

Geology, Geochemistry and Genesis of Manganese Ore Deposits of Vizianagaram District, Andhra Pradesh, India.

Dr. Gollamudi Veeraswamy¹, BH. Nagendra Rao², M. Venkataiah³

^{1,2}Department of Civil Engineering, Malla Reddy Institute of Technology, Hyderabad, India. Email: gvsgeology@gmail.com

³Department of Geology, Osmania University, Telangana, India.

Abstract

Manganese deposits of Vizianagaram district, Andhra Pradesh shows conformable bands like in the khondalite suite 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, K₂O over Na₂O, Ni over CO, Zn and Cu over Pb are the elemental characteristics of the deposit. Discrete apatite inclusions 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. 7000C 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.

INTRODUCTION

Andhra Pradesh contributes about 9% of the total production of manganese ore in the country. Manganese deposits in and around Kodur in Vizianagaram district, Andhra Pradesh, are among the oldest working mines in India. The manganese ore deposits of this area are thus a distinct type according to Fermor and the mother rock of these manganese ore deposits is what he termed "Kodurite". Kodurite, named after Kodur village is composed of quartz, feldspar, manganese pyroxenes, spandite, garnet and apatite. Fermor ascribed the origin of the manganese ores of this region to the alteration of these manganese rich rocks. The later workers in this area, Krishna Rao (1954, 1960), Raghava Rao and Srirama Rao (1955), Mahadevan and Krishna Rao (1956) agreed on the essentially hybrid nature of the kodurites due to the assimilation of manganeseiferous sediments by granitic intrusions. They also attributed the origin of these manganese deposits to the metamorphism of the originally bedded manganeseiferous sediments.

As these ore deposits are academically and economically important, it is proposed here to carry out detailed studies on manganese ores of Garbham, Sadanandapuram and Kondakinguva areas of Vizianagaram district with respect to geochemistry and genesis of these ores.

GEOLOGICAL SETTING

The general geology of the area has been described in detail by most of the previous workers (Fermor, 1909, Prabhakara Rao 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 metasedimentary rocks of the khondalite series of Precambrian Eastern Ghats group of rocks. The members of khondalite series are

garnet and sillimanite para gneisses and schists, garnetiferous quartzites and intercalated calc- silicate gneisses and marbles. There are several mines and pits scattered mainly in the two neighbouring villages, Koduru and Garbham, which lie at a distance of 5 and 20 kilometers respectively from Garividi railway station on Madras-Calcutta railway line. (Fig: 1).

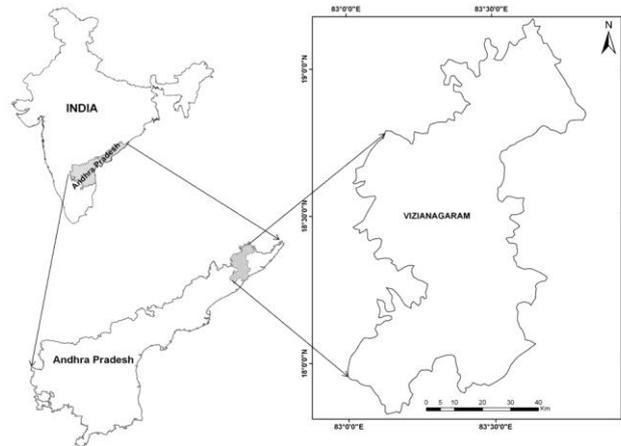


Fig: 1. LOCATION MAP OF STUDY AREA, VIZIANAGARAM DISTRICT

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 as hillocks in the N-W and S-W parts of the area. The calc-granulites occupied central part of the area, in the form of thin concentric lenses like. The bedded manganese ore occurs conformably underlying this calc-granulites. A number of quarries are working for manganese are at places like Garividi, Sadanandapuram and Koduru areas in this Kodurite belt.

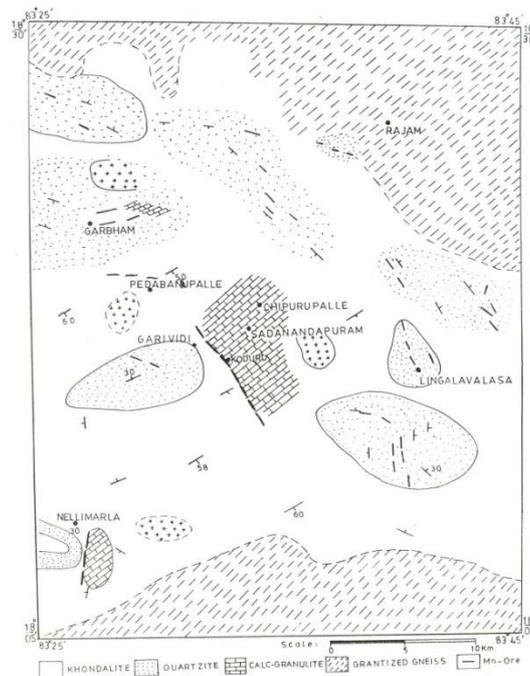


Fig: 2. GEOLOGICAL MAP OF GARIVIDI – GARBHAM AREA, VIZIANAGARAM DISTRICT.

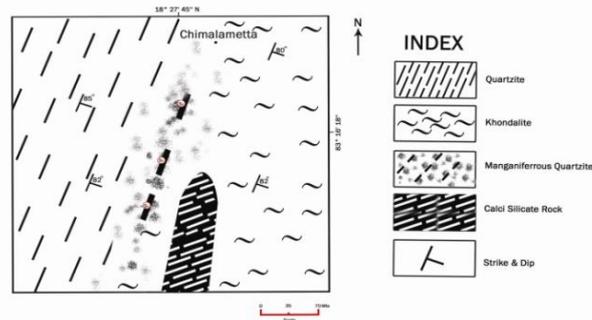


Fig: 3. GEOLOGICAL MAP OF KONDAKINGUVA AREA, VIZIANAGARAM DISTRICT.

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 form and can be treated along with the calc-granulite bands. Recently manganese ore occurrences are reported in Kondakinguva area near Salur (Nageswara Rao 2014). The ore bands are associated at the contact of quartzites and calc-granulites in the Eastern Ghats group of rocks. In all these areas ore occurs at shallow depths (2-3 Mts) and continued up to the maxim of 20 Mts.

Careful observation of the manganese quarries and the adjoining areas in the manganese belts reveals that the ore deposit is associated with two rock units namely garnetiferous quartzites 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 like. The ore bands having 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 loads being conformable with members of khondalite series. The primary manganese ore 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 relation between 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 an apparent discordant relation.

The manganese beds are of varying thicknesses ranging from less than a meter to four or five meters and contain primary mineral assemblages and their supergene alteration products (secondary). Krishna Rao (1960) considered the manganese bearing sediment to be the oldest member in the Precambrian Khondalite series. Calc-silicate rocks occur immediate contact with manganese beds in the Kodur group deposits, where as quartzites, and in places with K-Ba feldspars and garnets, occur as wall rocks at Garbham. The calc-silicate rocks consist of quartz, K-feldspar, calcite, scapolite and diopside

MINERALOGY OF THE ORES

Mineralogy of the manganese ores are 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 few cases. The present study revealed the presence of braunite, jacobsonite, pyrolusite, cryptomelane, other associated opaque minerals are graphite, hematite and traces of pyrite. The gangue minerals are quartz, orthoclase, garnet, Kaolinite with minor amounts of biotite and muscovite.

Braunite is identified in few samples with minor quantity and is replaced by cryptomelane. It is euhedral to subhedral and present in the Garbham and Sadanandapuram areas. The jacobsonites, which

are present both as individual free grains and also in intergrowth with pyrolusite. Cryptomelane forms colloform bands with or without pyrolusite. It replaces jacobite as well as silicate gangue minerals. Pyrolusite occurs as veins cross cutting the colloform bands. Pyrolusite replaces many manganese mineral.

Jacobite is granular, subhedral to tabular and isolated grains enclosed by secondary minerals in places. Islands of silicate minerals are found within jacobite. Hausmannite is found as exsolution lamellae in jacobite and is essentially a primary mineral.

SILICATE MINERALS

Quartz, orthoclase, garnet, Kaolinite and minor amounts of biotite, muscovite form 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 common. Kaolinite patches formed by alteration of orthoclase are distinct at a number of places within the manganese ore. Garnet occurs as subhedral to anhedral grains along with quartz and orthoclase.

PARAGENESIS

Based on textural relationships of various minerals, a paragenetic table (Table 1) mainly for oxides is given below

TABLE 1: MINERAL PARAGENESIS

	TIME	
	Primary	Secondary
Bixbyite	_____	
Braunite	_____	
Hausmannite I	_____	
Jacobite	_____	
Vredenburgite	_____	
Hollandite	_____	
Hausmannite II		_____
Hematite		_____
Pyrophanite		_____
Mn Silicates	_____	
K-Ba feldspars and other primary gangue minerals	_____	
Psilomelane		_____
Cryptomelane	_____	
Pyrolusite		_____
Ramsdellite		_____
Goethite		_____
Lithiophorite		_____
Wad	_____	
Kaolinite and quartz	_____	

Based on the primary associations it is inferred that Braunite, Bixbyite, Hausmannite and Jacobite formed at the same time. Secondary minerals were derived during supergene alteration. Psilomelane and Goethite are the earliest among the secondary oxides. Pyrolusite and cryptomelane are found as veins and cavity fillings in psilomelane and they are later than psilomelane.

GEOCHEMISTRY

The variations in geochemical composition of these ores have been studied and the results are presented in this chapter. The manganese ores from Koduru, Garbham and Kondakinguva areas have been analysed for their major, minor, trace and REE compositions using conventional and instrumental

analytical techniques.

The distribution of these elements help to understand not only the constituents in the ores but also the geochemical relations existing between them. Thus the probable geochemical processes and environment of formation of ores (primary and secondary) have been illustrated.

MANGANESE

Manganese is the twelfth in abundance in the elements of the Earth's crust, just after phosphorous. Geochemically manganese in the upper litho sphere is oxiphile and sometimes chalcophile in nature. Though a number of oxidation states are known for the manganese, from the laboratory experiments, there are only three oxidation states Mn^{+2} , Mn^{+3} , Mn^{+4} in which Mn^{+2} and Mn^{+4} are most common in nature.

Mn^{+2} has the ionic radius of $0.82A^\circ$ and has the electron negativity of 1.4. There is every possibility of a diadochy between Mn^{+2} and Fe^{+2} as well as Zn^{+2} due to similar ionic radius and charge. Barry Maynard (1983) found that the minerals that contain Mn^{+2} ions such as rhodochrosite, tend to be light colored, compared with Mn^{+4} minerals. Manganese in the igneous rocks is present exclusively in Mn^{+2} state.

Mn^{+3} has got the ionic radius of $0.65A^\circ$ and it can replace the ions like Fe^{+3} ($0.67A^\circ$), Ga^+ ($0.62A^\circ$), Cr ($0.64A^\circ$) due to similar ionic charge as well as radius. However, Rankama and Sahama (1950) observed that Mn^{+3} can readily transform into Mn^{+2} and Mn^{+4} as shown below.



Mn^{+4} has got the ionic radius of $0.54A^\circ$ and have a crystal field stabilization energy. Accordingly, Mn^{+4} in octahedral position in minerals should be strongly favored over Mn^{+2} in solution. (Crear et. al., 1980).

Chemical analysis of Manganese ores of Koduru (Table.2), Garbham (Table.3) and Kondakinguva (Table.4) areas. Analysis shows that in the Koduru area the manganese content varies from 22.01 to 63.10%, whereas in the Garbham it ranges from 19.61 to 59.62%. In the Kondakinguva area, manganese content varies from 16.01 to 46.92%. Manganese and iron is inversely proportional in the ores of all the three studied areas (Fig.4). It is from the literature that the primary manganese minerals having less manganese when compared with the secondary ores. The iron and manganese relationship is applicable to individual minerals also. It means that the increase of manganese content, iron content is decreasing. In the secondary minerals with the increase of manganese content silica content is decreasing. Grasselly et. al., (1969) observed a linear relationship between manganese and iron. Manganese ores of Vizianagaram district has got high iron content when compared to the other Indian deposits. Thus the ores of this area are of mixed type of iron and manganese. According to Henry Lepp (1968), the relative pre-penderance of both these elements is a function of depositional conditions as well as post depositional history.

MnO_2 and $Mn(OH)_2$ solutions and gels are negatively charged and therefore, there is greater tendency to absorb the cations like Na, K, Ca, Ba, Co, Ni, Cu, Pb, Zn in appreciable quantities. This is true in the case of minerals like pyrolusite, psilomelane and cryptomalane from the microprobe results. Edwards (1954) pointed out that the manganese oxide gels have a higher tendency to absorb salts of other metals, and that is how the psilomelane, pyrolusite and wad contain appreciable quantities of the above mentioned elements.

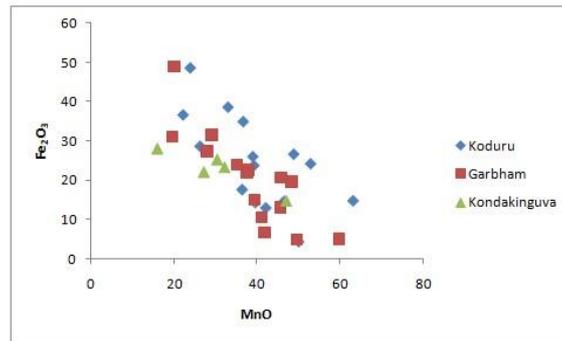


Fig.4. Fe₂O₃ VERSUS MnO FOR THE MANGANESE ORES OF VIZIANAGARAM DISTRICT.

IRON

Geochemically iron is siderophile, chalcophile as well as lithophile in nature. It has got two oxidation states of Fe⁺² and Fe⁺³. The ionic radius for the Fe⁺² and Fe⁺³ are 0.77Å° and 0.65Å° respectively. These are readily replaced by Mn⁺² and Mn⁺³ ions due to its similar ionic radius and charge. Goldschmidt (1929) called Fe, Mn, Ti, V, Co, Ni as the iron family and Landergreen (1943) called it as “Ferrides”.

Iron is the second most important element in the manganese ores. Besides iron rich manganese minerals like hausmanite, vredenburgite and jacobsonite, iron minerals like hematite, goethite and magnetite present in substantial quantities in these ores. However, in the microprobe analysis, it is observed that the secondary ores having minor amount of iron compared to that of the primary ores. Secondary ores are having the iron content less than 2% whereas the primary ores like jacobsonite consists of iron of about 70%. It means circulating waters which act on the primary ores give rise to secondary ores leaching away the iron content and this iron may form as iron minerals like hematite and goethite.

Iron content ranges from 4.21% to 48.44% in Koduru, whereas in Garbham it is from 4.96 to 48.92%. In the Kondakinguva area iron content varies from 14.78 to 28.09%. There is a geochemical affinity between the iron and phosphorous. There is a direct (sympathetic) relationship between iron and phosphorous in the ores (Fig. 5). However, this is also true in case of individual minerals from the microprobe analysis results. For example the Balaghat ores of Madhya Pradesh, Adilabad ores of Andhra Pradesh and Nikopol ores of Russia are iron poor whereas phosphorous is also poor. While the Goa ores, Vizianagaram ores of Andhra Pradesh as well (Sivaprakash 1980) as Nishkal ores of Orissa are iron rich in which phosphorous is also rich.

ALUMINA

Geochemically alumina is a lithophile element in the Earth's Crust. It is having only one oxidation state Al⁺³. Its ionic radius is 0.51Å°. Gallium, with the same charge and ionic radius close to alumina is camouflaged in the alumina – bearing minerals. Rankama and Sahama (1950) observed in the SiO₄ tetrahedra a part of Si⁺⁴ may be replaced by Al⁺³ but the substitution is never completed.

TABLE II: CHEMICAL ANALYSIS OF MANGANESE ORES OF KODURU AREA.

Oxide	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
SiO ₂	14.41	21.66	24.91	21.22	10.68	15.66	4.48	18.49	12.84	7.39	16.48	3.69	26.43	7.76	18.49
Al ₂ O ₃	2.05	2.26	3.26	4.91	3.64	2.64	2.26	4.68	0.92	0.29	0.12	0.03	1.06	1.08	2.32
Fe ₂ O ₃	25.87	4.21	12.81	14.19	48.44	36.48	26.49	28.49	38.46	14.64	23.62	24.06	17.48	34.79	14.49
TiO ₂	0.84	0.04	0.92	1.91	1.72	0.92	0.92	0.82	0.09	0.03	0.19	0.92	0.92	0.84	1.06
MnO	38.86	49.94	42.00	39.44	23.71	22.01	48.76	26.12	32.84	63.10	39.12	52.83	36.27	36.53	46.41
BaO	2.54	4.94	2.14	2.12	0.09	3.09	2.41	2.86	1.09	3.48	1.82	2.36	4.14	3.12	2.28
CaO	1.15	0.96	0.86	0.42	0.86	2.62	1.94	0.88	0.48	1.10	1.46	0.94	1.12	1.48	1.06
MgO	1.06	1.94	1.06	0.06	1.42	1.28	0.99	0.46	0.92	0.67	0.94	0.96	0.99	2.26	0.94
K ₂ O	0.88	0.28	0.96	0.09	0.14	2.14	1.06	1.02	0.68	0.98	1.08	1.02	1.23	1.09	1.23
Na ₂ O	0.52	0.12	0.48	0.51	0.32	0.06	0.52	0.92	0.34	0.56	0.54	0.54	0.59	1.24	0.59
P ₂ O ₅	0.81	0.29	0.29	0.14	0.42	1.06	0.19	0.29	0.74	0.82	0.38	0.64	0.26	0.34	0.74
H ₂ O ⁺	10.50	13.26	9.68	14.94	8.49	11.84	9.92	14.96	9.92	6.46	14.23	11.42	9.48	9.43	10.03
	99.49	99.9	99.37	99.95	99.93	99.8	99.94	99.99	99.32	99.52	99.98	99.41	99.97	99.96	99.64
Traces in ppm															
Pb	127	38	67	142	118	213	79	172	ND	179	69	212	5	229	370
Cu	86	112	89	93	163	24	113	129	23	5	136	164	113	ND	ND
Ni	448	714	286	119	116	664	242	612	236	116	249	314	229	550	648
CO	343	532	448	164	448	519	519	314	340	136	172	276	173	619	542
Zn	104	79	39	74	38	ND	36	28	129	72	34	32	28	12	39
Ga	79	116	64	68	69	112	132	69	73	ND	39	141	164	68	132
Cr	500	1000	100	139	776	514	942	430	440	339	243	544	339	736	492
v	100	149	112	216	72	134	116	120	120	72	120	112	143	49	38
Y	75	72	78	44	142	71	71	26	52	102	74	71	72	79	126

TABLE III: CHEMICAL ANALYSIS OF MANGANESE ORES OF GARBHAM AREA.

Oxide	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
SiO ₂	8.64	14.16	10.21	2.69	9.42	3.56	4.54	15.68	21.64	17.84	23.68	8.68	25.41	10.62	20.16
Al ₂ O ₃	15.96	5.42	3.49	3.87	4.68	3.99	3.32	2.52	2.68	2.82	2.41	1.06	2.96	2.49	0.14
Fe ₂ O ₃	10.48	5.06	22.64	19.64	21.96	20.64	23.91	31.04	27.41	4.96	14.98	48.92	6.68	31.58	13.14
TiO ₂	0.98	0.09	0.52	0.39	0.48	0.41	0.68	1.08	0.91	0.59	0.44	0.48	0.14	1.09	1.01
MnO	41.00	59.62	38.01	48.23	37.50	45.71	35.12	19.61	27.86	49.56	39.39	19.96	41.71	29.01	45.52
BaO	2.68	3.52	2.04	2.84	1.42	0.98	2.14	1.24	3.42	1.28	1.78	0.48	2.96	1.28	3.41
CaO	1.21	1.72	0.19	0.68	0.14	0.27	0.56	0.82	1.08	1.71	0.44	2.99	2.69	0.66	0.98
MgO	0.92	1.08	0.69	1.09	0.54	1.89	2.19	1.52	2.17	0.64	2.83	1.39	5.86	6.84	1.32
K ₂ O	1.98	2.98	1.09	1.82	2.29	1.76	0.84	1.58	0.52	3.48	0.88	1.06	1.01	1.92	2.92
Na ₂ O	0.68	0.79	0.34	0.51	0.86	0.48	1.09	0.72	1.49	2.16	1.39	0.58	0.42	0.09	0.42
P ₂ O ₅	0.26	0.22	0.59	0.37	0.54	0.51	0.59	0.68	0.32	0.76	0.16	0.64	0.09	0.52	0.24
H ₂ O ⁺	14.26	5.09	21.08	17.86	19.98	19.76	24.82	23.54	10.48	14.98	10.92	13.09	9.96	14.46	10.86
	99.05	99.75	100.89	99.99	99.81	99.96	99.80	100.03	99.98	100.78	99.20	99.33	99.89	100.56	100.12
Traces in ppm															
Pb	182	148	94	146	76	ND	126	122	196	170	ND	180	114	72	170
Cu	ND	ND	166	68	5	264	ND	269	292	42	134	5	10	156	78
Ni	569	720	426	492	776	139	740	243	240	260	146	700	149	440	430
CO	728	366	443	347	746	566	966	463	764	492	616	129	230	769	640
Zn	146	123	5	144	ND	42	74	5	176	ND	ND	48	40	ND	116
Ga	26	49	ND	12	24	29	110	19	139	126	5	68	64	128	66
Cr	640	1000	443	968	486	1000	964	274	990	643	349	389	350	713	790
v	142	128	26	138	142	126	246	62	166	62	138	40	ND	42	ND
Y	129	74	12	64	29	ND	ND	118	ND	ND	29	114	ND	38	48

TABLE IV: CHEMICAL ANALYSIS MANGANESE ORES OF KONDAKINGUVA AREA.

Sample no	1	2	3	4	5
SiO ₂	28.63	21.99	30.21	29.62	30.55
Al ₂ O ₃	6.67	9.12	12.12	6.97	5.82
Fe ₂ O ₃	25.32	14.78	28.09	23.35	22.13
TiO ₂	0.37	0.42	0.92	0.38	0.88
MnO	30.36	46.92	16.01	32.15	27.17
BaO	0.08	0.09	0.11	0.07	0.12
CaO	0.68	0.61	0.76	0.75	0.72
MgO	0.02	0.05	0.01	0.01	0.01
K ₂ O	0.25	0.86	0.64	0.56	0.13
Na ₂ O	0.04	0.19	0.05	0.05	0.06
P ₂ O ₅	0.92	0.45	0.72	0.85	0.72
H ₂ O ⁺	6.42	4.35	10.34	4.75	11.35
	99.76	99.83	99.98	99.51	99.66

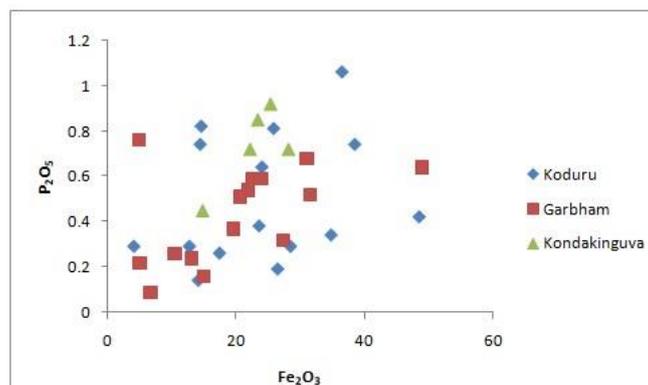


Fig.5. P₂O₅ VERSUS Fe₂O₃ FOR THE MANGANESE ORES OF VIZIANAGARAM DISTRICT.

This is also the most important element in the manganese ores in the area. In the primary ore minerals the Al_2O_3 ranges from 2-10% whereas in the secondary ore minerals it is less than 2%. This may be due to the circulating water which acts on the primary ores leaching the Al_2O_3 . The Al_2O_3 ranges from 0.03 to 4.91% in Koduru samples whereas in Garbham samples it is from 0.14 to 15.96%. In the Kondakinguva area the values are in the range of 5.82 to 12.12%. It is noted that high aluminium content (>5%) present in the Garbham and Kondakinguva ores. Sivaprakash (1980) noted hercynite and galaxite is present in solid solution in those areas and the presence of these minerals cause the enrich of alumina content in the ores. However, the wall rocks which contain more alumina incorporate alumina in to the ores.

SILICA

Geochemically silica is a lithophile element in Earth's Crust. In nature its native state is Si^{+4} . Its ionic radius is $0.39A^\circ$. Ringwood (1955) suggested the replacement of Si^{+4} by P^{+5} in the silicate minerals. According to Sigmund Koritrig (1965) replacement of Si^{+4} by P^{+5} is possible only in the igneous and metamorphic rocks.

Silica is one of the important elements in the manganese ores in these areas. Except in the silicate bearing minerals like rhodonite, braunite and garnets in all other minerals the silica content is less than 2%. This may be due to leaching phenomena. In the manganese ores of Koduru, the silica content ranges from 3.69 to 26.43% whereas in Garbham it is from 2.69 to 25.41%. Kondakinguva, the values are in the range of 21.99 to 30.55%.

PHOSPHOROUS

Geochemically it is of lithophile character. In nature it is having the two oxidation states of P^{+3} and P^{+5} . Vugt (1931) stated that phosphorous follows very closely with the course of titanium during the magmatic differentiation in spite of great difference in their chemical behavior. Tageeva (1942) found phosphorous and arsenic concentrated in waters connected with volcanic activity. Ringwood (1955) observed replacement of Si^{+4} by P^{+5} in silicate minerals.

The manganese ores of Vizianagaram district are known for their higher amounts of phosphorous. Since the phosphorous is a deleterious element, a study has been made to understand its behavior in different ores such that it may be helpful in eliminating this element from these ores. The analytical results for phosphorous content in these ores are quite interesting and they may be helpful in locating ores with less phosphorous. The variation of phosphorous content in these ores and its behavior with other elements like potassium (Fig. 6), sodium (Fig. 7), barium (Fig. 8), calcium (Fig. 9), silica (Fig. 10), is given.

In the present study phosphorous content is higher in the protores compared to that of the secondary ores. In the primary ore minerals, phosphorous content varies between 0.7 to 0.9% while in the secondary ore minerals it is from 0.4 to 0.5%. In the normal ore analysis from the Koduru area, phosphorous content is from 0.14 to 1.06% whereas in the Garbham samples it is from 0.09 to 0.76%. In the Kondakinguva area, phosphorous content varies from 0.45 to 0.92%.

As already mentioned there is a linear relationship between phosphorous and iron in the manganese ores. Mukherjee (1958) stated that phosphorous content increases with the iron content and this relationship is governed by certain physicochemical conditions.

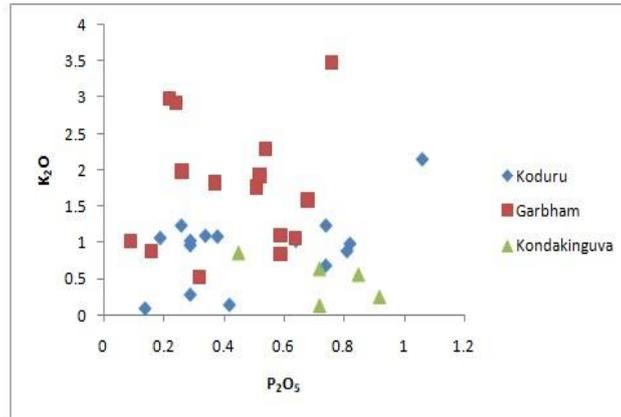


Fig.6. K₂O VERSUS P₂O₅ FOR THE MANGANESE ORES OF VIZIANAGARAM DISTRICT.

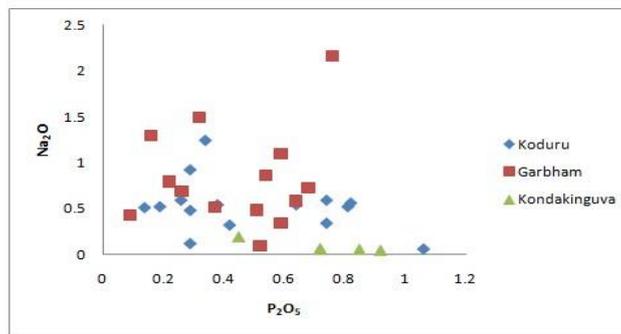


Fig.7. Na₂O VERSUS P₂O₅ FOR THE MANGANESE ORES OF VIZIANAGARAM DISTRICT.

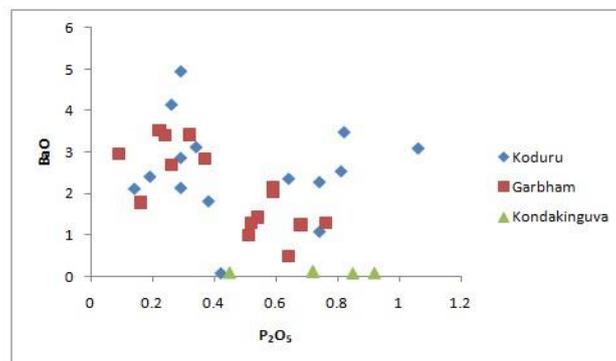


Fig.8. BaO VERSUS P₂O₅ FOR THE MANGANESE ORES OF VIZIANAGARAM DISTRICT.

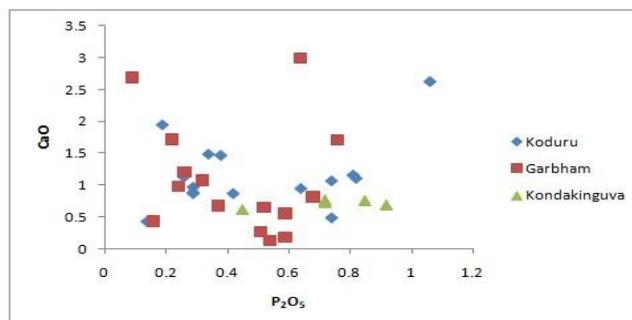


Fig.9. CaO VERSUS P₂O₅ FOR THE MANGANESE ORES OF VIZIANAGARAM DISTRICT.

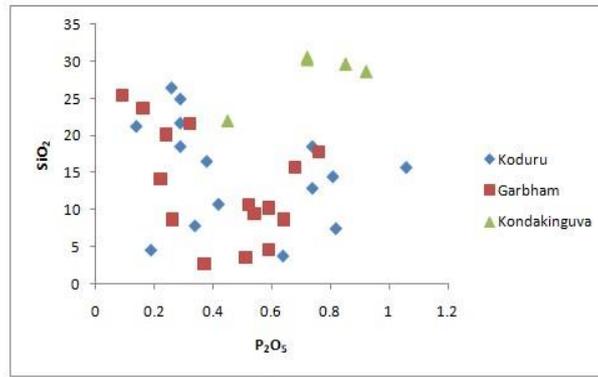


Fig.10. SiO₂ VERSUS P₂O₅ FOR THE MANGANESE ORES OF VIZIANAGARAM DISTRICT.

Mason (1958) pointed out that positively charged Fe(OH)₃ sols absorb the anions like (PO₄).

Regarding the nature of phosphorus in the manganese ores in this area, different workers postulated different theories. Krishna Rao (1975), Smirnov (1976), Krishna Rao et. al. (1981) stated that apatite is the main contributor for the phosphorus in the ores and entry of phosphorus through reorganization of the crystal lattice might have happened during the process of weathering. Kshirasagar (1971) pointed out phosphorous in the manganese ores in this area is largely due to apatite bearing pegmatites intrusion into the ores. Visweswara Rao (1980) suggested that phosphorous in the area is due to

Phosphorous content in the ores increases with the iron content, which indicates the possibility of some phosphorous entering into the manganese ores in the early stage of formation of colloidal absorption

Garnets are altered to secondary manganese ores and garnets might have played a role in the concentration of phosphorous in the ores.

Phosphorous ions from the associated (host) rocks might have gone into solution with the manganese and fixed in the ores.

Sivaprakash (1980) observed a manganese bearing phosphate mineral “gorceixite” from this area. Bhattacharayya et.al. (1984) observed that phosphorous in the manganese ores is contributed by the apatite and high intensity magnetic separation may reduce the phosphorous. Raju (1986) stated that phosphorous is derived into the ores during diagenesis from the associated pegmatites. The present author’s contention is that some phosphorous may precipitated at the early stage of manganese ore formation, with the result the protores contain high the phosphorous than that of the secondary ores.

SODIUM

Geochemically sodium is a lithophile element in the Earth’s crust. In nature its oxidation state is Na⁺¹ and its ionic radius is 0.98Å° with electro negativity of 0.9.

In the primary manganese minerals the Na₂O is less than 0.75% whereas in the secondaries it is between 1-2%. Manganese ores from Koduru shows that the sodium content is between 0.06 to 1.24% whereas in the Garbham it is from 0.09 to 2.16%. Kondakinguva the values varies from 0.04 to 0.19%. The presence of sodium in the manganese ores is due to absorption from the associated rocks. The circulating waters act on the primary ores giving rise to secondary ores and these circulating waters might have appreciable amounts of sodium, with the result the secondary ores having an appreciable amounts of sodium. The solutions might be of alkaline in nature.

POTASSIUM

Geochemically potassium is also a lithophile element. In nature it has the oxidation state of K⁺¹ having the ionic radius of 1.33Å° and electron negativity of 0.8. The substitution of potassium by

barium (Fig. 11) as well as strontium is possible due to their similar ionic radius.

Potassium content in the secondary ore minerals are much higher when compared to the primary minerals. In the primary ore minerals potassium content is generally less than 1% whereas in the secondaries it ranges from 1 to 3%. The explanation for the higher content of potassium in the secondary ores is that the circulating waters which act upon the primary ores increase the potassium content in the secondary ores.

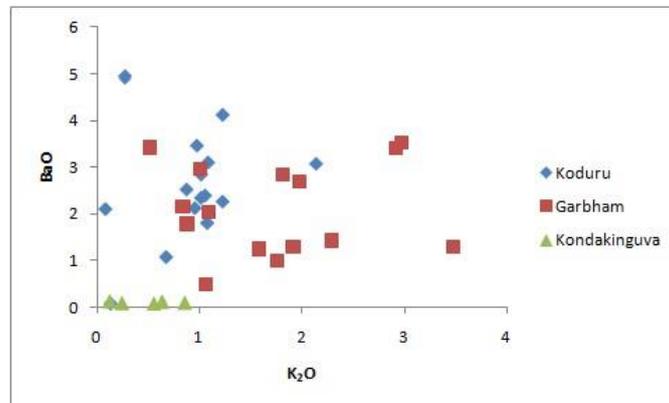


Fig.11. BaO VERSUS K₂O FOR THE MANGANESE ORES OF VIZIANAGARAM DISTRICT

Potassium content in the manganese ores of Koduru ranges from 0.09 to 2.14% whereas in the Garbham it is from 0.52 to 3.48%. Kondakinguva manganese samples contain 0.13 to 0.86% of potassium. Rankama and Sahama (1950) explained that more potassium present than sodium in many of the secondary manganese ores.

BARIUM

Barium is a lithophile element in nature. It has got the oxidation state of Ba⁺² with the electro negativity of 0.85.

Like sodium and potassium, barium content is much higher in the secondary ore minerals compared to that of primary ore minerals. In the primary ore minerals (except hollandite) barium content is less than 0.75% whereas in the secondary minerals it is from 1.5 to 7%.

The manganese ore analysis reveal that the barium content in the Koduru is from 0.09 to 4.94% while at Garbham it is from 0.48 to 3.52%. Kondakinguva ores contain 0.07 to 0.12%. Sivaprakash (1980) reported the barium feldspars from these areas and his argument for the high percentage of barium in the ores is due to the barium feldspars.

However, the present author contends that circulating waters which are of alkaline nature might have contributed much barium to the secondary ores.

COPPER

Geochemically it is of lithophile as well as chalcophile in nature. It has the oxidation state of +2 in nature. Cu⁺² very close to Fe⁺². In the normal ores from Koduru and Garbham the values are ranging from 5 to 292 ppm.

COBALT

Cobalt is having the oxidation state of Co⁺² and Co⁺³ and has the ionic radius of 0.72Å° and 0.63Å° respectively. Cobalt is ferromagnetic and siderophile in nature. However, the observation as well as the occurrence of cobalt and nickel in the upper lithosphere showing the tendency of chalcophile character. The bivalent cobalt ion is practically the same size (0.74Å°) as the ferrous ion (0.77Å°) and it has camouflaged with the ferrous ion. Ahrens (1953) observed that Co⁺³ with the ionic radius of 0.63Å°

would readily substitute for Mn^{+3} (0.66\AA) due to similar ionic radius and charge.

Cobalt content in the secondary ore minerals is in appreciable amounts. In the ore analysis from Koduru area, cobalt content is between 136 to 619ppm. Whereas from the Garbham area is from 129 to 966 ppm. The cobalt in the manganese ores has been added by circulating solutions and it is concluded that the presence of cobalt in these ores is due to absorption rather than substitution.

NICKEL

Nickel is strongly ferromagnetic and siderophile in character like iron and cobalt. It has the oxidation state of Ni^{+2} having the ionic radius of 0.68\AA . Nickel has got the same ionic radius and charge with that of magnesium and therefore, it is camouflaged with the magnesium. Mason (1958) stated that the ratio of Ni: Mg is highest in the early formed crystals (especially olivine) and shows a steady decline in the late formed rocks and minerals.

Nickel content is in appreciable amounts in a secondary ore minerals. In the normal ore analysis for the Koduru it ranges from 116 to 714 ppm whereas for Garbham it is 139 to 776 ppm. During the weathering nickel remains for long in the solid products and it is deposited in the hydrolyzate sediments. Nickel is very stable in aqueous solution contrary to Fe^{+2} and Mn^{+2} and is accordingly able to migrate for considerable distance under proper circumstances. The nickel in the manganese ores has been from the circulating water and it is concluded that the presence of nickel in these ores is due to absorption rather than substitution.

GALLIUM

Geochemically gallium is of chalcophile character. Gallium, with the same ionic radius and charge close to that of aluminium, is replaced in aluminium-bearing minerals. Mason (1958) mentioned the size of gallium and alumina ions (Ga^{+3} 0.62\AA , Al^{+3} 0.57\AA) and suggested that gallium would tend to be more abundant in the later-formed aluminium minerals. Gallium is enriched in pegmatite feldspars and micas. Though gallium is enriched in certain minerals and rocks but so far no mineral has been formed containing gallium as the essential constituents.

The ores from the Koduru as well as Garbham shows that the gallium ranges are from traces to 100 ppm. The presence of gallium in the ores is due to entry of gallium into Al^{+3} position or Fe^{+3} position (Fig. 12 & 13). However, the gallium in the manganese ores may be derived from the pegmatites which consist of substantial quantities of gallium. Goldschmidt and Petters (1931) noted the substantial quantities of gallium in some of the sedimentary rocks as well as in some manganese ores.

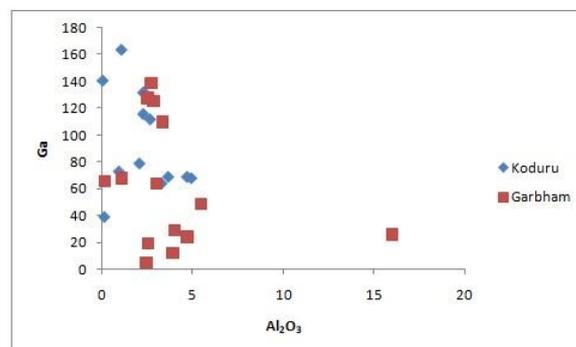


Fig.12. Ga VERSUS Al_2O_3 FOR THE MANGANESE ORES OF VIZIANAGARAM DISTRICT

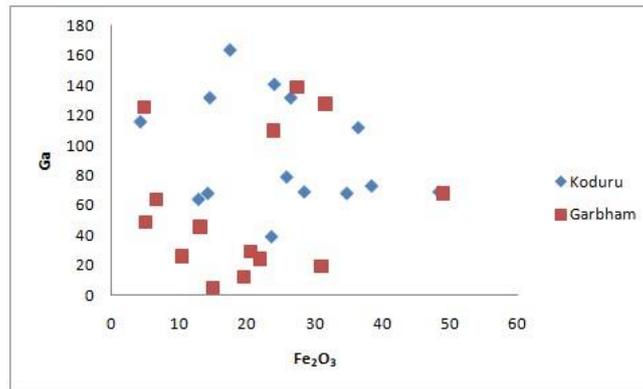


Fig.13. Ga VERSUS Fe₂O₃ FOR THE MANGANESE ORES OF VIZIANAGARAM DISTRICT

CHROMIUM

Geochemically chromium is strongly lithophile element on the Earth's Crust. It has the oxidation state of Cr⁺³ having the ionic radius of 0.64 Å and it resembles iron in many respects. Cr⁺³ (0.64 Å) is close with the Al⁺³ (0.57 Å) and in particular Fe⁺³ (0.67 Å), thus it replaces iron and aluminium diadochially. Shaw (1954) observed Cr, V, Ni in great amounts in Pelitic rocks. Vanadium and chromium are close associates of titanium in the manganese ores and those contents increase with the increase of Fe₂O₃. Magaritz and Brenna (1979) showed the coherence between MnO₂, Fe₂O₃, Fe(OH)₃ is due to absorption of negatively charged chromium hydroxide sols.

In the normal ore analysis from the Koduru shows that the chromium content is varying from 100 to 1000 ppm whereas in the Garbham also it is between 274 to 1000 ppm. Roy (1966) has also noted the appreciable amount of chromium in the Koduru manganese ores. Dhan Raju (1969) reported an appreciable amount of chromium in the granites and calc-granulites of this area.

VANADIUM

In the Koduru area, the vanadium content varies from 38 to 216 ppm whereas from the Garbham, it ranges from 26 to 246 ppm. It replaces Ti (0.64Å), Fe⁺³ (0.65Å) and Al⁺³ (0.57Å). V⁺⁵ may replace P⁺⁵ (0.35Å). Landergreen (1948) stated that vanadium also replaces chromium. It is strongly enriched in titaniferrous iron ores. Though the size of V⁺³ ion is close to that Fe⁺³ (0.67Å) but according to Landergreen (1948) the diadochic replacement in this case is not very probable. In comparison with the chromium, the vanadium content in both these areas are very less. The vanadium in the ores is due to absorption of (VO₄)₃ by Fe(OH)₃ sals.

Based on the above observations the following conclusions are arrived.

1. The manganese ores of this area are anomalously enriched in iron which sometimes concentrates in amounts equivalent to manganese.
2. The ores also shows high content aluminum.
3. In general, the ores are rich in phosphorous which is variable from area to area.
4. It is also noted that the ores rich in alkali elements such as barium strontium, sodium, potassium etc.

The ores of primary or bedded type has high phosphorous content when compared with the ores of other environments. The ores from high pegmatitic activity areas contain maximum amount of phosphorous, and obviously indicate the phosphorous enrichment due to addition and redistribution through apatite mineralization. Apatite of different sizes and composition have been reported and are very common in the study areas. The ores from secondary environments contain less phosphorous when compared to primary ore horizons. This could be explained to be due to the effects of leaching, due to which the phosphorous along with sodium, potassium, etc. leached out.

The phosphorous content in ores of powdered nature is very high especially if these are affected by pegmatitic activity. The powdered zones are the result of structural deformation and pegmatitic activity. The high phosphorous ores are common in structurally weak zones.

REE GEOCHEMISTRY

REE Geochemical study for the manganese ores of the study area was not yet been investigated. The REE geochemistry as a tool for sedimentary processes has been used by many authors. Slight change in REE patterns may reflect a change in redox potential. Hence the REE patterns can be used in tracing out the post – depositional processes (ie diagenesis). The analytical results of selected ore samples are listed in (Table: 5) and shale normalized REE patterns are given in (fig. 14). Manganese ore associated with calc granulites having higher concentration of REE (Koduru deposits) when compared with manganese associated with quartzites (Garbham deposits).

TABLE V: RARE EARTH ELEMENTS COMPOSITION OF MANGANESE ORES OF VIZIANAGARAM DISTRICT, ANDHRA PRADESH.

	1	2	3	4	5
La	25	150	31	6	4
Ce	37	290	6.9	7.5	6.6
Nd	17	120	25	-	-
Sm	2	21	6.5	1.15	6.8
Eu	0.9	3.8	1.3	0.9	2
Uu	5.3	14.7	4.3	2.5	1.5
Lu	6.2	13.8	4.8	2.1	15

1-3 from Koduru, 4-Garbham, 5-Kondakinguva.

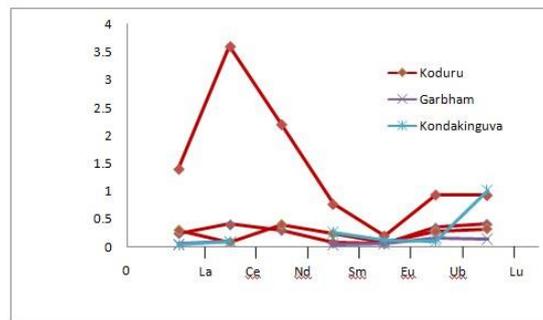


Fig.14. SHALE NORMALIZED REE PATTERNS FOR MANGANESE ORES OF VIZIANAGARAM DISTRICT, ANDHRA PRADESH.

The REE behavior of primary ores are believed to be rich in Eu (Komuro et al. 2006). However in the studied ores Eu was removed after extensive diagenetic modifications causing very low Eu values. Because of the oxidizing environment facilitated the oxidation of Ce^{3+} to Ce^{4+} , eventually this will develop a positive Ce anomaly. As the repeated oxic diagenesis continues it would enhances the Ce content in the ores more than other REE's. 1987). Therefore, the oxidation process would lead to REE enrichment. The Ce anomaly has been used as a redox measure of the environment of deposition by many authors (Glasby et al. 1987, Varentsov et al. 1964). The studied ore samples contain relatively low REE content and a positive Ce and low Eu anomalies. These patterns shows clear diagenetic features probably due to fresh water involvement in the ore formation. Positive Ce anomaly is indicative of terrigenous source and oxic conditions.

GENETIC MODAL

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 has been developed as a syngenetic part of the metasedimentary sequence of the Eastern Ghats Complex. These ores fall in the hydrogenous field and fresh water fields. In these deposits, metamorphic mineral 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. Manganese and 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 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 present within the oxide sediment.

The mode of solutioning 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 under alkaline conditions. Fe may be 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 (sivaprakesh 1980). Relatively high amounts of Si, Al and Ti in the Vizianagaram deposits are due to the admixture of detrital material during precipitation (choi and Hariya, 1992) Phosphorous is present as fine apatite crystals within silicates (Acharya 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 inferred based on the iron 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 giving rise to economically workable manganese deposits.

METAMORPHISM

After the deposition and diagenetic changes, the manganese rich sediments were metamorphosed along with conformable calcareous, pesammitic and pelitic sediments under granulitic faces conditions. The original oxides and hydroxides with an increase in P and T during metamorphism, transform to oxides / silicates. This is an essentially isochemical 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 country 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, hausmannite could result from the direct transformation of an early formed Fe-Mn hydroxide at 600°C -750°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)

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.

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 phosphorus in the original sediment and was enriched by granitic and pegmatitic activity in the area.

References

1. Acharya, B.C, Rao, D.S., 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) Phosphorus in the siliceous manganese ores of Nishikhal, Orissa, India. *Jour.Geol* 66(1); 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 Chiknaya Kanahalli — Green stone Belt, Karnataka studies in Earth Science Volume Bangalore University p.111-122.
5. Bhattacharayya. S, Krishna Rao. S.V.G, And Sharma. K.J 1984. On the nature of phosphorous in the manganese ores of Garbham – Garividi belt of Eastern Ghats *Indian Mineral*, V. 26, No:2
6. 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
7. Crerar.D.A, Cormick.R.K And Barnes.H.L 1980. Geochemistry of manganese, an over review. In I.M.Varenstov and Gy. Grasselly Eds. *Geology and Geochemistry of Manganese*. E.Schweizerbart'score. Verlagsbuchhandlung, Stuttgart, V. 1, pp 293-334.
8. Edwards.A.B 1954. *Texture of the Ore minerals and their significance*, Melbourne. Australasian Institute of Mining and Metallurgy (Inc), 2nd Edition.
9. Fermor, L.L., 1909, The manganese ore deposits of India: *Indian Geol, Survey Mem.*,v.37.
10. GOLDSCHMIDT.V.M 1929. *Die Naturgeschichte der Di sentamilie Sathal. D Eisen*, Heff. 18.
11. Goldschmidt.V.M AND PETERS.C.L 1931. *Zur Geochemie der. Scadinm Idib. Math – Physik. Klasse III, IV* pp 257.
12. Grassely.Gy, Szabe.Z And Bardossy.GY 1969. Data on the geology and mineralogy of the Eplency manganese ore deposits. *Ibid. Tonas XIX FASC*, 1 szeged Hungaria, pp 15-143.
13. Henry. Leep 1968. The distinction of manganese in the Animikian iron formations of Minnesota. *Econ. Geol.* V. 63, pp 61-75.
14. Krishna Rao, J.S.R., (1954). The geology of chipurupalle area, Vizagapatam district with special reference to the origin of manganese ores: *Geol., Mineralog. Metall. Soc. India Quart. Jour.*, v.26, p.35-44.

15. Krishna Rao, J.S.R., (1960). Structure and stratigraphy of the manganese deposits of Visakhapatnam and Srikakulam districts, India : *Econ. Geol.*, v.55 p.827-834.
16. Krishna Rao, S.V.G., Sarma, K.J and Bhattacharaya (1981) Potential characteristics of the low grade manganese ores in north coastal Andhra Pradesh, India. *Proc. Int symp.on recent advances in Beneficiation and Agglomeration held at Bhuvanesar.*
17. Krishna Rao. J.S.R. 1975. Some problems on the manganese ores of Andhra Pradesh. *Acta Mineralogica-Petrographic, Acta Univ. Szegediensis V. 22/1*, pp 133-141.
18. Krishna Rao. S.V.G, Sharma. K.J And Bhattacharayya. Samit 1981. Manganese silicate-carbonate protore (Quelzite) from the Srikakulam manganese belt, *A.P.Jour.Geol.Soc.India, V. 22, No.4.*
19. Kshirasagar.T.V.S.R 1971. Neutron activation instrumental analysis and its application to manganese ores and associated rocks (unpublished Ph.D Thesis submitted to Andhra University, Waltair).
20. Landergreen. Sture 1943. Geokemika studies over Grange bergsfaltets Jarnms.ma.Ing.Vetenskaps.Akad.Handl.No.172.
21. Magartiz.M And Brenner.I.B 1979. The geochemistry of lenticular manganese ore deposit, Uma, Bogma,Southern Sinai. *Mineral deposits (Berl)*, V. 14, pp 1-13.
22. 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.*
23. Mason.B(1958).*Principles of Geochemistry.* John.Wiley & Sons Inc, New York. (Text Book).
24. Mookherjee, A (1961). Distribution of minor elements in the gondote manganese ores and its geochemical significance. *Econ.Geo1.56:723-729.*
25. Mookherjee.A.1958. Paragenesis of the manganese minerals associated with the gonditic rocks near Khapa, Nagpur District, Bombay. *Quart. J. geol.Sco. India, V. 30*, pp 33-36.
26. 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.*
27. Nicholson, K (1988). An ancient manganese iron deposit of fresh water origin, Islay, Argyllshire. *Scott.J. Geo1.24 (2) 175-187.*
28. Okada, K., (1960) Thermal study on some todorokites: Japanese Assoc., Mineralogists, Petrologists, *Econ.Geologists Jour.*, v.45, p.49-53.
29. Pravakara Rao, G., 1950, The geology of manganese —bearing rocks of Garividi and Garbham, Vizagapatam : *Geol. Mineralog. Metall. Sco. India Quart. Jour.*, v.22. p.25-44.
30. Raghava Rao, K.V., and Srinivasa Rao, M., (1955). A Study of Khondalites, Charnockites and associated gneisses and manganese ores around Salur and Bobbili, Srikakulam district. *Geol. Mineralog. Metall. Sco. India. Quart. Jour.*, v.27. P.163-174.
31. 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, Maharashtra. *Geol. Survey. India. Spl.Publ.ser1:545-564.*
32. Raju. K. K. V. S 1986. Distribution and behavior of Phosphorous in the manganese ores minerals of Vijayanagaram, (A.P), India. Paper presented in the National Workshop on “ Removal of phosphorous from manganese ores” at R.R.L. Bhubaneswar.
33. Rankama, K., and Sahama, T.C., (1950) *Geochemistry* : Chicago, Univ. Chicago Press,912 p.
34. Rankama.K. And Sahama.G. 1950. “Geochemistry” The University of Chicago Press.
35. Rao, A.T (1999) Sappijine granulites from Marturu near Anakapalle in the EGMB, India : *Gondwana research memoris No.5,p.139-144.*
36. Ring Wood. A.E 1955. The principles governing trace elements distribution during magmatic crystallization. *Geochim. Cosmochim. Aeta, V. 7*, pp 542.

37. Roy,S (1960). Mineralogy and texture of the manganese ores of Koduru Srikakulam district, Andhra Pradesh, India: Canadian Mineralogist, v.6, p.491-503.
38. ROY.S. 1966. Syngentic manganese formations of India, Jadavpur University, Calcutta, pp 1-163. (TextBook).
39. 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.
40. Sigmundkoritrig 1965. Geochemistry of phosphorous the replacement of Si+4 by P+5 in the rock forming silicate minerals. Geochim. Et. Cosmochim. Acta., V. 29, pp 361-371.
41. Sivaprakash, C (1980). Mineralogy of Manganese Deposits of Koduru and Garbham, Andhra Pradesh, India. Econ. Geol.vol.75, pp.1083-1104.
42. Smirnov.V.I 1976. Geology of mineral deposits. Pp 1520. (Text Book).
43. TAGEEVA.N.V 1942. Flourine and boron in natural water and bearing on the occurrence of petroleum, Compt. Rend (Doklady) Acd. Sci., U.R.S.S., V. 34, pp 117.
44. Varentsov. I. M. 1964. Sedimentary manganese ores: Amsterdam, Elsevier, pp 119.
45. Visweswara Rao.K 1980. Studies on the geochemistry and mineralogy of manganese ore deposits of Srikakulam and Vizianagaram district, A.P., India. (Unpublished Ph.D. Thesis submitted to Andhra University, Waltair).
46. Vugt.J.H.L 1931. On the average composition of the Earth's crust with particular reference to the content of phosphoric and titanitic acid, Skrifta Norske videnskaps – Akd. Oslo. I. Mat-nature classes No.7.