Geochemistry and Genesis of Manganese Ore Deposits, Andhra Pradesh, India

T.Suryanarayana^{1,2}

Professor & Geology & Wollo University ¹Department of Geology, College of Science and Technology, Andhra University, Vizag 530013, India. ²Department of Geology, College of Natural Science, Wollo University, Dessie Campus, Ethiopia.

Abstract

Manganese deposits of Vizianagaram district, Andhra Pradesh occur as conformable bands in the Khondalite Group of rocks of Eastern Ghats complex. The dominant manganese ore minerals include cryptomelane, psilomelane, pyrolusite, hausmannite, bixbyite and wad etc., Quartz, orthoclase, garnet, kaolinite, hematite and mica are the associated gangue minerals. Presence of high silica and dominance of CaO over MgO, $K_2 O$ over $Na_2 O$, Ni over CO, Zn and Cu over Pb are the elemental characteristics of the deposit. Discrete apatite grains are identified in quartz and orthoclase. Continental weathering appears to be the source for manganese and iron. After deposition and diagenesis, the manganese rich sediments were metamorphosed under granulite facies (max.700°C and min. 6 kb pressure) conditions and subsequent deformation and supergene enrichment produced the present deposit. The manganese ores are generally of low grade with high phosphorus content.

Keywords - Manganese, Kodurite, Eastern Ghats, Phosphorous, Geochemistry, Genesis.

I. INTRODUCTION

Andhra Pradesh contributes about 9% of the total Production of manganese ore in the country. ManganeseDeposits in and around Kodur in Vizianagaram district,Andhra Pradesh, are among the oldest working mines inIndia. The manganese ore deposits of this area are thus adistinct type according to Fermor and the mother rock of these manganese ore deposits is what he termed"Kodurite". Kodurite, named after Kodur village iscomposed of quartz, feldapar, manganese pyroxenes,Spandite garnet and apatite. Fermor (1909)Ascribed theOrigin of the manganese ores of this region to the alterationof these manganese rich rocks. Later workers in this area, Krishna Rao (1954,1960), Raghava Rao and srirama Rao(1955), Mahadevan and Krishna Rao (1956) agreed on theEssentially hybrid nature of the kodurites due to theAssimilation of manganeferous sediments by graniticIntrusions. They also attributed the origin of theseManganese deposits to the metamorphism of the originallyBedded manganeferous sediments.

As these oredeposits are academically and economically important, it is proposed here to carrying out detailed studies on manganese ores of Garbham,Sadanandapuram and Kondakinguva areas ofVizianagaram district in respect to of these ores. Geological Settings:

The general geology of the area has been describedin detail by most of the previous workers (Fermor, 1909,PrabakaraRao 1950 and Krishna Rao 1954) and only a brief and relevant reference is given here. The manganese ore deposits of the study area are associated with Meta sedimentary rocks of the khondalite series of Precambrian Eastern Ghats group of rocks. The members of khondalite series are garnet and sillimanite para gneisses andschist's, garnetiferous quartzitesand intercalated calc- silicate gneisses and marbles. There are several mines and pits scattered mainly in the two neighboring villages, Koduru and Garbham, which lie at a distance of 5 and 20 kilometers respectively from Garividi railway station on Madras- Kolkata railway route. (Fig: 1 a & 1 b).



Fig. 1a. Location map of Andhra Pradesh. 1b. Location map of the Koduru and Garbham

The manganese ores in and around Garividi, Koduru and Sadanandapuram area are called Kodurites. The rock types associated with Kodurites are namely khondalites, quartzites, granite gneisses and patches of calc- granulites. The khondalites are very prominent and are cut by minor pegmatite bodies at places. Quartzites are also abundantly present in these kodurites and forming hillocks in the N –W and S- W parts of the area and the calc- granulitesoccupy central part of the area. The bedded manganese ore occurs conformably underlying the calc- granulites. A number of quarries are worked for manganese at places like Garividi, Sadanandapuram and Koduru areas in the Kodurite belt (Fig: 2&3).



Garbham area is characterized by the rock types mainly of quartzites, granite gneisses, Khondalites and patches of calc- granulites. The manganese ore generally occurs in the bedded from and can be treated along with the calc- granulite bands. Recently manganese ore occurrences have been reported in Kondakinguva area near Salur (NageswaraRao 2014). In all these areas, ore occurs at shallow depths (2-3 Mts)and continued up to the maximum of 20 Mts(Fig: 4 a & 4 b).

GEOCHEMISTRY AND GENESIS OF MANGANESE ORE DEPOSITS



Fig. 4 Manganese Quarries at A. Garbham



Fig. 4 B. Manganese Quarries at Sadanandapuram, Vizianagaram district

Careful observation of the manganese quarries and the adjoining areas in the manganese belts reveals that the ore deposit is associated with rock units namely garnetiferousquartzites and calc- granulites. The former dominated in the Garbham area and the later in the Koduru area. However, the manganese ore has a definite stratigraphic position in the sequence of deposition of khondalite suite of rocks. It can be stated that calc- granulite association with manganese ore is observable in all the places, even as minor, thin bands. The ore bands have a trend of NW-SE to E-W.

According to Mahadevan and Krishna Rao (1956) the manganese ores at Koduru are part and parcel of the Khondalite suite of metamorphosed sedimentary rock, the ore bands and lodes being conformable with members of khondalite series. The primary manganese ores are certainly conformable with respect to the enclosing rocks of the khondalite series. The primary layering of the ores was also conspicuous. The only unconformable relationbetween the ore and the wall rock was observed where the supergene ore migrated along the foliation and joint planes of the paragneisses and now present in an apparent discordant relation. The dimentions of each ore band are several hundreds of meters length and approximately 5 meters width. The manganese beds are of varying continous of thicknesses ranging from less than a meter to four or five meters and contain primary mineral assemblages and their supergene alteration products. Krishna Rao (1960) considered the manganeses bearing sediment to be the oldest member in the PrecambrainKhondalite series. Calc- silicate rocks occur in immediate contact with manganese beds in the Kodur group deposits, where asquartzites, and in places with K-Ba feldspars and garnets, occur as wall rocks at Garbham. The Calcsilicate rocks consist of quartz, K- feldspar, calcite, scapolite and diopside.

II. MINERALOGY OF THE ORES

Mineralogy of the manganese ores have been studied from a suite of samples systematically collected from the mines at Garbham, Sadanandapuram and Kondakinguva areas. Manganese minerals identification was based on ore microscopic study and supported by XRD in a few cases. The present study revealed the presence of braunite, Jacobsite, pyrolusite, cryptomelane, as also graphite, hematite and traces of pyrite. The gangue minerals are quartz, orthoclase, garnet, kaolinite with minor amounts of biotite and muscovite. Brauniteis identified in a few samples in minor quantity and is replaced by cryptomelane. It is euhedral to subhedral and present in the Garbham and Sadanandapuram areas. The jacobsites, which are present both as individual free grains andalso in intergrowth with pyrolusite. Cryptomelane forms colloform bands with or without pyrolusite. It replace Jacobsite as well as silicate gangue minerals. Pyrolusite occurs as veins cross cutting the colloform bands. Pyrolusite replaces many manganese minerals (Fig:5& 6).



Fig. 5 Photo Micrograph shows the replacement of hausmannite(dark grey) by pyrolusite(whitish) Silicate gangue(black)..Reflected light 50X



Fig: 6. Photomicrograph shows the replacement of braunite(white) by cryptomelane(light grey) and Silicate gangue(black).Reflected light 50X

Jacobsite is granular, subhedral to tabular and isolated grains enclosed by secondry minerals in places. Islands ofsilicate minerals are found in Jacobsite. Hausmannite is found as exsolutionlamelle in Jacobsite and is essentially a primary mineral formed under high grade metamorphism.

Quartz, orthoclase, garnet , Kaolinite and minor amounts of biotite, muscovite from the silicate gangue minerals. The silicates quantity increases from Garbham to Sadanandapuram and to Kondakinguva areas. Replacement of these silicate minerals along grain boundaries and in intergranular spaces by manganese ore minerals are very commom (Fig: 7). Kaolinite patches formed by alteration of orthoclase are distinct at a number of places in the manganese ore. Garnet occurs as subhedral to anhedral grains along with quartz and orthoclase.



Fig: 7. Photomicrograph of pyroxene granulite shows the pyroxene, orthoclase,garnet, quartz biotiteand sillimanite Plane polarised light 50X

III. PARAGENESIS

Based on textural relationships of various minerals, a paragenitic table (Table 1) mainly for oxides is given below. Table 1: Paragenetic Table for oxide minerals

←Time→						
	Primary	Secondary				
Bixbyite						
Braunite						
Hausmannite						
Jacobsite						
Vredenbrgite						
Psilomelane						
Goethite						

Wad	
Kaolinite	
Quartz	

Based on the primary association it is inferred that Braunite, Bixbyite, Hausmannite and Jacobsite formed at the same time. Secondary minerals were derived during supergene alteration. Psilomelane and Geothite are the earliest amoung the secondary oxides Pyrolusite and cryptomelaneare found as veins and cavity filling in psilomelane and they are later than psilomelane.

IV. GEOCHEMISTRY

A total of 10 samples from different manganese mines of Vizianagaram district were analysed for Major, Minor and Trace elements (by ICP - MS at NGRI, Hyderabad) and the data is given in (Table 2).

Table:	2. Chemical	analyses of Mar	iganese ores of	Vizianagaram District
--------	-------------	-----------------	-----------------	-----------------------

	1	2	3	4	5	6	7	8	9	10
SiO ₂	14.41	24.91	4.48	7.35	26.43	8.64	14.16	15.68	25.40	20.16
Al ₂ O ₃	2.05	3.26	2.26	0.24	1.06	2.94	5.42	2.52	2.96	0.14
Fe ₂ O ₃	25.87	12.81	25.35	12.14	17.48	10.28	5.06	31.04	6.68	13.14
TiO ₂	0.84	0.92	0.90	0.03	0.92	0.98	0.09	1.08	0.14	1.01
MnO	38.86	42.00	45.76	62.10	36.27	55.00	58.62	24.32	41.71	45.52
BaO	2.54	2.14	2.21	1.10	4.14	2.68	3.52	1.22	2.96	3.22
CaO	1.15	0.86	1.04	0.65	1.12	1.21	1.72	0.82	2.69	0.98
MgO	1.06	0.85				0.92	1.08	0.50	1.86	0.82
K ₂ O	0.88	0.96	1.02	0.94	0.99	1.98	2.98	1.55	1.01	2.92
Na ₂ O	0.52	0.48	0.52	0.47	0.49	0.68	0.72	0.75	0.42	0.42
$P_2 O_5$	0.81	0.25	0.15	0.82	0.50	0.26	0.22	0.68	0.09	0.24
LOI	11.50	9.68	8.82	7.35	9.48	14.26	5.05	13.54	9.95	10.86
Traces in	PPM									
Pb	127	65	72	140	5	110	108	110	12	70
Cu	186	87	112	15	112			218	10	78
Ni	445	420	435	110	225	357	420	225	248	430
Со	342	380	420	112	127	220	355	240	130	325
Zn	100	35	34	70	24	120	115	112	40	110
Ga	75	60	120		134	26	29	19	64	65
Cr	322	74	237	214	227	320	420	250	270	325
V	80	110	105	59	100	142	125	62		
Y	60	74	70	84	74	129	72	79		38

(1-3 samples from Garbham, 4-7 Samples from Koduru deposits and 8-10 samples from Kondakinguva areas)

The Mn ores show wide variation in MnO $Fe_2 O_3$ and SiO₂ values, Manganese and iron shows antipathetic relation in these ores (Fig: 8). The phosphorus content is very high in comparison to other manganese deposits eg.North Kanara, Karnataka, India (Ananta Murthy and Deva Raju, 1990), Balaghat District, Madya Pradesh (Roy 1960). Generally iron rich manganese samples contain high amounts of phosphorous (Acharya et al 1994), Dominance of CaO over MgO, K₂ O over Na₂ O and Co over Ni are also characteristic of vizianagaram manganese ores. Similar geochemical enrichments are reported from gondite manganese ores of Madya Pradesh and Maharashtra of Cu, Pb and Ni in these ores are similar to those found in Nishikhal manganese ores of Orissa, India (Acharya et al 1997). Bhandara , Maharashtra and Barbil, Orissa (Rai et al 1979. Ajmal,1990, Siddiquie and Raza, 1990). Vizianagaram manganese ores fall in the area of hydrogenous deposits (Fig.9)in the SI- Al discriminate diagram (Choi and Hariya, 1992). These ores have Lower concentration of Co, Cu, Ni, and Zn when compared to the famous manganese ore deposits of India.

Phosphorous contents in the manganese ores of Garbham and Koduru areas are in the range of 0.15 to 0.81% and

0.22 to 0.82% indicating higher content of phosphorous in these ores. However Kondakinguva area maintains some what Low (0.09 to 0.68%) concentration (Nageswara Rao, 2014) and indicating the decreasing trend of phosphorous from Koduru to Kondakinguva area through Garbham (SE to NW). phosphorous increases with the iron in these ores (Fig: 10) and not shown any trend with the manganese (Fig: 11). Phosphorous in these ores is mainly due to the apatite bearing pegmatite intrusions in these areas and also the host rocks contain apatite as an accessory mineral, which might have gone in to solution with the manganese and fixed in the ares. (Krishna Rao, 1960). Barium also quite high in these ores (1.10- 4.14). Siva prakash (1980) reported barium feldspars in these areas and argued for the high percentage of barium in the ores is due to the barium feldapars. Circulating waters might have contributed some barium to these ores.

These manganese ores have Lower concentration of Co,Cu, Ni and Zn and when plotted in a ternary diagram CO-Cu-Ni, they are comparable to the I slay (sedimentary fresh water), Nishikhal (meta sedimentary, supergene) and Barbil(sedimentary) manganese deposits (Data and figure is not given here). Diagnostic plots of Na₂ O versus MgO of the Vizianagaram manganese ore samples (Fig:12) Lie in the fresh water field of Nicholson (1988).



V. GENETIC MODEL

The occurrence of well defined bands of manganese ore having the same strike and dip as the dominant

foliation in Khondalite and quartzite and the similar folding of manganese ore bodies and the country rock strongly suggest that the manganese deposits of Vizianagaram district have been developed as a syngenetic part of the meta sedimentary sequence of the Eastern Ghats Complex. These ores fall in the hydrogenous field and fresh water fields. In these deposits, metamorphic minerals assemblages (primary) and their supergene enrichments (Secondary) are present. Metamorphism gave rise to primary oxides such as hausmannite, Jacobsite etc., and silicates such as manganese garnet and so on. Manganeseand iron oxides are abundant minerals in these deposits followed by manganese silicates and minor carbonates. Therefore, a predominantly oxide facies was deposited during the original sedimentation. This predominantly (Mn- Fe) oxide sediment probably contained abundant admixture of sand and/or clay in the metamorphosed sedimentary silicates which are also present. In these deposits, calc- silicate rocks are inter bedded with the manganese rich sediments. It is inferred that small pockets of carbonates are present within the oxide sediment.

The mode of solution and transportation Fe and Mn and their deposition under oxidizing conditions has long been known. Fe and Mn may be transported as fine particles etc and soluble in neutral and acidic solutions and become precipitated quite early than manganese under any given Ph- Eh conditions. During sedimentation, the Mn and Fe could have been precipitated in the form of Fe, Mn oxides, hydroxides and gels readily adsorbed by cations such as K.Ca and Ba (Rankama and sahama 1950), Such precipitated and adsorbed materials could reorganize themselves in to minerals such as pyrolusite, cryptomelane and psilomelane during diagenesis (sivaprakash 1980). Relatively high amounts of Si Al and Ti in the Vizianagaram deposits are due to the admixture of detrital materials during precipitation (choi and Hariya, 1992) Phosphorous is present as fine apatite crystals within silicates (A charya et al., 1994). The original sediments might contain some amount of Phosphorous (Sivaprakesh 1980; Bhathacharya et al; 1984) and more Phosphorous in the form of apatite appears to have been introduced in to the manganese ores through granitic and pegmatitic activities (Krishna Rao at. 1981; Acharya et al., 1994).

Source for manganese deposits have been traditionally cited as continental erosion, volcanic activity, or deeper parts of the depositional basin. However, continental erosion appears is to be adequate to account for the manganese ores of Vizianagaram deposits. This is inferredbased on the oxides present in the Mn ores. No recognizable volcanogenic sediments occurred above or below the manganese rich sediments. If the Mn derived from the bottom layers of the basin, it would have been concentrated in the calcareous and silicious sediments and would not have occurred in sharp, well- defined beds. All the above points pointing towards the chemical precipitation of manganese in the depositional basin.

Prolonged exposure of the manganese minerals to atmospheric oxygen and percolation of meteoric water has caused the primary minerals to undergo strong supergene alteration. During this, all manganese oxides tend to change to pyrolusite, cryptomelane, psilomelane. Repeated solution and deposition separates the primary protore, consisting of Mn- Fe mixtures into Mn – rich minerals such as pyrolusite, cryptomelane and psilomelane and Fe- rich minerals such as goethite. This gives rise to economically workable manganese deposits.

Metamorphism:

After the deposition and digenetic changes, the manganese rich sediments were metamorphosed along with conformable calcareous, psammitic and politic sediments under granulitic faces conditions. The original oxides and hydroxides with an increase in P and T during metamorphism, transform to oxides/ This is an essentially isochemical silicates. metamorphism. Temperature, pressure and oxygen fugacity are the important parameters in controlling the manganese oxide / silicate stability boundaries during metamorphism. The manganese beds along with the associated county rock have been affected by polyphase metamorphism and deformation. The presence of some of the primary minerals can be used to estimate their temperatures of formation. For instance, hausmannitecould result from the direct transformation of an early formed Fe- Mn hydroxide at $600^{\circ} \text{ C} - 750^{\circ}$ C (Okada, 1960) which is in agreement with the temperature of metamorphism of Eastern Ghats. The P-T conditions of metamorphism of Eastern Ghats in parts of Andhra Pradesh was determined as >700 C and >6Kb (Rao, 1999).

VI. CONCLUSIONS

Mode of occurrence, mineralogy, texture and chemical characters of Vizianagaram manganese ores suggest their formation as chemical precipitates and the source of which appears to be continental erosion. Manganese formation along with the country rocks have been metamorphosed under granulite facies conditions and later supergene enrichment to give rise to the present mineral assemblages. Koduru manganese deposits are controlled by calc-granulites whereas Garbham ores are by quartzites.Mineral assemblages have formed by metamorphism at peak temperatures of at least 700° C and minimum pressure was 6Kb.High phosphorous content is due to the probable presence of phosphorous in the original sediment and was enriched by granitic and pegmatitic activity in the area.

REFERENCES

- ACHARYA, B.C., RAO, D.S. and SAHOO, R.K. (1997) Mineralogy, chemistry and genesis of Nishikhal manganese ores of south Orissa, India. Mineralium deposita 32, p.79-93.
- [2] ACHARYA, B.C., RAO, D.S. SAHOO, R.K. and DASH, B. (1994) Phosphorous in the siliceous manganese ores of Nishikhal Orissa, India. Jour.Geol 66(1); 32, p.15-23.
- [3] AJMAL, M. (1990) Trace element study of manganese ores of the Barbil area, Keorshar district. Orissa, India.Mineral deposits 25; 160-162.
- [4] ANANTHA MURTHY, K.S. and DEVARAJU, T. (1990) Mineralogy, geochemistry and genesis of manganese ore deposits of the ChiknayaKanahalli - Green stone Belt, Karnataka, Studies in Earth Science. Bangalore University p.111-122.
- [5] CHOI, J.H. and HARIYA, Y. (1992) Geochemistry and depositional environment of manganese oxide deposits in Tokora belt, Japan. Econ. Geol 87 (5): 1265-1274.
- [6] FERMOR, L.L. (1909) The manganese ore deposits of India: Indian Geol, Survey Mem., v.3.7.
- [7] KRISHNA RAO, J.S.R. (1954) The geology of Chipurupalle area, Vizianagaram district with special reference to the origin of manganese ores: Geol., Mineralogy. Metall. Soc.India Quart. Jour., v.26,p.35-44.
- [8] KRISHNA RAO, J.S.R. (1960) Structure of stratigraphy of the manganese deposits of Visakhapatnam and Srikakulam districts, India : Econ. Geol., v.55 p.827-834.
- [9] KRISHNA RAO, S.V.G ., SARMA, K.J. and BHATTACHARYA, S. (1981) Potencial characteristics of the low grade manganese ores in north coastal Andhra Pradesh, India. Proc. Intsymp.on recent advances in Beneficiation and Agglomeration held at Bhubaneswar.
- [10] MAHADEVAN, C. and KRISHNA RAO, J.S.R. (1956) Genesis of manganese ores of Visakhapatnam –Srikakulam districts (India): Internat.Geol.Cong., 20th, Mexico 1956, Symposium del manganese, v.4. p. 133-139.
- [11] MOOKERJEE, A. (1961) Distribution of minor elements in the gondote manganese ores and its geochemical significance. Econ.Geol.56:723-729.
- [12] NAGESWARA RAO, V.V. (2014) Exploration and study of manganese ores of Kondakinguva area, near Salur. Unpubl. Report. Dept. of Geology, Andhra University. Pp.10.
- [13] NICHOLSON, K. (1988) An ancient manganese iron deposit of fresh water origin, Islay, Argyllshire. Scottish. J. Geol. 24 (2) 175-187.
- [14] OKADA, K . (1960) Thermal study on some todorokites: Japanese Assoc., Mineralogists, Petrologists, Econ. Geologists Jour., v.45, p.49-53.
- [15] PRAVAKARA RAO, G. (1950) The geology of manganesebearing rocks of Garividi and Garbham, Visakhapatnam: Geol. Mineralogy, Metall. Sco. India Quart. Jour.,v.22p.25-44.
- [16] RAGHAVA RAO, K.V. and SRINIVASA RAO,M. (1955) A Study of khondalites, Charnokites and associated gneisses and manganese ores around Salur and Bobbili, Srikakulam district. Geol. Mineralogy. Metall. Sco. India. Quart.Jour.,v.27.P.163-174.
- [17] RAI, K.L., SARKAR, S.N. and KONAR.G. (1979) A Statistical appraisal of stratigraphic and structural control of the geochemistry in the Sitasongi (chikla-B) manganese ore body, Bhandala district, Mahrashtra. Geol. Survey. India. Spl. Publ.serl:545-564.
- [18] RANKAMA, K. and SAHAMA, T.C. (1950) Geochemistry: Chicago, Univ.Chicago Press, 912p.
- [19] RAO, A.T. (1999) Sappirinegranulites from Marturu near Anakapalle in the EGMB, India:Gondwana research memoris No.5,p.139-144.

- [20] ROY, S. (1960) Mineralogy and texture of the manganese ores of Koduru Srikakulam district, Andhra Pradesh, India: Canadian Mineralogists, v.6, p.491-503.
- [21] SIDDIQUIE, F.N. and RAZA, M. (1990) Major and trace elements variability in manganese ores of Srikakulam districts, A.P.Bull. India.Geol Assoc.23 (2):99-109.
- [22] SIVAPRAKASH, C. (1980) Mineralogy of Manganese Deposits of Koduru and Garbham, Andhra Pradesh, India. Econ.Geol.vol.75, pp.1083-1104.