

Instrumental neutron activation analysis of beachrock samples of South East Coast of Tamilnadu, India

R.RAVISANKAR^{1*} P.ESWARAN² N.P.SESHADERSSAN³ Bramaji RAO³

(¹ Department of Physics, Sri Siva Subramania Nadar College of Engineering, Kalvakkam, Chennai – 603110, Tamilnadu, India;

² Department of Physics, SMK Fomra Institute of Technology, Thaiyur, Chennai- 603 103, Tamilnadu, India;

³ Nuclear Chemistry Section, Chemistry Groups, Indira Gandhi Centre for Atomic Research (IGCAR), Kalpakkam-603 102, Tamilnadu, India)

Abstract Element profiles of some beach rock samples collected from South East Coast of Tamilnadu, India have been determined using single comparator method of INAA. The geo-chemical behavior of the elements in the region is discussed. The irradiations were done at thermal neutron flux of $\sim 10^{11} \text{ cm}^{-2}\cdot\text{s}^{-1}$ at 20kW power using Kalpakkam Mini Reactor (KAMINI), IGCAR, Kalpakkam, Tamilnadu, India. Around 19 elements have been determined from 15 samples by high-resolution gamma spectrometry. The accuracy and precision were evaluated by assaying the irradiated Standard Reference Material (SRM 1646a Estuarine sediment) and were found to be in good agreement with certified values.

Key words Beach rock, Analysis, Instrumental neutron activation analysis, KAMANI Reactor

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1 Introduction

Geochemical composition of sedimentary rocks has been widely used in recent years to determine the composition of source area to evaluate weathering processes and to quantify the secondary processes such as sorting and diagnosis, to reconstruct tectonic setting of depositional basin and to evaluate the composition evolution of continental crust. Geochemical approaches have been considered to be more advantageous because a) they are equally applicable to coarse and fine grained sedimentary rocks, in contrast to petrographical approaches that are difficult to use in case of fine or very coarse sedimentary rocks, b) they can be applied even to mineralogical altered rocks where bulk chemistry has not been substantially affected, and c) they can be used to evaluate the evolution of source areas during pre-depositional period^[1]. In this regard, the beach rock samples were collected to study the elemental distribution by instrumental neutron activation analysis (INAA) and to infer the provenance of its sedimentary formation and also the geochemical be-

havior of the elements of interest are discussed.

The beach rock formations are found in many places in the world. One such beach rock formation is found in the South East Coast of Tamilnadu in India^[2]. Beach rock is commonly found along the tropical and subtropical coasts^[3-5]. Beach rock, most commonly appearing as a layer deposit inclined towards the sea, is a sedimentary formation indurated by the effects of carbonate cement-aragonite-or magnesium calcite initially formed in the layer in the intertidal zone. Beach rock also acts as a resistant barrier to erosion, thus affecting the rate of erosion and overall development. However, beach rock can be quite useful in describing and delineating environments of deposition.

A number of modern, non-destructive techniques which are rapid, highly sensitive and require small amounts of samples, have been commonly used for elemental analysis; electron scattering for chemical analysis (ESCA), X-ray fluorescence (XRF) and instrumental neutron activation analysis (INAA). INAA has many advantages over the other methods of ele-

* Corresponding author. Email: ravissn@gmail.com, ravi@ssnce.ac.in

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mental analysis. It differs from most other methods of chemical analysis in that it depends on the properties of the nuclides, rather than behavior of outer shell electrons of the atom. Moreover, full chemical separation, which is required in conventional chemical methods, can be left out in the activation method.

Instrumental activation analysis is being extensively used as an analytical tool in various fields such as environment, biology, geology and cosmology [6-10]. It provides precise and accurate results with high sensitivity and selectivity for a large number of elements in the periodic table and thus becomes most attractive for multi-element profile. INAA being non-destructive, samples need not be taken in solutions. Thus it provides a relative freedom from analytical blanks. The determination of trace elements in sediments and rocks has been carried out accurately by INAA [11-15]. INAA has been widely used for the determination of REE, in geological samples due to their nuclear characteristics particularly to neutron activation [16,17]. The advent of high-resolution gamma-ray spectrometry using HPGe detectors has increased the potential of this technique. The K_0 method is a versatile tool for multi-element analysis and easy to adopt [18]. In the K_0 NAA method a mono-standard (gold) and samples are irradiated together. The ratio of the induced specific activities of the nuclides in the sample to those in the comparator is multiplied by the predetermined composite constant consisting nuclear constants specific to each nuclide, reactor location parameter and detector efficiencies to arrive at the concentration of the elements present in the sample. In the present study an attempt has been made to study the elemental distribution in beach rock samples by INAA.

2 Experimental

2.1 Sample collection and preparation

The beach rock samples were collected from 15 sampling sites stretching from Rameshwaram to Kanyakumari of South East Coast of Tamilnadu covering around 360 km (Fig.1). Approximately 1 kg of bulk of each rock samples was sampled in a plastic bag from each location. All the samples were brought to the laboratory cleaned, weathered surface removed and the remaining fresh materials crushed into small pieces. These samples were powdered using agate

mortar and dried for 24 h at a temperature of 110°C and then pulverized to particle not greater than 2 mm mesh screen.

2.2 Sample irradiation and counting

Irradiations were performed in thermal neutron flux of $10^{11}\text{cm}^{-2}\cdot\text{s}^{-1}$ using pneumatic transport facility of KAMINI research reactor, Kalpakkam. With a view to assay the short and long-lived radionuclides, two sets of irradiation, 5 min and 5 h, were performed. In the case of short irradiation of 5 min, the samples were counted for 100 to 300s for about 30 min after a decay period of 10 min for the determination of ^{28}Al , ^{27}Mg , ^{49}Ca , ^{51}Ti and ^{52}V . Other short-lived nuclides like ^{165}Dy , ^{56}Mn and ^{24}Na were determined after an interval of 200-300 min.

The other set of the irradiations were done for a period of 5 h in the same location of the reactor 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). They were counted for 10,000-30,000 s after a cooling time of 2, 4 to 7 and 35 to 50 days. Data acquisition in all these cases was done using a PC based MCA, coupled to a vertical HPGe detector system.

2.3 Radioactive assay

After irradiation the polythene covers were removed and the polypropylene tubes containing the sample and the gold 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 cm³ 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.

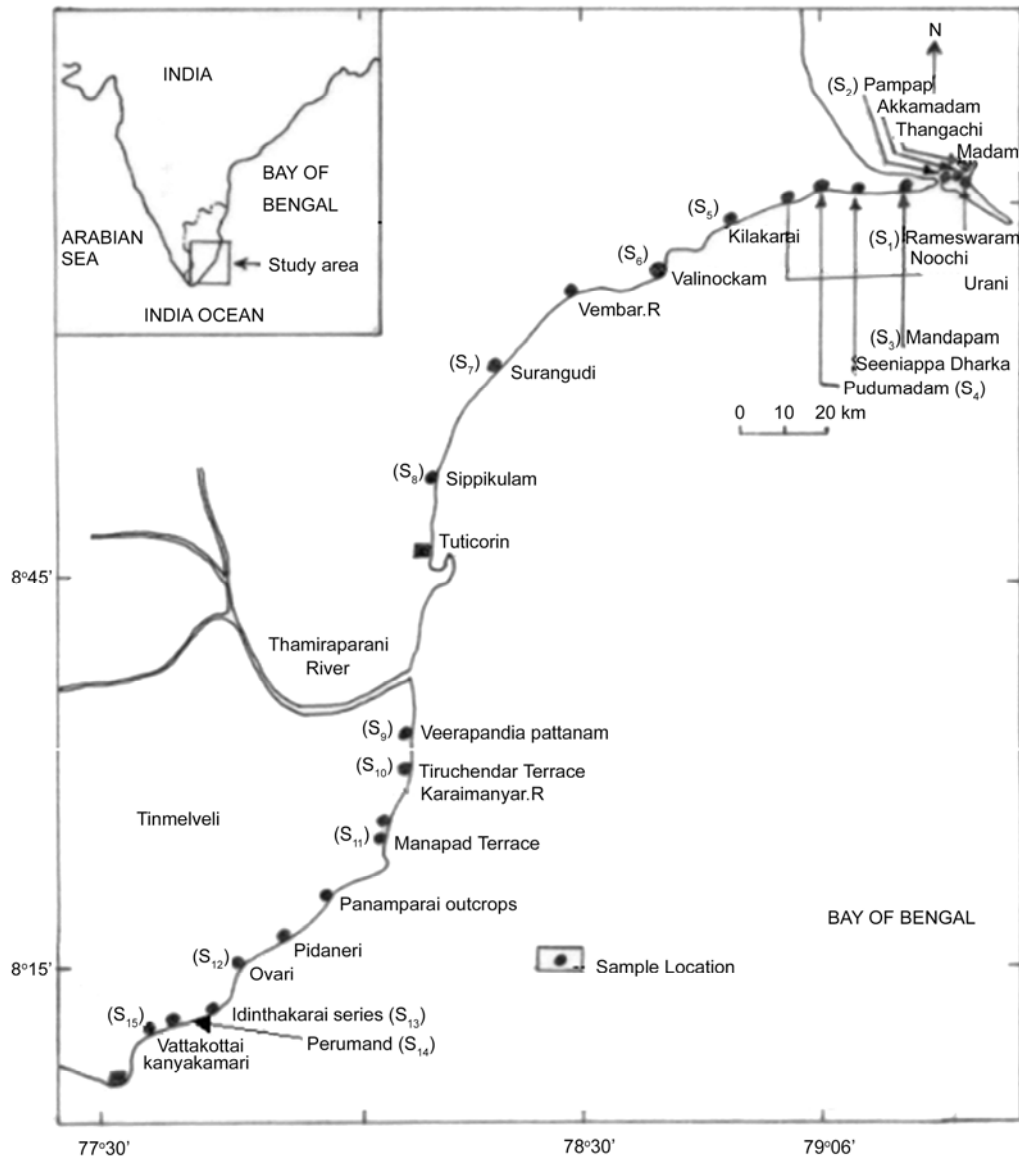


Fig.1 Sample location map.

2.4 Calculations

Peak areas corresponding to different photopeaks were calculated by summing the counts under the peak and subtracting the linear Compton background. The peak areas were converted to specific count rate (A_{sp}) by the equation:

$$A_{sp} = P_A / (SDCW)$$

where P_A =peak area, S =saturation factor, C =counting correction, D =decay correction, and W =weight of the sample.

The concentration of the i -th element (in 10^{-6}) was calculated using the relation

$$\text{Conc. (in } 10^{-6}) = A_{sp} / (A_{sp}^* \cdot K_{anal})$$

where A_{sp} =specific count rate corrected per gram of the sample, A_{sp}^* =specific count rate of the comparator (^{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 of the technique for the experimental setup has been 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. Analysis of the

Standard Reference Material in Table 1 shows a good agreement of measured values with the certified ones.

Table 1 Analysis of standard reference material (SRM 1646a Estuarine sediment) by INAA (in 10^{-6} unless % indicated)

Elements	Measured value	Certified value
Al %	$2.40 \pm 0.7^*$	2.30 ± 0.2
Ca %	0.53 ± 0.4	0.52 ± 0.2
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

* Standard deviation

Table 2 Elemental concentration of beach rock samples (in 10^{-6} unless % is indicated) from South East Coast of Tamilnadu, India*

Elements	S ₁ **	S ₂	S ₃	S ₄	S ₅	S ₆	S ₇	S ₈
Al %	0.15(9.4)	1.2(13.4)	1.3(11.7)	22.5(4.2)	0.61(1.5)	3.18(9.5)	2.03(8.7)	2.33(10.7)
Ca %	15.83(2.9)	22.44(4.9)	17.99(6.1)	24.28(4.9)	18.53(1.7)	15.31(4.9)	18.14(4.5)	12.18(4.9)
Mg %	0.70(5.6)	0.88(13.2)	3.04(2.7)	1.13(33.87)	2.63(17)	1.32(13.3)	2.55(30.8)	3.20(11.6)
Na %	0.42(0.4)	0.57(3.6)	0.43(2.9)	0.52(1.4)	0.39(3.2)	0.85(3.6)	0.59(2.3)	0.15(8.1)
K %	0.46(3.5)	0.69(10.1)	0.71(4.4)	ND	0.79(3.4)	1.89(11.9)	1.22(15.3)	ND
Ti %	0.07(10.9)	1.20(2.8)	0.49(21.6)	ND	0.04(9.8)	0.34(10.2)	0.12(16.8)	7.04(5.2)
Fe %	0.81(0.9)	2.37(5.9)	2.48(2.7)	0.29(9.9)	0.33(1.5)	1.39(0.8)	0.67(0.03)	15.83(0.82)
Co	3.91(15.3)	7.07(10.5)	9.58(16.1)	2.99(22.2)	4.99(10)	9.06(1.9)	5.5(6.5)	30(0.4)
Cr	14.94(2.1)	26.1(5.7)	53.95(8.8)	ND	21.75	36.31	102.84	187.04(3.9)
V	4.76(5.7)	62.66(18.3)	37.82(3.1)	5.66(9.2)	5.87(11.5)	28.25(14.4)	13.31(9.9)	416.28(11.4)
Mn	167.55(2.8)	407.50(8.2)	385.91(3.8)	215.55(3.5)	146.99(99.8)	686.55(3.5)	226.36(4.5)	2809.02(4.8)
Hf	5.21(5.9)	17.24(6.5)	26.0(11.8)	2.24(14.2)	3.81(2.9)	14.78(4.1)	9.14(14.1)	56.28(0.8)
Zr	ND	ND	2348.64(16.6)	ND	ND	ND	1612.24	2662.31(13.7)
La	101.03(0.1)	78.58(1.9)	27.14(0.2)	16.05(0.1)	9.49(0.3)	38.22(1.2)	16.58(1.4)	140.01(0.09)
Ce	18.14(3.1)	137.7(6.8)	37.32(16.8)	29.17(10.7)	16.57	87.29(8.5)	57.87(2.2)	221.92(4.9)
Sm	1.10(0.8)	5.62(2.7)	2.49(26.9)	1.64(1.3)	1.05(27.3)	3.08(2.2)	1.22(20.5)	11.05(3.4)
Eu	0.49(4.7)	1.06(5.8)	2.21	0.74	0.80	2.00(1.2)	0.96	2.85(2.4)
Tb	0.30	0.99	0.41	0.18	0.16	0.74	0.22	1.25
Yb	0.44(2.3)	0.19	0.65(5.1)	0.41	0.22	0.82	0.49-	2.61(3.9)

Elements	S ₉	S ₁₀	S ₁₁	S ₁₂	S ₁₃	S ₁₄	S ₁₅	Average
Al %	1.43(12.5)	2.25(2.7)	1.68(2.3)	2.23(11.3)	7.73(0.7)	0.72(13.3)	3.42(9.4)	3.52
Ca %	14.24(6.8)	23.59(1.9)	24.69(2.1)	18.22(5.9)	10.87(6.3)	20.52(3.9)	4.43(2.9)	17.42
Mg %	2.20(8.5)	2.27(10.6)	0.73(15.4)	1.22(9.7)	3.21(10.9)	0.70(15.3)	2.48(5.6)	2.15
Na %	0.51(3.3)	0.44(3.2)	0.43(2.3)	0.96(2.1)	1.79(12.2)	0.22(4.5)	0.52(0.4)	0.59
K %	1.04(12.4)	1.06(13.7)	0.52(8.8)	1.44(27.9)	4.61(8.0)	0.43	0.66(3.5)	1.19

* To be continued in next page.

3 Results and discussions

The concentrations of some elements in beach rock samples of South East Coast of Tamilnadu from 15 sampling sites are reported in Table 2. The samples were identified as S₁, S₂,...,S₁₅ in the order of sampling locations. From the table it is seen that calcium is present at higher levels than the other elements in almost all the samples. This is due to the high abundance of calcium carbonate in tropical and subtropical areas of ocean [19] and also typical beach rock formation [20].

The lowest and highest concentration of Al is recorded at S₁ and S₄ respectively. The highest concentration of Al at S₄ indicates the higher degree of weathering and reflects the degree of influence of sediment, whereas the lowest concentration at S₁ implies the finer nature of sediment containing clay minerals and iron oxides [21].

Table 2 (continued)

Elements	S ₉	S ₁₀	S ₁₁	S ₁₂	S ₁₃	S ₁₄	S ₁₅	Average
Ti %	0.06(23.2)	ND	0.52(4.1)	0.38(10.7)	0.30(7.6)	0.16(13.47)	15.66(10.9)	2.03
Fe %	0.44(11.9)	0.61(0.8)	0.73(7.5)	1.13(12.3)	5.45(3.8)	0.51(3.7)	23.12(0.9)	3.74
Co	7.2(3.5)	2.78(1.1)	3.57(4.9)	3.26(3.7)	14.83(5.5)	6.64(6.5)	45.85(15.3)	10.48
Cr	29.48(2.8)	55.58(6.2)	38.25	25.95(10.5)	97.2(6.1)	54.392(10.9)	304.53(2.1)	74.88
V	15.68(18.9)	72.45(7.9)	30.97(10.6)	27.98(9.6)	62.87(12.5)	11.87(7.5)	631.90(5.7)	101.60
Mn	778.84(3.5)	499.41(7.7)	114.17(5.6)	139.89(4.9)	580.33(4.1)	432.21(3.9)	2514(2.8)	673.62
Hf	5.63(1.5)	6.88(4.2)	45.43(8.1)	20.25(9.8)	14.73(0.4)	4.56(9.8)	101.43(5.9)	22.24
Zr	ND	1087.3(3.7)	1990	1525.08(5.3)	1532.57	1027.14	4692.86(7.7)	2053.13
La	10.06(10.9)	25.14(1.0)	121.13(1.2)	131.57(2.4)	56.80(2.9)	29.94(0.6)	678.03(0.1)	98.48
Ce	19.48(10.0)	77.22(1.7)	225.34(4.6)	247(8.9)	86.43(6.9)	51.29(16.1)	1288.33(3.1)	173.40
Sm	0.95	3.80(5.0)	11.06(2.2)	12.33(1.7)	4.07(2.4)	2.43(2.8)	60.36(0.8)	8.15
Eu	0.84-	0.68(9.6)	1.35(5.4)	1.34(8.1)	2.56(2.1)	0.55	5.69(4.7)	1.61
Tb	0.45	0.67	0.98	1.25	2.80	0.60	7.21	1.21
Yb	0.56	0.89	1.35	2.81	4.79(7.8)	1.08	14.08(2.3)	2.09

**S₁-Rameswaram, S₂-Pampan, S₃-Mandapam, S₄-Pudumadam, S₅-Kilakarai, S₆-Valinockam, S₇-Surangudi, S₈-Sippikulam, S₉-Veerapandia Pattanam, S₁₀-Tiruchendur, S₁₁-Manapad, S₁₂-Ovari, S₁₃-Idinthakarai, S₁₄-Perumnal, S₁₅-Kanyakumari.

ND-Not Determined. Figures in parenthesis: Relative Standard Deviation (RSD).

The higher concentrations of Na, K are recorded at S₁₃. This may be due to the extraction of sodium from rock during weathering, its absolute amount decreasing in the hydrolyzate sediments, whereas potassium first goes into solution but does not remain dissolved thus absorbed by the clay content [22]. The difference in the behavior of sodium and potassium during the weathering is due to the greater resistance of potash feldspar as compared with that of plagioclase feldspar [23].

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 [24] has pointed out that in the processes of ion exchange, the common ions inherited from soil environment (Ca²⁺ 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 concentrations of Na and Mg are found in the location at S₁₃. This may be due to the low content of Ca in the marginal environment such as tidal channel and, swamps can also be attributed to the above replacement of Ca by other ions [25].

The lowest and highest concentration of Fe, Ti, Cr, Mn and V were recorded for S₄, S₅, S₁₁, S₁ and S₁₅ respectively. The higher concentration of these elements may be due to the environment of Ti, V and Cr in minerals such as ilmenite, rutile and chromite present in the samples. This may be due to heavy minerals

present in the samples and also in sediments [26].

It is interesting that Mn and Fe concentration decrease with increasing Mg value in the study is found at S₅ and S₁₂ respectively. This may be due to the increasing distance from source which causes a progressive reduction in terrigenous content [27]. The low abundance of Mn was obtained at S₁₁ and S₅. This may be because the dissolution of carbonate causes the formation of bicarbonate ions that resulted in the formation of bicarbonate ions which is stable in anaerobic environment at low pH and Eh. Higher pH and oxidizing conditions retard the mobility of Mn ions [28].

When the distributions of Mn and Cr are compared in the study, it is seen that these elements can behave antithetically. Mn depletion is accompanied by immobility of Cr enrichments. This can be attributed to the contrasting behavior of Mn and Cr during redox transformations. Mn depletions and Cr enrichments are both the results of suboxic conditions. Mn will dissolve and the remain in solutions as Mn and Cr will be effectively scavenged as Cr or co-precipitated with Fe and Al. Therefore, the contrasting properties of Mn and Cr can be used to pinpoint the PE levels of an alteration suite, but the criterion that Mn be present in a leachable form should be meeting [29].

The low concentration of Co in the present study shows that its mobility is reduced in the carbonate dominant environment [30]. Another reason for dilution may be wind and fluvial material brought in by the streams in the study area and also this implies that the

sediment is free from this metal pollution [31].

The presence of Zr and Hf in the study indicates the possibility of heavy minerals present in the sediment. The concentration of Zr and Hf was found to be high at S₁₅. This may be because that these elements, weathered at least with respect to Ti, essentially be immobile in all profiles [32]. These observations agree very well with the predicated mobility of these elements. And also Hf and Zr concentrated mostly in sand size material such as zircon. Zircon in sediments is deriving mainly from mechanical sorting and therefore most of Hf could be sand-size fraction, leading its depletion in the clay [33].

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. To study the distribution of REEs chondrite normalization is widely applied. The chondrite-normalized pattern of the beach rock sample is shown in Fig.2.

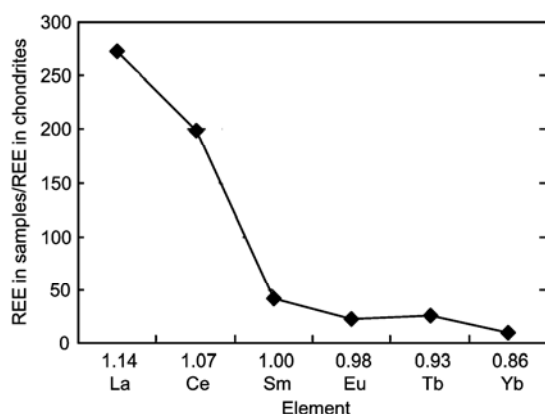


Fig.2 Chondrite-normalized pattern for beach rock samples.

The pattern of the graph shows LREEs enrichment and HREEs depletion. Compared with heavy REE, light REEs are enriched in the particles of the aquatic environment. In the aquatic environment, compared with crust or shales, LREE and HREE fractionation is widely observed as the LREE are preferentially absorbed to surfaces of particles while HREE are preferentially retained into the solution. The pattern also resembles the characteristic feature of carbonates. In the beach rock samples, the mineralogical composition will be important in the fractionation and enrichment of REE. Results of the heavy minerals are relatively stable in weathering process and therefore REE content depends on the accumulation of accesso-

ry phases in sediment fractions [34]. More stable minerals like zircon and monazite are present in REE than that evidenced by spectral studies and hence enrich the REE content. Geological studies also revealed that heavy minerals are present in the sediment of the study area [35].

The variation in the content of the metals and different trace elements in the present study is due to the nature of weathering process and also the velocity of transporting media [36].

4 Correlation analysis

In an attempt to deduce the inter-element relationships in the samples, the total geochemical data were subjected to a correlation analysis using the statistical package (SPSS 6.0 Software). The correlation matrix for the data set is given in Table 3.

A positive correlation of A1 with K and Na in the samples suggests that concentration of these trace elements is controlled by clay minerals and mica while the weak correlation existing between REEs suggests that minerals other than clays and mica control their REE. The correlation between A1 and Ti is poor in the study suggesting that Ti may be concentrated in other minerals such as black mafic rocks fragments and oxides (e.g. ilmenite, rutile and sphene) [37]. There appears to be little or no correlation between Fe, Mg and A1, which leads to the inference that both Fe and Mg contents are controlled by non- aluminous phases or accessory oxide minerals [38]. Ti and Al are both detrital elements, but being associated with complementary fractions (of sandy respectively) which should expect to be anti-correlated.

No correlation between Fe and Ca and Mn and Ca indicates that the concentration of Fe and Mn were controlled by fluctuating pore water Eh rather than the rate of cement precipitation [39].

Iron is strongly positively correlated with Ti, V, Cr, Co, Hf, Zr and REE. This suggested that Fe is present in two forms, a terrigenous contribution (with Ti etc) and hydrogenous contribution (with Mn etc) confirming the dual source of Fe [40]. The negative correlation of Mg with A1 does not suggest terrigenous or in-situ source.

Table 3 Correlation analysis

	Al	Ca	Fe	K	Mg	Na	Ti	La	Ce	Sm	Eu	Dy	Yb	Mn	Co	Hf	V	Cr	Zr
Al	1																		
Ca	0.06	1																	
Fe	-0.03	-0.06	1																
K	0.22	-0.58	-0.07	1															
Mg	-0.02	-0.59	0.49	0.40	1														
Na	0.23	-0.55	-0.06	0.94	0.27	1													
Ti	-0.02	-0.51	0.96	-0.23	0.36	-0.17	1												
La	-0.03	-0.51	0.87	-0.16	0.21	-0.02	0.94	1											
Ce	-0.04	-0.47	0.86	-0.17	0.21	-0.03	0.93	0.99	1										
Sm	-0.04	-0.47	0.85	-0.18	0.21	-0.03	0.93	0.99	0.99	1									
Eu	-0.01	-0.71	0.92	0.12	0.54	0.17	0.89	0.88	0.87	0.87	1								
Dy	-0.07	-0.57	0.83	-0.08	0.48	-0.05	0.871	0.84	0.83	0.83	0.79	1							
Yb	-0.03	-0.69	0.86	0.09	0.36	0.20	0.89	0.96	0.95	0.91	0.80	0.66	1						
Mn	-0.07	-0.56	0.93	-0.12	0.54	-0.19	0.86	0.69	0.66	0.66	0.78	0.80	0.66	1					
Co	-0.05	0.07	0.99	-0.03	0.52	-0.03	0.95	0.86	0.84	0.84	0.94	0.84	0.87	0.92	1				
Hf	-0.12	-0.45	0.90	-0.20	0.35	-0.12	0.91	0.91	0.90	0.91	0.90	0.79	0.84	0.78	0.88	1			
V	-0.05	-0.55	0.99	-0.17	0.45	-0.16	0.98	0.88	0.87	0.87	0.89	0.86	0.85	0.93	0.97	0.91	1		
Cr	-0.11	-0.65	0.96	-0.02	0.58	-0.04	0.93	0.86	0.84	0.84	0.89	0.81	0.87	0.87	0.95	0.87	0.94	1	
Zr	-0.14	-0.46	0.80	-0.07	0.56	-0.03	0.79	0.81	0.79	0.79	0.83	0.67	0.79	0.66	0.79	0.88	0.80	0.87	1

The poor correlation coefficient of Co with other elements like Al, Ca, Na and K in the present study may indicate no mineralization in the area and all the values are due to background dispersal. A strong correlation obtained with Fe, Ti, REEs and Mn shows a significant contribution of detritus from the rocks [38].

A significant positive correlation existing between Co and Cr, Mn and Fe are probably suggestive of post-depositional processes within sediment [41].

Vanadium has a good positive correlation with Fe, Mg, Ti, REEs, Co and Hf. This suggests that metal-liferous sediments and associated basalt are also enriched in V minerals in the study area [42].

The REE shows a good correlation with Mn and Fe while their correlation with Ca is inverse. This suggests that most of REE of this carbonate sequence are held adsorbed on clays, oxides and other minerals and removed by acid stripping. The positive correlation between REE and Fe and Mn could suggest that Fe-Mn oxhydroxide coatings on surface minerals probably played most important role in adsorbing and concentrating REE in sea water [43]. A strong positive correlation of Zr with total REE in the samples shows that zircon is more important than clay/mica in housing all REEs [44]. The positive correlation between Zr

and Ti indicates that they are considered to be immobile; their presence in sediments may represent a source rock composition [1].

The lack of relationship between metals and trace elements were found in the study suggests these metals in sediment are not significantly associated with natural aluminosilicates, iron hydroxides and calcium carbonate minerals.

5 Conclusion

Based on the geochemical studies on beach rock samples by INAA, it is inferred that the cementation of beach rock is due to the calcium carbonate. There is high abundance of calcium carbonate in tropical and subtropical areas of ocean and also typical beach rock formation. The presence of heavy metals and trace elements in Vattakoti shows significant place for elemental mineralogical investigations. Further this study also demonstrates a systematic non-destructive multi-elemental analysis in geological samples.

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References

- 1 Raza M, Casshyap S M, Khan A. *J Geo Soc Ind*, 2002, **60**: 505.
- 2 Ravisankar R, Dheenathayalu M, Ramaswamy V, *et al.* *Rad Prot Env*, 2003, **26**: 426.
- 3 Gischler E, Lomando J A. *Sed Geo*, 1997, **110**: 277.
- 4 Kneale D, Viles H A. *Sed Geo*, 2000, **132**:165.
- 5 Cooper J A G. *Mar Geo*, 1991, **98**: 145.
- 6 Nada A, El-Bahi S M, Abdel-Ghany H A, *et al.* *App Rad Iso*, 2001, **55**: 575.
- 7 Naidu G R K, Denschlag H O, Mauerhofer E, *et al.* *App Rad Iso*, 1999, **50**: 947.
- 8 Ting-Pang-Cheng, Morris J S, Koirtiyohann S R K, *et al.* *Nucl Instr Meth Phys Res A*, 1994, **353**: 457.
- 9 Joron J L, Treuil M, Raimbault L. *J Radioanal Nucl Chem*, 1997, **216**: 229.
- 10 Ni Bangfa, Yu Zhanqin, Wang Pingsheng, *et al.* *J Radioanal Nucl Chem*, 1997, **216**: 179.
- 11 Madaro M, Moauro A. *J Radioanal Nucl Chem*, 1987, **114**: 337.
- 12 Dim L A, Adetunji J, Okujeni C D. *J Radioanal Nucl Chem*, 1993, **168**: 101.
- 13 Mahaney W C, Hancock R G V, Stalker A. *J Radioanal Nucl Chem*, 1994, **180**: 5.
- 14 Randle K, Al-Jundi J. *J Radioanal Nucl Chem*, 2001, **249**: 361.
- 15 Lara L B L S, Fernandes F A N, Oliveria H, *et al.* *J Radioanal Nucl Chem*, 1997, **216**: 279.
- 16 Meloni S, Genova M, Oddone M, *et al.* *J Radioanal Nucl Chem*, 1987, **112**: 531.
- 17 Yusof A M, Akyil S, Wood A K H. *J Radioanal Nucl Chem*, 2001, **249**: 333.
- 18 Acharya R N, Burte P P, Nair A G C, *et al.* *J Radioanal Nucl Chem*, 1997, **220**: 223.
- 19 Shumilin E, Kalmykov S T, Sapozhnikov, *et al.* *J Radioanal Nucl Chem*, 2000, **246**: 533.
- 20 Els-Sayed M K H. *Mar Geo*, 1998, **80**: 29.
- 21 Rosales-Hoz L, Carranza-Edwards A, Lopez-Hernandez, *et al.* *Env Geo*, 2000, **39**: 378.
- 22 Rankama K, Sahama T G, *Geochemistry*, Chicago: The University of Chicago Press, 1950: 69.
- 23 Ashokkumar. *Ind J Env Prot*, 2001, **21**: 887.
- 24 Nelson B W. *Symposium on the environmental chemistry of marine sediments*. Occasional Publication, University of Rhode Island, 1962, **1**: 27.
- 25 Seralathan P, Seetaramaswamy A. *Ind J Mar Sci*, 1987, **16**: 31.
- 26 Subramanian V, Van Tadack L, Vangrieken. *Chem Geo*, 1985, **48**: 271.
- 27 Prasad Rao C, Adabi Mohammad. *Mar Geo*, 1992, **103**: 249.
- 28 Reedman J H. *Techniques in mineral exploration*, 4th Edition, London: Applied Science Publisher, 1979: 533.
- 29 Middleburg J, Cornelish Vander H, Weijden Joost R W, *et al.* *Chem Geo*, 1988, **68**: 253.
- 30 Naseem S, Shamim Ahmed Sheikh, Qadeeruddin, *et al.* *J Geochem Explo*, 2002, **76**: 1.
- 31 Gambhir S K. *Poll Res*, 1999, **18**: 545.
- 32 Nesbitt Cramerand J J. *Mass-balance relations and trace element mobility during continental weathering of various igneous rocks*. Symposium on petrology, Paris, 1983: 73
- 33 Nagendrenath B, Kunzendorf H, Pluger W L. *J Sed Petro*, 2000, **70**: 1081.
- 34 Chandrajith R, Dissanayake C B, Tobschall H J. *App Geochem*, 2000, **15**: 1369.
- 35 Angusamy N, Rajamanickam G V. *Ind J Mar Sci*, 2000, **29**: 283.
- 36 Priyadarshi N. *Ind J Env Prot*, 1998, **18**: 511.
- 37 Mc-Lennan S, Taylor S R, Eriksson. *Geochimica et Cosmochimica Acta*, 1983, **47**: 1211.
- 38 Asiedu Daniel, Suzuki Shiegyuki, Isugio Shibatta Keniinogami. *Geochimica et Cosmochimica Acta*, 2000, **155**: 173.
- 39 Sayed M R G. *J Geo Soc Ind*, 1993, **42**: 585.
- 40 Wijayananda N P, Cronan D S. *Mar Geo*, 1994, **117**: 275.
- 41 Ergin M, Saydam C, Basturk O, *et al.* *Chem Geo*, 1991, **91**: 269.
- 42 Nassem S, Gnesis of manganese ore deposit of Lasbela Area. Balochistan, Pakistan, Ph.D Dissertation, Department of Geology, University of Karachi, 1996: 299.
- 43 Woragh G, Valera R. *Chem Geo*, 2002, **182**: 395.
- 44 Condie C K, Noll P D, Conway C M. *Sed Geo*, 1992, **77**: 51.