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Study and Mineralogical Analysis of Zr, Ti-rich Minerals, Silicon Found in the Sand of Cox's Bazar Beach

[1] Dr. Mokhlesur Rahman, [2] Md.Ashiqur Rahman Alif, [3] Md. Abdul Hakim Shalim, [4] Arijit Saha Ayon, [5] Molla Md Zubaer, [6] Dr. Wan Mohd Norani

[1][2][3][4][5] Department of Nuclear Science & Engineering, Military Institute of Science and Technology, Mirpur Cantonment, Dhaka, Bangladesh

[6] Faculty of Ocean Engineering Technology and Informatics, Universiti Malaysia Terengganu, Kuala Nerus, Terengganu, Malaysia

Email: [1] mokhlesur@nse.mist.ac.bd, [2] alifashiq@gmail.com, [3] hakimmunna1999@gmail.com, [4] ayonarijitsaha2000@gmail.com, [6] niksani@umt.edu.my

Abstract— Zirconium is a naturally occurring element that is primarily derived from the mineral zircon (ZrSiO4). Zircon is typically created as a byproduct in the manufacture of rutile and ilmenite from underground extraction activities since it always exists in combination with minerals that are rich in titanium. Due to the high melting point, high mechanical and chemical strength, and good corrosion resistance of zirconium, It is used in a wide range of applications such as ceramics, cladding material of nuclear fuel rods, manufacturing thermal insulators, catalysts, pharmaceutical products, electronic gadgets. The primary source of titanium is various titanium minerals, the most important of which is ilmenite (FeTiO3). Other significant titanium minerals include rutile (TiO2) and leucoxene, which is an altered form of ilmenite. They can also be associated with metamorphic rocks formed under high-temperature and pressure conditions. Due to their high strength, low density, and high resistance to corrosion, they are used in the piping system of nuclear power plants, heat exchanger, and condenser system. Rutile, Ilmenite, and Zircon can be separated using an Induced Roll Magnetic Separator (IRMS) and Electrostatic Plate Separator (ESPS). Here in this study, a mineralogical analysis of Zr and Ti found in the sand of Cox Bazar coastal area is performed. The concentration of Zr and Ti is determined using Wave Dispersion X-ray Fluorescence (WDXRF).

Index Terms— zircon, titanium, ilmenite, electronic gadgets, Cox Bazar

I. INTRODUCTION

Located on the southeastern coast of Bangladesh, the immaculate beaches of Cox's Bazar not only showcase the splendour of the Bay of Bengal but also harbour a substantial reserve of minerals beneath their golden sands. Within the realm of readily observable objects are concealed treasures in the form of minerals abundant in Zirconium (Zr) and Titanium (Ti), eagerly poised to unveil their intricate chemical and mineralogical intricacies. This conference paper undertakes a scholarly exploration, delving into the significant ramifications of these minerals, encompassing both resource processing and evaluation.

The attractiveness of minerals rich in Zirconium (Zr) and Titanium (Ti) is not solely limited to their visual appeal, but also extends to their considerable industrial importance. These minerals are of utmost importance in a wide range of advanced applications, such as aerospace, electronics, and renewable energy technologies, and so have a significant impact on the development of contemporary technological environments. It is crucial to comprehend the availability, distribution, and chemical composition of these substances within the distinctive geological setting of Cox's Bazar in order to fully harness their potential and make valuable contributions to the global supply chain.

The objective of our research is to investigate the complex chemistry and mineralogy of Zr- and Ti-rich minerals obtained from the Cox's Bazar beach placer deposits. By utilising sophisticated analytical methodologies, our objective is to unravel the intricate structural characteristics and elemental makeup of these minerals, thereby providing insights into their provenance and geological chronology. Furthermore, our investigation examines the ramifications of resource extraction, taking into account the economic feasibility and ecological sustainability of using these mineral resources.

Through a comprehensive analysis of the chemical composition and mineralogical properties of minerals abundant in Zirconium (Zr) and Titanium (Ti) in the region of Cox's Bazar, our objective is to offer significant knowledge that beyond the boundaries of mere academic interest. The results of our study have the potential to provide guidance for strategic resource management, serve as inspiration for the development of sustainable processing technologies, and promote a balanced approach to the utilisation of these valuable minerals. We invite you to participate in this scientific expedition, where we want to explore the phenomenon of coastal alchemy. Through our research, we aim to provide a fresh perspective on the latent resources concealed beneath the sandy shores of Cox's Bazar.

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II. LITERATURE REVIEW

Zircon is a mineral that is frequently encountered in both volcanic rock formations and sedimentary accumulations. The mineral possesses a unique crystalline arrangement and can be employed in the process of radiometric dating to ascertain the chronological age of geological formations. Zircon is frequently seen in coastal sediments and is often found in conjunction with other dense minerals such as ilmenite, rutile, and garnet. This literature review aims to investigate a selection of scholarly works pertaining to the presence of zircon minerals in coastal beach environments.

The initial research article under consideration is titled " Chemistry and mineralogy of Zr- and Ti-rich minerals sourced from Cox's Bazar Beach placer deposits, Bangladesh: Implication of resources processing and evaluation" authored by Menezes et al. (2018). This study aims to assess the geochemical and mineralogical characteristics of zircon, rutile, and ilmenite in order to enhance our comprehension of their economic value and identify feasible beneficiation pathways for subsequent processing. The mineral was discovered within the sand of Cox Bazaar. The heavies found in the sands of Cox's Bazar beach had an average weight percentage of 2.8, 12.1, and 2.7, respectively. The mineralogical and geochemical diversity among Zr- and Ti-rich materials was investigated by the utilization of X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM), and electron probe microanalysis (EPMA) techniques. The availability and pricing of titanium and zirconium in global markets are influenced by the choice of feedstock, which is impacted by increasing technology and customer demands. The uses of these materials also play a significant role in shaping their market dynamics. The present study also included examinations into provenance and petrogenesis, in order to examine the geochemical diversity, including elemental impurities and trace elements that could potentially originate from parental sources. The study revealed that the concentrations of zircon are notably constrained within the size fractions ranging from 125 to 63 µm, while ilmenite and rutile are present across all size ranges [1].

A separate study examines the granulite facies units within the Grenvillian Oaxacan Complex (OC), wherein the process of rutile crystallization took place within a temperature range of 808 to 873 °C. The present research is entitled, "U-Pb geochronology of rutile: deciphering the cooling history of the Oaxacan Complex granulites, southern Mexico." Based on data obtained from multiple places, it can be observed that the cooling and exhumation processes subsequent to the Zapotecan granulite facies event, which occurred approximately 990 million years ago, exhibited variations among the diverse tectonic slices comprising the OC. Following the granulite peak, the cooling process commenced within the central sector (Nochixtlán-Oaxaca), characterized by notable cooling rates of approximately 40 °C per million years. The anticipated rates of cooling vary between approximately 3°C/Ma for the northern OC outcrops in Coatepec (Puebla) and around 6°C/Ma for the southern region in Ejutla (Oaxaca). Consequently, the cooling process to reach a temperature of approximately 600°C was notably slower in both the northern and southern areas [2].

The potential for Kalimantan to emerge as a significant new heavy mineral (HM) province has been examined through an analysis of two HM-rich river tailings and two zircon concentrates collected from the Sampit district in Central Kalimantan. The composition of the two tailings samples rich in heavy minerals primarily consisted of quartz, accounting for over 95% of the composition. Additionally, a small proportion of ilmenite, altered ilmenite, leucoxene, and rutile were present, contributing to the heavy mineral component. Based on the chemical composition and modal abundance data, it was determined that both samples had a combined level of heavy metals (HM) amounting to 2%. The B-Ore sample had a nearly equal proportion of zircon and titanate minerals, while the A-Ore sample displayed a significantly higher abundance of zircon compared to the combined quantity of titanates. The A-Con sample was discovered to contain 90% zircon, as indicated by the results of bulk chemical tests conducted on the zircon-rich concentrates, which demonstrated a relatively high level of purity. The sample contained rutile impurities at a concentration of 2.2% [3].

Significant quantities of heavy mineral sands were discovered in the Murray Basin, located in southeastern Australia. These deposits can be classified into two types: high-grade, coarse-textured strandline deposits, with a total estimated volume of 90 million metric tons, and low-grade, extremely fine sheet-like deposits, with a total estimated volume of 250 million metric tons. The deposits are predominantly composed of ilmenite, which constitutes 40-60% of the total heavy mineral assemblage (THM). According to the mineral prices recorded in 2011, it was estimated that the reserves possessed a total value of US$200 billion, with the majority of this value, namely over 85%, attributed to the fine-grained resources. Despite the limited economic value of ilmenite, commercial exploitation has primarily focused on high-grade coarse-grained deposits due to its rutile and zircon content [4].

According to a study, the predominant opaque mineral present in the beach sands of Cox's Bazar is ilmenite, constituting approximately 15-30% of the overall heavy mineral content. Ilmenite-hematite exsolutions are commonly observed, with the seriate texture being the prevailing characteristic among these occurrences. The extensive evidence suggests a greater level of support for the volcanic origins of the exsolutions, as opposed to their metamorphic origins. The composition of magnetite consists of less than 2% is called ulvospinel, rendering it chemically and visually homogeneous. The observed distribution of MnO within the coexisting minerals of ilmenite and titanomagnetite suggests that intrusive igneous rocks are the likely origin of these

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mineral formations. The temperature range for the oxide assemblage in the study spans from 450 to 850°C, whilst the fo2 values exhibit a range of 10-13 to 10-19 [5].

The present study employed neutron activation analysis (NAA) to quantify the elemental contents of uranium and thorium in zircon assemblages obtained from Cox's Bazar beach placers. The extraction of magnetite, ilmenite, zircon, garnet, and rutile from beach sands was conducted by a separation process within the pilot plant of the Beach Sand Minerals Exploitation Centre (BSMEC). The aforementioned procedure incorporates three magnetic separators: a Low-Intensity Magnetic Separator (LIMS), a Wet High-Intensity Magnetic Separator (WHIMS), and an Induced Roll Magnetic Separator (IRMS). These separators are utilized to separate the five minerals previously mentioned. The separated zircon assemblages were examined using a polarizing petrographic microscope and X-ray diffraction techniques. The analysis revealed that over 75% of the zircon was found to be of high purity. The uranium and thorium content inside zircon was subsequently ascertained using Neutron Activation Analysis (NAA) at the BAEC TRIGA Mark II research reactor. Subsequently, the zircon sample that had undergone irradiation was subjected to analysis using a High Purity Germanium (HPGe) detector. The presence of uranium (U) and thorium (Th) was ascertained based on the detection of gamma ray peaks with energy levels of 277 keV and 312 keV, respectively. The analysis revealed that zircon contains uranium concentrations ranging from 94 to 141 parts per million (ppm), as well as thorium concentrations ranging from 127 to 506 ppm. Hence, it is imperative to consider the significant presence of uranium and thorium in zircon when undertaking mining activities for placer minerals in the beaches of Cox's Bazar [6].

The present study, entitled "Recovery of zircon from Sattankulam deposit in India—problems and prospects" highlights the significance of zirconium and the obstacles encountered in the extraction of zircon from the mineral deposits found in the sand of Sattankulam, India. Zircon is mostly generated as a byproduct in the process of producing ilmenite and rutile. Recovering a higher-grade zircon poses various obstacles. The Sattankulam deposit in India faces several substantial challenges that hinder the achievement of high recoveries and the production of premium quality zircon. These hurdles include the occurrence of monazite, the presence of heavy iron oxide surface coatings on the zircon mineral, and a notable proportion of sillimanite among the non-magnetic heavy minerals. The zircon quality is enhanced through the implementation of a high-temperature acid leaching method. During this procedure, the hot zircon undergoes treatment with sulfuric acid within a kiln, followed by subsequent stages of attrition, neutralization, and drying. Another procedure that can be employed is the zircon upgrading process (ZUP). During this procedure, the zircon specimen is subjected to a thermal treatment at approximately 400°C, followed by a rapid cooling process in a solution of diluted sulfuric acid. Nevertheless, it has been discovered that the most efficient approach to economically produce high-quality zircon is by the process of hot acid leaching of crude zircon concentrate [7].

The research article entitled "Heavy Mineral Assemblages of The Beach Sands of Kuakata, Southern Bangladesh" gives a comprehensive examination of the heavy minerals found in the sand of Kuakata beach. The study encompasses both qualitative and quantitative analyses, with a focus on understanding the distribution patterns of these minerals. Additionally, the paper investigates the origins and sources of these heavy minerals. A total of 17 samples were obtained from the beach sand, out of which 5 samples were selected for the purpose of conducting a heavy mineral analysis. The process of separating the heavy minerals from the samples was conducted. The concentrations of garnet, hornblende, epidote, and opaque minerals exhibited elevated levels. In contrast, monazite, rutile, and chloritoid were observed in lesser quantities. The minerals were observed using a polarizing microscope, and each mineral was recognized based on its distinctive properties. These minerals also yield valuable insights into their origins, such as crystalline rocks, metamorphic rocks, dynamo-thermal metamorphic source rocks, intrusive acid igneous rocks, gneisses, and granitoid rocks, as well as mafic rocks. The writers provide a precise and instructive presentation of the heavy minerals. It would be advantageous if the technique of the separating process were supplied. Nevertheless, the authors' findings offer compelling evidence regarding the existence of heavy elements inside the beach sand of Kuakata, as well as their origins [8].

III. METHODOLOGY

In the current study, three samples of beach sand were gathered from various locations within the Cox's Bazar coastline area. The samples were denoted as L(location) with distinct numerical identifiers. The designation "L-1" signifies that the specimen was obtained from Kolatoli Beach. Sample L-2 was collected from the central region between Sugandha and Kolatoli Beach, while sample L-3 was taken specifically from Sugondha Beach. All three samples are collected from the back dune.

The sample preparation process encompasses two key steps: sample drying and sample pelleting. Next, the sample was placed into the wavelength-dispersive X-ray fluorescence (WDXRF) equipment. The sample’s elemental composition was determined through analysis using Wavelength Dispersive X-ray Fluorescence (WDXRF) spectroscopy. Figure 1 illustrates the comprehensive technique employed in our present investigation.

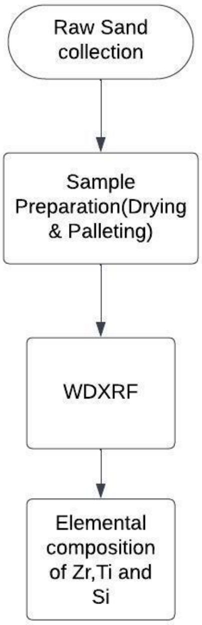

Figure 1: Determination of Elemental Composition of Zr, Ti and Si

IV. WDXRF

Wavelength-dispersive X-ray spectroscopy (WDXS or WDS) is an analytical technique employed to acquire elemental data for various materials non-destructively. In this process, atoms become excited as electrons are emitted from their orbitals due to high-energy radiation. The atom returns to a state where outer electrons occupy shells by releasing X-ray fluorescence radiation. The emitted radiation acts as an identifier. It is then analyzed by using a detector. By examining the wavelengths of the resulting X-ray, we can measure the various components present in the sample.

The Wavelength Dispersive X-ray Fluorescence (WDXRF) spectrometer is comprised of three primary components, namely an X-ray source, a sample chamber, and a detector. The X-ray source emits a high-energy X-ray beam, which is subsequently directed toward the sample located within the sample chamber. The X-ray radiation engages in interactions with the atomic structure of the specimen, thereby inducing the emission of fluorescent X-rays. then, the fluorescent X-rays undergo diffraction upon interaction with a crystal and are then directed towards the detector. The detector quantifies the magnitude of the fluorescence X-rays, a value that is directly related to the quantity of the element present in the sample.

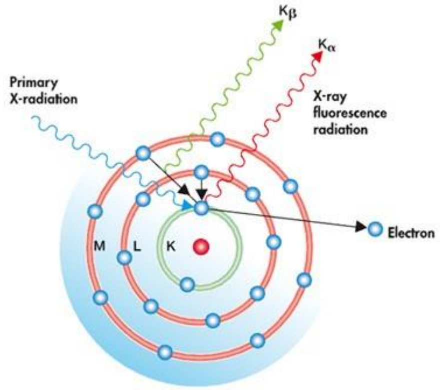

Figure 2: Working principle of XRF

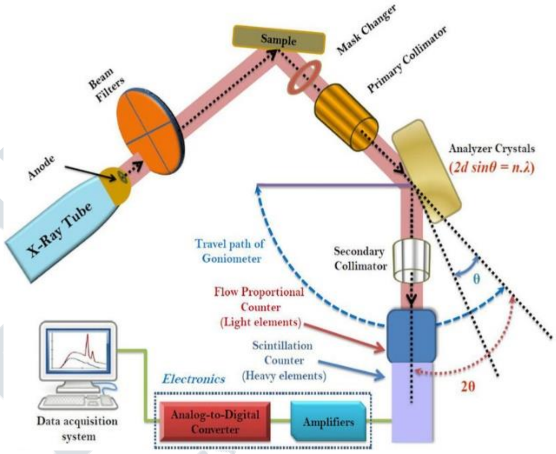

Figure 3: WDXRF diagram

WDXRF process obeys the Bragg's law. Based on this law, the phenomenon of constructive interference occurs when an incident X-ray beam with a wavelength denoted as "λ" interacts with a crystal surface at an angle denoted as "θ". Suppose the crystal possesses atomic lattice layers separated by a distance denoted as "d". In that case, the resulting diffracted X-ray beam will be released from the crystal at an angle also denoted as "θ" if the condition $n\lambda = 2d \sin\theta$ is satisfied, where "n" represents an integer. This implies that a crystal possessing a well-defined lattice dimension will alter the trajectory of an X-ray beam originating from a certain sample type at a predetermined angular displacement. The measurement of the X-ray beam can be accomplished by positioning a detector, typically a scintillation counter or a proportional counter, in the trajectory of the deviated beam. Given that each element possesses a unique X-ray wavelength, the presence of numerous crystals and detectors enables the determination of multiple elements. To enhance the efficiency of the process, the x-ray beams are commonly collimated using a collimator.

V. RESULT AND DISCUSSION

The result of the present is presented in Table 1. It represents the elemental composition of Zr, Ti, and Si of the three samples collected from three different locations in Cox's Bazar coastal area. Zr comes from Zircon ($ZrSiO_4$)

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which is a heavy mineral. On the other hand, Ti is originated from ilmenite ($FeTiO_3$), and rutile (TiO_2). Zircon is normally associated with rutile and ilmenite.

The elemental composition of Zr exhibits a range of 0.67 to 2.90% among the three samples. The largest percentage was seen in the sample obtained from Sugondha Beach, amounting to 2.9%. Following that, a smaller quantity was observed in the L-2 sample (0.67%). This implies that Sugondha Beach may have a greater abundance of heavy minerals. In the context of Ti, the sample denoted as L-1 exhibited the highest concentration (5.44%), whereas the sample designated as L-2 displayed the lowest elemental composition. The deposition of heavy minerals such as zircon, rutile, and ilmenite has been observed in the back dune area of Sugondha Beach. The elemental compositions of silicon were found to be much greater than those of zirconium and titanium in all three samples. The predominant presence of silicon in sands is the underlying cause.

Table 1. The elemental composition of Zr, Ti, and Si of the three samples

Analyte	L-1 (%)	L-2 (%)	L-3 (%)
Zr	1.33	0.67	2.90
Ti	5.44	1.56	4.15
Si	49.66	65.94	51.30

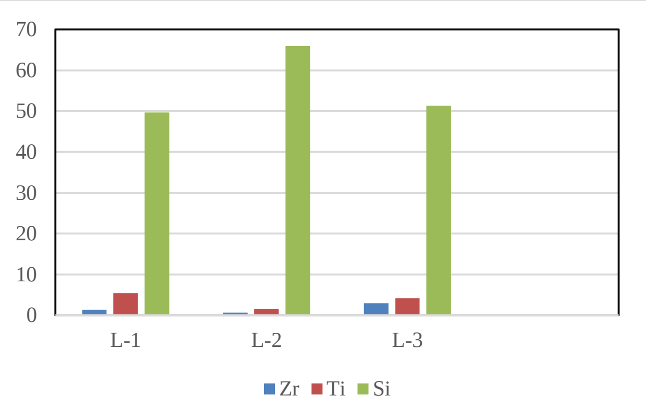

Figure 4: Elemental composition comparison among three samples

In prospective scenarios, the separation of heavy minerals such as zircon, rutile, and ilmenite from the individual three samples can be achieved. Additionally, the microstructure of zircon, rutile, and ilmenite can be discerned through the utilization of Scanning Electron Microscopy. The zircon samples can be subjected to irradiation in a 3 MW TRIGA Mark II Research Reactor of BAEC, employing the Neutron Activation Analysis (NAA) technique. Subsequently, the gamma-ray that is released can be quantified by the utilization of the High Purity Germanium (HPGe) detector. The determination of uranium and thorium will be conducted using gamma ray peaks at energies of 277 keV and 312 keV, respectively [6].

VI. CONCLUSION

In conclusion, the elemental composition analysis of Zr, Ti, and Si in the samples collected from three distinct locations in the Cox's Bazar coastal area provides valuable insights into the heavy mineral distribution. The prevalence of Zr, derived from Zircon, was notably higher in the Sugondha Beach sample, suggesting a potentially greater abundance of heavy minerals in this location. Ti, originating from ilmenite and rutile, exhibited variations in concentration among the samples, with L-1 showing the highest percentage. Silicon, with consistently higher concentrations across all samples, was identified as the predominant element in the sands.

The findings open avenues for prospective studies, particularly in the separation of heavy minerals and the detailed examination of the microstructure of zircon, rutile, and ilmenite using Scanning Electron Microscopy. The proposed use of Neutron Activation Analysis (NAA) on zircon samples, irradiated in a 3 MW TRIGA Mark II Research Reactor of BAEC, holds promise for quantifying gamma-ray emissions. This technique, along with the utilization of a High Purity Germanium (HPGe) detector, could further enable the determination of uranium and thorium concentrations in these heavy minerals. In conclusion, these results pave the way for a deeper understanding of the coastal area's mineral composition and provide a foundation for future research endeavors, contributing to the broader knowledge of geological processes and mineral resources in Cox's Bazar.

REFERENCES

[1]. A.S.M. Mehedi, Ismail Hossain, Md. Aminur Rahman, Mohammad Nazim Zaman a, Pradip Kumar Biswas, Md. Sha Alam, "Chemistry and mineralogy of Zr- and Ti-rich minerals sourced from Cox's Bazar beach placer deposits, Bangladesh: Implication of resources processing and evaluation",2022.

[2]. Miguel Gerardo Adame-Martínez, Luigi A. Solari, Carlos Ortega-Obregón, Fanis Abdullin, "U-Pb geochronology of rutile: deciphering the cooling history of the Oaxacan Complex granulites, southern Mexico",2020, v. 37, núm. 2, 2020, 135-145.

[3]. H. Aral, M. I. Pownceby, J. Im, "Characterisation and beneficiation of zircon rich heavy mineral concentrates from central Kalimantan (Borneo, Indonesia)",2008 Appl. Earth Sci. 117 (2), 77–87. https://doi.org/10.1179/174327508X339837.

[4]. Warren John Bruckard, Mark Ian Pownceby, Leanne Kathleen Smith and Graham Jeffrey Sparrow, "Review of processing conditions for Murray Basin ilmenite concentrates", 2015, 124, 47–63. https://doi.org/10.1179/1743285514Y.0000000083

[5]. Mitra, S., Ahmed, S.S., Moon, H.-S., "Mineralogy and chemistry of the opaques of Cox's Bazar (Bangladesh) beach sands and the oxygen fugacity of their provenance",1992, Sediment. Geol. 77 (3-4), 235247.https://doi.org/10.1016/0037-0738(92)90129-F

[6]. Zaman, M. M., Rajib, M., Kabir, M. Z., Deeba, F., Rana, S. M., Hossain, S. M., Latif, S. A. and Rasul, M. G., "Presence of uranium and thorium in zircon assemblages separated from

beach sands of Cox's Bazar, Bangladesh, Journal of Science, Technology and Environment Informatics",2016, Vol. 3, No. 1, p-161-168. doi: 10.18801/jstei.030116.18

[7]. V.G.K. Murty, Rashmi Upadhyay, Sundaresan Asokan, "Recovery of zircon from Sattankulam deposit in India-problems and prospects",2007.

[8]. Zahidul Bari, Mohammad Rajib, S.M. Mahbubul Ameen, "Heavy Mineral Assemblages of The Beach Sands of Kuakata, Southern Bangladesh",2011

[9]. Thermo Fisher Scientific, "WDXRF: How Does It Work?", 2023.

[10]. Wikipedia, "X-ray fluorescence",2023.

[11]. Barrington, C., Masbate, J., Podmeyer, D., "Zircon and zirconia: value-adding materials for the global investment casting industry. 14th World Conference Investment Casting",2016.

[12]. Corfu, F., Hanchar, J.M., Hoskin, P.W.O., Kinny, P., Atlas of zircon textures. Rev. Mineral. Geochem. 53, 469–500, 2003.

[13]. Curray, J.R., "Possible greenschist metamorphism at the base of a 22-km sedimentary section, Bay of Bengal". Geology 19, 1097, 1991.

[14]. Hoskin, P.W.O., "The Composition of Zircon and Igneous and Metamorphic Petrogenesis. Rev. Mineral. Geochemistry", 2003.

[15]. Hossain, M.S., Xiao, W., Khan, M.S.H., Chowdhury, K.R., Ao, S., Geodynamic model and tectono-structural framework of the Bengal Basin and its surroundings, 2020.