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Rare Earth Elements Determination in Rocky Shore Gastropod *Thais clavigera*

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Abstract. Interspatial and inter-tissue variations of rare earth elements (REEs) in *Thais clavigera* collected from particular sites along the east coast of Peninsular Malaysia, Malaysia were studied. All REEs yielded significant strong positive correlation ($p<0.05$, $p<0.01$) among each element in soft tissue and operculum, with some variations in shell. The typical REEs fractionation patterns normalized to chondrite were remarkably similar indicating a common source of the REEs for the whole east coast region. Identical deviations from this pattern were found for Eu and could be explained by their redox chemistry. The ratio of light to heavy REEs, La/Yb in the *T. clavigera* of 29.47 are remarkably similar to Terengganu River basin soil of 33.00 and Terengganu River sediment of 27.60. Consistent chondrite-normalized patterns suggested that light REEs and heavy REEs fractionation in coastline marine environment produces more light REEs and less heavy REEs.

Keywords: east coast peninsular Malaysia, rare earth elements, rocky shore, chondrite normalization

1. Introduction

REEs is a coherent group of elements whose chemical properties transform steadily and consequently being employed as a tool for exploring paleoclimatic environment, origin, erosion activities and soil-water connections [1]-[2]. REEs were initially isolated in the 18^{th} and 19^{th} centuries as oxides from rare minerals. In recent years, enrichments caused by anthropogenic factor have been increasing due to the growing uses and applications in various types of industries, resulting in contamination of mainly the aquatic environment [3]. REEs are used in enormous magnitudes in the mechanized of industrial goods including lasers, computers, pigments for glass and plastics, and additives [4]. REEs incline to be accumulated by biota and have contaminated consequences similar to those of heavy metals.

All aquatic invertebrates gather trace elements in their tissues, whether or not these elements are required to metabolism [5]. With admiration to REEs, no established biological functions have been described and thus these elements are considered as non-essential in biota. The soft tissues of marine molluscs are generally recognized as more efficient accumulators of metals than shells [6]. But recent studies have evidently used shell as one of the useful biomonitoring component of the molluscs on recording the environmental pollution. Shells also have some practical advantages over the use of soft tissue as they can reveal less variability, integrate metal concentrations over the life of the organisms, able to give an idea of the metal levels in the past and offer considerable advantages in easy preservation and storage [7].

The genus *Thais* is common in the intertidal rocky shores of Peninsular Malaysia [8]. Capability of *T. clavigera* to accumulate heavy metals and suitable as good bioindicator have been well discussed by several studies [9]-[11]. The objectives of this study are to provide an insight on interspatial and inter-tissue

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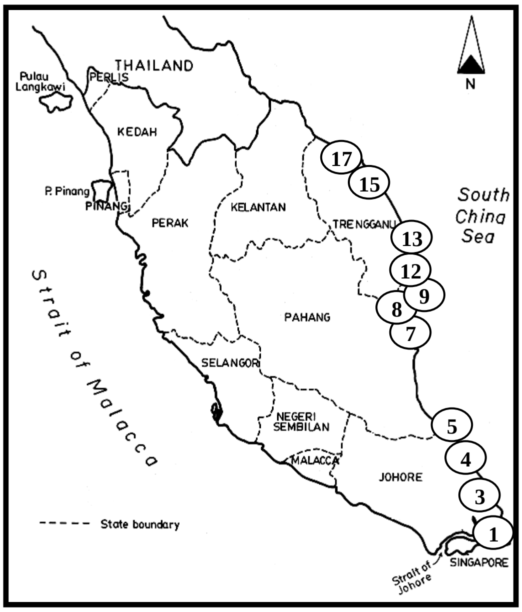
distribution of REEs in different tissues of *T. clavigera* from different rocky shore sites along coastal waters of the east coast of Peninsular Malaysia and investigate the degree of exposure of these elements as well.

2. Materials and Methods

11 sampling sites covered the area of latitude-north between 05^0 34' and 01^0 21' and longitude-east between 104^0 13' and 102^0 51' of east coast Peninsular Malaysia, Malaysia were done (Fig. 1). Sites particularly having rich numbers of *T. clavigera* population on natural rocky structures were occupied. Chosen samples of relatively identical size were hand collected during low tide phase. All samples were appointed in plastic loads, airtight, catalogued and kept at 4 – 6 ℃ during transference to the laboratory where the samples were scrubbed with running Milli-Q water (18.2 Ω) to remove sediment and salt particles prior to store frozen. Once allometric parameter measurement and tissue abstraction, obtained soft tissues were freeze dried before being pulverized and preserved at room temperature until analysis.



No	Site
1	Sungai Rengit, Johor
3	Tanjung Balau, Johor
4	Sedili Kechil, Johor
5	Mersing, Johor
7	Teluk Cempedak, Pahang
8	Tanjung Gelang, Pahang
9	Cherating, Pahang
12	Kijal, Terengganu
13	Kemasik, Terengganu
15	Tanjung Jara, Terengganu
17	Bari Kecil, Terengganu

Fig. 1: Map showing sampling sites along the east coast of Peninsular Malaysia, Malaysia

The analytical technique was based as in [12] with little modification. Analysis was carried out using Inductively Coupled Plasma Mass Spectrometer (ICP-MS) Perkin Elmer Elan 9000. Results were blank corrected and detailed as µg g^{-1} dry weight. Glassware used was submerged in 10% nitric acid (HNO_3) solution in advance for contamination prevention. SPSS was used for assessment of variance and noteworthy differences observed between REEs in different sites and correlation test. All comparisons were made at least at the 95% (p<0.05) and 99% (p<0.01) level of significance.

3. Results and Discussion

3.1. Interspatial variation

LREEs enrichment over HREEs is found in all body parts, as indicated in the Table 1. In general, the distribution patterns of LREEs and HREEs in *T. clavigera* have a comparable tendency with small deviation of fractionations between sites. Any deviation of LREEs and HREEs is considered natural, as the mean difference value was too minor. The dissimilarities in the REEs abundance for each site but at the same time resemblances in their REEs distribution patterns propose that they are of comparable origins.

The enrichment of LREEs appears to be consistent throughout the rocky shore areas along the east coast of peninsula. The enrichment throughout the coastal areas of the South China Sea might be due to adeptness of fluid dynamic mixing through sedimentation processes [13]. Also, the enrichment of LREEs is obvious in the increase of the ratio of LREE/HREE, which is constant with the ratio of La/Yb. The high ratio of La/Yb in *T. clavigera* at Site 17 is probably natural due to the lack of input sources as rivers and human built up areas. Correlation between LREEs is acquired by observing constant values of La/Sm and Ce/La at all sites. This identifies comparable sources of REEs and comparable fractionation patterns at all sampling sites.

Table 1: Total concentration (μg g^{-1} dry weight) of ΣREE, ΣLREE, ΣHREE and ratios of ΣLREE/ΣHREE, La/Yb, La/Sm, and Ce/La in soft tissue, operculum and shell of *T. clavigera*

Site	1	3	4	5	7	8	9	12	13	15	17
	Soft tissue										
ΣREE	1.44	2.97	0.73	1.45	0.79	0.29	0.45	1.42	1.11	0.65	0.36
ΣLREE	1.22	2.69	0.63	1.26	0.68	0.26	0.40	1.28	0.95	0.58	0.33
ΣHREE	0.22	0.28	0.10	0.20	0.11	0.03	0.05	0.14	0.16	0.07	0.03
LREE/HREE	5.51	9.60	6.45	6.32	6.21	9.19	7.44	9.16	5.80	8.47	10.94
La/Yb	17.92	45.68	24.49	19.83	18.32	42.51	21.43	33.26	23.75	24.78	52.18
La/Sm	3.06	7.74	4.95	3.14	3.49	8.09	6.86	4.92	3.13	6.20	9.97
Ce/La	2.75	1.99	2.01	2.72	2.36	1.91	1.45	2.65	2.88	2.55	1.58
	Operculum										
ΣREE	0.96	3.28	0.83	2.35	0.75	0.84	0.49	0.39	0.29	0.15	0.26
ΣLREE	0.86	2.94	0.74	2.12	0.67	0.75	0.43	0.35	0.25	0.12	0.22
ΣHREE	0.10	0.34	0.09	0.23	0.08	0.08	0.05	0.04	0.04	0.03	0.04
LREE/HREE	8.31	8.78	7.87	9.10	8.23	9.02	8.11	8.49	7.10	4.80	5.99
La/Yb	20.88	18.86	17.45	20.32	14.86	17.63	12.19	22.29	18.67	8.74	9.37
La/Sm	6.14	5.45	5.16	5.02	5.81	5.03	5.63	6.45	4.31	4.14	5.20
Ce/La	2.38	2.55	2.54	2.56	2.92	2.77	2.58	3.48	3.46	2.08	2.55
	Shell										
ΣREE	0.16	0.47	0.15	0.24	0.08	0.10	0.16	0.10	0.09	0.07	0.05
ΣLREE	0.14	0.44	0.13	0.21	0.07	0.08	0.14	0.08	0.08	0.05	0.04
ΣHREE	0.02	0.03	0.02	0.03	0.01	0.01	0.02	0.01	0.01	0.02	0.01
LREE/HREE	6.49	15.30	7.96	7.62	5.07	5.80	7.16	6.95	8.41	3.34	3.40
La/Yb	68.94	86.21	44.74	56.66	113.50	37.19	37.13	30.16	33.69	5.77	13.78
La/Sm	6.46	15.03	9.44	8.22	4.83	7.73	6.44	7.48	7.88	4.18	3.76
Ce/La	1.49	1.36	1.20	1.13	1.40	1.39	1.09	1.12	1.26	1.19	1.16

3.2. Inter-tissue variation

REEs concentrations in different body parts of *T. clavigera* indicate more variations found between different locations in soft tissue than in shell. This gives information that REEs accumulation varies among body parts. For marine shells, it has been shown that the outer shell layer contains higher REEs concentrations than the inner shell layer [14]. From this, it is implicit that the REEs distribution within shell is not homogenous. It is remarkable that REEs concentrations in soft tissues of *T. clavigera* are always higher than those in operculum and shells. This is in agreement with studies by [15] that described constant higher concentrations of REEs within tissues than those in shells in series of molluscs. All REEs yielded significant strong positive correlation (p<0.05, p<0.01) among each element in soft tissue and operculum. Correlation between REEs in shell however, shows a variation among locations. Strong positive correlation among REEs is considered natural, as REEs are very similar in their chemical and physical properties and expected to be similar as well in their distribution in biological tissue [16]. Yet, the accumulations in shell are thought to be different than other tissues as they reveal fewer correlations.

3.3. Chondrite normalization

Chondrite has been used for normalization of REEs since bulk composition of the earth is expected to be close to chondrite meteorites that describe the early earth [17]. The chondrite-normalized pattern in this study strongly recommends that the REEs accumulated by *T. clavigera* are originated mostly from indigenous rocks. The chondrite-normalized pattern in each sample was parallel to one another although the concentrations of REEs in each site were different. Fig. 2 shows the chondrite-normalized plots of REEs, reveals downward pattern of LREEs to HREEs and negative Eu anomaly in all locations and all body parts. Soft tissue and shell plots revealed less variation of chondrite-normalized ratios among locations compare with operculum. Eu deviations in the chondrite-normalized REEs pattern is predictable as these REEs are estimated to behave differently from the other REEs due to changes in their oxidation states in specific situation. They behave inversely in which under reducing condition Eu^{3+} becomes Eu^{2+} [18] resulting a negative Eu anomaly.

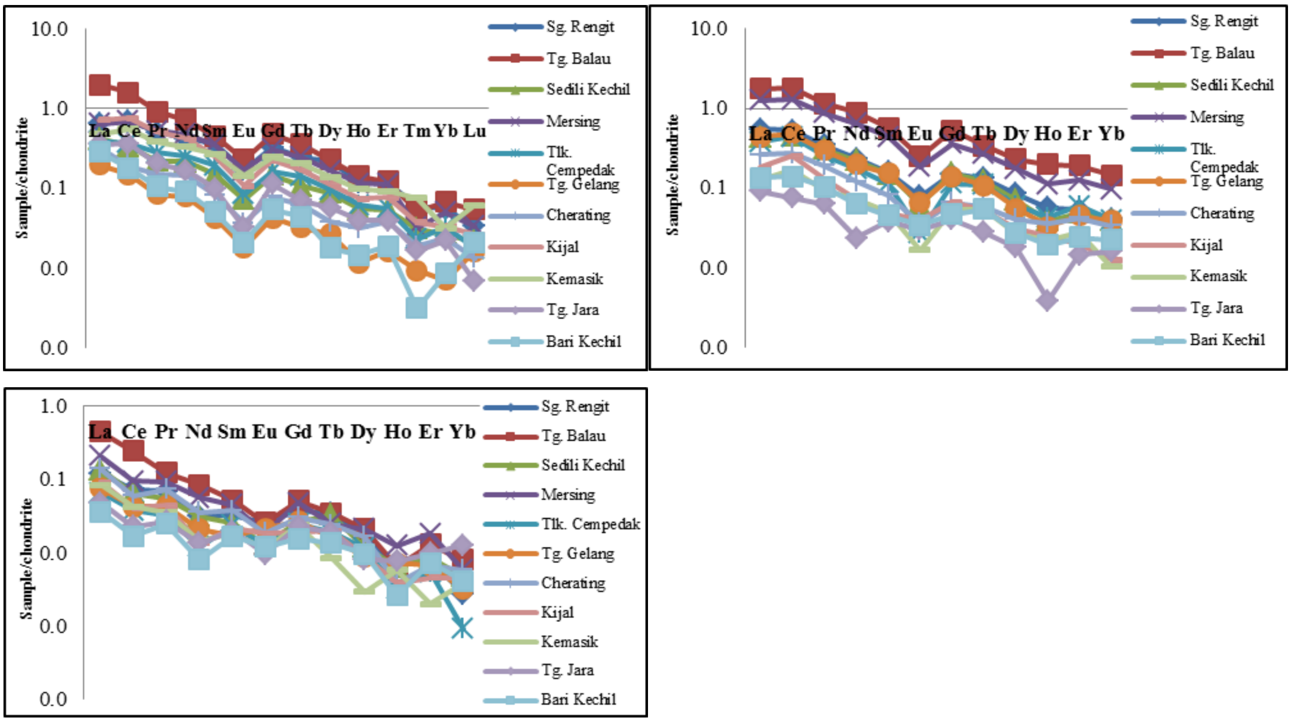


Fig. 2: Chondrite-normalized plots for the rare earth elements in the (a) soft tissue, (b) operculum and (c) shell of *T. clavigera* from paticular s ampling locations along the east coast of Peninsular Malaysia, Malaysia

Eu in the chondrite-normalized REEs pattern displays a range of anomalies. There is an insight that the negative Eu anomaly are derived from possible contamination as a result of discharge of organic materials and contaminations from industrial and agricultural wastes and municipal effluents from the cities and towns. Moreover, the deviations of Eu in all samples lead to the conclusion that REEs are not equally distributed between soft tissue, operculum and shell of studied samples. It cannot be assumed either the shell is not passing on all REEs equally or REEs is enriched in the shell after it formed.

The chondrite-normalized plots are remarkably similar, although the values are lesser than values from the Terengganu River sediment and granitic rocks of the Terengganu River basin which symbolizes the only published record of REEs measurements in riverine sediments in Malaysia as in [19]. Granite is the dominant rock of the east coast of peninsular Malaysia and thus the main natural source of REEs contributing the South China Sea. The ratio of light to heavy REEs, La/Yb in *T. clavigera* of 29.47 are remarkably similar to Terengganu River basin soil of 33 and of Terengganu River sediment of 27.6.

4. Conclusion

REEs are not equally distributed between body parts with more variation are significantly observed in soft tissue. The typical saw-tooth pattern for REEs concentrations was observed. Consistent chondrite-normalized patterns suggested that LREEs and HREEs fractionation in coastline marine environment produces more LREEs and less HREEs. Also, the enrichment of LREEs is consistent throughout the rocky shore areas along the east coast of the peninsula. Eu shows anomalies behaviour from the other REEs in all body parts as a result of their redox chemistry. The REEs fractionation patterns normalized to chondrite was remarkably similar indicating a common source of the REEs for the whole east coast region.

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