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Geochemical and Ore-mineralogical Characterization of Beach placer ilmenite from Srikurmam Deposit, Andhra Pradesh, India

M.Jagannadha Rao[1]*, J. Venkata Ramana[2], Aaron A.Jaya Raj[3], G.Raja Rao[3] and P.Rajesh[4]

[1-4]Department of Geology, Andhra University, Visakhapatnam-530003
[1]Department of Geosciences, Dr. B.R.Ambedkar University, Etcherla, Srikakulam
*Corresponding Author: mjrao.geology@gmail.com

ABSTRACT

Ilmenite ores from the Srikurmam placer sand deposit were investigated for their geochemistry and ore mineralogy. Studies indicated that the ilmenite of Srikurmam placer has TiO_2 content comparable to other placer deposits like Bhimunipatnam in east coast and Ratnagiri in west coast of India. The trace element data indicate that the elements such as Co (315 ppm to 320 ppm), Ni (45 ppm to 49 ppm), Zn (694 ppm to 698 ppm), V (1300 ppm to 1304 ppm) and Cr (648 ppm to 653 ppm) are in higher concentrations. Mn content in the ilmenites of the present study area has significantly low values (0.52 ppm to 0.93 ppm). Ore mineralogical studies indicate that the ilmenite exhibits conspicuous exsolution features. Studies reveal four types of intergrowths; hemo-ilmenite (complex exsolution and lamellar exsolved phase), ilmeno-hematite (Emulsion texture), and irregular exsolved phases exhibiting different grain level textures. Hematite phase in ilmenites incorporates excess iron (average 46.49%) in the structure of ilmenite. Based on the geochemical and ore mineralogical aspects, ilmenites of the Srikurmam placer area is more suitable for pigment-manufacturing. However, the higher concentrations of trace elements may affect the properties of pigment grade oxide. In addition the excess iron may cause environmental problems.

Key words: Beach placer ilmenite, Ore mineralogy, Geochemistry, Srikurmam, Andhra Pradesh.

INTRODUCTION

Ilmenite is a black iron-titanium oxide with a chemical composition of $FeTiO_3$. Ilmenite is the primary ore of titanium, a metal needed to make a variety of high-performance alloys. Most of the ilmenites mined worldwide is used to manufacture titanium dioxide, TiO_2, an important pigment, whiting, and polishing abrasive (geology.com › Minerals).Ilmenite is the most important ore of the element titanium. It has recently surpassed Rutile as the main ore mineral of that metal. Ilmenite was once used as a minor ore of iron prior to the discovery of titanium as an industrially important metal. (www.minerals.net/mineral/ilmenite.aspx).Ilmenite is named after the Ilmenski Mountains in Russia, where the mineral was first discovered. Ilmenite is slightly magnetic, which means that magnets can be used to separate it from other minerals in mineral sands. It is able to withstand extreme temperatures, and is used in the steel industry to line blast furnaces (www.australianminesatlas.gov.au/education/down_under/minerals.../ilmenite.html).

Placer ilmenite is the major source mineral of the world in the production of titanium metal, which has wide variety of applications. Titanium metal and its alloys are having excellent applications in aero-space industry, gas turbines and in machinery involved in high temperature operations and in defense equipment. Titanium carbide is used in commercial cutting tools.

World reserves of ilmenite are estimated at 740 million tons in terms of TiO_2 content. Major reserves are in China (27%), Australia (19%), India (11%), South Africa (9%), Brazil and Madagascar (6% each), Norway (5%), Mozambique (2%) and other countries. (Indian Minerals Yearbook 2015).

East coast of India has been known for the occurrence of the economically important ilmenite bearing placer sand deposits. During recent times, demand for ilmenite and its value added products has increased many fold. In this context, India, with an estimated total reserves of 278 million tons (Mukherjee, 1998), including Andhra Pradesh 103.05 million tons (Ravi et al., 2001) is at present placed comfortably. However, ilmenite ($FeoTiO_2$) being the important source for titanium, discovery of new ilmenite resources is essential keeping in view of growing need of titanium based products in various fields.

The present study deals with the study of ilmenite along Srikurmam coast in Andhra Pradesh (Figure 1) where one of the richest beach placer ilmenite deposits exists along the East Coast of India. Srikurmam with an extensive dunal belt system has an average grade of 34% Total Heavy Mineral (THM) concentration with abundant ilmenite and garnet occurrence. Preliminary studies hence indicated ilmenite and garnet to be predominant minerals with a grade ranging from 21.37% to 39.59% and 31.07% to 44.59%, respectively (Yugandhara Rao et al., 2001). However, baseline data pertaining to industrial utility of ilmenite geochemistry are scanty. This research note presents geochemical and ore mineralogical aspects of ilmenite of this deposit and their possible bearing on processing and value-addition.

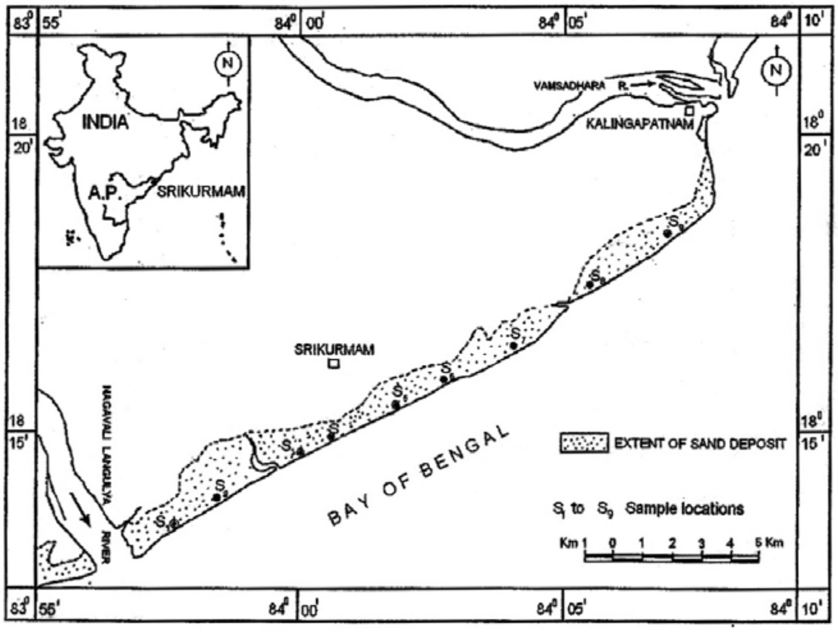

Figure 1. Srikurmam Beach Placer Deposit with Sample Locations.

METHODOLOGY

Keeping in view of the placer sand deposit in an extensive dunal environment, (Figure 2, 3 and 4) representative bulk samples, each of about 30 to 50 kg were collected at 9 locations (Figure 1). Each sample was reduced to required quantity by standard sample reduction techniques. The heavy minerals were concentrated by bromoform (sp. gr 2.89) and the magnetite was separated by hand magnet. The magnetite-free samples were then run through the isodynamic separator, set at ≡ 0.25 amp to separate ilmenite. The separation was repeated 10 to 15 times to ensure high purity of ilmenite (Figure 5.). The purity was checked under a binocular microscope and 99% pure samples were analyzed by Atomic Absorption Spectrophotometer and ICP-MS for major and trace elements. The standards used for the analysis are 100 ppm concentration supplied by Fisher scientific company, USA.

RESULTS

Geochemistry:

The ilmenite samples from the study area were analyzed for their major and trace elemental contents (Table 1.). The results indicate that the TiO_2 content varies from 50.04% to 52.05%. The total iron recorded in the range of 45.41% to 47.53%. Whereas major elemental concentrations such as SiO_2, Al_2O_3 and MgO recorded lower average values of 0.37%, 0.17% and 0.28% respectively, and had a range between 0.37 and 0.39%, 0.16 and 0.18% and 0.2 and 0.4%, respectively.

The trace elements, namely Cr, Mn, V, Co, Ni, Zn, and Cu are determined in the study. Among the trace elemental concentrations, Vanadium recorded highest concentration around 1300 ppm. Significantly Cr and Zn indicate almost similar concentrations. Cr ranges from 648 to 651 ppm and Zn is found to be in the range of 694 to 698 ppm, but Co is found to be in the range of 315 to 320 ppm, which is almost half that of Cr and Zn. Strikingly, these three elemental concentrations (i.e. Cr, Zn and Co) recorded much lower values than that of V. However, Ni occurs in the range between 45 and 49 ppm with an average abundance of 46.4 ppm, whereas Cu is found to be in the range between 65 and 68 ppm with an average of 66.6 ppm. More significantly Mn content is reported to be very much lower in concentration, ranging between 0.5 ppm and 0.93 ppm. These observations suggest that in the present deposit, the V (Average 1301.80 ppm) and Zn (Average 696.40 ppm) concentrations are comparatively higher than the other deposits, where as Cr (Average 650.40 ppm) is on par with other deposit and Mn (Average 0.73 ppm) is significantly reported very low concentrations. These observations are pictorially represented in the Figure 6.

Ore Mineralogy:

The detailed ore microscopic examination of the ilmenite grains from the present investigation revealed the wide variety of exsolutions mainly between the minerals hematite-ilmentite, ilmenite-hematite etc. In polished sections ilmenite appears grayish white with a light brownish tinge to pinkish tinge; the reflectivity is moderate. A number of exsolution patterns were observed

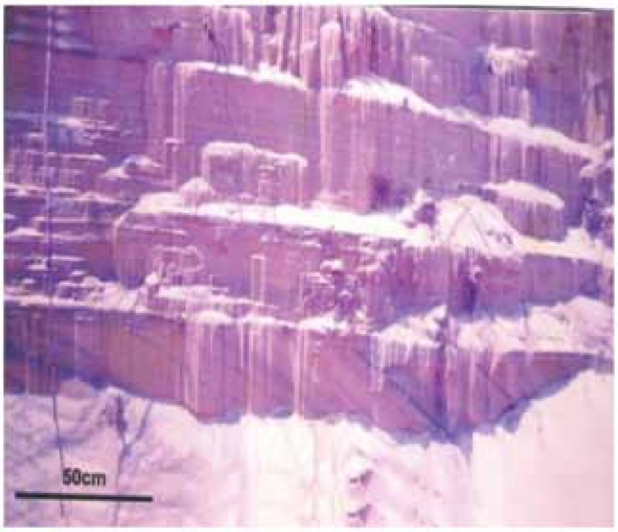

Figure 2. Excellent step and pillar like pattern in a dunal cross section, Srikurmam placer sand Deposit.

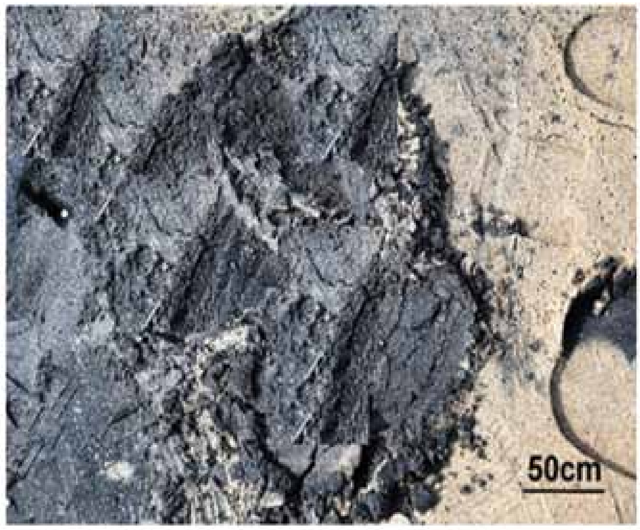

Figure 3. Rich ilmenite concentration in the Dune.

Figure 4. Density stratification of black sand with Ilmenite, in the berm cut.

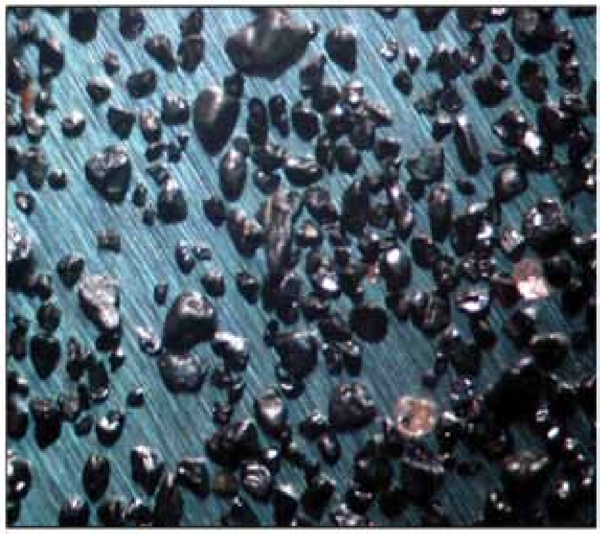

Figure 5. Separated ilmenite grains under binocular Microscope 30X.

in the present study. There are complex exsolved phase grains comprising hematite-ilmenite (Figure 7.a, complex exsolution), (Samsuddin Ahmed et al., 1992). Similarly the formation of ilmenite lamellae within the host hematite indicates the dominant hematite phase (more than 50%). This can be termed as "hemo-ilmenite" (hematite matrix) (Fig.7b, Lamellar exsolved phase) and the hematite exsolved phases within the host ilmenite indicate the dominant ilmenite phase (more that 50%) which can be considered as "ilmeno-hematite" (ilmenite matrix) (Figure 7.c Emulsion texture). This terminology is adopted from earlier reports from literature (Ramdohr, 1969, Samsuddin Ahmed et al., 1992). Similarly, the number of grains showing irregular exsolved phases of ilmenite and hematite can be seen in Figure 7.d. Some of the grains show pure ilmenite phase. Variations in optical properties such as reflectance, pleochroism, brightness, etc. are significant among the elements of present study. Wide variation in the width of intergrowth lamellae of both ilmenite and hematite phases is identified. The variations in the grain boundaries and micro fractures are very significant, indicating their differences in Ti and Fe contents. Some ilmenites show very fine needle-shaped (hair like) exsolution and are microcrystallline in nature.

The abundance of the lamellae of Hematite within ilmenite makes the grains to be called as Hemo-ilmenites or ilmeno-hematites depending upon the relative percentages of these two phases. The work done by Suzanne et al.,

Table 1. Chemical analysis of ilmenite (major radicals in wt % and trace elements in ppm) from the Srikurmam coastal sand deposit, Andhra Pradesh, compared with other deposits.

S.No	Location	TiO2	SiO2	Al2O3	T-Fe	MgO	Cr	Mn	V	Co	Ni	Zn	Cu
1	S1	51.12	0.38	0.17	46.66	0.2	651	0.74	1302	319	46	697	67
2	S2	51.26	0.37	0.18	45.69	0.4	650	0.53	1301	316	47	695	66
3	S3	52.05	0.37	0.16	45.84	0.3	653	0.52	1304	320	49	694	65
4	S4	51.75	0.38	0.17	45.5	0.2	649	0.64	1302	317	46	696	67
5	S5	50.65	0.39	0.18	47.53	0.2	648	0.93	1303	316	45	698	68
6	S6	50.36	0.36	0.16	47.35	0.3	651	0.81	1300	320	45	697	68
7	S7	50.04	0.38	0.18	45.41	0.4	651	0.69	1300	320	45	695	65
8	S8	51.27	0.37	0.18	47.41	0.22	652	0.90	1304	319	48	698	66
9	S9	51.95	0.37	0.17	47.02	0.3	649	0.81	1300	315	47	698	68
	Average	51.16	0.37	0.17	46.49	0.28	650.4	0.73	1301.8	318	46.4	696.4	66.6
10	B1	47.42	0.22	0.40	49.54	0.42	990	1120	600	90	44	103	8
11	B2	47.36	0.24	0.41	49.95	0.40	1016	1020	720	110	36	188	16
12	B3	50.30	0.29	0.54	46.90	0.30	910	1615	159	160	66	99	9
13	B4	48.18	0.50	0.28	49.29	0.20	416	1724	805	38	90	122	18
14	B5	49.66	0.22	0.50	46.23	0.26	844	1652	201	123	90	101	8
15	B6	50.50	0.80	0.30	46.34	0.32	444	1518	800	57	38	166	8
16	B7	48.12	0.18	0.52	49.26	0.26	1520	8100	512	120	62	124	4
17	B8	51.09	0.50	0.30	46.20	0.25	334	2020	714	88	22	106	12
18	B9	51.09	0.30	0.60	46.10	0.38	1110	1818	188	150	54	112	6
19	B10	52.30	0.44	0.32	44.10	0.18	212	1808	716	10	62	124	4
20	B11	50.05	0.11	0.19	47.28	0.65	504	1520	616	68	41	172	10
	Average	49.71	0.34	0.39	47.38	0.33	754	1628	584	92	55	136	10
21	84/1943-5	51.25	ND	ND	43.79	ND	621	2107	872	194	84	232	ND
22	84/1946-6	56.25	ND	ND	37.50	ND	773	2057	791	178	93	197	ND
23	84/1946-17	50.00	ND	ND	45.08	ND	513	2210	661	93	78	179	ND
24	84/1946-19	53.13	ND	ND	42.55	ND	583	2218	811	153	94	208	ND
25	91/2536-1	51.25	ND	ND	40.64	ND	724	2189	875	153	82	223	ND
26	91/2536-18	53.18	ND	ND	41.47	ND	740	2344	849	123	87	235	ND
27	84/KB/B-1	54.38	ND	ND	40.95	ND	508	2228	738	114	86	207	ND
	Average	52.77	ND	ND	41.71	ND	637	2193	799	144	86	211	ND
28	Q	60.00	0.90	0.10	35.20	0.60	416	3080	420	ND	ND	ND	ND
29	MK	55.00	0.90	0.80	39.80	1.00	256	3080	1232	ND	ND	ND	ND
30	OR	50.20	0.80	0.60	46.90	0.65	160	4235	672	ND	ND	ND	ND
	Average	55.066	0.866	0.833	40.633	0.75	277.33	3465	774.66	ND	ND	ND	ND

S1-S9 Samples of present study, S.No 10-20 Bhimunipatnam, (Jagannadha Rao et al., 2005), S.No 21-27 Ratnagiri (Sukumaran and Nambiar, 1994); S.Nos 28-30 Chatrapur (Mukherjee, 1998), ND-Not determined and T-Fe means total iron content.

(2000) indicated similar exsolved phases in Ilmenites of Skondel, Norway, which are derived from Norite parentage.

The ore mineralogical aspects indicate that the exsolution features of ilmenite under study have resemblance to that from Bhimunipatnam deposit (Jagannnadha Rao et al., 2015) and also Cox Bazar ilmenites (Samsuddin Ahmed et al., 1992).The resemblance indicates igneous parentage.

DISCUSSION

The TiO_2 content of ilmenite in the given samples is almost close to the theoretical ilmenite composition reported in literature which is 50.02% (Deer et al., 1965). The average TiO_2 of the present study area (51.16%) is comparable with that of Ratnagiri (52.77%) (Sukumaran and Nambiar, 1994). However, there is comparable variance in the presence of total iron contents of these two deposits (Table 1). The average total iron content of the ilmenite of the deposit is 46.49%, whereas Ratnagiri ilemenites have an average of 41.71%. The data thus demonstrate that ilmenite of SriKurmam deposit records higher total iron and lower TiO_2 contents as compared to the composition of ilmenites from the published data (Sukumaran and Nambiar, 1994, Mukherjee, 1998). Similarly the Chhtrapur ilmenite has TiO_2 in the range of 50.2% to 60% and total iron in the range of 35.20% to 46.90% (Mukherjee, 1998). However, the TiO_2 and total iron contents of the present study are comparable with those ilmenites reported from Bhimunipatnam where an average TiO_2 and total iron contents are 49.71% and 47.38%, respectively, (Jagannadha Rao et al., 2008). The SiO_2 content (0.36% to 0.39%) is comparable with Bhimunipatnam ilmenites (average 0.34%) and significantly less than that reported for Chhtrapur ilmenites (average 0.86%) (Mukherjee,1998).The Al_2O_3

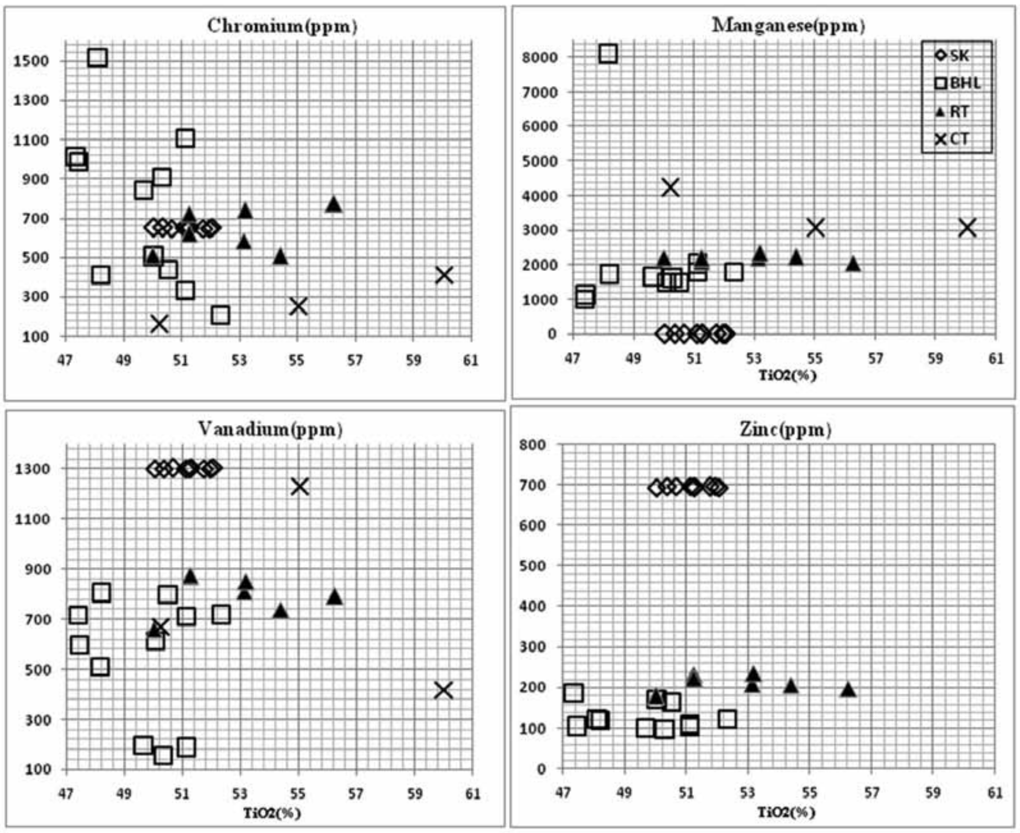

Figure 6. Scatter plots showing variation of Cr, V and Zn vs TiO_2 from different deposits Srikurmam (SK), Bhimunipatnam (BHI), Ratnagiri (RT) and Chhtrapur (CT).

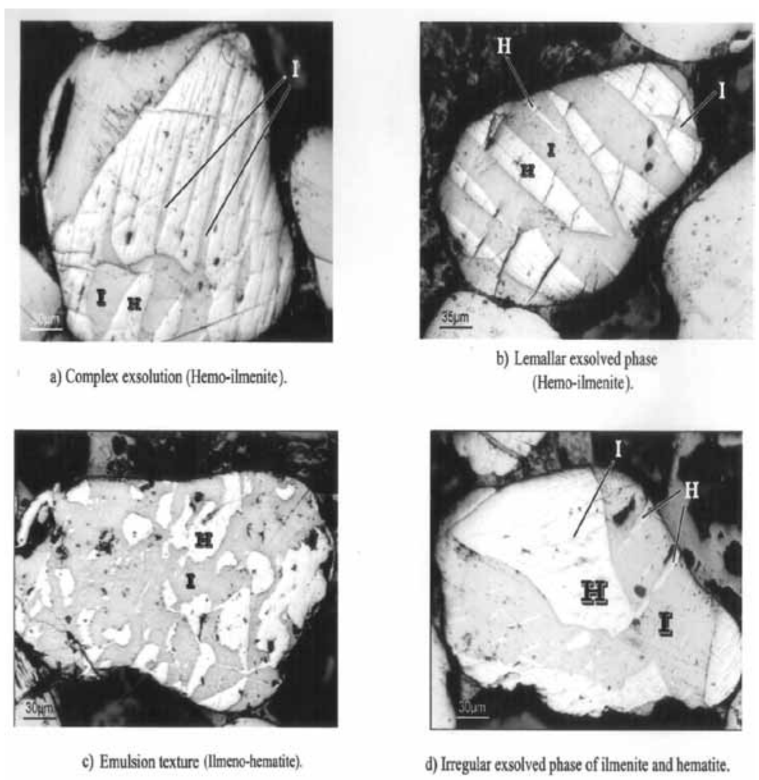

Figure 7. Ilmenite grain morphology with exsolved phases of ore minerals, Ilmenite (I) and Hematite (H).

values are comparatively less than Bhimunipatnam and Chhtrapur ilmenites. Similarly, the MgO% is in the range of 0.2% to 0.4%, significantly lower than that of Chatrapur ilmenites (Mukherjee, 1998) and Bhimunipatnam ilmenites (0.18% to 0.65%) (Jagannadha Rao et al., 2005). The trace elemental concentrations of Cr and V, which are in the range of 648 ppm to 653 ppm and 1300 to 1304 ppm respectively, are higher than that of ilmenites of Chhtrapur (Mukherjee, 1998) and Ratnagiri (Sukumaran and Nambiar, 1994). However, the Cr content of Bhimunipatnam ilmenites (Jagannadha Rao et al., 2005) is comparable with ilmenites of present study, but V concentration is less (average 584 ppm). The other trace elemental concentration, namely Co, Ni, and Cu of the present deposit are higher than the reported data (Table 1). The lower abundance of SiO_2 and higher abundance of Cr, Co, Ni and V suggest that the ilmenites of the present study are showing affinity to a possible basic parentage. Another striking observation is the vast difference in the abundance of the Mn content in the ilmenites of the present study area (0.73 ppm) compared with the other published data from Ratnagiri (2193ppm) (Sukumaran and Nambiar, 1994) and Chhtrapur (3465 ppm) (Mukherjee, 1998) and Bhimunipatnam (1628 ppm) ilmenites (Jagannadha Rao et al., 2005). The low Mn concentration contradicts the theory of the metamorphic parentage of ilmenites from the study area (Ramamohana Rao et al., 1983).

Zn concentration, which is found to be in the range of 694 to 698 ppm is comparatively higher than the other deposits. The report of occurrence of Zincanian ilmenite (Jagannadha Rao et al., 2008) from this area, perhaps explains high Zn concentration.

Earlier studies by (Jagannadha Rao, 1985); (Jagannadha Rao et al., (2005) on the ore mineralogy of Bhimunipatnam deposit indicated that the ilmenite shows high variability in terms of grain size, texture, pattern of exsolutions, composition of exsolved phases etc. In general the ilmenite of Srikurmam deposit is granular or rounded to irregular. Its grain size is around 80 microns.

From the above observations, it is very clear that the ilmenites of the study area recorded marginally less TiO_2 percent and high total iron content than the theoretical formula of the ilmenite. The higher total iron content can be explained due to the fact that these ilmenites are not pure and in fact they can be called as hemo-ilmenites or ilmeno-hematites as per the percentage of exsolved hematite phase. This is also established by the ore mineralogical observations as well. Similarly, the higher abundance of trace elements like V, Zn and Cr is a significant observation. The occurrence of wide variety of exsolutions in ilmenite as mentioned earlier, suggests their derivation from multiple sources or with different paragenesis, especially basic parentage.

(Hegde et al., 2006) have investigated the provenance of Honnavar beach, West coast of India. They have carried out the study with particular reference to ilmenite. They have concluded that the heavy minerals like ilmenite, magnetite and zircon, which are characterizing the Precambrian gneissic, granitic and basic rocks have been derived from the hinterland and subsequently transported by the river Saravathi. However, minerals like garnet, kyanite and staurolite are characteristic minerals of high grade metamorphic source and are derived from reworked paleo beach/off shore sediments. They further established that the high contents of trace elements namely Cobalt, Chromium, Vanadium and Nickel suggest basic source of their derivation.

Mohanty et al., (2003) have undertaken similar studies of geochemical characterization of ilmenite from Chhtrapur beach placer deposit using PIXE and EDXRF methods.

Suzanne et al., (2000) have carried out chemical and petrographic characterization of ilmenite and magnetite from Sokndal region, Norway. Their work emphasized the chemical features and micro textures reflecting the progress of magmatic evolution. They have indicated that the most primitive oxides of the region are ilmenites derived from Norites from Tellnes region.

Babu et al., (2009) carried out studies on recovery of ilmenite and other heavy minerals from Teri sands of Tamilnadu, India. They have established a method using spirals followed by dry high intensity magnetic separator and high tension separator to obtain 99.10% purity of ilmenite. The other minerals like zircon, sillimanite are separated by judicious combination of gravity and floatation process.

Ilmenite of the present study contains nearly 30% of iron as oxides, which is considered to be a polluting agent and consumes more chemicals in the process of manufacturing of TiO_2 or $TiCl_4$. In addition, ilmenite contains significant quantities of vanadium, chromium, Ni, Co etc., which affect the properties of pigment grade oxide. Chemistry of ilmenite also decides whether the given ilmenite can be processed by the following chloride route or by sulphate route, which will have significant technical and economic implications. The high iron content of ilmenites from the study area (Table 1) may result in excess iron, and as such is environmentally unwanted and consumes more acid in the process. This may have economic and environmental implications (Mukherjee, 1998).

CONCLUSION

The ore mineralogical study established extensive exsolved phases in Srikurmam ilmenite ores. These grain level textures strongly support a magmatic source of ilmenite derivation, rather than metamorphic parentage. The higher abundance of trace element concentration like V, Zn and Cr further support this observation. As far as the processing of ilmenite is concerned, the high Iron content will have problem of more acid consumption, which has an environmental impact.

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Compliance with Ethical Standards:

The authors declare that they have no conflict of interest and adhere to copyright norms.

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