

Geochemical Characterization and Presence of Rare Earth Elements in the Recent Depositions at the Islands of the Eastern Bay of Bengal, Bangladesh

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Abstract: This study presents geochemical characterization, as well as, quantification of rare earth elements in the recent beach deposition at the two major islands of the eastern Bay of Bengal-Kutubdia and Moheshkhali. Placer sand samples from near surface depositions were analyzed by heavy mineral separation, mineralogical identification, chemical composition and elemental mapping. X-ray diffraction (XRD), X-ray fluorescence (XRF), Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS) were used to obtain these results. The heavy mineral concentration in different raw sand samples resulted by heavy liquid separation technique revealed that the average abundance of heavy minerals is 69.67% in Kutubdia island and 9.32% in Moheshkhali island, respectively. The X-ray patterns of Kutubdia and Moheshkhali sand samples show the presence of zircon, quartz, hematite, magnetite, ilmenite, chromite, kyanite, anatase, rutile and garnet. Chemical composition of heavy mineral sands from Kutubdia and Moheshkhali islands were analyzed using X-ray fluorescence method (XRF) for major oxides and trace elements. The concentration is of Na₂O, MgO, Al₂O₃, SiO₂, P, K₂O, CaO, TiO₂, V₂O₅, Cr₂O₃, MnO, Fe₂O₃, CoO, ZnO, SrO, Y₂O₃, ZrO₂, Nb₂O₅, MoO₃, HfO₂, WO₃, ThO₂, U₃O₈, CeO₂, Nd₂O and Er₂O₃ were determined. A significant amount of various rare earth elements (REEs) in the elemental composition of few samples was also identified. The study is expected to be useful in the baseline and environmental aspects of both the islands.

Keywords: Kutubdia island, Moheshkhali island, Rare earth elements, elemental mapping.

Introduction

Bangladesh constitutes the major part of the Bengal basin, which is one of the most prominent Tertiary sedimentary basins in the world. It is located at the head of the Bay of Bengal and is bordered on its west by the Indian shield and in the north by Shillong plateau. The southern portion of the basin is open and gradually merges with the Bay of Bengal. The islands of Bangladesh are scattered along the Bay of Bengal and the river mouth of Padma. The word "Char" is used in many of the names and refers to floodplain sediment islands in the Ganges delta. The Kutubdia and Moheshkhali islands are located at the eastern Bay of Bengal.

The heavy mineral deposits along the coastal belt of Bangladesh constitute potential resources for Bangladesh. The Bangladesh Atomic Energy Commission (BAEC) has long been involved in exploration and research activities on heavy placer deposits along the coastal belt of Bangladesh.

Mineral sands on the beach and paleo-beach contain concentrations of the important minerals, mainly ilmenite, magnetite, zircon, rutile, garnet and monazite. These minerals grow as crystals in igneous rocks such as granite, pegmatite, basalt and some metamorphic rocks. Over millions of years, these igneous and metamorphic rocks were weathered and eroded. Grains of quartz and other minerals in the rock are washed

down to the sea by heavy rainfall and fast-flowing streams. The heavy minerals were then carried into the beach by waves and currents. As the waves washed up and down on the beach, also carry the lighter quartz grains with them back into the sea, leaving the grains of the heavy minerals behind on the beach. Wind also helped to concentrate the heavy minerals by blowing away the lighter quartz sand. These processes were repeated many times over millions of years, eventually creating a large deposit of mineral sands on the beach. As the sea level rose and fell over geological periods, the shoreline moved further inland and then backed again. As this happened, the deposits of mineral sand were covered by more sand and built up or eroded and re-deposited elsewhere. The area located between the foredune area and the eastern hills is characterized by sparsely distributed elongated paleo-sand dunes aligned parallel to the present coastline.

Many studies have been carried out on different physical and chemical aspects like mineralogical composition of the beach sands of Cox's Bazar (Biswas, 1977), mechanism of heavy mineral concentration in the beach sands of Cox's Bazar (Biswas, 1981), presence of radioactivity in Cox's Bazar beach of Bangladesh (Schmidt and Asad, 1963), difference in grain size among heavy minerals of Cox's Bazar to Tekaf foredune deposit (Deeba, et al., 2009), the natural radioactivity of the beach sand and their associated mineralogical components (Zaman et al., 2016 and 2012; Khan and Chowdhury, 2008;

Rahman et al., 2008; Alam et al., 1999; Mitra et al., 1992; Kasim, 1988). Many researchers have worked on grain size and textural properties (Biswas, 1982 and 1986; Samad and Hassan, 1982; Passega, 1964; Passega and Byramjee, 1969), but very limited work on coastal plain sediments of the Moheshkhali and Kutubdia islands of Bangladesh has been carried out by earlier workers.

Geologically, Kutubdia island is located in the western most portion of the eastern-northern frontier region of Arakan-Yoma folded belt. The geographical position of Kutubdia island is 21° 50' 06" N and 91° 50' 16" E.

the Arakan-Yoma folded belt. However, most of the area of the island is peneplain land with a narrow strip of beach. It is the present depositional area for progradational offshore island sequences form the continuation of the south-westwards structurally open Bengal fore deep. Maheshkhali Island is the main island of Maheshkhali upazila, in the Cox's Bazar district of Bangladesh. Maheshkhali is the only hilly island in Bangladesh (Fig. 1).

The study focuses on the geochemical characterization, heavy mineral distribution and their potential provenance identification to establish the baseline data

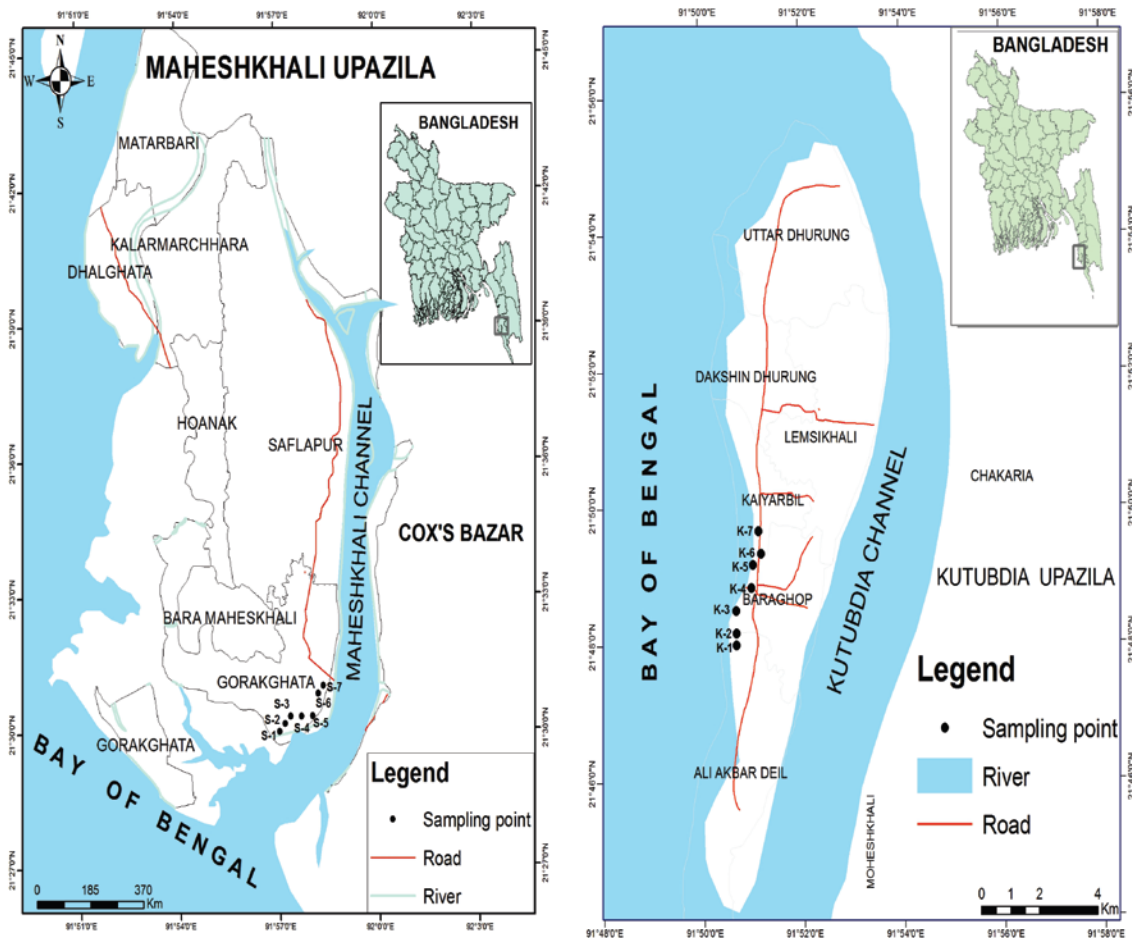


Fig. 1 Location map of the study area.
(Source: Government of Bangladesh, Local Government Engineering Department, LGED).

Kutubdia is an upazila of Cox's Bazar district in the division of Chittagong. The area is an island bounded by the Bay of Bengal on the north, west and south. In addition, Kutubdia channel, Banshkhali, Chakaria and Maheshkhali upazillas are on the east. It is an offshore island detached from Moheshkhali island which is separated by the narrow Kutubdia channel. A series of near shore islands have been developed along the eastern and western coast of the Bay of Bengal due to the Holocene sea level rise (Tarafder and Monsur, 2001). Tectonically the island is a part of Hatiya trough and originated due to the Neogene upliftment of

of the Moheshkhali and Kutubdia islands. Natural radioactivity was measured at the corresponding sampling areas by a portable Radiation Survey Meter (GS Austral Rad Mini). Placer sand samples from near surface deposition were analyzed through heavy mineral separation, mineralogical identification, chemical composition and elemental mapping. X-ray diffraction (XRD), X-ray fluorescence (XRF), Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS) were used to obtain these results.

Table 1 Sampling location and radiation ($\mu\text{Sv/h}$) at different stations of the collected samples.

Sampling station	Longitude (E)	Latitude (N)	Radiation ($\mu\text{Sv/h}$)	
			At surface	More than 1 m from surface
K-1	91°50'34"	21°48'32"	4.63	4.25
K-2	91°50'35"	21°48'35"	3.20	3.39
K-3	91°50'37"	21°48'40"	3.68	2.82
K-4	91°50'40"	21°48'44"	9.17	7.20
K-5	91°50'42"	21°48'47"	3.30	2.53
K-6	91°50'47"	21°48'51"	1.39	1.02
K-7	91°50'49"	21°48'55"	1.77	1.39
S-1	91°57'17"	21°30'16"	1.80	1.25
S-2	91°57'21"	21°30'18"	1.30	1.12
S-3	91°57'29"	21°30'21"	0.42	0.24
S-4	91°57'37"	21°30'21"	0.72	0.42
S-5	91°57'43"	21°30'21"	1.10	0.72
S-6	91°57'52"	21°30'21"	1.20	1.11
S-7	91°58'00"	21°30'21"	0.54	0.32

Table 2 Heavy and light mineral separation of Kutubdia and Moheshkhali islands.

Sample location	Sample ID	Heavy Mineral (%)	Light Mineral (%)
Kutubdia island	K-1	36.87	63.05
	K-2	65.1	34.82
	K-3	80.94	18.97
	K-4	79.14	20.77
	K-5	88.18	11.78
	K-6	79.72	20.25
	K-7	57.70	41.05
Moheshkhali island	S-1	20.01	79.00
	S-2	19.93	79.73
	S-3	4.00	95.87
	S-4	4.89	94.32
	S-5	3.82	96.18
	S-6	10.59	89.34
	S-7	1.99	97.90

Materials and Methods

Sample Collection

During the sample collection, samples were collected from 1.5m below the surface of the two islands. Seven samples were collected from Kutubdia island (K1-K7) and seven from Moheshkhali island (S1-S7). Radiation dose counts in $\mu\text{Sv/h}$ (micro sievert per hour) were recorded by a portable Radiation Survey Meter (GS Austral Rad Mini). About 3~4 kg of samples was collected at each counting location for subsequent laboratory investigation. The samples were kept in a plastic sample bag by marking the date, coordinates, sample type, etc. In the field, global positioning system (GPS, Magellan map) was used to locate the latitude-longitude values of the survey area. The radiation of the area varies from 1.39 to 9.17 $\mu\text{Sv/h}$ at the surface and 1.02 to 7.2 $\mu\text{Sv/h}$ at more than 1 m from the surface at Kutubdia island and 0.42 to 1.8 $\mu\text{Sv/h}$ at the surface and 0.24 to 1.25 $\mu\text{Sv/h}$ at more than 1 m from the surface at Moheshkhali island respectively (Table 1).

Heavy Mineral Separation

Heavy mineral separation was done to know the

percentage of heavy fraction in the raw sand. Bromoform (CHBr_3) was applied as heavy liquid for heavy mineral separation. It is used as a density separator to separate the heavy from light minerals in a lesser amount of 100 gm. Generally, 100-150 ml Bromoform is needed to separate 50gm of raw sand. The specific gravity of Bromoform is 2.9 at 20 °C.

The minerals that have specific gravity higher than the Bromoform are called heavy minerals. For this purpose, 50 gm of the raw sand sample was poured with stirring into 100-150ml Bromoform contained in a wide-mouthed separating funnel. The funnel was fitted with a stopcock, the bore of which is of greater diameter than the inner diameter. The mineral floating on the Bromoform was stirred and then left until all the heavy minerals had been settled. The heavy minerals with some Bromoform were then run through the bottom of the separating funnel into a funnel containing a filter paper. The heavy mineral in the filter funnel was washed, removing Bromoform using acetone, dried and weighed, and finally calculated as a percentage of the weight taken. Seven subsurface samples from Kutubdia island and seven from Moheshkhali island respectively have been taken for this analysis (Table 2).

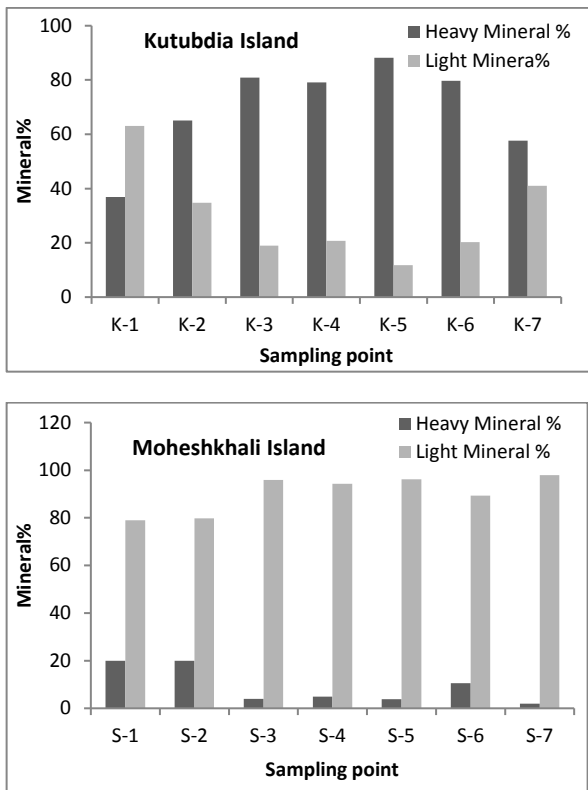


Fig. 2 Heavy and light mineral distribution of the Kutubdia and Moheshkhali islands.

The heavy fractions of the collected samples were analyzed by X-ray diffraction to identify the constituent minerals. After removing moisture using oven-dry at around 50°C for about 6 hours, samples were powdered fine enough for X-ray analysis with the help of automatic grinder. The mineralogical analysis was performed using a X-ray diffractometer of RIGAKU Rint-Ultima-III system. The operating conditions were continuous scanning between 3-75° at 4°/min, X-ray target of CuK α , tube voltage of 40 kV, and tube current of 40 mA.

X-ray Fluorescence Spectrometry Study

Sand samples were analyzed by X-ray fluorescence spectrometer (XRF) UniQuant 4 system of Philips

PW2400 that uses fundamental parameter (FP) method. Due to lack of sufficient quantity for using in XRF, four representative samples from two lines (2 each from S and K) were used. Fine powder of each sample was prepared to pellet form for the XRF system. Measurements were considered up to 0.01 wt%.

Scanning Electron Microscope Study

Scanning electron microscope coupled with energy dispersive spectrometer (SEM-EDS) was used to study the samples by micro-areal analysis as well as the elemental mapping to observe the presence of elements of interest. The apparatus used for the analysis was the scanning electron microscope JEOL JSM-5600LV with the initial operating condition of 20 kV, working distance 20 mm and spot size of 20 to take secondary electron image (SEI). Samples were dried in oven at around 50°C overnight to remove the moisture completely and then coated with gold for SEM analysis.

Results and Discussion

The heavy mineral concentration in different raw sand sample resulted from the heavy liquid separation technique (Table 2). It is found that the heavy mineral content of the Kutubdia island varies from 36.87% to 88.18% and Moheshkhali island varies from 1.99% to 19.93%. Light and heavy mineral distributions along with photomicrographs of some heavy minerals of the study area are given in Figures 2 and 3. In comparison with the other parts of the coastal area i.e., Sonadia island, the average concentrations of heavy and light minerals measured by Bromoform separation technique are 35.75% and 64.19%, respectively (Kabir et al., 2018).

The X-ray patterns of Kutubdia (K-line) samples (Fig. 4) show the presence of heavy minerals, which are found regularly in beach environment of Bangladesh i.e., zircon, hematite, magnetite, ilmenite, chromite, kyanite, anatase, rutile and garnet (almandine). However, the Kutubdia samples may indicate the

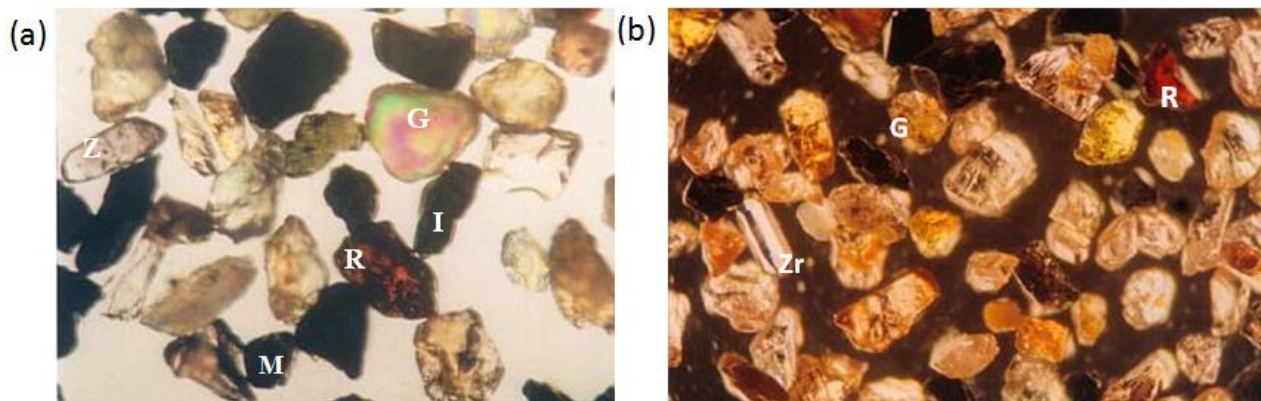


Fig. 3 Photomicrograph of heavy minerals (Ilmenite-I, Magnetite-M, Garnet-G, Rutile-R, Kyanite-K of (a) Kutubdia island and (b) Moheshkhali island.

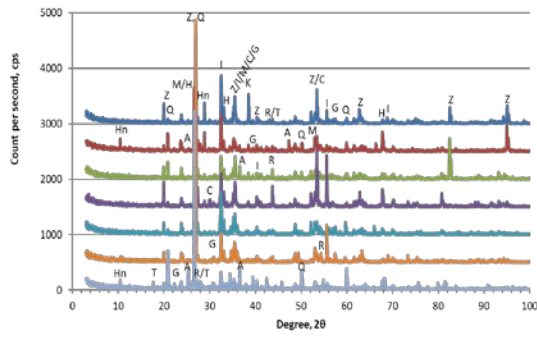


Fig. 4 XRD peaks of K-line samples. Z-Zircon, Q-Quartz, H-Hematite, M-Magnetite, I-Ilmenite, C-Chromite, K-Kyanite, A-Anatase, R-Rutile, G-Garnet (Almandine).

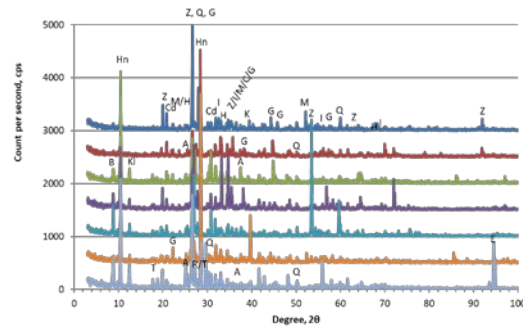


Fig. 5 XRD peaks of S-line samples. Z-Zircon, Q-Quartz, H-Hematite, M-Magnetite, I-Ilmenite, C-Chromite, K-Kyanite, A-Anatase, R-Rutile, G-Garnet (Almandine), T-Titanite, Cd-Cordierite, B- Biotite, Kl- Kaolinite, E- Epidote

Table 3 Chemical composition of heavy mineral sands from Kutubdia and Moheshkhali island.

Composition	K1		K7		S1		S2	
	Wt%	Std Error	Wt%	Std Error	Wt%	Std Error	Wt%	Std Error
Na ₂ O	0.205	0.032	0.917	0.092	1.76	0.13	1.51	0.12
MgO	0.72	0.079	1.51	0.12	2.32	0.16	4.56	0.22
Al ₂ O ₃	4.55	0.09	7.9	0.12	10.72	0.14	16.19	0.17
SiO ₂	19.11	0.43	59.67	0.54	47.49	0.55	41.78	0.55
P	0.459	0.016	0.348	0.013	0.359	0.013	0.745	0.022
K ₂ O	0.247	0.031	0.765	0.069	0.693	0.65	0.698	0.065
CaO	0.896	0.079	3.53	0.17	5.09	0.21	9.79	0.02
TiO ₂	24.57	0.47	10.06	0.33	8.62	0.31	5.97	0.26
V ₂ O ₅	0.221	0.034	0.085	0.015	0.105	0.018	0.063	0.012
Cr ₂ O ₃	1.33	0.03	0.437	0.015	0.292	0.011	0.126	0.006
MnO	0.823	0.023	0.462	0.016	0.66	0.02	0.505	0.017
Fe ₂ O ₃	35.68	0.03	12.86	0.02	19.72	0.02	17.18	0.02
CoO	0.033	0.002	0.013	0.001	0.017	0.0017	0.018	0.001
ZnO	0.036	0.002	0.035	0.002	0.079	0.00093	0.07	0.003
SrO	-	-	-	-	0.020	0.003	0.04	0.007
Y ₂ O ₃	0.119	0.006	0.033	0.002	0.036	0.001	0.035	0.001
ZrO ₂	9.12	0.31	1.01	0.1	1.56	0.13	0.393	0.052
Nb ₂ O ₅	0.044	0.003	0.021	0.001	0.014	0.001	0.019	0.001
MoO ₃	0.176	0.008	0.021	0.002	0.038	0.002	0.01	0.001
HfO ₂	0.285	0.011	0.031	0.002	0.043	0.002	0.013	0.002
WO ₃	0.026	0.003	0.02	0.002	-	-	0.01	0.002
ThO ₂	0.474	0.021	0.042	0.009	0.041	0.01	0.044	0.007
U ₃ O ₈	0.027	0.003	-	-	-	-	-	-
CeO ₂	0.469	0.016	0.1	0.005	0.119	0.006	0.063	0.006
Nd ₂ O ₃	0.199	0.008	0.041	0.003	0.046	0.003	0.017	0.004
Dy ₂ O ₃	0.028	0.006	-	-	-	-	-	-
Er ₂ O ₃	0.108	0.006	0.036	0.003	0.05	0.004	0.049	0.003
Yb ₂ O ₃	0.016	0.003	-	-	-	-	-	-
Others	0.01	-	0.05	-	0.05	-	0.01	-
Total	99.996	-	99.997	-	99.9717	-	99.968	-

existence of similar kind of minerals with different crystal phase like the titanium bearing minerals rutile and anatase. Almandine is mostly present as garnet group mineral. Like other areas, both magnetite and hematite were found as ferromagnetic minerals.

The X-ray patterns of Moheshkhali (S-line) samples show the presence of zircon, quartz, hematite, magnetite, ilmenite, chromite, kyanite, anatase, rutile, garnet (almandine), besides the presence of biotite type heavy and kaolinite type clay minerals, which are flaky in nature are also identified (Fig. 5). These minerals are not generally found in heavy fractions. However, as the samples were finer grains in size, clay size particles may be present in those parts. Like K-line, these samples also indicate the existence of rutile and

anatase. Epidote was also identified as an opaque mineral, like magnetite and hematite as ferromagnetic minerals.

Interestingly, XRD patterns of Moheshkhali samples may indicate the existence of chromite, a heavy mineral that was not previously observed or reported in the placer mineral deposits of Bangladesh. As a good amount of minerals were unidentified in the heavy fractions because of lesser quantity, it is possible that chromite is concentrated in the area in favorable depositional condition. The reasons of radioactivity of the study area may be from appreciable amount of radioactive elements such as zircon which contains some important radioactive elements.

X-ray Fluorescence Spectrometry Study

The main objective of the XRF analysis was to determine the concentration of all elements in the periodic table, besides giving special attention to rare earth elements present in the samples. Table 3 shows the results of the XRF of major and trace elements of the study area. The concentrations of TiO₂ was found in the highest amount among all the elements, ranging from 10.06-24.57 Wt% in Kutubdia and 5.97-8.62 Wt% in Moheshkhali islands. The concentrations of rare earth elements present in the Kutubdia samples are ThO₂ (0.042-0.474 Wt%), CeO₂ (0.1-0.046 Wt%), Nd₂O₃ (0.041-0.199 Wt%), Er₂O₃ (0.036-0.108 Wt%) and Moheshkhali samples are ThO₂ (0.044-0.041 Wt%), CeO₂ (0.063-0.119 Wt%), Nd₂O₃ (0.017-0.046 Wt%), Er₂O₃ (0.049-0.004 Wt%).

Scanning Electron Microscope Study

SEM analysis represents the spatial distribution of every element in the samples. Choosing a particular area of analysis, the sample image and the corresponding color-based images indicate the distribution of each element on that area.

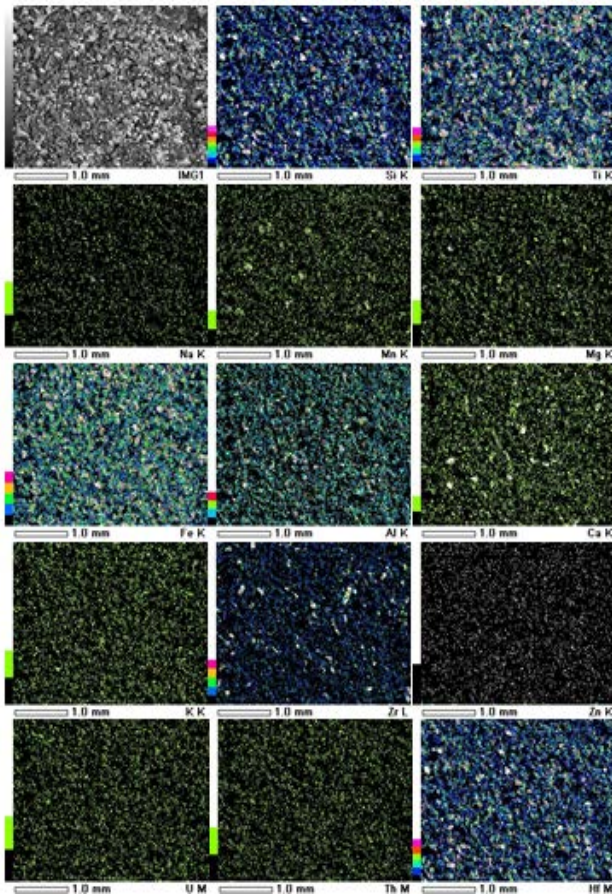


Fig. 6 Elemental mapping of K5 sample showing concentration of major elements and few other elements of interests in a particular section as shown in 1st image.

Figures 6 to 9 show the elemental mapping of two representative samples in respect of major elements

and few other elements of interests like uranium, thorium and hafnium.

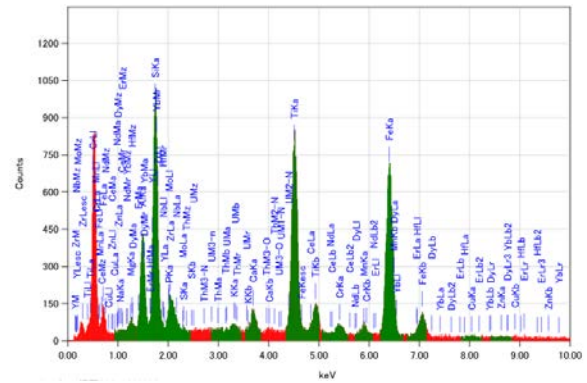


Fig. 7 Corresponding peaks of all the elements in SEM-EDX for the same section of K5 that is used for elemental mapping (Fig. 6).

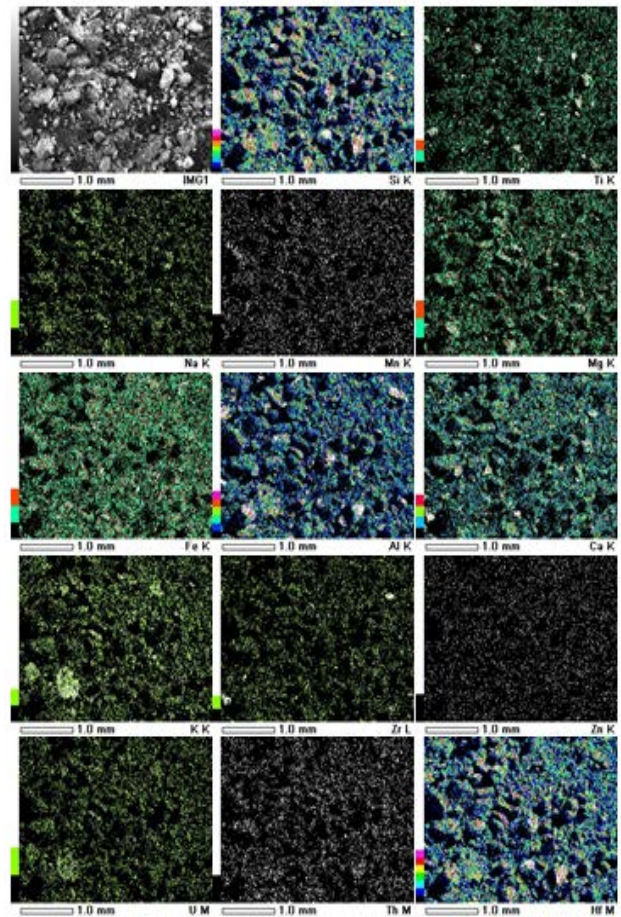


Fig. 8 Elemental mapping of S4 sample showing concentration of major elements and few other elements of interests in a particular section as shown in 1st image.

Conclusion

The study area is a region of active geomorphological changes, especially by erosion and deposition. Due to its geographic and complex tectonic positions along with active processes, most of the areas frequently suffer from cyclone, erosion, saltwater intrusion and water logging.

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