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Rare Earth Elements of Ajali Sandstone, SW, Anambra Basin in Nigeria: Implication for Soil Genesis

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ABSTRCT: The Ajali Sandstone, South-western, Anambra Basin, was studied for Rare Earth Elements (REEs), using a Phillips 45 channel Inductively Coupled Plasma (ICP) Emission Spectrometer. The standard deviation of the REEs (Dy, Er, Eu, Y, Yb, La and Nd) averages 3.5 mg/L, 0.34 mg/L, 0.32 mg/L, 3.93 mg/L, 1.96 mg/L, 4.02 mg/L and 2.24 mg/L respectively for each of the sampled locations. The REEs concentrations showed both positive and negative concentration anomalies. The enrichment or depletion of the REEs is generally attributed to their tendency to be incorporated into plagioclase preferentially over other minerals. The Ajali Formation is predominantly sand/sandstone, with clay occurring only as intercalations/thin beds of clay drapes with the increasing particle size of the sand grains, makes the rate of adsorption and distribution of REEs in the soil low, and explains the low values of REEs concentration. Soil organic matter (SOC) plays an important role in the adsorption and migration of REEs in the Ecosystems. The SOC is linearly associated with REEs Concentration as it increases with increasing content of SOC. The Ajali Sandstone studied falls in the vicinity of abandoned cropland to cropland in a lower/gentle slope region, correspondingly low in soil organic matter content and as such slow rate of distribution and migration of REEs concentrations in the Ajali Sandstone. The sesquioxides such as Fe oxides increases as REEs contents increases. The 0.46 mean value of Fe_2O_3 in the Sandstone of the area studied implies a low REEs adsorption rate and subsequently the very low REEs concentrations of the soils. The distribution of REEs within the Ajali Formation soils were grossly affected by the factors that influenced the adsorption and migration rate of the minerals during magmatic fractionation process, hence the low REEs concentration of the Sediments.

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Rare earth elements (REEs) include a series of lanthanide elements, and they have similar electronic structures and chemical properties. Two to three groups of REEs are generally distinguished into light rare earth elements (LREEs), heavy rare earth elements (HREEs), and sometimes middle rare earth elements (MREEs) based on their atomic mass and effective ion radius (Henderson, 1984; Laveuf and Cornu, 2009). REEs generally occur as trivalent ions, Ce can be also in tetravalent state, and Eu is in divalent state. REEs are widely used to investigate soil environmental change and weathering processes, and they are the powerful indicators of geochemical processes and soil development, (Mao, *et al., 2009;* Taylor and McLennan, 1985). The REE's from La to Lu (Z = 57-71) have been the basis of many geochemical studies. Most of these have considered hard rock problems but several studies have also been carried out on sediments and sedimentary rocks. Sedimentary deposits often seem to have REE distribution reflecting the different source rocks, sedimentary processes and grain size variation (Dyprik and Brunfelt, 1976; Dyprik and Brunfelt, 1979 and Haskin, *et al.*, 1966). Goldschmidt (1954) suggested that during the processes of weathering soil formation and sedimentation, all REEs are concentrated in the hydrolysate minerals (clays, and shale components, bauxite minerals and oxidates of iron and manganese). It is generally considered that weathering and erosion results in only minor amounts of REE going into solution for only a few percent of the REE entering the ocean are dissolved (Fleet, 1984; Fleet *et al.,* 1976; Martin *et al.*, 1976). The bulk of the REE is eroded material is contained in clays and Roaldset and Rosengvist (1979) believe that much of the REE hold on loosely in the clays and are therefore available to take part in exchange reactions. Haskin *et al*., (1966) have indicated that sandstones have lower REE contents than shale. However if detrital apatite and zircon are present in abundance in the sandstone, the REEs may be a typically enriched. The overwhelming concentrations of the REE in the detrital fraction of transported material rather than the dissolved portion suggest that the REE pass from weathering to deposition almost exclusive without taking part enroute in any significant chemical processes (Fleet,

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1984). This low solubility coupled with the very similar chemical properties of the REE and their resistance to fractionation in supercrustal environment (Nance and Taylor, 1977) has resulted in the use of the REE distribution patterns to identify parental materials of supercrustally altered rocks and sediments (Nance and Taylor, 1977; Taylor and Hallberg, 1977 and Willerman and Condie, 1973).

However mobilization and fractionation of the REE can occur during surface alteration of rocks (Balashove *et al.*, 1964; Willerman and Haskin, 1973). In humid tropical environment, chemical decomposition plays an important role in weathering and diagenetic processes, which affect redistribution of REE in the elastic sediments (Runov *et al.,* 1967).

Location of Study Area: The study area and its environs are situated in Fugar, Ayogwuiri, Auchi and Uzebba all enclosed within the Ajali Formation. The area is highly accessible with major and minor roads, together with other adjoining roots. The location map (figure 1) was generated using the GPS coordinates obtained from the field studies.

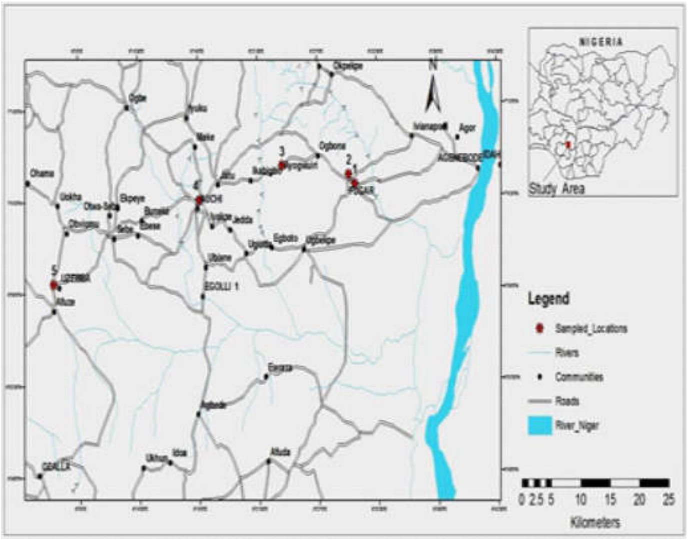

Fig. 1: Location map of study Area

Sample collection: A total of 51 samples were collected at an interval of 0.6m in 5 different locations (Fugar, Fugar II, Ayogwuiri, Auchi and Uzebba) in the South West, Ajali Formation, Anambra Basin. 10 samples were analyzed for Rare Earth Elements (REE).

Sample Treatment: Microwave assisted digestion. A mixture of 1.0 g of honey, 2.0 mL of concentrated HNO_3, 2.0 mL of 30% v/v H_2O_2, with 0.5 ml of yttrium (100.0 mg L^{-1}) as internal standard was submitted to a heating program in a closed microwave oven (Provecto Analitica – DGT 100; Campinas, Brazil) following the steps: 1 min at 320 W, 2 min at 0 W, 5 min at 320 W, 5 min at 520 W and 5 min at 740 W. The resulting solution was diluted with deionized water to 25.0 ml in a volumetric flask before to be analyzed by ICP OES.

Sample Analysis: The samples were analysed for REE using a Phillips 45 channel Inductively Coupled Plasma (ICP) Emission Spectrometer by method described in Wash *et al*., (1981). All reagents used in the experiments were of analytical grade. Deionised water (18.2 MW cm) obtained from a Milli-Q water system (Bedford, MA, USA) was used throughout. Stock solutions of all evaluated species were prepared with concentrations of 1000 mg L^{-1} in 2% v/v HNO_3, except for K, which was directly diluted in the multielementar standard solution.

Analytical calibration curves were prepared with Yttrium, as an internal standard, was used at a concentration of 2 mg L^{-1}. Only a total of 7 (Dy, Er, Eu, Y, Yb, La, Nd) REEs were determined.

RESULTS AND DISCUSSION

The results of the geochemical analyses of the REEs are sequentially presented.

Table 1, shows the standard deviation of the REEs (Dy, Er, Eu, Y, Yb, La and Nd) averages 3.5 mg/L, 0.34 mg/L, 0.32 mg/L, 3.93 mg/L, 1.96 mg/L, 4.02 mg/L and 2.24 mg/L respectively for each of the sampled locations (at Fugar, Fugar II, Ayogwuiri, Auchi and Uzebba).

Table 1: Mean Standard deviation of Rare Earth Elements.

Sample ID	**Analyte**						
	Mean standard deviation in (mg/L)						
	Dy	Er	Eu	Y	Yb	La	Nd
FG6	2.00	0.20	0.45	3.40	1.90	4.25	12.50
FG15	1.50	0.40	0.45	4.00	2.00	4.00	1.10
FGB6	7.00	0.30	0.10	4.50	2.50	4.50	1.00
FGB11	2.50	0.30	0.25	3.80	1.80	3.80	1.30
AY1	1.50	0.70	0.30	3.50	1.75	3.50	1.25
AY7	6.50	0.20	0.30	4.15	1.65	4.15	1.15
AU6	3.00	0.40	0.25	4.40	2.20	4.40	0.75
AU7	3.00	0.10	0.30	4.00	2.25	4.00	1.20
UZ2	1.00	0.50	0.45	4.10	2.10	4.10	1.60
UZ5	3.50	0.30	0.30	3.45	1.45	3.45	0.90

Key: *Dy – Dysprosium; Er – Erbium; Eu – Europium; Y – Yttrium; Yb – Ytterbium; La – Lantanum; Nd - Neodynium*

Figures 2-6 displays a positive concentration anomaly for Dysprosium (Dy), Yttrium (Y) and Latunium (La) and a negative concentration anomaly for Erbium (Er), Europium (Eu) and Ytterbium (Yb).

The enrichment or depletion of the REEs is generally attributed to their tendency to be incorporated into plagioclase preferentially over other minerals. If magma crystallises stable plagioclase, most of the Dy, Y, and La will be incorporated into the mineral, causing a higher than expected concentration, with respect to the other REE in that mineral.

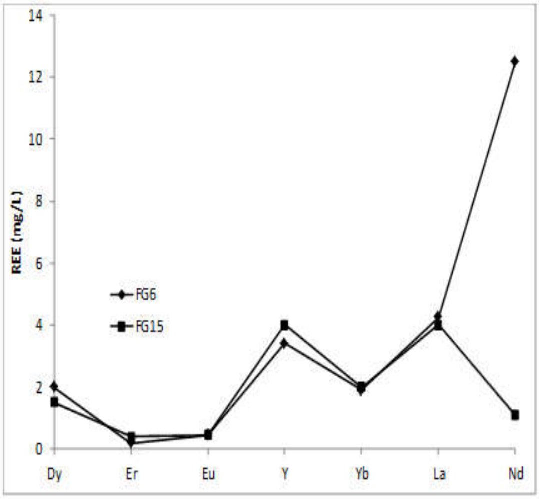

Fig. 2. REE concentrations of Ajali Sandstone at Fugar

The rest of the magma will then be depleted with the concentration of Eu, Er and Yb been lower than expected with respect to the other REEs in the magma (negative concentration anomally).

This explain the extremely low concentrations of Eu, Er, and Yb and the fairly high to high concentrations of Dy, Y, La as seen in the REE concentration plots (Figure 2-6).

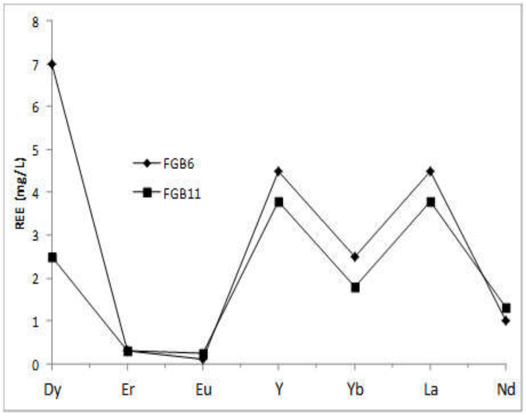

Fig. 3. REE concentration of Ajali Sandstone at Fugar II

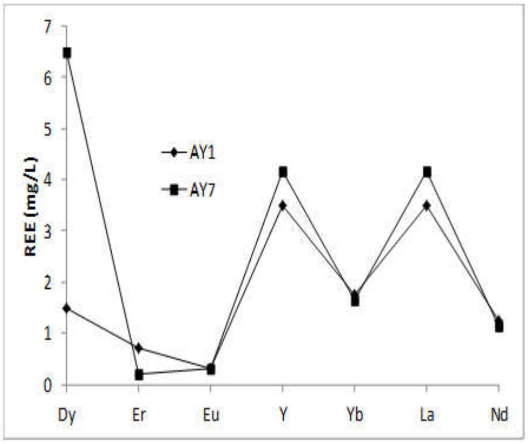

Fig. 4. REE Concentration of Ajali Sandstone at Ayogwuiri

Furthermore, this REE concentration anomaly is an indication of the provenance of the Ajali Sandstone in the area studied is likely sourced from a mafic-igneous source. Also, the formation of similar patterns of REEs concentration anomalies indicates that the Sandstone is mature, well mixed and most probably from a similar/common paleo - depositional environment. This finding corroborates with the findings of Imasuen and Imeokparia, (1992) and also in a related study on the Maturity of sediments and Ancient environment of deposition by Ilevbare and Imasuen, (2020); Ilevbare and Omodolor, (2020) respectively, the Ajali Sandstone in the study locality was reported as matured, moderate to well sort and from a fluvial paleo - environment of deposition. One main factor that influences REEs distributions in soils is clay minerals, which can adsorb the REEs (Laveuf and Cornu, 2009). Generally, REEs content increase with decreasing particle size and with increasing proportion of clay content (Rao *et al.,* (2011); Kimoto *et al.,* (2006). Ilevbare and Imasuen, (2020) ; Ilevbare and Omodolor, (2020) from their study revealed that the textural parameters show that the Ajali Sandstone are medium sand, poorly to moderately sorted, coarse to strongly coarse skewed with mesokurtic to leptokurtic grains shows a coarsening upward sequence, with dispersed intercalations of clay, been predominately sand/sandstone.

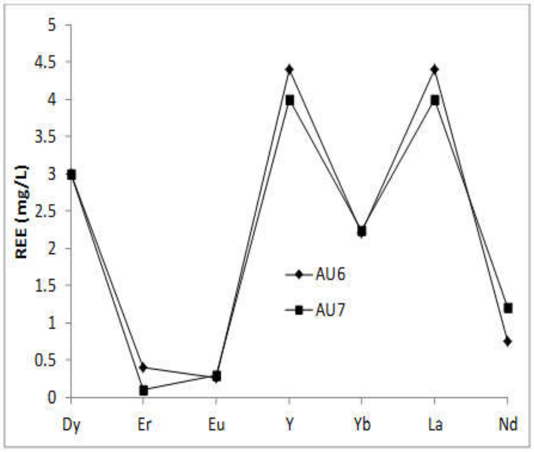

Fig. 5. REE Concentration of Ajali Sandstone at Auchi

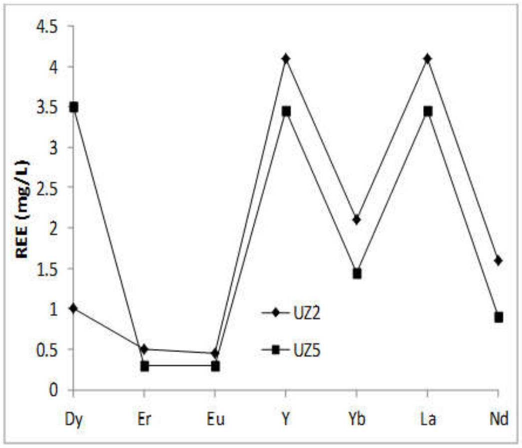

Fig 6. REE Concentration of Ajali Sandstone at Uzebba

The little or no clay within the Ajali Sandstone together with the increasing particle size of the grains, explains why the REEs of the Formation are very low, which is consistent with the already established trend by Rao *et al.,* (2011) ; Kimoto *et al.*, (2006). Soil organic matter (SOC) plays an important role in the adsorption and migration of REEs in ecosystems. The SOC contents in topsoil tends to decrease in the following order: secondary forest > shrub land > grassland > abandoned cropland > cropland, and SOC content decreases as the decreasing slope positions as follows: upper slope > middle slope >lower slope. The SOC contents were the highest in secondary forest soils, because the surface soils were covered by plant residues such as leaves and branches, and the original soil contains substantial humus, plant roots, and debris, (Wu, *et al.,* 2001; Tang *et al.,* 2003).

The SOC was positively and linearly associated with REEs Concentration as it increases with increasing content of SOC and vis-versa (Zhang, *et al*., 2019). The Ajali Sandstone studied falls in the vicinity of abandoned cropland to cropland in a lower/gentle slope region, which from the findings of (Zhang, *et al*., 2019), should be very low in soil organic matter content and as such correspondingly low REEs concentrations as evident from the results of table 1. This implies that, the SOC played a significant role in controlling REEs distribution within the Ajali Formation.

Another important factor influencing REEs distributions is the adsorption of REEs onto sesquioxides such as Fe oxides. Mihajlovic *et al.,* (2018), reported that REEs contents increases with increasing Fe oxide content (and vis-versa) and decreases with surface soils in this order: lower slope > middle slope >upper slope. Ilevbare and Imasuen, (2020), in a related study on the Ajali Sandstone, showed that the mean value of Fe_2O_3 from their table of weathering indices to be 0.46, which is extremely low, hence, low REEs adsorption rate and subsequently the very low Concentrations of the REEs within the Ajali Formation.

*Conclusion***:** This study demonstrates the distribution and influencing factors of REEs in the Ajali Formation, SW, Anambra Basin. The REE concentration anomaly is an indication of the provenance of the Ajali Sandstone in the area studied is likely sourced from a mafic-igneous source. Also, the similar patterns of REEs concentration anomalies indicates that the Sandstone is mature, well mixed and most probably from a similar/common paleo - depositional environment. All three factors (clay minerals, soil organic matter and sesquioxides) were all found to be low, indicating a low adsorption rate for the REEs minerals during magmatic fractionalization which account for the very low concentrations of the REEs in the studied area.

REFERENCES

Balashove, Yu, A; Ronov, AB, Migdisov, AA; Turanskaya, NV (1964). The effect of climate and facies environment on the fractionation of the rate of earths during sedimentation, *Geochem. Int.* 10: 995-1014.

Dyprik, H; Brunfelt, AO (1976). Rare earth elements in lower Paleozoic epicontinental and eugeosynclinical sediments from the Aslo and Tronheim Regions. S*ediment.* 23:.363-378.

Dyprik, H; Brunfelt, AO (1979). Distribution of rare earth elements in some North Atlantic Kimmeridgian Black Shales, *Nat.* 278: 339-341.

Fleet, AJ (1984). Aqueous and sedimentary geochemistry of the rare earth elements. In: P. Henderson (Editor). *Rare Earth Element Geochemistry*, Elsevier Amsterdam, 343-373.

Fleet, AJ; Henderson, P; Kempe, DRC (1976). Rare earth elements and related chemistry of some drilled southern Indian Ocean basalts and volcanogenic sediments, *J. Geolphy. Res.* 81: 4257-4268.

Goldschmidt, VM (1954). Geochemistry, Oxford University Press, Oxford, p.730.

Hallberg ROA (1976). Geochemical Method for Investigation of Palaeoredox Conditions in Sediments. Ambio Special Report, .4139- 147.

Haskin, LA; Wilderman, TR Frey, FA; Collins, KA; Keedy, CR; Haskin, MA (1966). Rare earth in sediments, *J. Geophys. Res.,* 71: 6091-6105.

Henderson, P (1984). Rare Earth Element Geochemistry: Developments in Geochemistry; Elsevier: Amsterdam, The Netherlands, 2: 510

Imasuen, OI; Imeokparia, EG (1992). REE Geochemistry of Soils of mid-western Nigeria. *AJST Series B,* 6(1): 39-48.

Ilevbare, M; Imasuen, OI (2020). Sedimentology and Maturity of Ajali Formation, Benin Flank, Anambra Basin, Nigeria. *Ife J. Sci.* 22(1): 123-135.

Ilevbare. M; Omodolor, HE, (2020). Ancient Deposition Environment, Mechanism of Deposition and Textural attributes of Ajali Formation, Western Flank of the Anambra Basin, Nigeria, Elsevier, *Case Studies in Chemical and Environmental Engineering*, https://doi.org/10.1016/j.cscee.2020.100022.

Kimoto, A; Nearing, MA; Zhang, XC; Powell, DM (2006). Applicability of rare earth element oxides as a sediment tracer for coarse-textured soils. *Catena,* 65: 214–221.

Laveuf, C; Cornu, S (2009). A review on the potentiality of rare earth elements to trace pedogenetic processes. *Geoderma,* 154: 1–12.

Mao, LJ; Mo, DW; Yang, JH; Shi, CX (2009). Geochemistry of trace and rare earth elements in red soils from the Dongting lake area and its environmental significance. *Pedosphere*, 19: 615–622.

Martin, JM; Hgdahl, O; Philipott, SC (1976). Rare earth element supply to the Ocean, *J. Geophys. Res.* 81: 3119-3124.

Mihajlovic, J; Rinklebe, J (2018). Rare earth elements in German soils—A review. *Chemosphere*, 205, 514–523.

Nance, W. Band; Taylor, SR (1977). Rare earth elements and crustal evolution II Archean sedimentary rocks from Kalgwrilie, *Australia Geochim, Cosmochim Acta*, 41: 225-231.

Rao, W; Tan, H; Jiang, S; Chen, *J (*2011). Trace element and REE geochemistry of fine- and coarse-grained sands in the Ordos deserts and links with sediments in surrounding areas. *Geochemistry*, 71: 155–170.

Roaldset, E (1979). Rare earth elements in different size fractions of a marine quick clay from Ullensaker and a till from Upper Numedal, Norway, *Clay Mineral*, 14: 229-240.

Runov, AB; Balashov, AY and Migdisov, AA (1967). Geochemistry of the rare earths in the sedimentary cycle, *Geochim. Inst.,* 4: 1-17.

Tang, J; Johannesson, KH (2003). Speciation of rare earth elements in natural terrestrial waters: Assessing the role of dissolved organic matter from the modeling approach. Geochim. Cosmochim. Acta, 67: 2321–2339.

Taylor, SR; Hallberg, JA (1977). Rare-earth elements in the Mards Calc-akaline suite: An Archaem geocgemical analogue of Andean type volcanism, *Geochim et Cosmochim Actai, 41: 1125-1129.*

Taylor, SR; McLennan, SM. (1985). The Continental Crust: Its Composition and Evolution; Blackwell: Oxford, UK, p. 312.

Wash, JN, Buckley, F; Barker, J (1981). The simultaneous determination of the rare-earth elements in rocks using conductivity coupled plasma source spectrometry, *Chem. Geol.,* 33, p.141-153.

Willerman, TR; Haskin, LA (1973). Rare earths in Precambrian sediments, *Geochim Cosmochim Act*, 37: 419-438.

Wu, Z; Jun, L; Guo, H; Wang, X; Yang, C (2001). Adsorption isotherms of lanthanum to soil constituents and effects of pH, EDTA and fulvic acid on adsorption of lanthanum onto goethite and humic acid. *Chem. Speciat. Bioavailab.* 13: 75–81.

Zhang, Q; Han, G; Liu, M; Wang, L (2019). Geochemical Characteristics of Rare Earth Elements in Soils from Puding Karst Critical Zone Observatory, Southwest China. In *Sustainability* https://www. researchgate. net/publication/ 335754544.