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Fractionation of Rare Earth Elements in Surface Sediment of Peninsular Malaysia Coastal Waters

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The environmental fate of rare earth elements (REEs) in the Malaysian environment is limitedly known; however, industrial emission is increasing. This study focused on the REE assessment of the surface sediments obtained from rocky shore ecosystems along the Peninsular Malaysia coastal waters, on deliberating interspatial variability, and on describing their partitioning. Samples were treated with the Teflon Bomb technique, and the concentration of 14 natural REEs was measured through inductively coupled plasma mass spectrometry (ICP-MS). Through quality control practices, the results were verified by employing a standard reference material BCR 667. The tendency of REE distribution was the most mutual property of particular places worldwide and in Malaysia. Among REEs present in sediment, strong correlations were observed, which indicated REEs they behave coherently to each other in different processes of geochemical fractionation. The contaminant metals, namely manganese, arsenic, cadmium and copper, were strongly correlated with REEs ($p < 0.01$ and $p < 0.05$); hence, these metals may be nonanthropogenic in origin because REEs are geogenic in origin. The enrichment factor (EF) values of the comparative results were divided by the region-specified deficiency to minimal enrichment in all the regions, except in the east coast region, which presented considerable enrichment, suggesting a probability of discharge of the anthropogenic effluent. The results of the analysis normalized to chondrite presented patterns of low atomic weight rare earth elements (LREEs) enrichment, gradual downward pattern and depletion through high atomic weight rare earth elements (HREEs) concentrations.

Keywords: Rare earth elements, Surface sediment, Enrichment factor, Chondrite.

INTRODUCTION

Even the name rare confusingly implies, most rare earth elements (REEs) were not uncommon in a nature environment. They are relatively plentiful in the earth's crust. The increasing industrial expenditures of REEs are accompanied by growing emissions, which primarily end up in the aquatic environment. Contamination of REEs into the environment may be attributed by the fact that REEs are incorporated in many modern devices. The key emission route is to surface water where the bulk of REEs ends up in the sediment owing to the low solubility properties. REEs commonly available at low concentrations in soil and water, but their low mobility could promote their accumulation in the environment as a result of anthropogenic inputs [1]. It can be concluded that anthropogenic inputs could

show characteristic signatures of the REEs composition. Comprehensive REEs studies in Malaysian environment from previous work have received much attention, with emphasis on sediment [2-6] along with detail explanations on REEs behaviour. Such studies measured the REEs behaviour in the South China sea and east coast of Peninsular Malaysia, with limited data observed covering REEs in Straits of Malacca, such as Pulau Pinang environment [2].

EXPERIMENTAL

Site survey has been done to ensure the approachability to the study sites and to minimize the sampling period as well. Fig. 1 displays the map showing sampling sites along Peninsular Malaysia coastal waters and Table-1 shows a list

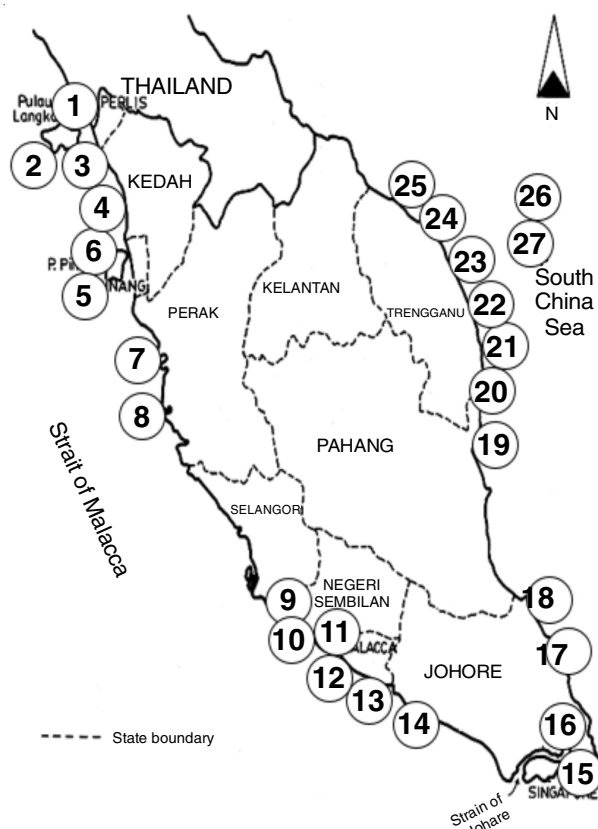


Fig. 1. Map showing sites location along Peninsular Malaysia coastal waters. Details of the investigated sites locations are showed in Table-1.

TABLE-1
LIST OF SAMPLING SITES AND COORDINATES

No.	Site	Latitude	Longitude
1	Pasir Tengkorak Beach, Langkawi	6.4309° N	99.7255° E
2	Tengah Beach, Langkawi	6.2712° N	99.7308° E
3	Beringin Beach, Langkawi	6.2969° N	99.8597° E
4	P. Sayak, Kedah	5.6548° N	100.3340° E
5	P. Betong, Penang	5.3092° N	100.1924° E
6	Bt. Feringghi, Penang	5.4799° N	100.2616° E
7	Tlk. Senangin, Perak	4.3111° N	100.5701° E
8	Tlk. Batik, Perak	4.1853° N	100.6093° E
9	Tmn. Tanjung, Negeri Sembilan	2.5549° N	101.7932° E
10	Tlk. Kemang, Negeri Sembilan	2.4640° N	101.8479° E
11	Blue Lagoon, Negeri Sembilan	2.4145° N	101.8542° E
12	Tg. Bidara, Malacca	2.2956° N	102.0787° E
13	Tg. Kling, Malacca	2.2160° N	102.1592° E
14	Bt. Pahat, Johor	1.7937° N	102.8876° E
15	Sg. Rengit, Johor	1.3498° N	104.2209° E
16	Tg. Balau, Johor	1.6132° N	104.2593° E
17	Sedili Kecil, Johor	1.8436° N	104.1493° E
18	Mersing, Johor	2.4294° N	103.8478° E
19	Tg. Gelang, Pahang	3.9659° N	103.4188° E
20	Cherating, Pahang	4.1254° N	103.3969° E
21	Kijal, Terengganu	4.3306° N	103.4922° E
22	Kerteh, Terengganu	4.5570° N	103.4674° E
23	Tg. Jara, Terengganu	4.8074° N	103.4246° E
24	Chendering, Terengganu	5.2995° N	103.1811° E
25	Bari Kecil, Terengganu	5.5671° N	102.8652° E
26	Dalam Bay, Tioman	2.8723° N	104.1838° E
27	Tekek, Tioman	2.8132° N	104.1474° E

of sampling sites. These recorded locations were also useful for further exploration. All samples were collected throughout the equivalent period, but from diverse sites to characterize the spatial variations in the samples. The top 10 cm depth of surface sediments were collected at each sampling site with triplicates for each site, respectively. Sediments were collected in clean polyethylene bags with a plastic scoop and then were stored in the ice chest. The sediment samples were oven dried at 60 °C for 3-4 days until constant weight was obtained. Samples were then grounded to a homogenous powder with porcelain mortar and pestle. The sediments were sieved through a 63 µm aperture stainless steel sieve, following the published method [7-9]. The sieved samples were then shaken vigorously to yield homogeneity.

Glassware used were treated with 10% nitric acid solution in advance for contamination prevention. Digestion of sediment sample was assisted by Teflon Bomb, following the published method [7]. The digested samples were then quantitatively transferred to a 15 mL labelled centrifuge tube and brought up to 10 mL volume with Milli-Q water (18.2 MΩ cm).

Analysis of REEs was carried out using ICP-MS Perkin Elmer Elan 9000 system, following published method [7] with modification to enhance the accuracy. The HNO₃ (Merck, Suprapur) used for measurement was less than 2% as to minimize the damage to the interference and isobaric molecular interferences. Aliquots were typically diluted 10 times for analysis with 2% HNO₃, made using a combination of pure HNO₃ and Milli-Q water.

The curve generated from the response obtained from serial dilutions of a multi-element calibration standard. The isotopes measured were ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴²Nd, ¹⁵²Sm, ¹⁵³Eu, ¹⁵⁸Gd, ¹⁵⁹Tb, ¹⁶⁴Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷⁴Yb and ¹⁷⁵Lu. Results achieved were blank corrected and expressed as µg g⁻¹ dry weight. Recovery procedure was executed using standard reference material BCR 667 Estuarine Sediment acquired from Institute for Reference Materials and Measurements (IRMM), Belgium.

To exclude the Oddo-Harkins' effect in the REEs concentration pattern of samples, concentration data were divided by the average chondrite taken from McDonough and Sun [10]. Therefore, the positive anomaly is defined as the value greater than unity while negative anomaly is defined as the value less than unity.

The enrichment factor was evaluated as the ratio of the REEs concentration in all samples divided by the concentration of that element in the North American Shale Composite (NASC) and Post-Archean Australian Sedimentary rocks (PAAS) values. The PAAS values might be more relevant for this study than those compiled from the North American and European continents and also, this composition has been most frequently used in normalization procedures, thus facilitating the comparison with literature data. For the calculation of total REEs, LREE and HREE, the calculation methods were as follow:

$$\Sigma \text{LREE} = \text{La} + \text{Ce} + \text{Pr} + \text{Sm} \quad (1)$$

$$\Sigma \text{HREE} = \text{Eu} + \text{Gd} + \text{Tb} + \text{Dy} + \text{Ho} + \text{Er} + \text{Tm} + \text{Yb} + \text{Lu} \quad (2)$$

$$\Sigma \text{REE} = \Sigma \text{LREE} + \Sigma \text{HREE} \quad (3)$$

A common approach to valuing the anthropogenic impact on the sample is to calculate the normalized enrichment factor (EF) for element concentration above uncontaminated background levels. The enrichment factor method normalizes the measured elements with respect to a sample reference such as Fe, Sc and Al [11]. Normalization accounts for the accumulation affected by the dissimilarity in the mobility of dissimilar elements. In this manner, the element equal or less than one (unity) indicated that the main source originally comes from the crust. If the enrichment factor is greater than one, it displayed that the main source has an anthropogenic contribution. The enrichment factor values interpretation used by worldwide researchers [12-14], were shown in Table-2.

Enrichment factor	Contamination category
< 2	Deficiency to minimal enrichment
2-5	Moderate enrichment
5-20	Significant enrichment
20-40	Very high enrichment
> 40	Extremely high enrichment

One-way analysis of variance (ANOVA) was employed for assessment of dissimilarity and notable variances detected between REEs in different sites. All comparisons were made at least at the 95% ($p < 0.05$) and 99% ($p < 0.01$) level of significance. The analytical results and field data were compiled to form a multi-elemental database using Excel 2016 software (Microsoft, Washington, USA) and SPSS software (SPSS Inc., Chicago, USA).

RESULTS AND DISCUSSION

The mean values of REEs concentrations across regions are illustrated in Fig. 2. Result by using ANOVA indicated that there are significant differences between concentrations of all REEs among sampling sites ($p < 0.05$). The pattern is quite consistent through all sites. In general, the abundance follows the order of Ce > La > Nd > Pr > Sm for the light REEs (LREEs) and Gd > Dy > Yb > Er > Eu > Ho > Lu > Tb for the heavy REEs (HREEs). There are dissimilarities in the REEs abundance for each site, but they demonstrate similarities in their REEs distribution patterns, which propose that they are of parallel origins. The distribution trends appeared to be the common feature of most coastal marine sediments of Malaysia [15], the Southeast Coast of India [16] and in the earth's crust [17].

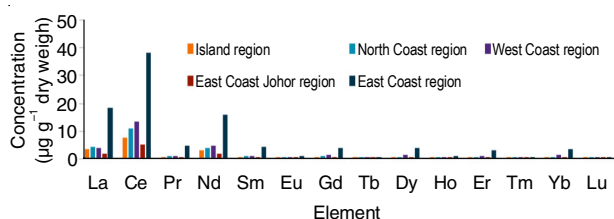


Fig. 2. Mean values of REEs concentration across regions ($\mu\text{g g}^{-1}$ dry weight)

Correlation among REEs and trace metals in surface sediment of rocky shore sites along Peninsular Malaysia coastal waters were given in Table-3. The contaminant metals *e.g.* As, Mn, Cu and Cd are significantly correlated with REEs ($p < 0.05$ and $p < 0.01$), consequently suggests that these metals are probably non-anthropogenic in origin as the REEs are geogenic in origin. Significant correlation of Fe and Al with REEs is expected, as they are abundant in rocks and sediments.

Element	Associated correlation
La	(+)Al**, (-)As**, (-)Mn*, (-)Fe*, (-)Se**
Ce	(+)Al**, (-)As**, (-)Mn*, (-)Fe*, (-)Se**
Pr	(+)Al**, (-)As**, (+)Cd**, (-)Mn**, (-)Se**
Nd	(+)Al**, (-)As**, (-)Mn*, (-)Fe*, (-)Se**
Sm	(+)Al**, (-)As**, (-)Mn*, (-)Fe**, (-)Se**
Eu	(+)Al**, (+)Cd**, (-)Mn**, (-)Cu**, (-)Se**
Gd	(+)Al**, (-)As**, (-)Mn**, (-)Fe**, (-)Se**
Tb	(+)Al**, (+)Cd**, (-)Mn**, (-)Se**
Dy	(+)Al**, (-)As**, (-)Mn*, (-)Fe*, (-)Se**
Ho	(+)Al*, (-)As**, (+)Cd**, (-)Mn**, (-)Se**
Er	(+)Al*, (-)As**, (-)Mn*, (-)Fe*, (-)Se**
Tm	(+)Cd**, (-)Mn**, (-)Cu**, (-)Se**
Yb	(-)As**, (-)Mn*, (-)Fe*, (-)Se*
Lu	(+)Cd**, (-)Se**

Only associated elements are displayed. (+) = Positive correlation, (-) = Negative correlation; **Correlation is significant at the 0.01 level (2-tailed). *Correlation is significant at the 0.05 level (2-tailed)

Inter-REE possible associations in the surface sediment using Pearson's correlation coefficient are presented in Table-4. It is interesting to note that significant positive correlations ($p < 0.01$) from all sites along the Peninsular Malaysia coastal waters were found for all of the REEs pairs. No negative correlation was exposed. The good correlations between the REEs are perhaps derived from the point that they behave coherently to each other in various geochemical fractionation processes.

Table-5 displays the enrichment factor (EF) values calculated for sediment along Peninsular Malaysia coastal waters. Referring to the contamination categories based on the enrichment factor values from Table-2, comparative results divided by regions indicated all mean values are deficient to minimal enrichment in all regions, except for East Coast region that showed the value of significant enrichment. The results also indicate constant low enrichment factor values, which is comparable with analysis of South China Sea sediment core [4]. Consistent values of enrichment factor < 1.0 in REEs series suggesting that there is sufficient retention of REEs from effluents discharge from rivers of such regions. High values of enrichment factor from East Coast region is very interesting, suggesting effluents discharge from rivers of Pahang and Terengganu are enriched with the anthropogenic elements.

Fig. 3 displays the pattern for REEs concentrations in surface sediment normalized to the average concentration of chondrite. Results were divided by region as to display clear information across sites. Generally, results of the analysis normalized to chondrite presented patterns of LREEs enrichment, gradual

TABLE-4
INTER-REE POSSIBLE ASSOCIATIONS IN THE SURFACE SEDIMENT USING PEARSON'S CORRELATION COEFFICIENT

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
La	1													
Ce	.990**	1												
Pr	.846**	.854**	1											
Nd	.988**	.992**	.891**	1										
Sm	.977**	.981**	.898**	.981**	1									
Eu	.721**	.729**	.964**	.767**	.811**	1								
Gd	.988**	.995**	.880**	.995**	.989**	.762**	1							
Tb	.750**	.765**	.973**	.801**	.840**	.984**	.803**	1						
Dy	.983**	.991**	.827**	.982**	.978**	.702**	.992**	.747**	1					
Ho	.890**	.907**	.963**	.925**	.951**	.920**	.932**	.949**	.906**	1				
Er	.954**	.968**	.849**	.965**	.979**	.753**	.977**	.795**	.984**	.942**	1			
Tm	.740**	.763**	.944**	.799**	.843**	.952**	.802**	.973**	.763**	.964**	.837**	1		
Yb	.931**	.948**	.782**	.943**	.943**	.668**	.951**	.712**	.971**	.894**	.987**	.779**	1	
Lu	.407**	.431**	.784**	.492**	.528**	.856**	.477**	.855**	.409**	.729**	.500**	.858**	.429**	1

**Correlation is significant at the 0.01 level (2-tailed)

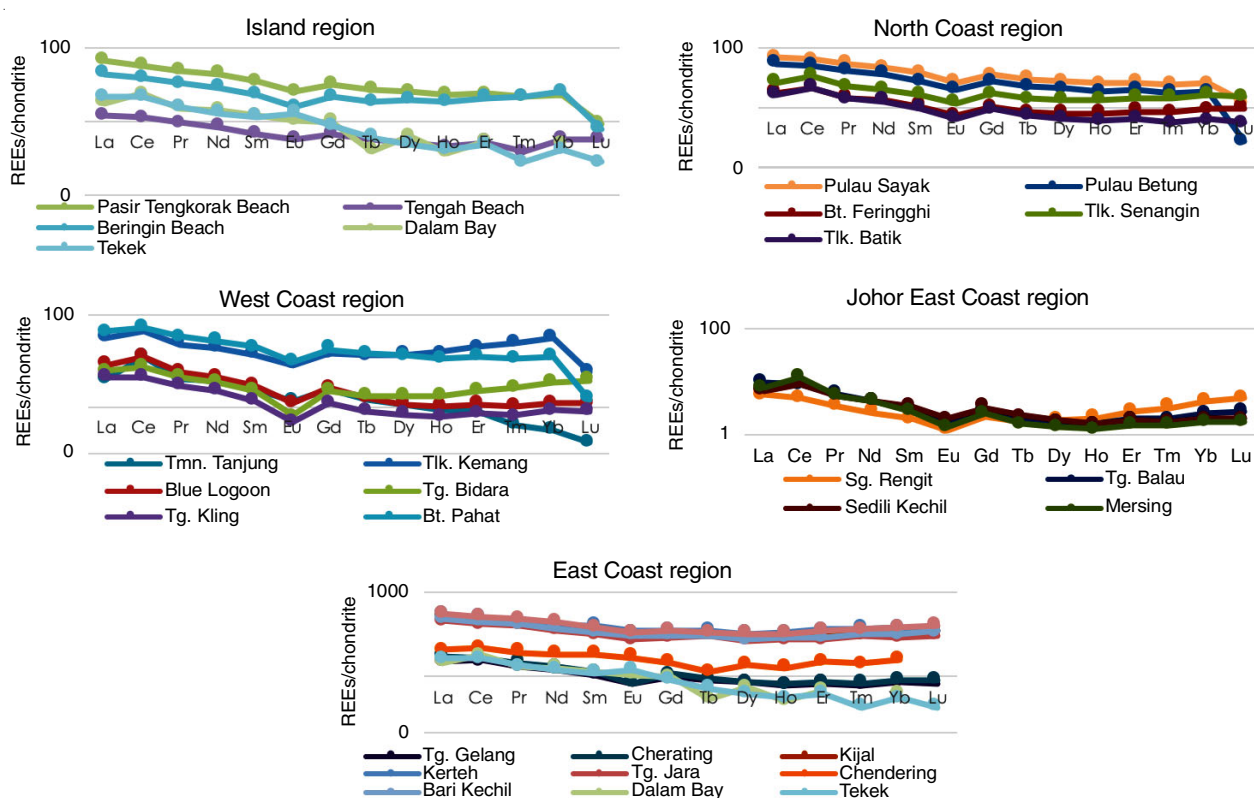


Fig. 3. Pattern for REEs concentrations in surface sediment normalized to the average concentration of chondrite

downward pattern and depletion through HREEs concentrations.

As calculation by region is considering site-specific value as negligible due to the mean calculation, the high values of enrichment factor in the East Coast region was derived from Kerteh site. Such fact could be related to the oil refineries industries that occur in this specific site. REEs pollution by the oil-related process has been reported by numerous studies [18-22]. Olmez *et al.* [19] reported the anthropogenic REEs indication of oil-refined petroleum products in aquatic sediments and stated that the sources of the REE enrichment were

petroleum cracking catalysts and their products. Yusof *et al.* [15] also suggested external inputs from the effluents of a large oil-refining complex of Singapore Island in their REEs analysis of core sediments of Johor Straits between Malaysia and Singapore.

Cerium anomaly, which was expected to deviate as a result of being redox element, displayed a little and weak anomaly. Such pattern is consistent with the patterns reported in Mae Klong River, Thailand [23] and in the Southeast Asian tin belt source rocks [24]. The chondrite normalized REEs plots from the different sampling sites are remarkably similar, although

TABLE-5
ENRICHMENT FACTOR VALUES
CALCULATED FOR SEDIMENT

	Island region	North Coast region	West peninsula region	East Coast Johor region	East Coast region
La	0.59	0.46	0.23	0.17	8.86
Ce	0.63	0.57	0.36	0.23	8.74
Pr	0.58	0.47	0.29	0.18	9.36
Nd	0.58	0.48	0.31	0.19	8.65
Sm	0.72	0.59	0.42	0.26	14.34
Eu	0.97	0.56	0.36	0.29	18.43
Gd	0.99	0.85	0.62	0.40	16.09
Tb	0.74	0.64	0.54	0.32	17.33
Dy	0.80	0.63	0.57	0.33	14.92
Ho	0.73	0.57	0.57	0.35	16.88
Er	0.91	0.66	0.69	0.45	20.04
Tm	0.92	0.63	0.79	0.53	25.82
Yb	1.16	0.68	0.89	0.61	23.99
Lu	0.26	0.42	0.60	0.98	35.67

the values are lower than values from the Terengganu river sediment and granitic rocks of the Terengganu river basin [5]. Sites along the East Coast of Peninsular Malaysia coastal waters displayed consistent REEs pattern as compared to sites of West Coast peninsula that displayed a variation, although, in a minor value.

Conclusions

From the present study, the followings observations can be concluded:

(a) There are dissimilarities in the REEs abundance for each site, but they demonstrate similarities in their REEs distribution patterns, which propose that they are of similar origins. cerium and europium show consistent anomalies behaviour from the other REEs as a result of their redox chemistry. The REEs fractionation patterns normalized to chondrite and shale were remarkably similar indicating a common source of the REEs.

(b) The good correlations between the REEs found in this study perhaps derived from the point that they behave coherently to each other in various geochemical fractionation processes.

(c) Consistent chondrite-normalized patterns suggested that LREEs and HREEs fractionation in coastline marine environment produces more LREEs and less HREEs. Correspondingly, the enrichment of LREE in selected species is consistent throughout the rocky shore areas.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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