, 1958 &amp; 1962)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>II</td>
<td></td>
</tr>
<tr>
<td>Braunite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bixbyite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vredenburgite (Metastable)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hausmannite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jacobsite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hollandite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manganite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrolusite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cryptomelane</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Almandine Zone</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ukwa area, (Roy, 1962)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>II</td>
<td></td>
</tr>
<tr>
<td>Braunite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bixbyite</td>
<td></td>
<td></td>
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<tr>
<td>Hollandite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manganite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hematite</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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 MnO$_2$ in composition, with mainly Mn$^{4+}$ 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.

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 deformatonal 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:

\[
\text{Mn}_x \text{MnO}_3 + \text{Fe}_2\text{O}_3 \rightarrow (\text{Mn,Fe}) \text{MnO}_3
\]

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 Mn$^{3+}$ 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 Table 3.

### Table 3: Specific assemblages of manganese oxide minerals in different metamorphic zones (Roy, 1964b)

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

### VI. 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 (MnO<sub>2</sub>, psilomelane [(Ba, H₂O)₂MnO₁₀, Wadsley, 1952, 1953], cryptomelane (K₃Mn₄O₁₀, Richmond and Fleischer, 1942), braunite (3Mn₂O₃, 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 and Siddiquie, 2010) and were taken into due consideration for unveiling the possible mineral paragenesis.
a) Primary ore minerals assemblages and mineral paragenesis

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

Rhodochrosite-braunite-bixbyte-rhodonite
Jacobsite-hausmannite-vredenburgite
Hausmannite-rhodonite-pyroxymanosite-spessartite

i Rhodochrosite-braunite-bixbyte-rhodonite

This assemblage is the characteristic of primary ores of Balaghat district. The diagenetic origin of rhodochrosite (MnCo$_3$) is evident in its morphology (Fig. 3 & 6) in many samples from hinge zone of folds. It is

$\text{MnCo}_3 + \text{SiO}_2 = \text{Mn(SiO}_3 + \text{Co}_2$ (Reaction -1)

(Rhodochrosite) (Quartz)

(Rhodonite)

The replacement of carbonate with pyroxenoid is seen in the banded ore (Fig. 4). The rhodochrosite crystals themselves contain numerous inclusions of both rhodochrosite and quartz (Fig. 7).

Braunite (Mn$_3$SiO$_{12}$) is an important lower oxide of manganese and takes up manganese during the

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

(Raunite) (Bixbyte) (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$^\circ$-900$^\circ$C) with varied composition due to Mn$^{3+}$, Fe$^{3+}$ exchange with bixbyte. Braunite is present in Archaean and Proterozoic manganese deposits of Kalaahari, S. Africa and India containing around 4.5% of SiO$_2$,Wt% and 4.5% of CaO (Roy, 1981). Depending upon the bulk composition (availability of Si, Fe etc.), temperature and oxygen fugacity, braunite and bixbyte 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 (Fig. 3). 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 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;

Increasing grade of metamorphism from bixbyte. 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 Mn. It breaks down as per the following process;

ii 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 (Fig. 5). Vredenburgite intergrown the hausmannite (Mn-rich member) and jacobsite (Fe rich member) in the primary ore samples are frequently observed in the studied ore (Fig. 5). The individual grains often show a well-developed lamellar twinning (Fig. 5). 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 (Bhat, 2014) (Fig. 5). 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.

iii 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, pieomontite

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

\[
\text{Tephoite} + \text{Solution} \quad \text{(Reaction-3)}
\]

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 (Fig. 4 & 7). 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 idioiblasts are seen embedded in secondary pyrolusite and epidote are sporadic (Fig. 4). 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 caryopilite (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);

b) Secondary ore mineral assemblages and mineral paragenesis

i 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 bixbite at 600°C. However the dominance of cryptomelane in some samples indicates least conversion. The presence of the higher oxides 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, 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 (Fig. 5 & 8). 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.

**Figure 3**: Ore microphotograph showing lineated rhodochrosite (Rhc) with secondary pyrolusite (Py) and psilomelane (Psi) preserving the granoblastic texture and granulitic fabric in manganese ores from Bharweli mine, Balaghat district, M.P India

**Figure 4**: Ore microphotograph showing rhodonite (Rhd), spessartite (Spt), and quartz (Qtz) as a metamorphic mineral assemblage in the metamorphosed ores from Ukwa Mine, Balaghat district, M.P India
Figure 5: Ore microphotograph showing sharp contacts between hausmannite (Hsm), jacobsite (Jcb), pyrolusite (Py) and cryptomelane (Crp) in the metamorphosed ores, Tirodi Mine, Balaghat district.

Figure 6: Ore microphotograph showing spherulites of rhodochrosite with bixbyite and secondary pyrolusite preserving the granoblastic texture and fabric as the metamorphic indicator from Bharweli mine, Balaghat district, M.P India.

Figure 7: Ore microphotograph showing rhodonite (Rhd), spessartite (Spt), quartz (Qtz) as a metamorphic mineral assemblage in the metamorphosed ores from Ukwa Mine, Balaghat district, M.P India.
Figure 8: Ore microphotograph showing bixbyite (Bxy), Rhodhocrosite (Rhc) and pyrolusite (Py) as a metamorphic mineral assemblage in the metamorphosed ores from Ukwa Mine, Balaghat district, M.P India.

Figure 9: Showing 2θ position of bixbyite and quartz (Bharweli mine, Balaghat district, M.P.)

Figure 10: Showing 2θ position of bixbyite, pyrolusite and Rhodochrosite (Ukwa mine, Balaghat district, M.P.)
VII. Conclusions

Braunite forms at a very low temperature, appearing in the chlorite zone of regional metamorphism, and it continues in stable form right up to the sillimanite zone. Schneiderhohn (1931) and Dunn (1936) considered bixbyite as a high temperature mineral appears first in biotite zone and also appears in the sillimanite and almandine zone in the Balaghat. It shows records, at places, of conversion to hausmannite, and a second generation of this mineral is also found to have been formed as conversion product in the cleavages of the latter in ore bodies of sillimanite zone in Tirodi areas. Bixbyite continues up to the sillimanite zone along with braunite and other high temperature lower oxides of manganese. Vredenburgite, free hausmannite and free jacobsite appear in the sillimanite zone. Hollandite appears in the almandine zone, apparently at the cost of psilomelane (Richmond and Fleischer, 1942; Wadsley, 1950) and continues to the sillimanite zone. In waning stages of metamorphism, bixbyite in all zones converts to second generation braunite. Magnetite and primary pyrolusite formed everywhere in the waning stage.

The phase equilibrium studies of systems involving magnetite, jacobsite, vredenburgite and hausmannite considerable data suggests regarding the formation and stability range of the minerals. The formation of jacobsite is dependent on two major factors, viz., (i) enough iron in the bulk composition and (ii) adequate temperature for the stability of manganese and iron in Mn$_3$O$_4$ and Fe$_3$O$_4$ stage. Van and Keith (1958) observed that the compositional range of jacobsite increases with higher temperature. In metamorphic manganese ores, jacobsite free of hausmannite lamellae would form in fairly high grade of metamorphism when the composition limit does not extend to the vredenburgite field or when the temperature never reaches for the mix crystal (metastable vredenburgite) to form. The presence of vredenburgite ensures high temperature in the range of approximately 500° to 700°C or higher (Mason, 1943b), a bulk composition rich in manganese (vredenburgite field) and a sufficiently slow cooling for the intergrowths to form. Wherever the delicate intergrowths of jacobsite and hausmannite are retained, it is evident that there was no further recrystallization. The presence of discrete grains of hausmannite, not oriented in the crystallographic directions of jacobsite in metamorphic ores, would indicate a bulk composition low in iron and a high temperature of formation. It has been shown by laboratory experiments that higher oxides of manganese such as cryptomelane and pyrolusite convert to hausmannite at high temperature (McMurdie and Golovato, 1948; Delano, 1950; Faulring, et al., 1960; etc.). In most of these cases, however, the Mn$_3$O$_4$ state (hausmannite) is attained through the Mn$_3$O$_3$ state (bixbyite). When hausmannite is present as discrete grains in addition to its presence as lamellae in associated vredenburgites, it apparently either indicates presence of excess Mn$_3$O$_4$ which could not enter into vredenburgite and crystallised independently, or that part of the exsolved hausmannite had segregated outside jacobsite after exsolution. This may indicate that subsequent to the exsolution of hausmannite in jacobsite, further recrystallization ensued, due to which the intergrowth was destroyed and the two minerals recrystallized as discrete grains.

In a very slow rate of cooling also the exsolved hausmannite would tend to migrate to the borders or interstitial spaces of jacobsite rather than to stay confined in them. The presence of hausmannite alone, in the absence of jacobsite, evidently reflects a high temperature of formation and a bulk composition rich in manganese but poor in iron.

The phase-equilibrium studies involving manganese, iron and silica and from investigations on different natural mineral assemblages of manganese...
ores of various metamorphic grades, it has been possible to throw some light on the formation and phase transformation of some important manganese minerals with change in temperature and possible variation of oxygen partial pressure. With the onset of metamorphism, and consequent increase in temperature, the higher oxides of manganese with dominant Mn$^{4+}$ in the sedimentary deposits, transform to the Mn$_2$O$_3$ state and combine with the available silica to form braunite. The stability range of braunite being very wide, it can form as a transformation product of MnO$_2$ in low grade metamorphism and can continue right up to the highest grade. Bixbyite, on the other hand, appears sometime later than braunite at a higher temperature and though its temperature of formation has been determined in the laboratory as around 500°C (Klingsberg and Roy, 1959; Mason, 1943b) it can appear in biotite zone, at a lower temperature, in natural metamorphic process. Bixbyite, in most cases, is accompanied by hollandite which is also a transformation product of psilomelane formed in elevated temperature condition (Richmond and Fleischer, 1942; Wadsley, 1950). The association of braunite, bixbyite and hollandite (in the absence of jacobsite, hausmannite and vredenburgite) continues to the almandine zone (Bharwell-Ukwa area).

The manganese oxide mineral assemblages and their paragenesis in higher metamorphic zones were related to the phase transformations shown in the phase-equilibrium diagrams given by Mason (1943b) and Muan and Somiya (1962). The coexistence of bixbyite, metastable vredenburgite (later exsolved to two phases) and hausmannite correspond to the isobaric binary invariant situation at 932°C (laboratory condition, in air) in the phase-equilibrium diagram furnished by Muan and Somiya (1962). With lowering of temperature, a small amount of bixbyite (2-3 %) may form either as exsolution or conversion product in hausmannite at Tirodi areas. The stability of this bixbyite will, however, depend upon the oxygen partial pressure prevalent at that time. With lowering temperature, the two-phase region of vredenburgite is reached and hausmannite lamellae exsolved in jacobsite-host. The vredenburgite thus formed may retain its intergrowth, or may recrystallize leading to the formation of discrete grains of jacobsite and hausmannite. Hollandite, manganese and sometimes primary pyrolusite form in lowering temperature condition in the waning stage.

After detailed studies and discussion, the author observed that a definite trend of formation and transformation of manganese oxide minerals with increasing of temperature in metamorphic condition.

Though definite or absolute temperature of formation cannot always be predicted when other supporting data regarding oxygen partial pressure etc. are lacking, the sequence of formation and transformation of the minerals is more or less constant.

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