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Beach Rocks from the South East Coast of Tamilnadu, India: A Spectroscopic Study

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ABSTRACT

Beach rock has only rarely been observed in the coasts. It is a hard costal sedimentary formations consisting of various beach sediments, lithified through the precipitation of carbonate cements. One such formation is noted on the South East Coast of Tamilnadu, India. The objective of this contribution is to collect and review information on reported occurrences, characteristics and formation mechanism of beach rocks and applying the spectroscopic techniques for beach rock formation and evolution. The FT-IR and XRD technique is used to identify the constituent of minerals and cementing materials of the beach rocks. The instrumental neutron activation analysis (INAA) is used to determine the elemental geochemistry of the beach rocks. Results are discussed and the conclusions are drawn. The combined spectroscopic techniques are used to throw light on the nature and cause of cementation.

Keywords: Beach rocks, Mineral Analysis, FT-IR, XRD, Multi-Elemental Analysis, INAA,

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INTRODUCTION

Earth’s crust is made up of various types of rocks.Large areas of the earth are covered with soil. But soil itself is a mixture of tiny rock fragments, decayed organic matter, water and air. Rocks are the largest accumulation of minerals cemented together and hence generally minerals constitute the crust of the earth. Some of the elements of the earth’s crust rarely occur individually in nature, but are generally found in chemical composition with some other elements in the form of compounds. In the earth’s crust the rocks can be classified, in general, into three types, according to their origin viz.,(1) Igneous, (2) Metamorphic and (3) Sedimentary. Igneous rocks are formed by the hardening of magma, i.e., molten masses rising to the surface from the entrails of the earth. Metamorphic rocks are formed from the subjection of pre-existing rocks to intense pressure and temperature, which promotes recrystallization and because of recrystallization new rock is produced with new texture and perhaps also with new mineral composition. The sedimentary rocks originate from detrital material and dissolved mineral matter produced due to decomposition of pre-exciting rocks and also from the degrading remains of plants and animals.

Beach rock comes under the classification of sedimentary rocks.Beach rock, most commonly appearing as layered deposit inclined towards the sea, is a sedimentary formation indurated by the effects of carbonate cement-aragonite or magnesium calcite initially-formed in the intertidal zone. Beach rock or beach sandstone consists of beach sand cemented together by calcium carbonate to form friable to well-cemented rock. 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 favoured the formation of beach rocks. Essential to beach rock development is ground water with enough calcium to provide cementing agent. The occurrence, cementation and formation of the beach rock is outlined below.

1.1. Occurrence

Beach rock is generally limited to tropical and subtropical climates, though not every tropical beach has beach rock [1-3]. Beach rock has also been reported from temperate regions, but such occurrences are rare. For example, Binkley and Wilkinson [4] describe beach rock from Ore Lake, Michigan. Furthermore, there appears to be no connection with rainfall as beach rock has been found in arid (Arabia) and humid (Pacific and Caribbean) regions [4-5]. Beach rock also shows no obvious preference for either a high-or low-energy beach environment [5].

The constituents of beach rock are generally similar to the surrounding unconsolidated beach material [5-9]. The sediment is generally carbonate [7] although beach rock with constituents of volcanic origin has been reported from Hawaii [10-11]. Purely silt-or clay-size beach rocks are not known [3].

1.2. Cementation

Beach deposits along many coasts are cemented with either aragonite or calcite. Cementation is assumed to have occurred in situ or beneath thin sediment cover [8]. Carbonate cement is formed in the intertidal zone of the world's tropical and sub tropical beaches [12]. Cemented beach rock from Mediterranean [6], the Red sea [13], Venezuela[14], and South Africa [15] has been studied and reviewed. Russell [1] reviewed several studies on beach rocks and their cementation.

Lithification of beach rock can occur very rapidly, even within just a few years [5-6, 9, 16-17]. However, the length of time during which precipitation occurs is not known, or whether the cement forms by slow continuous growth at levels of moderate super saturation, or sporadically at times of favorable conditions. Although all beach rocks are cemented by calcium carbonate [7].

Beach rock cements are commonly composed of aragonite or high-magnesian calcite or calcite, which are consistent with carbonate precipitation in a marine or, at least, saline environment.All theories of beach rock formation have one thing in common: cementation must take place within the intertidal zone.

1.3. Formation

Studies of the beach rock from other localities demonstrate that the usual cement in such rock is aragonite, calcite or high magnesium calcite or all of them. The occurrence of beach rock formation is a result of direct precipitation of calcite and/or aragonite from solution within the beach rock. Cementation occurs in two stages; an initial cryptocrystalline high-Mg calcite rim first coats grains, followed by the growth of fibrous carbonate (generally high Mg calcite or aragonite) commonly as isopachous coating around the framework grains. The presence of such cementing agents in most beach rock suggests that the cement was formed in contact with seawater, whereas in fresh water the low concentration of Mg ions favours formation of low Mg calcite [18].

The second possible water controlled driving mechanism of the aragonite-to-calcite transformation which is freshwater-seawater mixing is as follows. The mixing of water is saturated or supersaturated with respect to calcium carbonate at differing CO_2 pressures, temperatures to calcium carbonate and thus promotes dissolution [19-22]. In general, beach rock occurs in tropical and subtropical beaches as layers of cemented beach sediments and occupies a position within intertidal and low supratidal zone.

Based on the above discussion, a detailed examination is required to understand the process of cementation of the beach rocks in the marine environment. The present work aims to identify the cementing material for the beach rock formation using spectroscopic techniques.

MATERIALS AND METHODS

2.1. Sample collection and preparation

Beach rock samples were collected from 15 sampling sites, stretching from Rameshwaram to Kanyakumari along the South East Coast of Tamilnadu (Fig 1). From the sampling sites, approximately 1 kg sample was taken from the same rock and collected in a plastic bag. All the samples were brought to the laboratory, cleaned, weathered surface removed and the remaining fresh materials crushed into small pieces. These samples are powdered using agate mortar and dried for 24 hrs at a temperature of 110°C and then pulverized to particle sizes not greater than 2mm mesh screen.

2.2. FT-IR Analysis:

The major and minor minerals are qualitatively determined by using FT-IR. Sample of 2 mg is mixed with 40 mg of spectroscopic KBr in the ratio 1:20 using a mortar and pestle. The Nicolet Avator 360 series FT-IR at Annamalai University, Annamalainagar, Tamilnadu, India was used. The FT-IR spectra were taken in 4000-400cm^{-1}. The instrument scanned the spectra 16 times in 1 minute and the resolution was 5cm^{-1}. A typical FT-IR spectrum is shown in Fig-2.

2.3. XRD Analysis:

XRD patterns of beach rock powder samples were recorded at room temperature by X-ray diffractrometer (D500, Siemens) having a curved graphite crystal diffracted monochromator, with a source of Cu_Kα ray and NaI(Tl) scintillation detector from Material Chemistry Division, Chemical groups, Indira Gandhi Centre for Atomic Research (IGCAR), Kalpakkam, Tamil Nadu, India. A narrow slit of 0.1mm was used with a scanning speed of 1/2° per minute and time constant of two seconds. The diffraction patterns were obtained over the 2θ values in 20°–80°. A typical XRD spectrum is shown in Fig-3.

2.4. INAA Analysis

2.4.1. Sample irradiation and counting

Irradiations were performed in thermal neutron flux of $10^{11}cm^{-2}\cdot s^{-1}$ using pneumatic transport facility of **KAMINI** research reactor, Indria Gandhi Centre for Atomic Research (IGCAR), Kalpakkam, Tamilnadu, India. With a view to assay the short and long-lived radionuclides, two sets of irradiation, 5 min and 5 h were performed. The samples of 5-min irradiation were counted for 100 to 300s after 10-min cooling for the determination of ^{28}Al, ^{27}Mg, ^{49}Ca, ^{51}Ti and ^{52}V and a cooling of 200-300 min for analyzing ^{165}Dy, ^{56}Mn and ^{24}Na. The samples of 5-h irradiations to determine the medium and long-lived radionuclides (^{42}K, ^{51}Cr, ^{59}Fe, ^{60}Co, ^{95}Zr, ^{140}La, ^{141}Ce, ^{152}Eu ^{153}Sm, ^{175}Yb and ^{181}Hf) were counted for 10,000-30,000 s after a cooling time of 2, 4 to7 and 35 to 50 days.

2.4.2. Radioactive assay

After irradiation the polypropylene tubes containing the sample and the gold as the standard for quantitative analysis were washed under running water, wiped and mounted on standard Perspex plates. Samples were assayed for γ-activity of the activation products using an 80 cm^3 HPGe detector coupled to a PC based 4K analyzer in an efficiency calibrated position with reproducible sample to detector geometry. The sample to detector distance was maintained at 12-15 cm depending upon the level of activity to avoid true coincidences effects. The detector system had a resolution of 1.8 keV at 1332 keV. The activities of radionuclides were considered as a function of time to ensure purity and identity. Gamma-ray standard of ^{152}Eu was used for efficiency calibration of the detector, at different distances between the sample and detector in a stable source to detector geometry.

2.4.3. Calculations

Peak areas corresponding to different photo peaks, after subtracting the linear Compton background, were converted to specific count rate (A_{sp}) by $Asp=P_A/SDCW$, where P_A=peak area, S=saturation factor, C=counting correction, D=decay correction, and W=weight of the sample.

The concentration of the ith element (in µg/g) was calculated by Conc=$[A_{sp}/(A^*_{sp}K_{anal})]$, where A_{sp}=specific count rate corrected per gram of the sample, A^*sp=specific count rate of ^{198}Au, and $K_{anal} = K_0\ [(f+Q_0\ (\alpha))/(f+{}^*Q\ (\alpha))]\cdot(\xi/\xi^*)$, where ξ is the detection efficiency of the detector for the γ-ray energy used, f is the sub-cadmium to epi-cadmium neutron flux ratio, and $Q_0(\alpha)$ is the ratio of cross sections and is equal to $I_0(\alpha)/\sigma_{th}$, where $I_0(\alpha)$ is the infinitely dilute resonance integral corrected for the non-ideal epithermal neutron flux distribution. Validation for the experimental setup was done by irradiating the Standard Reference Material (SRM 1646a estuarine sediment) for the same period of time with comparator and the sample in the same location of the reactor (Table-1). The SRM analysis agreed well with the certified values.

RESULTS AND DISCUSSION

3.1. FT-IR Analysis

The i.r.absorption peaks were compared (Table 2) with available literature, the minerals identified as quartz, orthoclase, albite, kaolinite, montmorllinite, illite, calcite, aragonite, dolomite, ilmenite and rutile [23-25].. The large number peaks of calcite in the i.r. spectrum indicate the abundance of calcite in the samples and it may be due to the typical beach rock formation. Beach deposits along many coasts were cemented with either aragonite or calcite because some of these “beach rock” derive their cement from seawater. Seawater is several times supersaturated with respect to calcite and aragonite and also it is the source of the cementing agent calcium carbonate

3.2. XRD analysis

Qualitative mineralogy of the beach rock samples was determined with the standard interpretation procedures of XRD. Quartz, albite, orthoclase, kaolinite, calcite, aragonite, ilmenite, rutile and almandine garnet were identified from the peaks in diffractrogram. Major minerals in the samples are quartz and calcite. The presence of heavy minerals (ilmenite, garnet, rutile etc.) may be the contribution from the hinterland geology, laterization of gneissose rocks, occurrence of small streams and categorization by waves and tides.

The qualitative identification of the minerals in beach rock samples was carried out by using FT-IR and XRD techniques. The combined techniques reveal the presence of minerals such as quartz, orthoclase, albite, kaolinte and montmorlinte in the samples. Beach rock is mostly composed of marine shell fragments (e.g., molluscs, coralline algae, foraminifera) and terrigenous detritus (e.g., quartz and feldspar). The presence of quartz and feldspar in our study indicates that they also play a role for the cementation of beach rock samples.

From the IR and XRD spectra of the samples, the peaks indicating the abundance of minerals such as carbonate groups calcite and aragonite occupy large portion of total peak areas. The high abundance of calcite in the samples was due to the typical beach rock formation. This is may be due to the beach deposits along many coasts were cemented with either aragonite or calcite because some of these “beach rock” derive their cement from seawater. Seawater is several times supersaturated with respect to calcite and aragonite and also it is the source of the cementing agent calcium carbonate. The bulk mineralogy of beach rock samples from the IR and XRD studies reveals that calcite, aragonite and slightly lesser extent quartz are the dominant minerals. A similar mineralogical composition characterizes the beach rocks of other locality.

3.3. INAA Analysis:

The elemental contents in the beach rock samples are reported in Table 3. The calcium is the highest of all the elements in almost all the samples. This is due to high abundance of calcium carbonate in tropical and subtropical areas of ocean [26] and also typical beach rock formation [9] .The highest Al content at S_{13} indicates the higher degree of weathering and reflects the degree of influence of sediment, whereas the lowest Al content at S_1 implies the finer nature of sediment containing clay minerals and iron oxides [27].

The variation in the distribution of Ca, Mg, Na and K in some locations may be mainly controlled by clay minerals in the study area. Nelson [28] has pointed out that in the processes of ion exchange, the common ions inherited from soil environment (Ca^{2+} and H^+) by the absorption in surface particles are replaced by most abundant ions (Na^+ and Mg^+)^6. The net reaction between fluvial clays and seawater is primarily an exchange of seawater Na for bound Ca^+. The higher Na and Mg concentrations at S_{13} may be due to the low Ca content in the marginal environment such as tidal channel and, swamps can also be attributed to the above replacement of Ca by other ions [29].

Table-1 Analysis of standard Reference Material by INAA

Elements	Measured Value	Certified Value
Al %	2.40 ± 0.7	2.30 ± 0.2
Ca %	0.53 ±0.4	0.52 ± 0.6
K %	0.89 ± 0.7	0.86 ± 0.8
Fe %	2.17 ± 1.4	2.08 ± 1.2
Na %	0.78 ± 0.8	0.74 ± 0.9
Ti %	0.47 ± 0.7	0.46 ± 0.6
V	43.94 ± 0.2	44.84 ± 0.4
Mn	231.33 ± 1.2	234.50 ± 1.6
As	6.26 ± 0.17	6.23 ± ± 0.15
Cr	41.3 ± 0.6	40.90 ± 0.8
Ce	34.51 ± 0.7	34 ± 0.2
Co	5.6 ± 0.2	5 ± 0.3
La	20 ± 1.6	17 ± 1.2

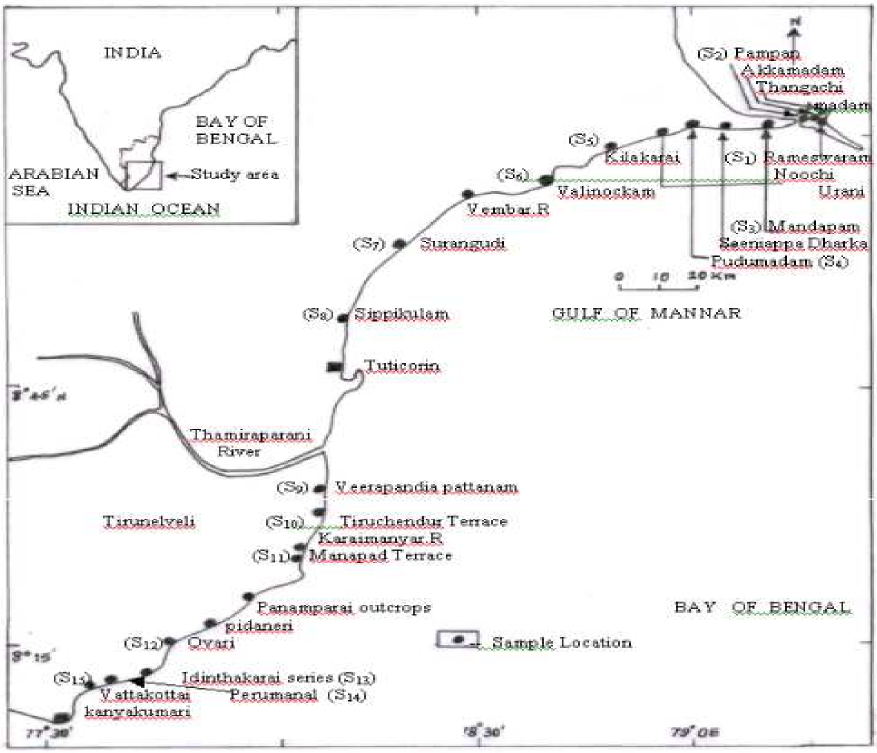

Fig.1.Location Map

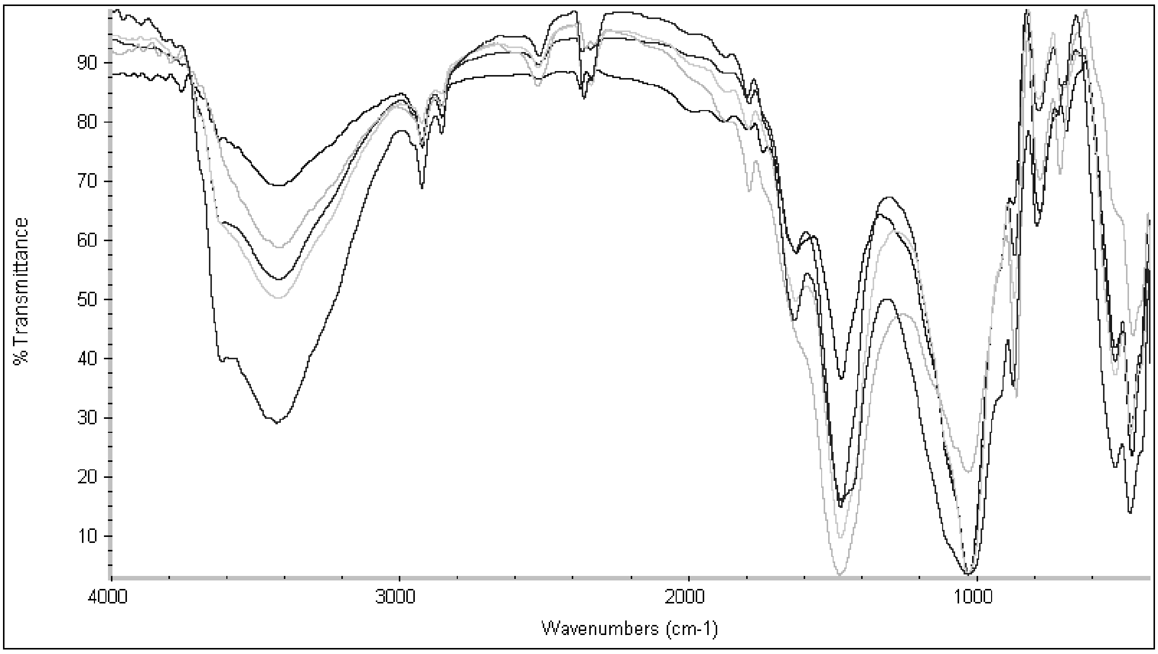

Fig.2. A typical FT-IR spectrum of Beach rocks of South East Coast of Tamilnadu

The presence of Fe, Ti, Cr, Mn and V were indicates the minerals such as ilmenite, rutile and chromite present in the samples as well as the study area. This may be due to heavy minerals present in the samples and also in sediments [30].The low concentration of Co in the present study shows that its mobility is reduced in the carbonate dominant environment [31].The presence of Zr and Hf in the study indicates the possibility of heavy minerals present in the sediment. In beach rock samples, the contents of REEs follow the order Ce>La>Sm>Yb. This is consistent with average abundance in the earth's crust.

The variation of the different trace elements in the present study may be due to the nature of weathering processes, and the velocity of transporting media. The total trace elements concentrations 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.

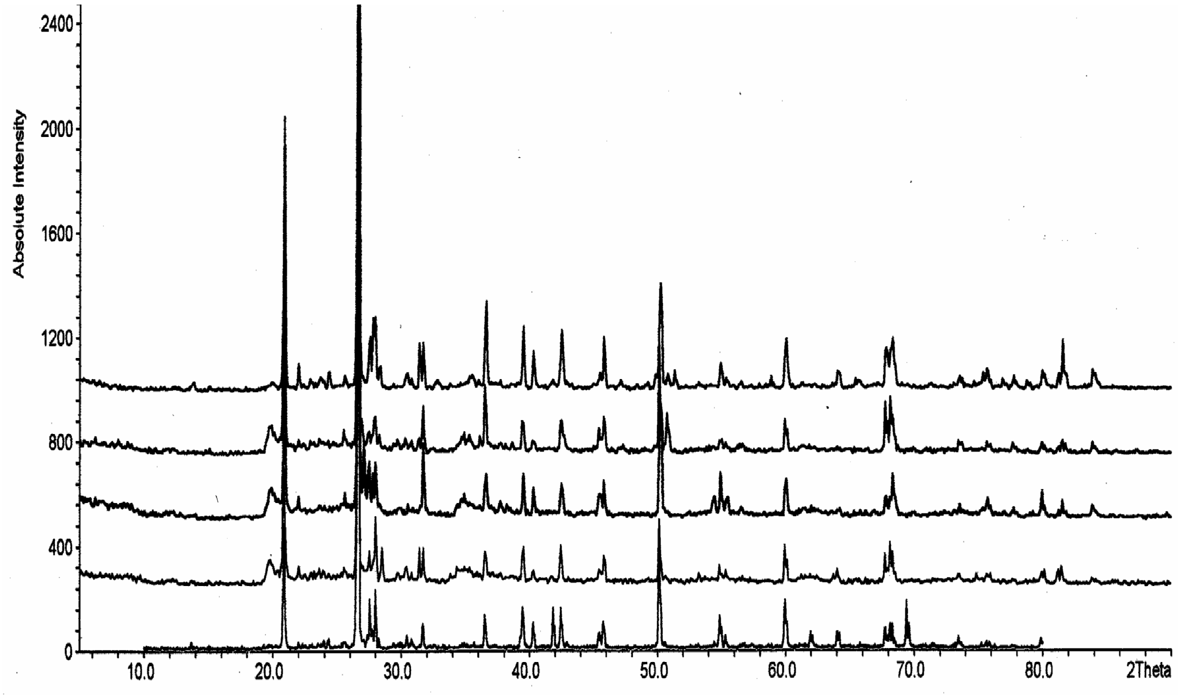

Fig.3. A typical X-ray diffractrogram of Beach rock of South East Coast of Tamilnadu

Table 2: Observed Absorption Frequency in the region of 400 – 4000 cm^{-1}

Sample No	**Quartz**	**Feldspar**		**Clay Mineral**			**Carbonate Minerals**		
		Orthoclase	**Albite**	**Kaoilinite**	**Montomorilinte**	**Iltite**	**Calcite**	**Aragonite**	**Dolomite**
S1	1160, 455, 775, 795	435, 540	405	1035, 3660	3440	-	715, 875, 1425, 1800, 2515	1080, 1475	-
S3	455, 775, 795	435	406, 585	1035, 3620	475, 3440	915	715, 875, 1800, 2515	855, 1080	-
S5	457, 695, 775	435, 540	405,	1035	475, 3445	915	715, 875, 1795,2515	855, 1080, 1475, 1785	2525
S7	456, 775, 795	435, 540	405, 585	1035, 3690	3445	-	715, 875, 1425, 2515, 2875	1080, 1475	-
S9	455, 775	435, 540	405	1035	3445	915	715, 875, 2515	855, 1080, 1475, 1785	-
S11	457, 695, 775, 795	435, 540	405	1035, 3690	3445	915	715, 875, 1425, 1800, 2515, 2875, 2875	855, 1080	2525
S13	455, 795	435	405, 585	1035, 3660,	475	-	715, 875, 1425, 1795	855, 1080, 1475, 1785	2525
S15	695, 775	435, 540	405, 585	1040, 3660, 3690	3445	-	715, 875, 1425, 1800, 2515, 2875	1085, 1785	2525

Table 3 Elemental concentration of Beach rock samples of South East Coast of Tamilnadu (in ppm unless % indicated)

Elements	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}	S_{11}	S_{12}	S_{13}	S_{14}	S_{15}
Al %	0.15	1.2	1.3	2.4	0.61	3.18	2.03	2.33	1.43	2.25	1.68	2.23	7.73	0.72	3.42
Mg %	0.70	0.88	3.04	1.13	2.63	1.32	2.55	3.20	2.20	2.27	0.73	1.22	3.21	0.70	2.48
Na %	0.42	0.57	0.43	0.52	0.39	0.85	0.59	0.15	0.51	0.44	0.43	0.96	1.79	0.22	0.52
Ca %	15.83	22.44	17.99	24.28	18.53	15.31	18.14	12.18	14.24	23.59	24.69	18.22	10.87	20.52	4.43
Ti %	0.07	1.20	0.49	ND	0.04	0.34	0.12	7.04	0.06	ND	0.52	0.38	0.30	0.16	15.66
Fe %	0.81	2.37	2.48	0.29	0.33	1.39	0.67	15.83	0.44	0.61	0.73	1.13	5.45	0.51	23.12
Co	3.91	7.07	9.58	2.99	4.99	9.06	5.5	30	7.2	2.78	3.57	3.26	14.83	6.64	45.85
Cr	14.94	26.1	53.95	ND	21.75	36.31	102.84	187	29.48	55.58	38.28	25.95	97.2	54.39	304
V	4.76	62.6	37.82	5.66	5.87	20.25	13.31	416.2	15.68	72.45	30.97	27.98	62.87	11.87	631.9
Hf	5.21	17.24	26	2.24	3.81	14.78	9.14	56.28	5.63	6.88	45.43	20.25	14.73	4.56	101.4
Zr	ND	ND	2348	ND	ND	ND	1612.24	2662	ND	1087	1990	1525	1532	1027	4692
Mn	167.5	407.5	385.9	215.5	146.9	686.5	226.36	2809	778.84	499.4	114.1	139.8	580.3	432.2	2514
La	101.0	78.58	27.14	16.05	9.49	38.22	16.58	140	10.06	25.14	121.1	131.5	56.80	29.94	678.0
Ce	18.14	137.7	37.32	29.17	16.57	87.29	57.87	221.9	19.48	77.22	225.3	247	86.43	51.29	1288
Sm	1.10	5.62	2.49	1.64	1.05	3.08	1.22	11.05	0.95	3.80	11.06	12.33	4.07	2.43	60.36
Eu	0.49	1.06	2.21	0.74	0.80	2	0.96	2.85	0.84	0.68	1.35	1.34	2.56	0.55	5.69
Tb	0.30	0.99	0.41	0.18	0.16	0.74	0.22	1.25	0.45	0.67	0.98	1.25	2.80	0.6	7.21
Yb	0.44	0.19	0.65	0.41	0.22	0.824	0.49	2.61	0.56	0.89	1.35	2.81	4.79	1.08	14.08

S_1-Rameswararm, S_2-Pampan, S_3-Mandapam, S_4-Pudumadam, S_5-Kilakarai, S_6-Valinockam, S_7-Surangudi, S_8-Sippikulam, S_9-Veerapandia Pattanam, S_{10}-Tiruchendur, S_{11}-Manapad, S_{12}-Ovari, S_{13}-Idinthakarai, S_{14}-Perumnal,S_{15}-Kanyakumari. ND-Not Determined

CONCLUSION

Beach rock formation is a special type of formation when compared to other types of formation.The detailed examination of cementing material in beach rock is analysed by the spectroscopic techniques. The qualitative identification of the minerals in beach rock samples was carried out by using FT-IR and XRD technique. Among the minerals identified by these techniques, calcite was the most abundant mineral. The presence of calcite indicates directly that they are the constituents of the cementation mineral in beach rock samples. The elemental distribution in the beach rock samples was determined by using instrumental neutron activation analysis (INAA). From the elemental analysis, calcium was more abundant than other elements and also it exhibited the highest concentration in almost all locations. This is due to the typical beach rock formation.

From the analysis, the beach rocks may derive the cement from seawater. Seawater is several times supersaturated with respect to calcite and aragonite and also it is the source of cementing agent calcium carbonate. Many workers reported that calcium carbonate is the cementing materials for beach rock formation and it supports the statement. The combined use of mineralogical and multi-elemental analysis is an adequate methodology to identify the source of cementing material for the beach rock formation. This study demonstrates the feasibility of spectroscopic techniques for the analysis of beach rock samples and it is proven that these techniques can be used for environmental matrix.

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REFERENCES

[1].R.J.Russell, *Zeit.fur Geo*, 6(1) **(1962),** 1-6.
[2].R.J.Russell, *J.Trop.Geo*, 17 **(1963),** 24-27.
[3].T.P.Scoffin and D.R.Stoddart, Chemical Sediments and Geomorphology,London: Academic Press, Inc, **(1983),** p.401-425.
[4].K.L.Binkley, and B.H.Wilkinson, *J.Sed.Petro,* 50 **(1980),** 953.
[5].O.P.Bricker,Carbonate Cements.,Baltimore, Johns Hopkins Press,**(1971a),** p.1.
[6].T.Alexandersson, The Mediterranean Sea: A Natural Sedimentation Laboratory, **(1972),** p.203-223.
[7].J.J.Scholten, *Zentralblatt fur Geologie and Palaontologie Teil,* 19 **(1972),** 351.
[8].J.D.Milliman, Berlin: Springer-Verlag**,(1974),** p. 375.
[9].M.K.H.El-Sayed,*Mar.Geo.*,80 **(1988)**, 29-35.
[10].K.O.Emery and D.C.Cox, *Pacific Science.*,10 **(1956),** 382.
[11].J.H.J.Meyers,*Sed. Petro.,* 57**(1987)** 558.
[12].D.R.Stoddart and J.R.Cann, *J.Sed.Petro.,* 35 **(1965),** 243.

[13].G.M.Friedman and E.Gavish, Carbonate Cements. Baltimore, Johns Hopkins Press, **(1971),** p.13.
[14].I.Reuber and L.Ellenberg, *Acta.Cient.Venez.*, 30 **(1979),** 462.
[15].J.H.Barwis and A.Tankard, *J.Sed.Petro.*, 53 **(1983),** 1281.
[16].J.S.Hanor, *J. Sed. Petro.*, 48 **(1978)** 489.
[17].A.Strasser, E.Davaud, and Y.Jedoui, *Sed.Geo.*, 62 **(1989),** 89.
[18].H.Holail, and R.Rashed, *Mar.Geo.*, 106 **(1992),** 141.
[19].J.Thrailkill, *Geo.Soc.Am.Bull.*, 79 **(1968),** 19.
[20].D.D.Runnels, *J. Sed. Petro.*, 39 **(1969),** 1188.
[21].L.N.Plummer, *Geo. Soc. Am. Mem.*, 142 **(1975),** 219.
[22].T.M.LWigley, and L.N.Plummer, *Geochimica et Cosmochimica Acta*, 46 **(1976)**, 989.
[23].R.Ravisankar,S.Kiruba,A.Chandrasekaran,G.Senthilkumar and C.Maheswaran, *Indian Journal of Science and Technology*, 3(8) **(2010),** 858-862.
[24].R.Ravisankar,S.Kiruba,A.Chandrasekaran,A.Naseerutheen,M.Seran andP.D.Balajai,*Indian Journal of Science and Technology*, 3(9) **(2010),** 1016-1019.
[25].R.Ravisankar,S.Kiruba, A.Naseerutheen, A.Chandrasekaran, and C.Maheswaran, *Der Chemica Acta*, 2(1) **(2011),** 157.
[26].E.Shumilin, S.T.Kalmykov, D.Sapozhnikov, E.Nava-Sanchez, D.Holguin-Quinones Gorsline,L.Godinez-Orta,Yu.Sapozhnikor,andA.Rodriguez-Castaneda, *J.Radioanal.Nucl.Chem.*, 246 **(2000),** 533.
[27].L.Rosales-Hoz, A.Carranza-Edwards and M.Lopez-Hernendez, *Env.Geo.*, 39 **(2000),** 378.
[28].B.W.Nelson, Occasional Publication, University of Rhode Island, 1**(1962),** 27.
[29].P.Seralathan and A.Seetaramaswamy,*Ind.J.Mar.Sci.*, 16 **(1987),** 31.
[30].V.Subramanian ,L.Van Tadack ,Vangrieken, *Chem.Geo*,48 ***(1985),*** 271.
[31].S.Naseem, Shamim Ahmed Sheikh, Qadeeruddin and Khaula Shirin, *J. Geochem.Explo.*, 76 **(2002),** 1.