

Article

Textural and Chemical Characters of Lean Grade Placer Monazite of Bramhagiri Coast, Odisha, India

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Abstract: The present study aims to investigate the textural, mineralogical and geochemical characteristics of lean grade placer monazite from the Bramhagiri beach sand deposit to assess the possibility for its use in industrial applications. The bulk back dune sand deposit with 18 samples showed the elements uranium and thorium in traces, phosphorus and calcium in minor amounts, and alumina, silica and titanium in major amounts. Since apatite was absent in this placer deposit, P and Ca were attributed to monazite only. Based on the chemical analysis, it was established that the monazite mineral exists in this deposit. The monazite is generally below the –150- to +90-micron size range, and the concentration of the monazite mineral in the bulk back dune sand is around 0.01% by weight. The structural data and complete chemical analysis established that the monazite is Ce-monazite. The monazites with other heavy mineral sands of the Bramhagiri beach placer deposits were derived from the Eastern Ghats, which closely resembles the mineralogical composition of khondalite, charnockite, leptynite and pegmatite groups of rocks. The Eastern Ghats' provenance appears to be the primary source for the heavy mineral assemblages of the Bramhagiri placer deposit. Thus, these monazite sands are derived from the granulite facies of metamorphic rocks such as khondalites and charnockites from the Eastern Ghats group of rocks. Garnet is the major mineral, following ilmenite and sillimanite. Zircon, rutile and monazite are minor minerals in the deposit. All these minerals are well liberated and have uniform shapes with variable densities and size ranges, with different magnetic, electrical and surface properties. Hence, the occurrences of these heavy minerals are of economic importance. Further, these minerals can be recovered individually for industrial applications.

Keywords: monazite; on-shore sand; lean grade; placer minerals; beneficiation; Bramhagiri; beach sand



Citation: Singh, D.; Basu, S.; Mishra, B.; Prusty, S.; Kundu, T.; Rao, R. Textural and Chemical Characters of Lean Grade Placer Monazite of Bramhagiri Coast, Odisha, India. *Minerals* **2023**, *13*, 742. <https://doi.org/10.3390/min13060742>

Academic Editors: Francesco Radica, Gianluca Iezzi and Claudio Finocchiaro

Received: 24 April 2023

Revised: 24 May 2023

Accepted: 26 May 2023

Published: 30 May 2023



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1. Introduction

Placer deposits are natural concentrations of heavy minerals. Monazite is one of the placer-heavy minerals. There is an increased demand for rare earths in modern civilisation, especially in electronics and battery-operated motor vehicles. Exploring new resources of rare earth deposits is necessary to meet this high demand for rare earths. Monazite is one of the atomic minerals that contains a high percentage of lighter rare earths (LRE) and a lesser percentage of heavy rare earths (HRE). The demand for the exploration and exploitation of monazite is the primary objective for a country such as India. Monazite is a phosphate mineral associated with rare earth elements and is also radioactive due to the presence of uranium and thorium. The notable diversified composition of rare earths allows monazite to be considered as a group of minerals that commonly include:

- i. Monazite-Ce [(Ce, La, Nd, Th) PO₄ or CePO₄],
- ii. Monazite-Sm [SmPO₄ or {(Sm, Gd, Ce, Th) PO₄}],

- iii. Monazite-Nd [NdPO_4 or $\{(\text{Nd}, \text{La}, \text{Ce}) \text{PO}_4\}$],
- iv. Monazite-Pr [PrPO_4 or $\{(\text{Pr}, \text{Ce}, \text{Nd}, \text{Th}) \text{PO}_4\}$],
- v. Monazite-La [LaPO_4 or $\{(\text{La}, \text{Ce}, \text{Nd}) \text{PO}_4\}$],
- vi. Gasparite-Ce [$(\text{Ce}, \text{La}, \text{Nd}) \text{AsO}_4$],
- vii. Cheralite [$(\text{Ca}, \text{Ce}, \text{Th})(\text{P}, \text{Si}) \text{O}$], and
- viii. Brabantite [$\text{CaTh}(\text{PO}_4)_2$].

The source rocks for monazite are khondalite, charnockites, pegmatites, etc. The khondalites exhibit uniformity in thorium content along the Granulites Belt of Eastern Ghats [1], but a significant diversification is reported in the charnockites group of rocks [2]. In monazite, ThO_2 ranges from 6% to 10% from the khondalite rocks and between 9% and 10% from the charnockites [3]. Kamineni et al., 1991 [3] reported that monazite contains 28.35%–31.08% Ce_2O_3 , 6.52%–10.39% Th_2O_3 , 11.35%–12.34% La_2O_3 , 9.75%–10.98% Nd_2O_3 , 3.79%–4.38% Pr_2O_3 , 28.26%–29.05% P_2O_5 and 1.57%–2.02% CaO . The ThO_2 content in monazite generally ranges from 4% to 12%, while in cheralite it is as high as 30% [4]. The average ThO_2 content in earlier studied samples was 9.42% and conformed to monazites and not cheralites. Cheralites have been reported at Bhimmunipatnam, AP coast [5]. The Th and Ca may be due to the substitution of REEs. The chemistry of monazites supports the interpretation that actinides substitute for LREE and implies other concomitant substitutions, such as Ca for REE and Si for P. It is reported that the chemical composition of monazite minerals such as Ce_2O_3 , La_2O_3 and P_2O_5 corresponds to 26.6%, 13.4% and 23.6%, respectively. The radioactive content includes U and ThO_2 , corresponding to 0.572% and 10.491%, respectively. The major constituents present in the mineral are in the order of $\text{Ce}_2\text{O}_3 > \text{P}_2\text{O}_5 > \text{La}_2\text{O}_3 > \text{Nd}_2\text{O}_3 > \text{ThO}_2 > \text{TiO}_2 > \text{SiO}_2 > \text{Pr}_2\text{O}_3 > \text{CaO} > \text{Al}_2\text{O}_3 > \text{Sm}_2\text{O}_3 > \text{CdO} > \text{U} > \text{Fe}_2\text{O}_3 > \text{Y}_2\text{O}_3 > \text{PbO} > \text{MgO}$. ZnO , IrO_2 , Gd_2O_3 and other heavy rare earths are also seen at the ppm-level [6].

A literature review revealed that globally many researchers have studied monazite chemistry and its occurrence in placer deposits [7,8]. A few researchers studied the granulometry, mineralogy and geochemistry of monazite all along India's East and West coasts [9–15]. However, the studies related to the Bramhagiri sand deposit specially on monazite is negligible [16–20].

It is reported [9] that in the heavy mineral deposits of Chavara and Manavalakurichi, the La content lies in the range of 9.73% to 12.04%, Ce between 23.23% and 27.68%, while that of ThO_2 and U_3O_8 is 10.50% and 0.04%, respectively. The total REE contents (TREE) range from 56.6% to 48.4%, in which the light lanthanides (LREE) compose 55.6% to 46.8%, and the heavy lanthanides (HREE) compose 1.55%–0.908%. The chemical composition of the monazite of the Bhimunipatnam–Konada coastal sand deposit has been reported by Bangaku Naidu et al. [10]. The ThO_2 content varies from 3.78% to 13.3%, Y_2O_3 from 0.00% to 2.26%, SiO_2 from 0.48% to 2.85%, CaO from 0.7% to 1.76% and UO_2 from 0.03% to 0.42%. The total REE ranges from 43.47% to 67.78%, total LREE from 42.90% to 64.08% and the total HREE varies from 0.57% to 3.70% in this study area. BC Acharya et al. 2009 [11] reported that Kontiagarh, Ganjam Dist, Odisha monazite contains 28.35%–31.08% Ce_2O_3 , 11.35%–12.34% La_2O_3 , 6.52%–10.39% ThO_2 , 3.79%–4.38% Pr_2O_3 , 9.75%–10.98% Nd_2O_3 , 28.26%–29.05% P_2O_5 and 1.57%–2.02% CaO . They also examined previously another study area, Ekaula Beach, Gahiramath coast, Odisha, in 1998 [12] for pre-concentrate of zircon and monazite. These data are not precise for monazite chemical analysis. Sunita et al. [16–21] studied the Bramhagiri coast for its heavy mineral concentration, granulometry of heavy minerals and assessment on mineralogical modal analysis and its influence on flowsheet development for the recovery of individual heavy minerals and value addition. The monazites with other heavy mineral sands of the Bramhagiri beach placer deposits were derived from the Eastern Ghats group of rocks, which closely resembles the mineralogical composition of the khondalite, charnockite, leptynite and pegmatite groups of rocks. The Eastern Ghats' provenance appears to be the major source for the heavy mineral assemblages of the Bramhagiri placer deposit. Thus, these monazite sands are derived from the granulite facies of metamorphic rocks such as khondalites and charnockites from the Eastern Ghats

group of rocks [11,12]. The Th and Ca present in monazite may be due to the substitution of REEs [3]. The paper aims to study the textural, mineralogical and chemical characteristics of Lean Grade Placer Monazite of Bramhagiri Coast, Odisha, India. A detailed study has not been attempted on this deposit by other researchers or academicians in India or elsewhere.

2. Materials and Methods

Around 118 bulk raw sand and auger bore samples were collected all along the coast of Brmhagiri to Sipasuribili, Puri Dist, Odisha, India. The source rock or parent rocks for the occurrence of these coastal placer minerals are khondalite rocks and recent alluvium deposits. The sample collection location map and parent rock can be seen in the Figure 1 location map.

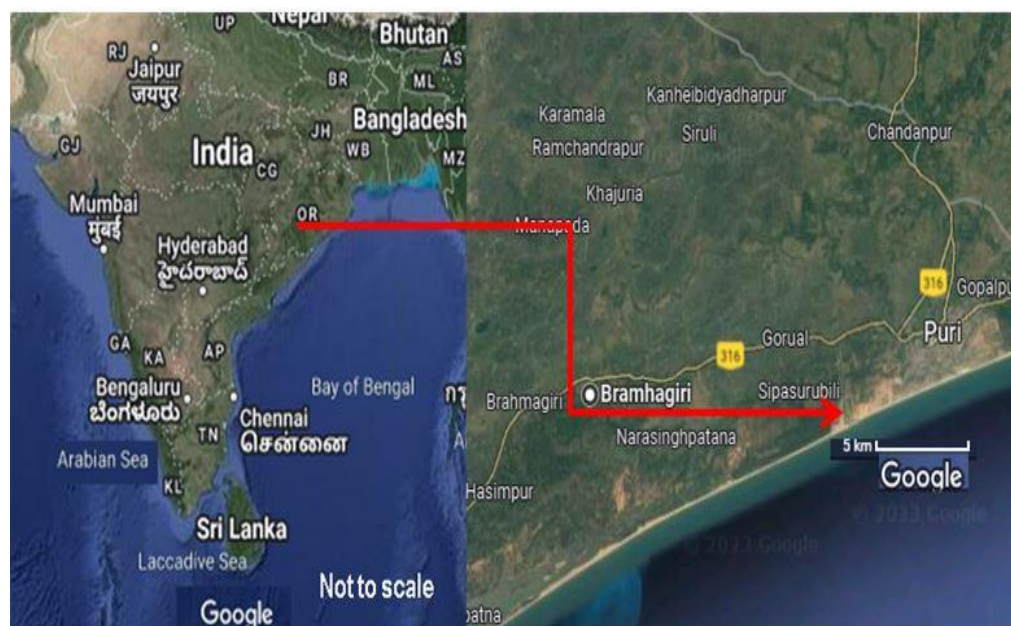


Figure 1. Sample location map: Bramhagiri, Odisha, India GPS coordinates. Latitude: 19.8000; longitude: 85.6500.

However, 118 samples were collected from five different shore/dune sands to assess the occurrence of the monazite mineral concentration. The five different category sands termed and shown in Figure 2 are [a] shore sand, [b] backshore sand, [c] frontal dune sand, [d] central dune sand and [e] back dune sand.

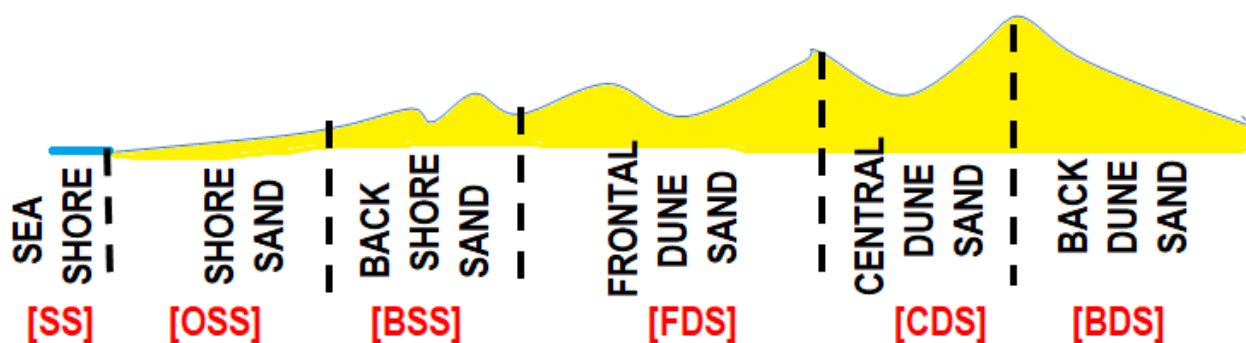


Figure 2. The terminology used for the shoreline topography to collect auger samples.

All 118 samples collected from the five zones shown in Figure 3 are sub-sampled using standard sampling methods. Samples were collected 1 km from north to south along the

coast and 2 km from east to west. Beach sand samples were collected up to water table for near to the shore. Each sample was collected about 50 kg.

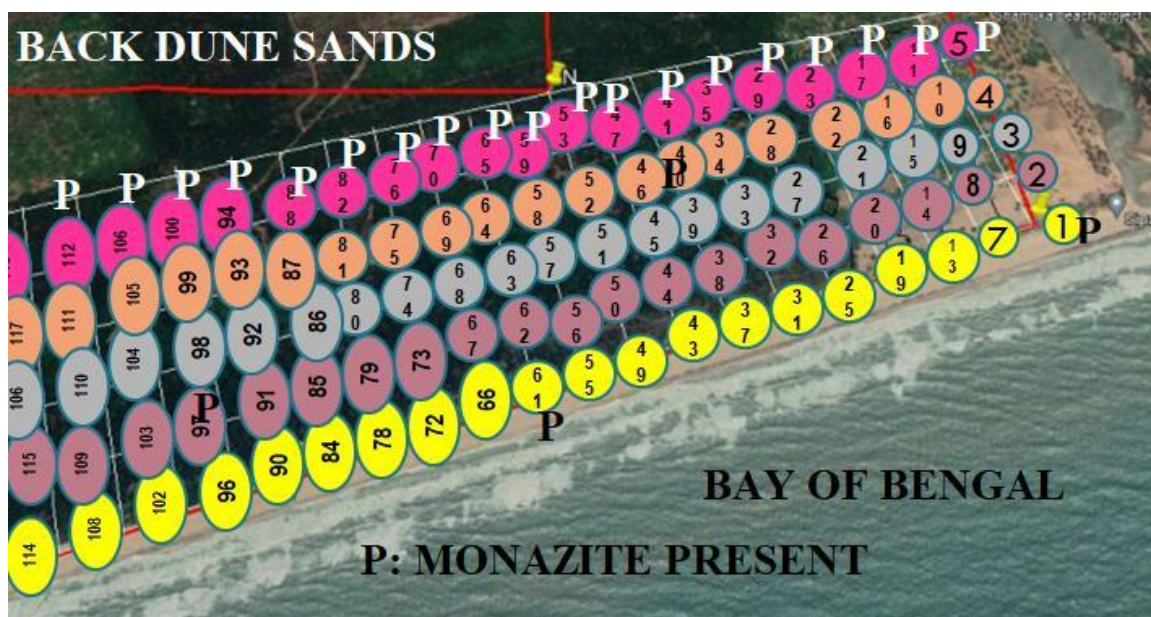


Figure 3. Grid samples collected in the IREL placer mining lease.

Farther to the shore, 50 kg samples were collected by auger but not up to the water table. All samples were sampled by coning and quartering methods at the coast. Each sub-sample was stored separately. Each sub sample was subjected to sink float studies. Bromoform an organic liquid (2.89 sp.gr) was used as media. The heavy minerals recovered by the sink and float studies were further subjected to magnetic separation to separate the magnetic minerals, such as ilmenite and garnet (monazite being a para-magnetic mineral). It is essential to mention that ilmenite is a magnetic mineral that can be separated at 0.6 T magnetic intensity, and garnet can be separated at around 1.0 T. This practice is widely accepted in the beach sand industries where garnet is separated by a magnetic separator. The float quartz mineral was stored separately. The nonmagnetic heavy minerals fraction containing zircon, rutile, sillimanite and other minerals was further subjected to diiodomethane, a 3.3 sp.gr organic liquid. The float mineral was sillimanite, and the others were zircon and rutile. Magnetic and nonmagnetic very heavy and light heavy minerals were subjected to a size analysis using Indian standard sieve sets. Each fraction was studied under the microscope for detailed mineralogical and modal analysis studies. The whole experimental procedure is shown in Figure 4.

The inductively coupled plasma spectrophotometer PlasmaQuant 9100 ICP OES spectrometer of Analytik Jena was used to analyse elements present quantitatively. The ASpect PQ software with an automatic baseline correction algorithm (ABC) and a tool for correcting spectral interferences (CSI) were also used. The sample was digested with concentrated sulphuric acid and evaporated to dryness. The mass was dissolved in hydrochloric acid and analysed by ICP. Standard working solutions were prepared for calibrations by suitable diluting of the stock solution in 5% (v/v) nitric acid. The elemental composition confirmed the concentration of monazite.

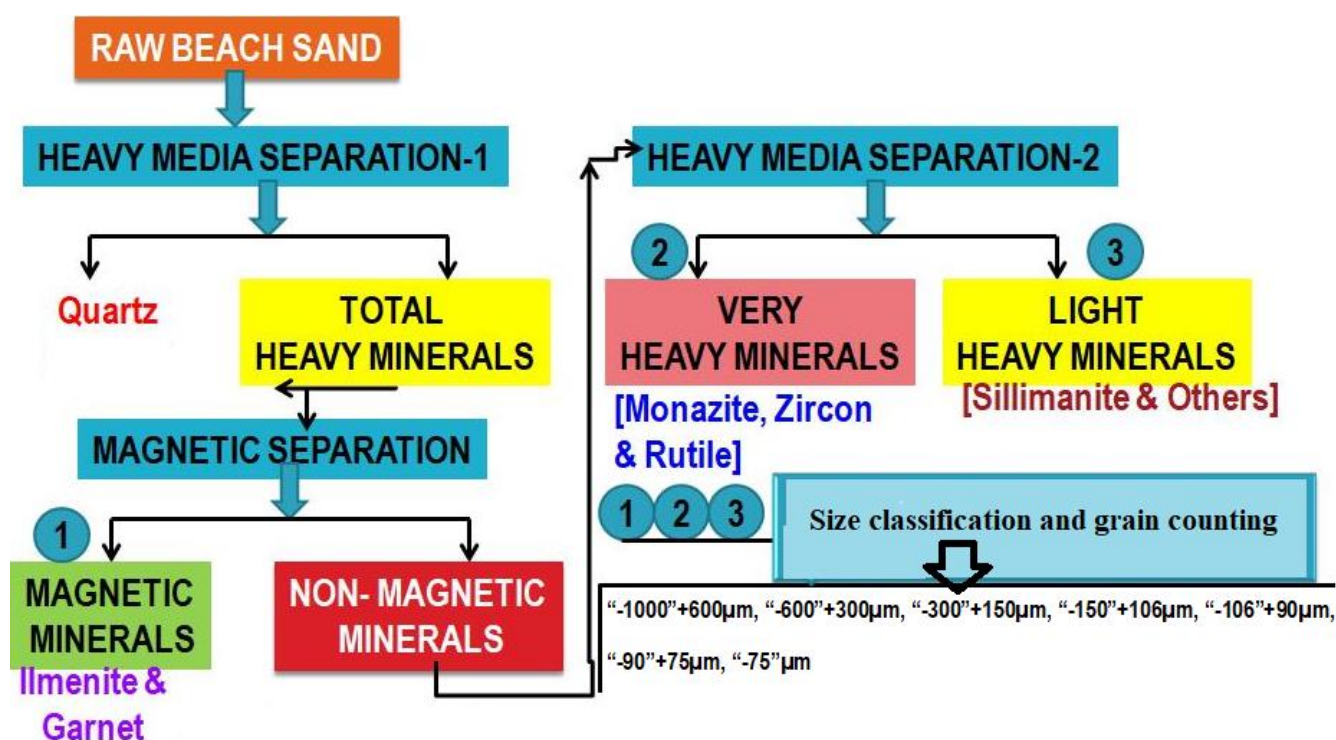


Figure 4. Experimental procedure for mineral grain counting.

In the microscopic study, slides were prepared from representative samples. The microscopic study used a polarising microscope (Leica DM2500P, Leica, Wetzlar, Germany) in plane-polarised and crossed-polarised lights. SEM and SEM EDAX studies were also performed on a product obtained from the present flowsheet based on novel approaches to recover enriched monazite. The EDS analysis results were semi-quantitative. The composition was determined by correlation with the mineral data. The uncertainty margin was generally less than 5%. XRD and Raman spectra studies were also attempted to assess the monazite mineral phases. The instruments used for these studies were SEM-EDS: JEOL JSM-6360LV Scanning Electron Microscope, XRD: PANalytical, Model X'Pert Pro, Source of X-Rays: Mo K α , 0.71 Å (wavelength), scan rate: 0.020/sec., Raman: the spectral range of the equipment was from a 50 cm⁻¹ to 4000 cm⁻¹ shift from the laser line, accomplished with optical microscopy from Radical Scientific, model RXLr-4 Pol microscopes with 20 $\times$ magnification.

The experimental setup to achieve the monazite mineral concentrate from the Bramhagiri back dune sand deposit is shown in Figure 5. The raw sand containing 0.01% monazite was subjected to spiral concentration studies to recover the total heavy minerals. The total heavy minerals were further subjected to a laboratory model rare earth drum magnetic separator followed by a laboratory-scale rare earth roll magnetic separator to recover the enriched monazite concentrate. The nonconducting and nonmagnetic fractions were subjected to sequential sink and float studies and the nonmagnetic very heavy minerals were taken up for characterisation. It is essential to mention that monazite is a para-magnetic mineral that can be separated at a 1.2 T magnetic intensity. Here, the magnetic intensity 1.0 T was used to separate monazite as nonmagnetic. Feed and product grades, yield and recoveries were calculated based on the mineralogical modal analysis.

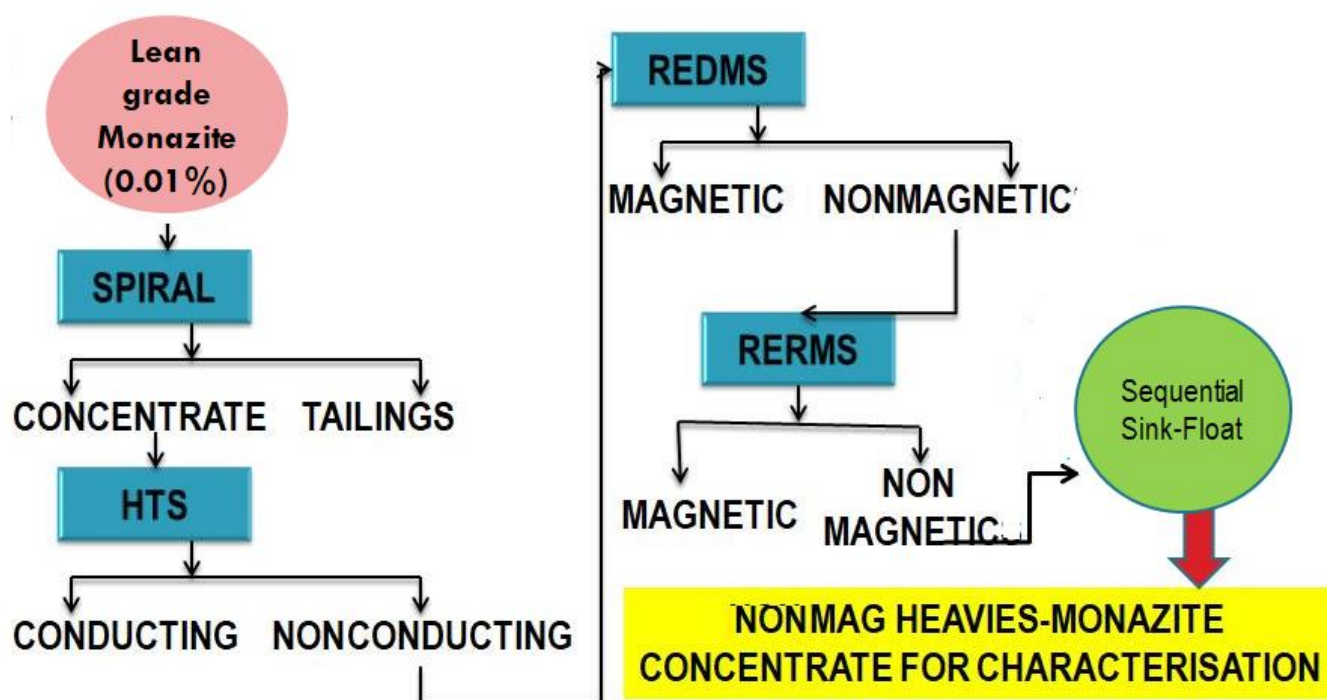


Figure 5. Experimental setup to achieve monazite from Bramhagiri to Sipasurubil dune sand deposit.

3. Results and Discussion

The textural, mineralogical and chemical characterisation of raw sand collected from different shore/dune sand deposits of Bramhagiri coast, the feed and the products of each unit operation are discussed in detail in the following for pre-concentration of the monazite mineral.

3.1. Textural Characterisation

The occurrence of total heavy minerals from all auger bore samples, of which there were around 118, all along the coast of Bramhagiri to Sipasurubil villages, Puri Dist, Odisha, India, and the concentration of minerals in each shore sand, back shore sand, frontal dune sand, central dune sand and back dune sand are presented in Figure 6. The data indicate that in all respects, the back dune sand sample all along the coast is rich in the total heavy mineral concentration than other sand deposits. Typically, the shore sand deposit is not following any trend in concentration, which may be due to the washings of sand with high currents of tides and shore winds.

The distribution of the individual heavy minerals and total heavy minerals in the different types of sand deposits, such as shore sand, backshore sand, frontal dune sand, central dune sand and back dune sand, is shown in Figure 7. In all respects, the back dune sand deposit contained the highest mineral concentration. The total heavy minerals (THM) in the back dune was 49.2% and the ilmenite concentration was 56.3% by weight. The monazite occurrence at the percentage level was noticed only at the shore and back dune sand. As explained earlier, the shore sand concentration was unstable due to high energy tides and wind. Hence, the minerals in the back dune sand may have been at the most stable concentration and suitable for mining to recover minerals.

Further, one can see from Figure 7 that the total heavy minerals and individual minerals were increasing from the back shore sand to back dune sand. However, the trend with the zircon mineral differed, which may have been due to the difference in particle characteristics.

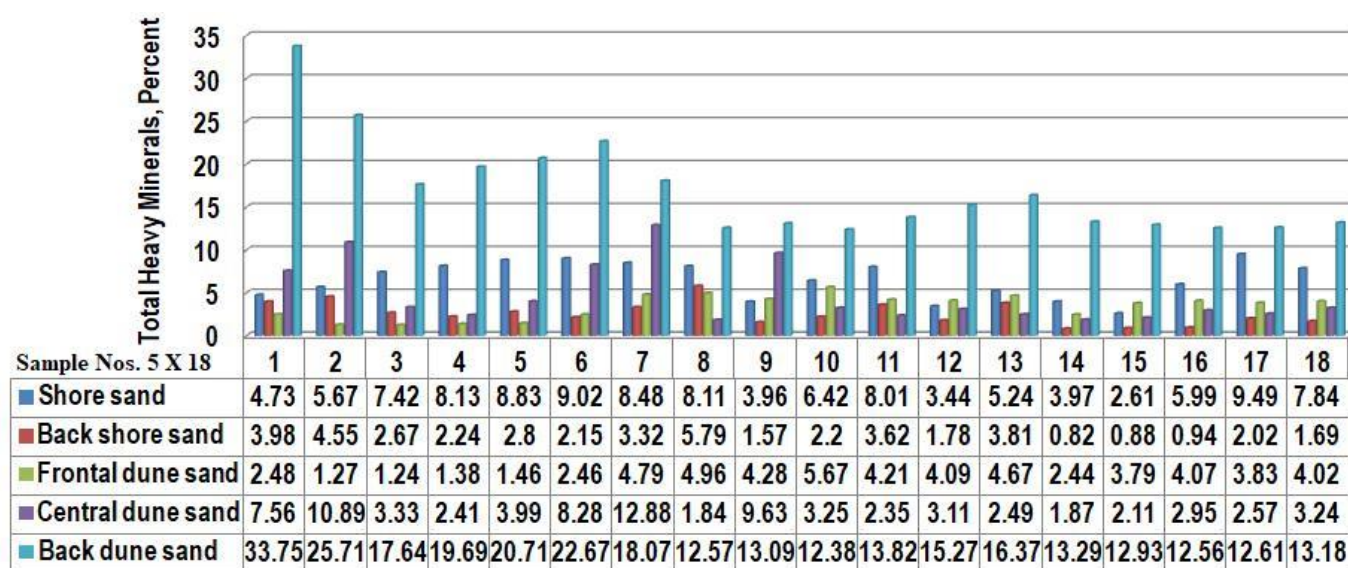


Figure 6. Total heavy mineral occurrence trend along the coast.

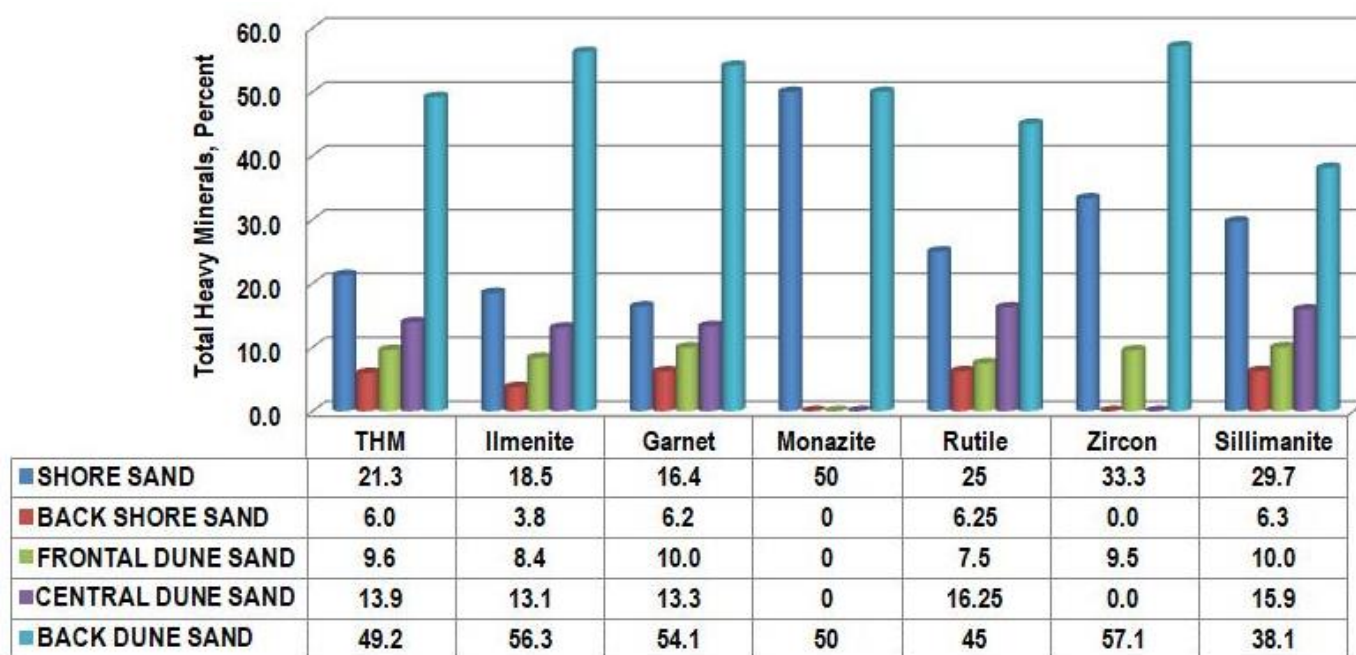


Figure 7. Distribution of THMs and individual heavy minerals in each zone.

Figure 8 shows the total heavy minerals and also individual minerals, including the ilmenite, garnet, monazite, rutile, zircon and sillimanite concentration in all 17 auger samples of the back dune sand deposit. All along the coastal line of Bramhagiri to Sipasurubili villages, the concentration of the heavy mineral pattern was not uniform. The heavy mineral concentration varied from a minimum of 14% to a maximum of 34% along this coast. The abundance of the garnet mineral was significant all along the coast, followed by the ilmenite mineral. Interestingly, the abundance of monazite mineral (0.01%) was almost the same all along the coast. Since this is a minor to trace quantity/abundance mineral in the heavy mineral assemblage, accurately determining the monazite percentage was difficult. The abundance of the zircon mineral was insignificant, whereas the sillimanite mineral concentration was more significant along the coast.

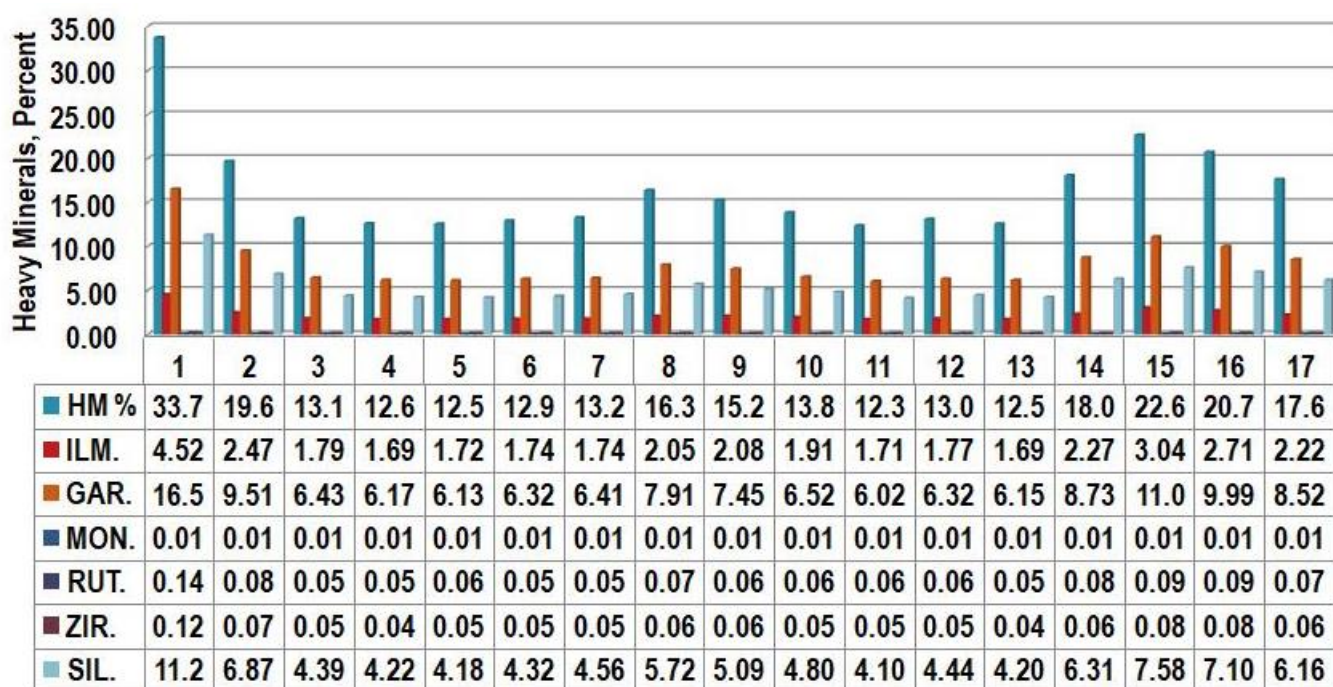


Figure 8. Heavy minerals in back dune sand samples.

The monazite content or the monazite grade in each auger sample (sample 5 to sample 107 along the coast) varied all along the coast in the back dune sand deposit (Figure 9). It was observed that the monazite grade was 0.01% minimum and the 0.02% was the maximum. The average trend line was 0.014% monazite in the back dune sand deposit. However, it may be noted here that the grain counting for monazite was difficult due to negligible concentration/abundance, as it is finer than other heavy minerals. Since monazite is heavier (relative to other heavy minerals), finer and has a lesser concentration, it suffers in deposition.

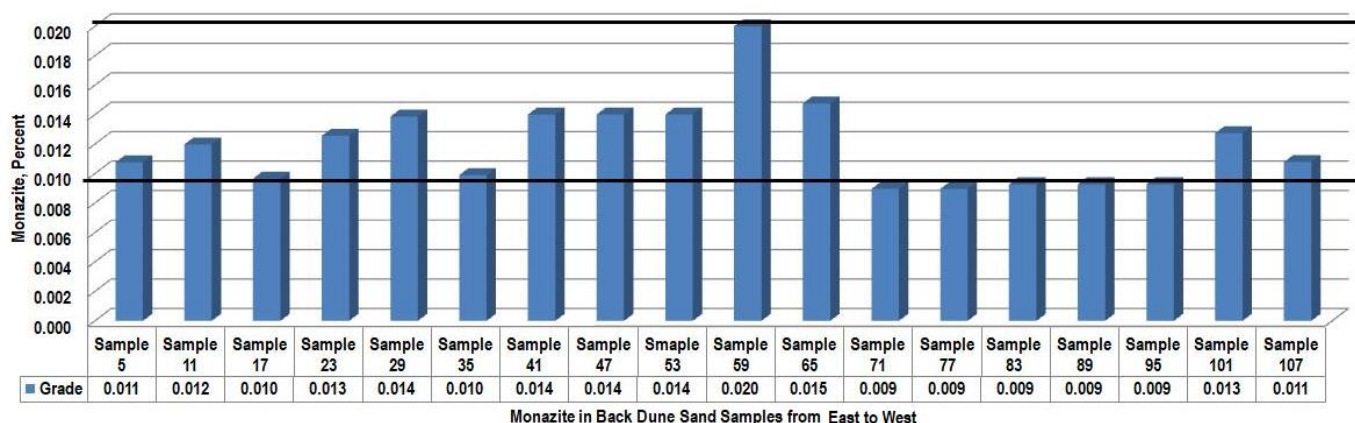


Figure 9. Monazite content in each sample exhibiting minimum and maximum.

3.2. Granulometric Characteristics

It is exciting to note the existence of monazite minerals in a particular size range only. The size analysis of monazite is shown in Figures 10 and 11. Figure 10 represents the size analysis of 18 auger samples along the coast in the back dune sand sample. The monazite was concentrated between $-150 + 106$ and $-106 + 90$ microns in all samples. Below the $-90 + 75$ micron size, monazite was significantly seen in sample no. 65 only. The

percentage of the monazite concentration was restricted to less than or equal to 0.01% in any size fraction or sample number along the coast of the back dune sand.

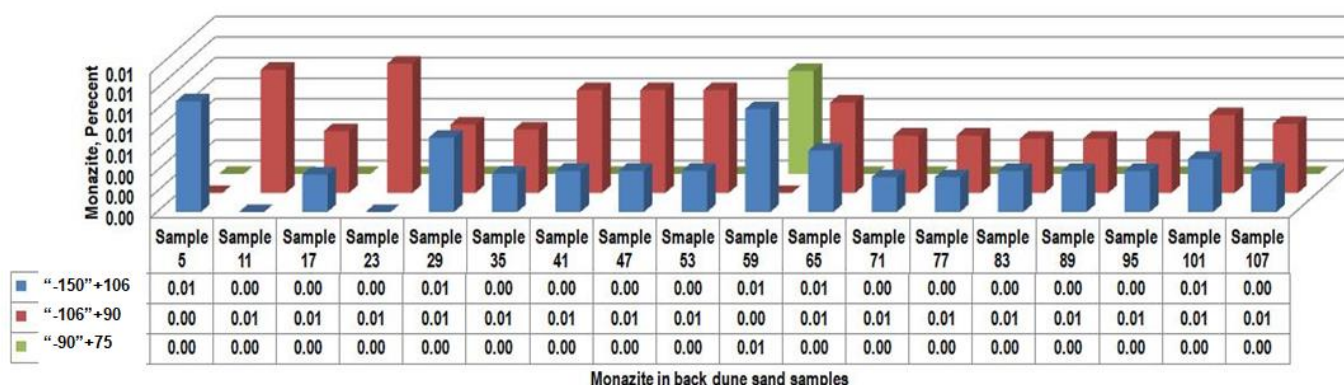


Figure 10. Size analysis of monazite in backdune sand samples.

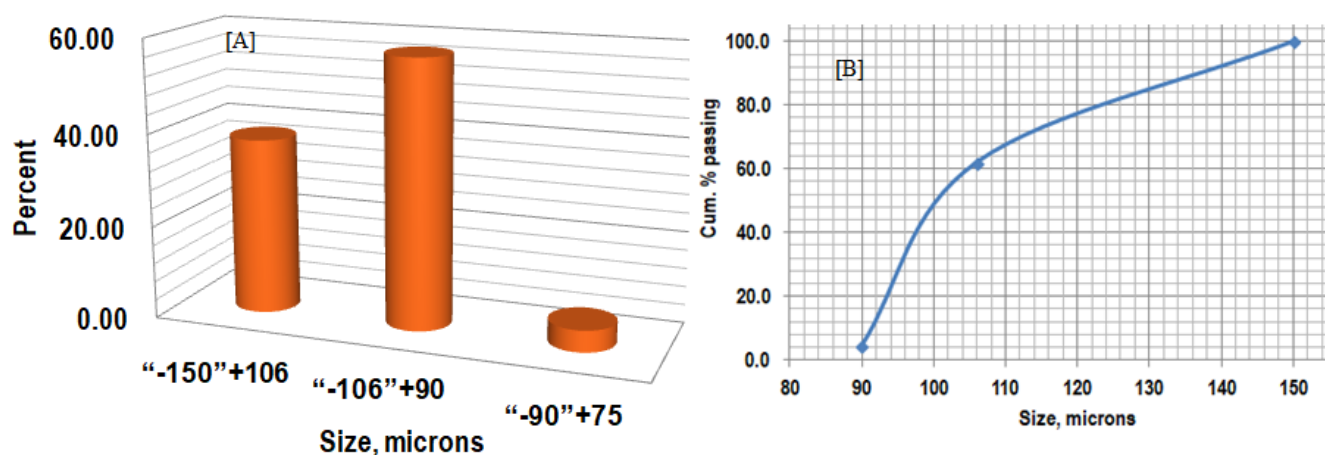


Figure 11. Size analysis of monazite in backdune sand sample by mineral abundance (A) and by cumulative passing (B).

The size analysis of monazite was determined by preparing and combined all 18 samples; the data are shown in Figure 11. The mono histogram of the $-160 + 90$ micron size fraction shows a maximum concentration of monazite in the particular size range, accounting for a maximum of 60% of monazite by weight. The $-150 + 106$ was 30% monazite, whereas $-90 + 75$ represents the ground-level concentration. The d_{80} passing size of monazite was drawn by plotting a graph between monazite's cumulative percentage passing size and the size in microns. The size distribution plot shows that 80% of the monazite in the back dune sand sample collected all along the Bramhagiri to Sipasurubili coast had a size finer than 124 microns. Since the particle size was below 150 microns, extracting radioactive and rare earth elements was easier without further grinding the sample. Notably, in general, all heavy minerals are finer than gangue mineral quartz, and the heavy minerals are not in uniform size. Monazite, zircon, rutile and ilmenite are finer in size than garnet minerals, followed by sillimanite.

3.3. Mineralogical Characterisation

The mineralogical modal analysis of raw sand (composite back dune sand), Total Heavy Minerals, Total Magnetic Heavy Minerals, Total Very Heavy Minerals, Total Non-magnetic Heavy Minerals and Total Nonmagnetic Light Heavy Minerals obtained by sequential sink–float and magnetic separation are given in Table 1. The data indicate that the monazite content in the bulk raw sand was 0.01% by weight, whereas the bulk sand

contained 15.3% THM. Spiral concentrators enriched this feed material to 0.07% monazite content, where the THM was 93.2% by weight. The garnet mineral was in the highest concentration in spiral concentrators accounting for 46.3% by weight, followed by sillimanite at 32.9% and ilmenite at 13.2% by weight. The total magnetic very heavy minerals were at 90.32% and the total very heavy minerals constituted 95.56%.

Table 1. Mineralogical modal analysis of raw sand (composite back dune sand), Total Heavy Minerals, Very Heavy Minerals, Light Heavy, Total Magnetic Minerals, Total Nonmagnetic Very Heavy Minerals, Total Nonmagnetic Minerals, Light Heavy Minerals.

Minerals	Raw Sand, % [THM 15.3%]	Spiral Con, % [THM 93.2%]	Magnetic & Sequential Sink Float, %	SINK-FLOAT [Sequential], %
Monazite	0.01	0.07	-	-
Ilmenite	1.97	13.2	-	-
Garnet	7.13	46.3	-	-
Sillimanite	4.97	32.9	-	-
Zircon	0.56	0.4	-	-
Rutile	0.66	0.4	-	-
Quartz	84.7	4.7	-	-
Very Heavy Minerals	-	-	-	95.56
Light Heavy Minerals	-	-	-	2.39
Total Magnetic Minerals	-	-	90.32	-
Total Nonmagnetic, Very Heavy Minerals	-	-	5.24	-
Total Nonmagnetic Minerals Light Heavy	-	-	2.39	-
Gangue Minerals	-	-	2.05	2.05

THM: Total Heavy Minerals.

Monazite mineral characterisation studies were performed on representative samples collected from para-nonmagnetic very heavy minerals products using the conventional coning and quartering method, which were studied under optical and stereo-microscopes and a scanning electron microscope (SEM).

The minerals present in the sample were monazite, zircon, rutile, ilmenite, sillimanite, garnet and quartz. Monazite was present as the predominant mineral constituent, followed by zircon. Other minerals such as ilmenite, garnet, sillimanite, rutile and quartz were present in lesser proportions. Monazite occurred in a spherical shape/egg-like shape. Monazite appears yellowish in colour and exhibits high relief with a pitted morphological structure, while zircon is rounded to sub-rounded in shape [11]. Rutile is honey red, sillimanite has an elongated or tubular shape, ilmenite is dark in colour and garnet has an irregular shape and isotropic nature. An optical photomicrograph of individual mineral grains of monazite, zircon, sillimanite, rutile, ilmenite and garnet recovered from the spiral concentrator can be seen in Figure 12.

Mineralogical modal analysis of bulk back dune sand samples, nonmagnetic very heavy minerals and nonmagnetic and nonconducting very heavy minerals are shown in Figure 13. The data indicate that garnet was the high-concentration mineral, accounting for 50.24%, followed by sillimanite for 35.18% and ilmenite for 13.7%, where zircon and rutile were minor constituents with monazite as a trace mineral constituent. Nonmagnetic very heavy minerals were represented by 49% rutile, followed by zircon at 43% and monazite at 8%. Nonmagnetic and nonconducting minerals accounted for 84% monazite, followed by 16% zircon. Shape and size of the monazite and other mineral grains, and backscattered

images for I: Ilmenite; S: Sillimanite; Z: Zircon; G: Garnet; R: Rutile; M: Monazite are shown in Figure 14. The data indicate that monazite is sub rounded to rounded.

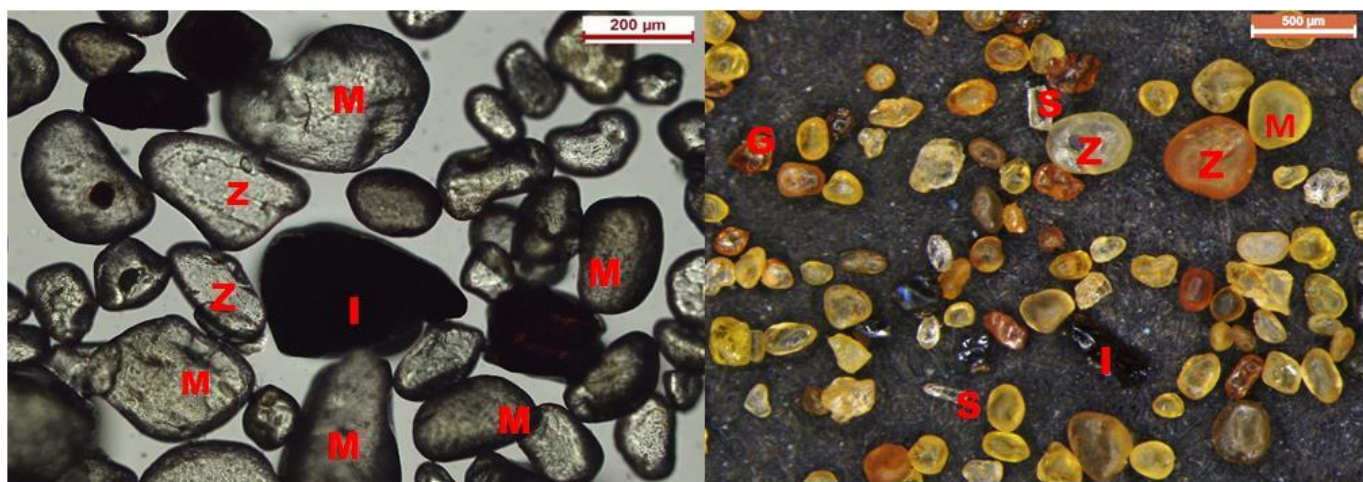


Figure 12. Optical photomicrographs of individual heavy minerals such as monazite, zircon, sillimanite, rutile, ilmenite and garnet.

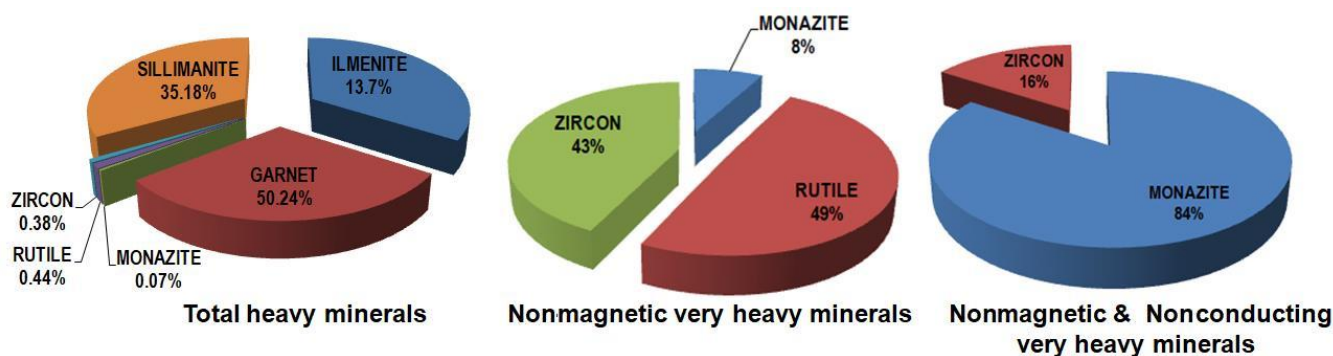


Figure 13. Mineralogical modal analysis of back dune sand sample.

SEM studies were performed using a scanning electron microscope (ZEISS EVO 18). An SEM photomicrograph of individual mineral grains of monazite, zircon, sillimanite, rutile, ilmenite and garnet recovered from the spiral concentrator can be seen in Figure 15. Backscattering images were taken and the semi-quantitative analysis (SEM-EDS) at different mineral phases was measured. The backscattering images, X-Ray elemental mapping and the EDX spectra and their semi-quantitative analysis can also be seen in Figure 15. It was observed that monazite was the primary mineral phase, along with other heavy minerals, zircon, rutile, sillimanite, ilmenite and garnet. Further, the monazite was observed as a spherical shape/egg-like with a bright shine. The X-ray mapping reveals the bulk mineralogy by the elemental distribution of Al in sillimanite; Fe, Ti in rutile; P, Th, Ce in monazite; Zr, Si in zircon, etc.

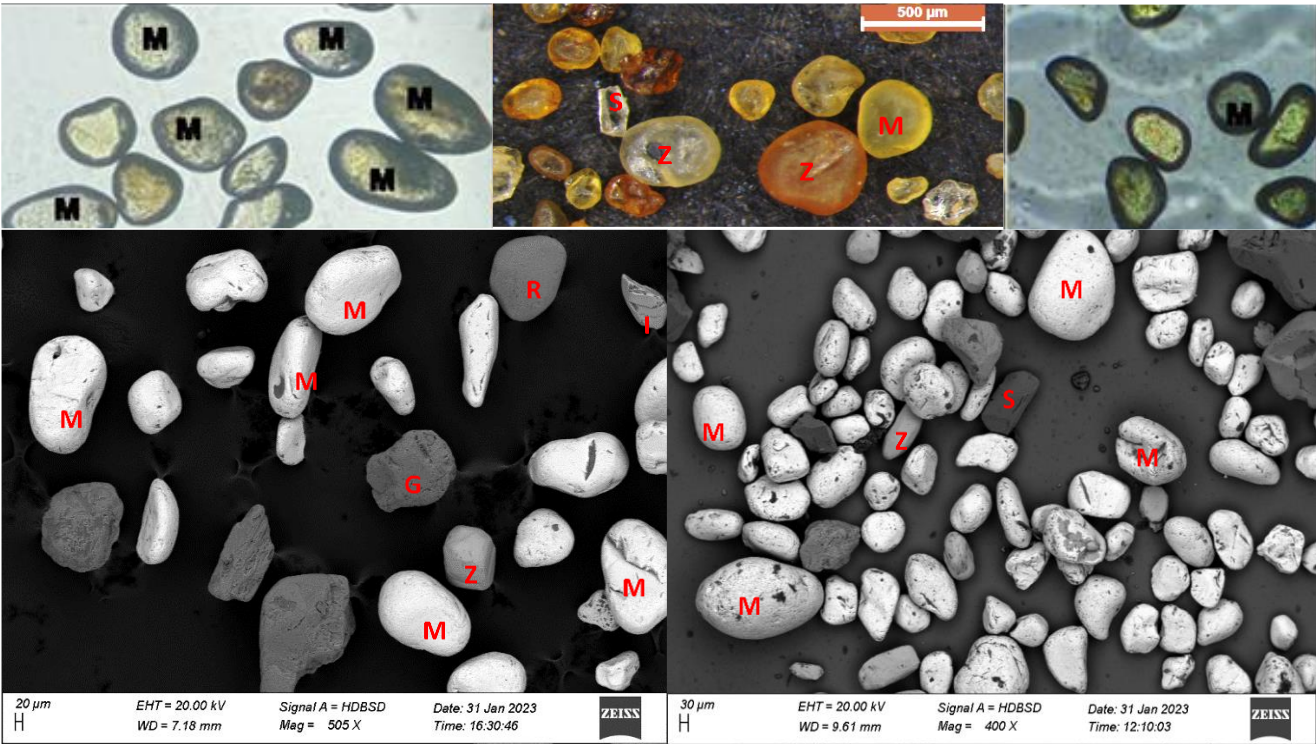


Figure 14. Shape and size of the monazite and other mineral grains, and backscattered images for I: Ilmenite; S: Sillimanite; Z: Zircon; G: Garnet; R: Rutile; M: Monazite. (all are projected in red colour).

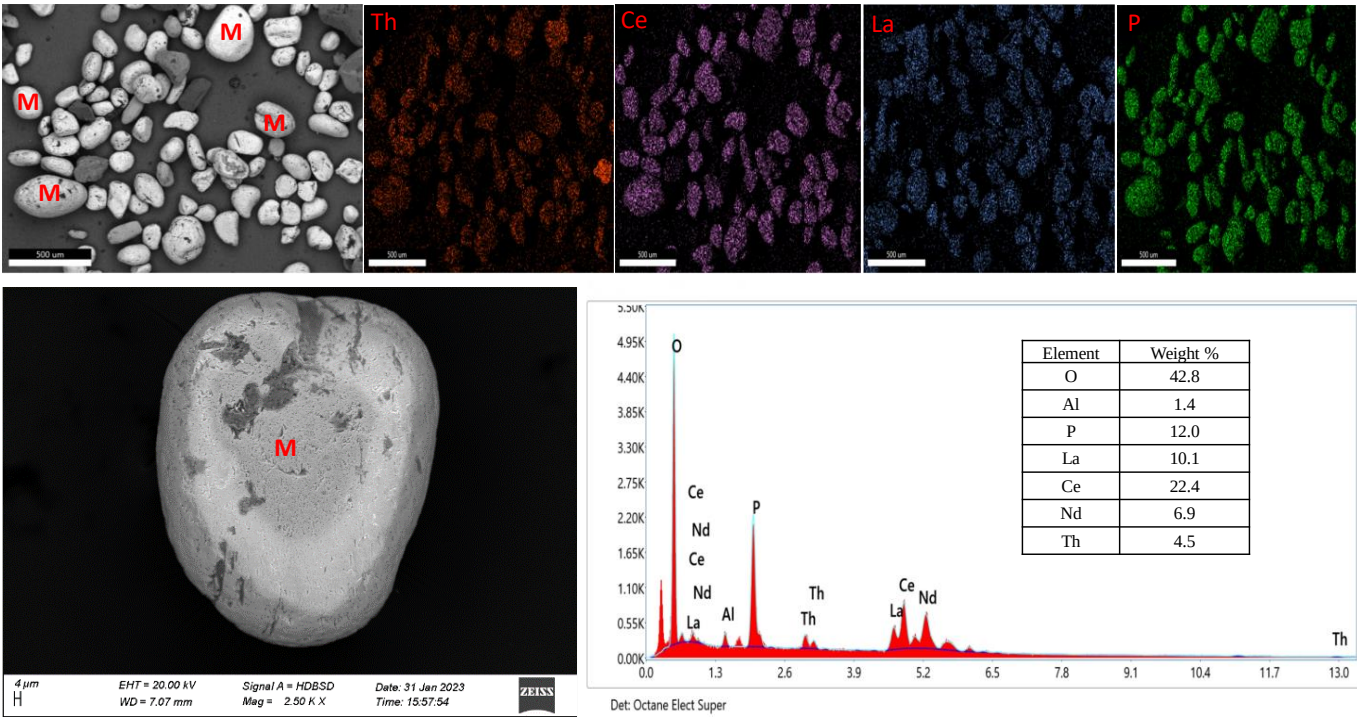


Figure 15. X-ray elemental mapping of monazite sample showing the distribution of different elements and EDX spectra of monazite.

3.4. Chemical Characterisation

A total of 18 back dune auger samples from samples 5 to 107 with an equal interval of each number are analysed (Table 2) for complete chemical analysis covering TiO_2 , Fe_2O_3 , Al_2O_3 , SiO_2 , MnO , Cr_2O_3 , V_2O_5 , MgO , CaO , P_2O_5 , ThO_2 , U_3O_8 , PbO and ZrO_2 . The presence of uranium, thorium, phosphorus and calcium indicated a monazite mineral in the back dune sample at a trace level. The reported values of Th and U in the raw sand agreed with the values reported by Routray et al. and Acharya et al. for the beach sand samples. The geochemical study of individual heavy minerals revealed that ilmenite and monazite minerals were weathered. It was also confirmed that individual heavy minerals increased with the increase in total heavy minerals, whereas the quartz mineral was falling.

Table 2. Complete chemical analysis of back dune sand collected from different auger samples.

Sample	TiO_2 %	Fe_2O_3 %	Al_2O_3 %	SiO_2 %	MnO %	Cr_2O_3 %	V_2O_5 %	MgO %	CaO %	P_2O_5 %	ThO_2 ppm	U_3O_8 ppm	PbO ppm	ZrO_2 %
5	2.510	1.440	10.060	74.450	0.600	0.002	0.010	0.833	0.581	0.011	1004.0	21.0	15.0	0.167
11	1.950	1.270	7.700	79.740	0.460	0.002	0.008	0.633	0.441	0.009	961.0	21.0	15.0	0.129
17	1.240	1.070	5.540	85.170	0.310	0.001	0.005	0.430	0.302	0.007	877.0	20.3	14.5	0.090
23	1.510	1.150	6.370	83.100	0.360	0.001	0.006	0.504	0.353	0.008	927.0	0.0	15.0	0.108
29	1.680	1.200	6.860	81.780	0.400	0.001	0.007	0.559	0.390	0.009	1254.0	29.1	20.8	0.112
35	0.020	0.010	0.010	0.180	0.000	0.000	0.000	0.000	0.000	0.000	1.3	0.0	0.0	0.000
41	0.940	0.980	3.930	88.470	0.220	0.001	0.004	0.310	0.216	0.005	695.0	16.2	11.5	0.062
47	0.980	0.990	4.110	88.120	0.230	0.001	0.004	0.319	0.223	0.006	856.0	20.2	14.4	0.067
53	0.950	0.980	3.850	88.570	0.220	0.001	0.004	0.304	0.212	0.007	1219.0	29.7	21.2	0.064
59	1.060	1.010	4.360	87.620	0.240	0.001	0.004	0.330	0.232	0.006	793.0	18.4	13.2	0.071
65	1.150	1.040	4.700	86.670	0.270	0.001	0.005	0.376	0.262	0.008	1285.0	31.0	22.1	0.079
71	1.140	1.040	5.160	86.010	0.290	0.001	0.005	0.399	0.280	0.006	814.0	21.0	15.0	0.167
77	0.970	0.990	4.200	88.000	0.230	0.001	0.004	0.324	0.227	0.006	1012.0	18.8	13.4	0.083
83	0.960	0.980	4.040	88.250	0.230	0.001	0.004	0.319	0.223	0.005	715.0	24.3	17.4	0.069
89	0.950	0.980	3.920	88.470	0.220	0.001	0.004	0.309	0.216	0.005	824.0	16.6	11.9	0.064
95	0.940	0.980	3.950	88.450	0.220	0.001	0.004	0.311	0.217	0.005	698.0	19.5	13.9	0.063
101	0.990	0.990	4.100	88.060	0.230	0.001	0.004	0.325	0.226	0.007	1109.0	16.2	11.6	0.062
107	0.200	0.770	1.110	94.680	0.070	0.000	0.001	0.098	0.066	0.001	0.0	26.8	19.1	0.068

The geochemical relations with elements and monazite minerals, as well as concentrations of major and minor amounts of element oxides of 18 bulk samples, are provided in Table 3. The SiO_2 concentrations of these samples ranged from 0.18% to 94.68%. The Al_2O_3 contents of these samples ranged between 0.01% and 10.06% and the TiO_2 contents in the samples varied from 0.02% to 2.51%. The ThO_2 and U_3O_8 concentrations of the samples ranged between 0–1285 ppm and 0–31 ppm, respectively. The Fe_2O_3 content of the area lied between 0.01% and 1.14%. Lower concentrations of MgO from 0.00%–0.83%, of MnO 0.00%–0.60% and of CaO 0.00%–0.581% were present in these samples. The ZrO_2 concentration varied from 0.06% to 0.16%. High TiO_2 , ZrO_2 , Al_2O_3 , ThO_2 and U_3O_8 concentrations exhibited high amounts of ilmenite, zircon, sillimanite, garnet and monazite in the 18 different auger sand samples.

The complete chemical analysis of the monazite mineral sample of the Bramhagiri back dune sand composite sample is given in Table 3. The data indicate that the sample contained ThO_2 9.5%, U_3O_8 0.2%, P_2O_5 28.5%, CeO_2 27.9%, La_2O_3 12.7%, Nd_2O_3 11.6%, CaO 0.8%, PbO 0.3%, Pr_6O_{11} 3.2%, Sm_2O_3 1.9%, Eu_2O_3 0.1%, Gd_2O_3 1.4%, Y_2O_3 0.5% and SiO_2 0.1%. The reported chemical analysis agrees with the work performed by many other researchers on monazite samples [1–20]. The lithology of the Bramhagiri area consists of charnockite and khondalite groups of rocks of the Eastern Ghats province. Granites

and granitic gneisses also exist in the rock assemblages. Large drainage systems such as the Mahanadi River may have brought a part of the sediment for the deposit formation, which flows through a range of lithologic successions covered with Katjodi, Kuvkai and Bhargavi rivers. The variation in the chemical composition of different heavy minerals is related to their association with different source rocks, such as charnockite, basic granulite, khondalite, calc-silicate granulite, gneiss, anorthosite, pegmatite and migmatite, and the degree of alteration/weathering.

Table 3. Complete chemical analysis of monazite mineral sample of Bramhagiri back dune sand composite sample.

Oxide	Weight, %	Oxide	Weight, %
ThO ₂	9.5	PbO	0.3
U ₃ O ₈	0.2	Pr ₆ O ₁₁	3.2
P ₂ O ₅	28.5	Sm ₂ O ₃	1.9
CeO ₂	27.9	Eu ₂ O ₃	0.1
La ₂ O ₃	12.7	Gd ₂ O ₃	1.4
Nd ₂ O ₃	11.6	Y ₂ O ₃	0.5
CaO	0.8	SiO ₂	0.1

An attempt was made to study the geochemical characteristics of these 18 auger samples where the data are given earlier in Table 2. Based on the complete chemical analysis of all 18 samples' data of the bulk sand, the geochemical study of uranium, calcium and phosphorus with THM was studied. Data are presented in Figure 16. The data indicate that increasing P₂O₅ increased the U₃O₈. Similarly, the U₃O₈ increased with increasing CaO and THM contents. Further, the P₂O₅ content followed an increasing trend with an increase in THM content.

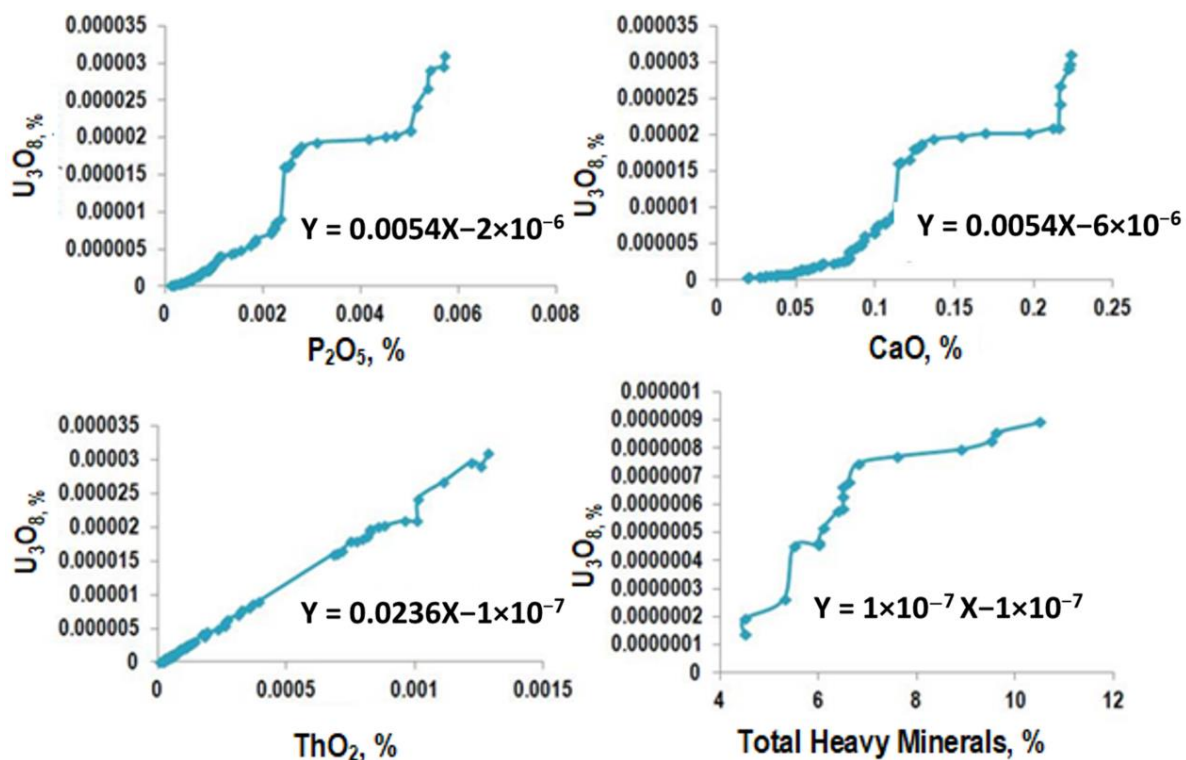


Figure 16. Geochemical study on THM vs. P, U and P vs. U and Ca vs. U.

The geochemical correlation for Th with U, Fe, Pb, P etc., are shown in Figures 17 and 18 and Table 4. The data indicate that with increasing the ThO₂ content, the other elements, such as U₃O₈, PbO and Fe₂O₃, increased. With increasing CaO, the P₂O₅ content increased. This correlation supports monazite mineral chemistry.

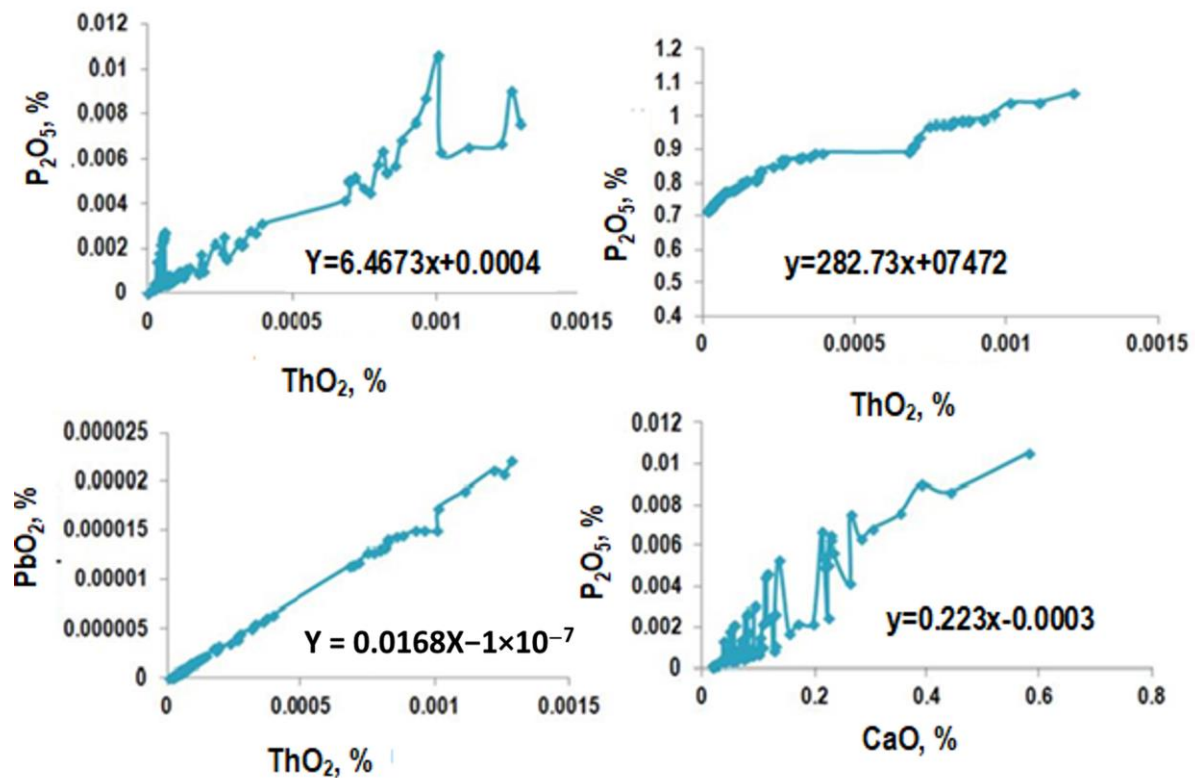


Figure 17. Geochemical study for Th vs. U, Fe, Pb and P.

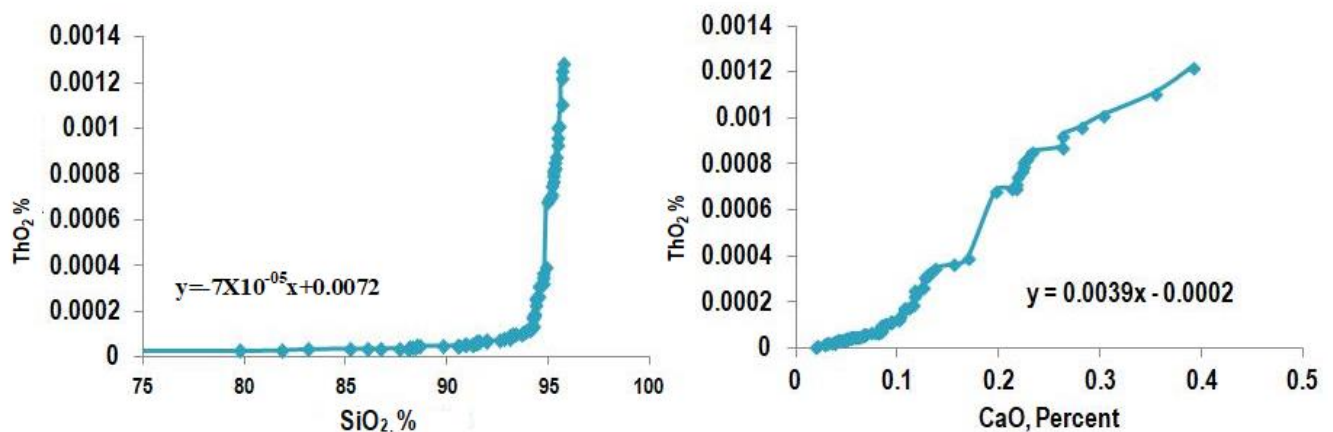


Figure 18. Geochemical studies for Th with Si and C.

Table 4. Geochemical correlation data.

S.No	Oxides	y	R ²
1	U ₃ O ₈ vs. ThO ₂	$0.0236x - 1 \times 10^7$	0.9976
2	Fe ₂ O ₃ vs. ThO ₂	$282.73x + 0.7472$	0.9468
3	PbO vs. ThO ₂	$0.0168x - 1 \times 10^7$	0.9976

Table 4. *Cont.*

S.No	Oxides	y	R ²
4	P ₂ O ₅ vs. CaO	0.0223x – 0.0003	0.8382
5	ThO ₂ vs. CaO	0.0039x – 0.0002	0.9607
6	U ₃ O ₈ vs. CaO	0.0002x – 6 × 10 ^{−6}	0.9006
7	U ₃ O ₈ vs. P ₂ O ₅	0.0054x – 2 × 10 ⁶	0.9389
8	THM vs. P ₂ O ₅	0.0004x – 0.0003	0.902
9	THM vs. U ₃ O ₈	1 × 10 ⁷ – 2 × 10 ⁷	0.8077

The geochemical correlations with uranium, thorium and total heavy minerals were studied and are shown in the figures earlier. The data with reference $y = mx + c$, y and R^2 values are noted in Table 5. The accuracy of the observations can be concluded with the R^2 values of these trends. The y and R^2 values for uranium and thorium vs. total heavy minerals, calcium and phosphorous are given in Table 5, indicating that the R^2 values for almost all elements are 0.9. The values agree with those reported using other characterisation techniques in different studies [1–20]. Thus, it was concluded that all monazite minerals were well-sorted, free grains and easy to transport for mechanical concentration or concentration by the mineral processing equipment. Hence, these back dune sand samples can be processed together to obtain individual concentrates of ilmenite, rutile, sillimanite, monazite, zircon and garnet by physical beneficiation methods. Complete chemical analyses, including a trace elemental analysis of monazite, recovered from the state-owned IREL (India) Limited, from different states, are presented in Table 6. The data indicate that all monazites were almost similar in chemical composition. However, the uranium content on the western coast was similar (0.33 to 0.35% U₃O₈), whereas the Odisha state monazite contained U₃O₈ at 0.19%. The cerium content was dominant among the rare earth elements and had a similar composition all over India concerning beach placer minerals. Hence, it could be established that the monazite was Ce-monazite.

Table 5. Complete chemical analysis of IREL plant-based monazite from different states.

	Manavalaaurichi, Tamilandu State (%)	Quilon, Kerala State (%)	Chattrapur, Odisha State (%)
U ₃ O ₈	0.35	0.33	0.19
ThO ₂	8.75	8.62	9.5
P ₂ O ₅	27.9	27.6	28.5
La ₂ O ₃	12.42	12.46	12.7
CeO ₂	28.5	27.9	27.85
Pr ₆ O ₁₁	3.81	3.58	3.16
Nd ₂ O ₃	10.73	10.48	11.58
Sm ₂ O ₃	1.56	1.61	1.9
Eu ₂ O ₃	0.02	0.026	0.08
Gd ₂ O ₃	0.68	0.69	1.37
Y ₂ O ₃	0.34	0.39	0.48
SiO ₂	0.95	0.95	0.95
CaO			0.76
PbO	0.2	0.2	0.27

Table 6. A comparison of XRD data of Ce-rich monazite with present experimental data of Bramhagiri sand deposit monazite.

Monazite (Ce Rich) ICDD Data			Monazite (Bramhagiri) Present Experimental Data		
$2\theta^{\circ}$	d_Value (Å)	I/I ₀	$2\theta^{\circ}$	d_Value (Å)	I/I ₀
17.013	5.2073	23.90	17.850	4.9690	22.90
18.458	4.8028	6.70	18.800	4.7200	25.20
18.941	4.6814	17.80	19.160	4.6321	26.37
21.205	4.1866	17.40	21.400	4.1521	30.64
25.257	3.5233	44.10	25.720	3.4636	30.03
25.281	3.5200	42.50	25.780	3.4557	23.56
27.128	3.2844	65.50	27.300	3.2667	100.00
28.751	3.1026	100.00	28.910	3.0883	49.20
29.997	2.9765	14.90	29.080	3.0706	61.82
31.171	2.8670	48.10	30.310	2.9488	33.00
31.214	2.8631	59.60	31.350	2.8533	42.06
36.773	2.4420	48.50	37.450	2.4014	17.77
36.885	2.4349	19.30	37.490	2.3989	19.82
37.636	2.3880	22.00	-	-	-
40.172	2.2429	8.50	40.280	2.2389	10.32
41.036	2.1977	20.60	-	-	-
42.056	2.1467	10.70	42.200	2.1414	54.10
48.339	1.8795	24.60	48.890	1.8629	19.25
48.419	1.8784	19.60	-	-	-
48.951	1.8592	19.10	-	-	-
48.966	1.8587	19.80	49.080	1.8561	17.87
51.910	1.7600	12.80	52.320	1.7486	48.56
51.940	1.7558	14.10	52.740	1.7356	58.42
52.530	1.7406	19.60	52.590	1.7402	54.38

The reported values of Th, U and other elements showed good agreement with the results of Acharya et al. [11,12]. Thus, the data further confirmed earlier findings that the back shore sand is rich with heavy minerals of economic importance. The parent rocks such as khondalite, quartzite, calc-silicate granulite, garnet biotite schist, gneisses, charnockites, anorthosite, granites and pegmatites present in the catchment area of Bhargavi River in the Eastern Ghats Mobile Belt, which contains the above heavy minerals as minor accessories, are the source of heavy minerals for this deposit.

3.5. Structural Data of Monazite

The structural data of monazite representing X-ray diffraction and Raman spectra image data are shown in Figure 19. The X-ray and Raman spectra data confirm the peaks of monazite (Ce). They also confirm from the peaks that these are well-crystallised minerals. The XRD data of the Ce-monazite standard and XRD data of the Bramhagiri monazite sample are given in Table 6.

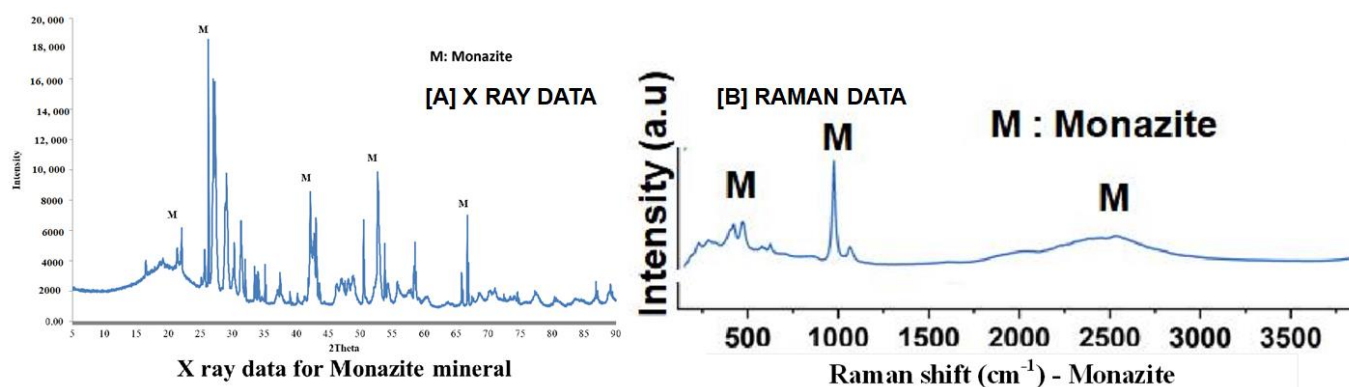


Figure 19. Structural data of monazite representing X-ray diffraction and Raman spectra image data.

Based on the XRD and Raman spectra, the crystal structure data of monazite may be assessed as Ce-monazite as per earlier reports of [21,22] for their La-monazite rare earth group, which is modified. The XRD data of Bramhagiri beach sand monazite almost matches the XRD peaks of the standard Ce-monazite standard sample.

Bangaku Naidu et al., 1990 [10] reported that monazite in the study area is hosted within the garnet-bearing paragenesis rocks such as metapelitic rocks (khondalites, pyroxene granulites) and charnockites, based on the high ratios of total LREE/Y and total LREE that were greater than those for actinides (Th + U). It is further confirmed from the studies of khondalite rock that wherever the garnet mineral exists, there the cerium rare earth element exists. Since the east and west coasts of India are surrounded by the khondalite group of rocks, it was concluded that the monazites occurring along the east and west coasts are Ce-monazites.

The mineral and chemical grade of monazite minerals in the present study reveal that the monazite is of high quality, contains fewer impurities and is within the limits of industrial specifications. The study on the textural and geochemistry of monazites confirms that the monazites are suitable for extraction of LREE and Th. Thus, these monazite minerals of the present study area are suitable for industrial applications.

4. Conclusions

The present investigation attempted to study the textural and geochemical characteristics of the lean-grade placer monazite of the Bramhagiri beach sand deposit.

- Based on the chemical analysis of bulk sand samples for uranium, thorium phosphorus, calcium, alumina, silica, and titanium, it is established that there exists monazite in this deposit.
- The monazite is below the 150-to-90-micron size range, and the monazite concentration in the bulk back dune sand is around 0.01% by weight.
- The lithology of the Bramhagiri area consists of charnockite and khondalite groups of rocks of the Eastern Ghats province. Granites and granitic gneisses also exist in the rock assemblages. Large drainage systems such as the Mahanadi River may have brought a part of the sediment for the deposit formation, which flows through various lithologic successions covering Katjodi, Kuvkai and Bhargavi rivers. The variation in the chemical composition of different heavy minerals is related to their association with different source rocks, such as charnockite, basic granulite, khondalite, calc-silicate granulite, gneiss, anorthosite, pegmatite and migmatite, and the degree of alteration/weathering. Thus, based on the mineralogical and geochemical studies, it is assessed that the probable provenance of the heavy minerals is from khondalite rocks.
- The mineral and chemical grade of monazite minerals of the present study reveals that the monazite is of high quality, contains few impurities and is within the limits of industrial specifications.

- The present study on the textural and geochemical characteristics of monazites confirms that the monazites are suitable for extraction of LREE and Th.
- The present study concludes, based on the structural data, that the monazites occur all along the southeast coast of Odisha, India, and especially in Bramhagiri beach sand deposits are there Ce-monazites, which are suitable for industrial applications such as for the recovery of uranium and thorium as well as light rare earths and heavy rare earths.

Author Contributions: Conceptualization and visualization, D.S.; methodology, R.R.; project administration, B.M.; supervision, S.B.; formal analysis, T.K.; Resource data curation, S.P.; writing—review and editing, D.S. All authors have read and agreed to the published version of the manuscript.

Funding: This Funding received from IREL (INDIA) Limited [Department of Atomic Energy].

Data Availability Statement: Not applicable.

Acknowledgments: The authours are thankful to IREL (India) Limited for providing funding and facilities to carry out the research work. One of the authors is duly acknowledging his research supervisors. He also sincerely thanks his parental organisation for providing research and financial facilities for this work.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Murthy, N.N.; Divakara, R.V. Geochemistry, provenance and depositional environment of the khondalites from the Eastern Ghats Mobile Belt. In *Eastern Ghats Granulites*; Rao, A.T., Divakara Rao, V., Yoshida, M., Eds.; Mem.5, Field Sciences Publisher: New York, NY, USA, 1999; pp. 15–30.
2. Mallikharjuna, R.M.; Divakara, R.V.; Murthy, N.N. Charnockite from EGMB—Geochemistry, protoliths character and tectonic relevance. *Gondwana Res. Group Mem* **1999**, *5*, 31–50.
3. Kamineni, D.C.; Rao, A.T.; Bonardi, M. The geochemistry of monazite types from the Eastern Ghats Granulite terrain, India. *Mineral. Petrol.* **1991**, *45*, 119–130. [\[CrossRef\]](#)
4. Bowie, S.H.U.; Horne, J.E.T. Cheralite, a new mineral of the monazite group. *Mineral. Mag.* **1953**, *30*, 93–99. [\[CrossRef\]](#)
5. Rao, A.T.; Rao, C.H.P. Cherlits from beach placers of Visakhapatnam-Bhimunipatnam coast. *Indian J. Mar. Sci.* **1980**, *9*, 214–216.
6. Anitha, J.K.; Sabu, J.; Rejith, R.G.; Sundararajan, M. Monazite chemistry and its distribution along the coast of Neendakara–Kayamkulam belt, Kerala. *India J. SN Appl. Sci.* **2020**, *2*, 812. [\[CrossRef\]](#)
7. Udayakumar, S.; Rezan, S.A.; Noor, A.F.M.; Putra, T.A.R.; Takip, K.M.; Hazan, R. Characterization of Malaysian Monazite Concentrate for The Recovery of Thorium Dioxide. *J. Phys. Conf. Ser.* **2017**, *1082*, 012090. [\[CrossRef\]](#)
8. Liu, X.H.; Li, B.; Xu, J.W.; He, B.; Liao, J.; Peng, H.W.; Wang, Y.H.; Lai, J.Q. Monazite geochronology and geochemistry constraints on the formation of the giant Zhengchong Li-Rb-Cs deposit in South China. *Ore Geol. Rev.* **2022**, *150*, 105147. [\[CrossRef\]](#)
9. Jeya, R.J.; Balasubramanian, G.; Thampi, P.K. Determination of rare earth elements in Indian coastal monazite by ICP-AES and ICP-MS analysis and their geochemical significance. *Curr. Sci.* **2008**, *94*, 1296–1302.
10. Bangaku, N.; Reddy, K.S.N.; Ravi, S.; Ganapati, R.; Murali, K. REE geochemistry of monazites from coastal sands between Bhimunipatnam and Konada, Andhra Pradesh, East Coast of India. *Curr. Sci.* **2016**, *110*, 1550–1559.
11. Acharya, B.C.; Nayak, B.K.; Das, S.K. Heavy Mineral Placer Sand Deposits of Kontiagarh Area, Ganjam District, Orissa, India. *Resour. Geol.* **2009**, *59*, 315–424. [\[CrossRef\]](#)
12. Acharya, B.C.; Panigrahy, P.K.; Nayak, B.B.; Sahoo, R.K. Heavy Mineral Placer Deposits of Ekakula Beach, Gahiramatha Coast, Orissa, India. *Resour. Geol.* **1998**, *48*, 125–136. [\[CrossRef\]](#)
13. Kathiravan, R.; Palanivel, K.; Rout, S.P.; Sudhakar, C.; Ramesh, K.K. Delineation of mineable heavy placer deposits using geospatial technology along Puri to Ichchapuram coastal tract of Odisha state India. *Appl. Sci. Comput.* **2018**, *5*, 1124–1438.
14. Mohanty, A.K.; Das, S.K.; Vijayan, V.; Sengupta, D.; Saha, S.K. Geochemical studies of monazite sands of Chhatrapur beach placer deposit of Orissa, India by PIXE and EDXRF method. *Nucl. Instrum. Methods Phys. Res. B* **2003**, *211*, 145–154. [\[CrossRef\]](#)
15. Rao, K.J.; Subramanyam, A.V.; Kumar, A.; Sunil, T.C.; Chaturvedi, A.K. Discovery of heavy mineral rich sand dunes along the Orissa-Bengal coast of India using remote sensing techniques. *Curr. Sci.* **2008**, *94*, 983–985.
16. Routray, S.; Mohanty, R.; Swain, R.; Sahu, S.; Mishra, B.R. Preparation and Characterisation of Zirconia Nano-materials Prepared from Zircon Minerals of Brahmagiri Coast. *J. Inst. Eng. Ser. E* **2001**, *102*, 87–95. [\[CrossRef\]](#)
17. Routray, S.; Jagadeeswari, V.; Ranjita, S. Placer Deposits of Brahmagiri Coast, Odisha—A New Resource For Industrial Heavy Minerals. *IOP Conf. Ser. Mater. Sci. Eng.* **2018**, *338*, 012012. [\[CrossRef\]](#)
18. Routray, S.; Swain, R.; Laxmi, T. Recovery of Heavy Minerals from Brahmagiri Deposit, Odisha using Gravity Table. *IOP Conf. Ser. Mater. Sci. Eng.* **2018**, *455*, 012084. [\[CrossRef\]](#)

19. Routray, S.; Swain, R.; Rao, R.B. A Study on Heavy Mineral Distribution Pattern Along Bramhagiri Coast of Odisha, India and Its Beneficiation to Recover Industrial Minerals. In *Advances in Production and Industrial Engineering, Select Proceedings of ICETMIE*; Springer: Singapore, 2020; pp. 299–307. [[CrossRef](#)]
20. Routray, S.; Swain, R.; Mohapatra, R.N. Studies on Recovery of Industrial Heavy Minerals from Lean Deposits of Bramhagiri Coast of Odisha, India. In *Materials Science Forum*; Trans Tech Publications Ltd.: Bäch, Switzerland, 2020.
21. Sharma, S.K.; Thomas, B.; Thomas, K.; Heitmann, J. Library of UV-Visible absorption spectra of Rare Earth Orthophosphates, LnPO_4 (Ln = La-Lu, except Pm). *Crystals* **2020**, *10*, 593. [[CrossRef](#)]
22. Schulz, B. Monazite Microstructures and Their Interpretation in Petrochronology. *Front. Earth Sci.* **2021**, *9*, 668566. [[CrossRef](#)]

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