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Sedimentology and Geochemistry of Heavy Minerals Along Kerala and Tamil Nadu Coast With Special Reference to Raman Spectroscopy

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Abstract

The Chavara and the Manavalakurichi regions are recognized as the two important heavy mineral deposits in India. The surface samples were collected from five locations and each was analyzed for their textural parameters and mineralogy. Sediments from both the regions are characterized by fine and to medium grained sand. The Chavara sands are moderately well sorted whereas, the Manavalakurichi sands are moderate to moderately well sorted. The sediments at both sites are positively and negatively skewed with very leptokurtic to very platykurtic nature. The linear discriminate function (LDF) of the textural parameters shows aeolian and shallow marine depositional environment. The major heavy mineral present in both the region is ilmenite followed by zircon, sillimanite, rutile, monazite, leucoxene and garnet. The heavy mineral content increases towards onshore in the upper and lower foreshore slope, but the grain size becomes finer and better sorted. The highest concentration of heavy minerals was found in the berms and the upper foreshore slope. The analysis shows that these heavy mineral placers are formed mainly from the palaeo-beach deposits being reworked and transported by the waves. The geochemical studies such as the XRF and the XRD analyses show that the major heavy mineral ilmenite has the alteration property by means of ilmenite- pseduorutile- leucoxene. The XRD data reveals about the transformation of rutile from anatase in both the sectors, and garnet phases were identified as almandine. The Raman spectroscopy data reveals that ilmenite has high vibrational frequency compared to the other heavies, mainly in case of the Chavara ilmenite than the Manavalakurichi. The Raman data for rutile shows that the polymorph of rutile *i.e.* anatase transformed into rutile at lower temperatures. This is well identified in the samples collected from the Manavalakurichi region. The Raman spectroscopy of sillimanite shows the initial stage of crystallization in the samples obtained from the Manavalakurichi region. Basically, the XRD allows the identification of different phases of minerals and the Raman spectroscopy is more sensible to observe the bassanite compound. In the Raman spectra, the differences between phases are related essentially to the movement of the main Raman band.

Keywords: Heavy Minerals, Sedimentology, Geochemistry, Raman Spectroscopy, Kerala and Tamil Nadu Coasts

Introduction

Geologically, textural and mineralogical studies have been carried out in the sediments of Kerala and Tamilnadu coast. All these sediments belong to Quaternary sediments. Several authors studied about surface and subsurface sediments for granulometric studies, especially Quaternary sediments from several parts across the world, and used them as a guide for the environment of deposition (El-Shahat and Abu- Ela, 1991; Niazy *et al.*, 1992, Lotfy, 1997; Abd-Allah *et al.*, 2012; Canline *et al.*, 2021).While considering the mineralogical part, most of the research are mainly focusing on the heavy minerals and their relation to provenance (Kameel *et al.*, 1994, El-Shahat *et al.*, 1999; Abu El- Eneien *et al.*, 1997; El – Balakassy *et al.*, 2005; Wahid *et al.*, 2010; Chaudhri *et al.*, 2016; Sajimol *et al.*, 2017; Anitha *et al.*, 2020). In spite of the vast studies on the Quaternary sediments in both the Chavara (Kerala) and Manavalakurichi (Tamil Nadu) coasts, a group of literature has revealed that a relatively some special kinds of works are done only concerning both to textural and mineralogical characters of the quaternary sediments. Heavy minerals are defined as high-density minerals, which have specific gravities of 2.9gcm^{-3} or greater than this. About 56 types of translucent species of heavy minerals are mainly described and have been regarded as the major indicators of sediment sources. The heavy minerals and its assemblage in sediments usually reflect their parent rocks as well as their origin. Thus, the specific heavy minerals including Ilmenite,

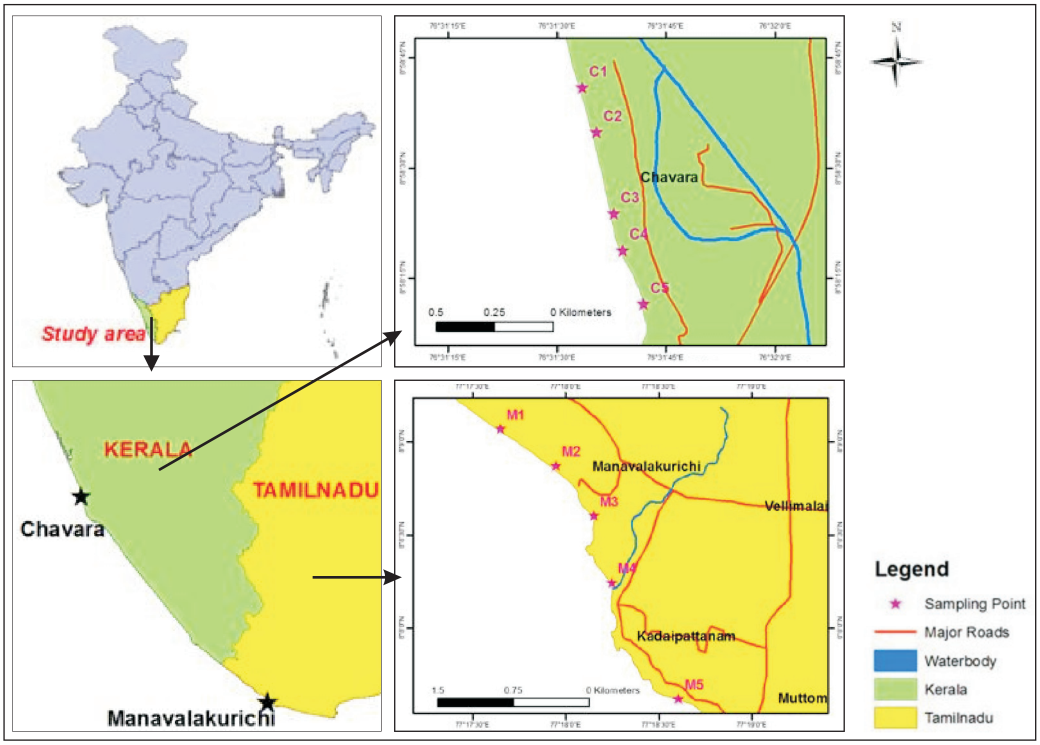

Fig.1. Location Map of the study area

Rutile, Monazite, Zircon, Sillimanite, Garnet, Leucoxene and other Ti-Fe oxide minerals have been widely used to designate the provenances of marine in terms of their unique varietal characteristics. According to the factors which influence the whole assemblage of the heavy minerals in a particular area include its weathering at different stages mainly between the source rocks and their own sedimentary environments, physical sorting, mechanical abrasion during transportation and diagenetic processes during buried. The main aim of this study is to identify the deposional conditions of heavy minerals in the Chavara and the Manavalakurichi regions. The present work also aims to shed clear and brief light on the textural as well as the mineralogical characters of the heavy minerals in these areas.

Study Area

The study area extends between latitudes 8° 58' 11.45" to 8° 58' 40.99" N and longitude 76° 31' 33.48" to 76° 31' 41.93"E in the Kerala state and 8° 9' 4.05" to 8° 7' 37.23"N and 77° 17' 39.1" to 77.310124E in the Tamil Nadu state. The sampling locations are approximately 1 km apart from each other (Fig. 1). The study regions are underlain by the crystalline rocks of Archean age consisting of gneisses, charnockites, granites and Quaternary sediments. The coastal stretch is rich in heavy minerals that include ilmenite and other heavy minerals such as rutile, leucoxene, sillimanite, garnet, zircon and monazite. The ultimate sources of heavy minerals seen in both the Chavara (CH) (Kerala) and the Manavalakurichi (MK) (Tamil Nadu) coast are the Western Ghats. The Kerala segment of the south Indian peninsula has the Precambrian basement and the overlying tertiary and quaternary formation overlying it along the coastal fringes. The rock types occurring in the Kerala region can be classified into three major age groups as belonging to Archean, Proterozoic and Cenozoic. The major units of the Archean continental crust are, granulites, granites, gneisses, and green stone .The bulk of the rocks of Kerala especially the granulites and associated gneisses belong to Precambrian. The Tamil Nadu crystalline rocks of Achaean to late Proterozoic age occupy over 80% of the area of state, while the rest covered by Phanerozoic Sedimentary Rocks mainly along the coastal belt and in few inland river valleys. The hard rock terrain comprises predominantly of Charnockitic and Kohondalitic groups and their migmatic derivatives, supra crustal sequences of Sathyamangalam and Kolar groups and Peninsular Gneissic Complex (Bhavani Group), intruded by ultramafic –mafic complexes, basic dykes, granites and syenites. The Sedimentary rocks of the coastal belt mainly include, the fluviatile, fluvio-marine and marine sequences.

Material and Methods

Totally ten samples were collected from the Chavara and the Manavalakurichi regions. The samples were taken carefully with an interval of one kilometer to represent the different textural and mineralogical varieties in each region.

Several investigation methods were subjected to the samples, mainly to determine their textural and mineralogical characters. For grain size analysis the samples were subjected to drying technique (Tucker, 1988). The bulk sample was reduced by coning and quartering and 100g of the sample was selected for laboratory analysis. Organic matters and ferruginous coatings were removed from the samples by treatment with 30 % by volume H_2O_2 and SnC_{l2}. After this pre-treatment, the samples were shifted at 0.50 ø intervals through ASTM sieve (from +18 to +230 mesh sizes)sets using a Ro-Tap sieve shaker for 15 min. The sieved materials were collected and weighed. The carbonates present in the sediments were estimated after sieving by treatment with 1:10 HCl. Weight percentage frequencies and cumulative weight percentage frequencies were computed (Folk and Ward, 1957). The sieved materials were weighed separately. Then the fractions were properly tabulated and the sands of the respective fractions were kept for further studies. The grain size parameters such as graphic mean (Mz), graphic standard deviation (SD), graphic skewness (Sk1) and graphic kurtosis (KG) were determined using the software package.

Heavy mineral separation was carried out using bromoform (SG- 2.89) and light heavies are separated by using acetone. The relative abundances of heavy mineral species were determined using point-counting of grain mounts under petrological microscopes using standard petrographic techniques. 300 grains were collected on each slide and the number percentages obtained by the counting procedure have been converted to modal percentages. Geochemistry of the sediments is carried out by using techniques such as XRF, which is running in Pan Analytical XRF instrument. Ominon software is used to interpret the data. For phase identification X-ray powder diffraction (XRD). Raman spectroscopy is a user-friendly, efficient innovative tool with tremendous potential, serving as a fundamental complement to a variety of provenance methods including heavy-mineral analysis and detrital geochronology. Because of its accuracy, efficiency and versatility, the results of the Raman technique are indispensable for fully reliable identification of heavy minerals in grain mounts or thin sections. Basic purposes of these two experiments are 1) XRD allows the identification of phases and that of 2) Raman spectroscopy is more sensible to observe the bassanite compound. In the Raman spectra, the difference between phases is related essentially to the movement of the main Raman band.

Results and Discussion

Textural attributes of sediments such as, mean, sorting, skewness and kurtosis are mainly used to reconstruct the whole depositional environment of sediments (Angusamy and Rajamanickam, 2006). Correlation between size parameters and transport processes of sediments has been established by elaborate studies from many modern and also from ancient sedimentary environments (Folk and Ward, 1957; Asselman, 1999; Malvarez *et al.*, 2001; Gandhi *et al.*, 2008; Nallusamy *et al.*, 2015). Figure 2 shows the descriptive statistics of the different grain size parameters. The grain size of the Chavara samples are completely fine grained; whereas the Manavalakurichi samples ranged between medium to fine sands. Sorting values of all the above-mentioned sediments show very narrow range of variations. The Chavara samples have moderately well sorted sediments, while the Manavalakurichi samples are moderately sorted to moderately well sorted. All the sectors in the Chavara region reached to fine skew, while the Manavalakurichi samples are both finely skewed and near symmetrical. Kurtosis values are varying in each field. The Chavara sector C1 shows platy kurtic and other shows meso kurtic, leptokurtic and very lepto kurtosis nature and in the case of MK sector, the samples shows platy kurtic, very platy kurtic, very lepto kurtic and extremely lepto kurtic. Friedman (1962) suggested that the extreme high or low values of kurtosis implies that part of sediment achieved there sorting elsewhere in high-energy environment. Variation in the kurtosis values is a reflection of the flow characteristic of the depositing medium, and the dominance of finer size of platykurtic nature of sediments reflects the maturity of the sand. This may be due to the aggregations of sediment particle size by compaction, and the variation in the sorting values. These are mainly due to continuous addition of finer/coarser materials in varying proportions.

The Raman spectroscopy data reveals that ilmenite has high vibrational frequency compared to other heavies, mainly in the case of Chavara ilmenite than Manavalakurichi. In the case of rutile, the Raman data gave the transformation of anatase into rutile at lower temperatures. This is well identified in the samples collected from the Manavalakurichi area. The Raman Spectroscopy of sillimanite shows the initial stage of crystallization. Here, it is well evidently seen in the samples obtained from the Manavalakurichi area. The property metamictization generally produced in the zircon samples, which is collected mainly from both the study areas. It can be only predicted by analyzing its intensity rate shown by the Raman peaks.

Bivarient plots

Sedimentologists have attempted to use scatter graphs of grain size parameters to distinguish between different depositional settings, via bivariate plots, which are based on the assumption that these statistical parameters reflect the differences in the fluid-flow mechanisms of sediments transportation and deposition (Sutherland and Lee, 1994). Figure 3 shows the relationship between mean grain size and sorting, sorting and skewness, skweness and kurtosis for the Chavara and the Manavalakurichi coasts. There is a clustering in medium sized and fine sand with moderately sorted and

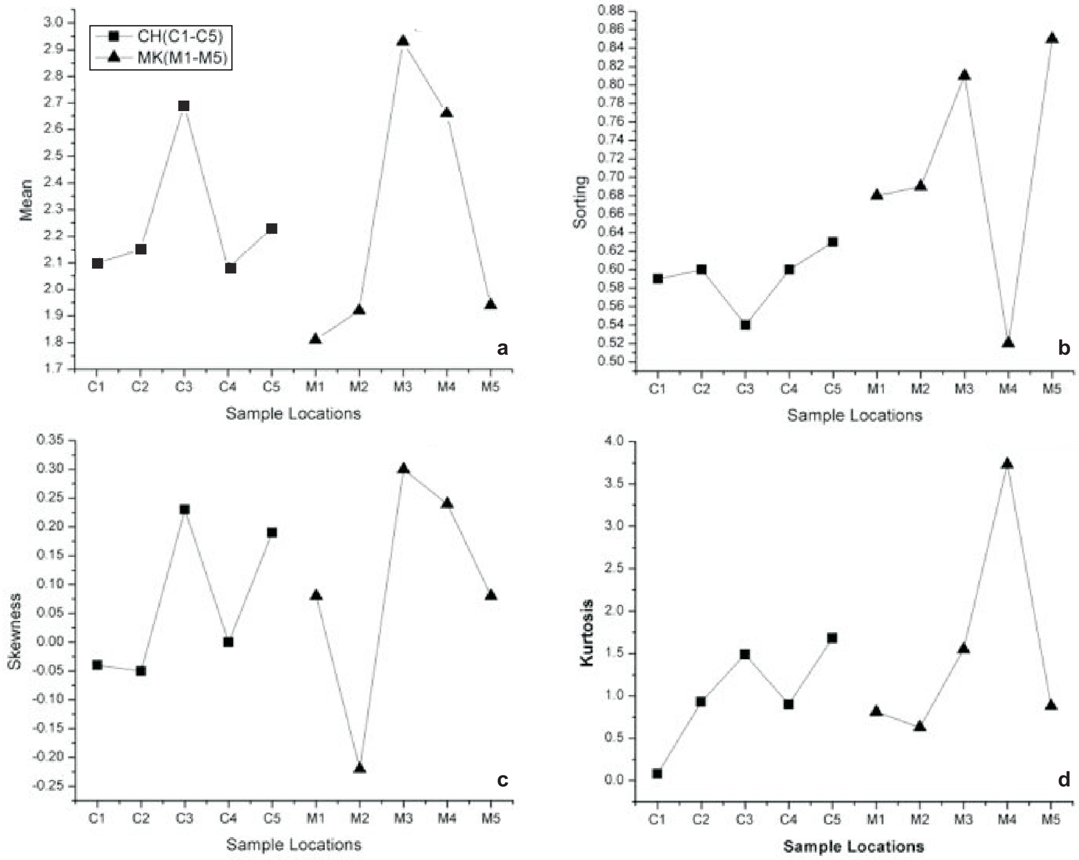

Fig.2. Variation of statistical parameters with location. (a)Mean v/s sample location (b) sorting v/s sample location (c) skweness v/s sample location (d) kurtosis v/s sample location

moderately well sorted. John (1967) explained that both mean grain size and sorting are hydraulically controlled, so that in all sedimentary environments the best-sorted sediments have mean size in the fine sand size range. The relationship between sorting and skewness for both the locations are moderately well sorted and nearly symmetrical. Sediments are moderately well sorted and near symmetrical and fine skew. By contrast, moderately well sorted to moderately sorted sediments are mainly clustered around the near symmetrical range and have positive skewness values. Plotting of skewness against kurtosis is one of the most powerful tool and help for interpreting the complete genesis of sediments, by quantifying the degree of its size distribution shows that the sediments from the Chavara and the Manavallakurichi coast lies within the positively skewed/very platy to very leptokurtic range (Folk, 1966). This suggests that the dominance of medium grain size population and the subordinate of coarse and fine grain size which gives positive skewness. However, most of the beach sediments from the Chavara and the Manavalakurichi coast show mixing of different size-range sediment populations, with one predominant population and a very subordinate population.

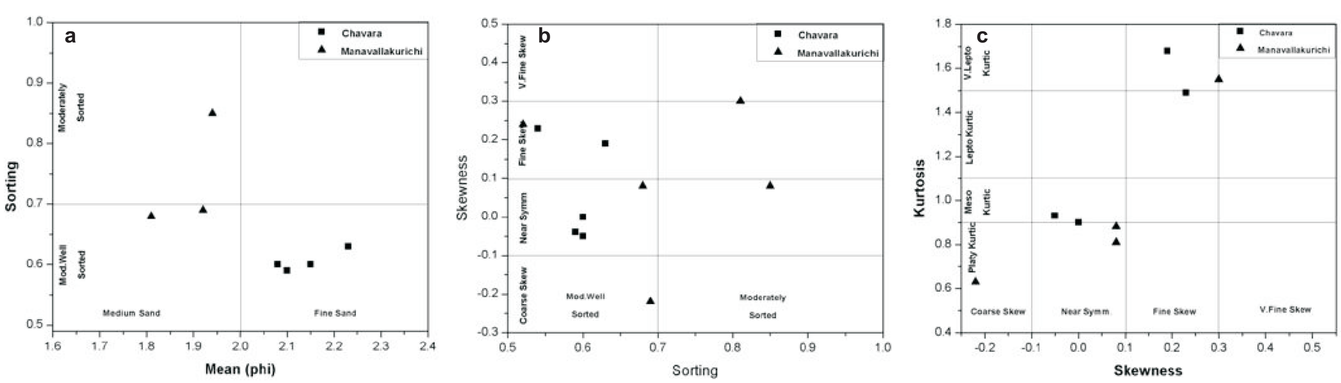

Fig.3. Bivarient plots. (a) Mean v/s sorting (b) sorting v/s skweness (c) skweness v/s kurtosis

Linear Discriminant Function (LDF)

The statistical method of analysis of the sediments helps to interpret the variations in the energy and fluidity factors seems to have excellent correlation with the different processes and the environment of deposition (Sahu, 1964). The LDF analysis of the sediment samples was carried out using the equations (1 - 4).

Y1 Aeolian

Beach = - 3.5688 (Mean) + 3. 7016 (Standard Deviation) 2 – 0.0766(Skewness) + 3.1135 (Kurtosis) (1)

If Y1>–2.7411, then the environment is 'Beach' and if Y1 <–2.7411, the environment is 'Aeolian'.

Y2 Beach

Shallow agitated water = 15.6534(Mean) + 65.7091 (Standard Deviation) 2 + 18.1071(Skewness) + 18.5043 (Kurtosis) (2)

If Y2 < 63.3650, then the environment is 'Beach' and if Y2 >63.3650, the environment is 'Shallow marine'

Y3 Shallow Marine

Fluvial = 0.2852(Mean – 8.7604 (standard deviation) 2 – 4.8932(Skweness) + 0.0482 (Kurtosis) (3)

If Y3>–7.4190, then the environment is 'Shallow marine' & if Y3 <–7.4190, the environment is 'Fluvial'

Y4 Fluvial

Turbidity = 0.7215(Mean) +0.403(Standard Deviation) 2+6.7322(Skewness) +5.2927(Kurtosis) (4)

If Y4>10.000, then the environment is 'Turbidity' and if Y4<10.000, the environment is 'Fluvial'

The process and environment of deposition were said by Sahu's linear discriminate functions were, Y1 is Aeolian, beach, Y2 is beach, shallow agitated water, Y3 is shallow marine, fluvialand Y4 is turbidity, fluvial. With reference to the Y1 and Y2 values, all the samples falls under an Aeolian process and beach process (Y1) and most of the samples falls in shallow marine waters (Y2) respectively. Further, all the samples (100 %) fall in the (Y3) shallow marine environment, Y4 values show that the samples were deposited by turbidity action by fluvial action (Fig. 4).

CM Pattern

Grain size parameters and the plots of CM patterns help to distinguish between the sediments of different environments of fluvial and deltaic deposits. In the present study, an attempt has been made to identify the modes of deposition of sediments of the Chavara and the Manavalakurichi coasts by the CM pattern. Parameter C (one percentile of the grain size distribution) and M (the median) were plotted with phi values of the C and M obtained from cumulative curves in microns (Fig. 5). The relation between C and M is the effect of sorting by bottom turbulence. The CM pattern is subdivided into in to five segments namely, NO (Rolling), OPQ (Bottom Suspension and Rolling), QR (Graded Suspension and No Rolling), RS (Uniform Suspension), S (Pelagic Suspensions). Out of the 10 locations from the South West coast of India, the analyses of samples from the Chavara and the Manavalakurichi regions were used to plot the CM diagram. These samples fall in the beach and tractive current environments. The tractive current diagram revealed that the berm samples fall in the beach environments, while the remaining samples fall in the beach and the tractive current environments mainly due to the wave actions (Kannaiyan *et al.*, 2017).

Heavy Mineral Study

The heavy mineral analysis is primarily used to understand the nature of the source from which the sediments

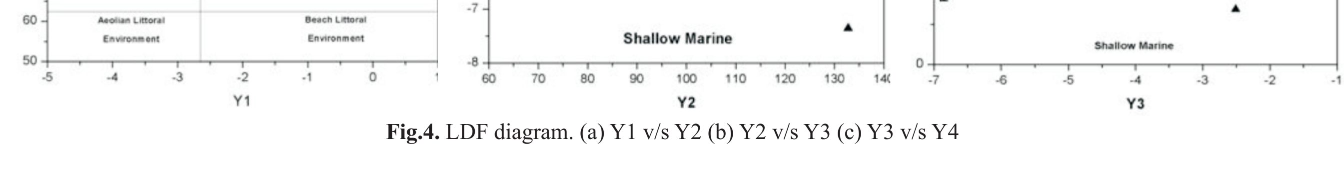

Fig.4. LDF diagram. (a) Y1 v/s Y2 (b) Y2 v/s Y3 (c) Y3 v/s Y4

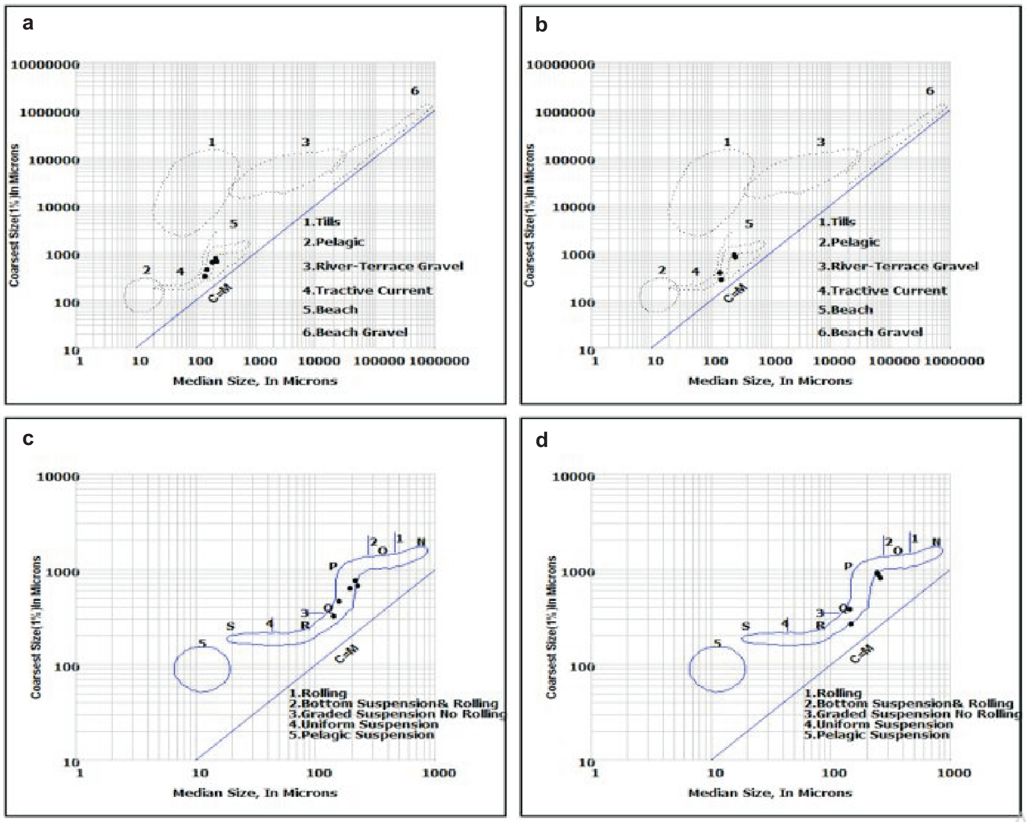

Fig.5. CM and TCD diagrams. (a) CM diagram of Chavara (b) CM diagram of Manavalakurichi(c) TCD diagram of Chavara (d) TCD diagram of Manavalakurichi

are derived because the heavy minerals are sensitive to the mode of transportation, type of weathering undergone, the distance transported, the period of stay and the nature of depositional basin. Once the material is taken out from the parent source, then the same is transported to the basin of deposition and redistributed according to their specific gravity, size, shape, etc. The distribution of heavy minerals is controlled by so many factors like destruction by wear and tear, stability of the mineral, density, grain size water motion, and energy in the depositional environment. Beach is temporary or short lived deposit on the shore. Most of the materials are sand and silt sized grains. The waves and tides have played a major role in the shaping of shoreline. Weight percentage of heavy minerals varies from (Table 1) 28.55 to 3.36 in Chavara with an average of 15.955 in medium grained samples, 67.04 to 50.43 with an average of 58.73 in fine grained samples and 29.66 to 4.03 with an average of 16.845 in very fine grained samples (Fig 6). But, the situation is quite different in the case of Manavalakurichi. Here weight percentage of heavy minerals varies from 27.77 to 0.87 with an average of 14.32 in medium grained samples, 55.24 to 30.42 with an average of 42.83 in fine grained samples and 28.7 to 3.5 with an average of 16.1 in very fine grained samples. Relatively higher percentage was shown at the Chavara region. This percentage is attributed to the intensive role of winnowing action of waves and currents.

Optical Microscopic Studies

The heavy mineral content in different size grades viz., medium (1-2 Ø), fine (2-3 Ø) and very fine (3-4 Ø) sands were mounted on the slides to study the mineralogical distribution. Sufficient care was taken to maintain a minimum of 300 grains in each mounted slide and to ensure the uniform spread of grains all over the slide and examined under the petrological microscope. The mineral counting was done by following the method of line counting. The different counts have been converted into percentages, and the values were tabulated. According to the grain count percentage values, the ilmenite is majorly present and is followed by rutile, leucoxene and

Table 1: Heavy Mineral weight percentage

		Heavy Minerals Weight %			
		THM*	Medium	Fine	Very Fine
Chavara	Avg	85.86	15.95	58.73	16.84
	Min	72.87	3.36	50.43	4.03
	Max	98.86	28.55	67.04	29.66
Manavalakurichi	Avg	61.76	14.32	42.83	16.1
	Min	46.86	0.87	30.42	3.5
	Max	76.67	27.77	55.24	28.76

*Total Heavy Minerals

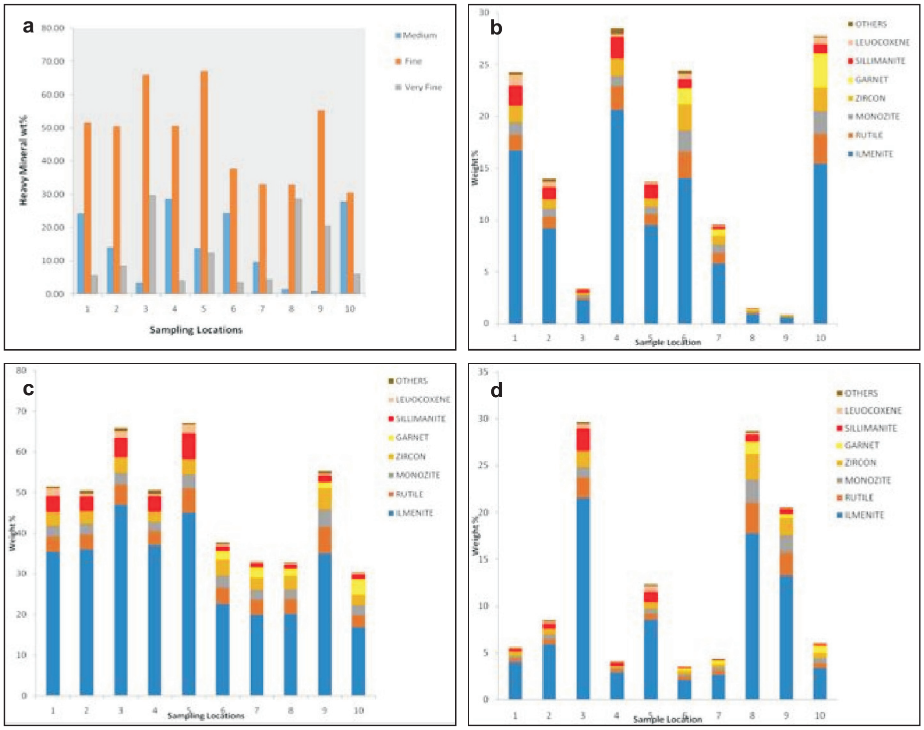

Fig.6. Graphs showing weight of the heavy minerals. (a) Total (b) Medium (c) fine (d) very fine

sillimanite. This is the case of the Chavara region and followed by ilmenite, monazite, zircon, garnet are abundantly present in the Manavalakurichi region (Fig. 7-8). These are in the case of fine grained sediments. All these abundance in minerals present in fine grained sediments (Table 2- 3).

XRF Analysis

The bulk geochemistry of the minerals present in the Chavara and the Manavalakurichi samples were analyzed using the XRF analysis along with the major oxides and trace elements.

Major oxides

Major elemental distribution (in weight %) of the seven heavy minerals of the Chavara (CH) and the Manavalakurichi (MK) samples are given in Table 4. The major oxides present in the ilmenite from CH is decreasing from CaO> MgO> SiO_2> Al_2O_3> Na2O> Fe_2O_3> TiO_2 and MK is decreasing from CaO> MgO> MnO> $V2O_5$> Al_2O_3> SiO_2> Fe_2O_3> TiO_2. The major oxides present in the rutile from the CH is decreasing from Al_2O_3>Fe_2O_3> SiO_2>V_2O_5>ZrO_2>TiO_2 and that of the MK is decreasing from Fe_2O>Al_2O_3>SiO_2>V_2O_5>P_2O_5>TiO_2. The major oxides present in the leucoxene from the CH is

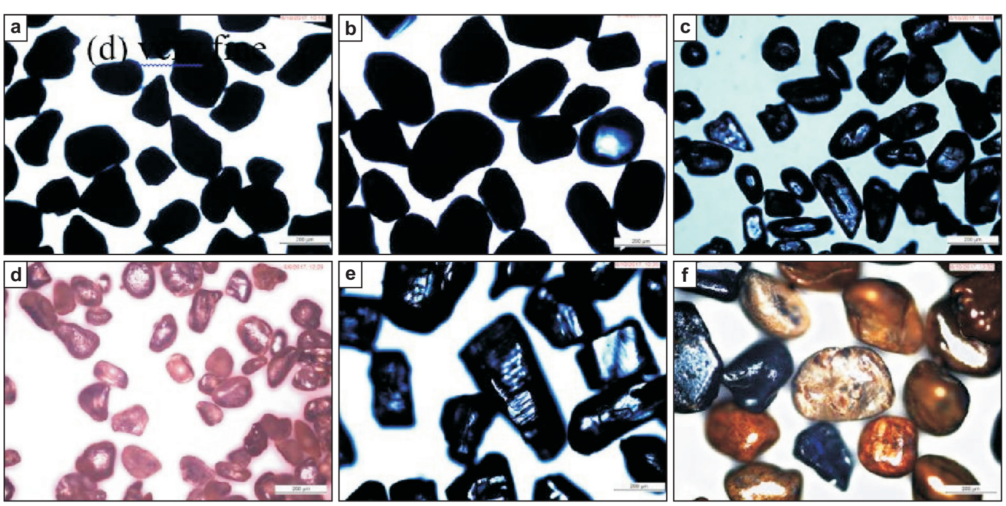

Fig.7. Optical microscope photographs of heavy minerals from Chavara samples Ilmenite (b) rutile (c) zircon (d) monazite (e) sillimanite (f) leucoxene

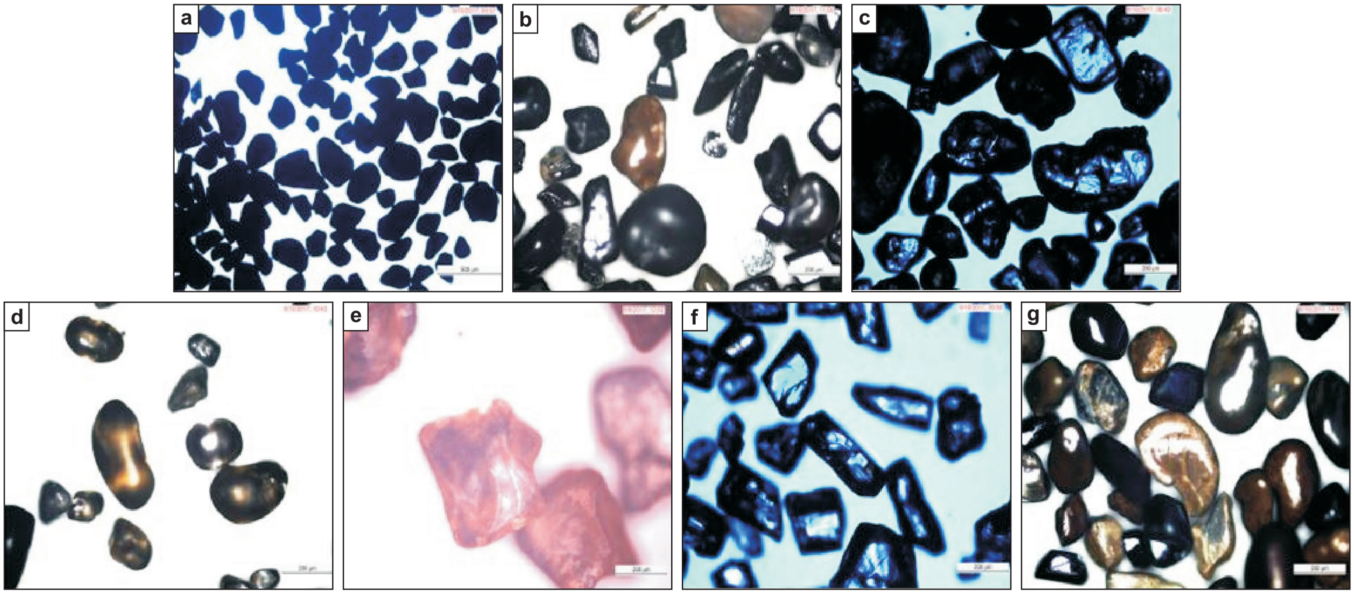

Fig.8. Optical microscope photographs of heavy minerals from Manavalakurichi samples. (a) Ilmenite (b) rutile (c) zircon (d) monazite (e) garnet (f) sillimanite (g) leucoxene

decreasing from P_2O_5>ZrO_2>Al_2O_3>SiO_2>Fe_2O_3>TiO_2 and that of the MK is decreasing from ZrO_2>P_2O_5>Al_2O_3>SiO_2>Fe_2O_3>TiO_2. But, generally we can say that ferric oxide dominates over the ferrous component in all the fractions of ilmenite samples from the CH.

Trace Elements

The trace elements are studied in ppm level (Table 5). Here, some trace elements are below the detection level. Rutile from the CH has the presence of MnO (91.7ppm) than that of

Table 2: Heavy mineral count percentages for the Medium, Fine, and Very fine fractions of Chavara

Heavy Mineral Count %		Ilmenite	Rutile	Monozite	Zircon	Garnet	Sillimanite	Leucoxene	Others
Medium	Avg.	11.667	1.23	0.775	1.060	0	1.336	0.407	0.275
	Max.	20.62	2.29	1.24	1.68	0	2.10	1.006	0.67
	Min.	2.321	0.22	0.18	0.25	0	0.23	0.074	0.06
Fine	Avg.	40.077	4.304	2.820	3.334	0.035	4.370	1.444	0.663
	Max.	46.97	5.87	3.45	3.87	0.176	6.20	2.25	0.95
	Min.	35.37	3.49	2.15	2.66	0	3.69	0.55	0.36
Very Fine	Avg.	8.564	0.812	0.547	0.723	0	0.9400	0.301	0.123
	Max.	21.54	2.175	1.16	1.69	0	2.42	0.613	0.240
	Min.	2.870	0.324	0.17	0.208	0	0.27	0.071	0.015

Table 3: Heavy mineral count percentages for the Medium, Fine, and Very fine fractions of Manavalakurichi

Heavy Mineral Count %		Ilmenite	Rutile	Monozite	Zircon	Garnet	Sillimanite	Leucoxene	Others
Medium	Avg.	7.342	1.336	1.055	1.180	1.116	0.406	0.274	0.109
	Max.	15.44	2.845	2.23	2.53	3.32	0.85	0.525	0.322
	Min.	0.545	0.104	0.075	0.076	0.02	0.02	0.009	0.006
Fine	Avg.	22.833	4.142	2.975	3.565	2.355	1.159	0.458	0.336
	Max.	34.89	6.57	4.42	5.14	3.88	1.71	0.620	0.600
	Min.	16.84	2.80	2.51	2.67	1.48	0.97	0.235	0.074
Very Fine	Avg.	7.812	1.429	1.082	1.155	0.627	0.336	0.091	0.086
	Max.	17.76	3.25	1.80	2.73	1.32	0.20	0.211	0.229
	Min.	2.109	0.36	0.28	0.34	0.247	0.086	0.015	0.014

Table 4: Results of Major elements from the study area

Ilmenite	Locations	TiO_2	Fe_2O_3	MgO	CaO	Na_2O	Al_2O_3	SiO_2
	Chavara	59.861	36.006	0.323	0.185	0.903	0.866	0.532
	Manavalakurichi	1.1792	1.152	0.485	0.244	0.274	46.136	48.586
Rutile		TiO_2	ZrO_2	V_2O_5	SiO_2	Fe_2O_3	Al_2O_3	
	Chavara	94.803	1.254	1.102	0.899	0.756	0.576	
		TiO_2	P_2O_5	V_2O_5	SiO_2	Fe_2O_3	Al_2O_3	
	Manavalakurichi	94.183	1.367	1.07	1.503	0.401	0.758	
Leucoxene		TiO_2	Fe_2O_3	SiO_2	Al_2O_3	ZrO_2	P_2O_5	
	Chavara	85.656	4.957	3.233	2.95	0.818	0.445	
		TiO_2	Fe_2O_3	SiO_2	Al_2O_3	ZrO_2	P_2O_5	
	Manavalakurichi	80.911	7.154	4.294	3.365	0.409	0.721	
Sillimanite		Al_2O_3	ZrO_2	CaO	P_2O_5	ZrO_2	Fe_2O_3	
	Chavara	58.99	37.27	1.46	0.748	0.721	0.366	
		Al_2O_3	SiO_2	ZrO_2	CaO	TiO_2	Fe_2O_3	
	Manavalakurichi	58.035	36.89	1.56	1.194	0.596	0.559	
Zircon		ZrO_2	SiO_2	Al_2O_3	HfO_2	CaO	TiO_2	
	Chavara	68.654	26.297	2.466	1.502	0.316	0.263	
		ZrO_2	SiO_2	Al_2O_3	HfO_2	CaO	TiO_2	
	Manavalakurichi	66.654	23.157	2.001	1.022	0.126	0.163	
Monazite		CeO_2	P_2O_5	La_2O_3	ThO_2	Al_2O_3	MgO	
	Chavara	30.12	24.725	10.95	8.26	0.547	0.217	
		CeO_2	P_2O_5	La_2O_3	ThO_2	Al_2O_3	MgO	
	Manavalakurichi	28.819	24.935	13.636	11.727	0.547	0.217	
Garnet		Fe_2O_3	SiO_2	Al_2O_3	MgO	TiO_2	CaO	
	Chavara	40.59	31.05	16.29	4.7	3.807	1.736	

the MK (69.9ppm). The CH samples show 14.2ppm but the Manavalakurichi sample is under Below Detection Level. Uranium is present in MK leucoxene.

Factor Analysis

R-mode factor analysis helps to identify the causes for the variation of the total heavy mineral distribution and its influence on the environment of deposition. Here the factors are influenced by heavy minerals like ilmenite, rutile monazite, zircon, leucoxene, sillimanite, garnet and other minerals. In the case of Chavara (Fig. 9a) and Manavalakurichi (Fig. 9b) heavy minerals, factor one is almost influenced with high order of positive score whereas, some second and third factor shows negative scores. The factors of these heavy minerals represent a dominant influence of mixture of low graded sediments.

Phase Identification

XRD studies were carried out for seven minerals which are collected from the coast of Chavara and Manavalakurichi. X-ray diffraction pattern of ilmenite in the Chavara and the Manavalakurichi sector were identified and show the major phase as ilmenite (Fig10a). In the Chavara sample, notable fractions have a dominance of altered phases of about or more than 64%. The first fraction represent, on the contrary, very well developed ilmenite peaks, pointing to the limited alteration suffered by these fractions. In Manavalakurichi too, the first four fractions represent the least altered fractions. But, all the Chavara magnetic fractions are highly altered than the corresponding magnetic fractions of the Manavalakurichi, indicating the advanced weathering undergone by the Chavara deposit. Though, the magnetic susceptibility has been described as being inversely related to the degree of alteration undergone, the highest magnetic fractions need not be the least altered.

The XRD patterns of Rutile in the Chavara and the Manavalakurichi fractions are given in (Fig. 10b). Here, both in the Chavara and the Manavalakurichi two types are identified. One is mainly for Anatase and another for Rutile. Anatase and Rutile are well-known as stable phases of TiO_2, the peaks are generally very diffuse, and the background is such that any amorphous phase. The transformation of Anatase to Rutile is clearly shown in the figure.

The XRD patterns of Zircon in the Chavara and the Manavalakurichi fractions are given in (Fig.10c). The XRD analysis of zircon-based samples did not show any significant differences. It should be noted, however, that the majority zircons are metamict in nature so that some retrograde reactions yielding zircon formation must be taken into account. $ZrSiO_4$ is the only present phase in the sintered samples at temperatures below 1500°C.

The XRD patterns of Monazite in the Chavara and the Manavalakurichi fractions are given in (Fig.10d). Monazite, the natural light-rare-earth phosphate is one of the most

Table 5: Trace elements (ppm) from the study area (BDL-below Detection Level)

Rutile		Mn	Pb	Bi	Se	P	Cu
	Chavara	71.01	13.18	1.345	0.8	BDL	BDL
		Mn	Pb	Bi	Se	P	Cu
	Manavalakurichi	54.13	BDL	BDL	BDL	BDL	BDL
Leucoxene		Zn	Y	As	Ge	Bi	Re
	Chavara	131.1	101.73	60.365	2.5	11.033	BDL
		Zn	Y_2O_3	As_2O_3	U	Au	SeO_2
	Manavalakurichi	192.3	105.3	76.9	71.8	22.6	BDL
Sillimanite		K	Th	Zn	Pb	Mn	Re
	Chavara	25.402	13.44	11.64	2.599	2.7	1.5
		K	Th	Zn	Pb	Mn	Re
	Manavalakurichi	32.54	61.95	17.914	5.105	11.308	BDL
Zircon		Ga	Pb	Cr	Mg	Co	P
	Chavara	90	72.68	71	27.5	1.7	BDL
		Ga_2O_3	PbO	Cr_2O_3	MgO	Co_3O_4	P_2O_5
	Manavalakurichi	89	65.3	48.57	16.58	1.248	BDL
Monazite		Zn	K	Cs	Nb	Sc	Re
	Chavara	89.97	BDL	BDL	BDL	BDL	BDL
		Zn	K	Cs	Nb	Sc	Re
	Manavalakurichi	114.07	BDL	BDL	BDL	BDL	BDL
Garnet		Cr	V	Y	Zn	K	Zr
	Manavalakurichi	421.66	246.56	299.37	301.57	304.83	368

important accessory minerals in geochemistry. Here, the succession of peaks and the intensities are almost identical in nature. Therefore, it is considered that those compounds have a true monazite structure. The XRD patterns of Garnet in the Manavalakurichi fractions are given in (Fig 10e). Here, the major phases are identified as almandine.

The XRD patterns of Sillimanite in the Chavara and the Manavalakurichi fractions are given in (Fig. 10f). The sharp and intense peaks clearly show the crystalline nature of the sample.

The XRD patterns of Leucoxene in the Chavara and the Manavalakurichi fractions are given in (Fig. 10g). As the altered variety of ilmenite, it have some similarities with ilmenite. Ilmenite is altered to leucoxene which is basically enriched in titanium and is economically very important.

The chemistry of alteration is mainly controlled by some important processes such as 1) simultaneous leaching and oxidation of ferrous iron from ilmenite and to form pseudoilmenite and then pseudorutile and 2) continuous leaching of iron during the transformation of pseudorutile to leucoxene. The process after this is also associated with hydrolysation ie, alumina and silica were introduced to the altered phases of ilmenite from the existing environment during alteration process. The reactions for transformation of ilmenite to pseudorutile and leucoxene phases are as follows.

Ilmenite – Pseudo Rutile -Leucoxene Alteration

Minerals formed by the help of several geological processes and then deposited at favorable locations give rise to economic valuable deposits. These minerals are when

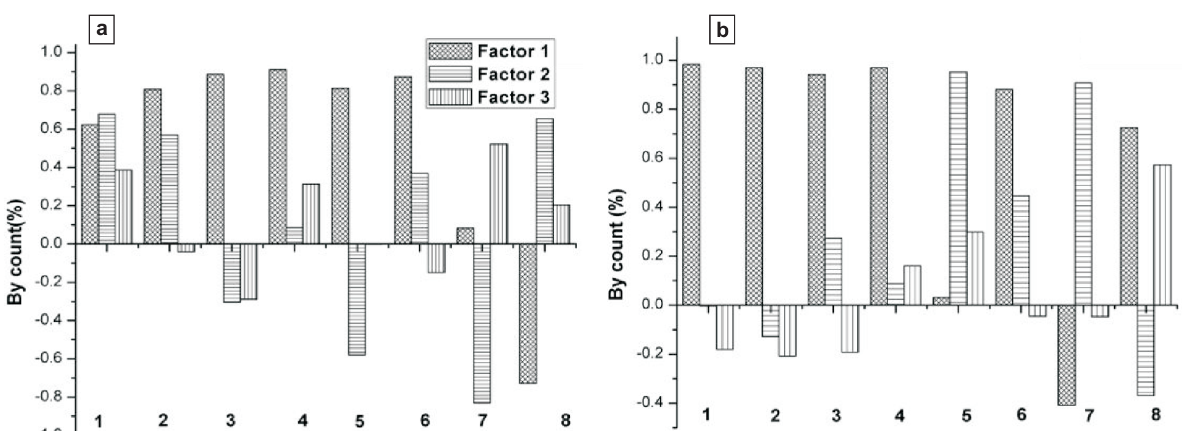

Fig.9. R-mode analysis factor for total heavy mineral data. (a) Chavara (b) Manavalakurichi

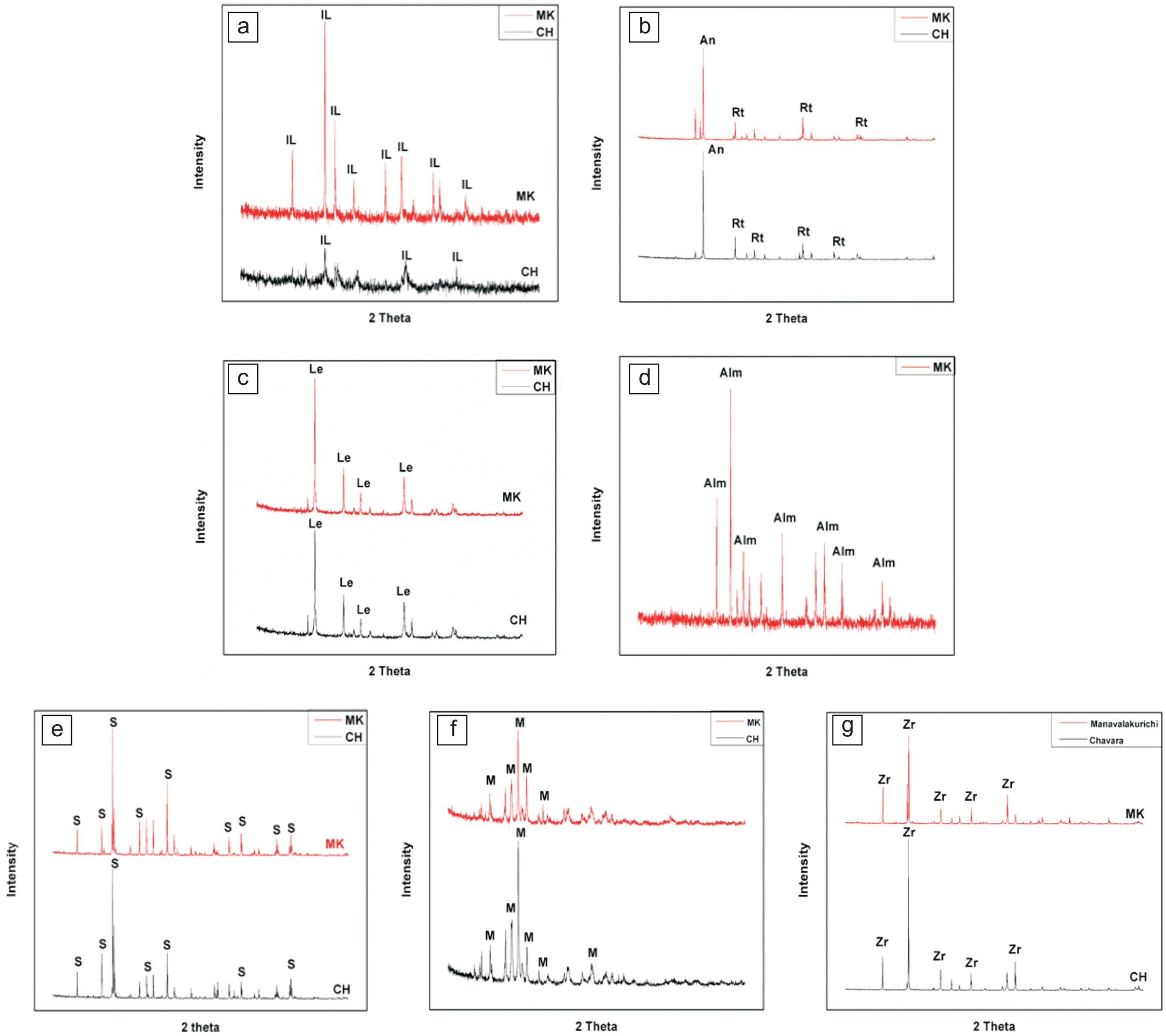

Fig.10. Phase identification using XRD Patterns for Chavara(CH) and Manavalakurichi(MK) samples, (a) Ilmenite (b) rutile (c) zircon (d) monazite (e) garnet (f) sillimanite (g) leucoxene

subjected to post-depositional physicochemical changes then undergo certain type of chemical reconstitution known as alteration. This causes either the enrichment of particular elements or depletion of elements. The alteration process gives rise to distinct phases, *i.e.* a parent phase and the newly formed authigenic phase distributed in an orderly or disorderly manner along with the parent. Most alteration leads to thermodynamically unstable, incomplete, irreversible phases that are extremely complex in elemental composition. The degree of alteration of ilmenite due to weathering is significant and is independent of the provenance. The famous Chavara placer deposit along the southwest coast of India is known for its huge reserves of heavy minerals (127 million tonnes; Abrahams *et al.*, 2001), particularly ilmenite of high industrial grade. In spite of the commercial implications and the viability of the deposit due to its high quality ilmenite and its exploitation and exploration from the beginning of the 20th century, not many studies have focused on the alteration patterns of beach ilmenite (Ramakrishnan *et al.*, 1997). The Chavara deposit represents a highly weathered,

Table 6: Chemical analysis and alteration stage of ilmenite (CH- Chavara; MK- Manavalakurichi)

Sample Locations	FeO	Fe_2O_3	Total Iron	TiO_2	Ti/Ti+Fe	Fe/Ti	Alteration stage
CH_ Ilmenite	16.199	36.006	25.1826	60.61	0.590689	0.692938	Hydrated Ilmenite
MK_Ilmenite	20.758	46.14	32.27032	48.59	0.474425	1.107815	Leucoxene
CH_ Leucoxene	16.196	4.957	21.1534	85.656	0.708246	0.411939	Leucoxene
MK_Leucoxene	20.758	7.154	27.91239	80.911	0.634743	0.57544	Pseudorutile

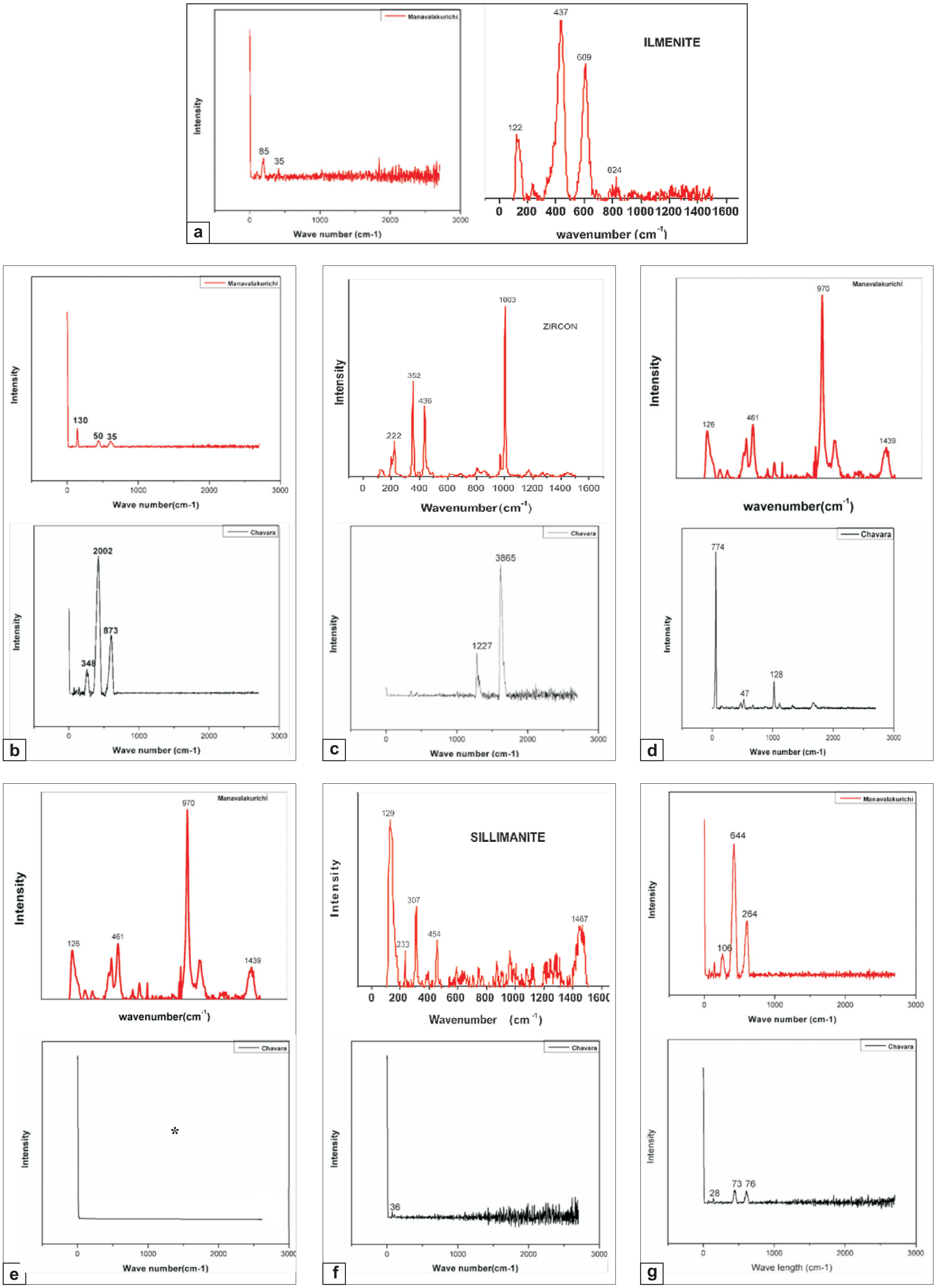

Fig.11. Raman graphs for Chavara (CH) and Manavalakurichi(MK) samples, (a) Ilmenite (b) rutile (c) zircon (d) monazite (e) garnet (*garnet content not detected in Chavara) (f) sillimanite (g) leucoxene

compositionally homogenous unit along its length (Ramakrishnan *et al.*, 1997). Both, the Chavara and the Manavalakurichi deposits are similar in terms of petrological setting, climate and groundwater conditions. Despite this, ilmenite from the two deposits shows compositional heterogeneity. Microscopic and XRD lines of evidence indicate that Chavara ilmenite is generally in a more advanced stage of alteration when compared to Manavalakurichi ilmenite. This might be attributed to the mature state of Chavara placers (Nair *et al.*, 1995).The chemistry of both iron and titanium in the Ilmenite heavy mineral structure is one of the most evident and direct indicator of the stage of alteration undergone. While the oxidation stage of iron is defined by ferrous to ferric conversion, as the first stage of alteration, and the latter process is the function of the leaching of iron from mineral structure and the corresponding enrichment of titanium. Forst *et al.* (1983) has classified the Ilmenite alteration into four stages based on the Ti/ (Ti+Fe) ratios. The terminology of those stages in the order of increasing stage of alteration is as follows. The Ti/ (Ti+Fe) values for different stages of alteration are Ferrian Ilmenite (<0.5), Hydrated Ilmenite (0.5-0.6), Pseudo rutile (0.6-0.7), Leucoxene (>0.7). From this classification, it is clear that the study area comprises of pure ilmenite and leucoxene (Table 6).

Raman Spectroscopy

Raman spectroscopy data reveals that ilmenite has high vibrational frequency compared to other heavies, mainly in the case of the Chavara ilmenite than the Manavalakurichi. In the case of rutile, Raman data gave the transformation of anatase into rutile at lower temperatures. This is well identified in the samples collected from Manavalakurichi. Raman spectroscopy of sillimanite shows the initial stage of crystallization. Here, it is well evidently seen in the samples obtained from Manavalakurichi. The property metamictization generally produced in the zircon samples which are collected mainly from both the study areas. It can be only predicted by analyzing its intensity rate shown by the Raman peaks (Fig. 11a-g).

Conclusions

The detail sedimentological studies of the samples revealed that the size distributions of the mean values indicate the dominance of fine grained nature in the Chavara samples and fine and medium grained both in the Manavalakurichi samples. The textural analysis indicates the dominance of medium to fine grained in high tide line and berm samples. Medium- to coarse-grained sediments are dominant in the low tide line samples due to the high-energy condition. The LDF results in both the study areas show the dominance of shallow marine deposits in the Aeolian beach and the influence of fluvial environment is less (~7%). The granulometric and the CM pattern indicate that most of the grains from both locations are formed by the rolling, the bottom suspension and the graded suspension. According to the grain count percentage values, ilmenite is majorly present in both the regions. All these minerals are dominantly present in the fine grained sediments. The major causes for the variation in the total heavy mineral distribution and its influence on the environment of deposition were analyzed through the R-mode statistics. In case of the Chavara and the Manavalakurichi heavy minerals, factor one is almost influenced with high order of positive score whereas, some second and third factors show the negative scores. The factors of these heavy minerals represent a dominant influence of the mixture of low graded sediments. The major heavy mineral, ilmenite has the alteration property by means of ilmenite- pseduorutile- leucoxene. The data reveals that ilmenite is pure in the Chavara region, while it gets transformed into leucoxene at the Manavalakurichi sector. The XRD data reveals about the transformation of rutile from anatase and garnet phases were identified as almandine in both the sectors. The Raman spectroscopy data reveals that ilmenite has high vibrational frequency compared to the other heavies, mainly in case of the Chavara ilmenite than the Manavalakurichi. The Raman data indicates the transformation of anatase into rutile at lower temperatures. This is well identified in the samples collected from the Manavalakurichi area. The Raman spectroscopy of sillimanite shows the initial stage of crystallization. Here, it is well evidently seen in the samples obtained from the Manavalakurichi region. The property, metamictization generally produced in the zircon samples mainly collected from both the study areas. It can be only predicted by analyzing its intensity rate shown by the Raman peaks.

Authors' Contributions

G. S. Gayathri: Conceptualization, Methodology, Formal Analysis, Investigation, Writing the Original Draft, Reviewing and Editing. **M. Suresh Gandhi:** Conceptualization, Supervision, Writing, Reviewing and Editing. **G. H. Aravind:** Formal Analysis, Reviewing and Editing. **S. R. Sreela:** Reviewing and Editing.

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