

# Chapter 8 Geochemical Studies of Ilmenite from Bhimunipatnam to Konada Coastal Sands, East Coast of India, North Andhra Pradesh, India

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Abstract Titanium is an important industrial element and a key component of heavy mineral assemblages. Electron probe microanalysis (EPMA) was used to analyze the chemistry of ilmenites collected from Bhimunipatnam to Konada coastal sands, Andhra Pradesh, India's East Coast. TiO<sub>2</sub> (total Fe) from 28.79 to 55.33 wt.% (avg. 45.67 wt.%), FeO (total Fe) from 28.79 to 55.33 wt.% (avg. 45.67 wt.%), and Si, Mg, Mn, Ca, Al, V, Cr, Cu, and Zn are all present in trace amounts in detrital ilmenite. The composition of end member of ilmenites was calculated, revealing that they are made up of ilmenite—hematite derived from magmasourced charnockites and ilmenite—geikielite, pyrophanite—hematite derived from the khondalite suite of the Eastern Ghats Granulite Rocks. They are characterized as ferrian ilmenites and have a Ti/(Ti + Fe) ratio of 0.35–0.64 (avg. 0.47), indicating that these ilmenite grains have undergone less modification. Ilmenite has an Mn/Mg ratio ranging from 0.04 to 113.23 (avg. 9.39), indicating that it is generated from metamorphic rocks. Backscattered electron (BSE) scans demonstrate their distinct angular to rounded shape, with some maintaining evidence of intergrowth, prior deformation, and rounded shape, all are influenced by the Gosthani and Champavathi rivers. In terms of environmental protection, the ilmenites (industrial specifications) in the current research area are better suitable for the Chlorate process, which extracts TiO<sub>2</sub> from ilmenite more efficiently than the Sulphate process.

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#### 8.1 Introduction

Mineral beneficiation of deposits and metallurgical treatment, stratigraphic correlation, and provenance investigations all benefit from physical and chemical characterization of economic heavy minerals. Sediment composition is influenced by the initial source rock's mineralogical composition as well as numerous other variables like weathering, transportation, deposition, and diagenesis that change over time (Morton 1985; Morton and Halls Worth 1999). Because of their major, trace, and REE fingerprints, detrital heavy minerals such as rutile, garnet, ilmenite, zircon, and monazite are commonly employed for provenance characterization. The chemical composition varies depending on the paragenesis of the parent rocks (Hutton 1950; Buddington and Linsley 1964; Darby et al. 1985).

Many researchers attempted to study the geochemistry of ilmenite intergrowths, alteration, and other impurities will not only affect the overall grade of the ilmenite and Provides but also sensitive information on the alteration of ilmenite (Suresh Babu et al. 1994; Bhattacharyya et al. 1997; Ramakrishnan et al. 1997; Rao et al. 2002, 2005; Jagannadha Rao et al. 2005; Nair et al. 2006; Sundararajan et al. 2009b; Mohapatra et al. 2015). Leaching of elements (Fe) from the titanium mineral lattice by hydroxylation and environmental conditions of the deposit play role in alteration. Geochemistry of ilmenite by provenances in different rocks (Darby and Tsang 1987; Nayak and Mohapatra 1998) and coastal sands (Basu and Molinaroli 1989; Mitra et al. 1992; Ramadan et al. 2012; Rahman et al. 2014; Jayalakshmi et al. 2003; Hegde et al. 2006; Bhattacharyya et al. 2006; Dinesh et al. 2007; Bangaku Naidu et al. 2016; Ganapathi Rao et al. 2019) has been studied. To better understand chemical composition change and evaluate the range of physicochemical alterations with weathering, ilmenite from distinct beach placer deposits has been examined (Nair et al. 2009; Sundararajan et al. 2010; Nayak et al. 2012; Rao and Sengupta 2014; Acharya et al. 2015; Bangaku Naidu et al. 2017) Ilmenite's industrial applications (Gazquez et al. 2014; Bangaku Naidu et al. 2018).

This research uses EPMA to investigate the provenance and industrial applicability of ilmenite from Bhimunipatnam to the Konada coastal sands, East Coast of India, North Andhra Pradesh, India.

#### 8.2 The Study Area's Geology and Location

The examined coastline length is between the Gosthani and Champavathi river mouths in the Visakhapatnam and Vizianagaram, Andhra Pradesh (17°52.005′ to 18°02.016′N latitude and 83°26.162′ to 83°36.545′ E longitude) and 20 km long, it

has 65 N/12, O/5, and O/9 Top sheets that belong to the Survey of India (Fig. 8.1). These transient rivers make up the drainage system and have their origins in the Eastern Ghats Mountain ranges. These rivers discharge huge quantities of sand into the Bay of Bengal in Konada, Bhimunipatnam, and Chepala Uppada. Numerous geological and geomorphic characteristics were created in the study area by rivers, tiny creeks, and brisk seasonal winds. The dunes, which have a thickness of 12 m and run parallel to the coast, contain an area with a significant concentration of heavy minerals. The width of the coastal sand deposit is an average of 120 m running NE-SW over 1400 km of India's east coast is covered by the Eastern Ghats Granulite Belt. Major rock units in the Eastern Ghats include khondalites, charnockites (Divakara Rao 1984), anorthosites (Leelanandam 1990), and pyroxene granulites (Narayana et al. 1995).

#### 8.3 Materials and Methods

#### 8.3.1 Heavy Mineral Analysis

Forty-seven ilmenite grains were chosen from ten representative sediment samples and collected along ten perpendicular to the beach traverses with a 1 km interval, as shown on the map (Fig. 8.1). The samples were transported to the lab where they were dried and carefully combined, after coning and quartering, samples are reduced to 100 g. The samples were treated with dilute HCl to remove shell materials and  $H_2O_2$  to remove the organic content after they have been properly washed and dried. The materials are subjected to textual analysis after they have been properly washed and dried. The sieved fractions, that is, coarse (+60 ASTM; 0.25 mm), medium (-60 to +120 ASTM; 0.25–0.125 mm), and fine (-120 to +230 ASTM; 0.125–0.062 mm) sands. These sieved samples were subjected to the mineral separation of lights and heaves by using bromoform.

#### 8.3.2 Grain Picking

Ilmenites were identified in several samples using a binocular petrological microscope and selected for geochemical research based on their optical characteristics. From ten representative samples collected from the coastal sands of Bhimunipatnam and Konada, 47 ilmenite grains were chosen for chemical analysis.



Fig. 8.1 Sample location map of the study area

#### 8.3.3 Sample Preparation

Each sample's selected grains were mounted using epoxy resin on a glass slide of standard size for additional lapping and polishing. With the use of this technique, imaging can be done with both transmitted and reflected light microscopy. Grinding and sample removal are done to make sure the resin blocks' top and bottom are parallel. In order to create a smooth surface, lapping was done with fine abrasives, often silicon carbide. Samples were polished using a combination of very fine alumina slurry and fine SiC paper, with particle sizes ranging from 6 to 0.30 microns. The polishing and then removed from the polished sample by washing it in an ultrasonic cleaner with clean water. After drying in the air and being cleaned with a blow duster.

Before being tested with EPMA, polished ilmenite grains are carbon-coated to prevent change accumulation. Utilizing carbon evaporation in a vacuum, the coating is applied. The specimens' carbon coats are measured for thickness on a polished glass block.

#### 8.3.4 Analytical Techniques

Chemical analysis of ilmenite is used by Electron Probe Micro Analyzer (CAMECA SX 100) in the Geological Survey of India, Hyderabad. Ilmenite grains were polished and sliced into 50 mm thin slices. Forty-seven ilmenite grains were exited by a beam current of 20 nA, the radius was kept at ~1  $\mu$ m, and voltage of 15 kV. For calibration, the standard of natural minerals was used for most of the elements (Corundum-Al; Wollastonite-Ca; Almandine-Fe; Hematite-Fe; Diopside-Mg, Orthoclase for Si and K; Chromite-Cr; Albite-Na, Al; Ca; Rhodonite-Mn; TiO<sub>2</sub>-Ti;). The other experimental settings are the same as those employed by Panday et al. in 2019. Table 8.1 provides ilmenite geochemical data and structure computed using two cations and three oxygens, as well as end-member compositions, from Bhimunipatnam to Konada coastal sands.

#### 8.4 Results and Discussion

#### 8.4.1 Distribution of Heavy Minerals

Total heavy minerals (THM) in beach sands range from 12.37 to 35.25 wt.% (avg. 21.41 wt.%), and their mineral composition is as follows, in decreasing order of weight percent abundance: ilmenite is 7.10, sillimanite is 6.09, zircon is 5.52, kyanite is 5.22, magnetite is 0.61, rutile is 4.33, leucoxene is 0.18, garnet is 0.25, monazite is 0.25, and other heavy minerals are 4.16.

	Tï/Fe + Tï	0.44	0.42	0.43	0.44	0.42	0.45	0.45	0.45	0.42	0.45	0.46	0.45	0.41	0.42	0.47	0.44	0.41	0.44	0.45	0.40	0.46	0.43	0.44
	Fe + Ti	67.47	67.74	66.26	67.22	67.63	66.87	66.48	66.48	68.03	65.54	65.68	66.38	68.29	68.22	66.68	67.30	67.21	67.17	64.99	66.83	67.04	67.18	67.36
-	Mn/ Mg	10.94	22.30	4.38	15.85	0.35	7.74	46.78	20.94	14.36	4.76	15.92	0.16	25.45	<i>I.52</i>	0.24	113.23	0.86	5.14	0.77	0.04	0.62	1.34	0.48
	Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
	lema- te	4.27	8.89	7.78	4.83	10.55	3.44	2.92	4.02	10.05	3.81	2.43	5.74	11.18	10.82	2.33	6.49	10.83	4.47	5.64	14.48	4.29	9.31	5.86
	men- ti	95.01	88.45	91.55	93.94	84.58	95.78	95.19	94.38	89.04	94.07	95.58	90.11	87.22	86.34	91.57	91.16	86.28	95.39	89.05	79.82	89.47	86.60	90.79
	sko- II ate it	0.07	0.21	03	0.07	0.28	0.08	0.14	9.18	30 8	.43	01.0	0.15	.08	0.03	6 11.0	02	00.00	0.08	00.00	.08	90.0	02	.14
	yro- ha- E ite li	.53 0	2.23 (	0.42 (	01 0	0.61 0	.54 0	.67 (	.28 0	53 0	.15 0	.66 (	0.26 (	.39 (	.13 0	.58 (	27 0	0 20	0.04 0	.34 0	0 60.0	.32 (	.51 0	.56 (
	ikie- p	0 11 0	0.23 2	0.22 6	0.14	.98 6	0.16 0	0.08 1	0.14	0.08 6	0.54 1	0.24 1	8.73 6	0.12	.68 1	6.42 6	05 2	0 60:	0.02 6	1 76.8	5.53 6	(.83 1	2.56 1	.65 6
-	tal lite	00	00	00	00	00	00	00	00	00	00	00	00	00	00	2 2	00	00	00	00	00	00	00	00
-	To	2.	2.	2.	2.	2.	2.	2.	2.	2.	2.	2.	2.	2.	2.	2.	2.	2.	2.	2.	2.	2.	2.	2.
	Ъ	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	C	0 0.0	0.0	0 0.0	0 0.0	0 0.0	0 0.0	0 0.0	0 0.0	0 0.0	0 0.0	0 0.0	0 0.0	0 0.0	0 0.0	0 0.0	0 0.0	0 0.0	0 0.0	0 0.0	0 0.0	0 0.0	0 0.0	0 0.0
	К	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1 0.0	0.0	0.0	0.0	0 0.0	0.0	0 0.0	0.0	0.0	0.0	0.0
	Na	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Ca	0.00	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Mg	0.00	0.0	0.00	0.00	0.0	0.00	0.00	0.00	0.00	0.01	0.00	0.0	0.00	0.02	0.05	0.00	0.02	0.00	0.0	0.06	0.05	0.03	0.03
	Mn	0.01	0.02	0.00	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.02	0.00	0.01	0.01	0.01	0.02	0.01	0.00	0.01	0.00	0.01	0.02	0.01
	Fe	1.03	1.06	1.06	1.03	1.05	1.02	1.01	1.02	1.08	1.00	1.00	1.01	1.09	1.08	0.96	1.04	1.08	1.04	1.00	1.08	0.98	1.05	1.02
	AI	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	ц	0.96	0.91	0.92	0.95	0.89	0.97	0.97	0.96	0.90	0.96	0.98	0.94	0.89	0.89	0.98	0.94	0.89	0.96	0.94	0.86	0.96	0.91	0.94
	Si	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	$P_2O_5$	0.00	0.00	0.01	0.02	0.03	0.03	0.00	0.03	0.01	0.04	0.00	0.02	0.04	0.02	0.01	0.03	0.03	0.01	0.07	0.02	0.02	0.01	0.03
	$Cr_2O_3$	0.03	0.11	0.02	0.04	0.14	0.04	0.07	0.09	0.15	0.21	0.05	0.08	0.04	0.01	0.05	0.01	0.00	0.04	0.00	0.04	0.04	0.01	0.07
	$\rm K_2O$	0.01	0.02	0.00	0.00	0.01	0.01	0.01	0.03	0.01	0.03	0.00	0.05	0.01	0.01	0.00	0.03	0.01	0.01	0.00	0.01	0.01	0.02	0.02
	$Na_2O$	0.01	0.03	0.05	0.00	0.03	0.04	0.00	0.05	0.00	0.02	0.03	0.07	0.15	0.03	0.02	0.05	0.00	0.02	0.03	0.01	0.02	0.03	0.00
	CaO	0.04	0.02	0.02	0.04	0.00	0.04	0.02	0.01	0.10	0.08	0.13	0.07	0.00	0.02	0.01	0.04	0.00	0.00	0.02	0.02	0.01	0.01	0.00
	MgO	0.03	0.06	0.06	0.04	1.07	0.04	0.02	0.04	0.02	0.14	0.06	0.99	0.03	0.45	1.45	0.01	0.55	0.01	1.03	1.47	1.30	0.68	0.71
	MnO	0.25	1.04	0.19	0.47	0.29	0.25	0.77	0.59	0.25	0.52	0.76	0.12	0.65	0.53	0.28	1.06	0.37	0.02	0.62	0.04	0.62	0.71	0.26
	FeO	48.38	50.11	48.89	48.18	50.37	47.47	46.86	47.35	51.06	46.24	45.95	47.37	51.68	51.33	45.84	48.83	50.62	48.36	46.14	51.29	46.91	49.63	48.46
	$Al_2O_3$	0.02	0.08	0.14	0.28	0.00	0.15	0.03	0.01	0.25	0.32	0.01	0.10	0.02	0.02	0.00	0.02	0.00	0.02	0.10	0.07	0.03	0.02	0.01
ľ	$TiO_2$	49.83	48.03	47.14	49.67	47.51	50.02	50.15	49.51	47.30	49.40	50.00	49.33	46.92	47.26	51.81	48.96	46.50	49.36	48.61	44.99	51.03	47.73	49.55
ľ	SiO <sub>2</sub>	0.01	0.05	0.03	0.00	0.03	0.01	0.01	0.02	0.07	0.10	0.07	0.03	0.02	0.03	0.00	0.02	0.01	0.03	0.12	0.05	0.02	0.04	0.03
ľ	Grain No	-	2	3	4	5	6	7	8	6	10	11	12	13	14	15	16	17	18	19	20	21	22	23
	Sam- ple. No	A					в					U				D				ш				

Table 8.1 Ilmenite composition from Bhimunipatm-Konada coastal sands

Ti/Fe + Ti	5 0.53	7 0.52	5 0.53	1 0.53	1 0.53	7 0.45	5 0.45	8 0.54	0.46	7 0.35	1 0.64	0.56	0.63	9 0.53	8 0.54	9 0.44	3 0.48	
Fe + Ti	5.50 8	66.37	65.65	64.8	64.9	67.63	67.75	62.68	67.60	62.93	62.91	64.20	63.90	64.09	63.98	62.99	66.5	
Mn/ Ma	0.28	0.83	0.0	0.10	0.51	6.52	2.73	0.90	0.64	0.75	0.35	0.05	0.48	2.35	1.51	6.15	0.46	
Total	001	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	
Hema-	0.00	0.00	0.00	0.00	0.00	3.43	3.33	0.00	4.44	25.45	0.00	0.00	0.00	0.00	0.00	5.32	0.06	
Ilmen-	93.36	96.98	94.87	94.11	99.24	95.69	95.88	97.07	94.10	69.92	95.55	89.54	96.30	99.89	96.53	93.13	93.02	
Esko- liate	0.17	0.15	0.18	0.16	0.31	0.13	0.04	0.17	0.39	0.02	0.19	0.16	0.22	0.06	0.09	0.03	0.06	
Pyro- pha-	0.72	0.77	0.19	0.24	0.08	0.56	0.41	0.79	0.23	1.15	0.55	0.24	0.61	0.02	1.36	1.11	1.15	
Geikie-	5.74	2.10	4.77	5.48	0.37	0.19	0.34	1.97	0.83	3.46	3.71	10.06	2.88	0.02	2.03	0.41	5.70	
Total	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	
	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
ځ	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
2	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Ž	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
ć	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Ma	0.06	0.02	0.05	0.05	0.00	0.00	0.00	0.02	0.01	0.03	0.04	0.10	0.03	0.00	0.02	0.00	0.06	
°.W	0.01	0.01	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.01	0.01	0.00	0.01	0.00	0.01	0.01	0.01	
di la cal	0.82	0.87	0.85	0.84	0.84	1.02	1.02	0.82	0.98	1.20	0.62	0.76	0.65	0.85	0.82	1.04	0.93	
4	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.01	0.02	0.01	0.01	0.03	0.00	0.00	0.00	
Ē	1.10	1.09	1.10	1.10	1.11	0.97	0.97	1.14	0.96	0.75	1.31	1.13	1.28	1.10	1.14	0.95	1.00	
5	0.00	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.02	0.00	0.01	0.00	0.01	0.02	0.00	0.00	0.00	
- C d	0.00	0.04	0.01	0.01	0.57	0.00	0.05	0.01	0.25	0.03	0.14	0.05	0.07	0.03	0.04	0.03	0.02	
ć	0.09	0.07	0.09	0.08	0.15	0.07	0.02	0.08	0.20	0.01	0.10	0.08	0.11	0.03	0.04	0.02	0.03	
K.O	0.00	0.03	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.02	0.01	0.02	0.02	0.02	0.03	0.02	
O.eV	0.03	0.03	0.05	0.02	0.00	0.02	0.01	0.02	0.05	0.03	0.01	0.01	0.08	0.04	0.04	0.01	0.04	
Ç	0.03	0.03	0.01	0.01	0.00	0.03	0.02	0.03	0.19	0.01	0.01	0.01	0.06	0.01	0.02	0.01	0.02	
MaO	1.54	0.56	1.26	1.44	0.10	0.05	0.09	0.50	0.23	06.0	0.97	2.70	0.76	0.01	0.52	0.11	1.53	
OuM	0.34	0.36	0.09	0.11	0.04	0.26	0.19	0.35	0.11	0.53	0.25	0.11	0.28	0.01	0.61	0.52	0.55	
Q	39.35	40.99	39.98	39.22	39.27	48.12	48.16	36.95	47.40	55.33	28.79	36.29	30.58	39.03	37.75	49.04	44.52	
	0.18	0.20	0.01	0.02	0.10	0.00	0.03	0.21	0.66	0.20	0.53	0.20	0.41	0.87	0.06	0.01	0.01	
C.E	58.37	57.58	57.70	57.27	57.37	50.50	50.58	56.66	51.32	38.32	67.63	60.05	66.96	56.32	57.79	49.84	53.27	
C S	0.19	0.10	0.03	0.05	1.65	0.01	0.01	0.08	0.90	0.13	0.43	0.10	0.38	0.85	0.04	0.04	0.00	
Grain	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	
Sam- ple.	2 ц					Ð		,		Н				I				

(continued)

(continued)	
8.1	
Table	

	Ti/Fe	+ Ti	0.42	0.46	0.44	0.44	0.45	0.47	0.35	0.64	0.47
	é +	ï	57.23	57.25	56.76	57.94	56.54	56.51	52.68	58.29	56.40
	'n/ F	g 1	1.12	0.47	2.82	2.57	0.29	0.15	0.04	13.23	9.39
	W	otal M	00	00	00	00	00	00,	00	1 00	00
	ema-	e 1	0.25	2.48	5.51	6.44	0.00	1.21	0.00	5.45	5.14 1
	nen- H	ti	5.52	4.98	2.08	2.30	6.43	4.96	9.92	9.89 2	1.74
	cko- Ilr	ute ite	01 8	05 9	90 9	16 9	9 00	9 11	00 6	16 9	16 9
-0-	a- Es	te lic	40 0.	43 0.	33 0.	06 1.	40 0.	23 0.	02 0.	27 I.	81 0.
£.	cie- ph	nin	81 1.	06 0.	07 I.	05 0.	16 0.	50 0.	02 0.	06 2.	32 0.
	Geil	1 lite	2.	2.	. I.	0.	3.	3.	0.0	0 10.	9 2.
		Tota	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.0(	2.00
		Р	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
		Cr	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00
		К	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Na	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
		Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Mg	0.03	0.02	0.01	0.00	0.03	0.03	0.00	0.10	0.02
		Mn	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.02	0.01
		Fe	1.06	1.00	1.03	1.04	1.01	0.97	0.62	1.20	0.97
		AI	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.03	0.00
		Ξ	06.0	0.98	0.94	0.94	0.95	0.99	0.75	1.31	0.99
		Si	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00
		$P_2O_5$	0.01	0.01	0.00	0.02	0.02	0.02	0.01	0.57	0.05
		$Cr_2O_3$	0.01	0.03	0.00	0.58	0.00	0.05	0.00	0.58	0.08
		${\rm K}_2{\rm O}$	0.01	0.02	0.01	0.00	0.03	0.01	0.00	0.05	0.01
		$Na_2O$	0.03	0.02	0.01	0.03	0.02	0.00	0.00	0.15	0.03
		CaO	0.03	0.01	0.01	0.03	0.01	0.00	0.00	0.19	0.03
		MgO	0.75	0.55	0.28	0.01	0.83	0.92	0.01	2.70	0.62
		MnO	0.66	0.20	0.62	0.03	0.19	0.11	0.01	1.06	0.38
		FeO	50.06	47.06	48.02	49.35	47.29	45.71	28.79	55.33	45.67
		$\mathrm{Al}_2\mathrm{O}_3$	0.03	0.00	0.04	0.29	0.01	0.01	0.00	0.87	0.14
		$TiO_2$	47.26	51.16	49.10	49.36	49.69	51.69	38.32	67.63	51.49
		$SiO_2$	0.00	0.01	0.06	0.04	0.01	0.08	0.00	1.65	0.16
	Grain	No	42	43	44	45	46	47			
Sam-	ple.	No	ŗ						Min.	Max.	Avg.

### 8.4.2 Ilmenite

Ilmenite is the most abundant ore mineral of titanium. This mineral has a solid solution with pyrophanite (MnTiO<sub>3</sub>), geikielite (MgTiO<sub>3</sub>), and hematite (Fe<sub>2</sub>O<sub>3</sub>). Ilmenite mineral has a large number of intergrowths of Ti–Fe oxides exsolutions, oxidation or hydrothermal process. Ilmenites contain low quantities of Ca., Zn, Cr, Al, Si, and Cu.

Ilmenite geochemistry is most important for the selection of processing methodology either chlorate route or sulfate route to produce titanium dioxide  $(TiO_2)$ . The mineral end-member compositions of ilmenite are essential for ore dressing and mineral beneficiation processes. Ilmenite's economic value can be determined by how much of it has weathered or been altered. Ilmenite's economic worth is determined by the degree of weathering or change. The mineralogy and geochemical characteristics of ilmenite are very useful for understanding its provenance and industrial applicability.

The main sources of titanium dioxide pigment are the minerals ilmenite, leucoxene, and rutile which contain titanium oxide. Titanium dioxide  $(TiO_2)$  pigment is made from titanium slag and synthetic rutile, which are both produced by ilmenite. The three minerals that can carry the most titanium are ilmenite, leucoxene, and rutile, with ilmenite acting as the main source of titanium. Ilmenite is immediately heated in an electro-furnace to melt it into ferrotitanium alloys. Cutting tools can be made of titanium carbide, a durable and silent material. Ferro-Carbon-Titanium is an alloy used to create high-speed tools.

Ilmenites are distinguished from other rock types using the rhombohedra quaternary system diagram (Haggerty 1976; Nayak and Mohapatra 1998). The endmember compositions of Fe-Ti oxides from coastal sands were shown in a rhombohedral quaternary diagram (FeTiO<sub>3</sub>–MnTiO<sub>3</sub>–MgTiO<sub>3</sub>–Fe<sub>2</sub>O<sub>3</sub>) in Fig. 8.2. Field 3 contains all of the samples, showing a basic rock suite, that is, khondalite and charnockite rocks.

Under varying temperature circumstances, the oxides in the  $TiO_2$ -FeO-Fe<sub>2</sub>O<sub>3</sub> triangle. The tie line in Fig. 8.3 depicts the overall chemical results of the examined ilmenites. These figures were derived quantitatively from a typical examination of ilmenite grains from the research area's beach and dune sediments.

Ilmenite from the Bhimunipatnam–Konada coastal sands has an average  $TiO_2$  value of 51.49 wt.%, whereas FeO (28.79–55.33 wt.%) has an average of 45.67 wt.% (Table 8.1). Cation leaching could explain the higher  $TiO_2$  content, while exsolved hematite phases in ilmenite could explain the lower  $TiO_2$  content (Jagannadha Rao et al. 2005). TiO\_2 concentrations in ilmenites were used by early researchers to determine the type of source rocks. Igneous sources had  $TiO_2$  less than 50 wt.%, whereas metamorphic sources had  $TiO_2$  greater than 50 wt.% (Darby and Tsang 1987; Basu and Molinaroli 1989). There is more iron and less  $TiO_2$  in ilmenite in feldspathic gneisses, whereas it has less iron and more  $TiO_2$  in khondalites–charnockites (Divakara Rao and Murthy 1998). Higher-grade metamorphic rocks have an average  $TiO_2$  of 51.49 wt.% in ilmenite grains.



**Fig. 8.2** Nayak and Mohapatra modified a quaternary diagram with proportions of pyrophanite, ilmenite, geikielite, and hematite as poles for ilmenite discrimination (1998). Mn-rich parametamorphites are found in field 1, intrusive acid suites, pegmatites, carbonatites, and extrusive acid suites are found in field 2, basic suites, such as amphibolites, granite gneisses, and basic igneous rocks are found in field 3, intrusive acid suites and anorthosite suites are found in field 4, and kimberlites are found in field 5

The FeO content of ilmenite from the research area's coastal sediments ranged from 28.79 to 55.33 wt.% (avg. 45.67 wt.%). The difference of FeO content in ilmenite could be linked to the degree of alteration, or leucoxenation, which results in SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, MgO, K<sub>2</sub>O enrichment, and FeO and MnO loss. Hematite exsolved phases inside the ilmenite could account for the considerable range in FeO (Jagannadha Rao et al. 2005).

The MnO content of the ilmenite from 0.01 to 1.06 wt.% (avg. 0.38%) and MgO content ranges from 0.01 to 2.70 wt.% (avg. 0.62 wt.%) from the coastal sands of Bhimunipatnam–Konada. Ilmenite grains contain trace amounts of  $SiO_2$  (0.01 wt.%) and  $Al_2O_3$  (0.01 wt.%).

The elemental geochemistry of ilmenite is very useful for geochemical characterization. Elemental ratios such as Mn/Mg are widely used as a provenance



**Fig. 8.3**  $\text{TiO}_2\text{-}\text{FeO-Fe}_2\text{O}_3$  solid system diagram showing the composition and approximate equilibrium, tie lines (dashed lines) of analyzed ilmenite.  $\text{TiO}_2\text{-}\text{FeO-Fe}_2\text{O}_3$  solid system diagram showing the composition and approximate equilibrium, tie lines (dashed lines) of analyzed ilmenite from the study area. (Modified after Buddington and Lindsley (1964), Broska et al. (2003))

indicator (Ganapathi Rao et al. 2019). The Mn/Mg ratios of ilmenite studied from Bhimunipatnam to Konada of coastal sands of this study vary from 0.05 to 113.23 (avg. 9.39) (Table 8.1). The present study area contains different rock types such as khondalites, calc-silicate rocks, quartzites, charnockites, basic granulites and granites of Archean to Precambrian age. These formations are highly migmatized and were termed as Eastern Migmatized zone (Ramam and Murthy 1997). The Mn/Mg ratios found in this study show that the majority of ilmenites come from metamorphic rocks (pyroxene granulites and khondalites), with a small percentage coming from basic charnockites and migmatizes.

Ilmenite's weathering mechanisms have been described in terms of several elemental ratios. Based on the Ti/(Ti + Fe) ratios (Forst et al. 1983) divided the four stages of ilmenite alteration. These stages are described using the following terminology in a sequence of increasing stages of modification. The Ti/(Ti + Fe) ratio for four phases of alteration: leucoxene (>0.7), pseudorutile (0.60–0.70), hydrated ilmenite (0.50–0.60), and ferrian ilmenite (>0.5). Based on the chemistry of the key elements, this system has been adopted and used for the chemical characterization of ilmenite in this work.

Ti/(Ti + Fe) ratio of the coastal sands of Bhimunipatnam–Konada ranges from 0.35 to 0.64 (avg. 0.47). Seventy-five percent of ilmenite grains have Ti/ (Ti + Fe) ratio is <0.50 which indicates that they are ferrian ilmenite and the remaining 25% of samples range from 0.50 to 0.60 which indicates that they are hydrated ilmenite. The low Ti/(Ti + Fe) values and fresh ilmenite grains imply that these grains have undergone less alteration and are more recent in input to the research region, whereas hydrated ilmenites are more weathered than ferrian ilmenites.

The higher concentration range of  $\text{TiO}_2$  content and MgO content <1.0% and Mn/Mg ratio  $\geq 1$  indicates that ilmenites are derived mainly from charnockites of calc-alkali magma. These ilmenites are formed from the khondalite suite of rocks with reduced TiO<sub>2</sub> content, MgO content >1.0%, and Mn/Mg 0.5%. In comparison to Chavara, Manavalakurichi, and Gopalpur dune ilmenites, the Ti/(Ti + Fe) values in the study region are low.

The scatter plot between Ti and (Ti/Ti + Fe) refers to the variation between different titanium mineral groups (Rahman et al. 2016) (Fig. 8.4). The studied ilmenite grains fall under the primary ilmenite field with less alteration in the narrow range of TiO<sub>2</sub>, MgO content <0.50% and Mn/Mg ratio < 1 most of samples indicates that the ilmenites are derived from metamorphic rocks.

The alteration of ilmenite in Kerala deposits (Sundararajan et al. 2009a, b), Tamil Nadu deposits (Suresh Babu et al. 1994), Orissa deposits (Mohapatra et al. 2015), and multistage South Africa (Hugo and Cornell 1991). The alteration of ilmenites of



Fig. 8.4 Scatter plot of Ti (wt %) versus Ti/ (Ti + Fe) for Ti-rich components (Ilmenite) of the coastal sands

the study area slightly changes to that of Orissa placer deposits. The investigated area is under a subtropical environment. There is high ferrous iron and less  $TiO_2$  ilmenite when compared to the west coast Manavalakurichi and Chavara deposits. It suggests that the present placer deposits are younger in age and have undergone the least weathering, because ilmenite contains considerable substitutions of Mn, Mg, V, and Cr (Deer et al. 1975).

Hematite is found in hematite laths, bands, and streaks in ilmenite, and they show polymodal distribution, fractures, and uneven patches within ilmenite. Ilmenite primary alteration pseudorutile with dark gray (1) and rimmed with secondary alteration product anatase (white) (2). Parallel bands of isolated ilmenite and/or pseudorutile surrounded by anatase (Fig. 8.5).

Partially altered ilmenite grains have a dark gray core or bands with anatase showing intense yellow internal reflection within and surrounding grains, according



Fig. 8.5 Photomicrographs (reflected light) of polished sections of changed ilmenite grains displaying different phases of alteration

to photomicrographs of polished sections obtained with reflected light (Fig. 8.5). During the intermediate stage of alteration anatase, the dark gray phase is pseudorutile, which appears in bands inside parallel sheets of original ilmenite/pseudorutile (Fig. 8.5). Isolated ilmenite/pseudorutile residues surrounded by anatase are common (Fig. 8.5). In the last stages of transformation, anatase completely replaces ilmenite (Fig. 8.5).

The difference in ilmenite content could be attributed to the origin and level of alteration of the parent rocks. Ilmenite and exsolved hematite can occur at lower temperatures and are miscible with  $Fe_2O_3$  and  $FeTiO_3$  in metamorphic rocks of the Eastern Ghats of Rocks (7–13 kbar, 900–1100 °C). Exsolved hematite has intergrown with some ilmenite grains and vice versa. Ilmenite and hematite lamellae have bimodal thickness distributions, which may indicate that they crystallized and exsolved at distinct periods from the FeTiO<sub>3</sub> to Fe<sub>2</sub>O<sub>3</sub> solid solution (Ramdohr 1969; Ahmed et al. 1992; Acharya et al. 1999).

There have been few geochemical studies of ilmenite placer deposits in India, especially coastal placer deposits in Bhimunipatnam–Konada (the current study region). Ilmenite (69–99 wt.%), hematite (0–25 wt.%), geikielite (0–10 wt.%), and pyrophanite (0–1 wt.%), according to end-member compositions of Fe–Ti oxides from Bhimunipatnam–Konada coastal sands (Table 8.1).

The chemical composition of ilmenite is shown in Table 8.2. Ilmenite from Bhimunipatnam–Konada (BK) in Andhra Pradesh has a superior chemical purity when compared to ilmenite from other sources.

In terms of  $TiO_2$ , ilmenites from the United States, Australia, and Malaysia are superior, with Quilon (Q grade) having the highest  $TiO_2$  concentration (60%) and Manavalakurichi (MK grade) having the lowest (55%). When compared to that of the United States, Australia, and India (Q, MK, and TN), the  $TiO_2$  concentration (avg. 51 wt.%) in the current study region, Bhimunipatnam–Konada (BK), is of lower quality, but it is superior to the OR Grade.

*Industrial specifications* TiO<sub>2</sub> greater than 50%, SiO<sub>2</sub> less than 1.5%, Al<sub>2</sub>O<sub>3</sub> less than 1.0%, MnO<sub>2</sub>.1.0%, Cr<sub>2</sub>O<sub>3</sub> 0.1%, P<sub>2</sub>O<sub>5</sub> 0.05% (sulfate route), P<sub>2</sub>O<sub>5</sub> 0.1%, CaO 0.2%, MgO 1.0% (chlorate route), U + Th1000 ppm, preferred 500 ppm, ore size 100 microns >50% and 40 microns >90% are the industrial specifications for ilmenite. Table 8.2 lists the ilmenite requirements for the sulfate and chlorate procedures for TiO<sub>2</sub> extraction.

The sulfate method is no longer considered since it generates gaseous hydrogen sulfide and sulfurdioxide during initial heating, causing air pollution. As a result, in terms of environmental protection, the chlorate method is preferable to the sulfate approach for extracting  $TiO_2$  from ilmenite. Ilmenite is appropriate for chlorate process in the current study region, based on chemical parameters, and U + Th concentration must be investigated, as it has not been determined in the current study.

Titanium, the 'lightweight champion' of metals, has a variety of uses. Titanium's high strength and corrosion resistance make it a significant and strategic material. Owing to its small weight, it has been utilized in the production of surgical equipment as well as in the chemical, electrical, aerospace, and aviation industries. Owing

Table 8.2 Ilm	enite quality fre	om various d	leposits arou	nd the world								
	United States	Australia					India					Present study area
Oxides (wt %)	Florida	Australia1	Australia2	Norway- Rock	Malaysia	South Africa	ø	MK	OR	IN	AP	BK (AP)
TiO <sub>2</sub>	63.5	54-56	61	43.8	52	49.5	60	55	50.2	51-54	48–52	51.49
Fe <sub>2</sub> O <sub>3</sub>	27–31	18–24	32.5	12.7	6.5	25	25.5	18.9	12.8	11.0– 16.0	7.0–17.4	45.67
FeO	4.7	16-22	3.6	34.3	34.3	22.5	9.7	20.9	34.1	28–33	30.9– 37.0	
Al <sub>2</sub> O <sub>3</sub>	0.73-1.38	0.5-1.0	1.2	1.2	1.3	0.7	1.1	0.8	0.6	0.5-0.55	0.30- 0.77	0.13
SiO <sub>2</sub>	0.06-0.79	0.4-0.7	0.85	1.9	0.7	0.6	0.9	0.9	0.8	0.44– 0.90	0.40– 0.45	0.16
ZrO <sub>2</sub>	0.04-0.19	0.05 - 0.15	0.25	0.01	0.13	NA	0.4	0.06	0.01	NA	NA	
MnO	0.86-1.63	1.4–1.7	1.06	0.33	26	1.2	0.4	0.4	0.55	0.3-0.37	0.38– 1.14	0.38
Cr <sub>2</sub> O <sub>3</sub>	0.1-0.12	0.03-0.04	0.11	0.02	0.02	0.2	0.13	0.08	0.05	0.04– 0.06	0.04- 0.07	0.08
V <sub>2</sub> O <sub>5</sub>	0.13-0.16	0.12-0.22	0.18	0.2	0.04	0.3	0.15	0.22	0.24	0.21 - 0.25	0.20- 0.22	
MgO	0.17-0.31	0.01-0.10	0.23	3.2	0.13	0.6	0.6	1	0.6	0.6-0.67	0.48– 0.82	0.62
CaO	0.04-0.15	0.01-0.10	0.02	0.5	0.13	0.1	0.2	0.2	0.2	0.02– 0.03	0.04– 0.13	0.03
$P_2O_5$	0.12-0.18	0.02-0.04	0.14	0.04	0.1	NA	0.2	0.12	0.03	0.02	0.02- 0.57	0.05
U + Th (ppm)	69–162	40-140	160	\$	NA	<20	150	225	50- 60	39–78	NA	NA
Q Chavara, Mł	Y Manavalakuri	ichi, OR Oris	ssa, TN Tami	l Nadu, AP Andl	hra Pradesł	ı, <i>BK</i> Bhimun	upatna	m-Koi	nada			

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to its outstanding qualities of low specific gravity, considerable hiding power, high refractory index, non-toxicity, opacity, and titanium dioxide  $(TiO_2)$  is a white pigment used in welding rod coating, ceramics, chemicals, textiles, cosmetics, paints, plastics, paper, rubber, fabric, and pharmaceuticals.

## 8.5 Conclusions

- 1. Ilmenite-hematite is from charnockite and ilmenite-geikielite-pyrophanitehematite is from khondalite suite of rocks.
- 2. The higher concentration range of  $\text{TiO}_2$  content and MgO content <1.0% and Mn/Mg ratio are  $\geq$ 1 indicating that some ilmenite grains are derived mainly from charnockites of calc-alkali magma.
- 3. The lower concentration range of  $TiO_2$  content, MgO content >1.0%, and Mn/Mg <0.5% suggest that the khondalite suite of rocks is also the main contribution of ilmenites in the study area.
- 4. The Ti/(Ti + Fe) ratio ranges from 0.35 to 0.64 (avg. 0.47), indicating that these ilmenite grains have undergone less alteration and have a fresh look. The subangular to subrounded appearance indicates that the ilmenites contributed to the red sediments recently and over a short distance.
- 5. The TiO<sub>2</sub> content of ilmenite from Bhimunipatnam–Konada (BK) is lower than that of the United States of America, Australia, and Q, MK, TN (India), but higher than that of Chhatrapur, Orissa, India (avg. 51.49 wt.%) (avg. 50.2%).
- 6. In this investigation, the chlorate process extracts  $TiO_2$  from ilmenite better than the sulphate method in terms of environmental protection.

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