

# Petrology of Mn carbonate–silicate rocks from the Gangpur Group, India

B.K. Mohapatra<sup>a,\*</sup>, B. Nayak<sup>b</sup>

<sup>a</sup>Regional Research Laboratory (CSIR), Bhubaneswar 751 013, India

<sup>b</sup>National Metallurgical Laboratory (CSIR), Jamshedpur 831 007, India

Received 11 April 2003; revised 6 February 2004; accepted 21 July 2004

## Abstract

Metamorphosed Mn carbonate–silicate rocks with or without oxides (assemblage I) and Mn silicate–oxide rocks with minor Mn carbonate (assemblage II) occur as conformable lenses within metapelites and metacherts of the Precambrian Gangpur Group, India. The petrology of the carbonate minerals: rhodochrosite, kutnahorite, and calcite that occur in these two assemblages is reported. Early stabilisation of spessartine, aegirine, quartz, and carbonates (in a wide solid solution range) was followed by pyroxmangite, tephroite, rhodonite through decarbonation reactions. Subsequently, jacobsonite, hematite, braunite, hollandite and hausmannite have formed by decarbonation–oxidation processes during prograde metamorphism.

Textural characteristics and chemical composition of constituent phases suggest that the mineral assemblages reflect a complex relationship between protolithic composition, variation of  $X_{\text{CO}_2}$  (<0.2 to ~0.3) and oxygen fugacity. A variation of  $X_{\text{CO}_2}$  and  $f_{\text{O}_2}$  would imply internal buffering of pore fluids through mineral reactions that produced diverse assemblages in the carbonate bearing manganiferous rocks. A minor change in temperature (from around 400 to 450 °C) does not appear to have had any major influence on the formation of different mineral associations.

© 2004 Elsevier Ltd. All rights reserved.

**Keywords:** Mn carbonates; Mn carbonate–silicate rocks; Gondites; Gangpur Group; India

## 1. Introduction

The Precambrian Gangpur Group, India comprises a volcanic free sedimentary sequence metamorphosed up to amphibolite facies. This sequence is well known for the occurrence of manganese oxide ores that are interstratified with Mn silicate rocks (Roy, 1966, 1981). Supergene alteration process enriched the manganese concentration and transformed these units into workable deposits that were exploited intermittently between 1907 and 1948. The manganese ores in this area are conformably enclosed within the pelitic Goriajhar Formation of the Gangpur Group. These manganiferous members interstratified with phyllite, mica schist, and meta chert, were deposited at about 1700–2000 Ma and metamorphosed at around 850 Ma (Sarkar et al., 1969). These manganese-rich assemblages are considered as analogs of the Precambrian

Sausar Group rocks in Madhya Pradesh and Maharashtra region of India (Roy, 1981). The manganiferous rocks that have been studied during the present investigation from Goriajhar and Manomunda area, Sundargarh district, Orissa, India are shown in Fig. 1.

The manganiferous rocks of the Goriajhar Formation have been often, if not always, assigned to be of gonditic nature (e.g. Fermor, 1909; 1911; Krishnan, 1937; Prasad Rao and Murty, 1956; Roy, 1966, 1981; Nicholson et al., 1997). Gondites are defined as a metamorphosed equivalent of non-calcareous, manganiferous, arenaceous and argillaceous sediment which is composed of spessartine and quartz with minor Mn silicates and oxides (Roy, 1965). These rocks do occur in the Goriajhar Formation of the Gangpur Group, but are of very minor abundance. However, spessartine, in general, is widely distributed in the rocks of the study area which do not have any affiliation with true gondite. Recent studies by the authors established for the first time that in addition to gondite (i.e. Mn silicate rocks with minor Mn oxides, type IIA of Dasgupta et al., 1990),

\* Corresponding author.

E-mail address: [bkmohapatra@rrihbhu.res.in](mailto:bkmohapatra@rrihbhu.res.in) (B.K. Mohapatra).

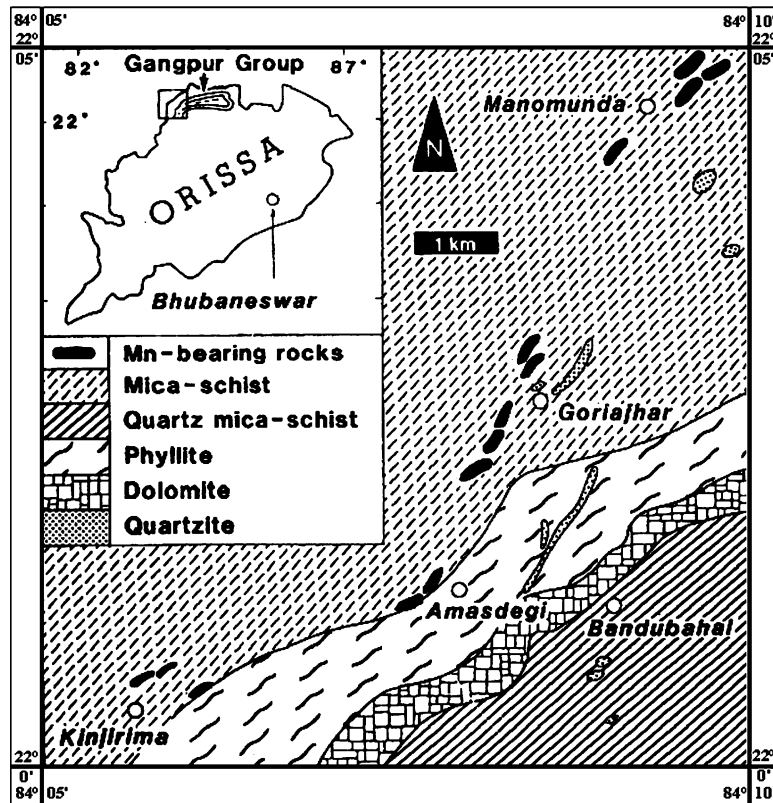


Fig. 1. Location and geological map of a part of Gangpur Group showing the distribution of Mn-bearing rocks around Goriajhar.

Mn silicate–oxide rocks (i.e. Mn oxide rocks with minor silicates, type IIB) and Mn silicate–carbonate–oxide rocks also occur in varying abundance in the Gangpur Group (Nayak et al., 1997). These assemblages were recognised through detailed petrological investigations, as these units are usually not distinguishable in the field. In the present investigation, we describe the petrological characteristics of Mn carbonate bearing mineral assemblages and evaluate the physico-chemical conditions of their formation.

## 2. Methods of microchemical analysis

Chemical compositions of coexisting mineral phases were determined by an ARL-SEM-Q-II electron microprobe (equipped with six spectrometers and four different crystals) in the Geochemisches Institut, Universität Göttingen, Germany. Operating conditions were 15 kV accelerating voltage and 15 nA sample current. The ZAF corrected representative mineral analyses are presented in Tables 1–3. Total iron was determined as  $\text{FeO}_{\text{tot}}$  and the amount of di- and trivalent iron were calculated according to the formulae of the minerals and expressed as  $\text{FeO}_{\text{calc}}$  and  $\text{Fe}_2\text{O}_3_{\text{calc}}$ . Total manganese was determined as  $\text{MnO}_{\text{tot}}$ ;  $\text{MnO}_2$  and  $\text{Mn}_2\text{O}_3$  were calculated in a similar manner. Carbon dioxide ( $\text{CO}_2$ ) was calculated according to the formula of the respective carbonate mineral.

## 3. Petrography and mineral chemistry of the Mn carbonate bearing rocks

Optical microscopic studies and geochemistry of individual mineral phases (by electron microprobe) in the studied rock types reveal the presence of carbonates (rhodochrosite, kutnahorite, calcite); silicates of pyroxenoid group (pyroxmangite, rhodonite), pyroxene group (Mn aegirine), garnet group (spessartine), olivine group (tephroite), mica group (phlogopite), and feldspar group (albite). Quartz is a common associate. The oxides that are associated with the silicate and/or carbonates are jacobsonite, braunite, hematite, hollandite, and hausmannite. Barite grains (in sizes up to 0.3 mm and <2 vol%) are randomly distributed in all the associations. It occurs either as corroded grains or sometimes as thin veins. The carbonate bearing rock types can broadly be grouped into the following two major assemblages:

- (I) Mn silicate–carbonate  $\pm$  oxide
  - (i) Tephroite + rhodochrosite + pyroxmangite + jacobsonite  $\pm$  quartz
  - (ii) Pyroxmangite + spessartine + rhodochrosite  $\pm$  quartz
- (II) Mn silicate–oxide + minor carbonate
  - (iii) Rhodonite + aegirine + braunite + hematite + kutnahorite  $\pm$  albite
  - (iv) Phlogopite + braunite + hollandite + hausmannite + calcite  $\pm$  albite

Table 1  
Microprobe analyses of Goriajhar carbonates

Wt%	rdh1	rdh2	kut	cal
CaO	0.31	2.18	34.00	54.82
MnO	56.29	56.93	24.25	0.75
FeO	3.70	1.71	–	–
MgO	0.78	0.17	0.17	0.17
CO <sub>2</sub> calc	38.27	38.25	41.89	43.58
Total	99.35	99.24	100.00	99.20
Cations	1	1	2	1
Ca	0.006	0.045	1.273	0.987
Mn	0.913	0.923	0.718	0.010
Fe	0.059	0.027	–	–
Mg	0.022	0.005	0.009	0.003
<i>Mol% of different carbonates</i>				
CaCO <sub>3</sub>	0.6	4.5	27.3	98.7
MnCO <sub>3</sub>	91.3	92.3	71.8	1.1
FeCO <sub>3</sub>	5.9	2.7	–	–
MgCO <sub>3</sub>	2.2	0.5	0.9	0.2

rdh1 and rdh2, rhodochrosite; kut, kutnahorite; cal, calcite. Each data set is average of point analyses of three points.

The carbonates are ubiquitous in assemblage I and constitute up to 25 vol% of the rock while in assemblage II, the modal abundance of carbonates is very low (maximum up to 12 vol%). Assemblage II is characterised by inhomogeneous distribution of the minerals due to a strongly developed layering. The three carbonates rhodochrosite, kutnahorite, and calcite occur mutually exclusive of each other (i.e. no two carbonates coexist). Chemical

Table 2  
Microprobe analyses of Mn silicates associated with Goriajhar carbonates

Wt%	pxm1	pxm2	sps	tp	rdn	aeg
FeO <sub>tot</sub>	3.59	1.87	1.31	6.06	0.16	26.82
SiO <sub>2</sub>	46.60	45.68	36.85	30.11	47.52	51.39
Al <sub>2</sub> O <sub>3</sub>	–	–	19.85	–	–	0.99
Fe <sub>2</sub> O <sub>3</sub> calc	–	–	1.24	–	–	28.69
FeO <sub>calc</sub>	3.59	1.87	0.23	6.06	0.16	–
MgO	0.53	0.08	–	0.22	0.77	0.71
CaO	0.14	0.67	1.53	0.15	5.48	2.96
MnO	49.12	50.83	40.51	63.98	46.42	4.35
Na <sub>2</sub> O	–	–	–	–	–	11.28
Total	99.98	99.13	100.21	100.52	100.35	100.37
Cations	14	14	8	3	10	4
Si	7.080	7.018	3.029	1.005	5.056	1.978
Al	–	–	1.923	–	–	0.045
Fe <sup>3+</sup>	–	–	0.077	–	–	0.831
Fe <sup>2+</sup>	0.456	0.240	0.016	0.170	0.014	–
Mg	0.120	0.018	–	0.011	0.122	0.041
Ca	0.023	0.110	0.135	0.005	0.624	0.121
Mn	6.321	6.614	2.820	1.809	4.184	0.142
Na	–	–	–	–	–	0.842

pxm1 and pxm2, pyroxmangite; sps, spessartine; tp, tephroite; rdn, rhodonite; aeg, aegirine. Each data set is average of point analyses of three points.

Table 3  
Microprobe analyses of oxides associated with Goriajhar carbonates

Wt%	jb	hm	br1	br2	hol	hs
FeO <sub>tot</sub>	71.77	86.08	17.22	6.56	6.34	8.97
MnO <sub>tot</sub>	20.66	3.37	64.35	71.57	60.47	81.11
SiO <sub>2</sub>	–	–	10.41	10.87	–	–
TiO <sub>2</sub>	0.62	0.97	–	–	–	0.31
Al <sub>2</sub> O <sub>3</sub>	0.25	–	0.11	0.12	0.42	0.36
MnO <sub>calc</sub>	20.66	–	–	–	5.00	29.74
Mn <sub>2</sub>	–	3.75	71.61	79.64	–	57.17
O <sub>3</sub> calc	–	–	–	–	–	–
MnO <sub>2</sub> calc	–	–	–	–	68.01	–
FeO <sub>calc</sub>	10.95	0.86	10.71	6.44	–	0.80
Fe <sub>2</sub> O <sub>3</sub> calc	67.47	94.71	7.24	0.13	7.05	9.08
MgO	–	–	–	1.82	–	–
CaO	0.28	–	0.45	0.61	0.23	–
BaO	–	–	–	–	17.59	–
Total	100.23	100.29	100.53	99.63	98.30	97.46
Cations	3	2	8	8	8	3
Si	–	–	1.042	1.074	–	–
Ti	0.018	0.019	–	–	–	0.009
Al	0.011	–	0.013	0.014	0.069	0.017
Mn <sup>2+</sup>	0.668	–	–	–	0.594	0.983
Mn <sup>3+</sup>	–	0.076	5.455	5.990	–	1.698
Mn <sup>4+</sup>	–	–	–	–	6.594	–
Fe <sup>2+</sup>	0.350	0.019	0.896	0.532	–	0.026
Fe <sup>3+</sup>	1.942	1.886	0.545	0.010	0.743	0.267
Mg	–	–	–	0.268	–	–
Ca	0.011	–	0.048	0.065	0.034	–
Ba	–	–	–	–	0.966	–

jb, jacobsite; hm, hematite; br1 and br2, braunite; hol, hollandite; hs, hausmannite. Each data set is average of point analyses of three points.

compositions of the carbonates, silicates and associated oxides are presented in Tables 1–3, respectively.

### 3.1. Texture and mineral chemistry of assemblage I

In association i, tephroite occupies 25–35 vol% and forms idiomorphic crystals having grain sizes in the range of 0.075–0.2 mm. The crystals sometimes show triple-junctions and occasionally, they are altered to either Mn-rich and Mg-poor minnesotaite or sepiolite (Mohapatra and Nayak, 2003) (Fig. 2). Rhodochrosite constitutes 15–20 vol%, while pyroxmangite occurs as a minor member (5–10 vol%). Idiomorphic grains of pyroxmangite and xenomorphic rhodochrosite grains are often embedded in tephroite. Minor amount of quartz as independent grains and as inclusions within pyroxmangite and tephroite have been recorded. The Mn oxide phase is represented by jacobsite (35–40 vol%) and it is distributed throughout the sample and sometimes contains minute inclusions of rhodochrosite grains. The replacement of rhodochrosite by manganite is also quite prominent in this association (Fig. 3).

In contrast to association i, pyroxmangite and rhodochrosite coexist with spessartine and quartz in association

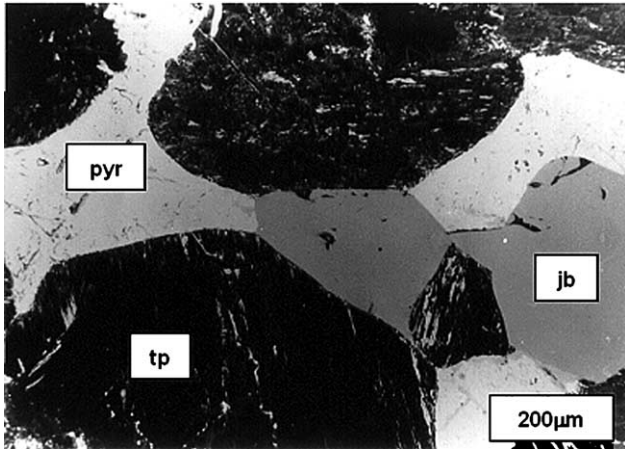


Fig. 2. Idiomorphic and partially altered tephroite crystals (tp) intergrown with jacobite (jb) and rhodochrosite. The rhodochrosite is now almost replaced by pyrolusite (pyr). Reflected light, oil immersion lens.

ii. The pyroxmangite crystals (av. 0.1 mm dia.) dominate with up to 80 vol%. Rhodochrosite is xenomorphic, fine-grained (av. 0.03 mm dia.) and occupies about 10–20 vol%. Inclusions of quartz and spessartine within pyroxmangite are also recorded (Fig. 4). Often, large rhodochrosite crystals show inclusions of spessartine (Fig. 5) and in most cases, rhodochrosite is replaced by manganite and is further oxidised to nsutite/pyrolusite (Mohapatra et al., 1995). Occasional presence of minute braunite or hematite crystals are recorded.

The carbonate phase in assemblage I, is a Mn–Fe–Ca–Mg solid solution, rich in rhodochrosite component with minor but variable siderite and magnesite end-members. The rhodochrosite in associations i and ii are compositionally different and for convenience are referred to as rdh1 and rdh2, respectively (Table 1). The rdh1 shows comparatively more siderite and magnesite contents ( $\text{cal}_{0.6} \text{rdh}_{91.3} \text{sd}_{5.9} \text{mgs}_{2.2}$ ), while rdh2 is enriched in the calcite component

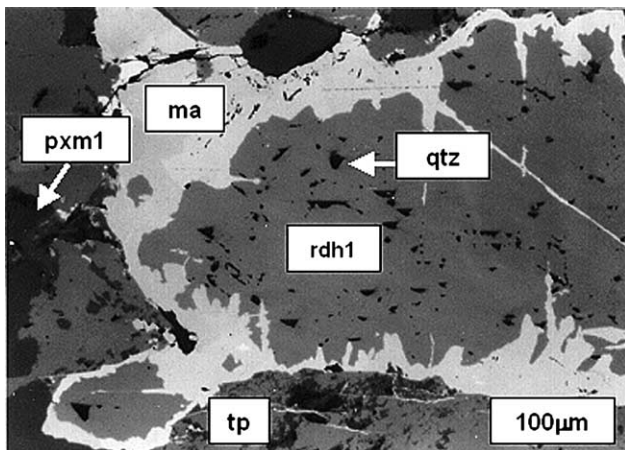


Fig. 3. Rhodochrosite (rdh1), tephroite (tp) and pyroxmangite (pxm1) in association i. Rhodochrosite is partially replaced by manganite (ma). Note the corroded grain boundaries between rhodochrosite and manganite and minute inclusions of quartz (qtz) in the former. Reflected light, oil immersion lens, crossed polars.

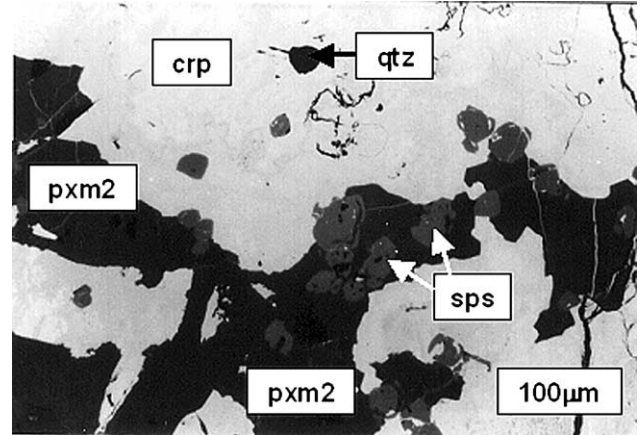


Fig. 4. Inclusions of quartz (qtz) and spessartine (sps) within pyroxmangite (pxm2) in association ii. Part of the pyroxmangite, and the original carbonate have almost been replaced by cryptomelane (crp). Reflected light.

( $\text{cal}_{4.5} \text{rdh}_{92.3} \text{sd}_{2.7} \text{mgs}_{0.5}$ ). Pyroxmangite in association i is also compositionally different from that of association ii and referred as pxm1 (iron rich) and pxm2, respectively (Table 2). Tephroite contains appreciable amounts of iron ( $\text{FeO}_{\text{tot}}=6.06$ ). The recalculated values for different valency states of iron indicate that jacobite in association i, may contain 67 wt% of  $\text{Fe}_2\text{O}_3$  in solid solution.

### 3.2. Texture and mineral chemistry of assemblage II

In association iii, the silicate-rich layers consist dominantly of rounded to idiomorphic, rhodonite crystals. Some crystals occasionally carry minute grains of hematite. Inclusions of kutnahorite within rhodonite show irregular grain boundaries (Fig. 6) and coexistence of kutnahorite, quartz, and rhodonite is recorded. Kutnahorite occurs as a subordinate phase (<10 vol%). Sometimes, it is partly altered and its low modal abundance may be due to its (pseudomorphic) replacement by cryptomelane. Mn-

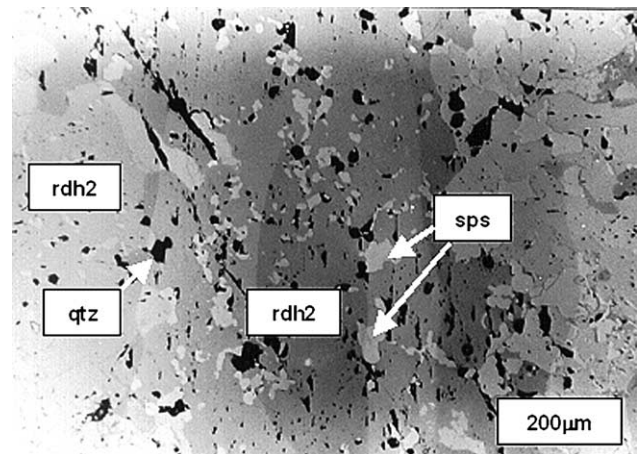


Fig. 5. Large rhodochrosite crystal (rdh2) in different orientations (dark position and bright position) showing inclusions of spessartine garnet (sps) and quartz (qtz) in association ii. Reflected light.

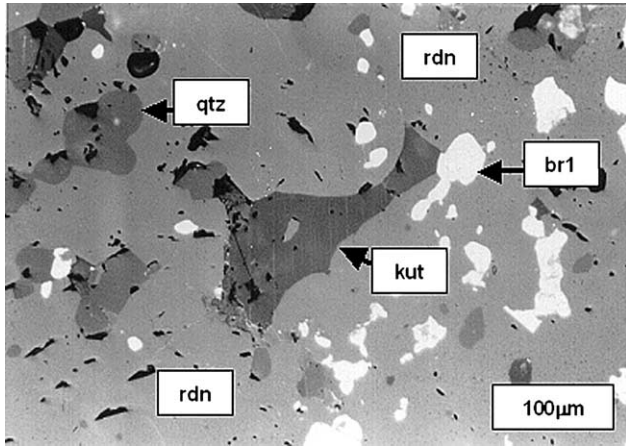


Fig. 6. Rhodonite (rdn), kutnahorite (kut), braunite (br1), and quartz (qtz) in association iii. Note the irregular grain boundary of kutnahorite. Reflected light.

aeigrine crystals (av. 0.15–0.2 mm) also appear in layers and are often partially replaced by minute needles/blebs of hematite. Braunite being the dominant oxide phase forms either independent thin layers or occurs together with hematite and rhodonite (Fig. 7).

Association iv consists of inhomogeneous distribution of ore dominated and silicate/carbonate dominated layers. Both braunite and hollandite are coarse-grained (grain sizes varying between 0.015 and 0.1 mm) (Fig. 8). The hollandite crystals occasionally contain small inclusions of braunite. The braunite and/or braunite–hollandite mineralisations associated with silicates/carbonates occurring as layers are obviously of the same age. On the other hand, in ore-dominated layers, the polycrystalline braunite crystals show overgrowths enclosing phlogopite, feldspar, and calcite. These two morphological varieties of braunite are compositionally different (Table 3). Layered braunite is similar to that of in association iii and is referred to as br1. Braunite crystals enclosing phlogopite, albite, and calcite are younger and are referred to as br2. Other associated oxide with

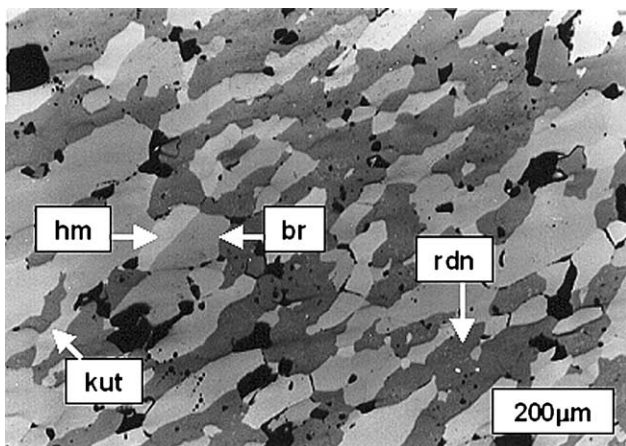


Fig. 7. Oriented crystals of braunite (br1), rhodonite (rdn), and hematite (hm). Kutnahorite (kut) is present as relics within braunite, black grains are albite (ab). Reflected light.

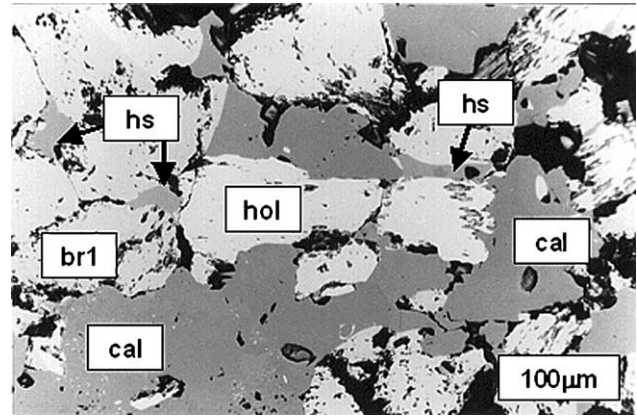


Fig. 8. Coarse grained hollandite crystals (hol) with braunite (br1) in association iv. The hausmannite (hs) grains are seen as isolated patches between hollandite and braunite. The matrix is calcite (cal). Reflected light.

braunite and hollandite is subordinate hausmannite that shows irregular grain boundaries. In silicate-rich zones, albite is the dominating mineral (~50 vol%), followed by phlogopite (30 vol%) and minor calcite (<12 vol%). Calcite occurs as idiomorphic to hypidiomorphic crystals, varying in size from 0.1 to 3 mm. Calcite grains also occur as inclusions within braunite (Fig. 9).

The carbonate in assemblage II is a Mn–Ca–Mg solid solution. In association iii, it is rich in the rhodochrosite component with subordinate calcite ( $\text{cal}_{27.3} \text{rdh}_{71.8} \text{mgs}_{0.9}$ ) while association iv mainly constitutes of calcite with minor rhodochrosite ( $\text{cal}_{98.7} \text{rdh}_{1.1} \text{mgs}_{0.2}$ ) (Table 1). The garnet is spessartine-rich with a considerable andradite and almandine component ( $\text{adr}_{3.85} \text{grs}_{0.67} \text{alm}_{0.53} \text{sps}_{94.95}$ ). The Mn-aeigrine is also iron rich ( $\text{FeO}_{\text{tot}} = 26.82$ ). Hematite may accommodate around 4 wt%  $\text{Mn}_2\text{O}_3$  in solid solution. In both cases br1 and br2 the manganese is expected to occur as  $\text{Mn}_2\text{O}_3$ . Braunite1 contains a considerable amount of iron ( $\text{FeO}_{\text{tot}} = 17.22$ ) in contrast to braunite2 that also has little Mg ( $\text{MgO} = 1.82$ ) in its structure. Hollandite is rich in barium ( $\text{BaO} = 17.59$ ) and contains around 7 wt%

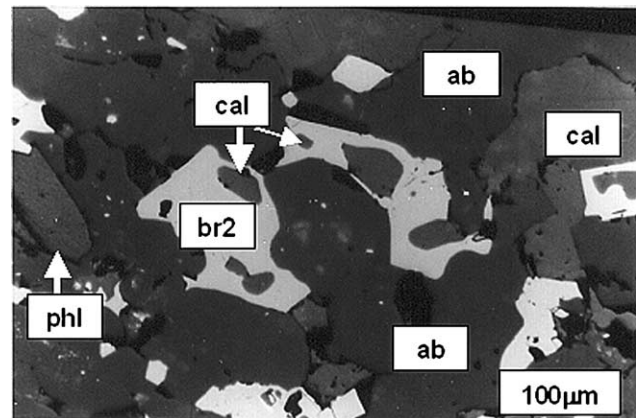


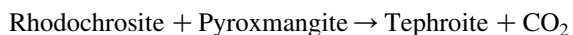
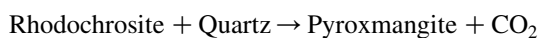
Fig. 9. The co-existing phases braunite (br2), calcite (cal), and albite (ab) with minor phlogopite (phl) in association iv. Note the relics of calcite within braunite grains. Reflected light.

$\text{Fe}_2\text{O}_3$  (calc) in solid solution ( $\text{FeO}_{\text{tot}}=6.34$ ). Hausmannite contains around 9 wt%  $\text{Fe}_2\text{O}_3$  (calc) ( $\text{FeO}_{\text{tot}}=8.97$ ).

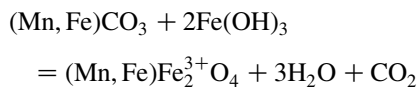
#### 4. Discussion

The textural peculiarities along with compositional characteristics of different coexisting minerals reflect several reaction paths in the Mn carbonate bearing rocks of the Gangpur Group. The formation of different mineral phases in these assemblages seems to be attributed to three important factors: bulk composition of the protolith, variation in  $X_{\text{CO}_2}$ , and oxygen fugacity during metamorphism. In both assemblages (I and II), the overall chemical composition of the rock/ore indicate that the original protolith was enriched in Mn along with variable abundance of Ca, Si, Fe, Al, Na, Mg, and Ba. From these, Na, Mg and Ba could have acted as sinks in phases like albite, phlogopite, hollandite/barite and did not influence the stability of coexisting manganese-bearing phases.

In association i, pyroxmangite, tephroite, and jacobsite coexist with rhodochrosite and minor quartz, where jacobsite, tephroite, and rhodochrosite appear to be in equilibrium. From the fact that (a) inclusions of quartz and carbonates occur within pyroxmangite and tephroite, (b) grains of pyroxmangite and rhodochrosite are embedded in tephroite, and (c) the existence of rhodochrosite inclusions within jacobsite, it may be inferred that both pyroxmangite and tephroite might have formed through decarbonation processes from a carbonatic precursor, while jacobsite has formed through decarbonation–oxidation reactions. Presence of little quartz in this association is probably due to its consumption during formation of pyroxmangite/tephroite. Therefore, we suggest that both tephroite and pyroxmangite formed during prograde metamorphism according to the following reactions (Peters et al., 1973):



In view of the fact that jacobsite does not form any association with braunite or hematite in association i; forms equilibrated assemblage with tephroite and rhodochrosite; and the presence of a single carbonate phase (sometimes as inclusions) suggest that jacobsite have been stabilised early in the metamorphic sequence (lower-mid greenschist facies) from a carbonatic precursor (admixed with Fe) by simple decarbonation–oxidation reactions with rising temperature. One such inferred reaction could be (Mücke et al., 2001)

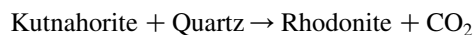


A similar origin of jacobsite from the Sausar Group, India has been reported by Bhattacharya et al. (1988). This decarbonation may originate from a local variation in the chemical potential of  $\text{CO}_2$  (Peters et al., 1978).

Peters et al. (1973) observed that rhodochrosite–quartz–tephroite occurred at very low-grade metamorphic conditions and rhodochrosite–quartz–pyroxmangite at mid-greenschist facies conditions in the mineral assemblages of Rhaetic Alps (Switzerland). This observation was also correlated with experimental studies at a pressure of 2000 bar. Starting from rhodochrosite and quartz at very low  $X_{\text{CO}_2}$  ( $X_{\text{CO}_2} < 0.2$ ), tephroite formed below 420 °C and pyroxmangite above 430 °C and at higher  $X_{\text{CO}_2}$  ( $X_{\text{CO}_2} > 0.2$ ). Considering the fact that tephroite and pyroxmangite occur together, the formation temperature in association i, probably lies in the temperature range between 420 and 450 °C. Similar temperatures can also be deduced from the experimental studies of Matthes (1961), who found a minimum temperature of 400 °C for the formation of pure spessartine. However, the associated jacobsite might have influenced the metamorphic reaction to a yet unknown degree. The presence of jacobsite as a stable phase in association i further suggests lower  $f_{\text{O}_2}$  conditions during metamorphism (below the Hematite–Magnetite buffer). This is also supported by the fact that, apart from jacobsite, no other  $\text{Fe}^{3+}$ -bearing minerals (like braunite, hematite, and  $\text{Mn}^{3+}$  silicates) occur in association i. Thus, the physico-chemical conditions of association i involved an iron-rich protolith, lower  $X_{\text{CO}_2}$  and lower  $f_{\text{O}_2}$  and a relatively low grade metamorphism.

Minerals in association ii, indicate that the protolith of this paragenesis consisted of the same constituents as those of association i, but contained considerably higher amounts of silica and alumina. This resulted in the formation of pyroxmangite and spessartine and the additional presence of spessartine suggests higher  $\text{CO}_2$ - and  $\text{O}_2$ -fugacities at mid-greenschist facies conditions. The (relatively) higher  $f_{\text{O}_2}$  is also reflected in occasional presence of braunite and hematite crystals.

The mineral association iii formed from a mixed Ca–Fe-rich bulk composition. The presence of hematite and Fe-rich braunite (br1, Table 3) indicates an iron-rich protolith. Similarly, the higher Ca content in rhodonite, 25–34 mol% of calcite component in kutnahorite, and appreciable calcium in coexisting aegirine (up to 3 wt% CaO) also support a calcium-rich protolith. Based on the coexistence of kutnahorite, quartz, and rhodonite in this association we propose the following decarbonation reaction:



The thermodynamically calculated  $X_{\text{CO}_2}$ – $T$  relation for the formation of rhodonite by Winter et al. (1981) yields an  $X_{\text{CO}_2}$  estimation of about 0.3. Thus rhodonite might have equilibrated in a moderately  $\text{CO}_2$ -rich ( $X_{\text{CO}_2} \sim 0.3$ ) environment. Braunite (br1) and hematite possibly formed during

prograde oxidation processes (Dasgupta et al., 1990). Braunite (br1) showing 7 wt%  $\text{Fe}_2\text{O}_3$  in solid solution and hematite having 3 wt% of  $\text{Mn}_2\text{O}_3$  in its lattice (Table 3) imply higher  $f_{\text{O}_2}$  (above Hematite–Magnetite buffer) during metamorphism. Thus, the constituent phases of this association developed from a Ca–Fe rich protolith under moderately rich  $\text{CO}_2$ —and higher  $\text{O}_2$ —fugacities.

In association iv, calcite is an important constituent. This association has formed from a Ca–Mn-rich bulk composition. It is devoid of hematite and rich in oxides like braunite (br1 and br2), hollandite, and hausmannite, and it confirms its Mn-rich protolithic composition. Other silicates, like phlogopite and albite, also contain manganese. Ba in hollandite and Mg in braunite (br2), probably, acted as inert components and did not influence the stabilisation of other oxides. Unlike other associations (i–iii), near absence of Mn silicates, and abundance of oxide with trivalent manganese of this association indicate an unusually high  $f_{\text{O}_2}$  environment (above  $\text{Mn}_2\text{O}_3$ – $\text{Mn}_3\text{O}_4$  buffer).

The chemical composition of the three carbonates are plotted in a ternary diagram  $\text{CaCO}_3$ – $\text{MnCO}_3$ –( $\text{MgCO}_3 + \text{FeCO}_3$ ), following Goldsmith and Graf (1960) (Fig. 10). In this plot, a slightly higher formation temperature for kutnahorite (association iii) compared with rhodochrosite (in associations i and ii) and calcite (in association iv) is observed. The presence of rhodonite along with kutnahorite but not pyroxmangite may also indicate that the metamorphic temperature was higher than that of pyroxmangite–rhodonite transition reaction. However, we believe that within a broad  $P$ – $T$  regime of greenschist metamorphic facies, such minor temperature differences ( $\sim 50^\circ\text{C}$ ) in closely spaced units may not result in a different mineral

association, but rather may reflect the bulk protolithic composition.

The carbonates associated with pyroxenoids and tephroite from Goriajhar are Al-free and their Mg content is negligible and may be represented in a chemographic triangle (Fig. 11). According to Peters et al. (1978), Fig. 11 depicts a decreasing  $X_{\text{CO}_2}$  from left to right. Except for quartz, all mineral phases of Fig. 11 show solid solutions for Ca- and Mn-end members and the gap between the two sets of schematic tie lines show the immiscibility-gap between the carbonates. Because of the solubility between Ca and Mn end-members in the pyroxenoid and in the carbonate association, respectively, some discontinuous exchange reactions are also possible. As  $\text{CO}_2$  was fixed in carbonates, the composition of protolithic fluids must have exerted a strong influence. In the tephroite–pyroxmangite association, the carbonate reflects the lowest  $\text{CO}_2$  activity ( $X_{\text{CO}_2} < 0.2$ ). A slightly higher  $\text{CO}_2$  activity ( $X_{\text{CO}_2} > 0.2$ ) only stabilised pyroxmangite. With the change from pyroxmangite to rhodonite, the  $\text{CO}_2$  activity increased further ( $X_{\text{CO}_2} \sim 0.3$ ) and the critical tie lines show a shift from rhodochrosite to kutnahorite. This variation of  $X_{\text{CO}_2}$  in close spaced areas at Goriajhar implies a buffering of the pore fluids by diverse mineral reactions (Greenwood, 1975). Similar mineral reactions in the presence of buffered  $X_{\text{CO}_2}$  have been reported by Dasgupta et al. (1993) in the Mn silicate–carbonate–oxide rocks from Parseoni, Sausar Group, India. Although the plots in Fig. 10 show a slightly higher metamorphic temperature for kutnahorite, the composition of the phases is mainly controlled by the Ca content of the bulk composition and considerable variation of  $\text{CO}_2$  in the respective mineral reactions.

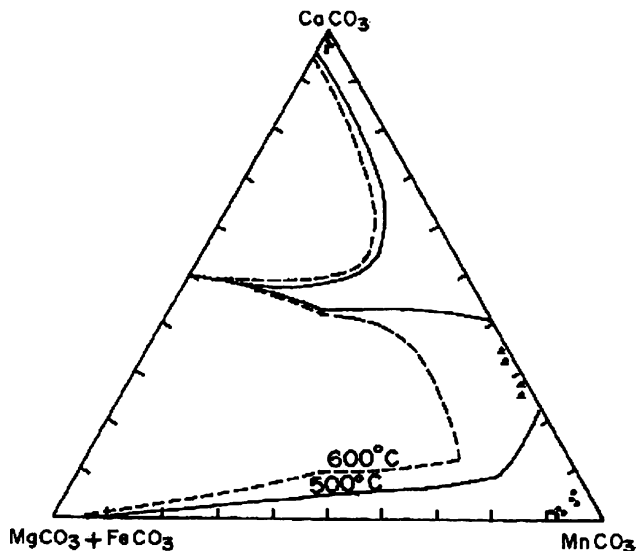


Fig. 10. Ternary diagram of the  $\text{CaCO}_3$ – $\text{MnCO}_3$ –( $\text{MgCO}_3 + \text{FeCO}_3$ ) system showing solvi at 500 and 600 °C (after Goldsmith and Graf, 1960). Solid dots, triangles, and circles represent the compositions of calcite, kutnahorite, and rhodochrosite, respectively, from the Goriajhar area.

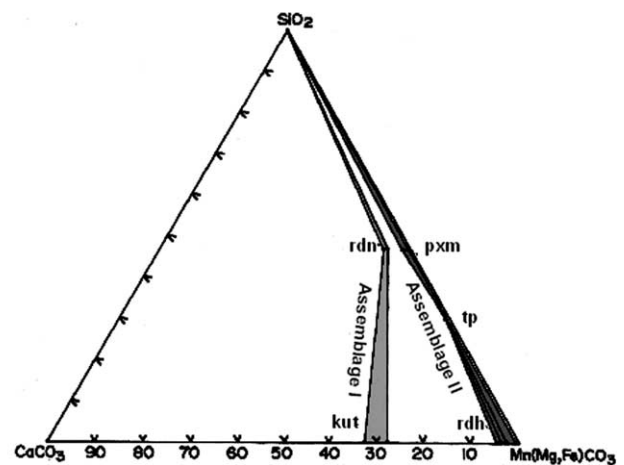


Fig. 11. Phase relations between Mn silicates and Mn carbonates of Goriajhar area. Tie lines connect the coexisting phases in assemblages I and II [rdn, rhodonite; pxm, pyroxmangite; tp, tephroite; kut, kutnahorite; rdh, rhodochrosite].

## 5. Conclusions

The manganeseiferous rocks of the Goriajhar Formation in the Gangpur Group, reflect a carbonate protolith. The compositional variations in the coexisting mineral phases are mainly attributed to the protolithic bulk composition, variation in  $X_{\text{CO}_2}$ , and to different oxygen fugacities during metamorphism rather than to the metamorphic temperature. The inferred variation in  $X_{\text{CO}_2}$  and oxygen fugacity at Goriajhar may be accounted for by a buffering of the fluid composition through complex mineral reactions. We also conclude that  $\text{CO}_2$ -diffusion did not occur across neighbouring rock-layers during metamorphism.

## Acknowledgements

Part of the work was carried out in Germany during the visit of BKM through Sr. DAAD fellowship and the authors wish to record their gratitude to Prof. A. Mücke, Georg-August-Universität, Göttingen (Germany) for electron microprobe support and for his critical comments on the preliminary manuscript. B. Nayak is grateful to CSIR, India for a research fellowship. Thanks are due to Sri P.K. Swain, Sr. Geologist, Geological Survey of India, for his help during the fieldwork. Prof. V.N. Misra (Director, RRL Bhubaneswar) is thanked for his permission to publish this paper. The constructive criticism and suggestions of the two reviewers, Prof. S. Dasgupta and Dr B. Pracejus, have greatly improved the manuscript.

## References

- Bhattacharya, P.K., Dasgupta, S., Chattopadhyay, G., Banerjee, H., Fukuoka, M., Roy, S., 1988. Petrology of jacobsonite bearing assemblages from Sausar Group, India. *Neues Jahrbuch Miner. Abh.* 159 (1), 101–111.
- Dasgupta, S., Banerjee, H., Fukuoka, M., Bhattacharya, P.K., Roy, S., 1990. Petrogenesis of metamorphosed manganese deposits and the nature of precursor sediments. *Ore Geol. Rev.* 5, 359–384.
- Dasgupta, S., Sengupta, P., Fukuoka, M., Roy, S., 1993. Contrasting parageneses in the manganese silicate–carbonate rocks from Parseoni, Sausar Group, India and their interpretation. *Contrib. Miner. Petrol.* 114, 533–538.
- Fermor, L.L., 1909. The manganese ore deposits of India. *Mem. Geol. Surv. India* 37, 610.
- Fermor, L.L., 1911. Notes on the manganese ore deposits of Gangpur State, Bengal, and on the distribution of gondite series in India. *Records Geol. Surv. India* 41, 12–21.
- Goldsmith, J.R., Graf, D.L., 1960. Subsolidus relations in the system  $\text{CaCO}_3$ – $\text{MgCO}_3$ – $\text{MnCO}_3$ . *J. Geol.* 68, 324–335.
- Greenwood, H.J., 1975. Buffering of pore fluids by metamorphic reactions. *Am. J. Sci.* 275, 573–593.
- Krishnan, M.S., 1937. The geology of the Gangpur State. *Mem. Geol. Surv. India* 71, 14–84.
- Matthes, S., 1961. Ergebnisse zur Granatsynthese und ihre Beziehungen zur natürlichen Granatbildung innerhalb der Pyralispit-Gruppe. *Geochim. Cosmochim. Acta* 23, 233–294.
- Mohapatra, B.K., Nayak, B., 2003. Mn-Olivine from Gangpur Group of rocks, Orissa. *J. Geol. Soc. India* 61, 581–587.
- Mohapatra, B.K., Nayak, B.R., Sahoo, R.K., 1995. Characteristics of nsutite ( $\gamma$ - $\text{MnO}_2$ ) in Goriajhar manganese deposit, Gangpur Group, India. *J. Miner. Petrol. Econ. Geol.* 90, 280–287.
- Mücke, A., Mohapatra, B.K., Nayak, B., 2001. The tephroite, spessartine, pyroxmangite and rhodochrosite-bearing mineral assemblages of the manganese ores in the Manomunda–Goriajhar area of the Gangpur Group, Orissa, India. Petrological and chemical investigations and their genetic implications. *Neues Jahrbuch Miner. Abh.* 176 (1), 21–43.
- Nayak, B.R., Mohapatra, B.K., Sahoo, R.K., 1997. Metamorphic Mn-rich assemblages from Gangpur Group of rocks Orissa. *Vistas Geol. Res. Spl. Publ. Geol., Utkal Univ.* 2, 137–148.
- Nicholson, K., Nayak, V.K., Nanda, J.K., 1997. Manganese ores of Ghorajhar–Monmunda area, Sundergarh district, Orissa, India: geochemical evidence for a mixed Mn source. In: Nicholson, K. et al. (Ed.), *Manganese Mineralisation: Geochemistry and Mineralogy of Terrestrial and Marine Deposits Geological Society (London) Special Publication No. 119*, pp. 117–121.
- Peters, Tj., Schwander, H., Tromsdorff, V., 1973. Assemblages among tephroite, pyroxmangite, rhodochrosite, quartz: experimental data and occurrences in Rhaetic Alps. *Contrib. Miner. Petrol.* 42, 325–332.
- Peters, Tj., Tromsdorff, V., Sommeraner, J., 1978. Manganese pyroxenoids and carbonates: critical phase relations in metamorphic assemblages from the Alps. *Contrib. Miner. Petrol.* 66, 383–388.
- Prasad Rao, G.H.S.V., Murty, Y.G.K., 1956. Manganese ore deposits of Orissa and Bihar, India. *Int. Geol. Cong., Mexico. Symp. Manganese 4*, 115–131.
- Roy, S., 1965. Comparative study of the metamorphosed manganese protore of the world. The problem of the nomenclature of the gondites and kodurites. *Econ. Geol.* 60, 1238–1260.
- Roy, S., 1966. Syngenetic Manganese Formations of India. Jadavpur University, Calcutta. 219 pp.
- Roy, S., 1981. *Manganese Deposits*. Academic Press, London. 458 pp.
- Sarkar, S.N., Saha, A.K., Miller, J.A., 1969. Geochronology of the Precambrian rocks of Singhbhum and adjacent regions Eastern India. *Geol. Mag.* 106, 15–45.
- Winter, G.A., Essene, E.J., Peacor, D.R., 1981. Carbonates and pyroxenoids from the manganese deposit near Bald Knob, North Carolina. *Am. Miner.* 66, 278–289.