



Stable Isotope Characteristics of Akiri Vein Copper Mineralization, Nasarawa, Nigeria

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ABSTRACT: The Akiri vein copper mineralization was investigated for its carbon and oxygen isotopic composition to determine the characteristics of the mineralizing fluid. Carbon and oxygen isotope analyses of Akiri siderite range between $\delta^{13}\text{C}$ values (-1.05 to -1.71‰) and $\delta^{18}\text{O}$ values (-14.94 to -15.18) respectively. $\delta^{13}\text{C}$ isotopic composition is comparable to values expected for Cretaceous marine carbonates. The ^{18}O depletion in the vein siderite indicates dominant meteoric water sources involved for carbonates precipitation. This significant depletion between the $\delta^{18}\text{O}$ compositions of Akiri siderite compared with carbonates from other parts of the basin probably indicate differential formational temperature or fluid composition. © JASEM

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KEY WORDS: Akiri, Copper Mineralization, Siderite, Isotope, Carbon, Oxygen.

Introduction

The Akiri copper mineralization is a significant copper deposit found in Akiri, Nasarawa, Nigeria (Fig. 1). The copper deposit is epigenetic vein mineralization cutting across the different stratigraphic lithologies within the Eze-Aku formation (Folorunso 2015). The veins occur on the flanks of domal structure (Anticlines) (Folorunso 2015). The aim of this research is to use stable Isotope geochemistry to determine the physicochemical characteristics of the mineralized

vein with a view to identify the possible source(s) of the mineralising fluids from which the ore and its gangue minerals were deposited. Isotopes of carbon and oxygen which are likely to be different for different ore districts and environments commonly give information on ore forming environments. In this study, the light isotopes of carbon and oxygen of vein minerals are examined in order to further understand the implications of their carbon-oxygen variation.

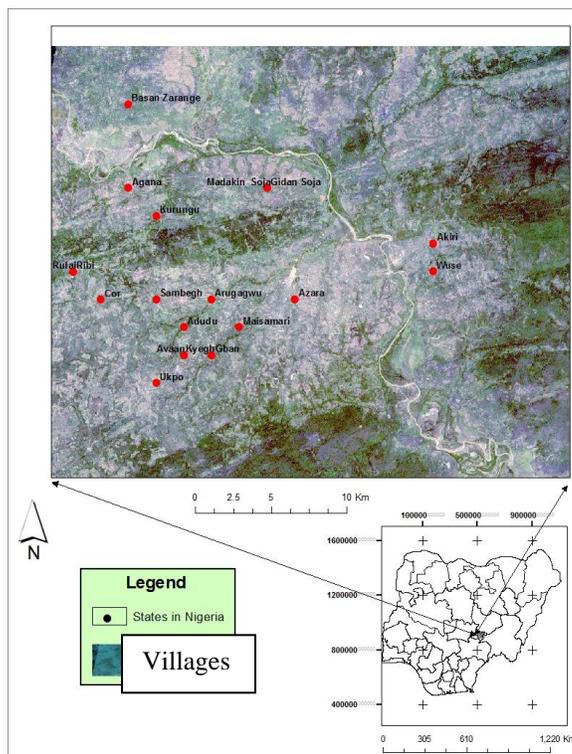


Fig. 1 Location of the study areas Akiri, Wuse and Azara on Landsat Image (Folorunso 2015)

Lithostratigraphy of the Middle Benue Trough: Offodile (1976) and Offodile and Reyment (1976) has described the geology and stratigraphy of the middle Benue region. Six upper Cretaceous lithostratigraphy formations were reported (Fig. II). Obaje *et al.* (1994) and Ojo (1997) also described some aspects of the middle Benue Trough stratigraphy. The formations recorded by the above mentioned authors from the oldest to the youngest are as follows: Asu River Group (Albian), Awe formation (late Albian - early Cenomanian), Keana Formation (middle Cenomanian), Eze Aku Formation (late Cenomanian – early Turonian) and the youngest Lafia Formation (Campanian - mastrichian). Previous works on the geology of Akiri and environs have been described by (Offodile 1976, Folorunso 2015).

Table 1 Generalized stratigraphy of the middle Benue trough (Offodile 1976)

Post-Cretaceous	Age	Formations	
Late Cretaceous	Maastrichtian	Lafia Formation	
	Santonian-Campanian	Volcanics	
	Coniacian	Awgu Formation	
	Late Turonian	Hiatus	
	Early Turonian		Ezeaku Formation
			Keana Formation
			Hiatus
Late Cenomanian			
Early Cenomanian		Awe Formation	
		Asu River Group	
Early Cretaceous	Middle-Late Albian		

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MATERIALS AND METHOD

Nine samples of siderite were obtained from hydrothermal siderite veins that cut the sedimentary rocks. About 0.5 mg of powder of each sample was analysed for its carbon and oxygen isotope composition. The analysis was performed in the stable isotope laboratory of the Activation Laboratories, Canada. Samples reacted with phosphoric acid at 72°C under helium (>99.996 vol. %) atmosphere in individual reaction tubes sealed with a septum. The released CO₂ from the siderite powders was collected, purified, and transported in a Helium flow via capillaries into the Isotope Ratio Mass Spectrometry (IRMS). Stable isotope measurements were determined using mass

spectrometer following procedures in Al-Aasm et al. (1990). The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are reported in ‰ relative to Vienna Pee Dee Belemnite (VPDB).

RESULTS AND DISCUSSION

Samples of siderite were taken from hydrothermal siderite vein that cut the sedimentary rocks and analysed for their carbon and oxygen isotopic composition. The isotope ratios are stated relative to Vienna PDB (Pee Dee Belemnite; $\delta^{13}\text{C}$ (VPDB) or $\delta^{18}\text{O}$ (VPDB). Results are given in Table II. The $\delta^{18}\text{O}_{\text{VPDB}}$ values of the siderite vary from -15.18 ‰ - 14.4‰ with a mean value of -14.82‰ while $\delta^{13}\text{C}_{\text{VPDB}}$ value vary from -1.71‰ to -1.05 with a mean value of -1.31‰ (Table 2).

Table 2 Results of carbon and oxygen isotope analysis.

Sample Number	$\delta^{18}\text{O}_{\text{VPDB}}$	$\delta^{13}\text{C}_{\text{VPDB}}$
AKP1SD1	-15.1	-1.71
AKP1SD2	-14.96	-1.15
AKP1SD6	-14.94	-1.05
AKP1SD1	-15.02	-1.71
AKP1SD1	-15.18	-1.7
AKP1SD3	-14.4	-0.91
AKP1SD9	-14.6	-1.25
AKP6SD4	-14.5	-1.18
AKP6SD7	-14.7	-1.09

The $\delta^{13}\text{C}_{\text{VPDB}}$ values of siderites from Akiri vein deposits ($\delta^{13}\text{C}$ from -0.91 to -1.71‰) is lower than the mineralized host limestones from Arufu Akwana area Middle Benue trough ($\delta^{13}\text{C}$ from 0.8 to 1.2 ‰) Akande and Abimbola (1989) and that of the unmineralized limestone from Yandev quarry (approximately 70 km from Arufu-Akwana lodes, middle Benue trough) (Fig. IV). However, Akiri $\delta^{13}\text{C}$ values (-0.91 to -1.71‰) lie within the range of values for Eyingba and Ameri siderites ($\delta^{13}\text{C}$ -2.6 to 2.3‰) analyzed according to Akande et al., (1989) and the values are comparable with marine carbonates (Fig. III). Also light $\delta^{13}\text{C}$ values in siderite suggest an organic carbon component (Hoefs 2009). The range of the values of Akiri vein siderite lie within carbonate precipitation from marine limestone's which have average $\delta^{13}\text{C}$ values near 0‰ as suggest by Moller et al. (1979).

A significant depletion in the heavy ^{18}O content with respect to the siderite occurred in the vein siderite (Fig. V) compared with carbonates from other parts of the basin. Lighter $\delta^{18}\text{O}_{\text{VPDB}}$ values revealed distinct group with very narrow variation ($\delta^{18}\text{O}_{\text{VPDB}}$ -

15.18‰ to -14.4‰). This group of $\delta^{18}\text{O}$ suggest a possible hydrothermal origin for the vein siderite (Huria et al 2002). The extreme depletion values in siderite compared to Cretaceous seawater $\delta^{18}\text{O}$ value is interpreted as diminishing isotopic fractionation with hydrothermal fluid temperature as the ore minerals precipitate. The isotopic composition of the fluid that precipitate the vein siderite can be calculated from the siderite-water fractionation relationship as given by O'Neil and Clayton (1969):

$$10^3 \ln \alpha = 2.78 * 10^6 / T^2 - 3.39,$$

If the mean value of vein siderite is -14.4‰ and filling temperature is 171.82°C

$$\text{Therefore, } 10^3 \ln \alpha = 2.78 * 10^6 / (273 + 171.8)^2 - 3.39 \\ = 2.78 * 10^6 / (444.8)^2 - 3.39$$

$$= 14.05 - 3.39$$

$$= 10.66,$$

$$\delta^{18}\text{O}_{\text{H}_2\text{O}} = (16.31 - 10.66) \text{‰}$$

$$= 5.65 \text{‰}.$$

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This value of 5.65 ‰ for the vein siderite corresponds to very saline fluid, which can be compared with the calculated fluid inclusion salinities. This supports vein minerals formation from highly saline brines. Although no estimate of the formation temperature of siderite was done, the fact that they are inter-grown with quartz and sulphides in the veins suggest hydrothermal origin (Akande et al. 1989). If equilibrium in the iron carbonate water system were assumed, the fractionation equation of O' Neil and Clayton (1969) predicts a $\delta^{18}\text{O}$ value of 5.65‰ per mil for the hydrothermal fluid which precipitate siderite at 171.8°C (using corrected Fluid inclusion temperature of quartz).

The observed difference between the $\delta^{18}\text{O}$ values of Akiri siderites ($\delta^{18}\text{O}$ values from -15.18 ‰ -14.4‰) and lower Benue siderite of (Akande et al. 1989) ($\delta^{18}\text{O}$ +19.5 to + 21.0) is perhaps a reflection of their formational temperature or fluid composition. The model isotope oxygen compositions of siderite fluids from Akiri lie within the $\delta^{18}\text{O}$ values between 5.7‰ and -2.9‰, typical of basinal brines precipitating the Mississippi valley-type (MVT) ores (McLimans 1977; Sicree and Barnes, 1996).

In addition, other fluid parameters of the siderite-forming fluids meet some typical features of basinal brines responsible for MVT ore deposition: Total salinity between 18 and 23 wt %; High CaCl_2 concentration; Temperatures between 60 and 220°C. Organic complexes also play important role in the MVT ore deposition (Sverjensky 1986; Sicree and Barnes, 1996).

It must be, however, emphasized that siderite of Akiri cannot be assigned to typical MVT ore, because of its failure to meet other important criteria. In contrast to the MVT ores, the siderite veins occur across sequence of sediments ranging from shale, sandstone, siltstone, mudstone facies. Also, the siderites have

crystallized at higher pressures and most importantly, they are dominated solely by copper sulphide ores.

Measurement of the oxygen and carbon isotope ratio ($\delta^{13}\text{C} = -1.71$ to -0.91 and $\delta^{13}\text{O} = -14.4$ to -15.1 ‰ relative to V-PDB) of fresh siderite at the Akiri Copper deposit, suggest origin of siderite veins is marine carbonate (rather than carbonatites). Moreover, the calculated isotopic compositions ($\delta^{13}\text{O} = 5.65$ ‰) of the hydrothermal fluid in the siderite imply that the fluid was meteoric water derived Choi et al., (2003). The carbon isotopic signature of the Akiri siderite veins shows similarities with isotopic signatures of siderites from lower Benue and distinction from other carbonates within the middle Benue trough.

The relative difference in $\delta^{18}\text{O}$ values of the Akiri vein siderite compared to the $\delta^{18}\text{O}$ lower Benue siderite mineralization may be as a result of the temperature gradient during alteration and or partial exchange of ^{18}O between the mineralizing fluid and the host sediments. The positive correlation between $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ ratios of Akiri siderites (Fig. VI) can be explained either by siderite precipitation due to mixing of two fluids with different NaCl concentrations as suggested by Zheng and Hoefs (2009). According to Akande and Abimbola (1989), the depletion of ^{18}O content of Arufu and Akwana host carbonate was caused by isotopic exchange between the carbonate rock and the mineralizing fluid as the areas close to the lode appear to be more influenced by the ore fluid thereby having $\delta^{18}\text{O}$ considerably less compared to the adjacent rocks 20m away. The significant difference between the $\delta^{18}\text{O}$ compositions of Akiri siderite compared with carbonates from other parts of the basin is perhaps a reflection of their formational temperature or fluid composition as suggested by (Akande et al. 1989).

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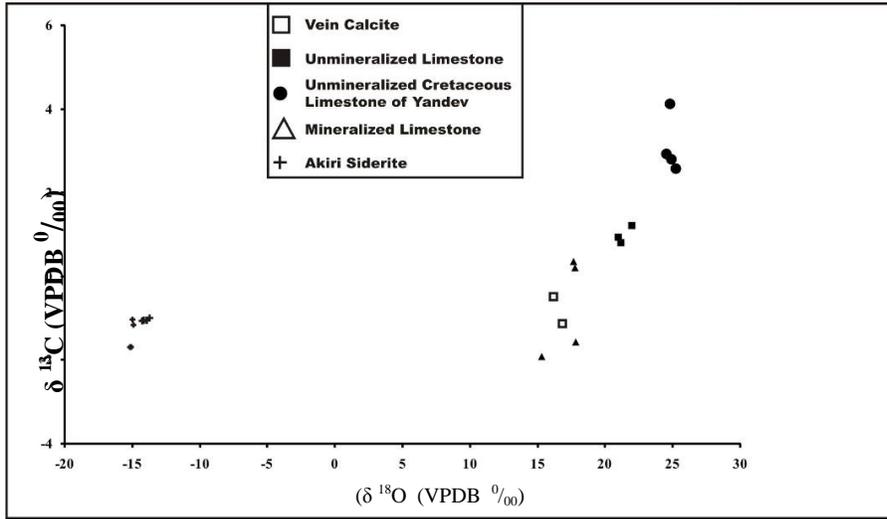


Fig. III: Carbon and oxygen isotopic composition of Akiri siderites compared with the Arufu and Akwana limestones and the Cretaceous unmineralized carbonate rocks from Yandev quarry (Akande et al. 1989)

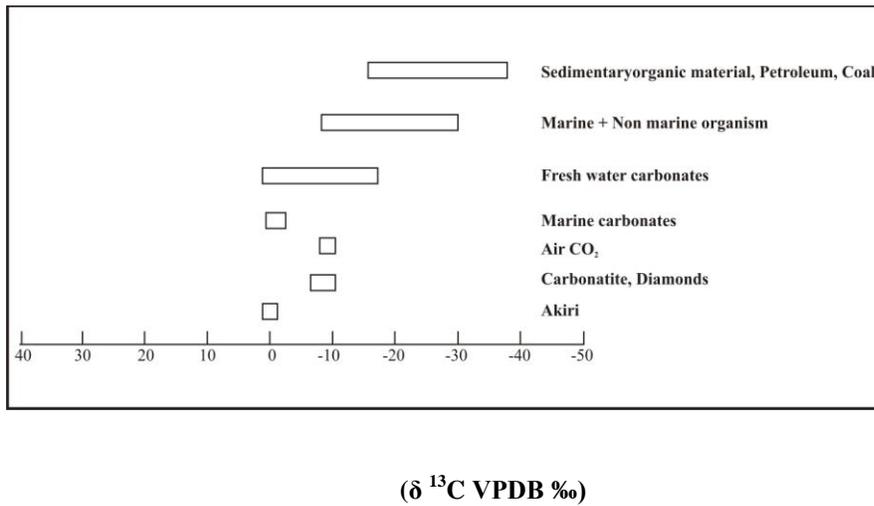


Fig. IV $\delta^{18}\text{O}$ values of Akiri compared with some important geological reservoirs (Hoefs 2009).

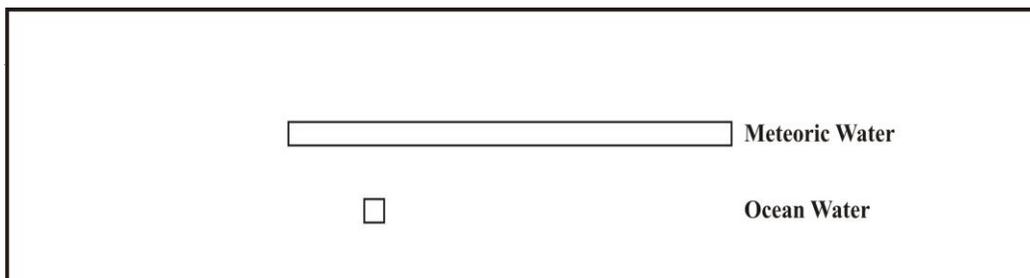


Fig. V $\delta^{18}\text{O}$ values of Akiri siderites compared with some important carbon reservoirs (Hoefs 2009)

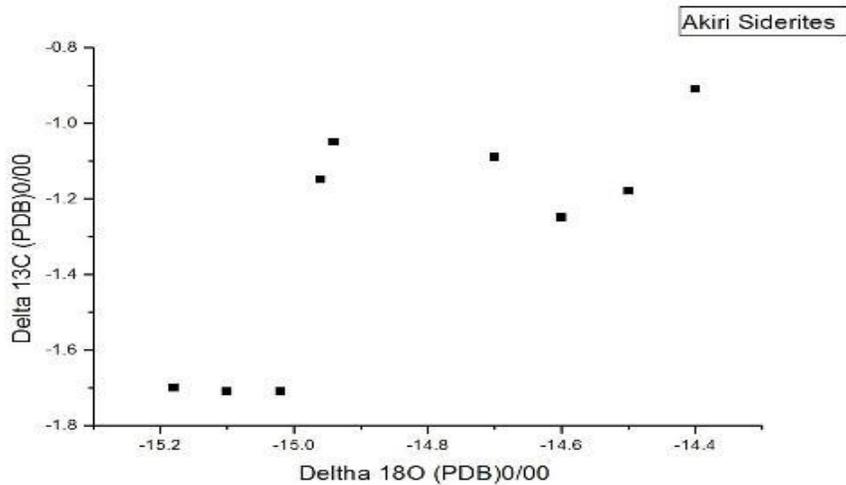


Fig. VI Plot $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ - values of hydrothermal carbonates from the vein Cu-deposits at Akiri (Zheng and Hoefs (2009))

Conclusion: Carbon and oxygen isotope analyses of Akiri siderites gave a narrow range of $\delta^{13}\text{C}$ values (-1.05 to -1.71‰) and $\delta^{18}\text{O}$ values (-14.94 to -15.18) respectively. Although such isotopic compositions is similar to values expected for Cretaceous marine carbonates. The ^{18}O depletion in the vein siderite

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respectively. Although such isotopic compositions is similar to values expected for Cretaceous marine carbonates. The ^{18}O depletion in the vein siderite

indicates probable dominant meteoric water sources involved for carbonates precipitation.

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