RARE EARTH ELEMENT DISTRIBUTION PATTERNS IN THE SOILS AROUND THE NIGERIAN RESEARCH REACTOR-1, (NIRR-1) IN ZARIA, NIGERIA

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Abstract

The Rare Earth Elements (REEs) are useful geochemical markers and retain group coherence in their geological environment. Here, the pattern of six REEs (La, Sm, Eu, Dy, Yb and Lu) determined by Instrumental Neutron Activation Analysis (INAA) of soils around the Nigeria Research Reactor-1 (NIRR-1), Zaria Nigeria is reported. REE distribution patterns for the soils covered in the investigation were identical, in other words exhibiting coherent fractionations from Low REE to High REE. The overall fractionation of the REEs for earth soil is depicted by the slope of the $(REE)_{cn}$ plot by the $(La/Lu)_{cn}$ in ratio. The REE plots obtained showed enrichment of $(LREE)_{cn}$ as against the $(HREE)_{cn}$, which is the usual trend for all geological matrices. The REE chondrite-normalized plots showed both Europium and Dysprosium anomalies for the upper plain and flood plain sites with the latter exhibiting the characteristic features of fadama wet land.

Keywords: Soil, Instrumental Neutron Activation Analysis, Rare Earth Elements, Chondrite –Normalized

Introduction

Soils are the main reservoirs for artificial radionuclide emanating from precipitation and they act as media for transfer of elements to biological systems (IAEA, 1990) or are critical environments where rock, air and water interface, most often subjected to a number of pollutants due to different anthropic activities (industrial, agricultural, transport, etc). They can also be a source of pollution to surface and ground waters, living organisms, sediments, and even oceans (Facchinelli, *et al*., 2001)**.** As the organic matter undergoes transformation by leaching, alteration, partitioning, microbial activity, weathering, crystallization, etc; from digenesis through late metamorphism, the rare earth elements (REEs) become uniquely altered, retaining some group peculiarities, depending on the nature of the geochemical environment (Ewa *et al*., 1996). Although the concentrations of most elements in the soils tend to vary with time, the rare earth elements (La, Sm, Eu, Dy, Yb, and Lu) remain unique, exhibiting group peculiarities in their environment through the geological periods (Taylor, 1964, Ewa *et al*., 1996; Funtua *et al*., 1999). REEs are representatives of similarity in sample composition and their patterns could be used as geochemical fingerprints of soil from different sites (Funtua *et al*., 1999).

This work was aimed at investigating the concentration of major, minor and trace elements from the soils around the Nigeria Research Reactor-1 (NIRR-1) as a measure of assessing the extent of enrichment of the soils if it so exists and using the data obtained to investigate the patterns of REEs which are known to be stable in their geo-chemical environments, thus establishing the REEs pattern of the soil around the location of NIRR-1 facility.

Experimental

Soil samples were collected at a depth of about 30 cm from specified locations around the NIRR-1 facility. The samples weighing about 1 kg were collected, loaded in a polyethylene bag and taken to the laboratory.

The soil samples were then exposed to ambient air in a dust - free environment before drying to a constant weight for 24 hours in a monitored oven maintained at 50 ^{0}C. Each dried sample was homogenized and re-quartered after which appropriate samples (100 to 200 mg in weight) of the dried soils were loaded into Vials and heat - sealed before irradiation. The

Standard (IAEA Soil 7) that was used as a comparator was also prepared in the same manner. The re-investigation of the Coal Fly Ash 1633b which was used as quality control to validate the analytical method is shown in Table 1.

Table 1: Re-investigation of coal fly ash 1633b used as quality control. (Concentrations in ppm)

Element	**This work**	**NIST 1633b**
La	88.9 (8.66)	94
Sm	20.9 (1.07)	20
Eu	2.58 (0.453)	4.1
Dy	-	-
Yb	8.17 (0.596)	7.6
Lu	1.14 (0.11)	1.2

Samples and Standards were irradiated at the Centre for Energy Research and Training (CERT), Ahmadu Bello University, Zaria, Nigeria using NIRR-1 at a thermal flux of 1.0×10^{11} n cm^{-2} s^{-1} for short lived radionuclides and 5.0×10^{11} n cm^{-2} s^{-1} for the long lived radionuclides as reported by Jonah *et al.*, (2006). Interference free analytical γ - energy lines, as shown in Table 2, were used for peak integration for the rare earth elements.

Table 2: Nuclear data used for the determination of REEs

Elements	**Radionuclide**	**γ – Energy**	**Half – life**
La	^{140}La	1596	40.3h
Sm	^{153}Sm	103.2	46.75h
Eu	^{152}Eu	1408	13.33y
Dy	^{165}Dy	94.7	122.33m
Yb	^{169}Yb	63	32d
Lu	^{177}Lu	208.4	6.71d

Results And Discussion

Six REEs were determined in soils around the NIRR-1, Zaria, Nigeria; two (La, Sm) of them were Light Rare Earth Elements (LREE), while three (Dy, Yb and Lu) were Heavy Rare Earth Elements (HREE) and one (Eu) Mddle Rare Earth Element (MREE).

Table 3 shows the Rare Earth Elements Chondrite-Normalized '(REE)cn' values were determined for each sample. The chondrite values used for the normalization were those reported by Laul, (1984).

The abundance of REEs in the soils can be used to investigate the geochemical transformation that might have occurred in the various sample sites. The $(REE)_{cn}$ values for each sample were plotted against their corresponding ionic radii. Fig. 1, Fig. 2 and Fig. 3 shows $(REE)_{cn}$ patterns for the difference soils investigated. The REE pattern for some of these soils was identical, exhibiting coherent fractionations from LREE to HREE. The overall fractionation of REEs for each soil is depicted by the slope of the $(REE)_{cn}$ plot by the $(La/Lu)_{cn}$ ratio as presented in Table 3.

In order to obtain the REE pattern for sample sites investigated the usual plot of the $(REE)_{cn}$ against their respective ionic radii was done (Fig. 1). The normal gradient was observed for all the sites with varying degrees of fractionation as evidenced in the $(La/Lu)_{cn}$ slope (Table 3). The anomalies (Eu, Dy) were not differentiated in the mixed plot. It was therefore necessary to separate the REEs obtained from sample upland sites with respect to these from the flood-plains and was accomplished in Fig. 2 and Fig. 3. All the plots show enrichment of $(LREE)_{cn}$ as against the $(HREE)_{cn}$. This is the usual trend for all geological matrices.

REEs of upland sites: The slope of the $(REE)_{cn}$ plot for the upland sites as shown in Fig. 2 were not as steep as these in the flood plain sites. Moreover the anomalies were not uniform with some exhibiting Eu anomalies as characteristic of soil samples.

REEs of flood-plain sites: The fractionating pattern of the REEs for samples obtained from the flood plain sites remained unique. The overall fractionation given by the $(La/Lu)_{cn}$ slope for these sites were found to be identical as could be seen in the plot (Fig. 3). This is in contrast to the pattern earlier discussed for the upland sites surrounding the reactor. The explanation for this could be attributed to the geochemical environment of the flood plains characterized by high soil moisture content of the samples as noticeable with fadama wetland flood plains leading to a shift from the usual Europium anomaly commonly encountered in geological matrices to a Dysprosium anomaly. The existence of Dy anomaly is the characteristics of argillaceous clay materials found in wet-land soils (Taylor, 1964). This trend shows a clear distinction of the $(REE)_{cn}$ values of sample obtained from flood plain sites when compared with those of the upland sites.

Table 3: Chondrite normalized data of REEs for all the sites investigated

Element (Ionic radii Å)	A12	A15	B11	B12	B13	B14	AB11	CD03	CD04	CD05
La (1.13)	112.6	179.1	94.2	127.5	170.9	148.0	125.6	162.7	155.3	146.4
Sm (1.03)	38.5	53.1	34.4	42.5	49.7	42.3	42.2	49.2	46.9	39.4
Eu (1.02)	9.45	11.2	9.04	20.3	29.2	22.6	17.5	19.9	20.3	12.3
Dy (0.99)	6.57	8.19	18.4	6.74	7.97	8.78	-	9.52	7.96	-
Yb (0.95)	22.1	21.9	22.8	20.7	27.1	23.7	23.2	26.4	17.5	21.0
Lu (0.94)	18.2	22.4	19.4	27.1	23.8	23.8	18.2	25.0	19.4	17.4
(La/Lu)cn	6.19	7.99	4.86	4.70	7.18	6.22	6.90	6.51	8.01	8.41

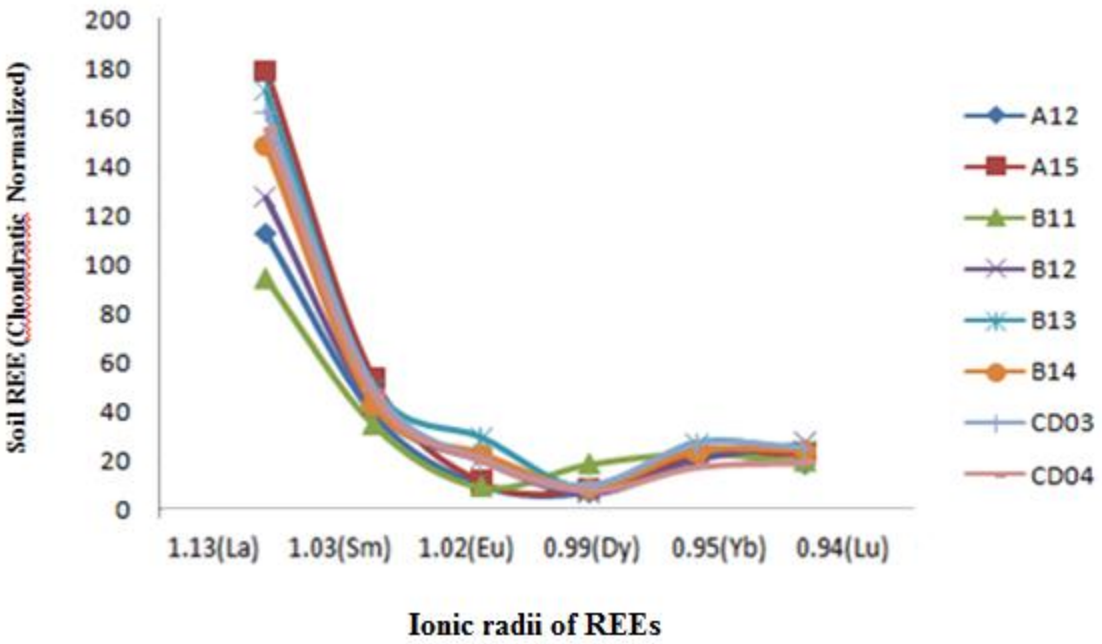

Fig. 1 Plot of soil REE for all the sites investigated

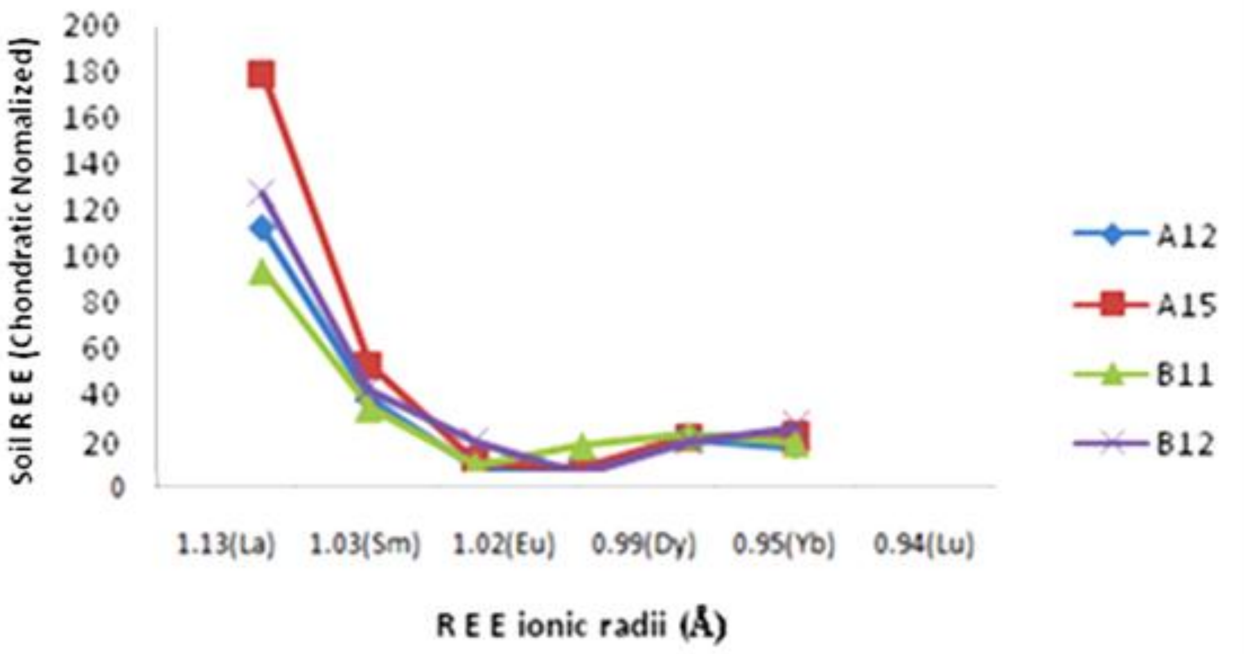

Fig. 2: REE Plot for 4 Upper Plain Sites

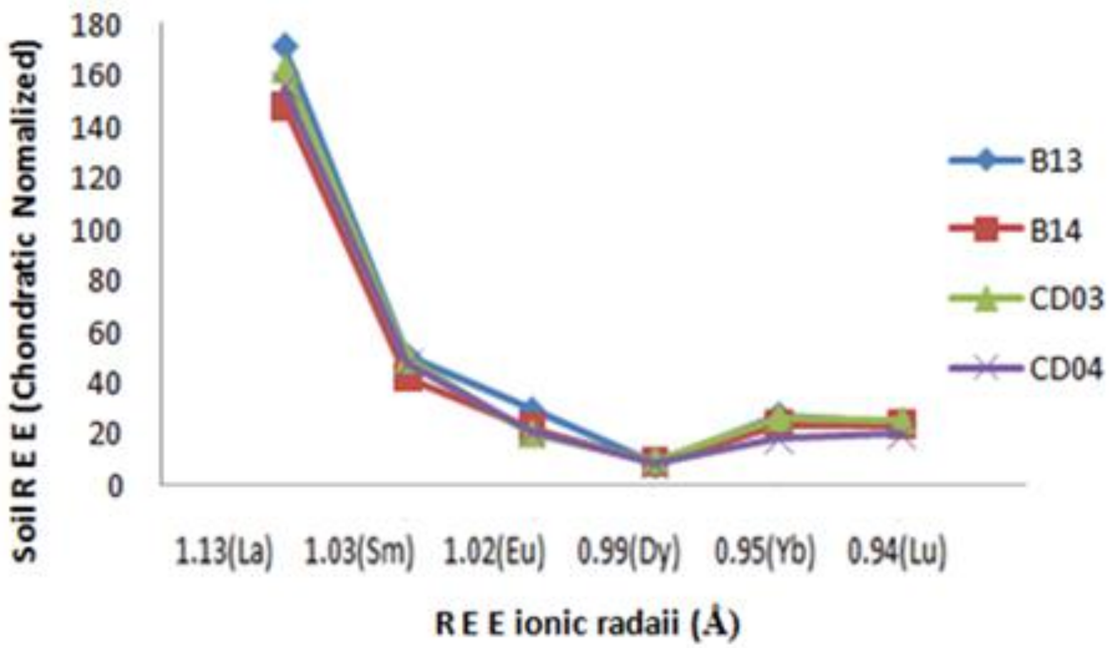

Fig. 3: REE plots for samples obtained from the Kubanni River flood sites

Conclusion

It is observed that samples at the upper plane of CERT with respect to the location of the NIRR-1 had concentrations relatively enriched than those of the lower plane. The six REEs identified are predominantly present in geochemical matrices such as the soils investigated. The REEs shows Dy anomaly for clay soils of the fadama flood plains which is a geochemical feature that this work has proved.

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