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GEOCHEMICAL ASSESSMENT OF ORE SAMPLES FROM ARTISANAL MINING SITES IN ZAMFARA STATE, NIGERIA

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ABSTRACT

This study focuses on the geochemical characterization of mineralized zones within Zamfara and its surrounding regions, located between latitudes 11°00'N–13°00'N and longitudes 5°00'E–7°00'E. The area is geologically underlain by the Migmatite Gneiss Complex and Schist Belts. Several researchers adopted magnetic filtration techniques such as vertical derivatives and analytic signal in order to delineate structures that may host mineralisation and hydrothermal alteration zones of solid minerals in the area. Other techniques adopted in the area include petrographic analysis. Even though, these methods can complement each other, some of the mineralisation and hydrothermal alteration zones are either too dispersed, in sufficient quantities, or of too low grade to be mined profitably and therefore does not economically contains concentration of ore minerals. Geochemical analysis utilizing X-ray fluorescence (XRF) was conducted to assess the elemental composition and concentration of mineral constituents within various alteration zones. The findings revealed significant concentrations of major oxides by weight, including CaO (18.29%), Al_2O_3 (31.13%), SiO (76.0) Fe_2O_3 (81.81%), SO_3 (0.18%), K_2O (25.29%), Mn_2O_3 (1.67%), P_2O_5 (0.91%), MgO (2.56%), Cr_2O_3 (1.28%), and CuO (0.04%) across multiple sampled locations. These compositions suggest zones of hydrothermal alteration and mineral enrichment, with variations in elemental distribution correlating with localized geochemical anomalies. Therefore, unveiling the rich subsurface geologic structures and mineral conduits coupled with identification of manifested minerals at the surface through geochemical method will improve the output capacity of the mining exploration and mitigate abandon mines. This study improved exploration efficiency by reducing investment risks in low-grade or uneconomic sites through understanding of the subsurface geology and structural controls of mineralization in a complex geologic setting.

Keywords: Geochemical Analysis, Zamfara state's schist belts, XRF, Solid Minerals

INTRODUCTION

Global mineral exploration faces growing challenges such as resource depletion, rising exploration costs, environmental concerns, and the need for responsible mining practices (Prior *et al*., 2012). These challenges are particularly relevant to regions like Zamfara, where artisanal mining is widespread but largely unregulated, leading to environmental degradation and public health risks (Olorede & Olorede, 2023). Addressing mineral exploration needs such as improved geological data, safer extraction methods, and sustainable resource management requires adapting global best practices to local conditions. Bridging this gap is essential for unlocking the region's mineral potential while safeguarding communities and ecosystems. Mining has been a significant economic activity in Nigeria for a very long time, dating back to 340 BC. In the early days, people extracted gold and other metallic substances. Although most of the mineral resources in the country have not been quantified, most states have identified extensive deposit of mineral resources (Alhassan, 2010)**.** Zamfara and its surrounding areas are widely recognized for their diverse mineral endowment, including occurrences of gold, copper, lead, and other economically significant metals (Danbatta *et al*., 2008b). However, challenges related to the identification of viable mineralized zones and the differentiation between ore-bearing and barren areas persist due to the heterogeneity of the underlying geology. Geochemical techniques, particularly X-ray fluorescence (XRF) analysis, have emerged as essential tools for quantifying elemental compositions and detecting geochemical anomalies associated with mineralization. By enabling rapid and precise assessment of rock and soil samples, XRF facilitates the evaluation of hydrothermal alteration zones and the delineation of potential ore deposits. The reviewed studies highlight key mineral and hydrocarbon exploration efforts across various Nigerian geological settings. Narimi *et al.* (2024) applied high-resolution aeromagnetic data to the Zamfara Basement Complex, successfully identifying structural features and magnetic source depths essential for guiding mineral exploration. Obaje *et al.* (2013) assessed the hydrocarbon potential of the Sokoto Basin, noting favorable total organic carbon (TOC) levels and recommending exploratory drilling to validate gas-rich prospects. Usman and Ibrahim (2017) emphasized the value of X-ray fluorescence over traditional petrographic methods for clarifying mineral composition in the Wonaka schist belt. Amuda *et al.* (2013) found eluvial gold deposits around Kutcheri and established copper and lead as reliable pathfinder elements. Shehu and Yelwa (2022) detected significant base metal concentrations in Kano's schist belt and advised radiometric surveys due to high potassium levels potentially linked to radioactive elements. Collectively, these studies underscore the integration of geophysical, geochemical, and analytical techniques in advancing Nigeria's mineral and energy resource assessments. The studies identified structural trends and the orientation of mineralized zones but did not validate the specific mineral types. Relying solely on secondary data, it lacked complementary geochemical analysis. This study employs XRF-based geochemical analysis to investigate the spatial distribution of major and trace elements within Zamfara's lithology's, aiming to contribute to a more effective mineral exploration strategy in the region. The study area is situated in Zamfara State and its surrounding regions in northwestern Nigeria, extending between latitudes 11°00'N and 13°00'N and longitudes 5°00'E and 7°00'E. This region lies within the Basement Complex terrain of Nigeria, which forms a part of the larger West African Craton Danjumma *et al.*, (2019a). The geology of the area is characterized by a diverse assemblage of rock units, including the Migmatite-Gneiss Complex (MGC), extensive Schist Belts, and a portion of the Sokoto Basin to the northwest Ajibade *et al.* (1987). The Migmatite-Gneiss Complex consists of ancient high-grade metamorphic rocks, including migmatites, banded gneisses, and granitic intrusives, forming the basement foundation (Osumeje *et al*., 2021a). The Schist Belts, which are of Proterozoic age, represent younger metasedimentary and metavolcanic sequences intruded by granitic rocks, often associated with significant mineralization. In contrast, the Sokoto Basin in the northwest consists of younger sedimentary sequences, primarily Cretaceous to Tertiary in age, indicating a transition from basement to sedimentary cover Dada (2006).

This geological diversity has contributed to the area's rich mineral potential, with known occurrences of gold, lithium, copper, zinc, and lead Danbatta, (2008a), Dada (2008). The structural complexity and metamorphic history of the region have also created favorable conditions for hydrothermal alteration and mineralization, making Zamfara a strategic target for mineral exploration activities Rahaman, (1988).

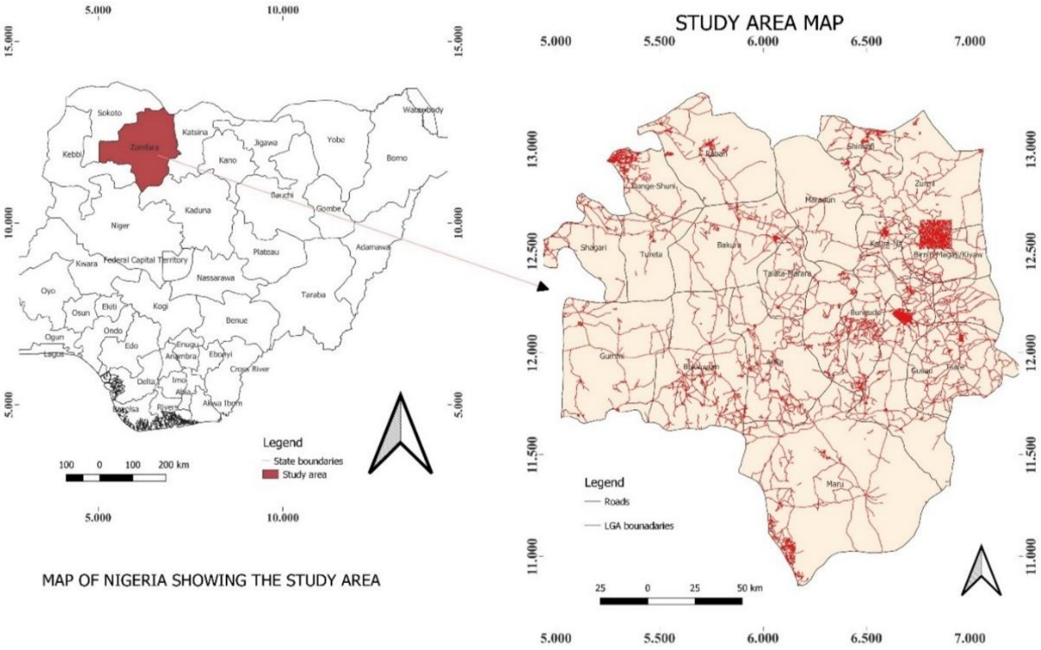

Figure 1: Shows the Location of the Study Area

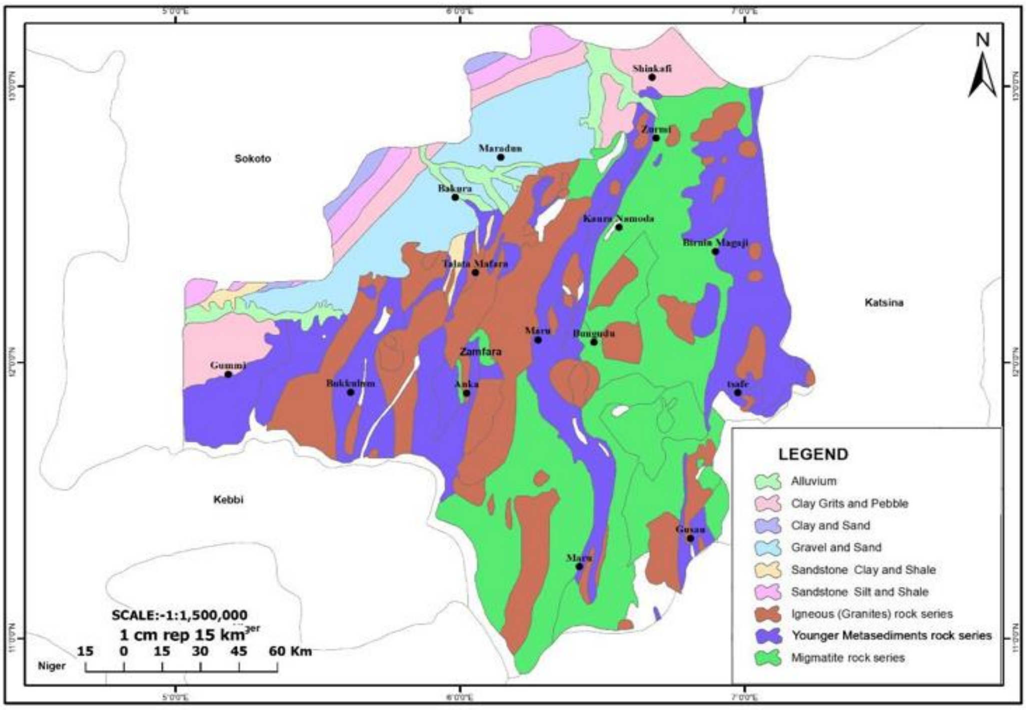

Figure 2: The Geology of Zamfara State Adopted After NGSA

MATERIALS AND METHODS

The following list includes several analytical methods for XRF examination of ore samples used in the lab.

Preparation of Sample for XRF

To characterize the geochemistry of major elements in the research region, rock samples from the man-made dug wells and outcrops were collected in 11 different locations as a follow up by the previous geophysical researches that identified mineralisation and hydrothermal alteration zones which collaborate with artisanal mining pits in the area. The samples were put into nylon container in order to avoid oxidation, the containers were level specimen: (A - K) which were taken to the of geology laboratory of Bayero University Kano for XRF analysis. In order to determine elemental composition, the samples were crush and grinded into a powder form (Jenkins *et al.*, 1981). After that, fused discs and pressed beads were created for analysis of the oxides. To ascertain the natural moisture contents of each prepared sample, they were oven-dried for an entire night at 105˚C. To ensure complete oxidation of sulfides and volatiles, enhances analytical reliability and avoids unwanted mineral melting. The samples were again roasted at 800˚C for a whole night in order to calculate the Loss on Ignition (LOI). The weight difference was then computed. In a platinum crucible, 1.5 g of powder from each sample for which LOI has been established was combined with 6 g of lanthanum oxide (La_2O_3) and lithium tetraborate ($Li_2B_4O_7$). The mixture was then fused at 1200˚C to create melt beads for the main element analysis (Jenkins, 1976).

Calibration of the XRF Analyser

National Institute of Standards and Technology (NIST) (USA) calibration standards that are similar in matrix to the (CaO, SiO_2, Al_2O_3, Fe_2o_3, SO_3, K_2O, Mn_2O_3, TiO_2, P_2O_5, MgO, Cr_2O_3, CuO and Ta_2O) were used. These standards ensure accurate quantification of elemental concentrations.

Instrument Calibration

Documented elemental composition known as (reference materials or known standard) were used while adjusting settings of the instrument as needed. These standards are similar as possible in matrix and composition to the samples.

Analysis Mode

XRF analyzers was set up and measured both qualitative (detecting elements) or quantitative (measuring element concentration).

XRF Analysis: Since the analysis is for ore minerals, focused were made on the elements of interest, which might include metals like iron (Fe), copper (Cu), lead (Pb), zinc (Zn), gold (Au), silver (Ag), and others depending on the ore type. The prepaid samples were then place the on the XRF sample holder or beam path, which was positioned well so that the X-ray beam can penetrate the sample properly. By Starting the analysis, and the XRF analyser emit X-rays onto the sample. The sample emits secondary X-rays (fluorescence), which the detector measures and analyses. The XRF device produced spectra corresponding to the elements present in the sample based on their atomic composition.

Data Interpretation: The XRF machine generated a spectrum showing peaks that correspond to the elements present in the sample. Using software, the machine converted the intensity of the X-ray peaks into concentrations of the different elements.

RESULTS AND DISCUSSION

The results in the Table 1, below were obtained from XRF analysis. Qualitative data obtained from XRF results shows the following minerals present in the samples and their respective percentages.

Table 1: Shows Sample of Minerals with Their Respective Oxides in Percentage

Oxides (wt.%)	Samples											Crustal abundance wt. %
	A	B	C	D	E	F	G	H	I	J	K	
CaO	0.28	0.00	0.26	18.3	1.66	0.23	4.46	0.00	81.8	0.19	0.00	4.24
SiO_2	65.2	41.7	43.1	41.0	35.86	38.9	47.9	67.9	88.8	75.6	76.0	66.8
Al_2O_3	8.38	19.3	24.6	16.0	31.1	14.6	15.4	0.18	4.40	11.5	9.40	15.1
Fe_2O_3	2.39	9.49	0.00	15.5	20.0	0.00	1.19	0.06	4.40	0.28	7.38	4.09
SO_3	0.40	0.16	0.18	0.22	0.15	0.18	0.18	0.16	0.00	0.40	0.00	0.06
K_2O	7.01	0.03	25.4	0.02	0.01	23.5	0.29	0.00	2.62	9.87	2.03	3.19
Mn_2O_3	0.16	0.08	0.61	0.29	0.65	5.65	0.04	0.02	0.19	0.00	1.67	0.07
T_iO_2	0.66	0.65	0.23	0.15	0.38	0.38	0.18	0.12	0.12	0.20	1.06	0.54
P_2O_5	0.00	0.00	0.00	0.60	0.14	0.00	0.00	0.00	0.00	0.91	0.00	0.15
MgO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.56	0.00	1.10	2.30
Cr_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.11	0.00	1.28	0.18
CuO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.00	0.00
Ta_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.00
BaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.36	0.00	0.04
ClO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.28	0.00	9.53
Rb_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.05

Table 1 above presents percentages by weight of each ore sample and their crustal abundance from the XRF analysis.

Table 2: Shows Sample of Minerals with their Respective Oxides in Percentage

Samples	Name of the Sites	Longitude	Latitude
A	Bingi	6° 32' 32" E	11° 41' 31" N
B	Maru	6° 24' 13.39" E	12° 20' 0.96" N
C	Gusau	6° 39' 50.83" E	12° 10' 12.86" N
D	Dansadau	6° 29' 42.72" E	11° 17' 46.36" N
E	Maradun	6° 14' 24.00" E	12° 33' 59.99" N
F	Chafe	6° 53'59.99" E	11° 55' 59.99" N
G	Zurmi	6° 47' 5.99" E	12° 45' 59.99" N
H	T/Mafara	6° 03' 44.10" E	12° 34' 6.28" N
I	Ruwan Gora	5° 59' 45" E	12° 14' 59" N
J	Kwandawa	6° 45' 05" E	12° 27' 50" E
K	Gandi	5° 44' 36.13" E	12° 57' 48.89" N

Table 2 above indicate the locations (longitude and latitude) of each sample that taken for geochemical analysis (XRF) Ultimately, economic viability is a balance between grade, demand, and the cost of extraction and processing. Figure 3 shows a pie chart of available ore composition in all the samples

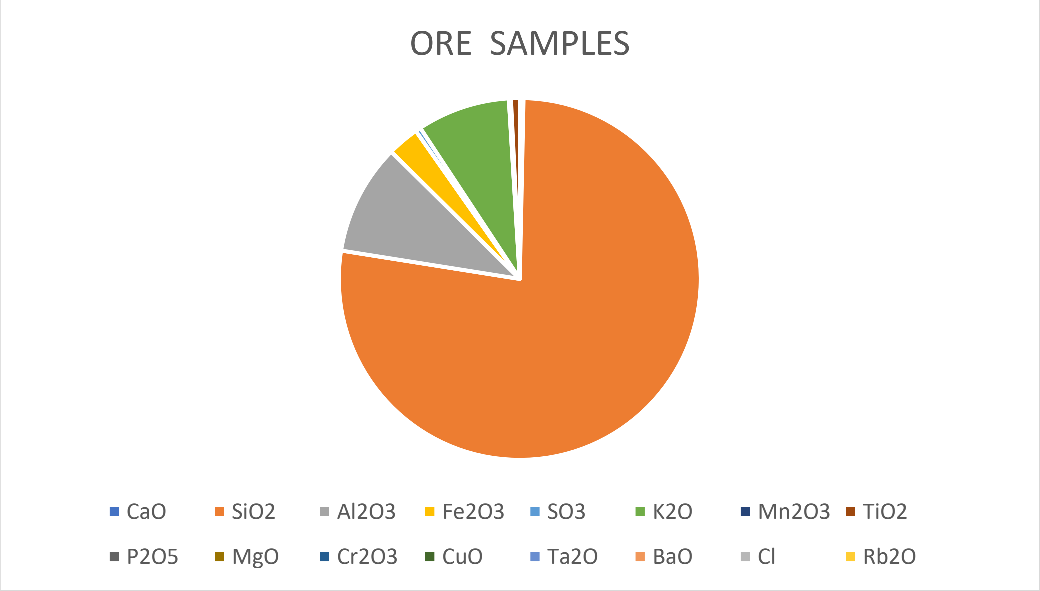

Figure 3: Shows a Pie Chart of Available Ore Composition in all the Samples

Figure 3 above indicates that silicon oxide constitutes the largest proportion of ore minerals in the geochemically analyzed samples, followed by chlorine oxide and potassium oxide, respectively."

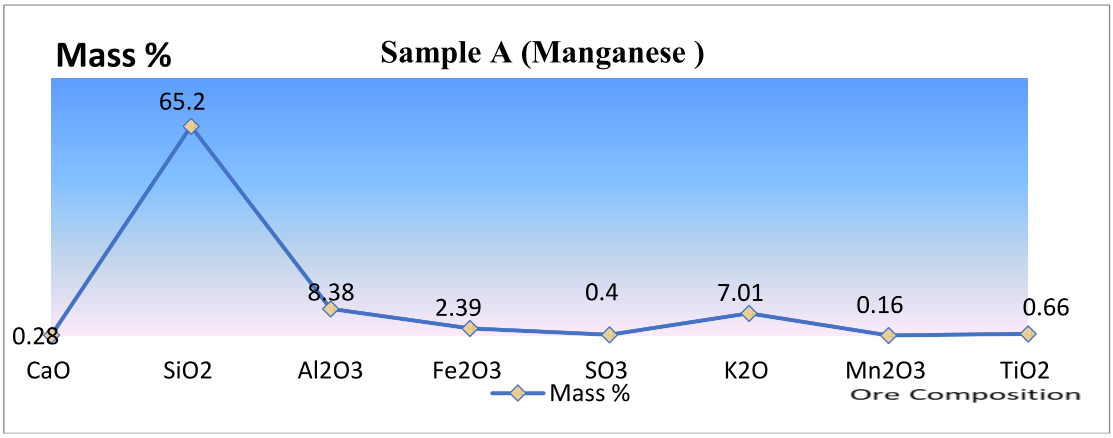

Figure 4: Line Showing of Sample A, (Manganese)

Figure 4 was labeled as manganese with the designation Sample A. However, the analysis shows that silicon oxide (SiO_2) makes up 65.2% by weight of the sample, whereas manganese oxide (MnO_3), at 0.16%, falls significantly below the 20% threshold required for economic viability.

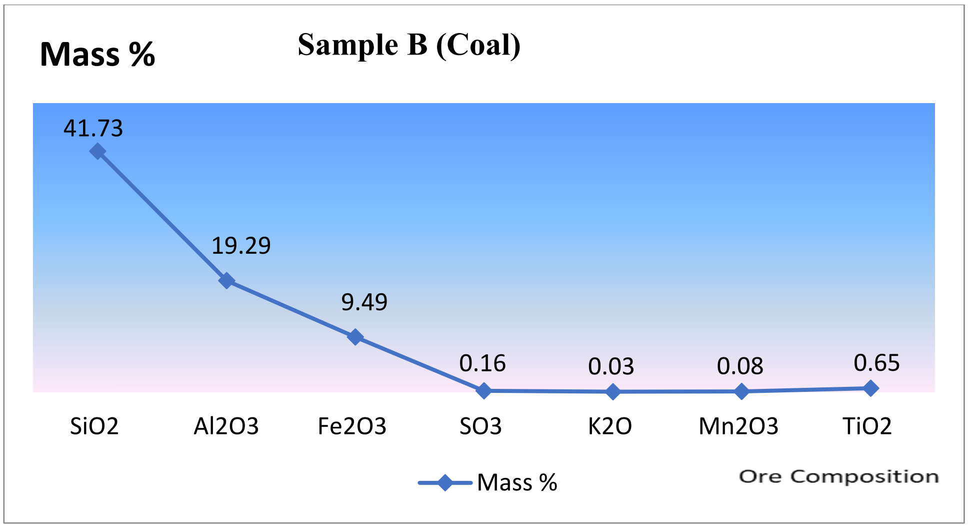

Figure 5: A Line Graph Showing Mass of Coal Against their Ore Composition

Figure 5 (Sample B) was initially identified as coal; however, geochemical analysis revealed that no traces of coal but the ore contains 19.29% by weight of aluminium oxide (Al_2O_3), suggesting potential for economically viable extraction.

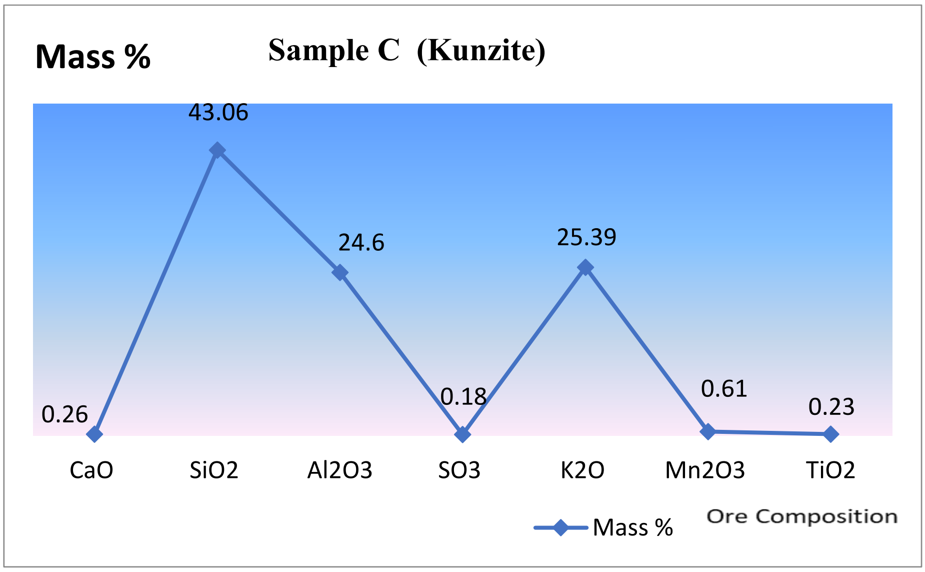

Figure 6: A line Graph Showing Mass of Kunzite Against its Ore Composition

Figure 6 (Sample C) was classified as Kunzite; however, geochemical analysis revealed significant concentrations of aluminum (24.6%) and potassium oxide (K_2O) (25.4%) by weight, indicating potential for economically viable extraction.

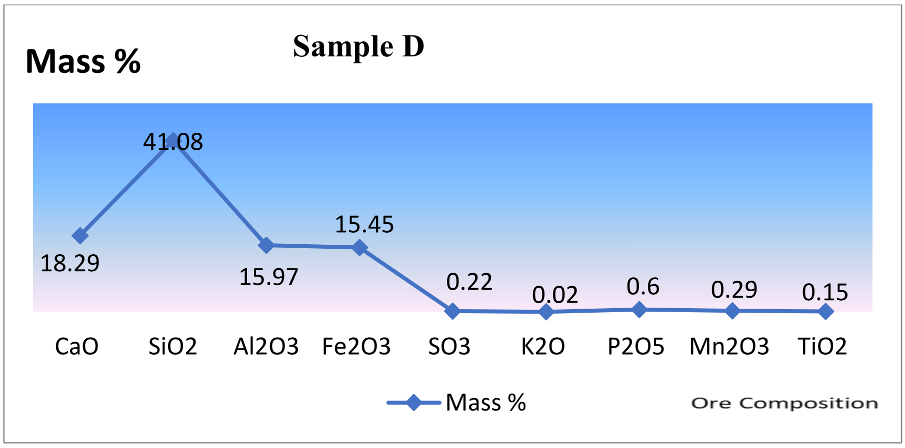

Figure 7: A Line Graph Showing Mass of Rutile Against its Ore Composition

Figure 7 (Sample D) was identified as rutile (TiO_2). The ore sample contains 0.15% by weight of TiO_2, which may suggest the presence of a potentially economically viable mineral.

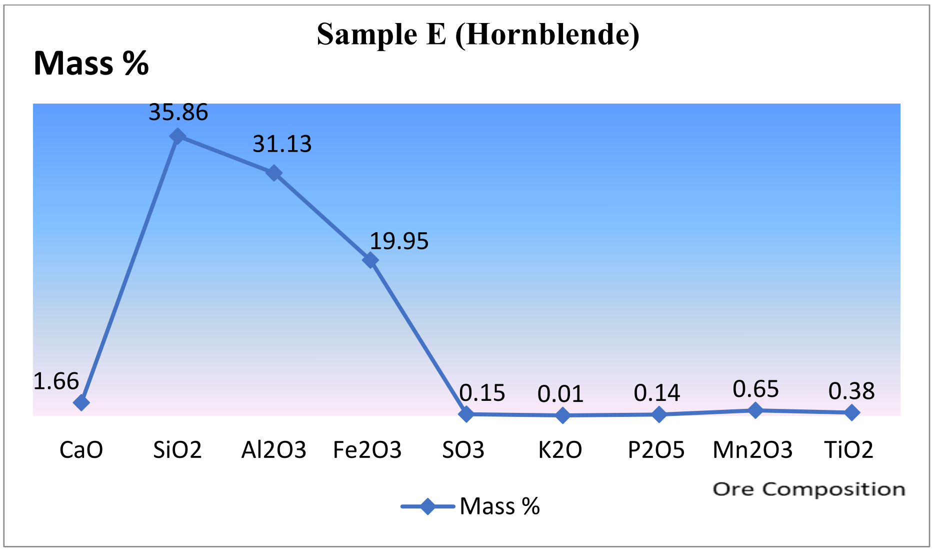

Figure 8: A Line Graph Showing Mass of Hornblende Against its Ore Composition

Figure 8 (Sample E) was identified as hornblende, it shows a content of aluminium oxide Al_2O_3 (31.13%) and iron oxide Fe_2O_3 which may suggest the presence of economic viability.

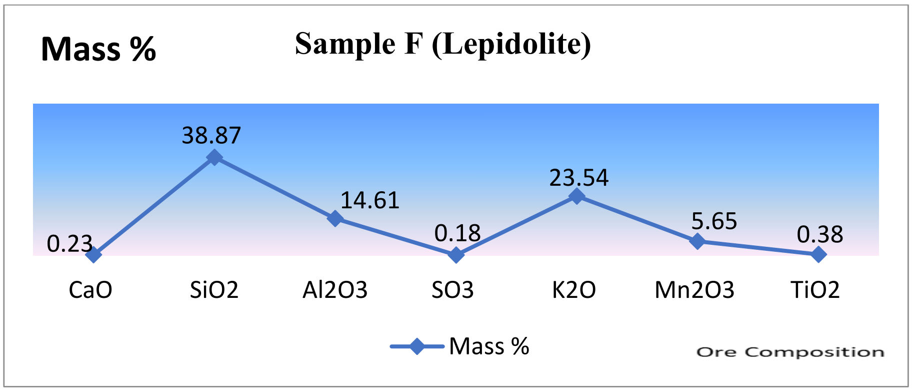

Figure 9: A Line Graph Showing Mass of Lepidolite Mica Against its Ore Composition

Figure 9 (Sample F) was classified as lepidolite mica ($LiAlSi_2O_6$), but no traces of lithium were detected. However, the analysis revealed a significant presence of potassium oxide (K_2O) at 23.5%, along with detectable amounts of TiO_2.

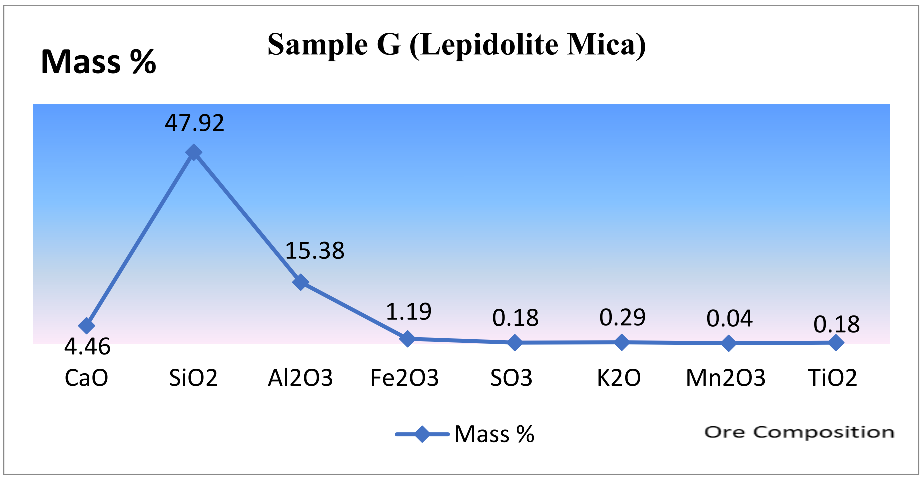

Figure 10: A Line Graph Showing Mass of Lead Oxide Copper Against its Ore Composition

Fugure 10 (Sample G) was also classified as lepidolite mica ($LiAlSi_2O_6$), but no traces of lithium were detected.

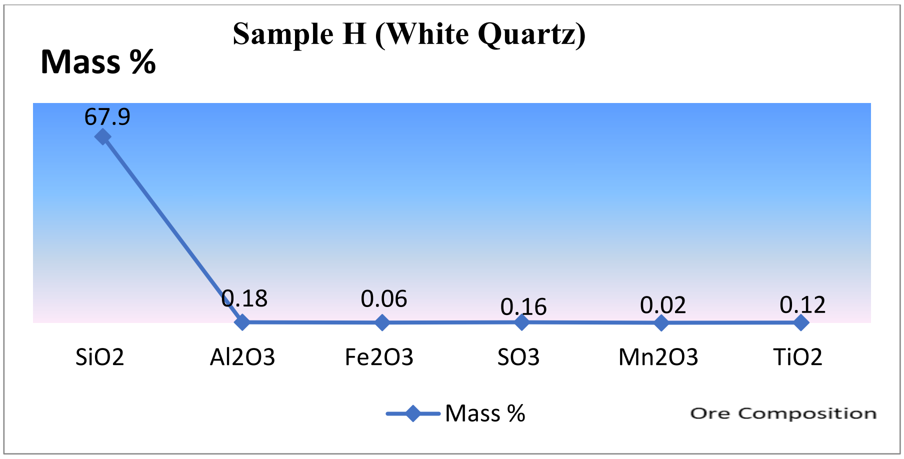

Figure 11: A Line Graph Showing Mass of White Quartz Against its Ore Composition

Figure 11 (Sample H) was identified as white quartz, with silicon oxide (SiO_2) making up approximately 67.9% by weight of the sample, indicating its economic viability.

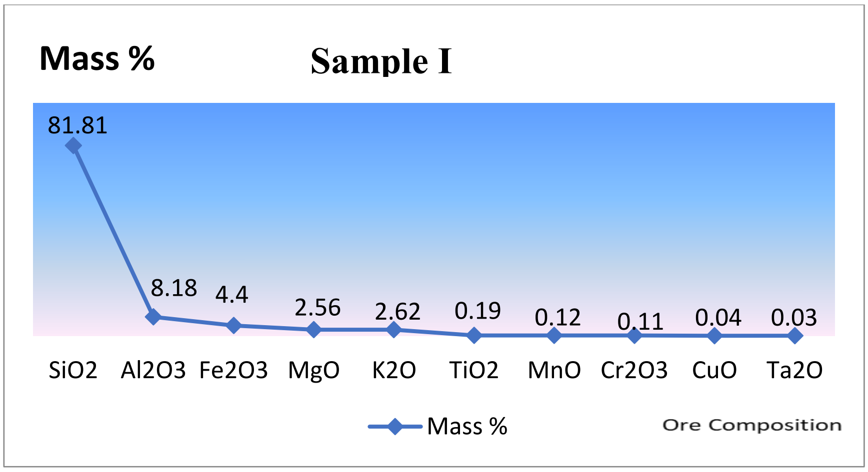

Figure 12: A Line Graph Showing Mass of White Quartz Against its Ore Composition

Figure 12 (Sample I) was also identified as white quartz, with silicon oxide (SiO_2) making up approximately 67.9% by weight of the sample, indicating its economic viability.

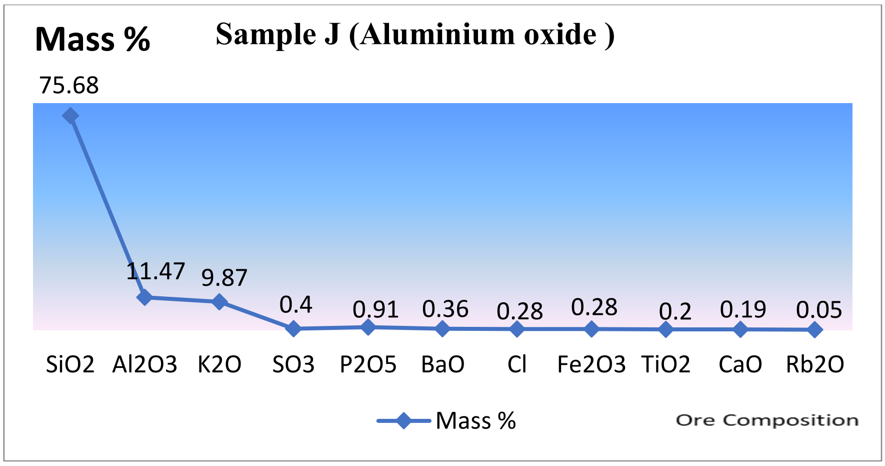

Figure 13: A line graph showing mass of Aluminium oxide against its ore composition

Figure 13 (Sample J) was identified as Aluminium oxide, however, aluminium oxide Al_2O_3 accounts for only (11.47 %) by weight of the sample which is not economically viable. Other oxides that found in the (sample J) in low quantity include Rb_2O (0.5 %), TiO_2 (0.2 %), P_2O_5 (0.915 %) with silicon oxide (SiO_2) making up approximately 75.68% by weight of the sample.

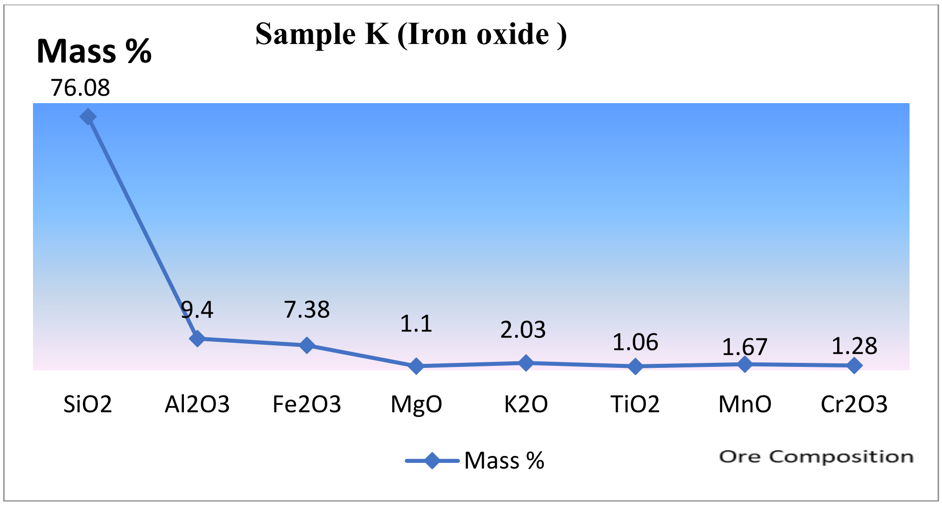

Figure 14: A Line Graph Showing Mass of Iron Oxide Against its Ore Composition

Figure 14 (Sample K) was identified as Iron oxide Fe_2O_3. However, the Iron and aluminium oxide constitute only (7.38 % and 9.4 %) by weight of the sample respectively, which is not economically viable.

The percentage required for an ore mineral to be of economic importance varies widely:

High-volume minerals: 20%–60%. Examples: Iron (Fe), Aluminum (Al), and Manganese (Mn) Medium-Value Metals: 0.5%–5%. Examples: Copper (Cu), Zinc (Zn), Lead (Pb) Precious metals: <0.01%. Examples: Gold (Au), Silver (Ag), and Platinum Group Metals (PGMs) Rare earth elements: 0.1%–1%. Examples: Neodymium (Nd), Dysprosium (Dy), Lanthanum (La) Jackson, (2007). The findings revealed significant concentrations of major oxides by weight, including Al_2O_3 (31.13 wt%), Mn_2O_3 (1.67 wt%), K_2O (25.29 wt%), CaO (18.29%) CuO (0.04%) and Fe_2O_3 (19.9 wt%). The medium volume oxides include P_2O_5 (0.91%), SO_3 (0.18 wt%), and MgO (2.56 wt%) While the low volume oxides includes Cr_2O_3 (1.28 wt%), T_iO_2 (0.66 wt%), Ta_2O (0.3 wt%) and Rb_2O (0.05wt%) across multiple sampled locations. These values however, do not collaborate well with findings from (Bala *et al*., 2020; MSF and WHO 2010).

The oxides and minerals analyzed in the geochemical study include coal, galena, hornblende, kunzite, lead oxide copper, lepidolite/mica, lithium, black mica, malachite, manganese, muscovite, white quartz, and rutile, as illustrated in Plate 1 below. Certain oxides, such as rutile, aluminum oxide, iron oxide, and lead oxide, show strong correlation with the geochemical results obtained from the samples. In contrast, others including copper oxide, magnesium oxide, lepidolite mica, lithium, and kunzite appear in insignificant or undetectable quantities.

Plate 1: Shows the Samples of Oxides that were Taking for XRF Analysis

CONCLUSION

The geochemical analysis conducted using X-ray fluorescence (XRF) in Zamfara and its surrounding regions successfully identified significant concentrations of major oxides indicative of hydrothermal alteration and potential mineralization. The spatial distribution of elements such as CuO, Cr_2O_3, and Ta_2O_5, alongside widespread occurrences of other oxides, provided clear geochemical signatures that distinguish mineralized zones from barren areas. These results validate the use of XRF as a powerful and reliable method for assessing elemental composition and guiding mineral exploration. The study demonstrates that geochemical data can effectively support the delineation of economically viable targets, offering a valuable framework for future exploration and resource evaluation in geologically complex terrains like northwestern Nigeria. It is recommended that future studies undertake exploratory core drilling in areas exhibiting promising mineral potential to validate and quantify the identified resources.

To build on the findings of this study, future research should integrate geochemical analysis with complementary geophysical and petrographic methods to enhance the accuracy of mineral identification and delineation. Detailed field-based sampling combined with higher-resolution spatial mapping can improve the understanding of mineralization patterns and structural controls. Additionally, isotopic and mineralogical studies could provide deeper insights into the genesis of the identified mineral deposits.

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