

Assessment of Trace and Rare Earth Element Distribution and Speciation in Bauxite deposits across Ekiti and Ondo States, Nigeria

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ABSTRACT: The growing significance of rare earth elements (REEs) in advanced electronic technologies and the nuclear industry, coupled with concerns about geopolitical dynamics and supply market vulnerabilities, has reignited global interest in securing domestic and economically viable sources of REEs through dedicated research and developmental pursuits. Bauxite, a naturally occurring mineral primarily composed of aluminum, has been identified to harbor an abundance of sought-after rare earth minerals, thereby rendering it a promising unconventional reservoir of REEs contingent upon geological and mineralogical characteristics. Nigeria, endowed with substantial bauxite deposits prominently situated in Ondo and Ekiti states, stands to offer an intriguing avenue for exploration. In this study, the utilization of inductively coupled plasma mass spectrometry (ICP-MS) facilitated the quantification of trace elements within samples obtained from six distinct production sites spanning Ondo and Ekiti states in Nigeria. The aim was to elucidate correlations between multi-elemental REE compositions and geographical origins. Employing both single quadrupole (SQ) and multi-collection sector field (MS) modes, concentrations of Pb, Cd, As, Zn, Mn, Al, Ca, Ni, K, Na, Mg, Cu, Fe, Ti, P, Cr, and Si were rigorously determined. Remarkably, ICP-MS analysis consistently revealed a palladium (Pd) concentration of 228.05 ppb across all sampled materials, factoring in a dilution factor of 175x. Consequently, the actual concentration of the digested solution was established at 39.91 ppm mg/L. The outcomes of this investigation hold potential significance in categorizing Nigerian bauxite deposits as viable REE sources, as well as in engineering tailored techniques to efficiently recover these elements. Such findings harbor promising economic prospects for the nation, positioning the solid mineral sector as a pivotal driver of Nigeria's burgeoning economy.

INTRODUCTION

In the midst of rapid technological advancement and unprecedented population growth over the last century, a global race has ensued for critical and strategic minerals and metals, which are essential for driving economic and technological progress. Notably, the significance of rare earth elements (REEs) has surged due to their integral role in advanced electronics technologies and the nuclear industry. Geopolitical concerns and supply instability on the global stage have sparked a renewed impetus among nations to secure indigenous sources of economically sustainable REEs through dedicated research and development endeavors.

Bauxite, a naturally occurring mineral primarily composed of aluminum, has emerged as a potential unconventional reservoir of REEs. The viability of bauxite as a REE source hinges upon the geological and mineralogical characteristics of the deposit. Within this context, Nigerian bauxite deposits, notably concentrated in Ekiti and Ondo states, present an intriguing prospect for exploration. REEs, encompassing 15 lanthanides ranging from lanthanum to lutetium, along with scandium and yttrium, inhabit the lower end of the periodic table. These 17 elements collectively exhibit similar chemical properties and can be categorized into three groups based on atomic number and mass: light rare earth elements (LREE),

including La, Ce, and Pr; middle rare earth elements (MREE), consisting of Na, Sm, Eu, and Gd; and heavy rare earth elements (HREE), spanning Tb to Lu (EPA, 2012).

Numerous soil parent materials harbor a diverse array of elements, including REEs, which, at elevated concentrations, pose environmental and human health risks. Taylor (2004) elucidated the significant influence of bedrock and its physicochemical attributes on soil REE content. Notably, the contamination of soil and water with trace and rare earth elements has captured scientific attention due to the associated hazards to human health (Loska et al., 2004). Ojo & Oketayo (2006) observed that mining activities have led to the contamination of rivers, streams, and sediments with trace elements like As, Fe, Hg, Mn, and Pb, exceeding established safety thresholds. It is pertinent to recognize that metals such as Fe, Cu, Co, Mu, Cr, and Zn, while essential as micro-nutrients, can also prove detrimental at excessive concentrations, as highlighted by Nair et al (2010).

The perilous nature of trace and rare earth elements as pollutants stems from their toxicity and resistance to degradation (Tijani et al, 2005). Furthermore, Hirano & Suzuki (1996) underscored the adverse effects and health risks posed by REEs to humans, emphasizing that prolonged exposure to REE dust could result in pneumoconiosis.

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Research by Wakita et al (2008) points to industrial waste, originating from atmospheric precipitation and urban/rural waste disposal, as a major contributor to the introduction of trace elements into marine and stream environments. Both heavy metals and REEs, characterized as toxic substances within ecosystems, find their way into hydrological systems through processes like rock weathering, volcanic activity, and atmospheric deposition. Senesi et al (1999) and Zhuang et al (2013) attribute the primary source of these elements to human activities such as industrialization, agriculture, urban expansion, and waste disposal.

The overall concentration of REEs surpasses 200ppm in the Earth's average crust, with applications spanning the production of hybrid batteries and motors, catalytic converters, potent permanent magnets, energy-efficient lighting, electronics, lasers, and more (BBC, 2019). Notably, the form and concentration of REEs within bauxite deposits are contingent upon the mineralogical composition and morphological distribution of the deposit (Bumeman et al, 2015).

Analytical techniques, particularly in atomic spectroscopy, have proven instrumental in studying REEs. Their broad applicability extends to environmental, geological, chemical, and industrial analyses. Consequently, investigating the REE potential of Nigerian bauxite deposits, specifically in Efon-Alaye (Ekiti State) and Ile-Oluji (Ondo State), assumes paramount importance. The objective of this study is to comprehensively analyze the concentration and speciation of trace and rare earth elements (REEs) through ICP-MS in these locations.

STATEMENT OF PROBLEM

The prevailing scenario within the rare earth elements (REE) landscape underscores a profound imbalance, with China accounting for over 75% of REE production, nearly half of the acknowledged reserves, and the preponderance of REE

metallurgical technologies (10, 27). Although the impending surge in demand for utilization in advanced technological devices is anticipated over the forthcoming decades, the confluence of factors including sustainability concerns, supply volatility, geopolitical intricacies, trade policies, processing methodologies, and the potential weaponization of resources has engendered a situation that not only bequeaths China with an almost complete market hegemony but also introduces fragilities into the global REE supply chain (5, 28).

This amalgamation of circumstances has galvanized a renewed impetus among nations, compelling them to endeavor towards safeguarding economically viable REE reservoirs through strategic research and development initiatives. These initiatives are meticulously geared towards bolstering REE retrieval efficiency and promoting recycling methodologies, thus mitigating the impact of supply constraints. Simultaneously, the pressing issue of trace and REE contamination in both soil and water reservoirs has elicited the attention of the scientific community, chiefly due to the potent health hazards it poses to human well-being (Loska et al, 2004).

OBJECTIVE

The objectives of this study encompass a comprehensive evaluation of the concentration and speciation of both trace and rare earth elements within the geographical regions of Efon-Alaye, situated in Ekiti State, and Ile-Oluji, located in Ondo State, Nigeria, employing the technique of ICP-MS. This analysis aims to unravel the multi-elemental and isotropic content of the gathered samples originating from these two distinct states. By achieving these objectives, the study is poised to offer valuable insights that hold the potential to invigorate Nigeria's solid mineral sector, thereby contributing positively to the overall economic landscape of the nation.



Figure 1: Map of Nigeria showing states with bauxite deposits



Figure 2: Map of Ekiti showing Efon Alaye bauxite deposit

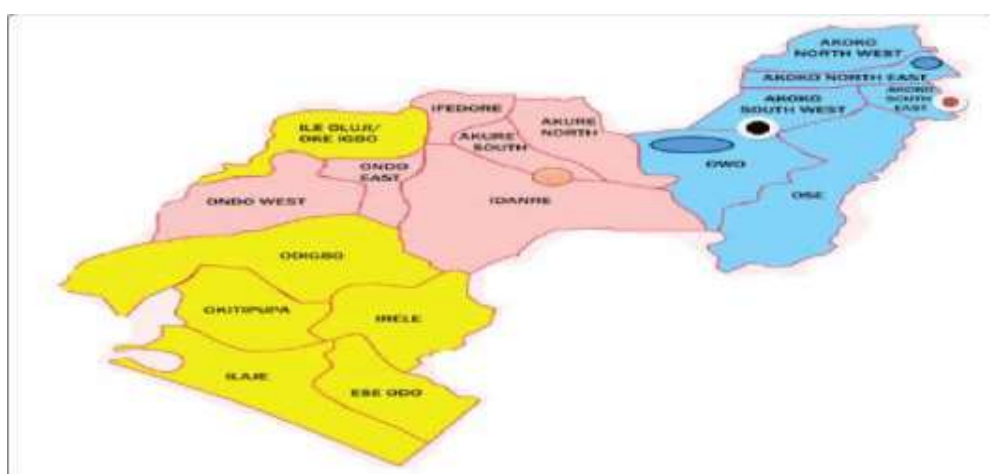


Figure 3: Map of Ondo state showing Ileoluyi bauxite deposit

RESULTS AND DISCUSSION

Table 1: Accuracy, Precision and Limits of Quantification Using Inductively Coupled Plasma- Mass Spectrometric (ICP-MS)

GA/ICPMS (ug/g, n=11)	KS 1	KS 2	KS 3	KS 4	KS 5	KS 6	GA/REC (1)	+/-CL (2) ug/g	Acc (%)
Rb	10± 0.10	12± 0.12	16± 0.12	12± 0.05	10± 0.15	12± 0.10	9	5	0.3
Sr	189± 0.10	158± 0.10	169± 0.04	192± 0.20	168± 0.22	190± 0.10	190	12	0.2
Yb	0.60± 0.10	0.50± 0.12	0.40± 0.09	0.20± 0.11	0.47± 0.08	0.652± 0.10	0.60	2.0	0.5
Si	76.27± 0.12	79.90± 0.42	77.36± 0.10	81.70± 0.11	72.56± 0.20	77.70± 0.18	80	10	12.2
Ti	0.25± 0.10	0.01± 0.22	0.45± 0.23	1.19± 0.12	0.42± 0.32	1.19± 0.13	0.3	0.2	3.2
Al	11.65± 0.30	13.18± 0.26	12.25± 0.10	10.50± 0.41	10.25± 0.14	8.50± 0.10	12	4.0	2.0
Fe	2.97± 0.22	0.40± 0.10	1.17± 0.20	0.94± 0.33	0.52± 0.18	0.94± 0.35	3	2.2	0.2
Ca	0.23± 0.10	0.27± 0.15	2.08± 0.32	0.78± 0.20	0.36± 0.21	3.78± 0.23	4	0.8	0.2
Zr	180± 0.12	157± 0.22	186± 0.14	177± 0.10	183± 0.10	180± 0.10	180	0.2	2.5
Nb	25± 0.12	22± 0.10	20± 0.08	22± 0.02	23± 0.22	23± 0.03	25	0.4	3.4

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Cs	1.20± 0.10	1.18± 0.10	1.24± 0.12	1.10± 0.20	1.22± 0.02	1.10± 0.05	1.20	0.2	5.2
Ba	1128± 0.10	1538± 0.20	1350± 0.07	1225± 0.12	1170± 0.06	1250± 0.12	1175	0.3	8.0
La	0.22± 0.10	0.20± 0.13	0.09± 0.10	0.12± 0.09	0.20± 0.10	0.20± 0.04	0.22	0.6	0.4
Ce	2.42± 0.10	2.40± 0.15	2.22± 0.15	2.52± 0.12	2.40± 0.03	2.26± 0.02	2.42	0.2	0.2
Pr	0.02± 0.10	0.04± 0.12	0.02± 0.10	0.22± 0.06	0.05± 0.01	0.02± 0.12	0.02	0.4	2.2
Nd	0.20± 0.10	0.26± 0.10	0.20± 0.11	0.15± 0.12	0.23± 0.04	0.24± 0.07	0.20	0.5	3.8
Pb	21± 0.10	21± 0.10	23± 0.08	16± 0.10	20± 0.06	17± 0.05	24	0.2	4.7
Mg	0.04± 0.18	0.11± 0.10	1.54± 0.10	0.97± 0.22	0.50± 0.02	0.95± 0.12	1	0.5	3.6
Na	3.02± 0.23	2.26± 0.15	3.65± 0.11	0.20± 0.12	3.20± 0.10	3.22± 0.09	4	0.3	7.7
K	5.20± 0.14	5.52± 0.22	1.30± 0.10	0.44± 0.16	3.22± 0.10	0.48± 0.06	5	0.5	5.3
Mn	0.01± 0.22	0.01± 0.26	0.32± 0.12	0.06± 0.24	0.01± 0.15	0.02± 0.12	0.03	0.4	3.6
Eu	0.33± 0.05	0.23± 0.02	0.36± 0.04	0.10± 0.02	0.31± 0.04	0.30± 0.10	0.4	0.6	6.3
Gd	0.22± 0.03	0.12± 0.12	0.24± 0.02	0.20± 0.05	0.12± 0.01	0.25± 0.06	0.25	0.2	2.2
Th	0.60± 0.05	0.30± 0.09	0.20± 0.05	0.62± 0.00	0.40± 0.03	0.62± 0.02	0.50	0.6	2.0
Zn	120± 0.06	112± 0.04	124± 0.03	122± 0.02	110± 0.05	122± 0.03	124	0.3	3.2

Table 2: The values of radioactivity concentration parameters for the six samples from Ondo and Ekiti states

Sample ID	²³⁶ RA	²³² TH	⁴⁶ K	Radium Equivalent Bq/Kg	External Index (Ncm)	Internal Index (N/cm)	Absorbed dose (nGy/h)	Annual effective dose (m5v/y)
KS 1	15.90	15.50	170.05	50.77	0.12	0.16	24.60	0.025
KS 2	12.72	15.70	162.22	46.22	0.10	0.14	22.35	0.020
KS 3	50.80	0.85	-	55.40	0.12	0.27	23.50	0.025
KS 4	53.50	-	20.20	52.67	0.08	0.10	10.20	0.015
KS 5	50.90	1.92	12.70	55.20	0.09	0.07	6.50	0.008
KS 6	52.45	0.82	-	53.70	0.01	0.17	12.80	0.010
Average	26.69	4.40	55.49	25.35	0.07	0.10	11.20	0.015

Table 3: The summary of Rare Earth and trace element concentration in the 10 samples KS1 to KS6.

Analyte	Mean(mg/L)	Standard(std)
Pb	2.50	283.31
Cd	0.62	228.80
As	0.25	234.98
Zn	0.20	213.86
Mn	0.20	213.86
Al	0.20	213.86
Ca	1.25	213.86
Ni	0.20	422.67

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K	0.20	232.00
Na	0.40	213.86
Mg	2.75	232.21
Cu	3.00	285.20
Fe	0.20	324.75
Ti	0.20	213.86
P	0.22	213.55
Cr	3.20	357.87
Si	0.20	213.86
Average	81.12	259.55

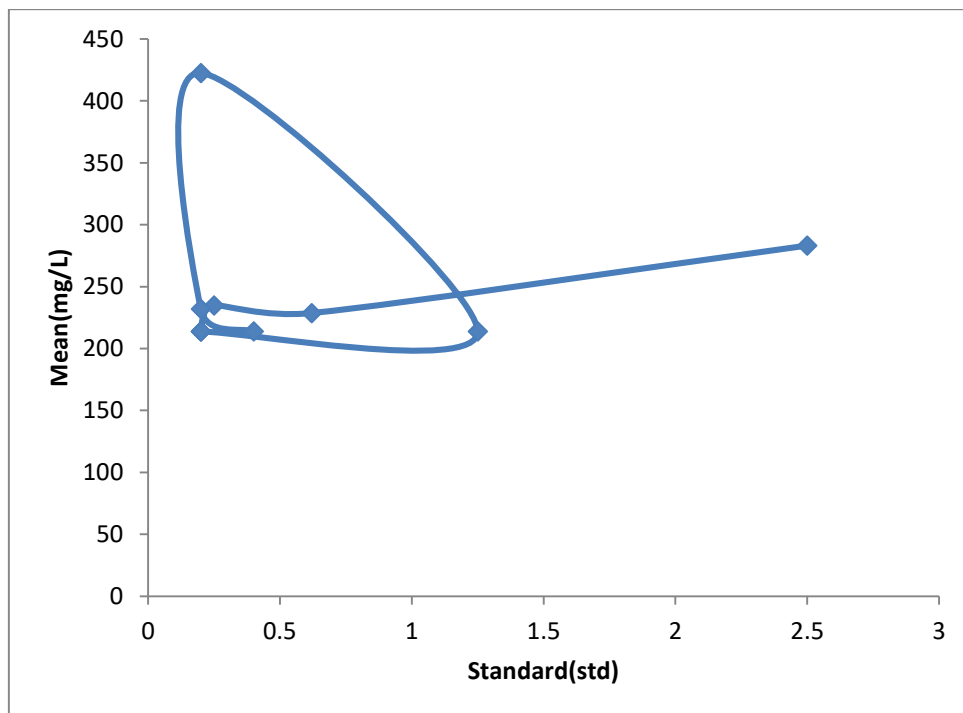


Figure 4: Plot of mean of analyte versus standard

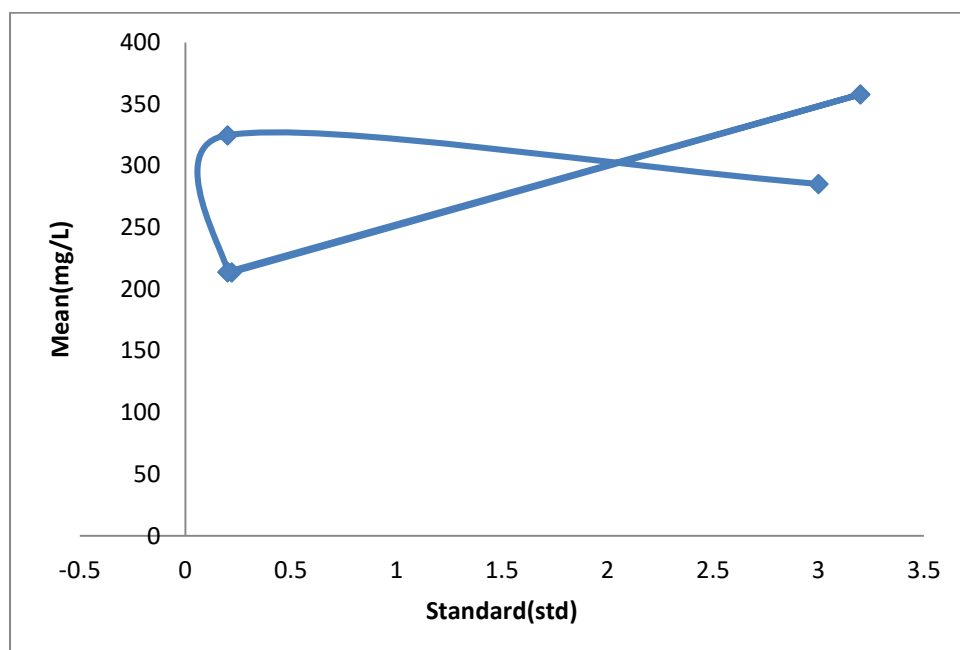


Figure 5: Plot of mean of analyte versus standard

Table 4. Summary of weight percentage of Trace elements concentration in the ID samples KS1- KS2.

Analyte	Standard(std)	Weight%
Pb	283.31	81.95
Cd	228.80	36.50
As	234.98	61.40
Zn	213.86	72.20
Mn	213.86	0.60
Al	213.86	29.00
Ca	422.67	1.80
Ni	232.21	51.00
K	213.86	0.90
Na	232.21	1.10
Mg	285.21	4.60
Cu	324.75	59.00
Fe	213.86	4.95
Ti	213.86	1.15
P	213.55	0.45
G	357.87	0.80
Si	213.86	76.50

The radioactivity concentrations of ²²⁶Ra, ²³²Th, and ⁴⁰K within the six samples were determined using the formula $A = N_c / (\epsilon \gamma)$, as outlined by El-Taher & Al-Zahrani (2014). In this equation, A represents the activity concentration in Bq/Kg, N_c signifies the net gamma counting rate, ϵ stands for the detector efficiency of the specific gamma ray, and γ corresponds to the absolute transition probability of gamma decay. The outcomes illustrate that the average emitted gamma-rays from the six samples are measured at 26.69, 4.40, and 55.49, respectively. The trace element spectrum, depicted in Figure 1, provides insight into phase identification and crystal structure verification, revealing multiple peaks indicative of the particles' polycrystalline nature.

Table 3 presents the results, effectively quantifying the presence of specific trace elements within the rare earth element samples under study. Meanwhile, Table 1 demonstrates the commendable capacity of ICP-MS for rapid, precise, multi-element analysis even at low concentration levels. The table underscores the effectiveness of calibration curves, converting measured analyte counts into concentrations within the low mg/L range, encompassing a high dynamic range. Notably, the ICP-MS analysis unveils a concentration of C (Pd) at 228.05ppb across all samples, with a dilution factor of 175x, resulting in a real concentration of the digestion solution at 39908ppb, equivalent to 39.91ppm (µg/L).

Figure 2 elucidates the distinct separation of trace elements from the rare earth elements present in the samples. Tables 2 and 3 further accentuate the presence of trace elements with relatively low concentrations. The study establishes a correlation between the concentration of trace and rare earth elements in the soil, utilizing the standard deviation of each element to assess differences across various sampling areas.

Overall, the study manifests a convergence of trace elements within both regions and states. This finding contradicts the assertion of Yanwang et al (2021) that substantial distinctions exist in trace element content between two divergent regions. Historically, a range of analytical techniques has been employed to assess trace element content; however, the study's outcomes diverge from these conceptions. The outcomes notably reveal a harmonious accord between laser ablation and solution methods, shedding light on the partitioning behavior of incompatible elements due to their size and charge constraints in mineral cation sites. The study underscores the remarkable sensitivity and operational range of ICP-MS.

Additionally, the SEM-EDS elemental analysis expounded in this work offers insights into the form of occurrence of rare earth element minerals within bauxite deposits across the two Nigerian states. Sequential extraction and gamma spectrometric analyses were conducted to inform method development for rare earth element recovery and the management of toxic and radioactive waste replete with Cd, Cr, As, Pb, Ra-226, U-238, Th-232, all stemming from REE recovery processes. The study highlights the contamination of REEs by trace elements such as As, Fe, Zn, Nb, Ca, Al, Yb, Sr, and Mn, with values surpassing established safety thresholds, corroborating prior findings (Ojo & Oketayo, 2006; Narrtey et al, 2011; Mudukwe et al, 2019). The significant challenge posed by trace and REEs as persistent, non-degradable pollutants is reinforced. Broadly, centuries of anthropogenic activities have led to widespread soil contamination globally (Wu et al, 2017; Zhang et al, 2001). Ultimately, the study concludes that the collected bauxite samples from both states manifest similar trace element

profiles within the REEs deposits, challenging the notion of regional differentiation.

CONCLUSION

In culmination, this comprehensive study delved into the intricate realm of trace and rare earth elements within the bauxite deposits of two Nigerian states, namely Ondo State and Ekiti State. Employing a spectrum of sophisticated analytical methodologies, including ICP-MS (inductively coupled plasma mass spectrometry) and gamma ray spectroscopy, the investigation aimed to unravel the intricate interplay of concentration, occurrence, and speciation of these elements. The study's scope also encompassed an exploration of toxic and radioactive elements intertwined with these deposits.

The utilization of cutting-edge techniques such as ICP-MS and gamma ray spectroscopy enabled the meticulous characterization of rare earth elements (REEs) within the bauxite deposits of the aforementioned Nigerian states. This in-depth understanding of mineralogical associations and concentrations holds immense significance, not only for pinpointing these bauxite deposits as potential sources of REEs but also for crafting tailored technologies conducive to the recovery of these precious elements. Such advancements carry the potential to invigorate Nigeria's economic landscape, with the solid mineral sector poised to emerge as a pivotal driver of the nation's growth.

The multifaceted applications of REEs, spanning from smartphone screens, computers, and flat-panel televisions to the motors of computer drives and batteries for hybrid and electric vehicles, highlight their pivotal role in modern technology. However, the inherent concern surrounding REEs stems from their association with low-level radioactive elements like thorium and radium within mineral deposits. Exposure to these radioactive elements has been linked to an elevated risk of developing cancers, notably lung and pancreatic malignancies.

In summation, this study lays the foundation for recognizing Nigerian bauxite deposits as potential reservoirs of valuable REEs. The insights garnered herein pave the way for the evolution of specialized recovery techniques and technologies, fostering economic growth while simultaneously addressing the health and environmental considerations tied to these crucial elements. As the global landscape embraces sustainable resource management, this study positions Nigeria's solid mineral sector to play a pivotal role in the country's economic journey, with far-reaching implications for both the nation and the broader realm of technological advancement.

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