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Provenance Studies of Ilmenite from Red Sediments, Bhimunipatnam Coast, East Coast of India

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ABSTRACT

Mineral chemistry of the ilmenites, drawn from the red sediments along the Bhimunipatnam coast, Andhra Pradesh, India was determined by EPMA technique. The major constituents are TiO_2 and FeO, and the value of $Ti/(Ti + Fe) < 0.5$ of these ilmenites indicate that they are relatively fresh 'ferrian ilmenites' and were contributed recently to the red sediments in the study area. Using the mineral chemical data, the end-member composition of the analyzed ilmenites was calculated, which reveals that they are of 'ilmenite - hematite' and 'ilmenite - geikielite - hematite' composition, derived from calc-alkaline magma-sourced charnockites and metapelitic khondalite suite of rocks respectively of the Eastern Ghats granulite belt. The TiO_2 content and Mn/Mg ratio of the study ilmenites indicate that these rocks constitute their provenance in the Gosthani river basin. Their back scattered electron (BSE) and scanning electron (SEM) images show their prominent sub-angular to sub-rounded shape, corroborating the study under microscope, with some preserving signatures of exsolution intergrowth, earlier deformation and rounded shape, all of which are attributed to their transportation by the Gosthani river, after their liberation from their provenance rocks.

INTRODUCTION

Geochemical characterization of coastal heavy minerals plays an important role in mineral beneficiation of their deposits and their metallurgical treatment as well as in their stratigraphic correlation and provenance studies. Generally in clastic sediments, quartz, feldspar and mica are major constituents and heavy minerals are minor constituents. Composition of sediment is primarily controlled by mineral composition of its provenance rocks and their paragenesis (Hutton 1950; Buddington and Lindsley 1964; Darby et al. 1985) as well as by different set of parameters, mainly weathering, transportation, deposition and diagenesis, operating during the sedimentation cycles (Morton 1985; Johnsson 1993; Morton and Hallsworth 1999). The variation of chemical composition depends on its source rocks paragenesis (Hutton, 1950; Buddington and Lindsley, 1964; Darby et al., 1985).

A few geochemical studies were carried out earlier on the red sediments along the Bhimunipatnam coast and these include on the clays from Bhimunipatnam (Rao and Raman 1986), Yerrampalem to Chepalakancheru (Malathi 2012), Bavanapadu - Ichapuram (Vaz et al., 1988) along the Andhra Pradesh coast. Ilmenite chemistry (Darby et al. 1985; Basu and Molinaroli 1989; Darby and Tsang 1987) and TiO_2 and MgO contents of ilmenite (Basu and Molinaroli 1989), and its Mn and Mg and Mn/Mg ratio (Dinesh et al. 2007) and MgO/MnO ratio (Bhattacharya et al. 1997) were used as provenance indicator. Ilmenite chemistry (Darby et al., 1985; Basu and Molinaroli, 1989; Darby and Tsang, 1987) and TiO_2 and MgO contents of ilmenite (Basu and Molinaroli, 1989), Mn and Mg and Mn/Mg ratios (Dinesh et al., 2007), MgO/MnO ratios (Bhattacharya et al., 1997) were used as provenance indicator.

Mineralogical and geochemical variations of heavy minerals from Valliyar river and beach sands (Nair et al., 1995); beach placers of Mandapam to Kanykumari region (Angusamy and Rajamanickam, 2001) and opaque minerals (Chandra Shekar and Rajamanickm 2001) of Tamil Nadu coast, heavy mineral deposits of Ambalapuza beach sands (Jayalakshmi et al., 2003) of Kerala coast, alteration characteristics of ilmenites (Rao et al., 2005), ilmenite from beach placers of the Visakhapatnam – Bhimunipatnam deposit (Jagannadha Rao et al., 2005), textural and heavy mineral studies on late Quaternary red sediments of Bhimunipatnam(Murali Krishna et al., 2016; 2017) of Andhra Pradesh coast and beach placer deposits (Acharya and Das, 2001); beach placer ilmenite from the Chhatrapur coast (Rao et al., 2002) of Odisha coast were studied.

For the first time, an attempt is made in this paper to study the mineral chemistry of the ilmenite, determined by EPMA, from the red sediments along the Bhimunipatnam coast, and using this to probe the nature of its provenance.

LOCATION OF THE STUDY AREA

The study area, comprising red sediments, of Bhimunipatnam is located between 17°51' and 17°53' N latitudes and 83°23' to 83°25' E longitudes, and is about 20 km north of Visakhapatnam in Andhra Pradesh (Fig.1). The red sediments cover an area of 10 km^2 and extend 5 km along the Bay of Bengal coast and 2 km inland. In the study area, four sedimentary sand units viz., (i) yellow sands, (ii) brick red sands, (iii) reddish brown sands and (iv) light yellow sands are present, from bottom to top in geological sections (Rao et al., 1993, 1993a).

Geology and Geomorphology

The following information about geomorphology of the study area in and around Visakhapatnam region is a summary from Prudhvi Raju and Vaidyanadhan, 1978; Prudhvi Raju et al., 1985; Nageswara Rao and Udaya Bhasakra Rao, 1999; Nageswara Rao et al. 2006. The Visakhapatnam region mainly consists of Eastern Ghats Group of rocks and Visakhapatnam to Bhimunipatnam coast with several headlands, bays, flat topped hills, wave cut terraces, sea caves, plains etc. The prominent geological formations of the study area are: Archaean – khondalites, leptynites and quartzites; Proterozoic - charnockites, granites, pegmatites, quartz veins and Quaternary – laterite, surficial soils and coastal sand deposits (Fig. 2).

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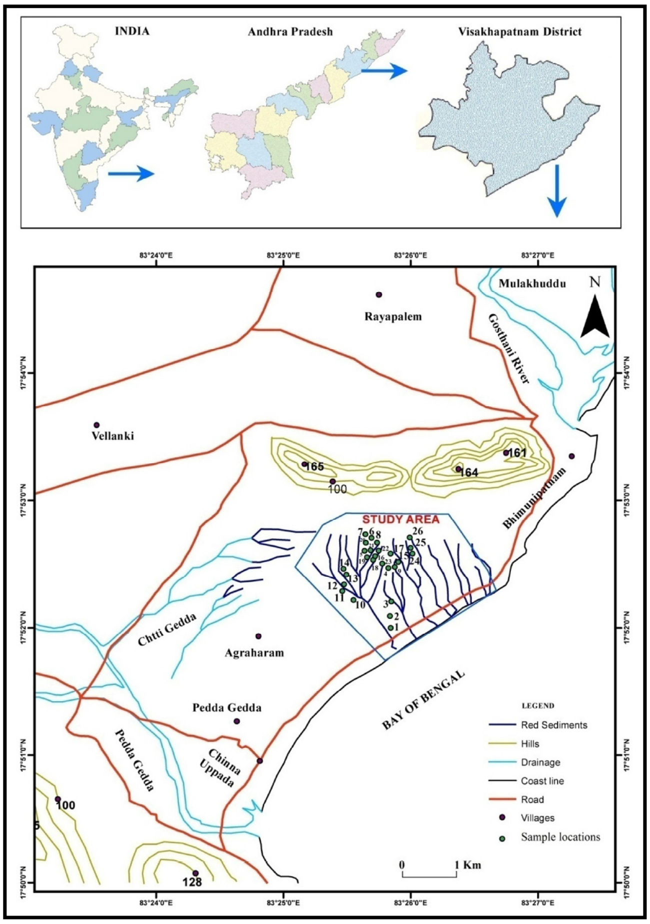

Fig.1 Sample location map of the study area

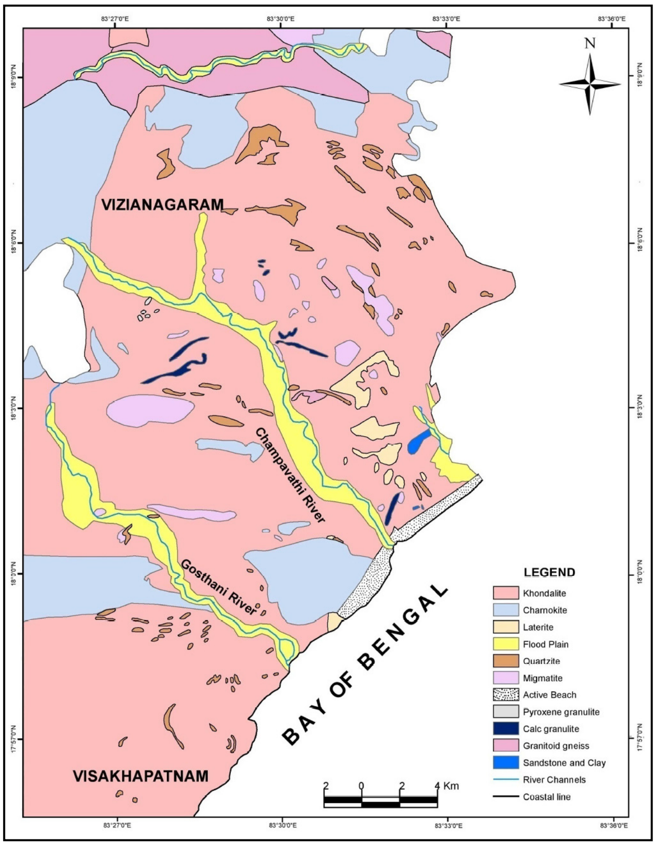

Fig. 2 Geological map of the study area

MATERIALS AND METHODS

Twenty eight representative samples (10 in yellow sands, 2 in reddish brown sands, 12 in brick red sands and 4 in light yellow sands) were processed for heavy mineral studies. Among the twenty eight samples ten representative samples are selected for geochemical analysis of ilmenite, these samples consists high concentration of ilmenite. Initially these samples were thoroughly washed with distilled water for removing of salts, treated with 15% Hydrogen Peroxide (H_2O_2) to remove organic matter and with 10% dilute HCl in order to remove the shell material and subjected to +230 mesh wet sieving. Then it was subjected to sieving +60 (>0.25mm), -60 to +120 (0.25 to 0.125mm) and -120 to +230 (0.125 to 0.062mm) ASTM mesh size fractions. These samples were subjected for heavy mineral separation by using bromoform (Sp. Gr. 2.88g/cm^3).

Grain Picking: Heavy mineral grains of ilmenites were identified under binocular petrological microscope in different fractions of each sample, based on their optical properties, 26 ilmenite grains (11 from yellow sand unit, 4 from reddish brown sand unit, 6 from brick red sand unit and 5 from light yellow sand unit) were selected from the red sediments of the Bhimunipatnam for chemical analysis by EPMA.

Sample Preparation: Selected grains in each sample were mounted onto a standard size glass slide with resin (epoxy) for further lapping and polishing. This method allows imaging to be achieved using both transmitted and reflected light microscopy. Removal of excess sample and grinding to ensure the top and base of the resin blocks are parallel. Lapping was carried out to produce a smooth surface by using fine (600 grade) silicon carbide abrasive. Samples were polished with fine SiC-paper and slurry of very fine alumina ranging in size from 6 to 0.30 microns. The polished sample was then washed with distilled water in an ultrasonic cleaner to get rid of the polishing grit and other surface dirt. The sample was then dried in air and cleaned with blow-duster.

Grain Mounting and Coating of Samples: For precise WDS (Wavelength Dispersive Spectroscopy) analysis, careful sample preparation is essential. Ilmenite grains were mounted in a non-conductive material and subjected to carbon-coating to dissipate excess charge produced by electrons beam. Furthermore, the standards and the sample were coated to the same thickness. Carbon coating was carried out by carbon evaporation under vacuum. A polished glass block was used to monitor the thickness of carbon coat deposited on the specimens.

Analytical Techniques: CAMECA SX 100 Electron Probe Micro Analyzer (EPMA), in the Geological Survey of India, Hyderabad, was used for chemical analysis of ilmenite samples. Polished surfaces of ilmenite samples, were exited with an electron beam of accelerating voltage kept at 15 kV and the beam current of 20 nA. The beam size was kept at ~ 1ìm. Natural mineral standards were used for most elements (Orthoclase Si and K; Corundum Al; Wollastonite Ca; Hematite Fe; Apatite P; Chromite Cr; Albite – Na and Al; Diopside- Mg and Ca ; Rhodonite- Mn; TiO_2 –Ti and Almandine- Fe).

RESULTS AND DISCUSSION

The EPMA-based mineral chemical data of ilmenite grains from red sediments, their structural formulae, calculated based on two cations and three oxygens, and end-member composition, calculated based on mineral chemistry, are given in Table 1. Summary of major observations of the mineral chemistry of ilmenite of the red sediments is given in Table 2.

Table 1. Chemical composition of ilmenite (by EPMA) in the Red sediments of Bhimunipatnam and its calculated structure.

Probe/Sample No./Gain No	8/1	8/2	8/3	27/4	27/5	12/6	12/7	12/8	13/9	13/10	13/11	10/12	10/13	10/14	23/15	23/16	24/17	24/18	25/19	25/20	5/21	5/22	5/23	7/24	7/25	7/26
SiO_2	0.04	0.03	0.02	0.01	0.03	0.04	0.00	0.01	0.12	0.02	0.03	0.01	0.03	0.00	0.07	0.00	0.02	0.01	0.06	0.11	0.01	0.02	0.05	0.02	0.08	0.04
TiO_2	49.91	50.13	49.76	50.38	49.74	49.13	47.45	51.54	49.84	48.80	48.99	50.42	52.49	48.58	50.33	48.28	51.80	49.26	48.94	50.66	50.55	51.71	50.71	50.23	51.50	50.21
Al_2O_3	0.04	0.03	0.05	0.01	0.03	0.01	0.00	0.02	0.04	0.06	0.02	0.03	0.01	0.02	0.02	0.03	0.02	0.06	0.00	0.05	0.04	0.00	0.02	0.00	0.01	0.00
MnO	0.41	1.35	0.36	3.00	1.33	0.26	0.14	0.28	0.53	0.69	0.77	0.41	0.36	0.37	0.46	0.04	0.18	0.42	1.32	0.89	0.16	0.28	0.57	0.84	0.09	0.59
MgO	0.30	0.07	0.69	0.20	0.04	1.28	1.01	0.39	0.25	0.28	0.28	0.53	1.29	0.31	0.56	0.24	1.99	0.14	0.12	0.52	1.85	1.21	0.99	0.05	1.52	0.51
CaO	0.02	0.01	0.03	0.00	0.03	0.02	0.03	0.02	0.02	0.03	0.01	0.02	0.02	0.03	0.01	0.00	0.00	0.00	0.01	0.03	0.02	0.02	0.03	0.01	0.01	0.00
Na_2O	0.01	0.02	0.01	0.02	0.00	0.00	0.02	0.02	0.03	0.03	0.03	0.04	0.02	0.02	0.00	0.01	0.00	0.03	0.01	0.01	0.00	0.02	0.00	0.03	0.01	0.02
K2O	0.01	0.06	0.04	0.01	0.00	0.01	0.02	0.01	0.02	0.01	0.01	0.01	0.05	0.01	0.03	0.00	0.01	0.00	0.00	0.03	0.01	0.01	0.00	0.03	0.02	0.00
Cr_2O_3	0.05	0.02	0.06	0.04	0.01	0.07	0.01	0.03	0.04	0.00	0.03	0.06	0.01	0.00	0.05	0.05	0.06	0.01	0.03	0.00	0.09	0.08	0.10	0.04	0.13	0.03
P_2O_5	0.00	0.01	0.02	0.03	0.02	0.04	0.05	0.03	0.02	0.04	0.04	0.02	0.02	0.03	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.02	0.01	0.00	0.03	0.07
(FeO)	47.10	47.00	47.09	44.35	46.72	49.27	50.71	47.87	48.35	50.12	49.74	48.58	45.63	50.44	48.79	50.23	46.14	50.13	49.39	46.67	47.30	46.43	47.62	48.87	46.49	48.46
FeO(c)	43.87	43.37	43.04	41.90	43.32	41.67	40.65	45.31	43.82	42.61	42.72	43.83	44.33	42.67	43.80	42.93	42.85	43.52	42.46	43.71	41.96	43.99	43.28	44.04	43.54	43.74
Fe_2O_3(c)	3.59	4.03	4.50	2.73	3.78	8.44	11.18	2.84	5.04	8.35	7.80	5.28	1.44	8.63	5.55	8.11	3.66	7.35	7.70	3.29	5.93	2.72	4.82	5.37	3.28	5.24
Total	98.25	99.11	98.57	98.31	98.34	100.98	100.57	100.48	99.75	100.91	100.72	100.65	100.07	100.67	100.87	99.71	100.58	100.80	100.66	99.30	100.61	100.06	100.57	100.65	100.22	100.45
On the basis of 2 cations																										
Si	0.0009	0.0007	0.0006	0.0003	0.0007	0.0009	0.0001	0.0002	0.0030	0.0005	0.0007	0.0002	0.0007	0.0001	0.0017	0.0000	0.0005	0.0002	0.0015	0.0027	0.0002	0.0004	0.0012	0.0005	0.0019	0.0009
Al	0.0011	0.0009	0.0014	0.0002	0.0010	0.0004	0.0000	0.0007	0.0012	0.0017	0.0005	0.0009	0.0004	0.0005	0.0007	0.0009	0.0005	0.0017	0.0001	0.0014	0.0012	0.0000	0.0005	0.0001	0.0004	0.0000
Ti	0.9637	0.9610	0.9550	0.9723	0.9615	0.9184	0.8935	0.9720	0.9484	0.9195	0.9247	0.9493	0.9862	0.9178	0.9456	0.9215	0.9647	0.9298	0.9255	0.9657	0.9431	0.9731	0.9520	0.9493	0.9655	0.9476
Mn	0.0088	0.0291	0.0078	0.0652	0.0290	0.0055	0.0031	0.0059	0.0114	0.0147	0.0163	0.0087	0.0076	0.0080	0.0097	0.0008	0.0037	0.0089	0.0282	0.0191	0.0034	0.0058	0.0119	0.0178	0.0020	0.0125
Mg	0.0114	0.0027	0.0263	0.0075	0.0016	0.0476	0.0376	0.0147	0.0094	0.0104	0.0104	0.0199	0.0482	0.0116	0.0209	0.0091	0.0733	0.0052	0.0045	0.0195	0.0683	0.0451	0.0370	0.0017	0.0566	0.0189
Ca	0.0006	0.0002	0.0008	0.0000	0.0009	0.0004	0.0009	0.0005	0.0005	0.0009	0.0002	0.0004	0.0006	0.0008	0.0001	0.0000	0.0000	0.0001	0.0002	0.0009	0.0005	0.0006	0.0009	0.0001	0.0002	0.0000
Na	0.0005	0.0011	0.0003	0.0007	0.0001	0.0000	0.0012	0.0008	0.0013	0.0012	0.0016	0.0017	0.0009	0.0007	0.0000	0.0003	0.0002	0.0013	0.0006	0.0004	0.0000	0.0007	0.0000	0.0014	0.0003	0.0011
K	0.0005	0.0018	0.0012	0.0002	0.0000	0.0004	0.0005	0.0002	0.0005	0.0002	0.0002	0.0002	0.0016	0.0004	0.0008	0.0001	0.0002	0.0001	0.0001	0.0009	0.0002	0.0004	0.0001	0.0010	0.0006	0.0000
Cr	0.0010	0.0003	0.0011	0.0009	0.0001	0.0014	0.0002	0.0006	0.0007	0.0001	0.0007	0.0011	0.0002	0.0000	0.0009	0.0011	0.0012	0.0002	0.0006	0.0000	0.0017	0.0016	0.0019	0.0009	0.0026	0.0006
P	0.0001	0.0003	0.0005	0.0007	0.0005	0.0008	0.0011	0.0006	0.0004	0.0007	0.0008	0.0004	0.0004	0.0005	0.0001	0.0002	0.0000	0.0002	0.0001	0.0001	0.0000	0.0004	0.0003	0.0001	0.0006	0.0015
Fe^{+3}	0.0693	0.0774	0.0863	0.0526	0.0732	0.1577	0.2109	0.0537	0.0959	0.1575	0.1473	0.0994	0.0270	0.1633	0.1042	0.1548	0.0682	0.1388	0.1457	0.0627	0.1106	0.0511	0.0905	0.1015	0.0614	0.0989
Fe^{+2}	0.9415	0.9245	0.9183	0.8985	0.9320	0.8655	0.8517	0.9502	0.9270	0.8934	0.8962	0.9171	0.9267	0.8971	0.9144	0.9101	0.8863	0.9135	0.8925	0.9273	0.8696	0.9197	0.9027	0.9249	0.9055	0.9174
End Member Compositions																										
Geikielite	1.14	0.27	2.63	0.75	0.16	4.76	3.76	1.47	0.94	1.04	1.04	1.99	4.82	1.16	2.09	0.91	7.33	0.52	0.45	1.95	6.83	4.51	3.70	0.17	5.66	1.89
Pyrophanite	0.88	2.91	0.78	6.52	2.90	0.55	0.31	0.59	1.14	1.47	1.63	0.87	0.76	0.80	0.97	0.08	0.37	0.89	2.82	1.91	0.34	0.58	1.19	1.78	0.20	1.25
Eskolaite	0.10	0.03	0.11	0.09	0.01	0.14	0.02	0.06	0.07	0.01	0.07	0.11	0.02	0.00	0.09	0.11	0.12	0.02	0.06	0.00	0.17	0.16	0.19	0.09	0.26	0.06
Ilmenite	94.15	92.45	91.83	89.85	93.20	86.55	85.17	95.02	92.70	89.34	89.62	91.71	92.67	89.71	91.44	91.01	88.63	91.35	89.25	92.73	86.96	91.97	90.27	92.49	90.55	91.74
Hematite	3.47	3.87	4.32	2.63	3.66	7.89	10.54	2.68	4.79	7.88	7.36	4.97	1.35	8.17	5.21	7.74	3.41	6.94	7.29	3.14	5.53	2.56	4.52	5.08	3.07	4.95

(Feo): As determined by EPMA; (c): indicates calculated values of FeO and Fe_2O_3 (Droop, 1987; Nayak et al. 2012)

Table 2. Summary of chemical data (wt. %) of ilmenites from red sediments

Probe	Minimum	Maximum	Average
SiO_2	0.00	0.12	0.03
TiO_2	47.45	52.49	50.05
Al_2O_3	0.00	0.06	0.02
FeO	44.35	50.71	48.06
MnO	0.04	3.00	0.62
MgO	0.04	1.99	0.64
CaO	0.00	0.03	0.02
Na_2O	0.00	0.04	0.02
K_2O	0.00	0.06	0.02
Cr_2O_3	0.00	0.13	0.04
P_2O_5	0.00	0.07	0.02

Distribution of Heavy Minerals

The weight percentage of total heavy minerals (THM) in red sediments ranges from 9.96 to 24.99% (av. 16.68%) and their mineral assemblage, in decreasing order of abundance in wt. %, is as follows: ilmenite - 6.49, magnetite - 3.07, rutile - 2.32, sillimanite - 2.08, zircon - 0.47, garnet - 0.24, monazite - 0.22, kyanite - 0.19 and other heavy minerals - 1.60.

Ilmenite

Most of the ilmenite grains are steel grey in colour and opaque in transmitted light. They are of various sizes and shapes, viz., some grains are well rounded to rounded with smooth surfaces and some are sub-angular to sub-rounded and some grains are numerous pits were observed under higher magnification. Different sizes and shapes of ilmenites identified under binocular microscope (Plate 1).

Mineral Chemistry of the Analyzed Ilmenite Grains

An examination of the EPMA-based chemical analysis of the ilmenite grains from the red sands of the Bhimunipatnam coast (Table 1) points to the following features of their mineral chemistry:

The range (in wt. %) and average (wt. %, in parentheses) of important chemical radicals in the analyzed ilmenite grains are as follows: TiO_2: 47.45-52.49 (av.50.05); FeO: 44.35-50.71(48.06), MnO: 0.04-3.00 (0.62), MgO: 0.04-1.99 (0.64); SiO_2: (0.03) and Al_2O_3 (0.02). Ratios of important elements (Table 3) show that Mn/Mg: 0.08-42.69, with more than 70% of the samples having value > 1 and rest < 0.50; Ti/(Ti + Fe): 0.42-0.47.

The large variation of FeO in the ilmenite could be due to hematite exsolved phases within ilmenite (Jagannadha Rao et al., 2005). The ilmenite in felsphathic gneisses are more iron and less TiO_2 compared to ilmenite in khondalites and charnockites where iron is less and TiO_2 is more (Divakara Rao and Murthy, 1998). A higher amount of FeO (44.35 to 50.71 %) is ascribable to higher presence of ilmenite – hematite exsolved phases (Gujar et al., 2007). The studied ilmenites have high values of FeO, ranging from 44.35 to 50.71%, which demarcate ilmenite - hematite exsolved phases. Back Scattered Electron (BSE) images (Fig. 3) of the ilmenite grains under study show sub-angular to sub-round shape and notable intergrowth of ilmenite and hematite phases, corroborating their mineral chemistry, showing pitted nature.

The Fe - Ti oxides and end-member composition, calculated indicate that ilmenite ($FeO.TiO_2$) component is predominant and varies from 85.17 to 95.02%, whereas hematite component (Fe_2O_3) is less and ranges from 1.35 to 10.54%, with minor geikielite and pyrophanite end-members varying from 0.16 to 7.33% and 0.08 to 6.25%, respectively; eskolaite component is negligible.

Rhombohedral quaternary system diagram, viz., ($FeTiO_3$ - $MnTiO_3$ - $MgTiO_3$ - Fe_2O_3) (Haggerty, 1976; Nayak and Mohapatra, 1998) is generally used to differentiate ilmenites derived from different suite of rocks. The end-member compositions of the analyzed grains, when plotted in the diagram, all the samples plot in its Field 3, which indicates that the analyzed ilmenite grains were derived from basic suite of rocks (Fig. 4).

Inferences from SEM images

An examination of the Scanning Electron images shows that the ilmenites grains are of variable shape, mostly from rounded, sub – angular to sub – rounded with off edges, corroborating microscopic study of the grains, with a little alteration and few pits. SEM technique reveals features like both mechanical and chemical weathering, pits, etch – Vs, grooves and so on with low intensity in ilmenite grains of the study area. The ilmenite grains of this area exhibit sub rounded to rounded shape along with deep pits are seen resulting from mechanical collision and later from solution activity (Fig.5a – f). Sub rounded edges of angular grains with flat surface indicating long distance transportation of the sediments (Fig. 5h). Corroded feature due to chemical weathering and leaching out behind the pits or grooves observed within the ilmenites grains and undulatory wavy surfaces due to solution effect were also observed on these ilmenite grains (Fig.6a–h).

DISCUSSION

The TiO_2 content of ilmenites in the study area is comparatively

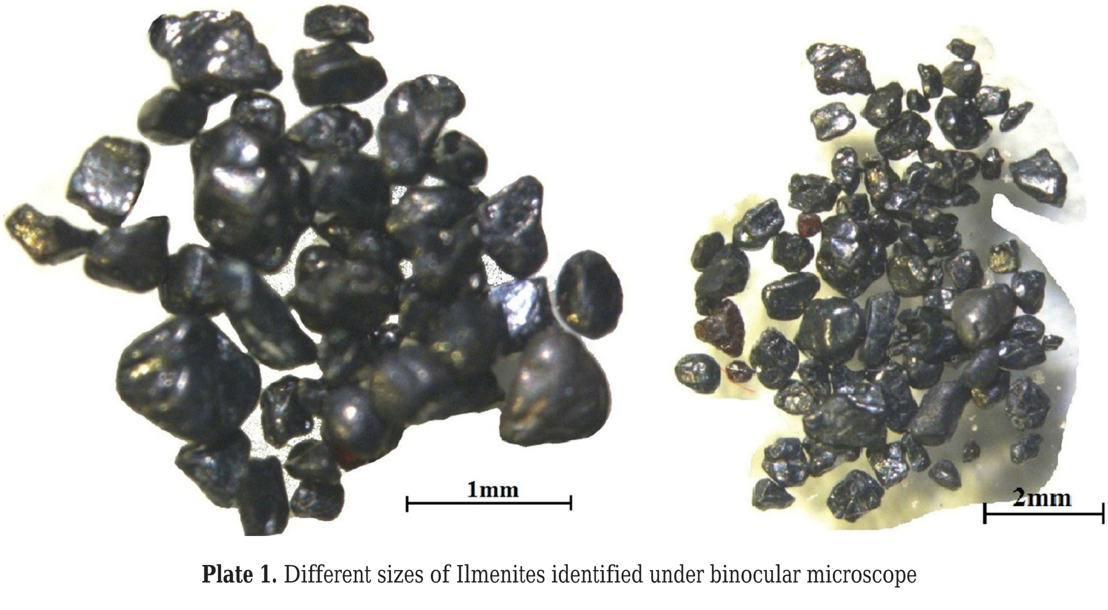

Plate 1. Different sizes of Ilmenites identified under binocular microscope

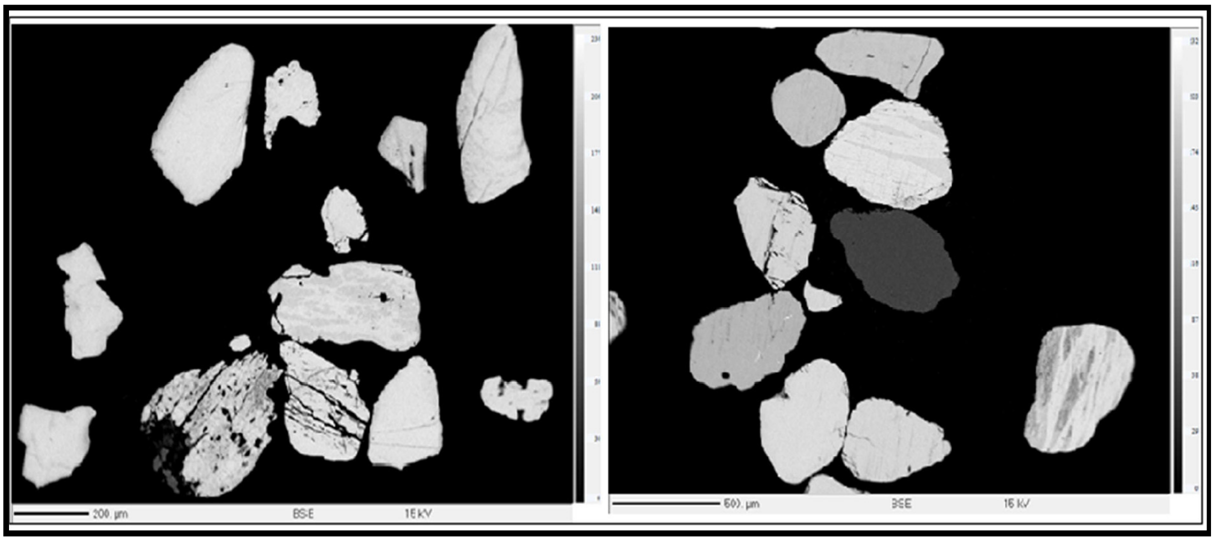

Fig. 3. Back scattered electron images (BSE) of ilmenite (grey) and hematite (white) phases in studied ilmenites from red sediments, Bhimunipatnam, Andhra Pradesh

either less or more than the theoretical value of ilmenite – 50%. (Deer et al., 1985) The variation of TiO_2 content in ilmenite may be ascribed to differences in the source rocks in the provenance, from which it was derived and any intergrowths, mainly hematite and magnetite, in ilmenites and leaching of FeO after deposition of ilmenites may be attributed to changes that took place in sedimentary environment of their deposition. Higher TiO_2 content may be due to leaching of the other cations and lower TiO_2 content and the higher amount of FeO than the theoretical value could be due to the presence of exsolved phases of hematite in ilmenite, which was noted in modern coastal sands of Bhimunipatnam - Visakhapatnam (Ramamohana Rao et al., 1983; Jagannadha Rao et al., 2005) region.

Hematite - ilmenite intergrowths of various proportions were noticed by Shunso (1977) in mafic rocks of magnetite series of Japan, which are generated in deep level (upper mantle and lower crust). Charnockites of the Araku area that forms a part of drainage basin of Gosthani River, Eastern Ghats of India were formed from mantle-derived magma by fractionation processes and crustal assimilation (Subba Rao et al., 1998) and are of calc - alkaline nature.

In the mantle-derived basaltic magma of high temperature and pressure conditions, magnetite - ulvospinel intergrowth forms and during ascending of such magma from depth, the early formed ulvospinel - magnetite series during sub-solidus oxidation at high temperature cubic solid solution series (ulvospinel - magnetite) transits through rhombohedral ilmenite - hematite solid solution series (Watkins and Haggerty 1968; Carmichael et al., 1974).

The ratios of Ti/(Ti + Fe) has been proposed to delineate weathering mechanisms undergone by ilmenite. The terminology of different stages of the weathering mechanism, with an increasing order of alteration, are: (a) Ti/ (Ti + Fe) < 0.50 (ferrian ilmenite); (b) 0.50 to 0.60 (hydrated

Table 3. Ilmenite chemistry (wt. %) of red sediments (EPMA)

Unit Name	Sample No./ Grain No.	MnO	MgO	Mn	Mg	Mn/Mg	FeO	TiO_2	Fe	Ti	Fe+Ti	Ti/(Fe+Ti)
Light Yellow sands	8/1	0.41	0.30	0.31	0.18	1.75	47.10	49.91	36.61	29.92	66.54	0.45
	8/2	1.35	0.07	1.04	0.04	24.76	47.00	50.13	36.53	30.05	66.58	0.45
	8/3	0.36	0.69	0.28	0.42	0.67	47.09	49.76	36.60	29.83	66.43	0.45
	27/4	3.00	0.20	2.32	0.12	19.26	44.35	50.38	34.48	30.20	64.68	0.47
	27/5	1.33	0.04	1.03	0.03	42.69	46.72	49.74	36.32	29.82	66.13	0.45
Yellow sands	12/6	0.26	1.28	0.20	0.77	0.26	49.27	49.13	38.30	29.45	67.75	0.43
	12/7	0.14	1.01	0.11	0.61	0.18	50.71	47.45	39.42	28.45	67.86	0.42
	12/8	0.28	0.39	0.21	0.24	0.92	47.87	51.54	37.21	30.90	68.10	0.45
	12/9	0.53	0.25	0.41	0.15	2.72	48.35	49.84	37.58	29.88	67.46	0.44
	13/10	0.69	0.28	0.54	0.17	3.16	50.12	48.80	38.96	29.26	68.22	0.43
	13/11	0.77	0.28	0.59	0.17	3.53	49.74	48.99	38.66	29.37	68.03	0.43
	13/12	0.41	0.53	0.32	0.32	0.99	48.58	50.42	37.77	30.23	67.99	0.44
	10/13	0.36	1.29	0.28	0.78	0.36	45.63	52.49	35.46	31.47	66.93	0.47
	10/14	0.37	0.31	0.29	0.19	1.53	50.44	48.58	39.21	29.12	68.33	0.43
	23/15	0.46	0.56	0.35	0.34	1.05	48.79	50.33	37.93	30.17	68.10	0.44
	23/16	0.04	0.24	0.03	0.14	0.21	50.23	48.28	39.04	28.95	67.99	0.43
Reddish brown sands	24/17	0.18	1.99	0.14	1.20	0.12	46.14	51.80	35.87	31.05	66.92	0.46
	24/18	0.42	0.14	0.32	0.08	3.85	50.13	49.26	38.97	29.53	68.50	0.43
	25/19	1.32	0.12	1.03	0.07	14.12	49.39	48.94	38.39	29.34	67.73	0.43
	25/20	0.89	0.52	0.69	0.31	2.20	46.67	50.66	36.28	30.37	66.65	0.46
Brick red sands	5/21	0.16	1.85	0.12	1.11	0.11	47.30	50.55	36.77	30.30	67.07	0.45
	5/22	0.28	1.21	0.21	0.73	0.30	46.43	51.71	36.09	31.00	67.09	0.46
	5/23	0.57	0.99	0.44	0.60	0.74	47.62	50.71	37.01	30.40	67.41	0.45
	7/24	0.84	0.05	0.65	0.03	21.57	48.87	50.23	37.99	30.11	68.10	0.44
	7/25	0.09	1.52	0.07	0.92	0.08	46.49	51.50	36.14	30.87	67.01	0.46
	7/26	0.59	0.51	0.46	0.31	1.49	48.46	50.21	37.66	30.10	67.77	0.44
	Min.	0.04	0.04	0.03	0.03	0.08	44.35	47.45	34.48	28.45	64.68	0.42
	Max.	3.00	1.99	2.32	1.2	42.69	50.71	52.49	39.42	31.47	68.5	0.47

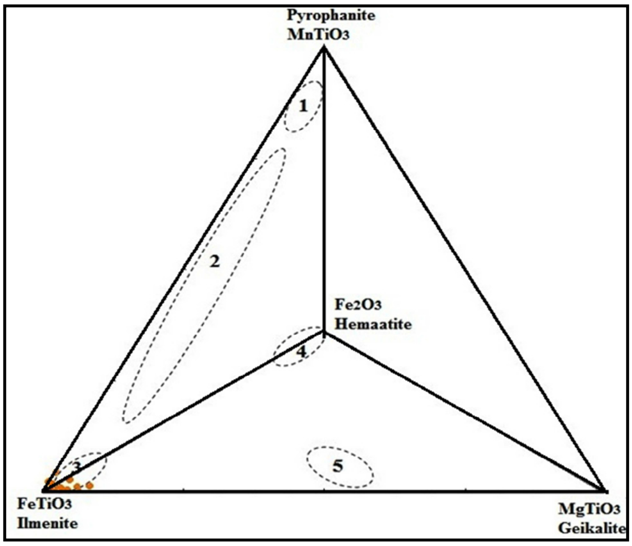

Fig. 4 Quaternary diagram with proportion of pyrophanite, ilmenite, geikielite and hematite as poles after Haggerty (1976), modified by Nayak and Mohapatra (1998) used for ilmenite discrimination. Field-1 Mn rich parametamorphites, Field-2 is intrusive acid suites, pegmatites, carbonatites and extrusive acid suites, Field-3 is basic suites i.e. amphibolites, granite gneisses and basic igneous rocks; Field-4 is intrusive acid suites and anorthosite suites and Field-5 is kimberlites

ilmenite); (c) 0.60 to 0.70 (pseudo rutile); and (d) > 0.70 (leucoxene) (Frost et al., 1983). On applying the above classification to the present work for the chemical characterization of ilmenite and its stages of alteration, the ilmenites under study with Ti/(Ti + Fe) <0.50 indicate that they are ferrian ilmenites characterized by little alteration.

The transformation of ilmenite to leucoxene happens, either through a series of intermediate products or directly, depending on the mode of alteration mechanism taking place (Hugo and Cornell, 1991; Mucke and Chaudhuri, 1991; Suresh Babu et al., 1994). The Indian placer deposits have different degree of alteration, (i.e.) Placer ilmenite deposits (i) along the Kerala coast of the west coast of India exhibit maximum alteration; (ii) along the Tamil Nadu coast of southern part of the east coast show moderate alteration; and (iii) along the Orissa coast of northern part of the east coast have undergone least alteration (Suresh Babu et al., 1996). Alteration of ilmenites increases towards equator due to increasing in temperature and rain fall. The present study area is the southern side of the Orissa coast along the east coast of India. The Ti/ (Ti + Fe) values for ilmenite from red sediments (Table 3.) of Bhimunipatnam are comparable with Ti/ (Ti + Fe) values of ilmenites from Honnavar dune sands (Hegde et al., 2006). From the present study area, Ti/ (Ti + Fe) values of ilmenite are low compared to that of the Chavara, Manavalakurchi and Gopalapur dune mineral sand deposits.

The low values (<0.5) of Ti/ (Ti + Fe) and fresh appearance of grains of ilmenite thus point out that the study ilmenite grains from the red sands have under gone less alteration and recent in contribution to red sediments. The Mn/Mg ratio is widely used as environmental indicator. Many studies on ilmenites of dune sands from the southern part of the west coast (Kerala) and Tamil Nadu coast of the southern part of the east coast of India (Table 4) indicate Mn/Mg ratio is d”1. The Mn/Mg ratios of ilmenites from source rocks and dune sands of south west coast of India, (Dinesh et al., 2007) is d” 1 and they suggested that the source rock for the ilmenites are mainly charnockites, khondalites and gneisses in hinterland, which was earlier reported by Aswathanarayana (1964) and Mallik et al., (1987). The ratio of Mn/Mg is 2.56 for Visakhapatnam dune ilmenites indicating multiple sources of meta-sedimentary and basaltic rocks (Bhattacharya et al., 1997). Mn/Mg ratio of the ilmenites from the Visakhapatnam - Bhimunipatnam coastal sands is ranges from 0.39 to 5.16 (Jagannadha Rao et al., 2005). Ilmenites of the coast Chhatrapur forming a part of the Orissa coast (Acharya and Das 2001; Rao et al., 2002) and Ekakula dune sands (Acharya and Das 2001) of Orissa show Mn/Mg ratio of d” 1. The Mn/Mg ratio of ilmenites ranges from 1.69 to 3.59 of south eastern Bangladesh (Ahmed and Islam 2001), which indicates that they were derived from plutonic rocks.

The river Gosthani that is main supplier of sediments to the study area originates in the Ananthagiri Hills of the Eastern Ghats and flows through the Borra caves and debouches its sediment at Bhimunipatnam, 4 km north of the study area. The drainage basin of Gosthani River constitutes mainly charnockites, khondalites and pyroxene granulites. The mineral assemblage of charnockite of Araku is (K-feld + Qtz+ Pl+ Opx ± Gt ± Ap± Zir ± Ilm (Subba Rao et al., 1998), and mineral assemblage of khondalite is quartz ± orthoclase ± plagioclase ± clinopyroxene ± silliminite ± garnet ± ilmenite ± magnetite ± spinel ± monazite ± zircon ± rutile (Kamineni and Rao, 1988). The geochemistry of ilmenite from charnockite and khondalites of the Gosthani drainage basin from the Araku – Padua area indicates that the MgO content of ilmenites from khondalites is higher than that of ilmenites from the charnockites (Divakara Rao and Murthy, 1998).

Of the Fe - Ti oxides (ilmenites) of the present study area, 70% of samples shows ilmenite - hematite end-member composition with Mn/

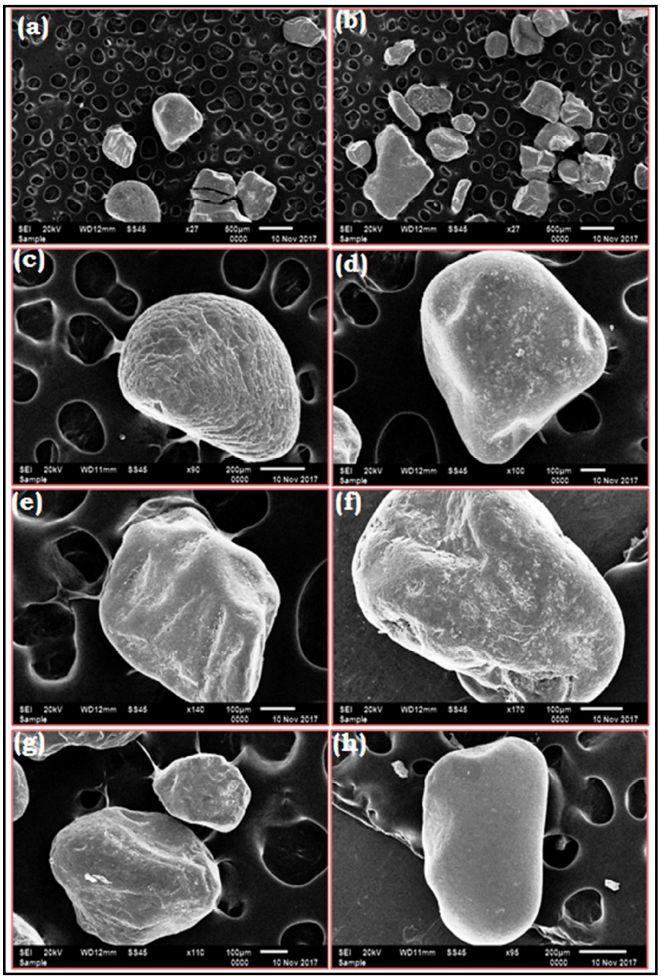

Fig.5 SEM images of ilmenite grains recovered from red sediments, Andhra Pradesh. (c - f) General view of ilmenites, Rounded to sub rounded ilmenite grains being pitted and fractured which could be due to mechanical collision of grains. (h) Sub rounded edges of angular grains with flat surface indicating long distance transportation of the sediments

Table 4. Mn/Mg ratio in ilmenites from different rock types and coastal sands compiled from published data

Author/Authors	Study Type/Area	Mn/Mg
Howie (1995)	Two pyroxenes granulites of charnockite series , Madras	0.8
Basu and Molinaroli (1989)	Igneous rocks and Metamorphic rocks	2.71 – 89.80 1.93 – 67.80
Sen (1986)	Deccan trap Basalts (Mahabaleswar)	0.28 – 1.06
Dinesh et al. (2007)	Charnockites (Nagral Kovil)Synite(Puttetti)Biotite gnesis	0.600.521.31
Divakara Rao and Murthy (1998)	CharnockiteKhondalite (Eastern Ghats	1.170.14
Jagannadha Rao et al. (2005)	Visakhapatnam to Bhimunipatnam coastal sands	0.39-5.16
Angusamy and Rajamanickam (2001)	Kanyakumari - Mandapam Beach Tamil Nadu Beach	0.182-1.61
Chandrasekhar and Rajamanickam (2001)	Velankanni – Pondicherry Central Tamil Nadu	0.375 – 1.26
Ramasamy (2001)	Tamil Nadu	0.51 – 2.85
Ahmed and Islam (2001)	South eastern Bangladesh	1.69 – 3.59
Kamineni and Rao (1988)	Sapphirine granulites from Kakanuru area, Eastern Ghats, India	0.060.02
Present Study	**Red sediments**	**0.08 – 42.69**

Mg ratio is <0.50 and remaining 30% of studied samples show ilmenite – geikielite - hematite end-member composition with Mn/Mg ratio of >1.

The Mn/Mg ratio and the end-member compositions of ilmenite from khondalite and charnockite rocks of the drainage basin of the Gosthani River show specific differences, namely, Fe - Ti oxides are of ilmenite - hematite nature in charnockites with Mn/Mg ratio of >1 and ilmenite – geikielite - hematite nature in khondalite rocks with Mn/Mg ratio of <0.5 (Kamineni and Rao, 1988; Divakara Rao and Murthy, 1998). Extrapolating these observations to the study ilmenites from the red sands, it is well corroborates with Mn/Mg ratios of ilmenites of red sediments of present study area which indicates that majority of ilmenites were derived from the igneous rocks, namely, charnockite suite of rocks and minor proportion is from meta-sedimentary khondalite suite of rocks in the Gosthani river basin.

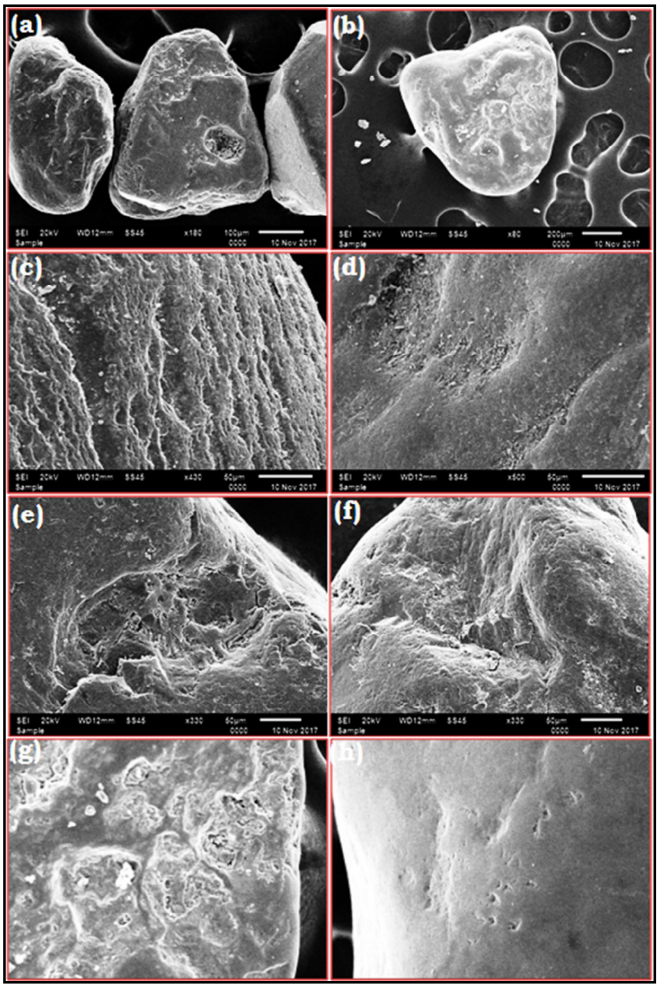

Fig.6. SEM images of ilmenite grains recovered from red sediments, Andhra Pradesh. (a, b) Mechanical and solution action (c) Corroded feature due to chemical weathering, (d) Smooth surface of ilmenite with pits (e - f) Sub rounded with impact 'v's (g) ilmenites grain leached out behind pits/grooves

Micro features like mechanical and chemical pits, solution pits, etch – Vs and grooves help to understand the physical and chemical energy levels, dissolution processes and post depostional diagenetic modifications prevailing at the surface and sub surface (Setlow and Karpovich, 1972; Morton, 1984) and also suggests that grains are formed by grain to grain collision in an aquatic environment (Mallik, 1986). The present study of micro morphological features detected by Scanning Electron Microscope (SEM) depicts the fact that two types of weathering processes such as mechanical and chemical, affected the ilmenite from red sediments that operated during their transportation as well as after deposition.

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