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

1* FOLORUNSO, IO; 2 BALE, RB; 3 ADEKEYE, JID

1 Department of Geophysics, University of Ilorin, Ilorin, Nigeria.
2, 3 Department of Geology and Mineral Sciences, University of Ilorin, Ilorin, Nigeria.
Corresponding Author: folorunso.io@unilorin.edu.ng, mobile: +2347033819230

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 δ¹³C values (-1.05 to -1.71‰) and δ¹⁸O values (-14.94 to -15.18) respectively. δ¹³C isotopic composition is comparable to values expected for Cretaceous marine carbonates. The ¹⁸O depletion in the vein siderite indicates dominant meteoric water sources involved for carbonates precipitation. This significant depletion between the δ¹⁸O compositions of Akiri siderite compared with carbonates from other parts of the basin probably indicate differential formational temperature or fluid composition. © JASEM

http://dx.doi.org/10.4314/jasem.v19i2.10

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.

Corresponding Author: folorunso.io@unilorin.edu.ng
Stable Isotope Characteristics of Akiri Vein Copper Mineralization

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 - Maastrichtian). Previous works on the geology of Akiri and environs have been described by (Offodile 1976, Folorunso 2015).

<table>
<thead>
<tr>
<th>Post-Cretaceous</th>
<th>Age</th>
<th>Formations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Late Cretaceous</td>
<td>Maastrichtian</td>
<td>Lafia Formation</td>
</tr>
<tr>
<td></td>
<td>Santonian-Campanian</td>
<td>Volcanics</td>
</tr>
<tr>
<td></td>
<td>Coniacian</td>
<td>Awe Formation</td>
</tr>
<tr>
<td></td>
<td>Late Turonian</td>
<td>Hiatus</td>
</tr>
<tr>
<td></td>
<td>Early Turonian</td>
<td>Ezeaku Formation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Keana Formation</td>
</tr>
<tr>
<td></td>
<td>Late Cenomanian</td>
<td>Hiatus</td>
</tr>
<tr>
<td></td>
<td>Early Cenomanian</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Awe Formation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Asu River Group</td>
</tr>
<tr>
<td>Early Cretaceous</td>
<td>Middle-Late Albian</td>
<td></td>
</tr>
</tbody>
</table>

1 FOLORUNSO, IO; 2 BALE, RB; 3 ADEKEYE, JID
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 δ¹³C and δ¹⁸O values are reported in ‰ relative to Vienna Peedee 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 (Peedee Belemnite; δ¹³C (VPDB) or δ¹⁸O (VPDB). Results are given in Table II. The δ¹⁸OVPDB values of the siderite vary from -15.18 ‰ to -14.4‰ with a mean value of -14.82‰ while δ¹³CVPDB value vary from -1.71‰ to -1.05 with a mean value of -1.31‰ (Table 2).

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>δ¹³CVPDB</th>
<th>δ¹⁸OVPDB</th>
</tr>
</thead>
<tbody>
<tr>
<td>AKP1SD1</td>
<td>-15.1</td>
<td>-1.71</td>
</tr>
<tr>
<td>AKP1SD2</td>
<td>-14.96</td>
<td>-1.15</td>
</tr>
<tr>
<td>AKP1SD6</td>
<td>-14.94</td>
<td>-1.05</td>
</tr>
<tr>
<td>AKP1SD1</td>
<td>-15.02</td>
<td>-1.71</td>
</tr>
<tr>
<td>AKP1SD1</td>
<td>-15.18</td>
<td>-1.7</td>
</tr>
<tr>
<td>AKP1SD3</td>
<td>-14.4</td>
<td>-0.91</td>
</tr>
<tr>
<td>AKP1SD4</td>
<td>-14.6</td>
<td>-1.25</td>
</tr>
<tr>
<td>AKP6SD4</td>
<td>-14.5</td>
<td>-1.18</td>
</tr>
<tr>
<td>AKP6SD7</td>
<td>-14.7</td>
<td>-1.09</td>
</tr>
</tbody>
</table>

The δ¹³CVPDB values of siderites from Akiri vein deposits (δ¹³C from -0.91 to -1.71‰) is lower than the mineralized host limestones from Arufu Akwana area Middle Benue trough (δ¹³C 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 δ¹³C values (-0.91 to -1.71‰) lie within the range of values for Eyingba and Ameri siderites (δ¹³C -2.6 to 2.3‰) analyzed according to Akande et al., (1989) and the values are comparable with marine carbonates (Fig. III). Also light δ¹³C 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 δ¹³C values near 0‰ as suggest by Moller et al. (1979).

A significant depletion in the heavy δ¹⁸O content with respect to the siderite occurred in the vein siderite (Fig. V) compared with carbonates from other parts of the basin. Lighter δ¹⁸OVPDB values revealed distinct group with very narrow variation (δ¹⁸OVPDB - 15.18‰ to -14.4‰). This group of δ¹⁸O suggest a possible hydrothermal origin for the vein siderite (Huria et al 2002). The extreme depletion values in siderite compared to Cretaceous seawater δ¹⁸O 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 171.8°C

Therefore, \[ 10^3 \ln \alpha = 2.78 * 10^6 / (273+ 171.8)^2 - 3.39 \]

\[ = 2.78 * 10^6 / (444.8)^2 - 3.39 \]

\[ = 14.05 - 3.39 \]

\[ = 10.66, \]

\[ \delta^{18}O_{H_2O} = (16.31 - 10.66) \% \]

\[ = 5.65 \%. \]
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 δ¹⁸O 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 δ¹⁸O values of Akiri siderites (δ¹⁸O values from -15.18 ‰ -14.4‰) and lower Benue siderite of (Akande et al. 1989) (δ¹⁸O +19.5 to +21.0) is perhaps a reflection of their formational temperature or fluid composition. The model isotope oxygen compositions of sidellite fluids from Akiri lie within the δ¹⁸O 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 sidellite-forming fluids meet some typical features of basinal brines responsible for MVT ore deposition: Total salinity between 18 and 23 wt %; High CaCl₂ 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 sidellite 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 sidellite veins occur across sequence of sediments ranging from shale, sandstone, siltstone, mudstone facies. Also, the sidellites have crystallized at higher pressures and most importantly, they are dominated solely by copper sulphide ores.

Measurement of the oxygen and carbon isotope ratio (δ¹³C = -1.71 to -0.91 and δ¹³O = -14.4 to -15.1‰ relative to V-PDB) of fresh sidellite at the Akiri Copper deposit, suggest origin of sidellite veins is marine carbonate (rather than carbonatites). Moreover, the calculated isotopic compositions (δ¹³O = 5.65 ‰) of the hydrothermal fluid in the sidellite imply that the fluid was meteoric water derived Choi et al., (2003). The carbon isotopic signature of the Akiri sidellite veins shows similarities with isotopic signatures of sidellites from lower Benue and distinction from other carbonates within the middle Benue trough.

The relative difference in δ¹⁸O values of the Akiri vein sidellite compared to the δ¹⁸O lower Benue sidellite mineralization may be as a result of the temperature gradient during alteration and or partial exchange of δ¹⁸O between the mineralizing fluid and the host sediments. The positive correlation between ¹³C/¹²C and ¹⁸O/¹⁶O ratios of Akiri sidellites (Fig. VI) can be explained either by sidellite 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 ¹⁸O 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 δ¹⁸O considerably less compared to the adjacent rocks 20m away. The significant difference between the δ¹⁸O compositions of Akiri sidellite 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).

FOLORUNSO, IO; BALE, RB; ADEKEYE, JID
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 $\delta^{18}$O values of Akiri compared with some important geological reservoirs (Hoefs 2009).
Fig. V $\delta^{18}$O values of Akiri siderites compared with some important carbon reservoirs (Hoefs 2009)

**Fig. VI** Plot $\delta^{18}$O and $\delta^{13}$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 $\delta^{13}$C values (-1.05 to -1.71‰) and $\delta^{18}$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
indicates probable dominant meteoric water sources involved for carbonates precipitation.

Acknowledgement: The study has benefited from financial support provided by the senate research grant of the University of Ilorin for field work.

REFERENCES


McLimans RK (1977) Geological, fluid inclusions, and stable isotopes studies of the Upper

Mississippi Valley zinc-lead district, southwest Wisconsin. Dissertation, Penn State University


Offodile ME (1976) The Geology of the Middle Benue, Nigeria. Special Publication Palaeontological Institute, University of Uppsala, pp:1-166


