Adamu, L. M.

Terrigenous Inputs, Redox Shifts, and REE Partitioning in Shankodi–Jangwa Coal, Middle Benue Trough, Nigeria: Implications for Green Energy Mineral Prospecting

Department of Earth Sciences,
Kogi State University,
Anyigba, Nigeria.
Email: lukman10musa@yahoo.com

TERRIGENOUS INPUTS, REDOX SHIFTS, AND REE PARTITIONING IN SHANKODI–JANGWA COAL, MIDDLE BENUE TROUGH, NIGERIA: IMPLICATIONS FOR GREEN ENERGY MINERAL PROSPECTING

Adamu, L. M.[1]; Alege, T. S.[2]; Ochu, G. D.[1]; Odoma, A. N.[2]; Ebeh, A.[1]; Ohiemi, A. F.[3]; Etukudo, N. J.[4]; Adesina, D. E.[1]; Umar, M. U.[5]; Obaje, N.G.[5].

[1]Department of Earth Sciences, Kogi State University, Anyigba, Nigeria.
[2]Department of Geology, Federal University Lokoja, Kogi State, Nigeria.
[3]Department of Geosciences, Confluence University of Science and Technology Osara, Kogi State, Nigeria.
[4]Department of Geology, Akwa Ibom State University, Mkpat Enin, AKS, Nigeria.
[5]Department of Geology, Ibrahim Badamasi Babangida University, Lapai, Niger State, Nigeria.
Email: lukman10musa@yahoo.com
[Date received: April 2025. Date accepted: June 2025]

ABSTRACT

This study investigated the concentration, distribution, and modes of occurrences of rare earth elements in coal from the Middle Benue Trough, northcentral Nigeria. This basin comprise one coal bearing Formation i.e. Awgu Formation. Using inductively coupled plasma mass spectrometry (ICP-MS), we analysed 28 coal samples from the Awgu Formation. Results indicated that the total REE concentrations (REE) were similar to REE-enriched shales, running as high as 110.01 ppm. The distribution patterns show LREE enrichment (LREE/HREE = 2.78–9.41) with positive Eu anomalies and suboxic Ce/Ce signatures, suggesting terrigenous input and redox shifts during deposition. Low LREE/HREE ratios and negative Ce anomalies imply a robust organic connection of REEs and little oxidative breakdown. These results identify the REE signature as B-type, suggesting stable provenance with no diagenetic change. The findings also highlight intricate depositional patterns in the Turonian–Santonian phase of the Benue Trough, hence stressing the impact of volcanic ash and hinterland weathering. Through the combination of trace element geochemistry and stratigraphic context, this study offers significant new information on the modes of occurrence and extraction potential of REEs in Nigerian coals. In addition to supporting the environmental viability of coal-based REE extraction in sub-Saharan Africa, the implications extend beyond energy transition plans, positioning Nigeria as a stakeholder in the geopolitics of essential minerals.*

Keywords: Coal; rare earth elements (REE); Awgu formation, Nigeria

1.0 INTRODUCTION

A key energy source and industrial feedstock, coal is the result of intricate biogeochemical processes taking place in ancient peat-forming settings. Despite its widely acknowledged commercial value, coal also preserves a unique geochemical record of the paleoenvironmental, paleoclimatic, and geodynamic conditions that shaped its creation. This duality - economic relevance combined with stratigraphic memory - positions coal as a topic of significant geological and technological interest. Rising in importance in coal research is the presence of rare earth elements (REEs), a collection of 17 chemically related metals that includes the lanthanides, scandium, and yttrium. Due to their remarkable magnetic, catalytic, and luminescent qualities, these elements support many modern technologies, including digital devices, defence systems, aerospace parts, high-performance magnets, and renewable energy sources (Hower et al., 2015; Dai et al., 2016). REEs are usually classified into light (LREEs: La–Sm ± Eu) and heavy (HREEs: Gd–Lu + Y) based on their geochemical behavior governed mostly by ionic radius, redox state, and volatility - with yttrium often grouped with the latter owing to its close ionic resemblance to holmium (Bau, 1996; Seredin & Dai, 2012). China now controls world REE output, producing almost 90% of the total (Department of Energy, 2017). This exclusivity has motivated world searches for substitute supplies. Among the most promising of these are coal seams and coal combustion byproducts (Seredin & Dai, 2012; Hower et al., 2015). Particularly, some coals have shown unusually high levels of REEs, which has led to research on their possible economic recovery and strategic use (Dai et al., 2016; Lin et al., 2017; Arbuzov et al., 2019; Mishra et al. 2019). Since then, other studies - mostly in China, Russia, and the United States have investigated the content, mineralogical relationships, and depositional sources of REEs in coal (Wenhui et al., 2000; Dai et al., 2006; Wen et al. 2024). Results imply that REEs exist in several forms, including inorganic carriers (such as phosphates, clays, and carbonates) and organic materials (Finkelman et al., 2018). Finkelman and colleagues, for example, discovered that in bituminous coals, more than 70% of LREEs are bound in phosphates, whereas low-rank coals tend to host most of the REEs in clay material. Both the leachability of REEs and the creation of economically feasible extraction procedures are greatly influenced by the host mineral's character. Although worldwide study on this topic has advanced significantly, the African continent especially Nigeria remains under-represented. Particularly in the Middle Benue Trough, a sedimentary basin of tremendous geological complexity and commercial potential, Nigeria holds large but underexplored coal reserves. Though interesting geological analogies with more thoroughly researched coal basins elsewhere, the Shankodi–Jangwa coalfields inside this trough have not yet been methodically assessed for their REE potential. Globally, volcanic ash inputs, sedimentary origin, depositional redox conditions, and post-depositional modification have all been connected to REEs in coal (Seredin et al., 2013; Liu et al., 2019). Researchers have often noticed that when there are clear signs of low europium levels showing that the source rocks are felsic there is a strong link between the amount of REEs and the ash produced in places like Russia's Zyryanka Basin. Similar revelations have come from Bulgaria (Eskenazy, 1987, 2009), Nova Scotia (Birk & White, 1991), and Kentucky (Hower et al., 2015). Though India is the second-largest coal producer in the world, research on the REE concentration of its enormous Gondwana coals has only lately picked up speed (IEA, 2018). REEs help scientists learn about where coal comes from and its potential as a valuable mineral. Their similar chemical behaviour in various geological situations allows researchers to piece together how and where the coal was formed, helping to understand the development of the area. Their fairly consistent chemical behaviour under different geological contexts lets one reconstruct depositional environments and thereby understand basin evolution. Furthermore, one cannot ignore the environmental effects of REEs in coal. These factors can create environmental problems during mining, burning, and waste disposal, as Baba and Kaya (2004) and Hower et al. (2020) point out, hence highlighting the importance of combined environmental and resource evaluations.

Amidst mounting anxiety about worldwide REE supply chains, Nigeria's underused coal reserves could be a major untapped resource. This study aims to close the information gap by reporting fresh data on the concentration, distribution, and mineralogical modes of REEs in coals from Jangwa/Shankodi, Middle Benue Trough, North-central Nigeria. This study aims to find out which minerals contain REEs and understand how they are affected by geological factors using inductively coupled plasma mass spectrometry (ICP-MS). Apart from its role in worldwide REE resource growth, this study also seeks to improve knowledge of sedimentary processes in the Benue Trough and to guide green economy policies by means of sustainable use of vital minerals in African coals.

2.0 GEOLOGY AND STRATIGRAPHY OF THE MIDDLE BENUE TROUGH

Obaje (2009) claims the Middle Benue Trough runs northeastward to a line linking Bashar and Mutum Biyu. This border shows the southern edge of the Gombe and Keri-Keri Formation, where the older layers of the Upper Benue Trough change sideways (Offodile 1976; Fig. 1). Though there are no detailed geological maps of the northeastern area of the Middle Benue Trough , the region just south of Bashar was included in a photogeological map (Obaje 2009; Obaje 2019; Patrick et al. 2013; Adamu et al. 2020, 2022a, 2022b, 2023, 2024a, 2024b). Usually, people undervalue the Middle Benue Trough. Offodile (1976), Offodile and Reyment (1977), and Nwajide (1985) provided maps of the Lafia-Keana-Awe area in the Makurdi neighbourhood. Among many others, Reyment (1965), Kogbe (1976), Offodile (1976), Petters (1982), Petters and Ekweozor (1982), and Obaje et al. (2020); Udo et al. (2020, 2023a, 2023b), Adamu et al. (2023, 2024a, 2024b) produced thorough stratigraphic descriptions of sediments in the Middle Benue Trough. The geologic sequence in the Middle Benue Trough is shown in Fig. 2. The Albian Asu River Group of Offodile (1976) and Nwajide (1990) hold the Middle Benue Trough's oldest marine deposits (Obaje et al. 2004; Abubakar et al. 2006; Adamu et al. 2023, 2024a, 2024b). Allix et al. (1997) and Brunet et al. (1989) refer to it as the Albian deposits, comprising the fossiliferous Arufu, Uomba, and Gboko Formations. Reyment and Dingle (1987) claim that this time period might show minor regression, possibly caused by a compressional event. The regressive Cenomanian-Turonian Awe and Keana Formations (Murat 1972) cover these areas. From the late Cenomanian to the early Turonian, the Benue Trough saw notable transgression that eventually suggested a link between the Tethys Sea to the north and the Gulf of Guinea to the south (Zaborski, 2000). Beneath the Awe and Keana Formations lie the marine facies of the Eze-Aku Group and the Awgu Formation, deposited until the Santonian period (Petters, 1982). Worldwide plate reorganisation caused all pre-Santonian strata to fold and rise during the mid-Santonian period (Guiraud & Bosworth 1997). Before a lot of volcanic activity began in the Tertiary period, the Lafia Formation, which is the only side layer matching the post-Santonian strata (Campanian-Maastrichtian) in the Benue Trough, finished being deposited in the Middle Benue Trough.

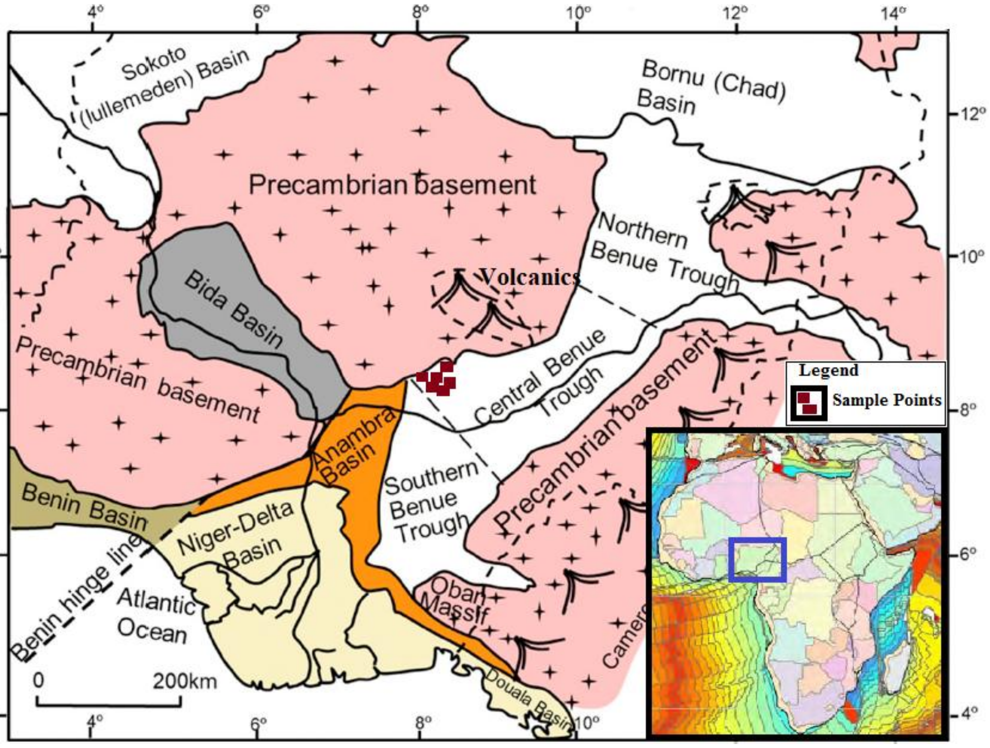
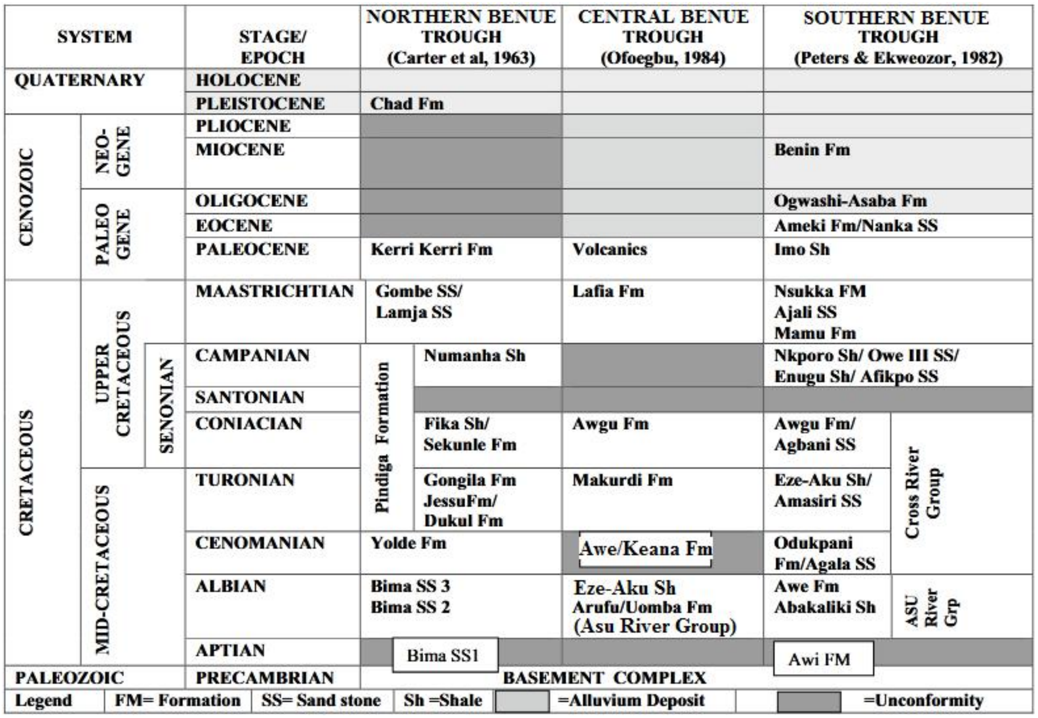


Fig. 1: Map of Nigeria showing regions covered by sedimentary and basement rocks and sampling locations (adapted from Benkhelil, 1989; Edegbai et al., 2019)



SYSTEM			STAGE/ EPOCH	NORTHERN BENUE TROUGH (Carter et al, 1963)		CENTRAL BENUE TROUGH (Ofoegbu, 1984)	SOUTHERN BENUE TROUGH (Peters & Ekweozor, 1982)	
QUATERNARY			HOLOCENE					
			PLEISTOCENE	Chad Fm				
CENOZOIC	NEO-GENE		PLIOCENE					
			MIOCENE				Benin Fm	
	PALEO GENE		OLIGOCENE				Ogwashi-Asaba Fm	
			EOCENE				Ameki Fm/Nanka SS	
			PALEOCENE	Kerri Kerri Fm		Volcanics	Imo Sh	
CRETACEOUS	UPPER CRETACEOUS		MAASTRICHTIAN	Gombe SS/ Lamja SS		Lafia Fm	Nsukka FM Ajali SS Mamu Fm	
		SENONIAN	CAMPANIAN	Pindiga Formation	Numanha Sh		Nkporo Sh/ Owe III SS/ Enugu Sh/ Afikpo SS	
			SANTONIAN					
			CONIACIAN		Fika Sh/ Sekunle Fm	Awgu Fm	Awgu Fm/ Agbani SS	Cross River Group
	MID-CRETACEOUS		TURONIAN		Gongila Fm JessuFm/ Dukul Fm	Makurdi Fm	Eze-Aku Sh/ Amasiri SS	
			CENOMANIAN	Yolde Fm		Awe/Keana Fm	Odukpani Fm/Agala SS	
			ALBIAN	Bima SS 3 Bima SS 2		Eze-Aku Sh Arufu/Uomba Fm (Asu River Group)	Awe Fm Abakaliki Sh	ASU River Grp
			APTIAN	Bima SS1			Awi FM	
PALEOZOIC			PRECAMBRIAN	BASEMENT COMPLEX				
Legend	FM= Formation	SS= Sand stone	Sh =Shale	▨ =Alluvium Deposit			■ =Unconformity	

Fig. 2: The stratigraphic sequence of the Benue Trough of Nigeria; the red boxes indicate the coal bearing formations (modified after Ehinola, 1995; Obaje, 2009)

3.0 MATERIALS AND METHODS

3.1 Coalfield Site, Sampling and Sample Preparation

Twenty-eight coal outcrop samples from the Awgu Formation coal exposed along the bank of River Dep in Jangwa/Shankodi near Obi were gathered in the Middle Benue Trough following the methods described in Adamu and Ayuba (2019). Proportional stratified random sampling provided the coal samples investigated in this work. The modest amounts of the samples used in this study result from the lack of road networks and insecurity caused by bandit activity in several areas of the Middle Benue region. To get fresh and representative samples, the sampling technique called for gathering coal sample fractions from each seam depending on band (lithotype) thickness. The whole seam's thickness ranged from 20 cm to 150 cm. At every sampling site, we scraped off the coal bed surfaces before lithological description and sample collection. Next, we packaged approximately 200 g of each coal into zip-locked polythene bags and transferred it to the laboratory for analysis. The coals were processed using the ASTM D-2013 standard (ASTM D2013/D2013M-12, 2012) guidelines. Before splitting with a sample riffler, a hammer mill crushed the samples to lower the particle size below 2.36 mm (mesh size -8). The ground and separated crushed samples were then split from the same sections of the complete sample into the <20-mesh and <60-mesh fractions. Every sample is represented by the top sizes of the <20-mesh and <60-mesh samples. We ground the 60-mesh fraction before the geochemical study.

3.2 ICPMS Analysis

Using Inductively Coupled Plasma Mass Spectrometry (ICPMS) at the ALS Geochemical Laboratory in Vancouver, Canada, we analysed the chemical makeup of 28 coal samples from the Awgu Formations, looking at rare earth elements. Each sample, weighing between 50 and 100 grams, was ground in a clean agate ring mill into small chips of 2-4 mm to avoid contamination before the analysis. Fifty to one hundred grams of each chosen sample were ground in a correctly cleaned agate ring mill and reduced to chips between 2 and 4 mm in size before being subjected to whole rock geochemical analysis, thereby preventing contamination. Heated to 980°C for 30 minutes, a graphite crucible holding 0.2 g of major element analysis samples was filled with the combination of 1.50 g of $LiBO_2/Li_2B_4O_7$ flux. The remaining material was then dissolved in 5% HNO_3 (distilled water diluted with ACS grade nitric acid). Replicate studies show that errors for significant elements fall between 1 and 2%. To study trace and rare elements over 48 hours, 50.0 mg of each sample was mixed in a tightly sealed Teflon jar on a hot plate at about 150°C with 3.0 ml of concentrated HF, 1.0 ml of concentrated HNO_3, and 1.0 ml of concentrated $HClO_4$. After drying, 1% HNO_3 in 60.0 ml was used to extract the solution. The findings for the traces and rare earth elements are correct to within five per cent. Using chemicals and a microwave to leach off elements in both their inorganic and organic states requires digesting the coal samples. The bombs were cleaned with 10 ml of 55% HNO_3 acid and 1 ml of 30% H_2O_2. Two stages of leaching occurred; the first used the most pure reagent in a ratio of 5 ml of 65% HNO_3 + 3 ml of 30% H_2O_2 at a temperature of 120°C. Digestion at 140°C in the second phase used 2 ml of 65% HNO_3 and 1 ml of H_2O_2. The solution was examined using ICP-MS (Perkin Elmer NexION x series) to determine the sample concentration percentage.

4.0 RESULTS AND DISCUSSION

4.1 Rare Earth Elements (REEs) Content and Distribution Patterns in Jangwa/Shankodi Coal

Often linked with high-tech sectors, Rare Earth Elements (REEs) can be found in coal and offer insightful analysis of its geological past, environmental consequences, and possible commercial value. Examining REEs in coal composition can serve to inform resource management, evaluate environmental concerns, and deepen our knowledge of coal creation and use. Table 1 and Fig. 3 display the characteristics of light rare earth elements (LREE) like Ce, Eu, La, Nd, Pr, and Sm, heavy rare earth elements (HREE) such as Er, Dy, Gd, Ho, Lu, Tb, Tm, Yb, and Lu, and how the amounts of LREE compare to HREE. The REE is much lower than the global average (68.5 mg/kg) and Chinese coals (137.9 mg/kg) (Ketris and Yudovich, 2009; Dai et al., 2012a). The specific types of REE found in coal deposits might be linked to processes like land-based material contributions, volcanic ash, water movement, and heat from the earth. Jangwa/Shankodi coals contain more REE than average Chinese coals, far more than US coals and normal coals around the world, and about the same as North American shales. The concentration of light rare earth elements is higher than that of heavy ones, consistent with the normal distribution of rare earth elements in coals (Dai et al. 2006; Dai et al. 2003; Dai et al. 2006). The higher amount of light rare earth elements in the Earth's crust and their ability to form soluble complexes likely explain why there are more light rare earth elements compared to heavy ones. The studied coal samples showed LREE/HREE levels between 0.84 and 0.87, far lower than the 41.16 and 43.24 of the typical coals from China and North China. Generally speaking, low LREE/HREE is a sign of the organic connection of HREE in peat and low-rank coals, which is still extant. All the coal samples tested had lower levels of LREE than the PAAS curve, indicating they were lacking in it, as shown in Fig. 3. This result suggests a reduced trace element content compared to PAAS. Cerium anomaly (Ce/Ce*) helps one to identify the palaeo-depositional environment. A ratio called Ce/Ce* helps determine the redox status of cerium (Ce) in a geological sample. It compares the observed cerium concentration (Ce) to the predicted concentration, depending on the behaviour of cerium in certain oxidation states. Values above 1 (Piper 1974) suggest oxidising conditions (Piper 1974; Milodowski and Zalasiewicz 1991; McDaniel et al. 1994). Roughly under 1, the Ce/Ce* values in the coal samples point to a suboxic depositional setting.

Figure 3 shows the distribution patterns of rare earth elements in Jangwa/Shankodi coal. Figure 3 clearly displays one type of REE distribution pattern. La-Lu's slope is low and glacis. Though the vale of Ce is unclear, it suggests a Ce discrepancy; the vale of Eu, on the other hand, is quite obvious with a small to medium "ʌ" shape and obvious Eu discrepancy. Fig. 1 shows that ΣREE is 110.01 ppm, LREE/HREE = 2.78 to 9.41 (avg. 4.07), positive europium and cerium anomalies - Eu* = 1.0 - 2.74 (avg. 1.65), Ce* = 0.49 - 1.10 (avg. 0.71). The study shows that the REE distribution patterns of the Late Turonian to Early Santonian Jangwa/Shankodi coal are B-type (Dahua et al., 2008). The distribution patterns are similar (Dahua et al. 2008; Wen et al. 2024), suggesting that the coals probably formed in the same place and have a similar background, and that the process of diagenesis did not affect the separation of the REE.

Sample ID N=28	LAWG 01	LAWG 03	LAWG 05	LAWG 07	LAWG 09	LAWG 11	LAWG 15	Average
Eu	0.11	0.23	0.12	0.30	0.21	0.30	1.51	0.40
Gd	0.33	0.40	0.21	0.41	0.34	0.51	0.60	0.40
Tb	0.07	0.12	0.04	0.20	0.17	0.31	0.46	0.20
Dy	0.32	0.50	0.15	0.54	0.48	0.75	1.02	0.54
Ho	0.08	0.15	0.05	0.20	0.16	0.30	0.57	0.22
Er	0.10	0.23	0.07	0.25	0.20	0.28	0.45	0.23
Tm	0.02	0.02	0.02	0.04	0.03	0.04	0.07	0.03
Yb	0.20	0.30	0.16	0.31	0.25	0.35	0.42	0.28

Lu	0.12	0.30	0.12	0.20	0.28	0.40	0.49	0.27
La	0.73	1.24	0.51	1.52	1.22	2.13	9.61	2.42
Ce	1.61	3.13	1.15	3.27	2.48	4.45	22.88	5.57
Pr	1.02	0.52	0.40	0.52	0.45	0.73	1.70	0.67
Nd	0.34	2.30	0.71	1.95	1.33	2.41	13.70	3.35
Sm	5.45	0.81	0.22	0.70	0.41	0.80	4.72	1.14
ΣREE	4.10	10.25	3.93	10.41	8.01	13.76	58.20	15.72
ΣLREE	1.35	8.00	2.99	7.96	5.89	10.52	52.61	13.15
ΣHREE	1.35	2.25	0.94	2.45	2.12	3.24	5.59	2.56
ΣLREE/ ΣHREE	3.04	3.56	3.18	3.25	2.78	3.25	9.41	4.07
ΣHREE/ ΣLREE	0.33	0.28	0.31	0.31	0.36	0.31	0.11	0.29
Ce/Ce*	0.58	0.76	0.49	0.72	0.65	0.69	1.10	0.71
Eu/ Eu*	1.00	1.24	1.71	1.71	1.72	1.44	2.74	1.65

Table 1. Rare Earth Elements (ppm) and ratios of some trace and rare earth elements normalized values of Awgu Formation coal in the Middle Benue Trough

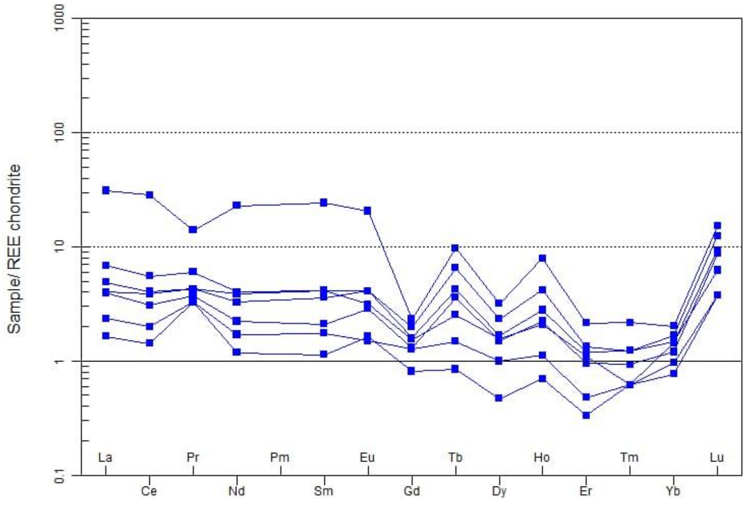


Fig. 3: Distribution pattern of rare Earth elements in the studied Awgu coal

4.2 Modes of Occurrence of Rare Earth Elements in Awgu Coal

Usually, three ways rare earth elements in coal exist are thought to be organic, independent mineral, and isomorphism (Palmer et al. 1990; Dai et al. 2005; Dai et al. 2003; Dai et al. 2002). According to detailed studies by Dai et al. (2005), Dai et al. (2003), and Dai et al. (2002), rare earth elements mostly exist in a silicate form, with very little that can dissolve in water or be exchanged. Different sedimentary settings affected the fractionation of rare earth elements in coal, while the same sedimentary setting affected the fractionation of rare earth elements in various lithologies (mostly coal, roof and floor) (Dai et al. 2008; Vivek et al. 2019). The modes of occurrence of rare earth elements are classified into six states-water-soluble state, exchangeable state, carbonate state, organic state, silicate state, and sulphide state-based on the approach developed by Dai et al. (2006) and Dai et al. (2005). Table 2 shows the procedure of sequential chemical extraction. Results of the stepwise chemical extraction of a coal sample from the Late Turonian to Early Santonian Awgu Formation were shown in Table 3. Rare earth elements primarily occur in silicate form, followed by organic matter, with a relatively low concentration in water-soluble and exchangeable states. The findings are consistent with several reported data, indicating that detrital material is quite significant in the modes of occurrence of rare earth elements in coal (Finkelman, 1993; Dai et al., 2006; Dai et al., 2006; Dai et al., 2008; Dahua et al., 2008; Kopobayeva et al., 2022).

5.0 CONCLUSION

The present investigation of the Shankodi–Jangwa coals of the Middle Benue Trough uncovers a distinctive and underappreciated resource environment under Nigeria's stratified crust. Through thorough geochemical investigation - especially via ICP-MS - the study has uncovered a REE-enriched coal profile with amounts comparable to those of widely acknowledged metalliferous shales. LREE enrichment patterns, unique europium anomalies, and redox-sensitive cerium signatures expose a complicated interaction over the Turonian-Santonian interval between terrigenous input, volcanic ash fallouts, and changing depositional chemistries. Geochemical leftovers of palaeoenvironmental memory today preserve this interaction in coal seams. These results have significant consequences for the green energy transition that go far beyond their geological relevance. The REE partitioning shows stable provenance with little diagenetic overprint - qualities that promote extractive feasibility. More importantly, the organic links between HREEs and suboxic depositional signatures reinforce the deposits' environmentally benign character, which makes them attractive from an ecological as well as economic point of view. Framed in the framework of global REE geopolitics, this paper not only validates Nigeria's untapped potential as a consistent player in the vital minerals arena but also charts a fresh path for sustainable resource exploitation in sub-Saharan Africa. By aligning the geological knowledge of REE occurrence with present strategic mineral demands, this study transcends academic significance and enters the realm of national politics and international energy diplomacy. Ultimately, the Shankodi-Jangwa coals represent dormant sources of green economic potential rather than only fossilised carbon. To release them, though, will require a coordinated political, technological, and scientific will endeavour. This basis is a crucial initial step in that way.

Table 2: The chemical occurrences and extraction methods of REEs Number Modes of occurrence

Number	Mode of occurrence	Extraction
I	Water soluble state	4g coal sample + 30ml water, 25°C, 24hours
II	Exchangeable state	Residue+30ml NH_4AC, 25°C, 24hours
III	Carbonate state	Residue of II+1.47g/cm^3 $CHCl_3$, sinking+10ml 0.5%HCl, 20min
IV	Organic state	Residue of II+1.47g/cm3 CHCl3, floating dried at 40°C, 1:1 HNO3 and HClO4 added, 5hours
V	Silicate state	Residue of III+2.89g/cm3 CHBr3, floating+1:1 HNO3 and HF, 5h
VI	Sulfide state	Residue of III+2.89g/cm3 CHBr3, sinking+1:1 HNO3, 5hours

Table 3: Recovery of sequential chemical extraction experiments for a Late Turonian to Early Santonian Awgu Formation (%)

Modes of occurrence	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	LREE	HREE	REE
Water soluble state	0.13	0.05	0.06	0.10	1.13	1.17	0.37	2.81	0.18	0.54	0.73
Exchangeable state	0.09	0.07	0.11	0.22	1.15	1.17	0.80	2.76	0.2	0.59	0.80
Carbonate state	2.97	4.36	5.64	7.29	7.97	9.28	30.97	27.80	3.53	8.50	12.03
Organic state	2.82	2.07	3.0	4.19	9.10	13.96	13.09	13.90	2.65	5.12	7.76
Silicate state	75.1	76.16	72.10	70.0	63.67	65.28	51.40	47.30	44.62	20.49	65.11
Sulfide state	19.88	16.27	19.01	18.05	17.15	8.24	4.37	5.66	11.29	2.28	13.57

Declaration of Competing Interest: We have nothing to declare

6.0 REFERENCES

1. Abubakar, M. B., Obaje, N. G., Luterbacher, H. P., Dike, E. F. C., & Ashraf, A. R. (2006). A report on the occurrence of Albian-Cenomanian elaterbearing pollen in Nasara-1 well, Upper Benue Trough, Nigeria. Journal of African Earth Sciences, 45(3), 347–354.
2. Adamu, L. M., & Ayuba, R. (2019). Guidelines for Geological Field Mapping of Basement and Sedimentary Terrain: With Examples from the Basement Rocks and Sedimentary Basins of Nigeria. Ahmadu Bello University Press, Zaria. ISBN: 978-978-8543-63-3.
3. Adamu, L. M., Andongma, W. T., Jiriko, N. G., Mazadu, D. B., Shinkafi, F., & Mohammed, D. A. (2022). A bivariate statistical analysis for coal exploration within parts of the Anambra Basin in Nigeria. Spatial Information Research. https://doi.org/10.1007/s41324-022-00440-x
4. Adamu, L. M., Obaje, N. G., Adeoye, J. A., Oladimeji, G. R. (2024b). Litho-Petro-Facies studies of the Cenomanian Awe/Keana sandstone, Middle Benue Trough, Nigeria: Implications for palaeodepositional environment and preliminary reservoir assessment. Science Forum (Journal of Pure and Applied Sciences), 24(2024), 1–34.
5. Adamu, L. M., Obaje, N. G., Adeoye, J. A., Oladimeji, R. G., & Yusuf, I. (2024a). Trans-Saharan seaway connection between the south Atlantic and the Tethys Sea during the Coniacian – Turonian: Evidence from bibliographical synthesis, field mapping, and seismic interpretation. Geosystems and Geoenvironment, 3(2024), 100243.
6. Adamu, L. M., Obaje, N. G., Adeoye, J. A., Oladimeji, R. G., & Yusuf, I. (2024). Trans-Saharan seaway connection between the south Atlantic and the Tethys Sea during the Coniacian – Turonian: Evidence from bibliographical synthesis, field mapping, and seismic interpretation. Geosystems and Geoenvironment, 3(2024), 100243.
7. Adamu, L. M., Obaje, N. G., Ayuba, R., Kovona, M. T., Adesino, D. A., & Etukudo, N. J. (2022). Litho-Bio Facies analysis and Systematic Paleontology of Sediments in Amansiodo-1 Well, Anambra Basin, Southeastern Nigeria. Earth Sciences, 11(3), 96–108. https://doi.org/10.11648/j.earth.20221103.16
8. Adamu, L. M., Obaje, N. G., Ngozi, O. P., & Umar, U. M. (2020). Integrated Geochemical and Multivariate Statistical Examination of Source Rocks in the Sokoto and Anambra Basins, Nigeria: Implications for Hydrocarbon Prospectivity. Petroleum Science and Engineering, 4(2), 39–50.
9. Adamu, M. L., Obaje, G. N., Adeoye, J. A., & Oladimeji, G. R. (2023). Geochemo-petro-biomarker analysis of the Mid Cretaceous Awgu coal in Nigeria's Middle Benue Trough: Implications for reconstructing the paleoenvironment. Journal of Mining and Geology, 59(2), 131–156.

10. Allix, P., Grosdidier, E., Jardine, S., Legoux, O., & Popoff, M. (1997). Découverte d'Aptien Supérieur à Albien Inférieur daté par microfossiles dans la série détritique Crétacé du Fossé de la Bénoué (Nigeria). Cretaceous Research, 18(1), 17–36. http://dx.doi.org/10.1006/cres.1996.0047
11. Arbuzov, S. I., Finkelman, R. B., Ilyenok, S. S., Maslov, S. G., Mezhibor, A. M., & Blokhin, M. G. (2019). Forms of finding rare earth elements (La, Ce, Sm, Eu, Tb, Yb, Lu) in the coals of Northern Asia. Chemistry of Solid Fuels, 1, 3–24. (In Russian)
12. Bau, M. (1996). Controls on the fractionation of isovalent trace elements in magmatic and aqueous systems: evidence from Y/Ho, Zr/Hf, and lanthanide tetrad effect. Contributions to Mineralogy and Petrology, 123(3), 323–333.
13. Benkhelil, J. (1989). The origin and evolution of the Cretaceous Benue Trough, Nigeria. Journal of African Earth Sciences, 8, 251–282.
14. Birk, D., & White, J. C. (1991). Rare earth elements in bituminous coals and underclays of the Sydney Basin, Nova Scotia: Element sites, distribution, mineralogy. International Journal of Coal Geology, 19, 219–251.
15. Brunet, M., Dejax, J., Brillanceau, A., Congleton, J., Downs, W., Duperon-Laudoueneix, M., ... Pilbeam, D. (1989). Mise en evidence d'une Sédimentations Précoce d'Âge Barrémien dans le Fossé de la Bénoué en Afrique Occidentale (Bassin de Mayo Oulo Léré, Cameroun). In J. Benkhelil, M. Guiraud, J. F. Posard & L. Saugy (Eds.), The Bornu—Benue Trough, the Niger Delta and its Offshore: Tectono-Sedimentary Reconstruction during the Cretaceous and Tertiary from Geophysical Data and Geology, In C. A. Kogbe (Ed.), Geology of Nigeria (2nd ed., pp. 277–309). Rock View Nigeria Limited.
16. Dai, S., Chou, C.-L., Yue, M., Luo, K., & Ren, D. (2005). Mineralogy and geochemistry of a Late Permian coal in the Dafang Coalfield, Guizhou, China: Influence from siliceous and iron-rich calcic hydrothermal fluids. International Journal of Coal Geology, 61, 241–258.
17. Dai, S., Han, D., & Chou, C.-L. (2006). Petrography and geochemistry of the Middle Devonian coal from Luquan, Yunnan Province, China. Fuel, 85, 456–464.
18. Dai, S., Li, D., Chou, C.-L., Zhao, L., Zhang, Y., Ren, D., Ma, Y., & Sun, Y. (2008). Mineralogy and geochemistry of boehmite-rich coals: New insights from the Haerwusu Surface Mine, Jungar Coalfield, Inner Mongolia, China. International Journal of Coal Geology, 74, 185–202.
19. Dai, S., Ren, D., Chou, C.-L., Li, S., & Jiang, Y. (2006). Mineralogy and geochemistry of the No. 6 Coal (Pennsylvanian) in the Junger Coalfield, Ordos Basin, China. International Journal of Coal Geology, 66, 253–270.
20. Dai, S., Ren, D., Chou, C.-L., Zhou, Y., Wang, X., Zhao, L., & Zhu, X. (2008).

Mineralogy and geochemistry of a superhigh-organic-sulfur coal, Yanshan Coalfield, Yunnan, China: Evidence for a volcanic ash component and influence by submarine exhalation. Chemical Geology, 255, 182–194.

21. Dai, S., Ren, D., Hou, X., & Shao, L. (2003). Geochemical and mineralogical anomalies of the Late Permian coal in the Zhijin Coalfield of southwest China and their volcanic origin. International Journal of Coal Geology, 55, 117–138.
22. Dai, S., Ren, D., Li, S. (2006). Discovery of the superlarge gallium ore deposit in Junger, Inner Mongolia, North China. Chinese Science Bulletin, 51(18), 2243–2252.
23. Dai, S., Ren, D., Tang, Y., Shao, L., & Hao, L. (2002). Influences of low-temperature hydrothermal fluid on the re-distributions and occurrences of associated elements in coal—A case study from the Late Permian coals in the Zhijin Coalfield, Guizhou Province, southern China. Acta Geologica Sinica (English Edition), 76(4), 437–445.
24. Dai, S., Ren, D., Tang, Y., Yue, M., & Hao, L. (2005). Concentration and distribution of elements in Late Permian coals from western Guizhou Province, China. International Journal of Coal Geology, 61, 119–137.
25. Dai, S., Ren, D., Zhang, J., & Hou, X. (2003). Concentrations and origins of platinum group elements in Late Paleozoic coals of China. International Journal of Coal Geology, 55, 59–70.
26. Dai, S., Ren, D., & Chou, C.-L. (2007). Effects of magmatic intrusion on mineralogy and geochemistry of coals from the Fengfeng-Handan Coalfield, Hebei, China. Energy & Fuels, 21, 1663–1673.
27. Dai S., Ren, D., Chou, C. L., Finkelman, R. B., Seredin, V. V., & Zhou, Y. (2012a). Geochemistry of trace elements in Chinese coals: a review of abundances, genetic types, impacts on human health, and industrial utilization. Int. J. Coal Geol. 94, 3-21.
28. Dai, S., Wang, X., Seredin, V. V., Hower, J. C., Ward, C. R., O'Keefe, J. M., ... Liu, H. (2012b). Petrology, mineralogy, and geochemistry of the Ge-rich coal from the Wulantuga Ge ore deposit, Inner Mongolia, China: New data and genetic implications. International Journal of Coal Geology, 90, 72–99.
29. Dai, S., Zhou, Y., Ren, D., Wang, X., Li, D., & Zhao, L. (2007). Geochemistry and mineralogy of the Late Permian coals from the Songzao Coalfield, Chongqing, southwestern China. Science in China Series D: Earth Sciences, 50, 678–688.
30. Dai, S., Sun, Y., & Zeng, R. (2006). Enrichment of arsenic, antimony, mercury, and thallium in a Late Permian anthracite from Xingren, Guizhou, Southwest China. International Journal of Coal Geology, 66, 217–226.
31. Dai, S., Ren, D., & Chou, C.-L. (2006a). Geochemistry of trace elements in Chinese coals:

a review of abundances, genetic types, impacts on human health, and industrial utilization. International Journal of Coal Geology, 94, 3–21.

32. Edegbai, A. J., Schwark, L., & Oboh-Ikuenobe, F. E. (2019). A review of the latest Cenomanian to Maastrichtian geological evolution of Nigeria and its stratigraphic and paleogeographic implications. Journal of African Earth Sciences, 150, 823–837.
33. Eskenazy, G. (1999). Aspects of the geochemistry of rare earth elements in coal: an experimental approach. International Journal of Coal Geology, 38, 285–295.
34. Finkelman, R. B., Dai, S., & French, D. (2018). The importance of minerals in coal as the hosts of chemical elements: A review. International Journal of Coal Geology, 212, 103251.
35. Guiraud, R., & Bosworth, W. (1997). Senonian basin inversion and rejuvenation of rifting in Africa and Arabia: Synthesis and implications to plate-scale tectonics. Tectonophysics, 282, 39–82.
36. Hower, J. C., Eble, C. F., Backus, J. S., Xie, P., Liu, J., Fu, B., & Hood, M. M. (2020). Aspects of rare earth element enrichment in Central Appalachian coals. Journal of Applied Geochemistry, 120, 104676.
37. Hower, J. C., Eble, C. F., O'Keefe, J. M., Dai, S., Wang, P., Xie, P., ... French, D. (2015). Petrology, palynology, and geochemistry of Gray Hawk coal (early Pennsylvanian, Langsettian) in eastern Kentucky, USA. Minerals, 5(3), 592–622.
38. Hower, J. C., Groppo, J. G., Joshi, P., Preda, D. V., Gamliel, D. P., Mohler, D. T., ... Schrock, M. (2020). Distribution of lanthanides, yttrium, and scandium in the pilot-scale beneficiation of fly ashes derived from Eastern Kentucky coals. Minerals-Basel, 10(2), 105. https://doi.org/10.3390/min10020105
39. Ketris, M. P., & Yudovich, Y. E. (2009). Estimations of Clarkes for carbonaceous biolithes: World averages for trace element contents in black shales and coals. International Journal of Coal Geology, 78(2), 135–148.
40. Kogbe, C. (1976). Paleogeographic history of Nigeria from Albian times. In Geology of Nigeria (pp. 237–252). Elizabethan Publishing Co.
41. Kopobayeva, A. N., Blyalova, G. G., Bakyt, A., Portnov, V. S., & Amangeldikyzy, A. (2022). The nature of rare earth elements accumulation in clay layers and coals of the Shubarkol deposit. News of the Academy of Sciences of the Republic of Kazakhstan. Series of Geology and Technical Sciences, 2(452), 117–130. https://doi.org/10.32014/2022.2518-170x.164
42. Liu, P., Huang, R., & Tang, Y. (2019). Comprehensive understandings of rare earth element (REE) speciation in coal fly ashes and implication for REE extractability. Environmental Science & Technology, 53, 5369–5377.

https://doi.org/10.1021/acs.est.9b00005

43. McDaniel, D., Hemming, S., McLennan, S., & Hanson, G. (1994). Resetting of neodymium isotopes and redistribution of REEs during sedimentary processes: The Early Proterozoic Chelmsford Formation, Sudbury Basin, Ontario, Canada. Geochimica et Cosmochimica Acta, 58(2), 931–941.
44. Mishra, V., Chakravarty, S., Finkelman, R. B., & Varma, A. K. (2019). Geochemistry of rare earth elements in lower Gondwana coals of the Talchir Coal Basin, India. *Journal of Geochemical Exploration*, *204*, 43-56.
45. Milodowski, A., & Zalasiewicz, J. (1991). Redistribution of rare earth elements during diagenesis of turbidite/hemipelagite mudrock sequences of Llandovery age from central Wales. Geological Society, London, Special Publications, 57(1), 101–124.
46. Nwajide, C. S. (1985). Lithostratigraphy and depositional history of the Albian Asu River Group in the Middle Benue Trough, Nigeria. Journal of Mining and Geology, 22(1), 15–25.
47. Nwajide, C. S. (1990). Sedimentation and paleogeography of the Middle Benue Trough, Nigeria. In The Benue Trough: Structure and Evolution (pp. 19–38). Vieweg+Teubner Verlag, Braunschweig.
48. Obaje, N. G. (2009). Geology and Mineral Resources of Nigeria. Springer-Verlag.
49. Obaje, N. G. (2019). Update on the Geology and Mineral Resources of Nigeria. Ajiboye Printers Nig. Ltd.
50. Obaje, N. G., Umar, U. M., Aweda, A. K., & Ozoji, T. M. (2020). Nigerian Cretaceous coal deposits and their petroleum source rock characteristics. International Journal of Petroleum and Gas Exploration Management, 4(1), 1–14.
51. Obaje, N. G., Wehner, H., Scheeder, G., Abubakar, M. B., & Jauro, A. (2004). Hydrocarbon prospectivity of Nigeria's inland basins: From the viewpoint of organic geochemistry and organic petrology. AAPG Bulletin, 88(3), 325–353.
52. Ofodile, M. E. (1976). The geology of the Middle Benue, Nigeria. Palaeontological Institute, University of Uppsala, Special Publication, 4, 1–166.
53. Offodile, M. E., & Reyment, R. A. (1977). Stratigraphy of the Keana-Awe area of the Middle Benue Region of Nigeria. Bulletin of the Geological Institutions of the University of Uppsala, N.S., 7, 37–66.
54. Palmer, C. A., Lyons, P. C., & Brown, Z. A. (1990). The use of rare earth and trace element concentrations in vitrinite concentrates and companion whole coals to determine organic and inorganic associations. In L. L. Chyi & C. L. Chou (Eds.), Recent Advances in Coal Geochemistry (pp. 55–63). Geological Society of America Special Paper 248.
55. Patrick, N. O., Fadele, S. I., & Adegoke, I. (2013). Stratigraphic report of the Middle

Benue Trough, Nigeria: Insights from petrographic and structural evaluation of Abuni and environs part of Late Albian–Cenomanian Awe and Keana formations. The Pacific Journal of Science and Technology, 14, 557–570. http://www.akamaiuniversity.us/PJST.htm

56. Petters, S. W. (1982). Central West African Cretaceous–Tertiary benthic foraminifera and stratigraphy. Palaeontographica Abteilung A, 179, 1–104.
57. Petters, S. W., & Ekweozor, C. M. (1982). Origin of mid-Cretaceous black shales in the 56. Benue Trough, Nigeria. Palaeogeography, Palaeoclimatology, Palaeoecology, 40, 311–319.
58. Piper, D. Z. (1974). Rare earth elements in the sedimentary cycle: A summary. Chemical Geology, 14(4), 285–304.
59. Reyment, R. A. (1965). Aspects of the Geology of Nigeria. Ibadan University Press.
60. Reyment, R. A., & Dingle, R. V. (1987). Palaeogeography of Africa during the Cretaceous period. Palaeogeography, Palaeoclimatology, Palaeoecology, 59, 93–116.
61. Udo, I.G., Etukudo, N.J., Abia, U.B., and Ibanga, I.M. (2020). Facies analysis and depositional environment of conglomeritic deposits in the northern part of the Niger Delta Basin, Nigeria, IOSR Journal of Applied Geology and Geophysics, 8(3), 11-30.
62. Udo, I.G., Udofia, P.A., Etukudo, N.J., and Adesina, D.A. (2023a). Paleoenvironmental Interpretation of the exposed section of the Benin Formation in Southeastern part of the Niger Delta Basin, Nigeria: A pebble morphometric approach, IOSR Journal of Applied Geology and Geophysics, II(3), 12-19.
63. Udo, I.G., Udofia, P.A., Etukudo, N.J., and Ibanga, I.M. (2023b). Sedimentary facies analysis of sandstone member of the Imo Formation in Northern part of the Niger Delta Basin, Nigeria, The International Journal of Engineering and Sciences, 12(6), 25-37
64. Wang, Z. (1989). Geochemistry of Rare Earth Elements. Beijing: Science Publishing House. (in Chinese)
65. Wen, L., Huang, W., Zhang, Y., & Jiu, B. (2024). Geochemical characteristics of rare earth elements in late Palaeozoic coals from North China. *Frontiers in Earth Science*, *12*, 1374780.
66. Zaborski, P. M. (2000). Tectonic and palaeogeographic evolution of the Benue Trough and its surroundings. In B. C. Schreiber & A. J. Redmond (Eds.), The Benue Trough: Structure and Evolution (pp. 9–21). Geological Society of London.