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Geochemical and Mineralogical Secrets of Cretaceous Coals in the Upper Benue Trough, Nigeria

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Abstract

The accelerating global demand for strategic minerals and rare earth elements (REEs), compounded by geopolitical supply constraints and market volatility, has intensified exploration of unconventional resource streams, including coal and coal combustion by-products. Beyond their traditional role as energy resources, certain coal deposits have emerged as potential repositories of critical elements of economic and technological importance. This study presents a comprehensive mineralogical and geochemical characterization of Cretaceous coal deposits from the Upper Benue Trough (UBT), Nigeria, thereby contributing essential baseline data to the limited body of literature on strategic element enrichment in West African coals. Seven representative coal samples collected from four distinct localities were analyzed using thermogravimetric analysis (TGA), bomb calorimetry, X-ray diffraction (XRD), X-ray fluorescence (XRF), and inductively coupled plasma-mass spectrometry (ICP-MS). Proximate analysis yielded mean moisture content of 6.8 wt.%, volatile matter of 27.7 wt.%, fixed carbon of 48.4 wt.%, and ash yield of 17.6 wt.%, indicating moderate-rank coal characteristics. The average calorific value of 24.11 MJ/kg, coupled with low sulfur content (0.85%, dry ash-free basis), suggests favorable combustion performance with comparatively reduced environmental risk. Ultimate analysis revealed average elemental concentrations of carbon (74.30 wt.%), hydrogen (5.88 wt.%), nitrogen (1.72 wt.%), and oxygen (16.46 wt.%), consistent with sub-bituminous to high-volatile bituminous classification. Mineralogical assemblages are dominated by kaolinite and quartz, with subordinate occurrences of gismondine, cadmium cyanide, and zinckenite. Geochemical data demonstrate enrichment in Ba, Mn, Cr, Cu, Sr, Zn, Zr, and light REEs including La, Ce, Nd, Sm, and Eu. The combined mineralogical and trace element signatures indicate that UBT coals represent a viable secondary source of critical minerals. Strategic recovery from coal ash residues could therefore provide an economically feasible and environmentally adaptive complement to conventional hard-rock REE exploitation.

Keywords

Critical minerals,
Rare Earth Elements,
Geochemistry,
Thermogravimetric,
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Introduction

Coal has long served as a major energy source. Beyond its energy applications, increasing research has revealed coal to be an important reservoir of valuable trace and rare earth elements (REEs), which are critical for modern industries including electronics, clean energy technologies, defense, and healthcare [1, 2, 3, 4, 5, 6, 7, 8]. REEs are particularly essential for the manufacture of high-performance magnets, phosphors, catalysts, batteries, and advanced defense systems. Rising global demand and escalating prices have positioned coal as a viable unconventional source of these critical elements [9, 10, 11].

Although coal is often criticized for its environmental impacts, its geochemical complexity makes it a unique repository for both common and strategic metals. Coal commonly contains elements such as Al, Cr, Ni, and Se, along with notable concentrations of Ce, La, Ga, and Ge. Its mineralogical composition is dominated by Si, Al, Fe, Ca, Mg, Na, and K, largely hosted in refractory minerals. Trace elements including As, B, Cd, Co, Cu, Ga, Mn, Pb, Sr, V, Zn, and Zr are often present in variable proportions [12, 13, 14]. Despite extensive geological investigations of the Upper Benue Trough (UBT), detailed geochemical and mineralogical characterizations of its coal deposits remain limited. This study therefore aims to provide new data on the elemental and mineralogical compositions of the Cretaceous coals in the UBT, with particular emphasis on their potential as sources of REEs and strategic minerals [15, 16].

Geological Background

The Benue Trough is a prominent inland rift basin extending approximately 800 km in length and 150 km in width, oriented NNE-SSW across Nigeria [17, 18, 19]. It forms part of the Central West African Rift System and records the early tectonic evolution associated with the opening of the South Atlantic Ocean. The Trough is filled predominantly with Cretaceous-Cenomanian sediments and has been the subject of considerable geological research [20, 21]. Coal seams within the Gongola Basin are hosted in the Maastrichtian Gombe Sandstone, which lies conformably on the Yolde Formation. In the Yola

Basin, coal-bearing units occur within the Lamja Sandstone, along with the Dukul, Jessu, and Sekuliye Formations and the Numanha Shale, which represent Cenomanian-Turonian-Santonian equivalents of the Gongola and Pindiga Formations [20, 21, 22, 23, 24, 25]. Regional deformation during the mid-Santonian initiated folding and basin partitioning, ultimately giving rise to the proto-Anambra Basin [26, 27].

Materials and Methods

Seven coal samples were collected from four localities in the Gongola and Yola arms of the UBT. Samples included surface excavations, open-pit mine materials, and borehole cuttings. Each sample was carefully labeled, sealed in airtight bags to minimize alteration, and prepared for laboratory analyses. Analytical Techniques:

- X-Ray Diffraction (XRD): Powdered samples were analyzed using a PANalytical X'Pert Pro diffractometer (40 kV, 40 mA) over a 2 θ range of 0-80° for mineralogical identification.
- X-Ray Fluorescence (XRF): Fused pellets prepared with lithium nitrate flux were analyzed to quantify major oxides [28].
- Inductively Coupled Plasma-Mass Spectrometry (ICP-MS): Samples were digested using microwave-assisted acid leaching with HNO₃ and H₂O₂. Elemental concentrations were quantified using a Perkin Elmer NexION ICP-MS.

Proximate and Ultimate Analysis: Thermogravimetric analysis (TGA) was used for proximate analysis, while gross calorific values were determined with a Dry-Cal bomb calorimeter (ISO 1928:2009). Ultimate analyses measured elemental C, H, N, O, and S contents.

Results

Proximate analyses indicated average moisture content of 6.8 wt.%, volatile matter of 27.7 wt.%, fixed carbon of 48.4 wt.%, and ash yield of 17.6 wt.%. The mean calorific value was 24.11 MJ/kg with sulfur content averaging 0.85% (daf) (Table 1). Ultimate analyses yielded mean values of 74.30 wt.% C, 5.88 wt.% H, 1.72 wt.% N, and 16.46 wt.% O.

Table 1. Proximate, GCV, and Ultimate data [28]

Proximate Analysis (Wt. %)					CV	Ultimate Analysis (%) (Daf)					
Sample I. D	V M	Fix C	Ash	Moist	(MJ/Kg)	S	C	H	N	O ^a	
11	24.0	39.4	31.0	5.6	20.28	0.79	76.40	5.98	2.05	14.78	
12	29.8	58.8	6.8	4.6	28.70	0.81	75.13	5.42	1.94	16.69	
13	27.7	47.8	21.8	5.6	24.55	0.51	78.50	6.40	1.58	13.00	
14	25.1	51.5	18.3	5.1	24.64	0.48	76.67	5.56	1.62	15.66	
15	31.1	52.1	6.8	10.0	26.19	0.32	73.47	5.82	1.48	18.91	
UBT	16	28.7	40.6	21.1	9.6	20.27	7.34	65.64	6.07	1.24	19.70
	17	14.0	3.8	79.0	3.2	1.90	2.19	39.75	7.68	1.63	48.76
						0.8					16.4
Areal Ave.	27.7	48.4	17.6	6.8	24.11	5	74.30	5.88	1.72	6	

XRD results showed dominance of kaolinite and quartz, with accessory phases including gismondine, zinckenite, cadmium cyanide, and pyrite (Table 2). XRF analysis revealed high SiO₂, Al₂O₃, and Fe₂O₃ contents (Table 3), while ICP-MS analyses indicated enrichment in Ba, Mn, Cr, Cu, Sr, Zn, and Zr (Table 4). Rare earth elements (La, Ce, Nd, Sm, Eu) were also enriched in several samples, particularly sample 17 (Table 5).

Table 2. UBT X-Ray Diffraction (XRD) (Indicative and not quantitative)

Sample ID	Minerals / Compounds Identified			
	Phase 1	Phase 2	Phase 3	Phase 4
11	Quartz	Sodium Aluminium Silicate.	N/A	N/A
12	Kaolinite	N/A	N/A	N/A
13	Kaolinite	Magnesium Iron Phosphate	Quartz	N/A
14	Beryllium, Manganese Oxide hydrate	Cadmium Cyanide Cd(CN) ₂	Quartz	N/A
		Zinckenite (Lead Antimony Sulfide)	N/A	N/A
15	Quartz		Potassium Hydrogen Germanium Oxide	Pyrite
16	Gismondine, (hydrated Alumino-Silicate)	Kaolinite	Potassium Beryllium Phosphate	Quartz
17	Kaolinite	N/A		

Table 3. X-Ray Fluorescence Data (Mass %) (The LOI of the samples was not measured during the XRF sample prep).

Trace Element	11	12	13	14	15	16	17
Al ₂ O ₃	21.23	17.25	24.49	23.6	9.04	16.33	21.62
BaO	NR	NR	0.18	0.18	0.22	0.07	0.05
CaO	0.52	2.74	3.71	3.72	11.73	2.98	0.29
Cr ₂ O ₃	NR	NR	NR	NR	NR	NR	NR
Fe ₂ O ₃	9.4	4.39	5.48	6.15	12.66	31.16	3.48
K ₂ O	1.59	0.86	0.36	0.35	14	0.64	1.36
MgO	1.16	1.95	1.19	1.21	4.02	0.92	0.33
MnO	NR	0.05	0.13	0.14	0.43	0.39	NR
Na ₂ O	0.16	3.86	NR	NR	NR	NR	NR

NiO	NR	NR	NR	NR	NR	NR	NR
P ₂ O ₅	NR	0.05	0.11	0.1	0.08	0.08	0.08
SiO ₂	63.59	62.31	57.9	56.31	47.26	40.46	68.98
SO ₃	0.19	4.11	2.89	3.99	11.46	4.24	NR
TiO ₂	1.31	1.1	2.06	2.01	1.38	1.18	2.66
V ₂ O ₅	NR	NR	NR	NR	NR	NR	NR
Mass %	99.15	98.66	98.49	97.75	98.41	98.44	98.84

FOOT NOTE: NR=NO RESULT

The trace element (TE) and rare earth elements (REE) results are presented in Tables 4 and 5. Quite some few trace elements show high composition in Ba, Cr, Cu, Mn, P, Sr, Ni, V, Zn, and Zr than the 18 (Table 4). Ba and Zr are exceptionally high for samples 13 and 14 above 18. Mn is high in Samples 13,14,15 and 16 above 18. The few rare earth elements (La, Ce, Nd, Sm and Eu) in this study are high in samples 11, 13, 14, and 17 than the 18 (Table 5).

Table 4. Trace Element concentrations (ppm).

Trace Element	11	12	13	14	15	16	17	18
As	2.0	1.2	1.4	1.5	0.7	7.8	2.8	0.71
Ba	101.4	37.2	256.5	259.6	202.1	133.9	125.8	79.99
Be	4.3	5.6	2.6	2.6	0.5	2.6	1.4	3.36
Cd	0.1	0.1	0.2	0.2	0.0	0.1	0.3	0.05
Co	11.4	5.6	6.4	6.4	4.2	38.5	17.5	5.33
Cs	1.1	0.3	0.1	0.1	0.0	0.4	2.1	0.78
Cr	26.0	12.8	17.1	16.5	6.1	26.5	36.4	10.89
Cu	23.6	16.6	18.0	16.6	6.2	10.4	22.0	4.14
Hf	0.2	0.1	5.5	5.4	0.1	0.4	1.7	0.86
Mn	39.4	56.5	213.9	224.2	310.1	666.3	80.6	18.29
Mo	0.4	0.7	0.7	1.0	0.6	4.8	0.6	0.81
Ni	19.9	6.1	10.8	9.6	6.7	29.2	10.9	3.63
P	46.5	35.8	84.2	83.3	40.5	49.5	143.8	22.65
Pb	10.3	5.2	8.9	8.7	2.6	7.3	19.8	4.44
Rb	6.7	1.6	1.4	1.4	0.4	1.5	7.6	2.51
Sb	0.0	-0.1	0.0	-0.1	-0.1	0.1	-0.1	-0.05
Sr	30.7	74.0	82.0	84.3	77.8	57.1	48.5	43.73
Th	6.4	2.5	8.6	8.2	1.1	3.8	15.8	2.98
U	0.3	0.6	0.9	0.9	0.2	0.8	1.6	0.91
V	25.4	14.6	12.5	12.6	5.8	27.8	41.9	15.46
W	0.0	0.0	0.0	-0.1	0.1	0.1	-0.1	0.92
Zn	50.1	38.8	16.9	15.6	6.8	246.5	83.7	8.50
Zr	7.2	4.1	249.1	240.1	5.7	13.1	61.1	34.88

FOOT NOTE: SARM 18 = SOUTH AFRICAN REFERENCE MATERIALS

Table 5. Select light Rare Earth Element concentrations (ppm).

REE	11	12	13	14	15	16	17	18
La	9.7	5.8	26.3	24.1	2.7	9.7	45.5	7.60
Ce	24.5	13.7	61.7	56.2	4.7	22.7	112.7	17.63
Nd	12.9	7.0	24.7	22.8	1.9	10.4	46.4	7.73
Sm	2.6	1.4	5.0	4.6	0.4	2.1	9.2	1.59
Eu	0.5	0.3	0.9	0.8	0.2	0.5	1.9	0.32

FOOT NOTE: 18 = SOUTH AFRICAN REFERENCE MATERIALS

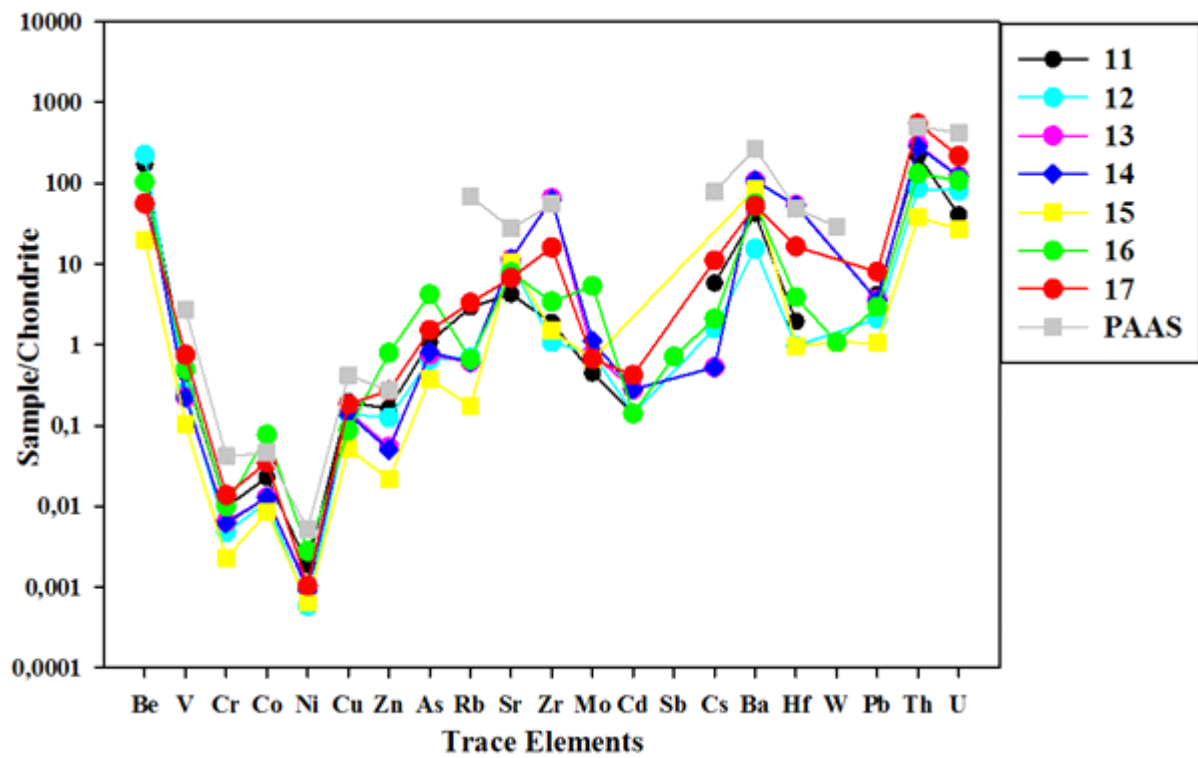


Figure 1. UBT Chondrite-Normalized TEs and PAAS.

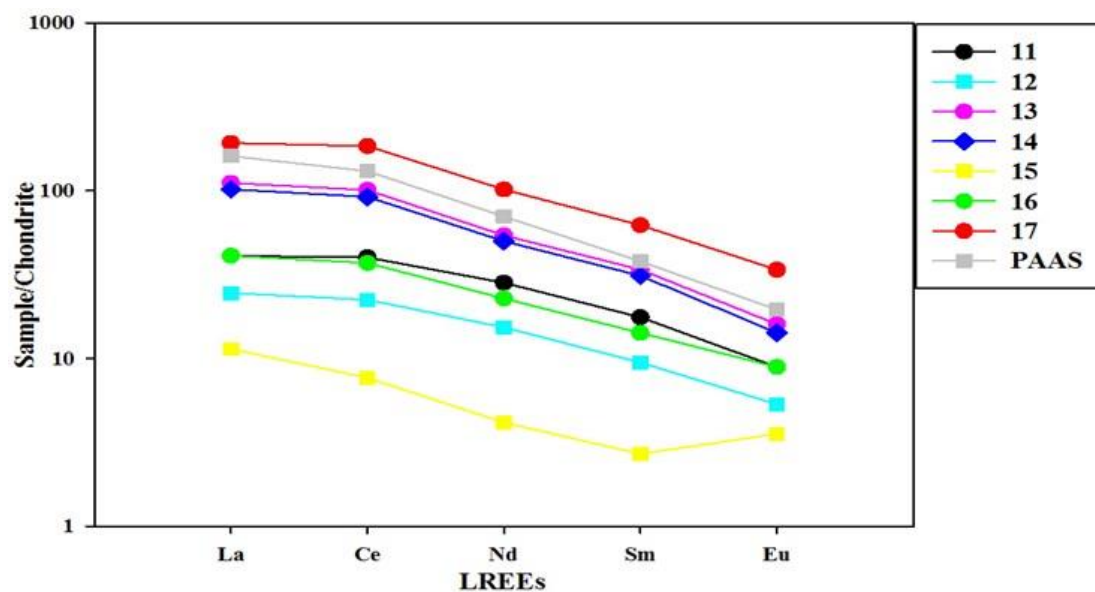


Figure 2. UBT Chondrite-Normalized LREEs and PAAS.

The chemical and mineralogical characteristics of the Upper Benue Trough coals reveal that significant insights into their genesis, provenance, and potential applications. The relatively low sulfur and ash contents observed across most samples confirm that these coals are of good combustion quality, comparable to global averages for Cretaceous coal deposits. High calorific values (up to 28.7 MJ/kg) and substantial fixed carbon contents further reinforce their utility as an energy resource (Table 1) [28].

Mineralogically, kaolinite and quartz dominate the coal assemblages (Table 3), reflecting the input of terrigenous clastics derived from weathering of feldspathic source rocks in surrounding highlands [28]. The presence of accessory minerals such as gismondine, cadmium cyanide, zinckenite, and pyrite (Table 2) points to multiple diagenetic and epigenetic processes. Kaolinite, often formed in humid tropical climates, suggests intensive chemical weathering of aluminosilicate precursors. The occurrence of sulfide phases (pyrite, zinckenite) (Table 3) implies localized reducing conditions and possible hydrothermal influence during coal formation [28].

The geochemical data indicate significant enrichment in trace elements including Ba, Mn, Cr, Cu, Sr, Zn, and Zr (Table 4) [28]. These elements are of considerable industrial and environmental importance. For instance, Ba and Sr often substitute in carbonate minerals and may serve as indicators of freshwater influx in depositional systems. Elevated Zn and Co, particularly in the Maiganga coals (Table 4), are consistent with their association with sulfide phases such as sphalerite and pyrite. Zirconium enrichment in certain samples indicates input from felsic igneous sources, suggesting provenance links to surrounding basement terranes [28].

Rare earth element (REE) concentrations in the studied samples are noteworthy (Table 4).

Although overall LREE contents are modest compared to average post-Archean Australian shales (PAAS) (Table 5), several samples exhibit significant enrichment, particularly sample 17 [28]. The chondrite-normalized REE patterns suggest derivation from felsic source rocks, consistent with the mineralogical evidence for zircon contributions. The occurrence of REEs in amorphous or clay-bound phases suggests potential recoverability from coal combustion products, supporting the idea that coal ash can be a secondary resource for REE extraction [28].

Comparisons with global datasets show that the UBT coals share similarities with other Cretaceous coals in Asia, North America, and Europe, particularly in terms of trace element enrichment. However, the elevated levels of Ba, Zn, and Zr highlight a unique geochemical signature that may reflect the interplay of deltaic to shallow marine depositional settings and tectonic processes active during the Santonian deformation phase [28].

From an applied perspective, the dual energy and critical-element potential of the UBT coals makes them strategically important. Coal combustion by-products (CCPs), especially fly ash, could serve as a viable source of REEs and strategic metals if appropriate processing technologies are applied. This aligns with global initiatives to diversify critical mineral supply chains and reduce reliance on conventional mining. Environmentally, understanding the distribution and modes of occurrence of potentially hazardous elements (e.g., As, Pb, Cd) is vital for mitigating pollution risks during coal utilization [28].

In summary, the UBT coals provide a valuable case study of the intersection between traditional energy geology and critical mineral exploration. Their geochemical complexity underscores the need for integrated approaches combining petrography, mineralogy, geochemistry, and industrial process research to fully unlock their resource potential.

The UBT coals are characterized by relatively low ash and sulfur contents, high calorific values, and mineralogical assemblages dominated by kaolinite and quartz. The clay minerals likely originated from chemical weathering of feldspar-rich source rocks, while carbonate phases may reflect epigenetic inputs from marine or hydrothermal fluids.

Major oxides indicate aluminosilicate dominance, consistent with felsic to intermediate provenance. Trace element enrichment in Ba, Zn, Co, and Zr suggests both detrital and sulfide mineral associations. For example, Zn is likely hosted in sphalerite and pyrite, while Zr enrichment reflects zircon input from felsic igneous sources.

The elevated concentrations of REEs, particularly La, Ce, and Nd, highlight the potential of UBT coals as alternative REE sources. Their occurrence within amorphous and clay-rich phases suggests partial organic and mineral binding, making coal ash processing a viable extraction route.

Conclusion

The crystalline mineral in coal is a complex and heterogeneous in composition; hence it is only through a thorough and holistic analysis that the geochemical and mineralogical secrets of the Cretaceous coal can be unpacked for an appropriate coal value chain utilization. The proximate data show that the coal is rich in volatile matter and fixed carbon with a low ash content except sample 17 with high ash content.

The calorific value of all the samples were high which correlates to their corresponding fixed carbon content. The minerals examined in this study consist majorly of kaolinites and quartz and minor quantities of secondary minerals (calcite). The mineral assemblage suggests that the coal-based minerals originate largely from detrital source. The abundance of Ba and Sr in the coal sample 11 could be ascribed to calcite, dolomite or phosphate. Trace elements Cr, Mo, Ni, V, and U in the studied coal samples is ascribed to clay mineral (kaolinite). The X ray fluoresces data shows that the oxides are dominantly Al_2O_3 , SiO_2 , and Fe_2O_3 . The major oxide elemental association (Al_2O_3 / TiO_2 , Cr/Th vs Sc/Th and Co/Th vs La/Sc) suggest sediments were source from intermediate, felsic or mafic constituents. The presence

of LREEs in amorphous forms in the studied coal is potentially useful for future industrial applications

These findings underscore the potential of UBT coals as unconventional reservoirs of strategic elements, with coal ash processing offering a sustainable approach to supplement conventional mining.

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Author Contributions

A.D. Mangs developed this manuscript from his Ph.D. thesis at the University of Johannesburg, supervised by Prof. N.J. Wagner and co-supervised by Prof. U.A. Lar. Prof. Wagner provided funding through DSI-CIMERA and offered technical guidance, while Prof. Lar contributed to restructuring and refining the manuscript.

Declarations

Conflict of Interest: The authors declare no conflicts of interest.

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