# **Research Paper**

# **Earth Science**



# Occurrence and Composition of Manganese Oxide Minerals From the Chikkanayakana Halli Manganese Deposit, Dharwar Craton, Southern India,

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ABSIKACI

X-ray diffraction, ore microscopy and electron microphobe studies have been done on ore samples obtained the mine site at chikkanayakana halli. Manganese ore minerals identified nsutite, cryptomelane, pyrolusite and lithiophorite, chemical composition of minerals indicate by other elements quartz schistose rocks feature as gangue in most samples, texture are varied and modes of occurrence are metasedimentary manganese ores have been subjected to lateritoid manganese ores in weathered supracrustal rocks-phyllite and quartzite) occur as fracture/cavity filling along cracks, network of joints, schistosity/bedding planes, crevices and vugs and precipitation, mineral association seems rather complex, as a result of which definitive paragenetic relation could not be established. Supergene formation of the manganese oxide ore is shown by the abundance if manganese minerals in solution channels such as fractures and cavities within the silicate gangue much of the ore however, appears to have been enriched by leaching of gangue minerals and the later addition of manganese. Key word: Chikkanayakanahalli, Nsutite, cryptomelane, pyrolusite, lithiophorite.

# **KEYWORDS**

Chikkanayakanahalli, Nsutite, cryptomelane, pyrolusite, lithiophorite.

#### Introduction.

The Chikkanayakanahalli schist belt represents the southern extension of ~ 460 km long Chitradurga schist belt and it is about 25 km long and 15 km wide. Precambrian terrains, the world over, are bestowed with metasedimentary manganese mineralization belonging to oxide, silicate, carbonate or mixed facies. In several such terrains, the metasedimentary manganese ores have been subjected to lateritization, which brought about changes in texture, mineralogy and chemical composition of manganese ores. Further, lateritization caused dissolution of metasedimentary ores and consequent release of manganese and other metals to the circulating waters, which later reprecipitated at new locales within the weathered profile and on the contemporary land surface

In the study areas, viz., Chikkanayakanahalli area, metasedimentary manganese ores have been subjected to lateritization resulting in the development of diverse textural, mineralogical and geochemical features. Based on these features, different manganese ore types confined to various locales in the weathered profile and the eroded surface have been recognized.

The manganese ores of Chikkanayakanahalli belt were made by the officers of the Karnataka State Geology Department. Sen (1921) and Venkataramaiah (1926) examined the manganese ores of Janehara, Karekurchi and Honnebagi and reported that manganese ores occur as lenses, patches and bands associated with quartz and ferruginous bands in the altered members of the schistose rocks. Naganna (1971, 1976) and Ramiengar (1977) also reported the occurrence of manganese ores in the area but did not provide details on their textural features, mineralogy and genetic aspects. Devaraju and AnanthaMurthy (1976) briefly dealt with the geology, mineralogy and genesis aspects of manganese ores of the area. This paper may therefore investigation aimed at the mineralized and chemical characteristic of the mineralization of genetic pro-

# Geological setting of chikkanayakanahalli schist belt:

Chikkanayakanahalli schist belt (Fig.1) one of the earliest accounts of the geology of the area around Dodguni, which constitutes the area of interest of the present investigation, was given by Jayaram (1917), who assigned the rocks to the "Champion gneiss series". Radhakrishna (1952) subdivided the rocks of the area into an upper ' Dodguni series' and a lower 'metamorphic series'. Srinivasan and Srinivas (1968,

1972) proposed a geosynclinal scheme of evolution for the rocks of the Dharwar group and described the rocks of the Dodguni series, which forms part of the Dharwar Supergroup, as geosynclinal shelf sediments belonging to the second cycle of sedimentation in the evolutionary cycle of the Dharwars. Mukhopadyay, et al., (1981) and Mukhopadyay and Ghosh (1983) carried out detailed structural mapping around Dodguni area and concluded that the rocks in the area have been affected by multiple episodes of deformation.

The rock formations in the Chikkanayakanahalli area can be subdivided into two main groups; the older group made up of amphibolite and chlorite schist interbedded with quartzite and the younger group consisting of BIF, marble, pelitic and semipelitic schists with amphibolite. Lateritoid manganese associated with discontinuous exposures of oligomitic conglomerate demarcates the boundary between the two groups. The older group has been correlated with Bababudan group (Swaminath, et al., 1976) and the younger group with the Chitradurga group (Mukhopadyay, et al., 1981).

The lithostratigraphic succession for the rock formations of the area, as proposed by Devaraju and Anantha murthy (1977, 1984) and (Devaraju, et al., 1986) is given in Table 3.1.

The supracrustal rocks have been folded into antiforms and synforms and have been subjected to greenschist to amphibolite facies metamorphism. The general physiographic trend of the Chikkanayakanahalli schist belt is North – South, whereas the schistose rocks trend NNW to NW and exhibit dips ranging from 30° to 80° (averaging 55°). A brief description of the rock formations encountered in the study area is provided below.

The oldest lithounit is the gneiss, followed upwards respectively by quartzite, chlorite schist, carbonate and dolerite. The quartzite and carbonate are at places associated with manganese and iron formations.

Gneisses, which are considered to be Peninsular gneisses (~ 3.0 Ga.), are encountered mainly in the western and eastern part of the Chikkanayakanahalli schist belt. Quartzites overlie the gneisses and occur as thick continuous beds mainly in the eastern part of the Chikkanayakanahalli schist belt. In the Dodguni, Hanumanthanahalli and Kondli areas, quartzites occur as lenses and patches within the chlorite schist and basic

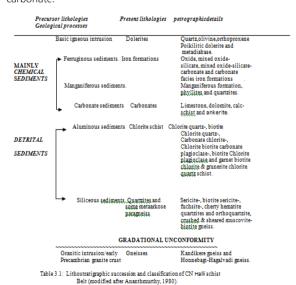
rocks. The quartzites exhibit primary sedimentary structures like current bedding, ripple marks and laminations indicative of shallow water depositional conditions. Based on modal composition, Ananthamurthy (1980) the cementing silica has been attributed to volcanic exhalations by Devaraju and Anantha murthy (1978).

Amphibolites are encountered as flows and minor intrusions associated with quartzites and as bands and lenses in the chlorite schist and carbonates. Anantha murthy (1980) to propose a mantle origin for the amphibolites. Chlorite schist overlies the quartzites and is composed of chlorite, grunerite, garnet, carbonate, biotite and guartz. Ferruginous and graphite-rich shales also occur associated with the chlorite schist. The chlorite schists are rich in Cr and MgO contents possibly indicating a 'Sima' source (Pichamuthu and Srinivasan, 1984).Carbonate rocks are essentially made up of cherty dolomite and limestone, the former predominating over the latter. Highest concentration of manganese has been noted in the phyllites that are spatially associated with carbonate rocks, suggesting existence of favourable pH conditions (Garrels, 1960). Devaraju and Anantha murthy (1984) opined that precipitation of limestone marked the beginning of carbonate deposition in an open basin with low salinity, pH and Mg:Ca ratio. Srinivasan et al., (1989) reported stromatolitic limestone from Dodguni (Plate 3.1), in the proximity of manganese mineralization, in the south eastern part of Chikkanayakanahalli area.

Manganiferous formation, spatially associated with Iron formation, occur as massive layers interbanded either with chert or phyllite. The manganiferous formation has been subjected to weathering along with host phyllite and quartzite. Details on the geological aspects of manganiferous formation are provided elsewhere, since it forms the topic of the present investigation.

Banded iron formation in the area is represented mainly by oxide and mixed oxide-silicate facies and less frequently by carbonate and mixed oxide-silicate-carbonate facies. Magnetite, ankerite, ferroan ankerite, siderite, grunerite and quartz are present in the banded iron formation. Banded iron formation is purported to have been deposited over platform of shelf region under quiescent conditions.

Dolerite dykes in the area are restricted to the gneisses and quartzites and rarely encountered in the chlorite schist and carbonate.



III.Procedure and methods of investigations: Ore samples from various localities of the manganiferous zone at chikkanayakana halli were obtained from the mine. Data acquisition for this paper consisted of X-ray diffraction, ore microscopy and electron probe microanalysis (EPMA). Petrographic studies on samples of manganese ore types of Chikkanayakanahalli area were carried out using Leitz Labrolux 12pol. incident light microscope provided with a photographic The properties examined for identification of attachment. minerals were colour, reflectivity and bireflectance, reflection pleochroism, anisotropic colours, internal reflections, polishing hardness, crystal form and cleavage.

X-ray investigation was carried out on both whole rock (ore) samples and scooped out mineral phases of ore minerals (with the help of a hand drill) identified by petrographic studies. X-ray studies on manganese were done on a JEOL X-ray diffractometer. Whole-rock samples for X-ray investigations were prepared by powdering them in an agate mortar and the finely powdered (>200 mesh) ore samples were filled evenly in the window provided in the sample holder slide. The upper surface of the sample powder was rendered flat by pressing it with a flat glass plate. A JEOL-8P X-ray diffractometer, equipped with an Iron target was operated at 40 KV and 29 MA. A manganese filter was used to eliminate  $K\alpha 2$  radiations.  $K\alpha 1$  radiations (1.934 A°) were used for determining the diffraction patterns of the sample. The scanning rate was fixed at 40 per minute and the chart speed maintained at 40 mm per minute. A diffraction pattern recording 20 angle (between 5° and 96°, corresponding to d values of 22.169 A° and 1.3012 A° respectively), against intensity was obtained. ASTM cards were used to identify the mineral phases. The ore microscopic studies and X-ray investigations revealed the presence of the following minerals in various structural/textural types of ores: nsutite, cryptomelane, pyrolusite, and lithiophorite.

# Petrography:

#### 1. Nsutite

Nsutite is encountered in the infiltration type. It is identified by its crystalline nature, white/cream colour, high reflectivity, marked bireflectance, strong anisotropism (in shades of grey) and high polishing hardness. It occurs as aggregates of finegrained material. In the colloform variety of infiltration-type ore, nsutite occurs as well developed crystals (Plate 6.12 B) and as bands alternating with pyrolusite, cryptomelane and (Plate 6.5 A)

# 2. Pyrolusite

Pyrolusite is medium- to coarse-grained, yellowish white in colour, with high reflectivity, distinct bireflectance and light yellow to greenish white reflection pleochroism. It shows strong anisotropism in yellowish brown shades, prismatic cleavage, straight extinction, and differential polishing hardness. Morphologically, pyrolusite occurs as tabular, interlocked crystal aggregates, medium- to coarse- grained prismatic crystals, fine-grained and needle-like crystals. In the intensely unaltered metasedimentary ores, Pyrolusite (I) is medium- to fine-grained and well crystalline (Plate 6.1 A). In the altered metasedimentary ores, pyrolusite (I) is replaced by diverse supergene minerals like cryptomelane (Plate 6.2 B), Pyrolusite Il occurs as bands alternating with nsutite (Plate 6.5 A & 6.6 A), cryptomelane as coarse-grained, randomly oriented aggregates or needle-like or fan-shaped crystals (Plate.6.11 B). Pyrolusite III occurs as fillings in vugs/dissolution cavities of colloform ores (Plate 6.12 A).

# 3. Cryptomelane

Cryptomelane in the study area is of supergene origin. In the altered metasedimentary manganese ores, cryptomelane occurs mainly as (i) irregular cryptocrystalline masses, (ii) fibrous patches and (iii) fracture/joint fillings. Bulk of the cryptomelane in the altered metasedimentary ore was deposited through low-temperature replacement of the metasedimentary pyrolusite (Plates 6.9 A & B) and only a small proportion is encountered as fracture/joint fillings. In the least altered metasedimentary manganese ore exhibiting banded texture, cryptomelane exhibits relict grains of pyrolusite, implying replacement origin of cryptomelane (Plate 6.2 B). In the colloform type, cryptomelane occurs as thin bands alternating with pyrolusite, goethite and nsutite (Plate 6.5 A).

#### 4. Lithiophorite

Lithiophorite is encountered in the colloform ores of infiltration type. Under the microscope it exhibits grayish white colour, moderate reflectance and distinct bireflectance in shades of grey, strong anisotropism in shades of black and white.

Lithiophorite is encountered as dissolution cavity-fillings in colloform variety of the infiltration type manganese ores. The cavities probably developed after the formation of botryoidal manganese ores by the processes of dissolution and have been subsequently filled by lithiophorite (Plate 6.8 B).

#### V. Chemical composition of mineral:

- **1. Nsutite:** EPMÅ analysis of nsutite are given in table XXX. It is essentially an MnO $_2$  minerla with traces of Si, Na, K, Al, Ca, Fe, in all cases, MnO $_2$  is 93%; Fe $_2$ O $_3$  is nil; SiO $_2$  up to 0.5%; CaO up to 0.2%; Na $_2$ O up to 0.07%; MgO up to 0.09% Al $_2$ O $_3$  up to 0.2%; and K $_3$ O up to 0.04%.
- 2. **Pyrolusit:** table XXX. gives the results of EPMA analysis of pyrolysite, the mineral is almost devoid of other elements MnO2 was found to be around 94%;  $Fe_2O_3$  is nil;  $SiO_2$  up to 0.3%; CaO up to 0.1%;  $Na_2O$  up to 0.2%; MgO up to 0.4%  $Al_2O_3$  up to 0.5%; and  $K_2O$  up to 0.5%.

3. **Cryptomelane:** Analysis of optically homogeneous layers are shown in Table XXX. These are from colloform types, concentric bands composed of cryptomelane, pyrolusite, nsutite and goethite, occur as discrete colloform bands. Other textural types were mostly found, under back scattered electron image to be heterogeneous. It is seen thet the K contents are exceptionally low when compared to cryptomelane from some other localities (Frenzel, 1980; Ostwald, 1988). Impurities are essentially the same as in nsutite and pyrolusite. Chemical composition of the mineral is as follows: MnO<sub>2</sub> around 92.8%; Fe<sub>2</sub>O<sub>3</sub> is nil; SiO<sub>2</sub> up to 0.07%; CaO up to 0.2%; Na<sub>2</sub>O up to 0.4%; MgO up to 0.04% Al<sub>2</sub>O<sub>3</sub> up to 0.5%; and K<sub>2</sub>O up to 0.05%.

**Lithiophorite:** In EPMA analysis of lithiophorite is encountered as dissolution cavity filling in colloform variety of the infiltration type manganese ores. The cavities probably developed after the formation of botryoidal manganese ores by the process of dissolution and have been subsequently filled by lithiophorite.

Chemical composition of the mineral is as follows:  $MnO_2$  around 75%;  $Fe_2O_3$  is nil;  $SiO_2$  up to 0.8%; CaO up to 0.2%;  $Na_2O$  up to 0.1%; MgO up to 0.1%  $Al_2O_3$  up to 11.5%; and  $K_3O$  up to 1.5%.

Table 2. Electron probe microanalysis of nsutite, pyrolusite, cryptomelane and lithiophorite (wt%)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Na20	0.071	0.135	0.04	0.051	0.201	0.03	0.02	0.02	0.02	0.74	0.72	0.48	0.62	0.27	0.13	0.09	0.09	0.13	0.23
K20	0.11	0.033	0	0.025	0.688	0.12	0.27	0.02	0.02	2.6	3.02	3.55	3.32	3.06	1.64	1.52	1.67	1.56	1.56
Ca0	0.25	0.28	0.22	0.169	0.13	0.18	0.16	0.22	0.25	0.08	0.12	0.12	0.12	0.41	0.18	0.31	0.21	0.18	0.21
Si02	0.46	0.667	0.47	0.674	0.483	0.51	0.23	0.43	0.34	0.11	0.11	0.14	0.14	0.02	0.73	1.16	0.91	0.76	0.73
Al203	0.306	0.412	0.12	0.34	0.561	0.35	0.09	0.28	0.3	0.78	1.88	1.09	1.94	0.16	10.9	12.9	12.3	10.8	10.9
Mg0	0.098	0.153	0.05	0.076	0.305	0.01	1.79	0.06	0.02	0.06	0.03	0.08	0.07	0.03	0.1	0.16	0.06	0.1	0.09
Fe203	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mn02	96.05	90.05	92	94.89	93.58	95.7	95.6	94.8	95.8	93	90.8	91.1	87.8	91.5	74.9	71.7	75.6	74.5	76.5
Total	97.58	91.94	94	96.28	96.26	97.1	98.2	96.3	96.8	97.4	96.7	96.6	94	95.4	88.5	87.9	90.9	88	90.2
	Analysis 1-4 nsutite, 5-9 pyrolusite, 10-14 cryptomelane and 15-19 lithiophorite																		

### VI. Discussion:

The Chikkanayakanahalli manganese oxide ores noted that a representative profile through the ore (then only manganese oxides) revealed a metasedimentary and lateritoid types of manganese oxide ores showing relict sedimentary feature. Further indicated that structures reminiscent of the effects of weathering and lateritization were prominent, according to Sorem and Cameron (1960). The mineral assemblage, paragenetic sequence and the structure and textures of the ores were consistent with supergene deposition of the manganese oxides. It may be of interest to note that several workers have emphasized the apparent difficulty in identification of manganese oxide minerals, especially in many of their concentrations in weathering environments (Potter and Rossman, 1979; Parc et al 1989; Ostwald, 1988). Thus difficulty has usually been attributed to the often poorly crystallized, finally particulate and disordered nature of manganese oxide concentration in such environments.

Powder diffraction pattern obtained from ore samples in the present study are generally broad and diffuse. Some pattern are characterized by quite prominent peaks, but most could not be assigned to either nsutite, cryptomelane or pyrolusite due to similarities in d-values, textural charecteristics, were prominent facilitated identification amongst the manganese oxide minerals, notably according to the identification procedures of Sorem and Cameron (1960). Pyrolysite in the ores is almost always crystalline, cleavase is distinct, and strong an-

isotropism. Lithiophorite is encountered as dissolution cavity filling in colloform variety of the infiltration type manganese ores. The major obstacle was between cryptomelane and nsutite especially in their cryptomelane and colloform varieties. However, in mode of occurrence types, texture, anisotropic character and mode of occurrence of the minerals served to distinguish between them.

Pyrolusite is encountered both in the metasedimentary and altered metasedimentary manganese ores. Different generations of pyrolusite are encountered in the metasedimentary/altered metasedimentary ores and based on their grain size, association and morphology; they have been designated as pyrolusite I to pyrolusite III.

In the altered metasedimentary ore, four varieties of pyrolusite are encountered, viz., pyrolusite (I, II, III & IV). In the moderately altered metasedimentary ore, pyrolusite (I& II) are encountered either as small broken-up fragments or islands of tiny specks/ particles, having concave surfaces amidst supergene minerals. In the altered metasedimentary ores, pyrolusite (I) is replaced by diverse supergene minerals like cryptomelane. Pyrolusite (III) occurs as large fan-shaped crystals along with other supergene manganese. Pyrolusite (IV) is encountered as veinlets/stringers confined to tensional fractures/joints and as vug-fillings in the altered metasedimentary ores.

Cryptomelane in the study area is of supergene origin. In

the altered metasedimentary manganese ores, cryptomelane occurs mainly as (i) irregular cryptocrystalline masses, (ii) fibrous patches and (iii) fracture/joint fillings. Bulk of the cryptomelane in the altered metasedimentary ore was deposited through low-temperature replacement of the metasedimentary pyrolusite and only a small proportion is encountered as fracture/joint fillings.

In the least altered metasedimentary manganese ore exhibiting banded texture, cryptomelane exhibits relict grains of pyrolusite, implying replacement origin of cryptomelane. Depending on the intensity of lateritization, the metasedimentary manganese ores show varying degrees of replacement of pyrolusite (I) by cryptomelane and the proportion of cryptomelane compared to pyrolusite also increases with increase in the degree of alteration.

Infiltration-type ores exhibit evidences of low temperature cavity filling and replacement textures. The textural features noted in the non-colloform and colloform varieties of infiltration-type manganese ores. Non-colloform varieties of infiltration-type manganese ores exhibit an intricate network texture, laminated texture. This variety generally consists of supergene manganese- and iron- minerals represented by cryptocrystalline cryptomelane and minor goethite respectively. In the quartzite-hosted manganese ores, the supergene minerals occur amidst quartz implying that they were precipitated by the replacement of quartz. In case of phyllite-hosted manganese ores, the Mn minerals are encountered as sub-parallel streaks, bands and irregular patches, indicating that both processes of replacement and cavity filling were responsible for their formation. In the colloform type, concentric bands composed of cryptomelane, pyrolusite, nsutite, occur as discrete colloform bands. Pyrolusite is represented by coarse-grained crystal aggregates that are commonly oriented perpendicular to banding and rarely occur as randomly oriented crystals. Colloform bands exhibit contraction (syneresis) cracks which may or may not be filled with supergene manganese minerals.

Banded texture composed of micro layers of single minerals or polyminerals is commonly noticed in colloform ores. The single mineral may be either cryptocrystalline manganese oxide (pyrolusite, nsutite, cryptomelane). Sometimes, radiating crystals of pyrolusite, nsutite are also encountered. Pyrolusite is a common constituent of both colloform and non-colloform types of infiltration-type ores. In the colloform type, pyrolusite II and III are encountered. Pyrolusite II occurs as bands alternating with nsutite. Pyrolusite III occurs as fillings in vugs/dissolution cavities of colloform ores. In the non-colloform ores, pyrolusite occurs either as a monominerallic phase or the box-work type consists of large prismatic crystal aggregates of pyrolusite II and cryptocrystalline cryptomelane. Cryptomelane is the major phase in both the colloform and non-colloform varieties. In the colloform type, cryptomelane occurs as thin bands alternating with pyrolusite and nsutite. In the non-colloform type, cryptocrystalline cryptomelane is associated with pyrolusite. In the colloform variety of infiltration-type ore, nsutite occurs as well developed crystals and as bands alternating with pyrolusite, cryptomelane. Lithiophorite is encountered as dissolution cavity-fillings in colloform variety of the infiltration type manganese ores. The cavities probably developed after the formation of botryoidal manganese ores by the processes of dissolution and have been subsequently filled by lithiophorite.

Chemical composition of nsutite, pyrolusite, cryptomelane and lithiophorite indicate very little contamination from other elements. A comparision of the elemental composition of pyrolusite and nsutite (Table 2) shows that apart from Si and Ca pyrolusite seems to have less affinity for other elements. It is therefore seen that the Fe contents is also negligible in nsutite, pyrolusite, cryptomelane and lithiophorite. The Al and k contents are also slightly Mg contents are almost negligible in pyrolusite compared with quite significant traces in nsutite. Na contents are also slightly higher in pyrolusite than nsutite, Cryptomelane, on the other hand, seems to be associated with Na more than either nsutite or pyrolusite. The rather

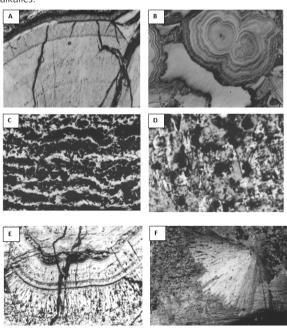
low content of potassium in the cryptomelane analysis may be quite interesting. Si contents are also higher in lithiophorite than nsutite pyrolusite and cryptomelane. The relatively high Si content in pyrolusite may indicate the element's presence in cleavage planes (Ostwald, 1988),

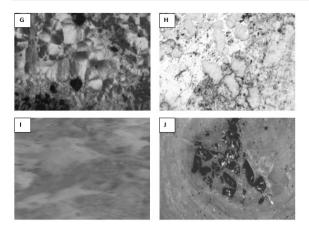
#### VII. Conclusions:

Metasedimentary manganese ore bodies, composed of well- crystalline medium-grained pyrolusite (I) admixed with argillaceous material of similar size, exhibit equigranular texture. Pyrolusite (I) is of sedimentary, diagenetic origin. Metasedimentary manganese ores also rarely exhibit inequigranular texture, which may be attributed to recrystallization of pyrolusite (I) to pyrolusite (II) due to greenschist facies metamorphism. Altered metasedimentary ores, in addition to other textures of metasedimentary ors, also exhibit replacement textures. Pyrolusite (I & II) were replaced mainly by cryptomelane. Pyrolusite (III) occurs as coarse-grained crystals of supergene origin and pyrolusite (IV) is found as vug-fillings and veins.

Non-colloform variety of infiltration-type manganese ores exhibit network and laminated textures, which are characteristic of cavity-filling and replacement processes. These ores are essentially made up of cryptomelane, and pyrolusite. Colloform variety of infiltration-type manganese ore, consisting of concentric bands of one or more manganese- and iron-minerals indicate their possible derivation from colloidal solutions. These ores are composed of cryptomelane, pyrolusite, nsutite, and lithiophorite. Of these minerals, cryptomelane, pyrolusite, and nsutite occur as discrete colloform bands, whereas lithiophorite is found as dissolution cavity fillings. At places, cryptocrystalline cryptomelane is found as syneresis crack fillings.

Chemical composition and nature of the ore forming solution can be evaluated from the textural features of the ores, mineralogical composition and their site of deposition. In the study areas, infiltration-type manganese ores are encountered at shallow depths localized along the secondary structures of the associated rock formations. The mineral composition and the cryptocrystalline nature of the minerals of these two types of supergene ores suggest that the majority of the lateritoid ores were derived from colloidal solutions rich in Mn, Fe and alkalies.





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