EDXRF analysis of beach rock samples of Andaman Island

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Abstract Elemental contents of beach rock samples were analyzed using EDXRF. The samples were collected from three locations of Andaman Island. The Al, Ca, K, Fe, Ti, Si, V, Co, Cu, Ba, Zn, Pb, Cd and Mn contents were determined. The geochemical behavior of elements in the region is discussed. The elemental contents of beach rock samples from Andaman Island are much below the values of both earth crust and that of Tamilnadu region. However, content of the biogenic element Ca was the highest of all elements. This is due to the typical beach rock formation.

Key words Beach rock, Andaman, Multi-element analysis, EDXRF

1 Introduction

Beach rock formation is peculiar compared to other types of rock formations. It is a sedimentary formation commonly appearing as layered deposit inclined towards the sea. It is influenced by the effects of carbonate cement-aragonite or magnesium calcite initially formed in the inter-tidal zone. Like the beach itself, beach rock represents a transition between the marine and meteoric environments, where processes from each environment commonly affect it. Beach rock also acts as a resistant barrier to erosion, thus affecting the shoreline's rate of erosion and overall development. However beach rock can be quite useful in describing and delineating environments of deposition[1]. Beach rock forms most commonly on beaches composed of calcareous shell and coral grains, but it can also develop in beaches of quartz sand or other mineral composition. It forms best on sand beaches; shingle or conglomeratic beach rock is less abundant. The natural factor of the beach, such as gentle slope of the foreshore, sufficient shell content and ground water temperature have also favored the formation of beach rocks. Essential to beach rock development is ground water with enough calcium to provide cementing effect.

Beach rock formation is found in many places in the world[2-5] and few places in India[6-8]. The beach rock samples of Tamilnadu were analyzed for cementation processes by studying elemental analysis using INAA and PIXE[9,10]. One such beach rock formation is found in the Andman Island[6]. The Quaternary rocks of Andaman-Nicobar Archipelago are very significant as they have various types of sediments capable of unravelling the climatic history, sea level variations and neotectonic activity, shore sand, beach rock, raised beaches, corals and sediments associated with mangroves are important constituents of the Holocene deposits. Of the beaches, rocks are significant as they represent the former strandline and hence sea level variations. The beach rocks are common all along the coastal tract of Andaman-Nicobar Archipelago[6]. These islands are represented by an active sub-ariel ridge located between the Arakan-Yoma in the north and Java-Sumatra in the south (Lat 6.45–13.43 N; Long 92.15–94.00 E). Geologically the Andaman basin is interesting as they have a long sedimentary record ranging from Cretaceous to Recent. The basin is studied for its geology and paleontology and valuable contributions have been made[11,12]. A detailed

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examination is required to understand the process of cementation of beach rocks of Andaman Island by studying the elemental composition.

EDXRF is chosen for the study due to its advantages of non-requirement of chemical treatment of the samples and less time-consuming non-destructive method. It has been used in studies on elemental composition of various environmental matrices[13-19].

2 Sample Collection and Preparation

At three locations (Fig.1), using global positioning system (QueM5 with accuracy up to 10 m), the samples were collected along the tide line, i.e. along the horizontal transect. A detailed geological survey was carried out before the fieldwork. In each location, 3–5 pieces of 2 kg bulk of beach rock samples were collected in a polythene bags. They were cleaned, weathered surface removed and the remaining fresh materials crushed into small pieces. The samples were powdered using agate mortar and dried for 24 h at 110℃ and then pulverized to particle sizes not greater than 2 mm mesh screen[10].

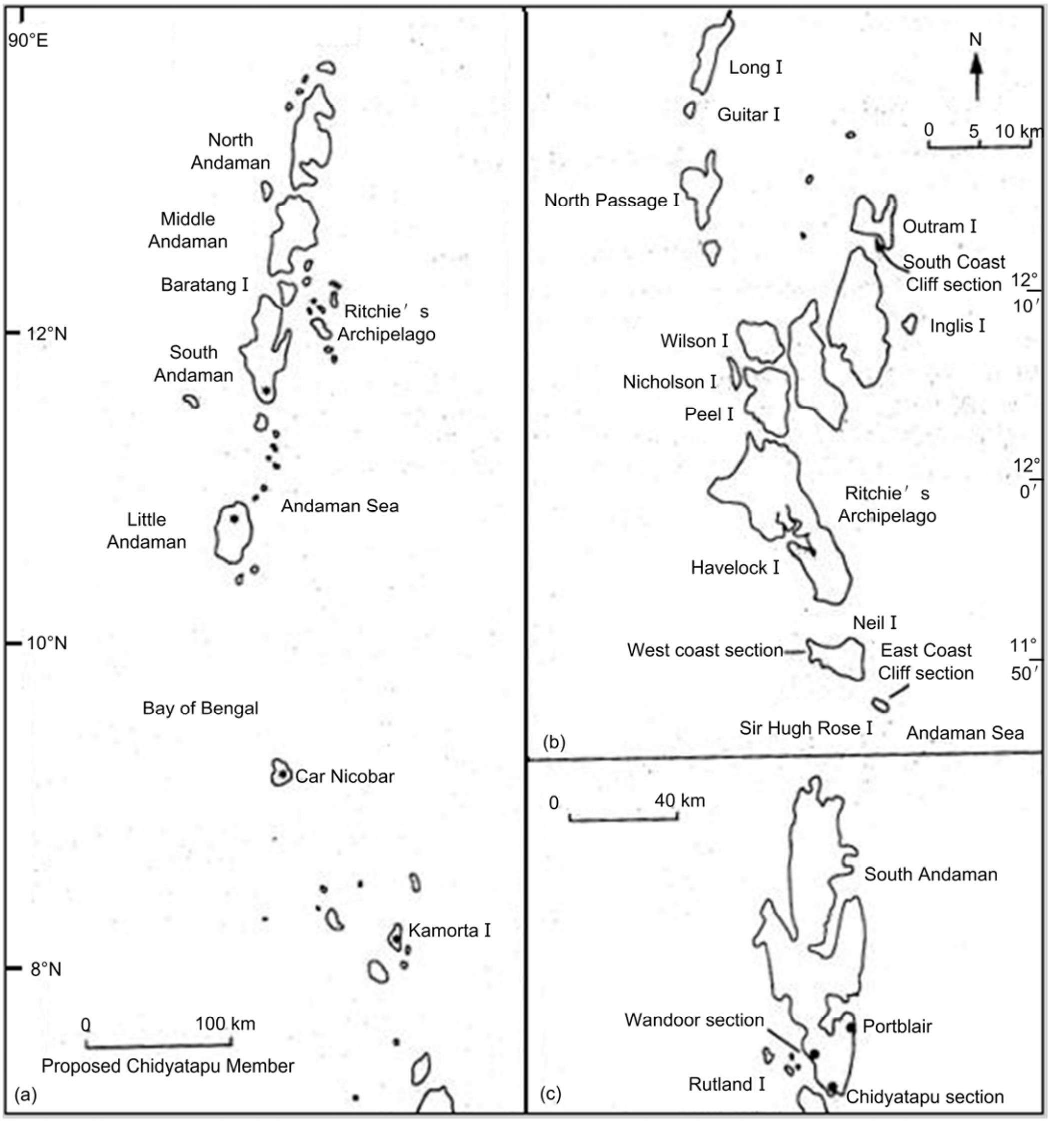

Fig.1 Location Map.

The powders were dried at 110℃ until no further weight loss was observed. One gram of the fine ground sample and 0.5 g of the boric acid were mixed sufficiently. The mixture was then thoroughly grounded and pressed to a 30-mm pellet using a 15-ton hydraulic press.

3 Experimental

The beach rock samples were analyzed using the EDXRF at Environmental and Industrial Safety Section, Safety Group, Indira Gandhi Centre for Atomic Research (IGCAR), Kalpakkam, Tamilnadu. It is a PW 4025 Minipal (M/s Philips, Netherlands), fitted with a side window X-ray tube (9 W) of a Rh anode. The sample exchanger accommodates 12 samples. Selection of filters, tube voltage, sample position and current are fully computer controlled. The beam spot (elliptical) is 81.7 mm^2. Standardless determination and automatic gain correction are performed with the MCA. Gain correction is performed when the beam stop is in the reference position. Beam stop contains a reference sample (an Al/Cu alloy). Cu is used for gain correction. Al and Cu are used for energy calibration. The standard stream sediment (GBW 7305) was used as reference material for standardizing the instrument (Table 1).

Table 1 Stream sediment standard values and the EDXRF results (in μg/g unless % is indicated)

Elements	Certified values	EDXRF
Al %	7.84	7.46
Ca %	3.17	3.18
K %	1.62	1.63
Fe %	4.32	4.28
Ti %	0.52	0.52
Si %	31.92	32.37
V	109	109.7
Co	18.5	18.0
Cu	137	138.9
Ba	440	633.9
Zn	243	261.3
Pb	112	159.6
Cd	0.82	0.88
Mn	1160	1137

Kα lines of Al, Ca, K, Fe, Si, Ti, V, Cu, Zn and Mn, and Lα lines of Ba, La and Pb, were used for X-ray analysis. The region of interest for Co is 3.025–3.240 keV while that of Cd is 6.815–7.120 keV. For Cd and Co an exposure time of 300 s was used, and for Al, Ca, K, Fe, Si and Ti, it was 60 s. For Ba, Cu, Mn, Pb, V and Zn, time of exposure was 200 s.

4 Results and discussion

Elemental contents of Al, Ca, K, Fe, Ti, Si, V, Cu, Co, Cd, Ba and Zn in beak rock samples of Andaman are reported in Table 2. They were compared with the crustal average and also beach rocks of Tamilnadu in Table 3. The quantitative and qualitative analyses of elements are discussed below. Al, Fe, K and Ti contents are much less than both the values of earth crust and beach rocks of Tamilnadu. While Si content is less than the crustal average, Ca is much higher than both crustal average and Tamilnadu region. Trace metals of V, Co & Mn are much less than both crustal average and Tamilnadu region. While trace metals of Cu, Ba, Zn, and Cd are less than the crustal values. However, there is no change in the Pb values.

Table 2 Elemental contents of beach rocks of AndamanIsland (in μg/g unless % is indicated)

Element	Neill Island (S_1)	Chidayatapu (S_2)	Wandoor (S_3)	Average
Al %	0.21	0.97	0.13	0.44
Ca %	29.37	22.46	29.04	26.95
K %	0.32	0.34	0.31	0.32
Fe %	0.37	1.48	0.23	0.69
Ti %	BDL	0.04	BDL	0.01
Si %	1.75	6.43	0.78	2.98
V	10.4	33.9	7.7	17.3
Co	BDL	1.3	BDL	0.4
Cu	7.5	9.4	1.8	6.2
Ba	166.6	255.9	159.5	194.0
Zn	0.7	6.4	BDL	2.4
Pb	BDL	12.9	BDL	4.3
Cd	1.0	0.78	0.98	0.92
Mn	BDL	137.6	BDL	45.9

Table 3 Comparison of the EDXRF results to crustal Average and beach rocks of Tamilnadu, India (in μg/g unless % is indicated)

Elements	Present study	Crustal average[20]	Beach rocks of Tamilnadu[10]
Al %	0.44	8.13	3.52
Ca %	26.95	3.63	17.42
K %	0.32	2.59	1.19
Fe %	0.69	5.00	3.74
Ti %	0.01	0.44	2.03
Si %	2.98	27.72	-
V	17.3	135	101.6
Co	0.4	25	10.48
Cu	6.2	55	-
Ba	194.0	400	-
Zn	2.4	70	-
Pb	4.3	13	-
Cd	0.92	0.2	-
Mn	45.9	900	673.6

4.1 Aluminum, Calcium and Potassium

Aluminum is a chemically stable and usually non-anthropogenic element. It is considered as an index of the aluminosilicate content of sediment and also used as an indicator of terrigenous debris of which the clay minerals and feldspar are quantitatively the most important. In Table 3, the Al content varied from 0.13% to 0.97% with an average of 0.44%. S3 and S2 recorded the lowest and highest, respectively. The lowest value at S3 may be due to the increased percentage of sand and $CaCO_3$. The highest value at S2 suggests a higher degree of weathering and reflects the degree of influence of finer nature of sediments. The variation of Al content of the samples probably reflect the diverse influence of terrigenous and authigenic materials[21].

In general, Ca is the most abundant element in beach rock samples, as was found in the present study. This may be due to typical beach rock formation[10]. It varied from 22.46% to 29.37% with an average of 26.95%. The lowest and highest value of this element was recorded in S2 and S1, respectively. Variation of calcium in the samples may be thought of as being controlled by clay minerals. The highest concentration of Ca in the samples may be due to the significant incorporation of clay sized $CaCO_3$ material in sediments.

K content in the beach rock samples varied from 0.31% to 0.34% with an average of 0.32%. The lowest and highest K contents were recorded for S3 and S2, respectively. As K first goes into the solution but does not remain dissolved, it is absorbed by the clay content. The difference in the behavior of sodium and potassium during the weathering is due to greater resistance of potash feldspar as compared to plagioclase feldspar[22]. Presence of feldspar mineral in the study area has been confirmed by FT-IR and XRD techniques.

4.2 Iron, Titanium and Silicon

Iron is a common and abundant element in earth's crust. It is present in the environment as a result of natural as well as anthropogenic activity and has frequently been used as an indication of natural changes in the heavy metal carrying capacity of the sediments. The Fe content varied from 0.23% to 1.48% with an average of 0.69%, with the lowest and highest values at S3 and S2, respectively. This may be due to iron being incorporated within calcite during primary precipitation of calcite in reducing condition and the result of input and sedimentation rate of detrital mineral into the depositional environment[23].

As an abundant element in the earth's crust, Ti is a common constituent of rocks, soils and sediments and is primarily found in rutile (TiO_2), ilmenite ($FeTiO_3$) and sphene ($CaTiSiO_5$). Ti content is lower than the crustal average value. This may be attributed to decreasing oxidative precipitation or currents and turbulence at the confluence might have dispersed considerably the flocculated particles to the sea before settling as has been interpreted for Fe.

Silicon content in the beach rock samples varied from 0.78% to 6.43% with an average of 2.98%. The lowest and highest Si contents were recorded for S3 and S1, respectively. Si has lower value compared to the crustal average. This may be due to the typical beach rock formation.

4.3 Trace elements: V, Co, Cu, Ba, Zn, Pb, Cd and Mn

As a ubiquitous element, V is emitted into the air, water and terrestrial ecosystem from a large number of diverse sources, which include waste effluents from vanadium metal industries, alumina plants, textile mills, iron and steel industries (which use vanadium as alloying material) and chemical industries. In Table 3, V content varied from 7.7 to 33.9 μg/g with an average of 17.3 μg/g. The lowest and the highest levels were recorded for S3 and S2, respectively. V content is lower than the crustal average. The V distribution in marine sediments is largely controlled by the input and sedimentation of detrital mineral in which it is principally located in mineral lattice position[24]. This may be one of the reasons for the V variation in the beach rock samples.

Co is among the most widely distributed heavy metals in terrestrial and aquatic environment. Co content is lower than the crustal average values. The low Co content may be attributed to its mobility, which is reduced in the carbonate dominant environment[25].

There are several sources of Cu emission to the atmosphere. The natural sources include wind blown, dusts, vegetation exudates, volcanic emissions and sea salt sprays. The anthropogenic sources include metal production, wood and fossil fuel combustion and waste incineration. The lowest and highest Cu contents are at S3 (1.8 μg/g) and S2 (9.4 μg/g), respectively. The Cu content in this study is lower than the crustal average.

From the Table 3, Ba varies from 159.5 to 255.9 μg/g with an average of 194 μg/g. S3 and S2 recorded the lowest and highest concentration, respectively. The Ba concentration may be explained by the formation of sizable amount of barites ($BaSO_4$) in the carbonates[26].

Zinc is one of the most ubiquitous and mobile of heavy metals and is transported in natural water systems to a great extent in dissolved form. The mean value of zinc concentration in the present study is lower than the crustal abundance. This may be due to the carbonate in the environment diluting the heavy metal concentration.

To understand the fate and transport of anthropogenic lead, its geochemistry in terrestrial and marine environments must be considered. The Pb content in the present study is 12.9 μg/g, while Pb content in the earth crust is estimated at 13 μg/g.

Cd is poorly concentrated in all the beach rock samples, ranging from 0.78 μg/g to 1 μg/g. The low Cd concentration may be attributed to its mobility, which is reduced in the carbonate dominant environment. Mn is an essential micronutrient for plant and animals. Processing of iron ores, in which manganese is present in significant concentration, constitutes the major sources of manganese pollution. In this study, Mn content (137.4 μg/g) is higher than crustal abundance (0.5 μg/g). This may be due to dissolution of carbonate causing the formation of manganese bicarbonate, which is stable, in aerobic environment at low pH. Another possible reason under oxic water condition is that Mn occurs as insoluble Mn (III) and Mn (IV) oxides, whereas in anoxic conditions it occurs as Mn (II) in the dissolved phase. During sub-oxic and anoxic condition Mn^{2+} diffuses upwards in the sediment column and Mn can precipitate in the form of Mn oxide/hydroxides at or near the freshwater-seawater interface. The variation of different trace elements may be due to the nature of weathering processes, and the velocity of transporting media. The total trace elements contents in sediments depend not only on the trace element input but also on the mineral composition of the sediment, which can be different from area to area. Another possible reason may be attributed to the hydrothermal alteration and metamorphism processes, i.e. the area was subjected to surface and subsurface processes of alteration.

5 Conclusion

Beach rock samples were collected from Andaman Island to study their geochemical nature. From the EDXRF analysis, content of the biogenic element Ca is the highest of all the elements. This may be due to the typical beach rock formation. Al in the samples shows the presence of aluminum silicates in the area. Si and K in the samples indicate that they were derived from terrigenous materials and play a role for the beach rock formation. The presence of Ba and V in the samples indicates the possibilities of their bearing minerals in the area. The lithogenic elements Ti and Fe show variable concentration in all the samples. This may be due to the distribution of K-and Plagioclase feldspar as well as clay minerals in the sediment.

Pollution related elemental (Co, Cu & Zn) concentrations are lower in all the samples than the crustal average values. This may due to carbonates generally possess a diluting effect on most metal concentration. The variation of the different trace elements may be due to the nature of weathering processes, and the velocity of transporting media.

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