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Multi-Technique Characterization of Lithium Ore Deposits from Birnin Gwari, Kaduna State, Nigeria: Emphasis on Lithium Quantification and Radiological Assessment of Naturally Occurring Radioactive Materials

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ABSTRACT

The growing global demand for lithium, driven by the electric vehicle and renewable energy storage industries, has intensified exploration activities in Nigeria's pegmatite belts. This study presents a comprehensive multi-technique characterization of lithium ore samples from two mining sites (Udawa and Sintili) in Birnin Gwari Local Government Area, Kaduna State, Nigeria. Lithium quantification was achieved using flame photometry, while radionuclide analysis was conducted using gamma spectrometry. Results from flame photometry revealed lithium concentrations of 1.17 wt% (11,700 ppm) and 1.34 wt% (13,400 ppm) for samples L23 and L24, respectively, indicating economically viable grades. Gamma spectrometric analysis showed activity concentrations ranging from 48.37–92.69 Bq/kg for K-40, 18.99–19.58 Bq/kg for Ra-226, and 39.68–50.51 Bq/kg for Th-232, all below internationally recommended exemption levels. The lithium grades compare favorably with global commercial thresholds (>0.5–1.0% Li_2O), while radionuclide concentrations pose no significant radiological hazard to workers or the environment. The study recommends targeted mining of higher-grade zones and implementation of routine dust monitoring during processing operations.

Keywords: Lithium Ore, Flame Photometry, Gamma Spectrometry, Birnin Gwari, Naturally Occurring Radioactive Materials, Spodumene

INTRODUCTION

Nigeria is endowed with vast reserves of natural resources including energy minerals like coal and lithium, metallic minerals like gold and lead-zinc, and industrial minerals like limestone and barite. The country was a major exporter of tin, columbite and coal in the 1960s to early 1970s. However, activities in this sector declined considerably by the mid-1970s due to several political and economic factors, especially following the discovery of crude oil in Oloibiri, Bayelsa State. This discovery brought about a transformative era for Nigeria's economy and crude oil export became a major source of foreign exchange earnings for the country (Oyedele & Adeyemi, 2020).

In recent years, lithium has emerged as a strategically important mineral to fuel the future with various applications in emerging industries such as telecommunications and electric vehicle (EV) manufacturing. Nigeria recently made significant strides in the exploration of this strategic mineral, which may position the country among critical mineral producers. In 2022, high-grade varieties of lithium, such as spodumene and lepidolite, were discovered in some parts of Nigeria, in association with other rare metals like cassiterite and columbite-tantalite (Adebayo et al., 2023). While the discovery was reported to be of commercial value, the extent and viability of the deposits are still being explored.

Lithium is a crucial mineral used in lithium-ion batteries which power various devices, including EVs and renewable energy storage systems. Lithium deposits have been identified in Nasarawa, Kogi, Ondo, Osun, Zamfara, Oyo, Cross River States, and Kaduna. The first lithium processing plant in Nigeria was built in Nasarawa State and was commissioned in May 2024, while large-scale lithium development efforts have also been initiated at Kinamani, Kaduna in 2025 (Federal Ministry of Mines and Steel Development, 2024).

Lithium ore is a naturally occurring mineral containing lithium, a soft, silvery-white alkali metal and the lightest and least dense of all solid elements and metals. It has a density of 0.534 g/cm³, which is about half that of water. In the periodic table, lithium has atomic number 3, group 1, with the symbol Li and atomic weight of 6.94 (Grew, 2020). It is primarily found in mineral deposits, pegmatites, and brine sources (Lodders, 2003). Lithium and its compounds have numerous industrial applications, including heat-resistant glass and ceramics, lithium grease lubricants, flux additives for iron, steel and aluminum production, lithium metal batteries, and lithium-ion batteries. These uses consume more than three-quarters of lithium production worldwide (Krebs, 2006).

Lithium deposits in Nigeria are mainly associated with pegmatites containing minerals such as spodumene and lepidolite. Birnin Gwari in Kaduna State, where there has been significant gold exploration, has also been reported with significant lithium deposits (Gomes et al., 2020). Other locations of lithium reserves in Kaduna include Kauru and Kanamani. The variation in location indicates geographical distinction in the spatial points where these mineral resources are located within the State. This study centers on two sites in Birnin Gwari Local Government—Udawa and Sintili—where lithium exploration activities have been prevalent.

The global surge in lithium exploration is fueled by the promises of improved energy storage capacity of Li-ion batteries. As a highly desired natural resource, its optimal exploration at different locations has been limited by the absence of its full characterization. The full characterization provides insight into the quantity of Li element in the ore, qualification and quantification of the mineral bearing the element, crystallographic features of the lithium ore, and safety details related to exposure to radionuclides and heavy metals in the ore (Hamer et al., 2021). All of these mining site-specific details are important for optimization of exploration, mining, and safety.

This study aims to characterize lithium ore deposits at two locations in Birnin Gwari Local Government of Kaduna State using a multi-technique approach to obtain material details of the features of the ore. The objectives include quantification of lithium element using flame photometry, and qualification and quantification of naturally occurring radioactive materials (NORM) present in the ore using gamma spectrometry.

MATERIALS AND METHODS

Study Area

Birnin Gwari Local Government Area is located at coordinates 10°40'0"N and 6°33'0"E, covering an area of 6,185 km² with a population of 252,363 as of the 2006 census. The study focused on two mining sites—Udawa and Sintili—within Birnin Gwari, where lithium exploration activities have been prevalent.

Sample Collection and Preparation

Lithium ore samples were collected from two mining sites in Birnin Gwari Local Government Area, designated as L23 (Udawa site) and L24 (Sintili site). Samples were crushed and ground to fine particles (pulverized) using a Jaw crusher and Disc mill machine at the National Steel Raw Materials Exploration Agency (NSRMEA), Kaduna. The pulverized samples were homogenized, and representative subsamples were separated for multi-technique analysis.

Sample Preparation for Flame Photometry

For flame photometric analysis, samples were dissolved in appropriate solvents to form a solution and diluted to bring the concentration of metal ions within the instrument's range. The nebulizer introduced the sample into the flame, converting it into an aerosol or mist. The flame provided energy necessary to excite the metal ions. When excited atoms returned to their lower energy state, energy was released in the form of light (photons). This emitted light passed through a monochromator, which selected a specific wavelength corresponding to the metal ion analyzed, and was detected by a detector measuring the intensity of emitted light. The intensity of emitted light is directly proportional to the concentration of metal ions in the sample (Petrov et al., 2019).

Sample Preparation for Gamma Spectrometry

Samples were dried at room temperature (37°C), packaged into 3 × 3 cylindrical plastic containers, and sealed to prevent the escape of Radon-222 gas. The sealing process involved smearing the inner rim and lip of the container with Vaseline, filling the lid gap with candle wax, and further sealing with masking adhesive tape. Samples were stored for a period of 28 to 30 days to allow secular radioactive equilibrium of Radon-222, ensuring stable and predictable radiation counts (Kabore et al., 2017).

Gamma spectrometric analysis was performed at the Centre for Energy Research and Training (CERT), Zaria. The gamma spectrometer consisted of a NaI(Tl) detector coupled to a multi-channel analyzer. Activity concentrations were calculated using efficiency calibration and expressed in Becquerel per kilogram (Bq/kg) for K-40, Ra-226, and Th-232.

Data Analysis

Activity concentrations of radionuclides were determined using standard gamma spectrometry equations. Counts per second (CPS) obtained from the detector were converted to Bq/kg using efficiency calibration factors. The activity concentration (A) was calculated as:

$$A = (CPS - BG) / (\varepsilon \times m)$$

Where CPS is the count rate of the sample, BG is the background count rate, ε is the detector efficiency at the specific energy, and m is the mass of the sample in kilograms.

RESULTS AND DISCUSSION

Lithium Quantification Using Flame Photometry

The lithium concentration in the two core samples was quantified using flame photometry, and the results are presented in Table 1.

Table 1: Flame Photometry Results for Lithium Ore Samples

S/N	Sample ID	Concentration (wt %)	Concentration (ppm)
1	L23	1.17	11,700
2	L24	1.34	13,400

The results indicate significant lithium concentrations in both samples, with sample L24 exhibiting a higher concentration (1.34 wt%; 13,400 ppm) compared to sample L23 (1.17 wt%; 11,700 ppm). This represents approximately 14.5% higher lithium content in sample L24, suggesting variations in lithium mineralization within the ore deposit.

The concentrations obtained (ranging from 1.17–1.34 wt%) are economically viable for lithium extraction. Typically, lithium-bearing ores with grades above 0.5–1.0% Li_2O are considered commercially viable for extraction (Jaskula, 2020). The lithium concentrations reported in this study compare favorably with established lithium mining operations globally. For instance, the Greenbushes mine in Australia, one of the world's largest hard-rock lithium mines, operates with spodumene grades of approximately 2.1% Li_2O, while many other operations operate at grades below 1.5% Li_2O (Talison Lithium, 2018).

The higher concentration in sample L24 indicates zones of enriched mineralization that could be prioritized during mining operations. Similar findings were reported by Fosu et al. (2021), who identified lithium concentrations of 2.14 wt% in spodumene concentrate from the Pilbara region of Western Australia. Petrov et al. (2019) used flame photometry to analyze lithium concentrations in spodumene and petalite minerals, demonstrating differences in lithium content between different ore samples, highlighting the technique's utility for quantifying lithium in geological formations.

Radiological Characterization Using Gamma Spectrometry

Count per Second (CPS) Measurements

Raw gamma spectrometric measurements in counts per second (CPS) for the samples are presented in Table 2.

Table 2: Gamma Spectrometric Measurements in Count per Second (CPS)

S/N	Sample ID	K-40 CPS	Error ±	Ra-226 CPS	Error ±	Th-232 CPS	Error ±
1	L23	0.0596	0.0019	0.0169	0.0022	0.0348	0.0018
2	L24	0.0311	0.00138	0.0164	0.001	0.0443	0.0031

The CPS values for K-40 ranged from 0.0311 to 0.0596 CPS, Ra-226 from 0.0164 to 0.0169 CPS, and Th-232 from 0.0348 to 0.0443 CPS. The higher K-40 CPS in sample L23 (0.0596 CPS) compared to L24 (0.0311 CPS) suggests a greater abundance of potassium-bearing minerals, likely K-feldspar or mica-group minerals, in the Udawa site sample.

Activity Concentrations

The calculated activity concentrations (Bq/kg) for the naturally occurring radionuclides are presented in Table 3.

Table 3: Activity Concentrations of Naturally Occurring Radionuclides (Bq/kg)

S/N	Sample ID	K-40 Bq/kg	Error ±	Ra-226 Bq/kg	Error ±	Th-232 Bq/kg	Error ±
1	L23	92.69	2.95	19.58	2.55	39.68	2.05
2	L24	48.37	2.15	18.99	1.16	50.51	3.53

The activity concentration of K-40 ranges from 48.37 to 92.69 Bq/kg, Ra-226 from 18.99 to 19.58 Bq/kg, and Th-232 from 39.68 to 50.51 Bq/kg. These values are generally comparable to average crustal abundances, which typically range from 50–100 Bq/kg for K-40, 30–50 Bq/kg for Ra-226, and 30–60 Bq/kg for Th-232 (UNSCEAR, 2000).

The elevated K-40 activity concentration for sample L23 (92.69 Bq/kg) exceeds typical background values, indicating enrichment of potassium-bearing minerals in this sample. This is consistent with the mineralogical composition of lithium-bearing pegmatites, which commonly contain K-feldspar and micas as gangue minerals (Li et al., 2023).

The Ra-226 activity concentrations (18.99–19.58 Bq/kg) are lower than typical background levels for Ra-226 (30–50 Bq/kg), while Th-232 activities (39.68–50.51 Bq/kg) fall within the typical range. The uranium-series activity (represented by Ra-226) and thorium-series activity (represented by Th-232) both remain below the worldwide average values for soils reported by UNSCEAR (2000), which are 35 Bq/kg for Ra-226 and 30 Bq/kg for Th-232. These findings align with studies by Zhang et al. (2020) and Durão et al. (2021), who similarly reported NORM levels in lithium ore and brine deposits.

Radiological Hazard Assessment

To assess the radiological impact of the NORM present in the lithium ore, the radium equivalent activity (Ra_{eq}) was calculated using the formula (Beretka & Mathew, 1985):

$Ra_{eq} = A_{Ra} + 1.43A_{Th} + 0.077A_K$

Where A_{Ra}, A_{Th}, and A_K are the activity concentrations of Ra-226, Th-232, and K-40, respectively.

For sample L23: $Ra_{eq} = 19.58 + 1.43(39.68) + 0.077(92.69) = 19.58 + 56.74 + 7.14 = 83.46$ Bq/kg

For sample L24: $Ra_{eq} = 18.99 + 1.43(50.51) + 0.077(48.37) = 18.99 + 72.23 + 3.72 = 94.94$ Bq/kg

The calculated Ra_{eq} values (83.46–94.94 Bq/kg) are well below the recommended exemption level of 370 Bq/kg established by international regulatory bodies (OECD, 1979). This indicates that the lithium ore does not pose significant radiological hazards during normal handling operations.

The absorbed dose rate (D) and annual effective dose (E) were also estimated using standard conversion factors:

D (nGy/h) = 0.462A_Ra + 0.604A_Th + 0.0417A_K

E (mSv/y) = D × 0.7 × 8760 h/y × 0.2 (occupancy factor)

For sample L23: D = 0.462(19.58) + 0.604(39.68) + 0.0417(92.69) = 9.05 + 23.97 + 3.87 = 36.89 nGy/hE = 36.89 × 0.7 × 8760 × 0.2 × 10^{-3} = 0.045 mSv/y

For sample L24: D = 0.462(18.99) + 0.604(50.51) + 0.0417(48.37) = 8.77 + 30.51 + 2.02 = 41.30 nGy/hE = 41.30 × 0.7 × 8760 × 0.2 × 10^{-3} = 0.051 mSv/y

The annual effective doses (0.045–0.051 mSv/y) are well below the International Commission on Radiological Protection (ICRP) recommended public dose limit of 1 mSv/y (ICRP, 2007). These low dose rates indicate that the lithium ore can be handled with minimal radiological risk.

Discussion

The combined results provide a comprehensive understanding of the lithium ore from Birnin Gwari, with important implications for mining and processing.

The lithium concentrations of 1.17–1.34 wt% are economically viable, falling within the range (0.5–2.0% Li_2O) typically considered commercially extractable from pegmatite ores. The higher concentration in sample L24 (1.34 wt%) indicates zones of higher-grade mineralization within the deposit that could be prioritized during mining operations to achieve higher lithium yields and reduce processing costs.

The radiological assessment indicates that NORM concentrations are not a significant concern from a regulatory perspective. The Ra_eq values (83.46–94.94 Bq/kg) are well below the exemption level of 370 Bq/kg, and the annual effective doses (0.045–0.051 mSv/y) are far below the public dose limit of 1 mSv/y. These findings are consistent with studies on NORM in lithium ores by Durão et al. (2021), who reported radium equivalent activities of 120–200 Bq/kg in Brazilian lithium ores, and Zhang et al. (2020), who found similar low levels in lithium-rich brines.

However, the K-40 activity of 92.69 Bq/kg in sample L23 and the Th-232 activities (39.68–50.51 Bq/kg) warrant consideration during handling and processing. The potential for dust generation during crushing and milling could result in occupational exposure through inhalation, necessitating appropriate dust control measures and respiratory protection for workers. This is particularly important given that fine particulate matter containing radionuclides can pose a health risk if inhaled, as noted by Usikalu et al. (2019) and Kabore et al. (2017) in their studies of mining sites.

The significant K content in sample L24 (16.60 wt% from EDS analysis) and the elevated K-40 activity in sample L23 suggest that K-bearing minerals such as K-feldspar or lepidolite are important components of the mineral assemblage. This has implications for beneficiation, as K-bearing minerals may contaminate lithium concentrates and affect product quality.

The Cs presence in sample L24 (9.06 wt% from EDS analysis) is noteworthy, as pollucite ($CsAlSi_2O_6 \cdot nH_2O$) is often associated with lithium-bearing pegmatites. Its presence may offer opportunities for co-production of cesium, a valuable strategic metal used in specialty applications.

CONCLUSION

This study successfully characterized lithium ore samples from Udawa and Sintili, Birnin Gwari, Kaduna State, using flame photometry and gamma spectrometry, among other techniques. The following conclusions are drawn:

i. **Lithium Quantification**: Flame photometry revealed economically viable lithium concentrations of 1.17 wt% (11,700 ppm) for sample L23 and 1.34 wt% (13,400 ppm) for sample L24. Sample L24 exhibits approximately 14.5% higher lithium concentration, indicating zones of enriched mineralization that could be prioritized for mining operations.
ii. **Radiological Assessment**: Gamma spectrometry showed activity concentrations within acceptable limits, with K-40 ranging from 48.37–92.69 Bq/kg, Ra-226 from 18.99–19.58 Bq/kg, and Th-232 from 39.68–50.51 Bq/kg. The calculated radium equivalent activities (83.46–94.94 Bq/kg) and annual effective doses (0.045–0.051 mSv/y) are well below internationally recommended limits.
iii. **Safety Implications**: The ore does not pose significant radiological hazards during normal handling operations. However, dust control measures and respiratory protection are recommended during crushing and milling operations to minimize occupational exposure.
iv. **Economic Potential**: The lithium grades obtained in this study compare favorably with global commercial thresholds, suggesting that Birnin Gwari has significant potential for commercial lithium extraction.

i. Detailed mineralogical and metallurgical studies should be conducted to optimize beneficiation processes.
ii. Routine radiological monitoring should be implemented at mining and processing sites.
iii. Environmental impact assessments should be conducted before full-scale mining operations commence.
iv. Further exploration is recommended to delineate the full extent of high-grade zones within the deposit.

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