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Geochemistry of Major Oxides in Host Rocks in Vizianagarm Manganese Ores Belt (A.P.), India

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Abstract

The abundance, distribution trends and significance of the major oxides in the host rocks in Vizianagarm Manganese Ores Belt (A.P.) (between N latitude 18˚12' and 18˚30' and E longitudes 83˚20' and 83˚45'), 15 samples of host rocks from different localities of the area under study were collected and analyzed for major oxides. We describe here in major oxides geochemistry of host rocks and manganese ore deposits associated with Precambrian Khondalite and Charnockite in Vizianagarm Manganese Ores Belt (A.P.): 1) Preponderance of SiO_2 over Al_2O_3; 2) Dominance of K_2O and CaO over Na_2O; 3) Abnormally high concentration of phosphorus and a positive relationship of P_2O_5 with CaO and Ti contents; 4) Manganese increases with increases of iron, lime and soda and *vice versa*, 5) CaO increases with the increases of Al_2O_3, Ti, K_2O and *vice versa*. High P_2O_5 content in these manganese ores appears to be the result of precipitation from secondary manganese rich solutions containing dissolved phosphorus from the P_2O_5 enriched host rocks. Another source of P_2O_5 may be the associated granitic and pegmatitic intrusions. Elements like K, Na, Ca, Mg, Co, Ni, Pb and Zn etc. appear to be mostly concentrated in the Mn-minerals viz. psilomelane, cryptomelane, hollandite and pyrolusite and related secondary phases [1] and [2]. Stratigraphically, the study area includes within a thick succession of Precambrian Group belonging to the Khondalite and Charnockite Groups of Dharwar Supergroup, that form a part of Eastern Ghat Complex of India. The manganiferous rocks that have been encountered in the Vizianagarm Manganese Ores Belt (A.P.) India are known as Kodurites.

Keywords

Vizianagarm, Manganese Ores, Major Oxides, Khondalite, Charnockite, A.P., Geochemistry, Eastern Ghat, Dharwar Supergroup

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1. Introduction

A large number of manganese deposits occur in the Precambrian Eastern Ghats complex of Andhra Pradesh, India. These are dominantly low to medium grade metamorphic deposits with high iron, phosphorus and silica. These manganese bands (deposits) are generally syngenetic and syntectonic with metasedimentry country rock of Khondalite, quartzite and calc-granulites [3].

Manganese ores are widely distributed throughout the Peninsular India. Stratigraphically, these are mainly confined to the Precambrian terrain and are encountered in the Sausar Group and Aravalli Supergroup of central and western India, Iron ore Group and Gangpur Group of eastern India. In Andhra Pradesh, there are major occurrences of manganese ores in Srikakulam-Visakhapatnam Manganese ores belt. The deposit is in this belt over an area of 50 kms in length and 20 km in width. The study area lies 150 km NE of Visakhapatnam and includes Garividi, Garbham and Chipurupalle areas (**Figure 1**). Systematic geochemical study of these manganese ores in the present study area was not carried out by earlier workers. Fifteen samples of host rocks were selected from different localities of the study area. They were analysed for number of major oxides and trace elements.

2. General Geology and Stratigraphy

The manganiferous rocks that have been encountered in the Srikakulam-Visakhapatnam manganese belt of Andhra Pradesh belongs to Kodurite Series which is typically exposed at Koduru (18˚16': 83˚36') a locality about 80 km north of Visakhapatnam, the rock series which constitutes an integral part of the Eastern Ghat complex of India. The rock series is composed of an intimate assembalges of metamorphosed argillaceous (garnet-sillimanite gneisses) as at Chipurupalle, Rayagada and Garbham, Arenaceous (Quartzite and garnetiferous

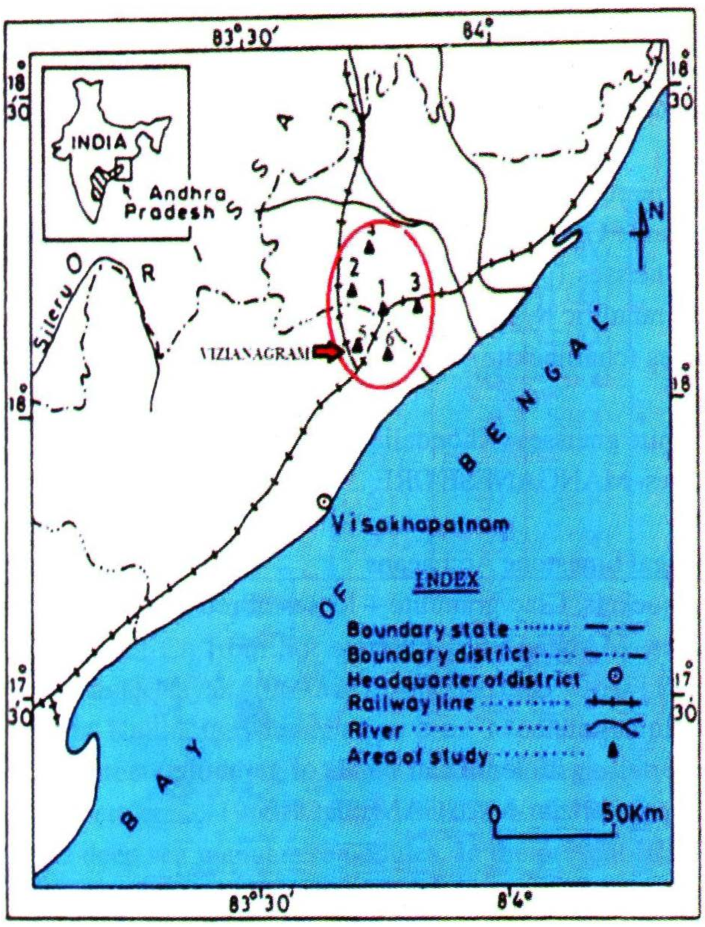

Figure 1. Location map of (1) Garividi, (2) Garbham (3) Chipurupalle manganese deposits, Vizianagram Manganese Ores Belt, (A.P.), India.

quratzite) as at Garbham, Koduru, Perapi and Avagudem and calcareous sediments (calc-granulites and gneisses) as at Koduru and Gadabavalasa areas, this sequences belonging to granulite facies.

The manganese ores in the area occur primarily in association with calc-granulites, less often with quartzite and still less with the quartz garnet ± sillimanite graphite gneiss. According to [4] who made radiometric determination of the Precambrain rocks of India, the Eastern Ghat Complex was included in the Precambrain-II (2500 - 3000 m.y.) of the classification of Indian Precambrain rocks. The calc-granulite, quartzite and Khondalites being syn-sedimentary rock bodies, are conformable and co-folded with the associated lithic units such as garnetiferous quartzite, gneisses and garnet-sillimanite gneisses, etc. [5]. Subsequently, granitic and migmatitic activities of different intensities played their respective roles on these metasediments transmuting their earlier textural and mineralogical characters. However, their impact on quartzite and manganese ore is minimal, probably because these units are considered to be the resisters during migmatisation [6]. At places hypersthene gneisses (Charnockite) occur as intrusive bodies in the synsedimentary rock units. All these rocks have in turn been intruded by granite, pegmatite and quartz veins [7].

[8] recongized several rock types ranging from ultrabasic to acidic in the mineralogical composition of Kodurite and ascribed them to differentiation prior to intrusion. [9] indicated that the Kodurite series might be due to hybridism on a large scale in which a granitic intrusion bodily assimilated the manganese of the Khondalites. [10] observed that by and large the manganese ore occurs associated either with quartzite (East Garbham) or with calc-granulite (Sadanandapuram).

However, the geological association in Saibaba main, Saibaba Central, Jai Bhavani-Kottakarra quaries is not clear owing to the highly weathered nature of the rocks. [11] suggested the following stratigraphic succession of the area under study and consider the granites to be intrusive bodies into the Khondalite and Kodurite series.

$$\left.\begin{array}{lr} 4 & \text{Granites} \\ 3 & \text{Charnockites} \\ 2 & \text{Kodurites}\cdots\text{Hybrid} \end{array}\right\}\text{Peninsular and Crystalline Complex}$$

$$\left.\begin{array}{ll} 1 & \text{Calc-granulites, crystalline limestone} \\ & \text{and associated manganese ores} \\ & \text{Garnet-Sillimanite gneisses} \\ & \text{Quartzite-Garnetiferous, Feldspathic} \\ & \text{and graphite-bearing} \end{array}\right\}\text{Khondalite Series}$$

These rocks at places exhibit relict banding. The Garbham main quarry and the Srinavasa quarry at Garbham show weathered calc-granulite-quatzo-feldslpathic rock underlying quartzite. The rock formation and associated manganese ore deposits belonging to the Khondalite and Charnockite suit of metasediments are of the Archaean age [7]. The generalised stratigraphic sequence of the rock formations of Srikakulam area which has been suggested by [7] and supported by [12] is presented as follows:

Granite, pegmatitie and quartz vein

Hypersthese-gneisses (Charnockites?)

$$\text{Khondalite Series}\left\{\begin{array}{l} \text{Garnet-sillimanite gneisses (khondalites)} \\ \text{Garnet-granulites} - \text{Ore horizon I} \\ \text{Calc-granulites} \\ \text{Garnet-granulites} - \text{Ore horizon II} \\ \text{Garnet-sillimanite gneissess (khondalites)} \\ \text{Coarse grained quartzites)} \\ \text{Feldspathic quartzite} \\ \text{Garnetiferous quartzite} - \text{Ore horizon III} \\ \text{Feldspathic quartzites} \\ \text{Coarse grained quartzites} \\ \text{Garnet-sillimanite gneisses (Khondalites)} \\ \text{Biotite-gneisses} \end{array}\right.$$

Crystalline algal limestone belonging to Knondalite Group (Archaean) [13]-[17] and gritty sandstone (Miocene?) in the form of rubble and laterite capping are also observed.

The present authors finds no evidence to differ from the suggestion made by [7] and [18], regarding the stratigraphic succession in Srikakulam except that the occurrence of crystalline algal limestone and shales (red and green) which did not find place in their classification. The modified sequence is presented [13]-[17] as follows:

Some of the earlier workers have also made an attempts to classify and establish the sequence of rock formations encountered at Garividi, Garbham and Chipurupalle areas (**Table 1** and **Figure 2**). They are as follows:

Garividi area [10]

Soil
Laterite-pisolites and concretions of
Mn-ore and calc-tufa
Pegmatite and quartz veins
Granites/garnetiferous biottie gneiss
Garnet-sillimanite gneiss (with or without graphite)
Calc-granulite and lenticles of crystalline limestone
Manganese ore and garnet granulites
Quartz-feldspar rock with occasional incidence of apatite
Garnet-sillimanite gneiss interlayered with quartzite and occasional lenticles of crystalline limestone

Garham Area [10]

Soil
Laterite-calc tufa calcreta
Pegmatite: pegmatite and quartz veins
Garnet/granite gneiss
Garnetiferous and non-garnetiferous quartzo-feldspathic rock
Biotite-gneiss
Charnockite
Garnet-sillimanite gneiss with or without graphite
Calc-granulite with manganese ore associated with bands and pockets of lithomarge and highly kaolinised

Table 1. Geological succession of the Garividi area, Srikakulam-Visakhapatnam belt (A.P.).

Age	Group	Rock types
Recent		Alluvium and soil
Pleistocene (?)		Laterite-limonite and ochre
Miocene (?)		Sandstone
		Pegmatite and quartz vein
		Granite and granite gneisses
Archaeans ←	Charnockite Group ←	Hypersthene gneisses (porphyro-blastic) (Charnockite)
		granulitic hypersthene diorite and granite gneisses (Charnockite).
		Garnet sillimanite gneisses (Khondalite)
	Khondalite Group ←	Garnet granulite—MAGANESE ORE HORIZON – I
		* Crystalline algal limestone Archaeans
		* Green shale pockets, calc-granulite + lenses of red shale
		Garnet granulites—MANGANESE ORE HORIZON II
		Coarse grained quartzite
		Feldspethic quartzite with lenticular bands of garnetiferous quartzite—MANGANESE ORE HORIZON III
		Coarse grained quartzite
		Garnet-sillimanite-gneisses (Khondalite)
		Biotite gneisses

Two horizons were not reported by earlier workers, reported for the first time [15] and [19].

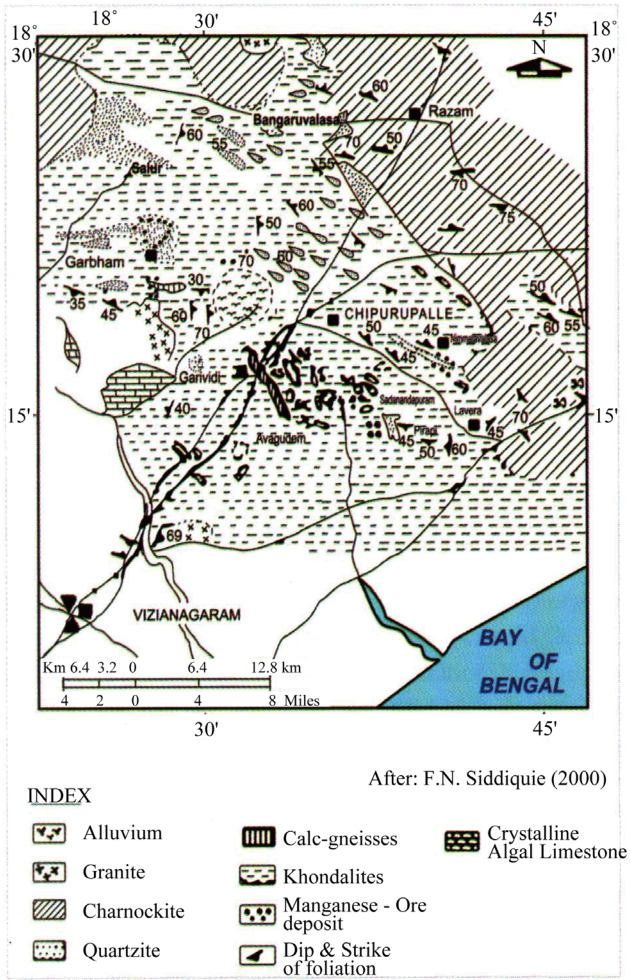

Figure 2. A generalised geological map of Garividi, Garbham and Chipurupalle manganese deposits, Vizianagram district (A.P.), India.

quartzo-feldspathic apatite rock, the latter in the majority of cases seen underlying the Mn-ore zone.

Calc-granulite highly weathered with intermixture of quartz-feldspar-apatite rock

Manganese ore with chert and lemonite quartzite

Garnet-sillimanite gneiss (with or without graphite) interlayered with quartzite

Chirpurupalle area [20]

Archaean:
- Recent laterite and loamy alluvium
- Granite gneisses
- Manganese rich rocks, "Kodurites"
- Khondalite series:
- Calc-granulites
- Quartz-garnet-sillimanite gneisses
- Quartzites

3. Major Oxides in Host Rocks

General Statement

In the area of study, the host rocks for manganese mineralization, are mainly Khondalite and Charnockite Group of rocks.

Fifteen samples of host rocks were selected out of a large number of samples collected for their chemical analysis out of which ten samples were of Khondalites and remaining five of Charnockites. The samples were analysed chemically for the determination of their major oxides—SiO_2, Al_2O_3, TiO_2, MnO, Fe_2O_3, FeO, P_2O_5, MgO, CaO, Na_2O, K_2O and H_2O^+ and some trace elements which are discussed [21]. The relative variation trends of various major oxides are shown in **Figure 3**. The analytical data are presented in **Table 2**.

4. Distribution of the Major Oxides

The abundance and variation range with average (wt%) of different major oxides of Khondalites and Charnockites are given in (**Table 2** and **Table 3**) and the distribution of various major oxides are discussed as below:

4.1. Silica (SiO_2)

The quantitative variation trend of silica in the host rocks from 47.84 percent to 70.45 percent and gives an average value of 61.81 percent (**Table 3**, **Figure 3**). Khondalite, Charnockite rocks have wide variation of silica (**Table 3**). [22] reported 58.04% to 74.38% SiO_2 from Srikakulam area, [11] reported 58.4% from Garividi, [23] reported 67.10% and 69.90% respectively from Charnockites of Tamil Nadu and Karnataka. The histogram (**Figure 4(a)**) represents frequency percent distribution, showing polymodal nature of SiO_2 in the host rocks. The maxima is at 65 - 70 percent class. The typical mode of SiO_2 falls between 65 - 70 percent.

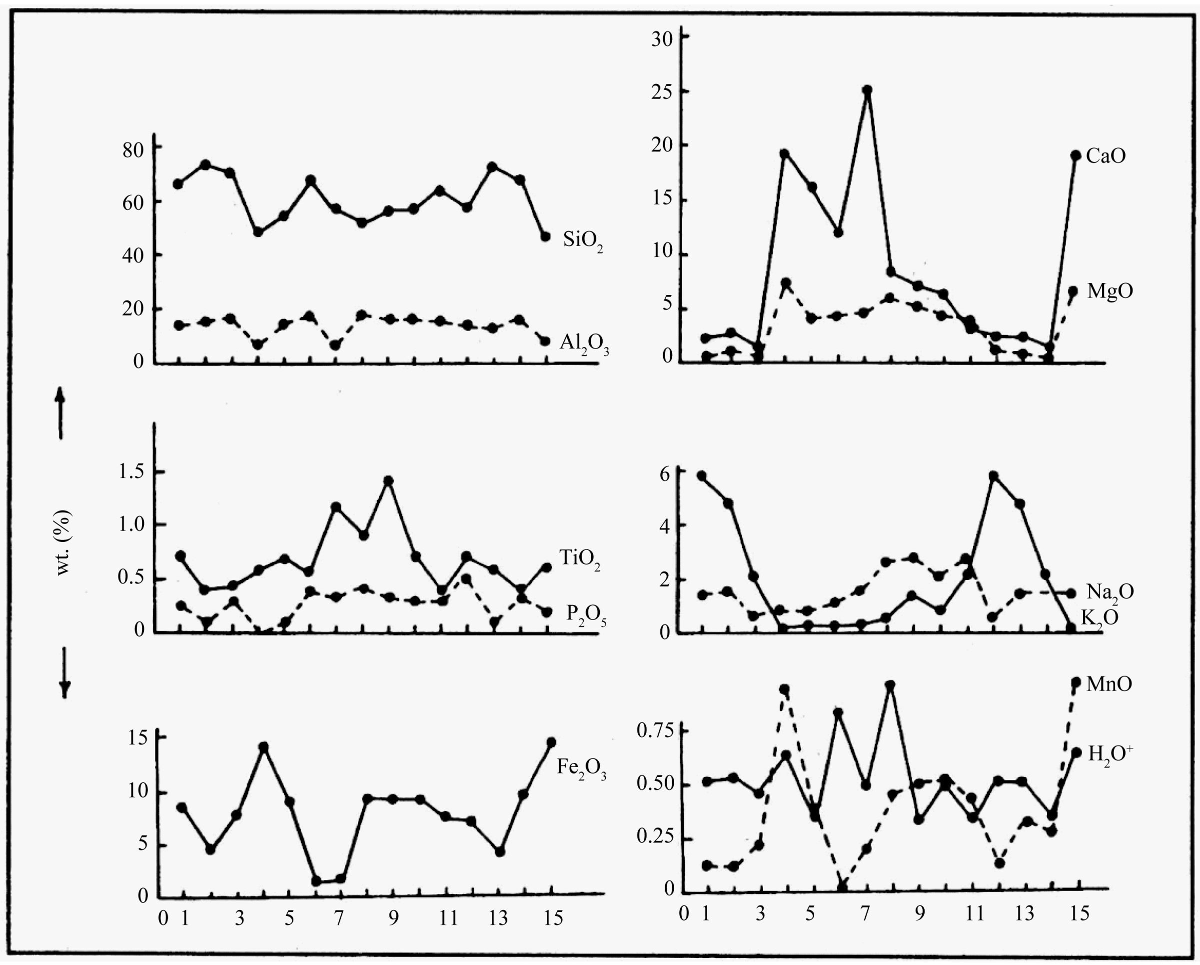

Figure 3. Variation diagrams of major oxides in Khondalite and Charnockite Groups of Garividi, Garbham and Chipurupalle areas, Srikakulam-Visakhapatnam Belt (A.P.).

Table 2. Distribution of major oxides of Khondalite and Charnockite Groups of Garividi, Garbham and Chipurupalle areas, Srikakulam-Visakhapatnam Belt (A.P.).

	KD1	KD2	KD3	KD4	KD5	KD6	KD7	KD8	KD9	KD10	CK11	CK12	CK13	CK14	CK15
SiO_2	69.35	70.3	70	48.84	56.1	68.46	58.29	52.24	56.1	59	64.16	69.09	70.45	68	47.84
Al_2O_3	13.09	13.45	16.75	6.42	13.4	10.94	6.32	17.42	16.34	16.02	15.66	13.35	13.12	16.4	7.42
MnO	0.12	0.12	0.21	0.94	0.36	0.08	0.21	0.4	0.5	0.52	0.38	0.12	0.3	0.26	0.9
Fe_2O_3	1.21	1.16	3.36	1.3	1.06	0.44	0.54	2.2	1.48	2.22	2.07	1.21	1.64	3.36	2.3
FeO	4.52	3.64	4.6	13.11	7.19	1.2	1.45	7.48	6.7	5.74	4.25	3.16	4.59	12.11	7.2
P_2O_5	0.24	0.1	0.3	n.d.	0.1	0.42	0.36	0.45	0.35	0.33	0.32	0.51	0.1	0.35	0.14
TiO_2	0.73	0.4	0.47	0.6	0.79	0.58	1.18	0.9	1.45	0.72	0.44	0.72	0.6	0.48	0.6
CaO	2.37	2.42	1.25	19.83	16.2	12.44	25.61	8.86	7.32	6.77	3.2	2.33	2.4	1.25	19.83
MgO	0.86	1.09	0.86	7.9	4.14	4.17	4.58	5.8	5.03	4.6	3.12	1.9	1.11	0.86	6.9
Na_2O	1.52	1.6	0.34	0.67	0.7	1.2	1.6	2.48	2.56	2.08	2.84	0.56	1.4	2.16	1.67
K_2O	5.94	4.96	2.16	0.02	0.24	0.16	0.2	0.64	1.42	0.94	2.2	5.9	4.97	2.09	0.02
H_2O^+	0.51	0.53	0.49	0.62	0.35	0.8	0.5	0.96	0.3	0.5	0.3	0.52	0.52	0.34	0.62
Total	100.46	99.77	100.79	100.25	100.63	100.89	100.76	99.55	100.33	100.4	100.43	100.46	99.77	100.14	100.35

KD = Khondalite; CK = Charnokite; n.d. = Not Detectable.

Table 3. Range of variation and average oxide % of Khondalite and Charnockite Groups of Garividi, Garbham and Chipurupalle areas, Srikakulam-Visakhapatnam Belt (A.P.).

Oxides	Minimum	Maximum	Average
SiO_2	47.84	70.45	61.81
Al_2O_3	6.32	17.42	13.07
TiO_2	0.12	0.94	0.36
MnO	0.44	3.36	1.45
Fe_2O_3	1.20	13.11	5.79
FeO	0.10	0.51	0.27
P_2O_5	0.40	1.45	0.70
CaO	1.25	25.61	8.80
MgO	0.86	7.90	3.52
Na_2O	0.34	2.84	1.55
K_2O	0.02	5.94	2.12
H_2O^+	0.30	0.96	0.52

4.2. Alumina (Al_2O_3)

The quantitative variation trend of Alumina in the host rocks of the study area ranges 6.32 percent to 17.42 percent and gives an average value of 13.07 percent (**Table 3**).

Khondalite and charnockite rocks show wide variation of Al_2O_3 (**Table 3**). [22] reported 9.65% to 20.64% Al_2O_3 from Srikakulam area. [24] reported 14.08% from feldspar garnetiferous granite-gneiss of Peddapantupalli, and [23] reported 14.10% and 15.10% from Charnockites of Tamil Nadu and Karnataka. The histogram (**Figure 4(b)**) represents frequency percent distribution, showing polymodal nature of Al_2O_3. The maxima is at 12 - 14 and 16 - 18 percent classes.

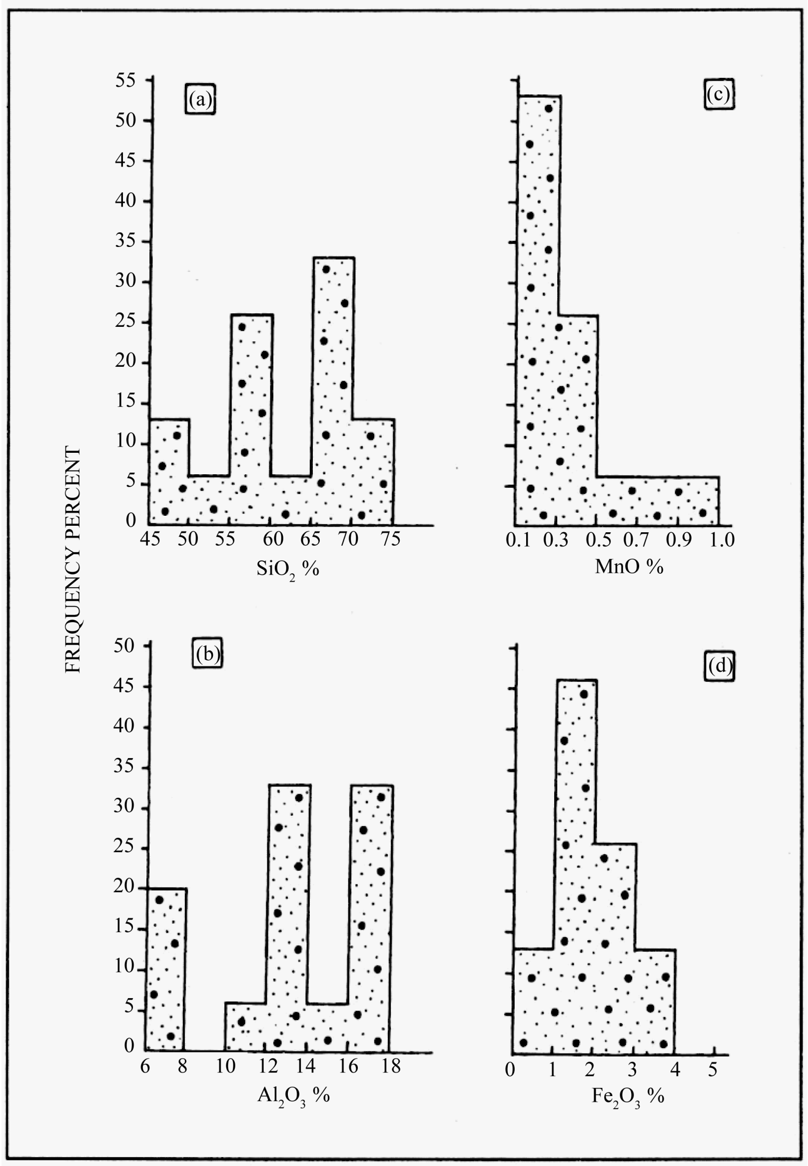

Figure 4. Histograms showing frequency percent distribution of SiO_2, MnO, Al_2O_3 and Fe_2O_3 in Khondalite and Charnockite Groups of Garividi, Garbham and Chipurupalle areas, Srikakulam-Visakhapatnam Belt (A.P.).

4.3. Manganese (MnO)

The quantitative variation trend of manganese monoxide in the Khondalite and Charnockite rocks ranges from 0.12 percent to 0.94 percent and gives an average value of 0.36 percent (**Table 3**).

[22] reported 0.09% to 3.70% from the Srikakulam area whereas Khondalites of Sri Lanka consist 0.18% MnO [25], [23] reported 0.05% and 0.02% from Charnockites of Tamil Nadu and Karnatka.

The histogram (**Figure 4(c)**) represents frequency percent distribution, showing unimodal positively skewed nature of MnO. The maxima is at 0.1 to 0.3 percent class and the typical mode of MnO also lies in the same class.

4.4. Ferric Oxide (Fe_2O_3)

The quantitative variation trend of Fe_2O_3 in the host rocks ranges from 0.44 percent to 3.36 percent and gives an average value of 1.45 percent (**Table 3**).

[22] reported 0.86% to 3.76% from Srikakulam area. [24] reported 1.22% from feldspar garnetiferous granite-gneiss of Peddapantupalli area, [23] reported 4.36% and 2.36% from the Charnockite of Tamil Nadu and Karnataka (**Table 3** and **Table 4**).

The histogram (**Figure 4(d)**) represents frequency percent distribution, showing unimodal positively skewed nature of Fe_2O_3. The maxima is at 1 to 2 percent class and the typical mode also lies in the same class.

4.5. Ferrous Oxide (FeO)

The quantitative variation trend of FeO in the host rocks ranges from 1.20 percent to 13.11 percent and gives and average value of 5.79 percent (**Table 3** and **Table 4**).

The Khondalites and Charnockites having higher concentration of FeO as compared to Fe_2O_3 (**Table 3** and **Table 4**), [22] reported 1.12% to 8.04% from same area, [26] reported 9.98% from hypersthene-granulite of Narasimhunipeta, [11] reported 8.04% from Khondalites of Garividi and [23] reported 3.60% and 1.30% from Charnockites of Tamil Nadu and Karnataka (**Table 3** and **Table 4**).

The histogram (**Figure 5(a)**) represents frequency percent distribution, showing polymodal nature of FeO. The maxima is at 3 to 5 percent class and typical mode also lies in the same class.

4.6. Phosphorus (P_2O_5)

The quantitative variation trend of P_2O_5 in the host rocks ranges from 0.10% to 0.51% and gives an average value of 0.27 percent (**Table 3**, and **Table 4**).

The concentration of P_2O_5 is abnormally on the higher side in the manganese ores as well as in the host rock of the study area, whereas [22] reported 0.18% to 1.01% from the various areas of Srikakulam district, [11] reported 0.75% from Khondalites of Garividi, and [24] reported 0.24% from feldspar garnetiferous granite-gneiss of peddapantupalli (**Table 3** and **Table 4**).

The histogram (**Figure 5(b)**) represents frequency percent distribution, showing bimodal nature of P_2O_5. The maxima is at 0.3% to 0.4% class. The typical mode of P_2O_5 is also lies between 0.3 percent to 0.4 percent class.

4.7. Titania (TiO_2)

The quantitative variation trend of TiO_2 in the host rocks ranges 0.40 percent to 1.45 percent and gives an average value of 0.70 percent (**Table 3**).

Table 4. Average major oxide (wt%) of the host rocks (Khondalite and charnokite) compared with other Khondalites and Charnockites.

	I	II	III	IV	V	VI	VII	VIII
SiO_2	60.86	63.90	68.36	60.75	60.08	58.04	67.10	69.90
Al_2O_3	13.01	13.19	14.08	14.49	12.38	17.30	14.10	15.10
TiO_2	0.77	0.56	0.73	0.36	0.65	1.65	0.80	0.41
Fe_2O_3	1.49	2.10	1.22	1.75	3.28	1.20	4.36	2.36
FeO	5.70	5.97	4.51	9.98	4.20	8.04	3.60	1.30
MnO	0.35	0.39	0.11	0.10	0.18	2.27	0.05	0.02
MgO	3.90	2.77	0.85	3.26	1.95	5.90	2.31	1.09
CaO	10.30	5.80	2.37	5.10	9.43	1.40	2.82	3.20
Na_2O	1.47	1.72	1.52	2.62	2.59	0.88	3.91	4.79
K_2O	1.66	3.03	5.93	1.20	3.06	3.24	2.23	1.49
P_2O_5	0.26	0.28	0.24	0.05	-	0.75	0.02	0.08
H_2O	0.55	0.46	0.44	0.51	1.80	0.15	0.47	0.16

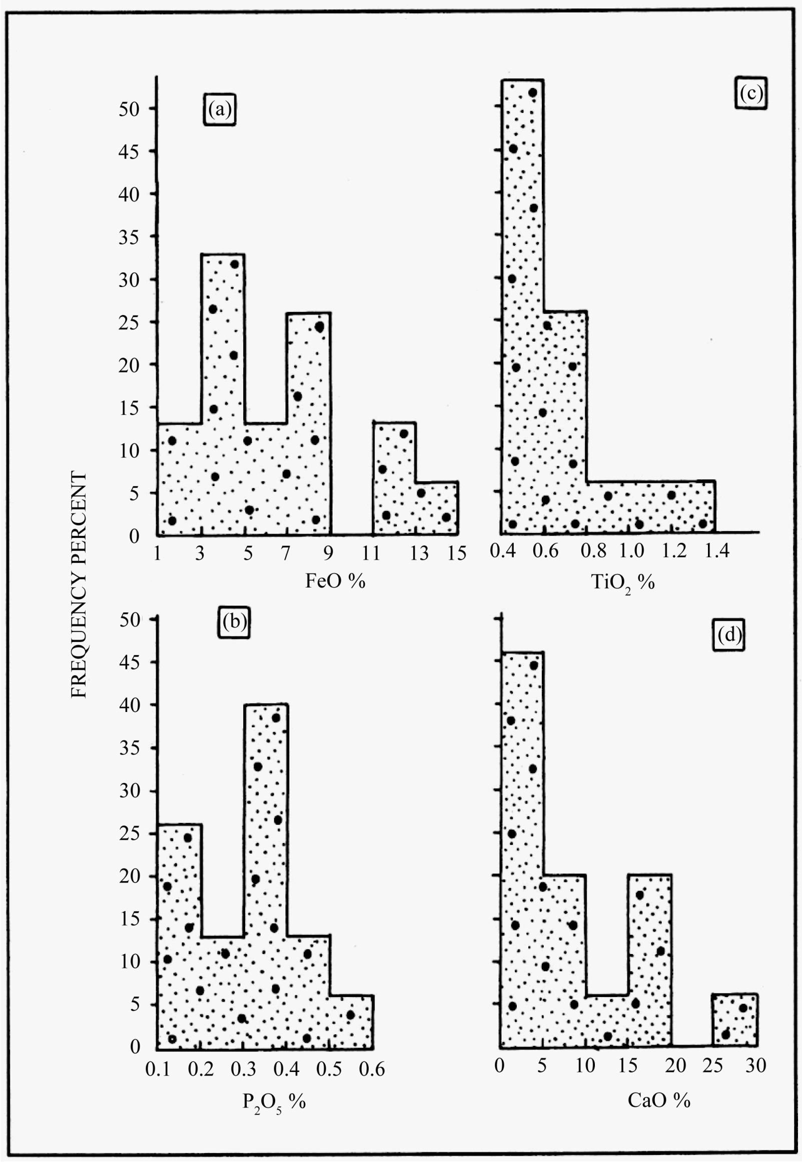

Figure 5. Histograms showing frequency percent Distribution of FeO, TiO_2, P_2O_5 and CaO in Khondalite and Charnockite Groups of Garividi, Garbham, and Chipurupalle areas, Srikakulam-Visakhapatnam Belt (A.P.).

[24] reported 0.73% from feldspar garnetiferous granite-gneiss of Peddapantupalli, Khondalite of Sri Lanka shows 0.65% TiO_2 [25]. [11] reported 1.65% from Khondalite of Garividi and [23] reported 0.80% and 0.41% from Charnockites of Tamil Nadu and Karnataka.

The histogram (**Figure 5(c)**) represents frequency percent distribution showing unimodal, positively skewed nature of TiO_2. The maxima is at 0.4 to 0.6 percent class and the typical mode also lies between 0.4 to 0.6 percent class.

4.8. Lime (CaO)

The quantitative variation trend of calcium oxide in the host rocks of the study area ranges from 1.25 percent to 25.61 and gives and average value of 8.80 percent (**Table 3** and **Table 4**).

The CaO in the Khondalites and Charnockites of the study area shows a wide variation range from 1.25% to 25.61% (**Table 3** and **Table 4**), Rao, K.V.R. (1955) reported 5.10% from hypersthene-granulite from the Narasimhunipeta and Krishnan (1934) reported 9.43% CaO in Khondalites of Sri Lanka (**Table 3** and **Table 4**).

The histogram (**Figure 5(d)**) represents frequency percent distribution, showing bimodal nature of CaO. The maxima is at 1 percent to 5 percent class. The typical mode lies between 1 percent to 5 percent class.

4.9. Magnesia (MgO)

The quantitative variation trend of MgO in the host rocks ranges from 0.86 percent to 7.90 percent and gives and average value of 3.52 percent (**Table 3** and **Table 4**).

Rao, K.V.R. (1955) reported 3.26% from hypersthene-granulite of narasimhunipeta, [11] reported 5.90% from Khondalites of Garividi and [23] reported 2.31% from Charnockites of Tamil Nadu (**Table 3** and **Table 4**).

The histogram (**Figure 6(a)**) represents frequency percent distribution, showing bimodal nature of MgO. The typical mode of MgO and maxima lie between 0 to 2 and 4 to 6 percent classes.

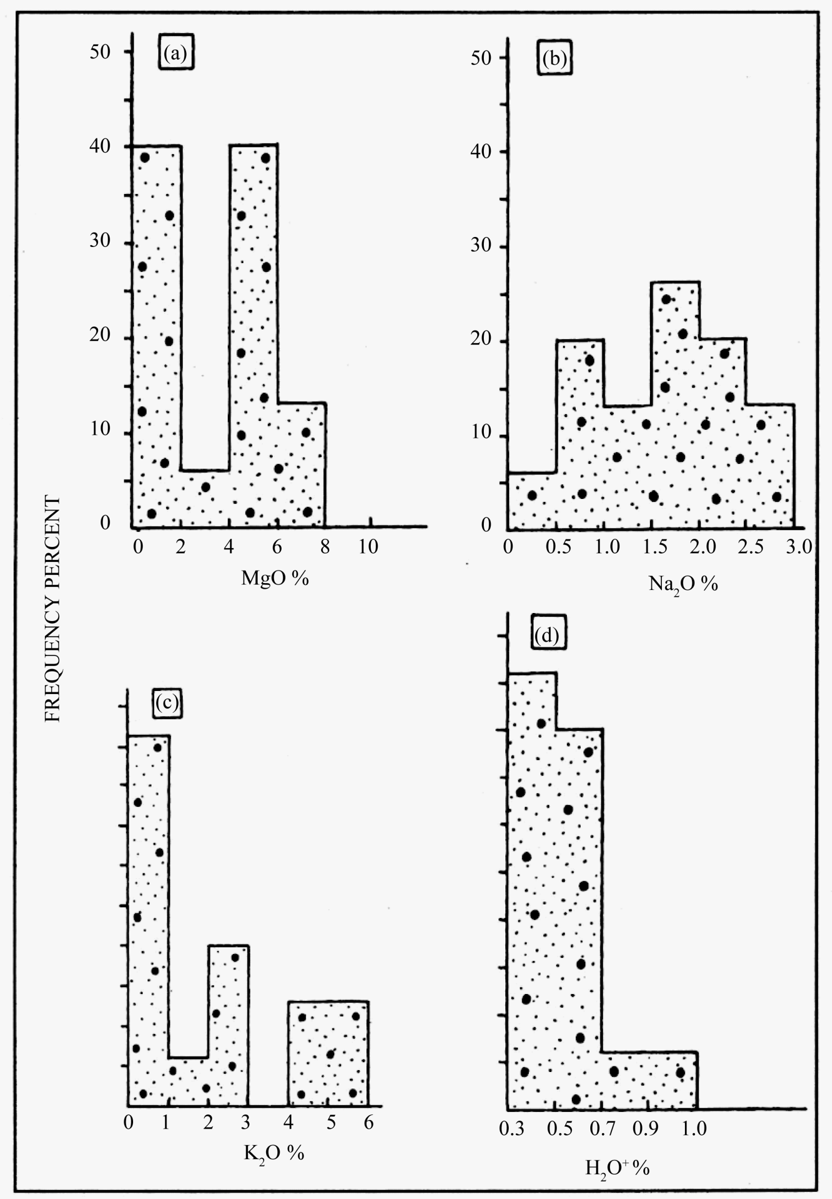

Figure 6. Histograms showing frequency percent distribution of MgO, K_2O, Na_2O and H_2O^+ in Khondalite and Charnockite Groups of Garividi, Garbham and Chipurupalle areas, Srikakulam-Visakhapatnam Belt (A.P.).

4.10. Soda (Na_2O)

The quantitative variation trend of Na_2O in the host rocks ranges from 0.34 percent to 2.84 percent and gives an average value of 1.55 percent (**Table 3** and **Table 4**).

Rao, K.V.R. (1955) reported 2.62% from hypersthene granulite of Narasimhunipeta, 2.59% reported in Khondalites of Sri Lanka Krishnan (1934), and [23] reported 3.91% and 4.79% from Charnockites of Tamil Nadu and Karnataka (**Table 4**).

The histogram (**Figure 6(b)**) represents frequency percent distribution, showing polymodal nature of Na_2O. The maxima is at 1.5 percent to 2.0 percent class, and the typical mode also lies in the same class.

4.11. Potash (K_2O)

The quantitative variation trend of K_2O in the host rock ranges from 0.02 percent to 5.49 percent and gives an average value of 2.12 percent. [24] reported 5.93% from feldspar garnetiferous granite-gneiss of peddapantupalli, 3.06% reported from Khondalites of Sri Lanka [25].

[11] reported 3.24% from Khondalites of Garividi, and [23] reported 2.23% from Charnockites of Tamil Nadu (**Table 4**).

The histogram (**Figure 6(c)**) represents frequency percent distribution, showing polymodal nature of K_2O. The maxima is at 0 to 1 percent class and typical mode also lies in the same class.

The Khondalites and Charnockites have wide variation of potassium oxide. This higher amount of K_2O is due to the presence of potash feldspar and micaceous mineral in these rocks. The high potash contents in Khondalites and Charnockites are possibly due to the migmatisation, which took place by the injection of feldspathic (K-feldspar) fluid. The megacrystic K-feldspar in them crystallised from the injected fluid and also by the segregation of the neo-mobilised feldspathic components during migmatisation. According to [27], the main supply of alkalies came probably from the intrusive igneous rocks, another probable source might be the quartz with its numerous fluid inclusion.

4.12. Water (H_2O^+)

The quantitative variation trend of H_2O^+ in the host rocks ranges from 0.30% to 0.96% and gives an average value of 0.52 percent.

[24] reported 0.44% from feldsdpar garnetiferous granite-gneiss of peddapantupalli, [26] reported 0.51% from hypersthene-granulite of Narasihunipeta, and [23] reported 0.47% from Charnockites of Tamil Nadu.

The histogram (**Figure 6(d)**) represents frequency percent distribution, showing unimodal positively skewed nature of H_2O^+. The maxima is at 0.3 to 0.5 percent and typical mode also lies in the same class.

5. Mutual Relationship

An attempt has been made to determine the geochemical relationship of MnO with SiO, Al_2O_3, FeO, K_2O, Na_2O, CaO (**Figures 7(a)-(f)**), and Fe_2O_3 in Khondalite and Charnockite Groups of Garividi, Garbham and Chipurupalle areas, Srikakulam-Visakhapatnam Belt (A.P.). The mutual relationships of significant oxides are plotted in various diagrams and discussed as follows:

5.1. Silica (SiO_2)

The computed correlation coefficient of silica shows strongly antipathetic relationship with MnO (**Figure 7(a)**) and FeO (relationship of SiO_2 with Fe_2O_3 and FeO and Al_2O_3 with Fe_2O_3 in Khondalite and Charnockite Groups of Garividi, Garbham and Chipurupalle areas, Srikakulam-Visakhapatnam Belt (A.P.)) and MgO and shows slightly negative relationship with TiO_2, Na_2O and H_2O^+ (**Table 5**).

These relationships reveal that with the increase of SiO_2 there is correspondingly decrease in MnO, FeO, TiO_2, CaO, MgO, Na_2O and H_2O^+ and *vice versa*. The negative relationship of silica with manganese and FeO probably indicates that manganese and FeO are the substitutes of silica. It appears that the negative relationship of MnO with silica is possibly due to the alteration of manganese bearing minerals into silicate minerals. The highly variable silica/alumina ratio (**Table 6**) and sympathetic relationship of silica with Al_2O_3, Fe_2O_3 and K_2O favours the coexistence of quartz and aluminosilicate minerals in the Khondalite and Charnockite rocks. The

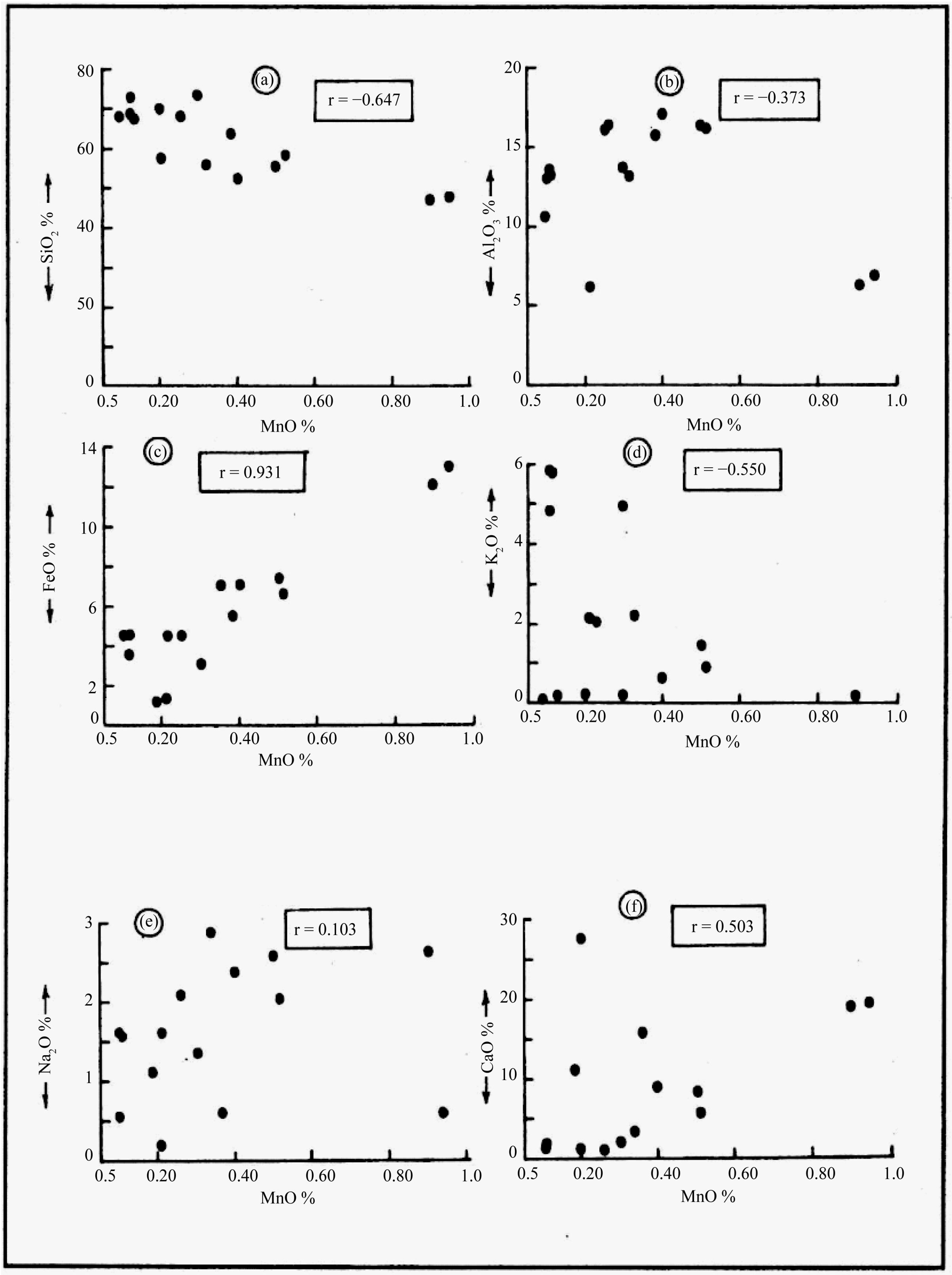

Figure 7. Relationship of MnO with SiO_2, Al_2O_3, FeO, K_2O, Na_2O and CaO in Khondalite and Charnockite Groups of Garividi, Garbham and Chipurupalle areas, Srikakulam-Visakhapatnam Belt (A.P.).

Table 5. Correlation coefficient between the various constituents of Khondalite and Charnockite Groups of Garividi, Garbham and Chipurupalle areas, Srikakulam-Visakhapatnam Belt (A.P.).

S.No.	SiO_2	**Al_2O_3**	**MnO**	**Fe_2O_3**	**FeO**	**P_2O_5**	**TiO_2**	**CaO**	**MgO**	**Na_2O**	**K_2O**	**H_2O^+**	Ni	Co	Pb	Zn	Cr	Sr	V	Li
SiO_2	1	0.3863	−0.0348	0.0348	−0.7988	0.2349	−0.4119	−0.7385	−0.9348	−0.1741	0.7329	−0.2199	0.1747	0.0957	0.6072	−0.2634	0.0899	0.0178	−0.2974	0.0779
Al_2O_3		1	−0.3746	0.5374	−0.2285	0.4139	−0.0116	−0.7976	−0.4863	0.3681	0.2813	−0.2005	0.3542	0.2514	0.0668	0.0683	0.239	−0.0308	−0.1491	−0.3063
MnO			1	0.1993	0.9319	−0.474	0.0923	0.5032	0.7941	0.1035	−0.5504	0.0573	−0.0163	0.2032	−0.249	0.0689	−0.2299	−0.219	0.1018	0.1688
Fe_2O_3				1	0.2476	0.0803	−0.3351	−0.4456	−0.2154	0.1929	−0.0402	−0.1686	0.3964	0.6076	0.2426	−0.3531	0.1611	−0.3805	−0.1415	0.091
FeO					1	−0.467	0.0407	0.3514	0.6977	0.0139	−0.4058	0.0484	−0.1092	0.1699	−0.2559	0.0429	−0.0546	−0.0091	0.1808	0.0044
P_2O_5						1	0.298	−0.2433	−0.1491	0.2804	0.0272	0.1629	0.2422	0.1302	−0.1324	0.0787	0.2954	−0.3134	0.3457	−0.3347
TiO_2							1	0.3417	0.3732	0.2686	−0.2434	−0.0778	−0.1786	−0.4448	−0.5717	0.4041	0.2491	0.0493	0.5239	−0.1731
CaO								1	0.7822	−0.1503	−0.7267	0.2387	−0.225	−0.3526	−0.5382	0.1953	−0.2272	0.0612	0.238	0.0786
MgO									1	0.1214	−0.7766	0.3612	−0.1259	−0.1526	−0.6402	0.3623	−0.2005	−0.0782	0.2634	−0.0911
Na_2O										1	−0.1265	−0.1089	0.0251	0.3904	−0.0253	0.0677	0.1261	−0.3141	−0.0978	−0.4564
K_2O											1	−0.1963	−0.1984	0.0819	0.6583	−0.2417	0.2086	0.0984	−0.0662	0.1648
H_2O+												1	−0.4218	−0.365	−0.2954	0.2541	0.1423	0.1041	−0.005	−0.0424
Ni													1	0.429	0.0073	−0.0018	−0.5629	−0.4311	−0.0747	0.2016
Co														1	0.5297	−0.347	−0.1564	−0.5655	−0.2778	0.0288
Pb															1	−0.6955	0.0855	−0.338	−0.2282	0.3454
Zn																1	−0.2832	0.3346	−0.2687	−0.125
Cr																	1	0.2135	0.3407	−0.4597
Sr																		1	−0.1375	−0.378
V																			1	−0.1025
Li																				1

higher concentration of silica is due to the presence of quartz and other siliceous minerals a characteristic feature of the original pellitic sedimentary rocks. Furthermore the high concentration of silica in the rocks of study area is possibly due to the presence of scapolite.

Silica shows a sympathetic relationship with Al_2O_3, Fe_2O_3, P_2O_5 and K_2O ($r = 0.732$) (**Table 6**). The positive relationship of silica with these elements is possibly due to the presence of potash feldspar and other alumino-silicate minerals.

5.2. Alumina (Al_2O_3)

The alumina is negatively but insignificantly related with MnO (**Figure 7(b)**), FeO (**Figure 7(c)**), TiO_2, MgO, and H_2O^+ and strongly antipathetic with CaO ($r = 0.79$. As evident from the (**Table 6**), alumina shows positive relationship with SiO_2, Fe_2O_3 ($r = 0.73$, P_2O_5, Na_2O and K_2O). However, a strong positive relationship appears between Al_2O_3 & Fe_2O_3 ($r = 0.73$). By correlation coefficient it therefore appears that like other few oxides, e.g., FeO, TiO_2, MgO, H_2O^+, the alumina is also not significantly related with MnO. Further the positive relationship of alumina with silica, Fe_2O_3, Na_2O and K_2O indicates the presence of sillimanite, kyanite, andalusite, orthoclase, microcline. The high Al_2O_3/Fe (total iron) ratio (**Table 6**) in both Khondalite and Charnockite is identical to that found in alumino-silicate minerals.

The abnormally high Al_2O_3 content is some samples of host rocks may be due to the presence of white specks of kaoline, found in cleavages and cracks of garnet [11]. These specks appear to be the cause of these abnormally high values. The abundance of alumina and silica can be assigned to the argillaceous nature of the parent rocks.

Table 6. Fe_2O_3/FeO, SiO_2/Al_2O_3, Na_2O/K_2O, CaO/MgO, MnO/P_2O_5, MnO/CaO, Al_2O_3/TiO_2, MnO/Fe (total iron) Al_2O_3/Fe (total iron) ratios of Khondalite and Charnockite Groups of Garividi, Garbham and Chipurupalle areas, Srikakulam-Visakhapatnam Belt (A.P.).

Sample Nos.	Fe_2O_3/FeO	SiO_2/Al_2O_3	Na_2O/K_2O	CaO/MgO	MnO/P_2O_5	MnO/CaO	Al_2O_3/TiO_2	MnO/Fe (Total Iron)	Al_2O_3/Fe (Total Iron)
1	**0.26**	**5.29**	**0.255**	**2.75**	0.5	0.050	17.93	0.020	2.284
2	0.318	5.22	0.322	2.22	1.2	0.049	33.62	0.031	3.539
3	0.730	4.17	0.157	1.45	0.7	0.168	35.63	0.026	2.104
4	0.099	7.60	33.5	2.51	0.94	0.047	10.7	0.065	0.445
5	0.147	4.18	2.91	3.91	3.6	0.022	16.9	0.043	1.625
6	0.366	6.25	7.5	2.98	0.42	0.014	18.86	0.109	6.67
7	0.372	9.22	8.0	5.59	0.58	0.008	5.74	0.105	3.175
8	0.305	2.99	3.87	1.52	0.88	0.045	18.35	0.042	1.853
9	0.197	3.43	1.80	1.45	1.42	0.068	11.26	0.056	1.823
10	0.331	3.68	2.21	1.47	1.57	0.076	22.25	0.058	1.795
11	0.360	4.09	1.29	1.02	1.18	0.118	35.59	0.048	2.005
12	0.284	5.17	0.094	1.22	0.23	0.051	18.50	0.021	2.445
13	0.518	5.36	0.281	2.16	3.0	0.125	21.86	0.062	2.733
14	0.732	4.14	1.03	1.45	0.74	0.208	34.16	0.032	2.062
15	0.189	6.44	83.5	2.87	6.42	0.045	12.36	0.062	0.514

The generally high concentration of alumina is possible due to the presence of alumina-silicate minerals, *i.e.*, feldspar, micaceous minerals and sillimanite (in garnet-sillimanite gneisses). In feldspar Si^{4+} (radius 0.42 Å) is replaced by Al^{3+} (radius 0.50 Å) in Si-O tetrahedra [28].

5.3. Manganese (MnO)

The MnO shows strong antipathetic relationship with SiO_2 ($r = -0.84$) and K_2O (**Figure 7(d)**), whereas it shows feebly negative relationship with Al_2O_3 and P_2O_5.

As evident from **Table 4**, the MnO, in the Khondalite and Charnockites of the present area have strong positive relationship with FeO ($r = 0.93$) and MgO ($r = 0.79$) and slightly positive relationship with Fe_2O_3, TiO_2, Na_2O (**Figure 7(e)**), Cao (**Figure 7(f)**) and H_2O^+, MnO/CaO ratio is constant. The positive relationship of MnO with Fe_2O_3, FeO and the constant MnO/Fe (total iron) (**Table 6**) ratio indicate that iron and manganese were delivered in the same proportion. The constant MnO/Fe ratio suggests coprecipitation of Mn and Fe under fairly oxidizing condition. The small quantity of manganese determined from the country rocks has most probably been derived from the manganese silicate minerals like manganese bearing garnets, pyroxenes, and other Mn bearing minerals presents in the host rocks ([14] [29]-[31]) possibly in association of ferruginous magnesium rich calc-granulite and garnet sillimanite gneiss and hypersthene gneisses.

5.4. Iron Oxides

The relationship of Fe_2O_3 with TiO_2, CaO, MgO, K_2O and H_2O^+ is negative as Fe_2O_3 increase with the decrease of these elements or *vice versa*.

The antipathetic relationship of Fe_2O_3 with MgO in Khondalite and Charnockite rocks may be explained by the replacement of Fe^{3+} (0.67 Å) by Mg^{2+} (0.66 Å) [32]. The higher FeO/Fe_2O_3 values is Khondalite from the Eastern Ghat granulite belt of India indicate lower oxidation conditions in Early Proterozoic [33]. In Eastern Ghat granulite belt of India the variation in FeO/Fe_2O_3 ratio from one area to the other suggests that these sediments were deposited in different basins with different pH. Eh conditions of deposition [33]. The Khondalite and charnockite rocks of the area under study, exhibit composition variation in iron (total iron), ranging from 1.64% to 14.41% and exhibit high MgO values. Random variation is also observed in K_2O, Na_2O and iron in ternary diagram showing high and random distribution of MgO in Khondalites (Δ) and Charnockites (•) of Garividi, Garbham and Chipurupalle areas, Srikakulam-Visakhapatnam Belt (A.P.) Fe_2O_3 (Total Iron), (**Table 7** and **Table 8**).

The significant relationship between various other oxides are also taken into consideration for example relationships of Al_2O_3 with TiO_2 (**Figure 8(a)**), CaO with MgO (**Figure 8(b)**) and Fe_2O_3 (**Figure 8(c)**) and FeO (**Figure 8(d)**).

5.5. Titania (TiO_2)

Titanium oxide shows positive correlation with MnO, FeO, P_2O_5, CaO, MgO and Na_2O whereas SiO_2, Al_2O_3 (**Figure 8(a)**), Fe_2O_3, K_2O and H_2O^+ are negatively correlated with TiO_2. The positive correlation of TiO_2 with CaO (r = 0.34), MgO (r = 0.37) and Na_2O (r = 0.26) clearly indicates that much of the TiO_2 contains in Khondalite and Charnockite rocks were possibly derived from the titanium bearing minerals like sphene.

5.6. Lime (CaO)

The graph and computed correlation coefficient of calcium show positive relationship with MnO in relationship of MnO with SiO_2, Al_2O_3, FeO, K_2O, Na_2O and CaO in Khondalite and Charnockite Groups of Garividi, Garbham and Chipurupalle areas, Srikakulam-Visakhapatnam Belt (A.P.), FeO, TiO_2 and H_2O^+ and strongly positive relationship with MgO (r = 0.78), (**Figure 8(b)**). CaO show antipathetic relationship with Fe_2O_3, P_2O_5 and Na_2O and strongly antipathetic relationship with SiO_2 (r = 0.78), Al_2O_3 (r = −0.79) and K_2O (r = 0.726). The ratio of CaO and MnO is constant. The Khondalite and Charnockite rocks of the study area having fairly high concentration of CaO (range from 1.25% to 25.61%). Furthermore diopside, wollastonite, anorthite, scapolite, piedmontite and calcite also contributed varying proportion of CaO to the Khondalite and Charnockite rocks. The lime content seems to be of migmatitic origin [38]. The relationship between various other oxides are also taken into consideration for example relationships of Fe_2O_3 (**Figure 9(a)**), SiO_2 with FeO (**Figure 9(b)** and **Figure 9(c)**) and in these host rocks of Garividi, Garbham and Chirpurupalle areas.

5.7. Phosphorus (P_2O_5)

The concentration of P_2O_5 is abnormally on the higher side in the manganese ores as well as in the host rocks of the study area. However, P_2O_5 shows insignificant negative relationship with MnO, FeO, CaO and MgO.

The ratio of MnO and P_2O_5 is variably low and high. Whereas P_2O_5 shows positive relationship with SiO_2, Al_2O_3, Fe_2O_3, TiO_2, Na_2O, K_2O and H_2O^+. The positive relationship of P_2O_5 with SiO_2, Al_2O_3 and K_2O appears

Table 7. Recalculted to 100 wt% of bulk components (Fe_2O_3 + MgO), Na_2O and K_2O in Khondalite rocks of Garividi, Garbham and Chipurupalle areas, Srikakulam-Visakhapatnam Belt (A.P.).

Sample No	(Fe_2O_3 + MgO)	Na_2O	K_2O
1	46.9	10.8	42.2
2	42.7	13.9	43.3
3	77.9	3.0	19.0
4	97.0	2.9	0.08
5	92.9	5.2	1.8
6	81.0	16.7	2.2
7	78.4	19.1	2.3
8	82.9	13.5	3.4
9	77.8	14.2	7.9
10	81.7	12.5	5.6

Table 8. Recalculated to 100 wt% of bulk components (Fe_2O_3 + MgO), Na_2O and K_2O in Charnockite rocks of Garividi, Garbham and Chipurupalle areas, Srikakulam-Visakhapatnam Belt (A.P.).

Sample No	(Fe_2O_3 + MgO)	Na_2O	K_2O
1	68.4	17.7	13.7
2	53.2	4.0	42.6
3	48.1	11.4	40.4
4	67.4	16.5	16.0
5	92.6	7.2	0.08

Fe_2O_3 total iron.

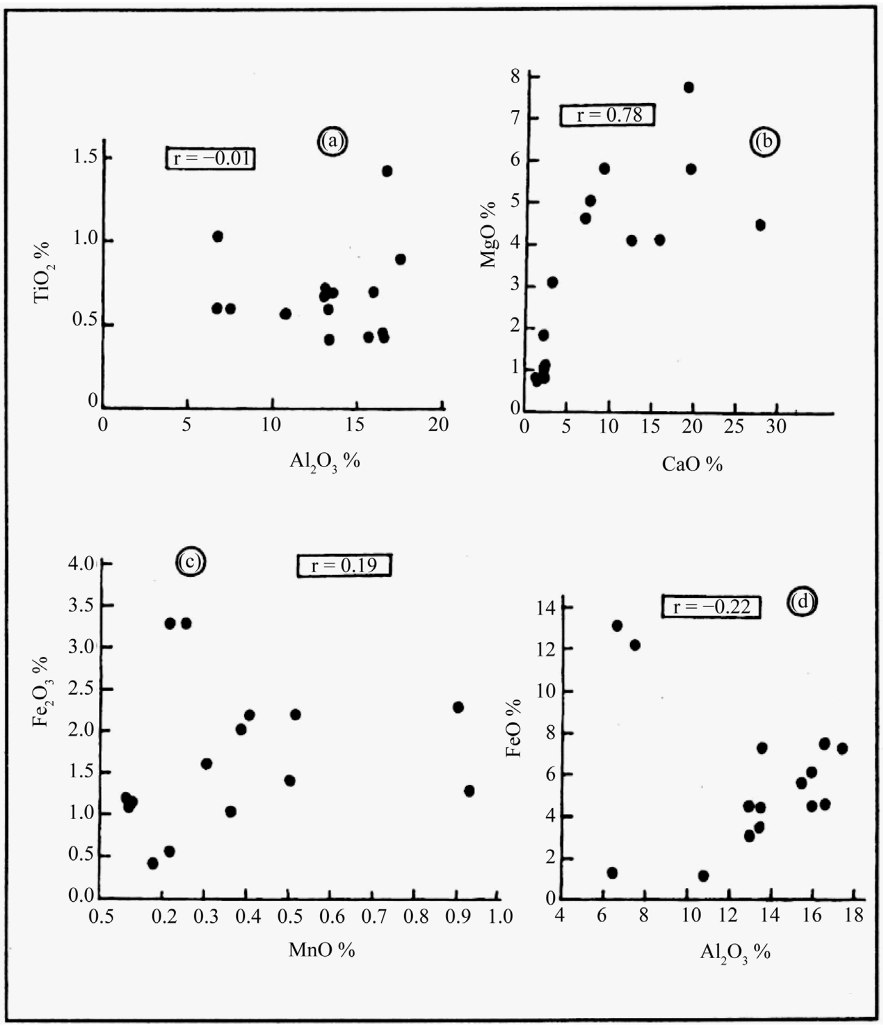

Figure 8. Relationship of Al_2O_3 with TiO_2 and FeO, and CaO with MgO and MnO with Fe_2O_3 in Khondalite and Charnockite Groups of Garividi, Garbham and Chipurupalle areas, Srikakulam-Visakhapatnam Belt (A.P.).

to be due to the presence of alumino-phosphate minerals probably leucophosphate formed by the reaction of phosphate rich solutions with clay minerals. The chemical reaction which indicates the formation of leucophosphate as given by [34] is as follows:

$$Al_2Si_2O_5(OH)_4 + 2HPO_4^{2-} \rightarrow 2AlPO_4 \cdot 2H_2O + 2SiO_2 + H_2O$$

$$2AlPO_4 \cdot 2H_2O + KOH \rightarrow KAl_2(PO_4)_2 OH \cdot 2H_2O + 2H_2O$$

Further the positive relation of P_2O_5 with Fe_2O_3 clearly indicates the ferruginous nature of phosphate minerals. According in [1] [27] [31] [35], the source of phosphorus in the original manganiferous rocks is apatite and spessartite which are the common constituent of the rocks associated with gondite and Kodurite types.

[36] reported up to 4.10 percent P_2O_5 in spessartite. The presence of apatite in the host rocks indicates that they were subjected to metamorphism in a more hydrous environment as also suggested by [37].

The manganese silicate-carbonate, clay and silica. In few mines as in Avagudem the manganese carbonate was either deposited in the form of carbonate or formed through diagenesis of manganese oxide [39].

5.8. Magnesia (MgO)

The present study reveals that MgO is positively correlated with FeO, CaO, MnO, TiO_2, Na_2O and H_2O^+ whereas it is negatively correlated with Al_2O_3, Fe_2O_3, P_2O_5, SiO_2 and K_2O (**Figures 9(a)-(c)**).

The Khondalites and Charnockites of the study area show higher concentration of MgO (ranges from 0.86% to 7.90%). [33] also reported higher concentration of MgO in Khondalites from the Eastern Ghat granulite belt of India.

These Khondalite with high MgO content can be compared with Late-Archaean-Early Proterozoic metapelites. In the area under study the Khondalite and Charnockite rocks exhibit compositional variations (**Table 9** and

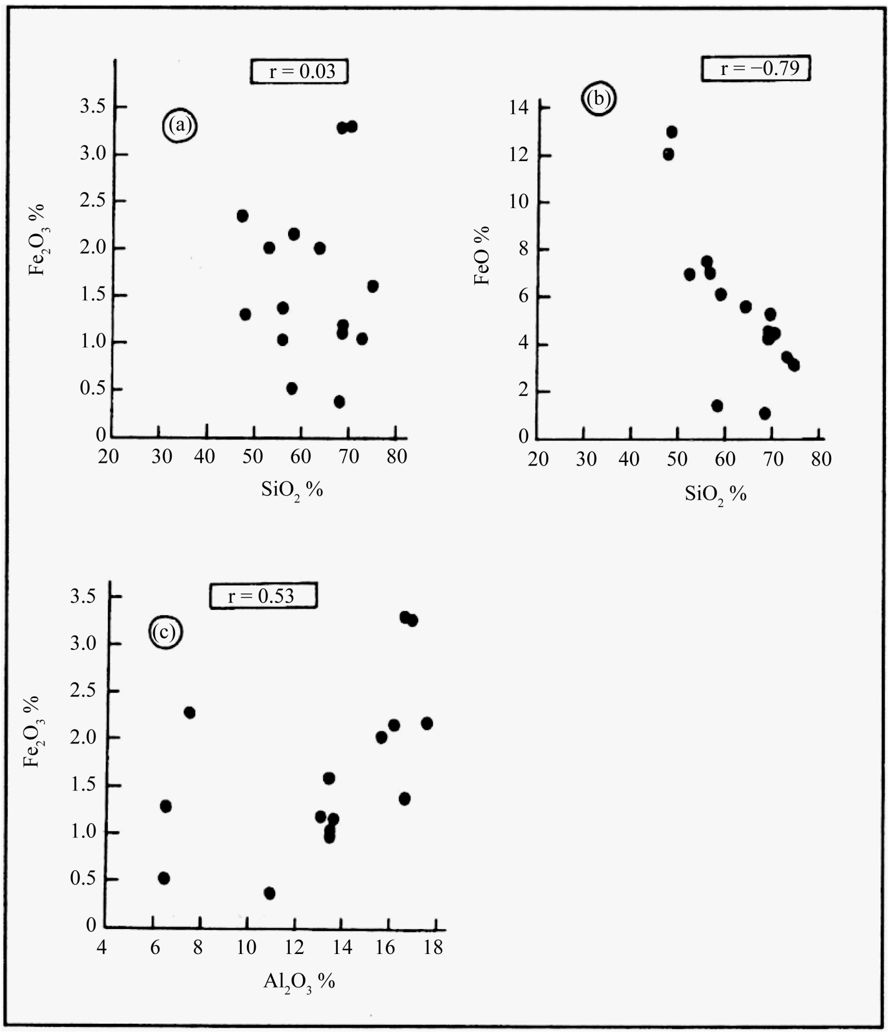

Figure 9. Relationship of SiO_2 with Fe_2O_3 and FeO and Al_2O_3 with Fe_2O_3 in Khondalite and Charnockite Groups of Garividi, Garbham and Chipurupalle areas, Srikakulam-Visakhapatnam Belt (A.P.).

Table 9. Recalculated to 100 wt% of bulk components MgO, Na_2O and K_2O in Khondalite rocks of Garividi, Garbham and Chipurupalle areas, Srikakulam-Visakhapatnam Belt (A.P.).

Sample No	MgO	Na_2O	K_2O
1	10.3	18.2	71.3
2	14.2	20.9	64.8
3	25.5	10.1	64.2
4	92.9	7.8	.2
5	81.4	13.7	4.7
6	75.4	21.6	2.8
7	71.7	25.0	3.1
8	65.0	27.8	7.1
9	55.8	28.4	15.7
10	60.3	27.2	12.3

Table 10) in MgO (ranges from 0.86% to 7.90%), K_2O (ranges from 0.02% to 5.94%) and Na_2O (ranges from 0.34% to 2.84%). The ternary diagram (**Figure 10**) shows wide scatter distribution of MgO, K_2O and Na_2O.

The concentration of magnesium oxide is possibly due to the presence of garnet, spinel, hornblende, magnesium rich pyroxenes and biotite in the rocks of the study area. All these minerals pointing to the argillaceous nature of the original sediments which gave rise to these rocks.

5.9. Soda (Na_2O)

In the Khondalite and Charnockite rocks soda shows positive relationship with Al_2O_3, MnO in relationship of MnO with SiO_2, Al_2O_3, FeO, K_2O, Na_2O and CaO in Khondalite and Charnockite Groups of Garividi, Garbham and Chipurupalle areas, Srikakulam-Visakhapatnam Belt (A.P.), Fe_2O_3, FeO, P_2O_5 and TiO_2.

These rocks in few samples show exceptionally high Na_2O/K_2O ratio. The ternary diagram (**Figure 11**) shows wide scatter distribution of K_2O and Na_2O.The presence of soda is due to the presence of feldspar and also due to the presence of scapolite in the Khondalites of study area [11]. The main supply of alkalies probably came from the igneous intrusion which cut across the Khondalite and Charnockite rocks. The high soda concentration in these rocks suggests the existence of predominantly tonalite/trondhjemite rocks in the source area. A study of granitic/gneissic episodes of the South Indian shield [40]-[42] indicates that the Early Archaean.

Post-greenstone granitic and gneissic episodes of the stable craton are mostly tonalitic/trondhjemitic in nature and K-rich granites appeared only in Late Proterozoic which explains better the high soda content in Proterozoic Khondalites of the Eastern Ghats. Predominance of soda rich tonalites and trondhjemites in Early Archean crust is also reported from other shield areas [43] [44]. Wide distribution in Na_2O from area to area may indicate to different temperatures of Na-rich and mafic source material indifferent basins [33].

5.10. Potash (K_2O)

K_2O shows insignificant negative relationship with CaO, MgO, MnO in relationship of MnO with SiO_2, Al_2O_3, FeO, K_2O, Na_2O and CaO in Khondalite and Charnockite Groups of Garividi, Garbham and Chipurupalle areas, Srikakulam-Visakhapatnam Belt, Fe_2O_3, FeO, TiO_2, Na_2O and H_2O^+. However, it shows strongly positive relationship with SiO_2 and slightly positive relationship with Al_2O_3 and P_2O_5 (**Table 4**). The dominance of K_2O over Na_2O is characteristic of parametamorphic rocks [20] and these rocks have exceptionally high and variable Na_2O/K_2O ratio. Potassium and sodium also show close coherence with aluminium, which is possibly due to the presence of soda and potash feldspar in these rocks.

5.11. Water (H_2O^+)

Water shows positive relationship with MnO, FeO, P_2O_5, CaO and MgO and negative relationship with SiO_2, Al_2O_3, Fe_2O_3, TiO_2, Na_2O and K_2O.

Table 10. Recalculated to 100 wt% of bulk components MgO, Na_2O and K_2O in Charnockite rocks of Garividi, Garbham and Chipurupalle areas, Srikakulam-Visakhapatnam Belt (A.P.).

Sample No	MgO	Na_2O	K_2O
1	38.2	34.8	26.9
2	22.7	6.6	70.5
3	14.8	18.7	66.4
4	16.8	42.2	40.9
5	80.3	19.4	0.2

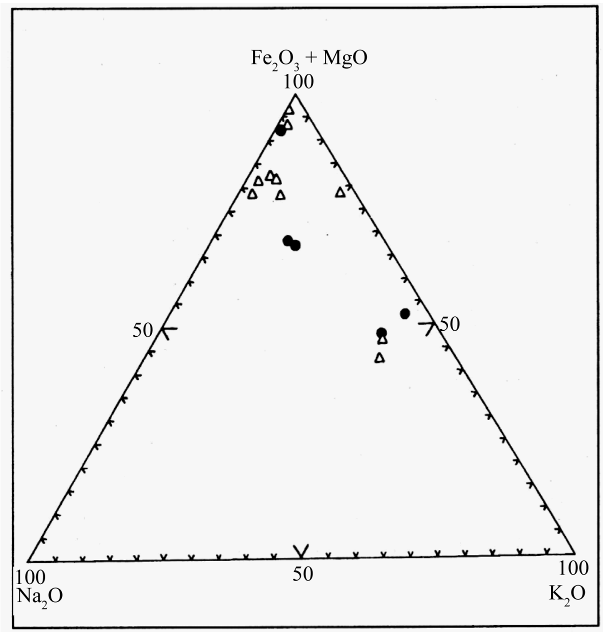

Figure 10. Ternary Diagram showing high and random distribution of MgO in Khondalites (Δ) and Charnockites (•) of Garividi, Garbham and Chipurupalle areas, Srikakulam-Visakhapatnam Belt (A.P.) Fe_2O_3 (Total Iron).

6. Conclusions

The analysis of 15 host rocks samples reveals that:
- Silica increases with the increases of Al, phosphorous and potash and *vice versa*.
- Alumina increases with the increases of SiO_2, P_2O_5, Na_2O and K_2O and *vice versa*.
- Mn increases with the increases of Fe and *vice versa*.
- MnO also shows strong sympathetic relationship with MgO and Na_2O.
- Phosphorous decreases with increase of MnO and *vice versa*.
- Ti increases with the increases of Mn and *vice versa*.
- Lime increases with the increases of Mn and *vice versa*.
- Mg increases with the increases of MnO and *vice versa*.
- Soda increases with the increases of both Mn and Fe and *vice versa*.
- Potash decreases with the increases of both Mn and Fe and *vice versa*.

The geochemical behavior of the host rocks indicate that the evolution of the ores took place in two different stage.

In first stage, sediments were rich in Mn, deposited in a basin during typical condition of oxidation. The chemical alteration and metamorphism of these sediments gave rise to the formation of primary metamorphic

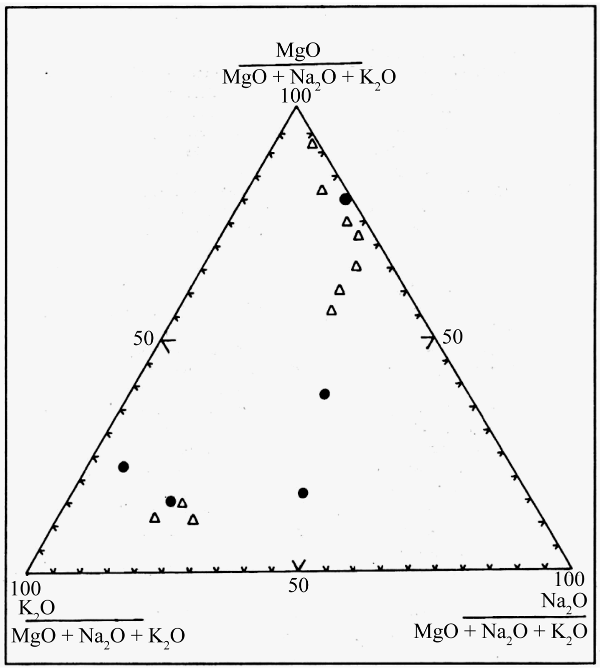

Figure 11. Ternary Diagram showing Wide Scatter of Na_2O and K_2O in Khondalites (Δ) and Charnockites (•) of Garividi, Garbham and Chipurupalle areas, Srikakulam-Visakhapatnam Belt (A.P.).

Mn minerals. In the later stages these metasediments suffered metasomatism due to intense igneous intrusions which caused hybridization at places.

In the second stage, the previously formed Mn ores and Mn-silicates of the country rocks like Mn-rich garnets and pyroxenes which played an important role in the formation of secondary Mn minerals viz. psilomelane-cryptomelane, hollandite, pyrolusite and wad etc. by the alteration. The meteoric water rich in CO_2 played an important role in solution, transportation, precipitation, concentration and finally redeposition of the secondary Mn ores.

The concentration and redeposition have largely taken place from colloidal state or solution in oxidizing environment. It is assumed that Mn and Fe are in colloidal state. The anions and cations of minor and trace elements are adsorbed on the surface of negatively charged $Mn(OH)_4$ and positively charged $Fe(OH)_3$ particles. The high K_2O/Na_2O, CaO/MgO and Co/Ni ratios in these ores are due to high adsorption capacities of K_2O, CaO and Co then Na_2O, MgO and Ni:

Presumably the Mn and Fe solutions first form in feebly acidic medium with at pH value around 7. However with an increase in alkalinity Mn^{2+} and Fe^{2+} they are converted to colloidal $Mn(OH)_4$ and $Fe(OH)_3$. The solubility of SiO_2 also increases with the increase pH (about 9), the Al_2O_3 dissolves into solution. The addition of $Al(OH)_3$ into solution causes drastic changes in character of $Mn(OH)_4$ colloids which are precipitated as oxide ores. Originally the Mn deposits have been derived from sources on the bordering Cratons, which are also the probable provinces for the sediments in this part of the basin.

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