

Determination Of Rare Earth Elements And Its Distribution Pattern From The Core Sediments By K_0 -Instrumental Neutron Activation Analysis

Ebenezer Aquisman Asare ^{1,2*}, Rafeah Wahi ¹, Alexander Obiri Gyampoh ³, and Omolayo Ajoke Omorinoye ⁴

1. *Universiti Malaysia Sarawak, Resource Chemistry Programme, Faculty of Resource Science and Technology, Kota Samarahan, Sarawak, Malaysia*

2. *University of Ghana, Graduate School of Nuclear and Allied Sciences, Kwabenya-Accra, Ghana*

3. *Kibi Presbyterian College of Education, Departments of Science, Kibi, Eastern Region, Ghana*

4. *University of Ilorin, Faculty of Physical Sciences, Department of Geology and Mineral Sciences, Ilorin, Nigeria*

*Corresponding author, Email : aquisman1989@gmail.com

This work aimed to assess rare earth elements and their distribution pattern from the core sediments from the central coast of Ghana by K_0 instrumental neutron activation analysis. The rare earth element content was evaluated with uncertainty less than 8% (at 95% confidence level) and demonstrated to be accordant with the IAEA-soil 7 certified concentrations. The calculated concentration of light rare earth elements and Fe normalized enrichment factors suggested that sediment samples were not enriched with light rare earth elements (LREEs) obtained from discharges of anthropogenic activities. The chondrite-normalized pattern of rare earth elements exhibited LREEs, Tm, Tb, Eu and Ho enrichment. The total contents of rare earth elements calculated can be used to establish baseline information about environmental contamination determination and to develop the relationships between the Ce/Ce* and Eu/Eu* anomalies and the source appointment of both LREEs elements and heavy rare earth elements (HREEs).

KEYWORDS

Rare earth element, Marine core sediment, Neutron activation analysis, Shale average, Enrichment factor

1. INTRODUCTION

Many years ago, anthropogenic activities have been an important source of trace metallic elements, in the end polluting the surface of the planet earth. These activities overburdened the existence of the environment (aquatic and terrestrial) with a huge amount of trace metallic contaminants. Exploitation and utilization of trace metallic elements in high-value goods and also as the main constituents of infrastructure became a foundation in human development advancement. Therefore, considering the local, national and global scale, human realization and individual responsibility on the ecological constituents to control and improve deteriorated terrestrial and aquatic environments have been intensified [1,2]. Rare earth elements (REEs) are being extensively overexploited because of their escalating request for the manufacture of gadgets includ-

ing alloy, magnet, glasses, catalyst and assorted electronics [3,4]. The benthic groups are immensely at risk since they assemble the toxic contents in sediments followed by transferring them to the higher trophic level [3,4]. Consequently, the health conditions of living organisms on higher trophic levels of the food chain in terrestrial and aquatic ecosystems will be affected because for instance humans obtained most of their protein sources from aquatic ecosystems [4,5,6].

Assessment among rare earth elements is augmented by normalizing the analyses with chondrite and average shale serving as a reference standard. In such assessments using chondrite or average shale for normalization, certain fractionation impacts may lead to an increase of light rare earth element concentration relative to the heavy rare earth element concentration. Additionally, the rates of normalized significant effects can be calculated [4]. Rare earth elements (REEs) in sediments have been widely employed as important tools for ecological studies owing to their characteristics during geochemical processes. Furthermore, rare earth elements are widely accepted as a depend-

able source of tracers due to their water-immobile behaviour and therefore, act conservatively throughout the processes of sedimentary. Marine and river sediments have the prospects of being the source of REE and usually serve as storage first by sorption of REEs from the water path and then as a source at elevated levels because of changing conditions, such as temperature, pH, Eh, etc. [4,7].

Customarily, discharges from wastewater do not go through suitable water treatment. Vegetation and the land tenure system have also increased the transportation and accumulation of REEs in soils and sediments. The coast of the central part of Ghana has been expanded outwards through sequential land repossession which has changed the position of the estuary seaward and the outcome varies due to saline water intrusion in the course of high tides that could affect the distribution of rare earth element contaminants. There are different types of analytical instruments for multi-elemental determination and instrumental neutron activation analysis is one of them. In general, there are three approaches to standardization in working using instrumental neutron activation analysis (INAA). These are the relative method, absolute method, and k_0 -standardization method (that is single comparator) [8]. The major standardization methods used for determining rare earth elements are relative and k_0 -standardization. The k_0 -standardization method is practically simpler but the main disadvantage is that the formulation and calculations including computational programming are more complex. Also, the k_0 -INAA method requires experts to explain the spectrum of specific elements in the sample, which are tedious to work on [8,9]. On the other hand, the relative method requires preparing standards for the individual element to be analyzed whereas the absolute method is more of a direct analysis of the irradiated samples without going through the process of standard preparation [8,9].

Instrumental neutron activation analysis (INAA) has been employed for rare earth elements determination in several geological materials. In 1978, the radiochemical separation was used to obtain the concentration of rare earth elements in rock samples after irradiation and they managed to assess all the fourteen REEs with a shorter cooling time of 12 days [10]. The study carried out by Danko reported that they were able to determine the concentration of 13 rare earth elements except for gadolinium (Gd) in biological materials by neutron activation analysis with pre and post-irradiation separation in a month [11]. Many works have been conducted to determine rare earth elements using the k_0 -neutron activation analysis method. According to

Ravisankar La, Ce, Sm, Eu, Tb concentrations were determined in beach rock samples with a cooling time of 30-50 days [12]. Silachyov study depicted that La, Ce, Nd, Sm, Eu, Tb, Yb and Lu were able to assess with a decay time of 7 days and 30 days when comparing internal standard method and single comparator method for assessing REEs in rock samples [13]. Extensive works on the geochemical characterization of sediments in the coastal part of Ghana have been recounted by some researchers. Nonetheless, there is little data baseline regarding the central coast of Ghana. Thus, this work aimed to investigate the concentration of rare earth elements in core sediments of the coast of the central part of Ghana using the NAA k_0 -standardization method.

2. MATERIAL AND METHOD

2.1 Study area, sampling and sample treatment

Core sediments were collected at three stations. The three sediments core were labelled as Komenda (5.050000 °N, 1.489444°W), Elmina (5°05'N, 1°21'W), Cape coast (05°06'N, 01°15'W). The samples were collected at a sea depth between 3.0-10.0 m from the coast of Komenda to the coast of Cape coast in the central part of Ghana with the help of a box corer (20.0 × 25.0 cm cross-sectional area). The maximum depth collected was 60.0 cm with the central core cut into the section between 3.0 and 4.0 intervals. The core sediment samples were placed into polyethylene bags before further treatment and laboratory analyses.

2.2 Preparation of standard solution for k_0 -instrumental neutron activation analysis method

To assess the concentration of REEs by employing the k_0 -instrumental neutron activation analysis method, standard samples were prepared from mono REEs plasma standard solution, Specpure® Alfa Aesar with the concentration of 1000 ppm accurate to 0.3 % wt. 20 ppm of the standard solution was pipetted on the filter paper (Whatman 42) with dimensions of 16 × 103 mm with polyethylene for support. A stopwatch was used between the starting of pipetting and weighing. A correction was conducted to take evaporation into consideration. The filter papers were rotated into 10 mm diameter cylinders after drying. The rolled filter papers were placed into 16 mm long polyethylene vials followed by heat-sealed [14].

2.3 Irradiation of prepared standard solution for k_0 -instrumental neutron activation analysis method

Irradiations of standard samples were carried out in

Table 1. Nuclear properties of rare earth element radio isotopes employed in this study [that is gamma energies, k_0 , and Q_0 values for the target (TI) and formed isotopes (FI)]

Target isotopes	Formed isotopes	Half-life	γ -ray energy (keV)	K_0	Uncertainty (%; 1sd)	Q_0	Uncertainty (%; 1sd)
^{139}La	^{140}La	1.6781 day	1397.8	1.34E-01	1.10	1.24	5.00
^{140}Ce	^{141}Ce	32.508 day	139.9	3.66E-03	0.90	0.83	5.00
^{142}Ce	^{143}Ce	33.039 day	299.6	6.89E-04	0.50	1.20	5.00
^{141}Pr	^{142}Pr	19.120 hr	1609.2	6.12E-03	0.60	1.51	5.00
^{146}Nd	^{147}Nd	10.980 day	96.9	1.02E-03	2.50	2.00	1.20
^{148}Nd	^{149}Nd	1.728 hr	598.1	4.56E-04	1.10	2.00	1.20
^{152}Sm	^{153}Sm	46.284 hr	117.5	2.31E-01	0.40	14.40	2.10
^{151}Eu	^{152}Eu	13.537 year	1397.0	9.36E+00	0.60	0.66	5.00
^{151}Eu	$^{151\text{m}}\text{Eu}$	9.3116 hr	798.8	3.02E+00	5.00	0.66	5.00
^{152}Gd	^{153}Gd	240.40 day	110.1	4.54E-03	4.00	0.77	15.00
^{158}Gd	^{159}Gd	18.479 hr	363.5	8.49E-04	1.60	29.90	3.10
^{159}Tb	^{160}Tb	72.30 day	796.2	8.25E-02	1.20	17.90	3.80
^{164}Dy	^{165}Dy	2.334 hr	99.4	3.57E-01	0.90	0.19	3.80
^{165}Ho	^{166}Ho	26.830 hr	89.0	4.94E-02	1.40	10.90	5.00
^{170}Er	^{171}Er	7.516 hr	328.4	1.04E-02	2.50	4.42	2.40
^{169}Tm	^{170}Tm	128.60 day	79.7	3.45E-02 ^a	5.00	14.3	3.30
^{168}Yb	^{169}Yb	32.026 day	192.3	1.04E-02	5.00	4.97	2.10
^{174}Yb	^{175}Yb	4.185 day	412.0	1.64E-02	0.60	0.46	5.00
^{176}Lu	^{177}Lu	6.648 day	213.8	7.14E-02	5.00	3.49	5.00
^a k_0 and Q_0 values for ^{169}Tm							

the Ghana research reactor 1 with a neutron flux of $5 \times 10^{11} \text{ cm}^{-2}/\text{s}$ for 30.0-90.0 min, operated at half-power of 15.0 kW. Counting was performed on an HPGE detector with an efficiency level of 50% at 1.33 MeV. Samples were then counted sequentially at a length of 2.50 mm (position PA₁), 36.0 mm (position PA₂) and 100.0 mm (position PA₃) on the detector and they were counted long enough to attain a net peak area with a statistical error less than 0.1%. Uranium and thorium samples were prepared in the same procedure as the REEs samples to complete the libraries for spectral and nuclear interference. Neutron self-shielding and gamma-ray attenuation correction modules were confirmed by employing 100.0 mg of 99.9% pure rare earth oxides (REO) and it was then followed by dilution with 2.0 g of silicon dioxide (SiO₂). The REE oxide samples were also irradiated in a neutron flux of $5 \times 10^{11} \text{ cm}^{-2}/\text{s}$ for 25 sec to 6 min. The oxides were calculated on position PA₃ to prevent methodical errors initiated by coincidence summing [14].

2.4 Certified reference material

IAEA soil-7 certified reference material was employed

to validate the k_0 -neutron activation analysis method at Ghana research reactor 1 (GHARR1). About 50-150 mg of IAEA soil 7 samples were weighed and mixed with 0.88 mg of silicon dioxide (SiO₂). It was then placed into a 1.4 mL polyethylene vial followed by irradiation which was varied between 25 sec and 7 hr. The means by which the samples were transferred to the reactor is known as the pneumatic transfer system operated at a pressure of 0.25 atm [15]. After cooling times of 25 min, 2-6 days and 1-3 weeks after irradiation, samples were counted for 10 min, 60 min, 5 hr, 1 day and 10 days decay time [15].

2.5 Core sediments preparation for k_0 -instrumental neutron activation analysis method

Marine core sediments on the central coast of Ghana were tested. The procedure for irradiation and counting followed the same as the certified reference materials (IAEA soil 7).

3. RESULT AND DISCUSSION

3.1 Sensitivity factors and GHARR1 library

The individual chemical element combined with the

Table 2. Rare earth elements concentration in IAEA soil-7 reference material

Element	Conc. _{cert} ± Δ (mg/kg)	Conc. _{measured} ± Δ (mg/kg)	Conc. _{measured} /conc. _{cert}
La	28.5 ± 1.1	27.2 ± 1.1	0.95
Ce	60.8 ± 2.1	58.9 ± 3.0	0.97
Pr	7.5 ± 0.6	7.25 ± 0.6	0.97
Nd	27.2 ± 1.2	26.1 ± 1.2	0.96
Sm	4.34 ± 0.4	3.89 ± 0.4	0.90
Eu	1.7 ± 0.08	1.54 ± 0.12	0.91
Gd	4.89 ± 0.16	4.51 ± 0.26	0.92
Tb	1.0 ± 0.02	0.96 ± 0.06	0.96
Dy	3.8 ± 0.18	3.46 ± 0.18	0.91
Ho	0.72 ± 0.08	0.68 ± 0.11	0.94
Er	2.46 ± 0.11	2.21 ± 0.19	0.90
Tm	0.54 ± 0.03	0.49 ± 0.03	0.91
Yb	2.60 ± 0.12	2.41 ± 0.17	0.93
Lu	0.74 ± 0.04	0.69 ± 0.08	0.93

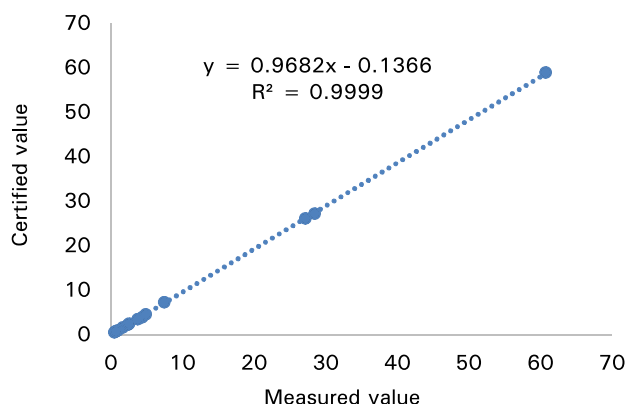


Figure 1. The correlation coefficient for the linear regression between certified and measured values

formed isotope, energy of the characteristic gamma-ray and its half-life, GHARR1 libraries has three sensitivity factors (B), computed for a sample with a fixed geometry placed in three kinds of reproducible counting positions : PA₁, PA₂ and PA₃. Table 1 shows the selection nuclides, formed isotopes, their gamma-rays, k₀ and the Q₀ plus their uncertainty with a standard deviation of one expressed in percentage. The data was fetched from the k₀ official database while the Q₀ values for europium-152, europium-152 m, ytterbium-169 and lutetium-177 were obtained from Abdollahi and Santoro studies and also k₀ and Q₀ for thulium-170 Abdollahi and Zawisza from [14,16,17,18].

3.2 Method validation

Table 2 depicts the results of concentrations of rare earth elements measured in IAEA soil-7 reference material. The calculated concentrations of Ce and Pr had higher consistent with the certified values. The correlation coefficient for the linear regression between certified and measured concentrations = 0.999 (Figure 1). Therefore, it can be concluded that k₀-NAA was able to quantify the concentration of REEs in IAEA soil-7.

3.3 Assessment and distribution patterns of rare earth elements in core sediments

Table 3 shows the calculated concentrations of different rare earth elements in three sampling locations. The content of REEs varied by a factor of 1- 5 between the three sampling locations. Considering each metal there is no significant difference within a single core and between various cores that varied by a factor of more than 6 in each station. Overall, the vertical distributions of all the calculated REEs of core sediments collected from three locations of the central coast of Ghana showed similar trends in each given core.

3.4 Enrichment factor

Ravichandran and Khadijeh opined that the enrichment of any metal compared to the crustal mean shale's is measured by enrichment factors (EF) [4,19]. The EF for rare earth elements was computed by the formula:

$$EF = (Cn/Fe)_{\text{sample}} / (Xn/Fe)_{\text{crust}} \quad \dots(1)$$

Where (Cn/Fe)_{sample} represents ratios of arithmetic average concentrations (mg/kg, dry wt) of the target trace element; (Xn/Fe)_{crust} represents the iron element in the investigated sediments and continental earth crust according to Lide [20]. An enrichment factor less or greater than one (1.0) indicates depletion or enrichment relative to crustal abundance whereas an EF equal to 1.0 shows that the rare earth element concentrations in sediments are at the crustal level. Since one of the objectives was to examine the features of light rare earth elements (LREEs) relative to heavy rare earth elements (HREEs). Lanthanum and ytterbium were selected to represent LREEs and HREEs. Figure 2 shows the vertical profiles of EF for lanthanum and ytterbium in three sampling locations. The enrichment factor recorded for La varied from 0.54 to 0.86 whereas Yb varied from 0.65 to 1.11. There was no significant enrichment of both light rare earth elements and heavy rare earth elements of core sediments collected from the three locations of the central coast of Ghana. It can be concluded that lanthanum and ytterbium depicted

Table 3. Rare earth element concentrations (mg/kg) in the core sediment from the central coast of Ghana

Station depth (cm)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Fe ₂ O ₃ (%)
Komenda															
16-20	31.2	36.5	8.1	29.5	6.7	4.1	5.3	3.3	5.5	2.3	2.1	1.9	1.5	0.4	5.1
21-25	29.7	35.8	8.0	29.3	5.4	4.4	4.7	3.6	5.2	2.1	1.9	2.3	1.6	0.2	4.6
26-30	30.6	33.9	7.3	26.7	5.1	4.2	5.1	3.1	5.4	2.1	1.7	2.1	1.2	0.4	4.9
31-35	24.7	29.3	5.2	30.1	6.1	3.9	5.4	3.1	5.3	1.8	2.0	1.6	1.2	0.1	4.1
36-40	26.3	31.2	6.6	28.4	5.1	3.9	5.2	3.3	5.1	2.1	1.9	1.9	1.1	0.2	4.3
41-45	27.2	29.9	4.7	29.6	5.2	4.3	5.4	3.1	5.2	1.9	2.0	1.7	1.4	0.3	4.9
Elmina															
16-20	26.4	31.3	6.2	22.2	5.7	6.2	5.1	2.9	4.9	2.6	3.4	2.2	1.3	0.8	5.4
21-25	22.7	33.5	7.2	23.5	5.2	5.6	4.6	3.3	5.2	2.1	2.6	2.0	1.1	0.2	5.2
26-30	24.3	33.1	6.6	24.5	4.9	5.9	5.0	3.3	4.4	2.4	3.1	2.6	1.4	0.4	5.7
31-35	21.9	29.7	5.9	23.1	4.4	5.7	4.8	3.0	4.5	2.1	3.1	2.4	1.7	0.6	5.3
36-40	22.9	29.4	5.9	23.5	4.6	5.6	4.5	2.6	4.4	2.1	3.3	2.3	1.2	0.6	5.7
41-45	25.8	26.4	4.9	20.2	5.1	5.4	4.5	2.9	4.4	2.3	3.6	2.4	1.4	0.6	5.1
Cape coast															
16-20	27.8	29.9	4.7	24.6	4.2	3.6	5.4	3.1	5.2	1.8	2.0	1.7	1.7	0.2	4.4
21-25	24.2	33.1	6.6	24.5	4.9	5.9	5.1	3.3	4.4	2.4	3.1	2.6	1.4	0.5	5.2
26-30	30.4	33.1	7.3	26.7	5.1	3.7	5.1	3.1	5.8	2.3	1.5	2.1	1.4	0.3	4.8
31-35	28.9	28.9	5.9	24.1	4.4	5.7	4.8	3.0	4.5	2.1	3.1	2.4	1.6	0.8	4.6
36-40	28.2	32.8	8.4	29.1	5.4	4.4	4.7	3.6	5.2	2.1	2.9	2.7	1.6	0.9	4.9
41-45	27.2	31.2	6.9	28.2	5.7	3.6	5.2	3.4	5.1	1.9	1.9	2.4	1.7	0.5	5.0

alike trends in EF profiles.

Iron contents in sediments could be affected by the process, such as redox reaction and enrichment as results of coagulation by salt influence in the coastal ecosystem and affecting the calculated enrichment factor outcomes, the EF was also computed by normalizing the contents of all the REEs relative to their average shale content [3]. The North American shale composite (NASC) was used to normalize the rare earth element concentrations in sediments (Table 4). The EF was measured as the rate of rare earth element contents in any segment to the concentration of that metal in the North American shale composite. The three sampling locations were divided into three portions of layers: the upper layers (16 – 21 cm), middle layers (26 – 35 cm) and lower layers (36 – 45 cm). Figure 3 shows the shale normalized ratios for rare earth elements. The calculated shale normalized ratios for all the REEs were greater than one for the three layers except for Ce and Yb which were less than 1. This indicates that there is inadequate retention of rare earth elements

from the various industrial refinery effluents that are released into lagoons, streams and rivers of Komenda, Elmina and Cape coast.

To evaluate the potency of the effect of endogenic processes, Shatrov suggested indicator ratios based on REEs and these ratios are examined below [6] :

$$\text{Ce/Ce}^* = \text{Ce}_{\text{NASC}} / (1/2 (\text{La}_{\text{NASC}} + \text{Pr}_{\text{NASC}})) \quad \dots(2)$$

Ce/Ce* values < 1 indicate negative anomalies, that is depletion of Ce in sediment. This means there is a reductive dissolution of insoluble Ce(IV) to soluble Ce(III) [21]. Ce/Ce* values > 1 suggests positive anomalies (that is enrichment of Ce in sediment). Cerium subsists in marine water in the form of Ce⁴⁺ and it can easily undergo hydrolysis and co-precipitation with manganese. Consequently, manganese nodules found in the marine environment have positive cerium anomaly whereas other cerium which formed as a result of biogenic and chemical deposition processes have negative cerium anomalies. The results from table 5 indi-

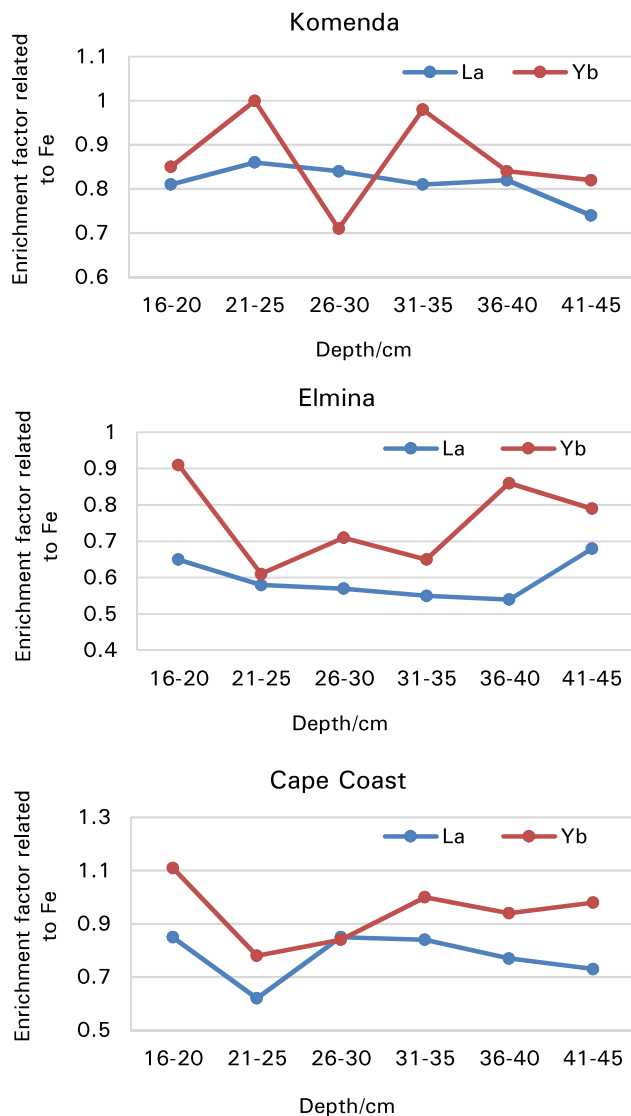


Figure 2. Fe normalized enrichment factors for La and Yb plotted as a function of depth in three sampling locations

cate that the core sediments collected from the coast of central parts of Ghana have low concentrations of rare earth elements and noticeable cerium anomalies proving that the core sediments perhaps carry biogenic detritus [4].

$$\text{Eu/Eu}^* = 0.5\text{Eu}_{\text{NASC}} / (\text{Sm}_{\text{NASC}} + \text{Gd}_{\text{NASC}}) \quad \dots(3)$$

Eu/Eu* values less than 1 suggest depletion in Eu. This is a result of reflecting oxidation of Eu(II) to Eu(III) and a drop of Eu values from the core sediments [21]. Eu anomaly indicates the input of unfathomable substances into the stretch of sediment genesis as fluids, hydrothermal solutions and volcanic rocks [4,21]. It was found from the results that the shale normalized style exhibits a negative Eu/Eu* anomaly. The Eu deple-

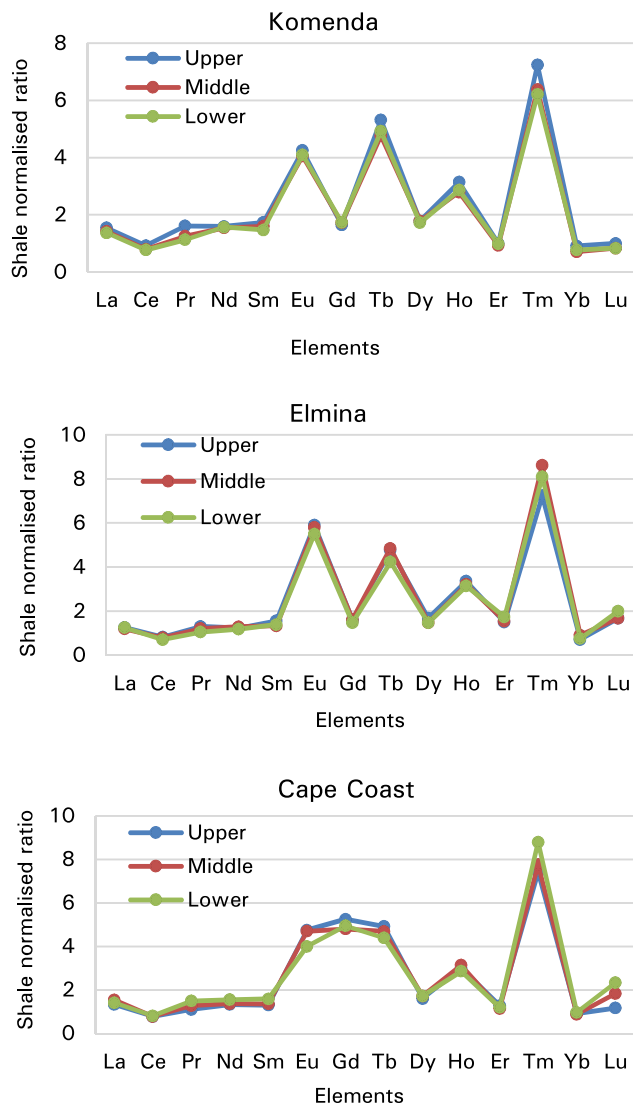


Figure 3. Shale normalized ratios for rare earth elements at a distance from 16 – 21 cm (upper layers), 26 – 35 cm (middle layers) and 36 – 45 cm (lower layers) in core sediments collected from the central coast of Ghana

tion is a result of strong reducing conditions, aeolian and hydrothermal inputs and the existence of waste feldspar [4,5]. Eu/Sm is a measure of the permeability level of fluid moving from the lower to the higher-order in the earth's crust [4]. Eu/Sm varies with crust thinning in the course of periods of maximum misdeed and rearrangement of the systemic patterns of areas. Based on the Eu/Sm ratio, permeability has been grouped into three values greater than 0.3 represent high, Eu/Sm values greater than 0.2 but less than 0.3 as medium while values less than 0.2 are considered low. The calculated Eu/Sm ratios for core sediments collected from the part of the central coast of Ghana were greater than 0.3 (Table 5). Ce/La ratios describe the connec-

Table 4. Rare earth elements concentrations in aliquant of the North American shale composite

Element	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
NASC (mg/kg)	39.0	79.0	10.3	37.0	7.0	2.0	6.1	1.3	6.0	1.4	4.0	0.58	3.4	0.6

Table 5. Sum of rare earth element, light rare earth element, higher rare earth element, Ce/Ce*, Eu/Eu*, Eu/Sm, Ce/La and La/Yb ratios in the core sediments from the central coast of Ghana

Station	ΣREE	ΣLREE	ΣHREE	ΣLREE/ΣHREE	Ce/Ce*	Eu/Eu*	Eu/Sm	Ce/La	La/Yb
Komenda									
16-20	138.4	112.0	26.4	4.24	0.58	0.56	0.61	1.17	20.80
21-25	134.2	108.2	26.0	4.16	0.59	0.71	0.81	1.23	18.56
26-30	128.9	103.6	25.3	4.10	0.57	0.67	0.82	1.11	25.50
31-35	119.8	95.4	24.4	3.89	0.90	0.56	0.64	1.19	20.58
36-40	122.3	97.6	24.7	3.95	0.60	0.62	0.77	1.19	23.91
41-45	121.9	96.6	25.3	3.82	0.66	0.66	0.83	1.10	19.43
Mean	765.5	613.4	152.1	24.16	3.90	3.78	4.48	6.99	128.78
Elmina									
16-20	121.2	91.8	29.4	3.12	0.62	0.94	1.09	1.19	20.31
21-25	118.8	92.1	26.7	3.45	0.66	0.93	1.08	1.48	20.64
26-30	121.9	93.4	28.5	3.28	0.66	0.97	1.20	1.36	17.64
31-35	112.6	84.7	27.9	3.04	0.66	1.00	1.30	1.36	12.88
36-40	112.9	86.3	26.6	3.24	0.64	1.00	1.22	1.28	19.08
41-45	109.9	82.4	27.5	3.00	0.59	0.92	1.06	1.02	18.43
Mean	697.3	530.7	166.6	19.13	3.83	5.76	6.95	7.69	108.98
Cape coast									
16-20	115.9	91.2	24.7	3.69	0.65	0.60	0.86	1.08	16.35
21-25	122.0	93.3	28.7	3.25	0.66	0.96	1.20	1.37	17.29
26-30	127.9	102.6	25.3	4.06	1.25	0.59	0.73	1.09	21.71
31-35	120.2	92.2	28.0	3.29	0.56	1.00	1.30	1.00	18.06
36-40	132.0	103.9	28.1	3.70	0.54	0.72	0.81	1.17	17.63
41-45	124.9	99.2	25.7	3.86	0.58	0.54	0.63	1.15	16.00
Mean	742.9	582.4	160.5	21.85	4.24	4.41	5.53	6.86	107.04

tion between hydrothermal (less than 2) and hydrogenic (greater than 2) effects on sediments and REE contents in the coastal sediments. The values of Ce/La in sediment ranged from 1.0-1.37. This range of values are similar to that of average shale and crust materials, suggesting low enrichment of cerium because of its potential reduction from insoluble Ce(IV) to soluble Ce(III). La/Yb values varied from 16.0 - 25.5 indicating enrichment of heavy rare earth elements compared to light rare earth elements in sediments. Insignificant enrichment of light rare earth elements may be attributed to a rise in the complexation of rare earth elements with marine water carbonate ligands with in-

creasing proton number [4].

The pattern of the chondrite – normalized rare earth elements of the coastal core sediments collected at the central part of Ghana was distinguished by higher light rare earth elements compared to heavy rare earth elements except for Tm, Tb, Eu and Ho and this is due to the influence of covering sediments close by an outlet for fluid rare earth element constituent, rock and hot-water interaction (Figure 4).

4. CONCLUSION

The current work analytically examined the efficiency

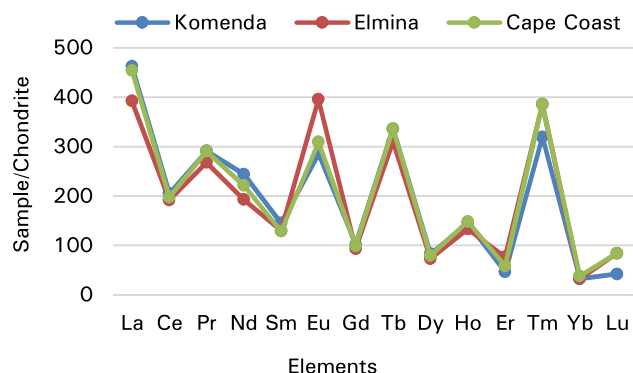


Figure 4. Chondrite-normalized rare earth element pattern of Komenda, Elmina and Cape coast samples

of the k_0 -NAA technique for calibrating rare earth elements in IAEA soil 7 reference material samples. The concentrations of REEs from lanthanum to lutetium were determined in three locations collected at the coast of the central part of Ghana. The concentrations of LREEs in the sediment samples were higher especially La and Ce. There are similar trends of Fe normalized enrichment factor for La and Yb and ytterbium (Yb) was significantly enriched than lanthanum (La). Thus, the distribution pattern of REE in core sediment samples could be used as a non-steady-state tracer in this creek. Overall, chondrite-normalized rare earth element pattern trends are similar in all the stations and this indicated that the sediment samples were from similar sources.

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