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Geochemistry of Cu–Pb–Zn Sulphide Ores: Implications for Hydrothermal Mineralization in the Nigerian Basement Complex

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Abstract **Original Research Article**

Cu–Pb–Zn sulphide mineralization represents an important metallogenic feature of Precambrian basement terrains worldwide. This study presents the geochemical characteristics of Cu–Pb–Zn sulphide ore samples analyzed at the Nigerian Institute of Mining and Geosciences (NIMG), Jos, with the aim of constraining their mineralization styles and genetic implications. Mineralogical and geochemical data reveal a sulphide assemblage dominated by chalcopyrite, galena, and sphalerite, with subordinate pyrite and trace accessory phases. Elemental associations and relative metal abundances indicate deposition from hydrothermal fluids under evolving physicochemical conditions. Although the precise field provenance of the ore samples is unknown, their mineralogical and geochemical signatures closely resemble hydrothermal base-metal sulphide mineralization commonly associated with the Nigerian Basement Complex. The study provides useful geochemical criteria for recognizing Cu–Pb–Zn hydrothermal systems in basement terrains and contributes to the understanding of polymetallic sulphide mineralization in Nigeria.

Keywords: Cu–Pb–Zn sulphides; Geochemistry; Hydrothermal mineralization; Basement Complex; Nigeria.

1. Introduction

Base-metal sulphide mineralization involving copper, lead, and zinc constitutes a significant component of global metallogenic systems, particularly within Precambrian basement terrains globally (Bafor, 1981; Elueze, 1982; Robb, 2005; Pirajno, 2009; Oyeladun *et al.*, 2012; Seck *et al.*, 2020, Akintola *et al.*, 2021). Such mineralization commonly occurs in hydrothermal veins, shear zones, and granitoid-related systems, where metal-bearing fluids migrate through structurally controlled pathways and precipitate sulphides under favorable physicochemical conditions (Large *et al.*, 2001; Garba, 2003; Wilkinson, 2013; Ali et al., 2014 and Jatau et al., 2014; Akintola, 2024).

In Nigeria, Cu–Pb–Zn sulphide occurrences have been documented within the Basement Complex, notably in association with Pan-African tectono-magmatic events (Olade,1976; Akande, & Zentilli,1984; Olade, & Morton,1985;Ajibade *et al.,* 1987; Woakes *et al.*,1987; Mucke, 2005). Previous studies have linked these mineralizations to shear-zone-controlled hydrothermal systems and late- to post-orogenic granitoids (Garba, 2003;

Okunlola, 2001; Godwin *et al.,* 2022; Agunleti, 2023). However, detailed geochemical characterization of many sulphide ores remains limited, especially for laboratory-archived samples without precise field provenance. This study investigates the geochemical characteristics of Cu–Pb–Zn sulphide ore samples analyzed at the Nigerian Institute of Mining and Geosciences (NIMG), Jos. The objective is to interpret the ore-forming processes and evaluate its affinity with hydrothermal mineralization styles typical of the Nigerian Basement Complex.

2. Geological background

The Nigerian Basement Complex forms part of the Pan-African mobile belt situated between the West African and Congo Cratons (Ajibade *et al.,* 1987). It comprises migmatite-gneiss complexes, schist belts, and Pan-African granitoids, collectively referred to as the Older Granites (Dada, 2006; Obaje, 2009; Olaolorun & Akintola, 2018). These lithological units have been extensively affected by deformation, metamorphism, and hydrothermal fluid activity during the Pan-African orogeny (±600 Ma) (Dada, 2006; Akintola, 2024). Hydrothermal mineralization within the Basement Complex is commonly structurally controlled and includes gold, base metals, and iron-manganese occurrences (Garba & Adamu, 2008; Nwajide, 2013; Akintola *et al.*, 2021; Akintola; 2024). Cu–Pb–Zn sulphide mineralization is typically associated with quartz veins, shear zones, and granitoid contacts, reflecting fluid circulation driven by tectonic and magmatic processes (Okunlola, 2001; Pirajno, 2009; Agunleti, 2023, Oluyede *et al.*, 2021; Nyajon *et al.*, 2025).

3. Materials and Methods

The sulphide ore samples investigated in this study were submitted to the Nigerian Institute of Mining and Geosciences (NIMG), Jos for laboratory analysis. Although the precise field locations of the samples are unavailable. However, the study focuses on their mineralogical and geochemical characteristics, independent of field provenance. Geochemical analyses were conducted using standard laboratory procedures at NIMG. Major and trace elements relevant to base-metal mineralization were determined following appropriate sample preparation, digestion, and instrumental analysis protocols using AAS. Quality control was ensured through calibration with certified reference materials (Jenkins & Snyder, 1996; Bish & Post, 1989; Atkins, & de Paula, 2010).

4. Results

The ore samples are dominated by sulphide minerals, principally chalcopyrite ($CuFeS_2$), galena (PbS), and sphalerite (ZnS). Subordinate pyrite (FeS_2) occurs as disseminated and intergrown phases. Minor accessory minerals include trace iron oxides and gangue quartz (Vaughan, & Craig, 1978; Anthony *et al.*, 1990; Sillitoe, 2015; Zhang *et al.*, 2021). The coexistence of Cu–Pb–Zn sulphides across the analyzed samples indicates a polymetallic sulphide assemblage typical of hydrothermal systems, where metal precipitation occurs in response to changes in temperature, pressure, and sulphur fugacity as presented in Table 1.

Table 1: Sulphide Mineral distribution across Samples 1–16

Sample No.	Dominant Sulphide Minerals Accessory / Trace	Phases Interpretation
Sample 1	Chalcopyrite + Pyrite Minor Zn, Fe Cu-rich	hydrothermal sulphide
Sample 2	Chalcopyrite + Sphalerite Fe, trace Ag Cu–Zn	sulphide assemblage
Sample 3	Galena + Sphalerite Minor Pyrite Pb–Zn	dominant sulphide
Sample 4	Chalcopyrite + Galena Fe, trace Bi	Polymetallic sulphide
Sample 5	Sphalerite ± Pyrite Zn, Fe Zn-rich	hydrothermal phase
Sample 6	Chalcopyrite + Pyrite Minor CuO	Primary Cu sulphide
Sample 7	Galena + Sphalerite Cd, trace Ag Pb–Zn	sulphide enrichment
Sample 8	Chalcopyrite + Sphalerite Fe Cu–Zn	Transitional assemblage
Sample 9	Pyrite + Chalcopyrite Fe dominant	Early sulphidation stage
Sample 10	Galena ± Pyrite Pb, Fe	Lead-dominant sulphide
Sample 11	Sphalerite + Chalcopyrite Zn, Cu	Mixed Cu–Zn sulphide
Sample 12	Chalcopyrite ± Pyrite Fe	Cu-rich sulphide phase
Sample 13	Galena + Sphalerite Minor Bi Pb–Zn	polymetallic sulphide
Sample 14	Chalcopyrite + Galena + Sphalerite Ag, Cd	polymetallic ore
Sample 15	Pyrite ± Chalcopyrite Fe Early	hydrothermal sulphide
Sample 16	Chalcopyrite + Sphalerite Trace Ag, As	Evolved hydrothermal assemblage.

Elemental distribution and metal association

Geochemical data show enrichment and variability in Cu, Pb, Zn, and Fe. The contents of Cu range from very low (0.01) to very high (20.25 wt. %), Pb (78.25 wt.%), and Zn (40.65 wt.%), the variability in Fe content reflects the presence of pyrite and early sulphidation processes in table 2. These variations in Table 2 indicate a significant heterogeneous polymetallic sulphide system. These features are consistent with hydrothermal mineralization (Olade, 1976; Akande, & Zentilli, 1984; Pirajno, 2009; Robb, 2005; Garba, 2003). Trace elements such as Ag, Cd, and As occur in minor concentrations, consistent with polymetallic hydrothermal sulphide systems rather than sedimentary or magmatic segregation processes (Olade, & Morton, 1985; Large *et al.*, 2001; Salehi, S.; Noaparast *et al.*, 2016). The relative abundance of Zn compared to Cu and Pb suggests evolving hydrothermal fluids, where decreasing temperature favored sphalerite precipitation following chalcopyrite and galena formation (Dutrizac & MacDonald, 1974; Dutrizac *et al.*, 1985; Koleini et al., 2010; Olvera *et al.*, 2016). This geochemical zoning pattern is widely reported in Nigeria within the Basement hosted-sulphide deposits and this suggests characteristics consistent with Cu–Pb–Zn hydrothermal sulphide assemblage (Garba, 2003; Garba & Adamu, 2008; Wilkinson, 2013).

Table 2: The contents of Cu–Pb–Zn in Sulphide Ore

Samples	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Element Zn		0.01	0.88		0.02		0.66	0.07	40.65	4.95			4.98	0.08	2.15	0.33
Cu	0.25	4.5	0.62	0.15	0.014	5.52	0.08	0.01	0.2	20.25	12.75	13.75	20.25	14.9	0.049	7.08
Pb	0.09	0.04	0.65	0.03	0.21	0.13	0.96	0.6	6.22	0.55	0.094	0.51	0.55	0.16	78.25	1.78
Fe	12.7	8.75	5.97	12.32	28		0.64	12.8	4.35	16.45	13.9	11.2	16.45	1.22	0.49	5.58
Ag		0.012		0.003		0.004	0.03	0.03	0.0018	0.012		0.028	0.012	0.03	0.0037	0.012
Ni				0.02		0.15			0.16			0.29				
Mn					0.06										0.08	
As						0.19			0.18	0.11						
Bi									0.04							
Cd									0.1			0.01				
S2-									18.5	25.3			25.34	0.004	10.41	

The relative proportions of Cu, Pb, and Zn suggest geochemical zoning commonly observed in hydrothermal deposits, where chalcopyrite, galena, and sphalerite precipitate sequentially during fluid evolution. The geochemical relationships between Cu, Pb, and Zn were further evaluated using binary and ternary diagrams (Figures 1–4). The Cu–Zn plot shows an inverse relationship, suggesting fractionation during hydrothermal evolution (Figure 1). The Pb–Zn association reflects co-precipitation at lower temperatures (Figure 2), while the Fe–Cu plot indicates early pyrite formation followed by chalcopyrite deposition (Figure 3). The ternary diagram confirms the polymetallic nature of the ore and highlights geochemical zoning consistent with hydrothermal mineralization processes presented in Figure 4 present the ternary geochemical distribution of Cu-Pb- Zn , while Figure 5 present the paragenetic sequence diagram of ore

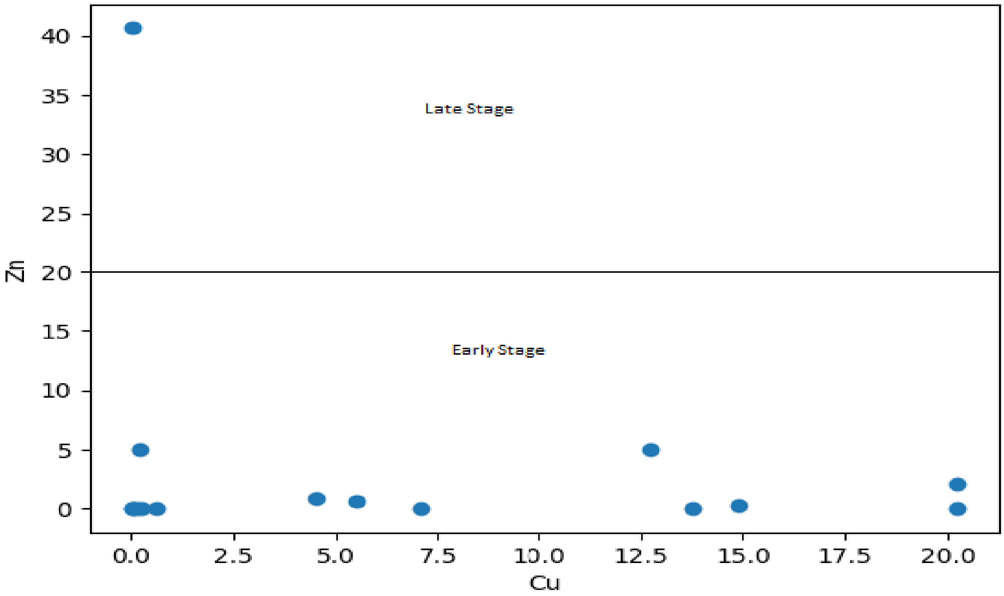

Figure 1: Binary plot of Cu versus Zn showing an inverse relationship, reflecting metal fractionation during hydrothermal fluid evolution and progressive cooling (after Robb, 2005; Pirajno, 2009).

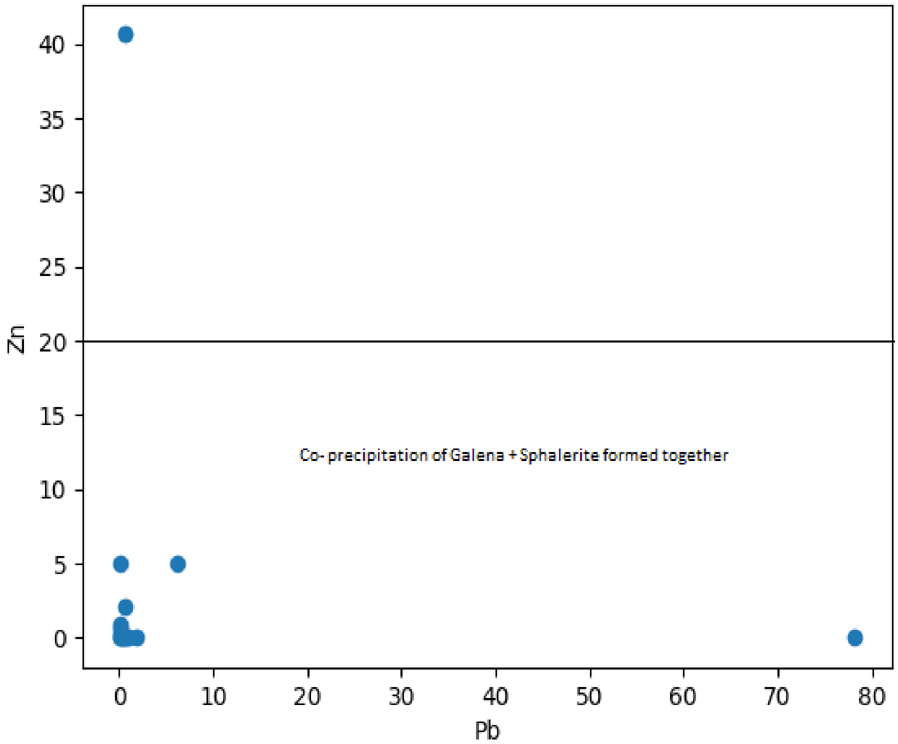

Figure 2: Pb versus Zn plot indicating partial co-precipitation during late-stage hydrothermal mineralization, consistent with polymetallic sulphide systems (Large et al., 2001).

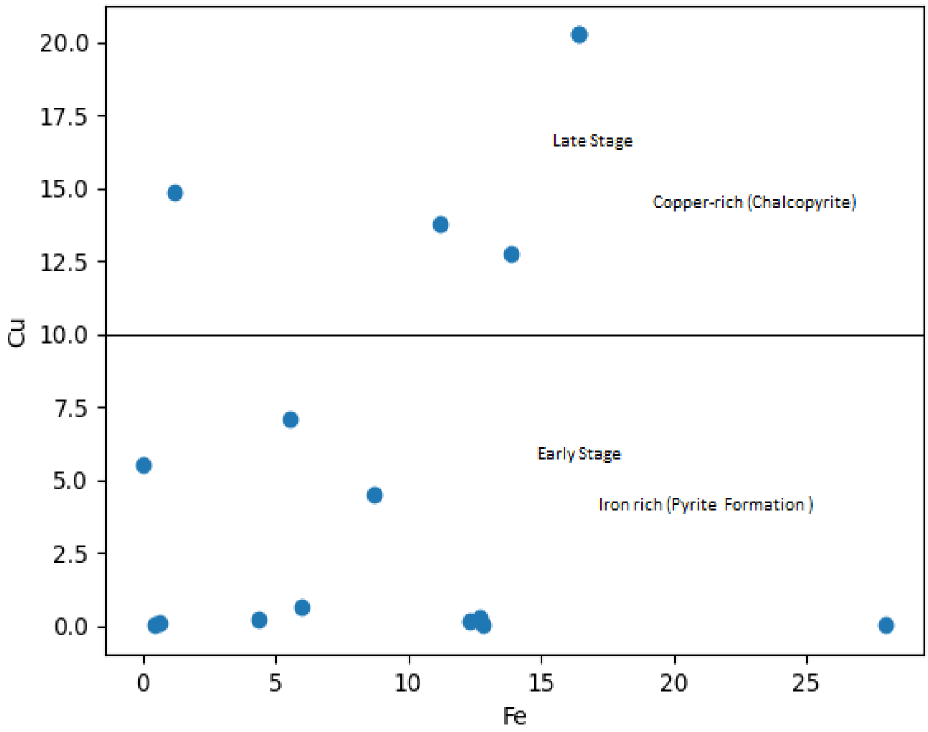

Figure 3. Binary plot of Fe versus Cu showing an inverse relationship, indicating transition from early Fe-rich pyrite mineralization to later Cu-rich chalcopyrite deposition during hydrothermal fluid evolution (Wilkinson, 2013).

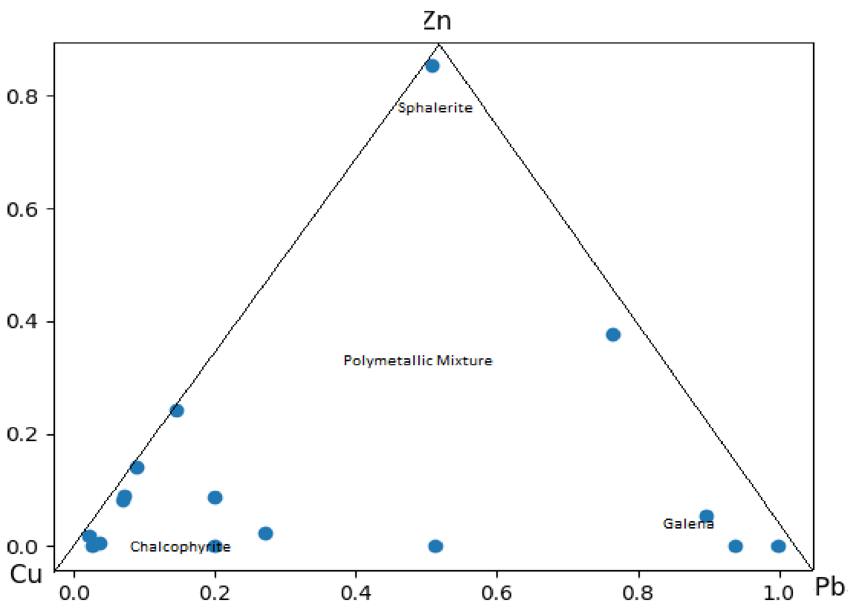

Figure 4. Ternary diagram of Cu–Pb–Zn showing polymetallic distribution and geochemical zoning typical of hydrothermal sulphide deposits in basement terrains (Pirajno, 2009; Robb, 2005).

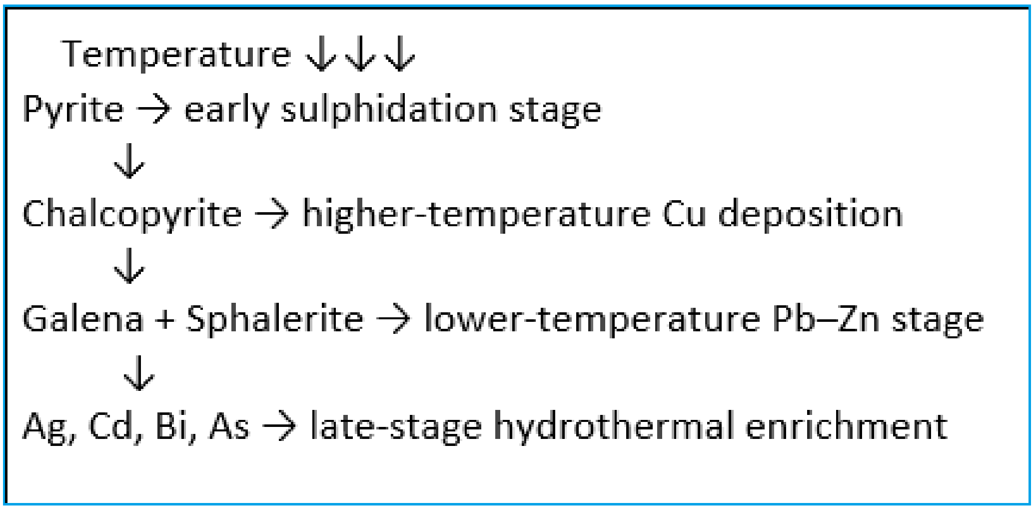

Figure 5: Paragenetic sequence diagram of ore

5. Discussion

Nature of Mineralization, Implications for the Nigerian Basement Complex and economic and exploration significance. The mineralogical and geochemical characteristics of the analyzed ore samples indicate formation from hydrothermal fluids rather than magmatic segregation or sedimentary processes (Garba, 2003; Pirajno, 2009). The geochemical pattern presented in Table 1 clearly reflects hydrothermal zoning, which is typical of evolving ore fluids (Pirajno, 2009): Zonation Trend as Early stage: Fe-rich (pyrite dominant) → Samples 1, 5, 9; Intermediate stage: Cu-rich (chalcopyrite) → Samples 6, 10–14; Late stage: Pb–Zn enrichment → Samples 7, 8, 15; With the Key Evidence of Zn spike (Sample 8) → late-stage cooling fluid; Pb extreme (Sample 15) → terminal hydrothermal phase. Cu dominance (Samples 10–14) → higher temperature deposition. This zoning trend reflects temperature-controlled sulphide precipitation, consistent with hydrothermal systems (Robb, 2005; Koleini *et al.*, 2011; Wilkinson, 2013 Salehi *et al.*, 2016). The geochemistry of trace elements (Ag, Cd, As, Bi, Ni, Mn) provides important genetic clues. Ag (Silver) is associated with galena and indicates Pb-rich fluids. Cd substitutes into sphalerite → confirms Zn mineralization. As and Bi: typical of late hydrothermal fluids Ni and Mn: minor fluid-rock interaction indicators. These elements confirm: Hydrothermal origin; Fluid evolution and fractionation, polymetallic enrichment. The high contents of Sulphur (S^{2-}) in (Samples 9, 10, 13, and 15) indicate high sulphidation conditions and efficient metal transport as sulphide complexes in reduced hydrothermal fluids and equilibrium precipitation of sulphide minerals (Large *et al.*, 2001; Fleet, 2006). The Cu versus Zn binary plot (Figure 1) shows an inverse relationship, indicating fractionation of metals during hydrothermal fluid evolution (Salehi *et al.*, 2016). Copper-rich samples correspond to early high-temperature mineralization dominated by chalcopyrite, whereas zinc enrichment reflects later, lower-temperature deposition of sphalerite. This trend is consistent with hydrothermal sulphide zoning reported in basement-hosted polymetallic systems. Figure 2 shows the Pb versus Zn plot shows a positive association, indicating co-precipitation of galena and sphalerite during the late stage of hydrothermal mineralization. Figure 3 The binary plot of Fe versus Cu relationship illustrating transition from early pyrite-dominated mineralization to chalcopyrite-rich stages and the Cu–Pb–Zn ternary diagram (Figure 4) reveals a broad dispersion of samples across the compositional field, reflecting the polymetallic nature of the sulphide mineralization (Klauber, 2008). Samples plotting toward the Cu apex represent early high-temperature chalcopyrite deposition, whereas those trending toward the Pb and Zn apexes indicate late-stage galena and sphalerite formation. Intermediate compositions suggest overlapping mineralization stages and fluid mixing. This distribution pattern is characteristic of hydrothermal sulphide systems exhibiting progressive cooling and metal zoning. The association of chalcopyrite, galena, sphalerite, and pyrite is diagnostic of hydrothermal base-metal sulphide mineralization as shown in the paragenetic sequence diagram (Figure 5). Such assemblages typically form in structurally controlled environments, where fractures and shear zones act as conduits for metal-bearing fluids. Although the exact field provenance of the ore samples is unknown, its mineralogical and geochemical signatures closely resemble Cu–Pb–Zn sulphide mineralization reported from the Nigerian Basement Complex. Comparable assemblages have been documented in the Ilesha schist belt, Egbe-Isanlu schist belt, Zungeru schist belt, Anka area and other basement terrains (Elueze, 1981; Kinnaird, 1985; Okunlola, 2001; Garba, 2003, Agunleti, 2023). The results therefore suggest that the analyzed ore represents a Basement Complex–type hydrothermal sulphide system, likely associated with Pan-African tectono-magmatic activity.

The polymetallic Cu–Pb–Zn sulphide mineralization is economically attractive due to the potential for multi-commodity extraction (Agunleti, 2023; Akintola 2024). The geochemical signatures identified in this study provide useful criteria for recognizing similar hydrothermal systems during mineral exploration in Nigerian basement terrains.

6. Conclusions

The Cu–Pb–Zn sulphide ore samples analyzed at the Nigerian Institute of Mining and Geosciences (NIMG), Jos, are characterized by hydrothermal sulphide assemblages dominated by chalcopyrite, galena, sphalerite, and subordinate pyrite. Geochemical evidence indicates that the mineralization was deposited from evolving hydrothermal fluids under varying physicochemical conditions. Mineralogical associations across Samples 1–16 reveal a consistent polymetallic Cu–Pb–Zn sulphide system, with pyrite representing an early and widespread mineralizing phase. Variations in dominant sulphide minerals among the samples reflect geochemical zoning during hydrothermal fluid evolution, ranging from Fe-rich early-stage mineralization to Cu-rich and later Pb–Zn-enriched phases. Minor occurrences of Ag, Cd, As, Bi, Ni, and Mn further support a polymetallic hydrothermal origin. The geochemical relationships observed in the binary and ternary plots indicate progressive cooling, fluid evolution, and metal fractionation during ore formation. Although the precise field provenance of the samples is unknown, their mineralogical and geochemical characteristics are consistent with hydrothermal Cu–Pb–Zn sulphide mineralization commonly associated with the Nigerian Basement Complex and Pan-African tectono-magmatic processes.

This study demonstrates the importance of integrated mineralogical and geochemical analyses in understanding ore genesis and provides useful geochemical criteria for identifying hydrothermal polymetallic sulphide systems in Nigerian basement terrains and similar geological environments elsewhere, where field information is limited.

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