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Isotope studies and Source of Brines in the Middle Benue Trough, Nigeria

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Abstract* - Samples from five brine vents mapped on or around the Keana Anticline Middle Benue Trough, Nigeria, reveal isotopic signatures ($\delta^{18}O$ and $\delta^{2}H$) that indicate evaporative enrichment and mixing with isotopically distinct deep waters, modeled by structurally controlled brine migration and stratigraphic confinement within permeable Keana sandstones Formation. The synthesis of geological, geochemical, and isotopic data in the MBT brine system is best explained by a hydrothermal-evaporative model where connate and geothermal fluids ascend through fault-controlled pathways, mingled with meteoric inputs and dissolved evaporite minerals, leading to the formation of highly saline brines. The geochemical and isotopic evidence points to a predominant meteoric origin for the brines in the study area, modified by intense evaporation and interaction with host rocks. Structural features and sandstone aquifers significantly control the migration and accumulation of these brines. The presence of both cold and hot brines can be attributed to differential geothermal gradients and fault-controlled fluid pathways. The elevated concentrations of dissolved solids, particularly at Ribi and Keana, indicate long-term geochemical evolution, making these brines potential sources of industrial salts.

Keywords: Brine, Migration, Middle Benue Trough, Isotopic Evidence

1.0 INTRODUCTION

Brine is defined as water containing a total dissolved solids (TDS) concentration exceeding 50 g/L. These solutions typically include cations such as K^{+}, Ca^{2+}, Na^{+}, Mg^{2+}, Li^{+}, B^{3+}, Sr^{2+}, Rb^{2+}, and Cs^{+}, and anions including SO_4^{2-}, Cl^{-}, HCO_3^{-}, CO_3^{2-}, Br^{-}, and I^{-} (Dobson, Stringfellow & Whittaker, 2021). Several of these dissolved ions have economic value; for instance, Li_2CO_3 and KCl are commercially important, while humans have long exploited halite. Historically, natural brines have been harnessed for sodium salts and other minerals for millennia (Dobson, Stringfellow & Whittaker, 2021). Based on their chemical composition, brines are generally classified into sulfate-, chloride-, and carbonate-dominated types (Dobson, Stringfellow & Whittaker, 2021). Within the Earth's crust, brines are commonly found in Quaternary salt lakes, in sedimentary rock pores, pre-Quaternary depositional layers, fractures of crystalline basement rocks, and even on the deep seafloor, such as areas in the Red Sea (Dobson, Stringfellow & Whittaker, 2021).

This research presents combined isotopic and geological evidence to elucidate the origin, migration pathways, and accumulation mechanisms of brines in the Middle Benue Trough. Analyses of stable isotopes ($\delta^{18}O$, $\delta^{2}H$, d-excess), integrated with stratigraphic and structural observations, are used to develop a hydrothermal-evaporative model in which fault-guided upflow, permeable Keana sandstones, meteoric recharge, and surface evaporation collectively generate and trap saline bodies. The study contributes site-specific data for Nasarawa State, differentiates between cold and hot brines, and identifies Keana and Ribi as locations of advanced geochemical evolution with industrial potential (Abubakar, 2014). These datasets represent one of the few detailed isotopic surveys of brines in the Middle Benue Trough, enhancing the understanding of brine provenance (Abubakar, 2014). Additionally, the study formulates a coherent conceptual model linking tectonic structures, reservoir characteristics, and surface evaporation processes to brine formation and entrapment, with practical implications for resource exploitation and water safety (Dobson, Stringfellow & Whittaker, 2021; Abubakar, 2014).

1.1 Study Area

Nigeria contains extensive brine deposits, notably in the Wuse-Akiri and Azara areas of the Middle Benue Trough (Abubakar, 2014). Brines are widely distributed in global geothermal systems and may serve as a significant industrial salt resource (Dobson, Stringfellow & Whittaker, 2021). The research area comprising Akiri, Ribi, Awe, and Keana is located within the Middle Benue Trough, an intracontinental rift basin that formed during the Cretaceous as a result of the separation of South America from Africa (Wright, 1968; Nwachukwu, 2009). The region is underlain by Cretaceous sedimentary sequences reflecting alternating marine and continental depositional environments. Stratigraphically, the succession begins with the Asu River Group (Albian), consisting of

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dark shales, limestones, and sandstones indicative of early marine transgression. The overlying Awe Formation (Cenomanian), composed of coarse sandstones, siltstones, and minor shales, represents fluvio-deltaic depositional settings. The Keana Formation (Turonian) includes cross-bedded sandstones interlayered with shales and mudstones, reflecting fluvial to shallow marine deposition. The Ezeaku Formation consists of calcareous shales and limestones, marking a deeper marine depositional phase (Abubakar, 2014). NE-SW trending faults and folds dominate the area's structural features, which have influenced sedimentation and hydrothermal fluid movement (Abubakar, 2014; Nwachukwu, 2009). The presence of brines and hydrothermal alteration features points to significant post-depositional geochemical processes, often associated with tectonic reactivation and deep fluid circulation (Abubakar, 2014).

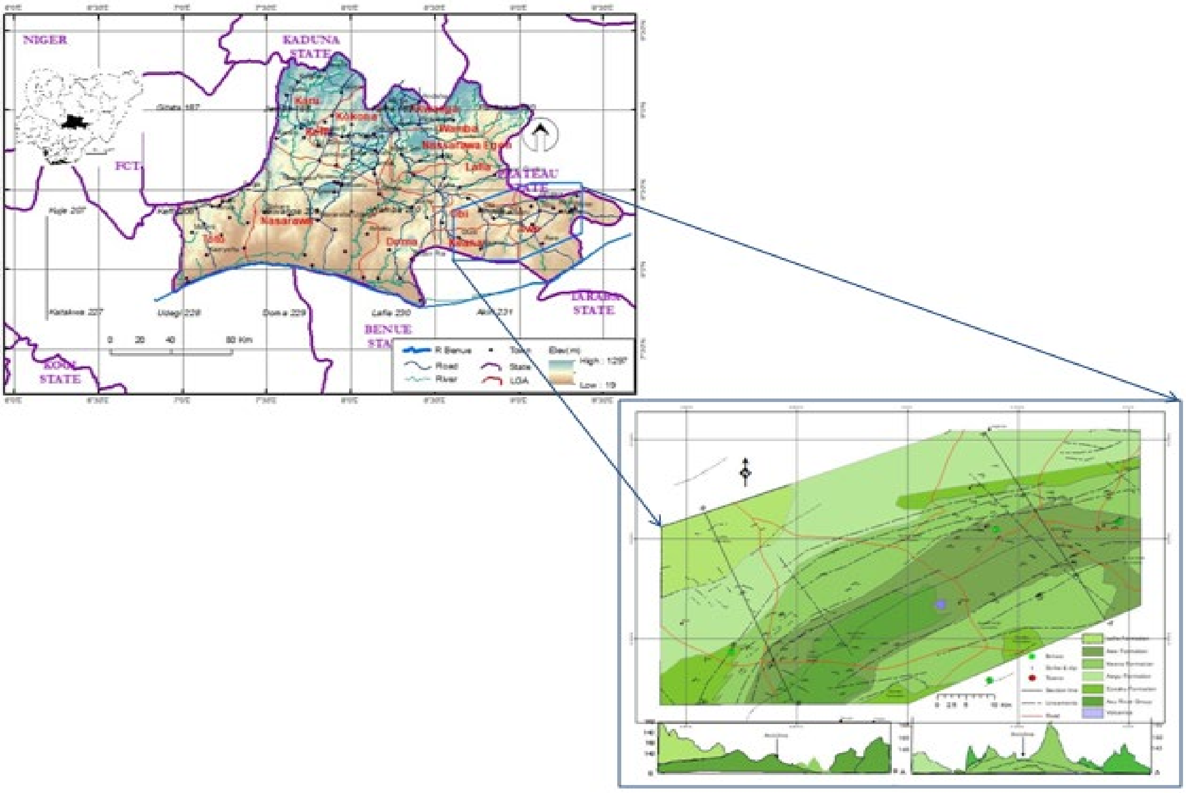

Figure 1.1: Research Location (adopted and modified from Map of Nasarawa State

2.0 GEOLOGICAL SETTING

The Benue Trough is part of the West African rift system (Genik, 1992, 1993; Mangs, Wagner & Moroeng, 2022). It stretches from the northern Niger Delta Basin to the Chad Basin and is bounded to the north and south by the Basement Complex. Sedimentary deposits are largely of Middle-Late Albian age (Offodile, 1976). The trough strikes NE-SW, with widths ranging from approximately 130 km to 200 km. Recent structural reconstructions and stratigraphic interpretations from Nwachukwu (2009) and Mangs, Wagner & Moroeng (2022) provide updated insights into the tectonic framework of the region.

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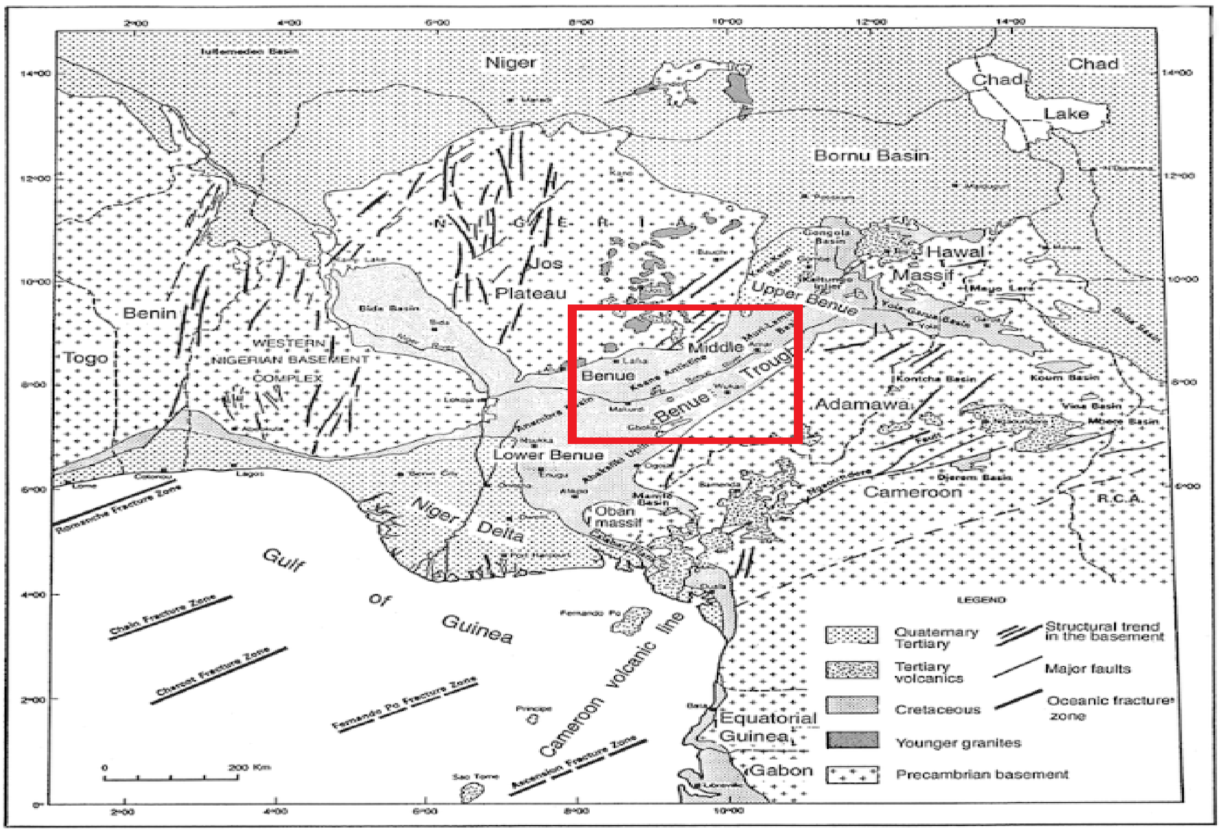

Figure 2.1: Structural framework of the Middle Benue Trough highlighting fault trends, anticlines, and major brine sites [Adopted from Benkelil *et al.,* 1997 in Osinowo *et al*. (2023)].

3.0 MATERIALS AND METHODS

This chapter describes the procedures adopted in investigating the structural control on brine migration in the Middle Benue Trough. The methodology integrates desk-based research, fieldwork, laboratory analyses, and data interpretation techniques designed to provide a comprehensive understanding of the geological, geophysical, hydrochemical, and isotopic characteristics of the study area.

3.1 Desk Study

The desk study in this work is categorized into three major components: the literature review, reconnaissance survey, and geophysical data analysis.

The literature review involved an extensive assessment of published articles, technical reports, geological maps, theses, and government documents relating to the geology, hydrogeochemistry, and geophysics of the Middle Benue Trough. This review established the existing level of knowledge, identified methodological approaches used in previous studies, and highlighted data gaps, thereby refining the research design and analytical strategies adopted for this investigation.

A reconnaissance survey was conducted to validate the information derived from the desk study and to assess accessibility and field conditions. This initial field visit enabled the observation of geomorphological features, major geological structures, and zones of saline groundwater discharge. It also assisted in identifying appropriate sampling locations and in planning field logistics for subsequent detailed investigations.

3.2 Geophysical Data Analysis

Aeromagnetic datasets and satellite imagery were acquired from the Nigerian Geological Survey Agency and the National Centre for Remote Sensing. These datasets were processed using ERDAS Imagine, ILWIS, ArcGIS, Oasis Montaj, and Surfer to enhance structural lineaments, delineate geological boundaries, and infer subsurface geometries. The analysis facilitated the identification of

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magnetic anomalies, fault orientations, and basement configurations that are potentially associated with the occurrence and migration of brines.

3.3 Field Work

Brine samples were collected from strategically selected locations based on structural features, evidence of evaporite dissolution, and hydrogeological indicators of saline discharge. High-density polyethylene bottles prewashed with nitric acid were used for sample collection, and each bottle was rinsed with sample water prior to filling. Samples for cation analysis were acidified to a pH below 2 using ultrapure nitric acid, whereas samples for anion analysis were kept unacidified and stored at 4°C. Stable isotope samples were collected in airtight glass vials without headspace to avoid isotopic fractionation. Field parameters such as temperature, pH, electrical conductivity, and total dissolved solids were recorded using calibrated multiparameter probes.

Rock samples were collected from exposed stratigraphic sections located along riverbanks, stream channels, and road cuttings. Only fresh and unweathered specimens were selected using a geological hammer. Each sample was immediately labeled and its coordinates documented using a handheld GPS device. Structural measurements—including strike and dip of bedding planes and fractures were recorded with a compass-clinometer to aid geological and structural interpretation.

This study utilized hydrochemical sampling, petrographic examination, and isotopic analyses to assess structural influences on brine migration. Stable isotope analyses of $\delta^{18}O$ and $\delta^{2}H$ were carried out on selected brine samples to determine origin, evolution, and hydrological interactions. Isotopic signatures were plotted against the Global Meteoric Water Line (GMWL) to differentiate between meteoric, evaporated, and connate water sources. Deuterium excess (d-excess), calculated as d-excess = $\delta^{2}H - 8 \times \delta^{18}O$, was used to identify evaporation effects and mixing processes. Cluster analysis was applied to the isotopic dataset to group samples with similar characteristics and validate isotopic interpretations related to brine modification.

3.4 Sample Analyses

Thin sections of selected rock samples were prepared to a thickness of 0.03 mm and examined under a polarizing microscope using plane-polarized and cross-polarized light. This analysis enabled the identification of mineral assemblages, textural relationships, and diagenetic features that influence reservoir properties such as porosity and permeability. The petrographic results provided insights into the lithological framework and post-depositional alterations affecting the rocks within the study area.

Geochemical analyses of the brines included major cations and trace elements determined using Flame Atomic Absorption Spectrometry and Agilent 7700 ICP-MS, while major anions were measured using ion chromatography. Mercury concentrations were determined using an HG-5000 atomic mercury analyzer. Instrument precision ranged between ±2–5% for ICP-MS, approximately ±2% for AAS, and below 3% for ion chromatography. Calibration was maintained with multi-element standards traceable to NIST reference materials, and analytical quality was ensured with blanks, duplicates, and reference standards.

Stable isotope ratios of $\delta^{18}O$ and $\delta^{2}H$ were determined using isotope ratio mass spectrometry, with analytical precisions of about ±0.1‰ for $\delta^{18}O$ and ±1‰ for $\delta^{2}H$. Measurements were calibrated against international standards including VSMOW, SLAP, and GISP. These isotopic results were used to infer recharge pathways, evaporation history, and mixing between meteoric and deep-circulated waters.

3.5 Data Analysis and Presentation

The resulting datasets were processed and interpreted using statistical tools, geochemical modeling software, and graphical methods. Petrographic results were analyzed to evaluate mineral proportions, textures, and diagenetic trends. Hydrochemical data were interpreted using Piper, Schoeller, and Stiff diagrams to classify water types and identify hydrochemical facies. PHREEQC was used to compute saturation indices, ion ratios, and mineral equilibria, thereby revealing water–rock interactions and processes governing brine chemistry.

Trace element data were statistically summarized to identify spatial trends and anomalous concentrations related to lithological variations or structural controls. Stable isotope data were interpreted using isotopic plots relative to the GMWL to assess evaporation effects, recharge mechanisms, and the potential mixing of meteoric and connate waters. All findings were presented through well-labeled tables, maps, diagrams, and geological cross-sections to ensure clarity and enhance interpretative accuracy.

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4.0 RESULTS AND DISCUSSION

4.1 Geology of the Study Area

Geologically, the MBT is underlain by a thick succession of Cretaceous sediments, predominantly composed of alternating marine and continental facies. These include, in ascending order, the Asu River Group (Albian), characterized by marine shales, micaceous siltstones, and mudstones; the Awe Formation (Late Albian–Cenomanian), comprising feldspathic sandstones and carbonaceous shales; the Keana Formation (Cenomanian–Turonian), noted for its massive, poorly sorted cross-bedded sandstones and subordinate shales; and the Ezeaku Formation (Turonian), consisting of calcareous shales, shelly limestone and friable sandstones (Offodile, 1976). These formations are exposed across various brine-bearing towns, including Keana, Awe, Akiri, and Ribi.

The geological map of the study area (Figure 4.1) illustrates the surface distribution of these litho-stratigraphic units and their spatial relationships. Importantly, field investigations indicate that most brine occurrences are associated with formations containing interbedded shales and sandstones, which provide both sources of salinity and conduits for fluid flow.

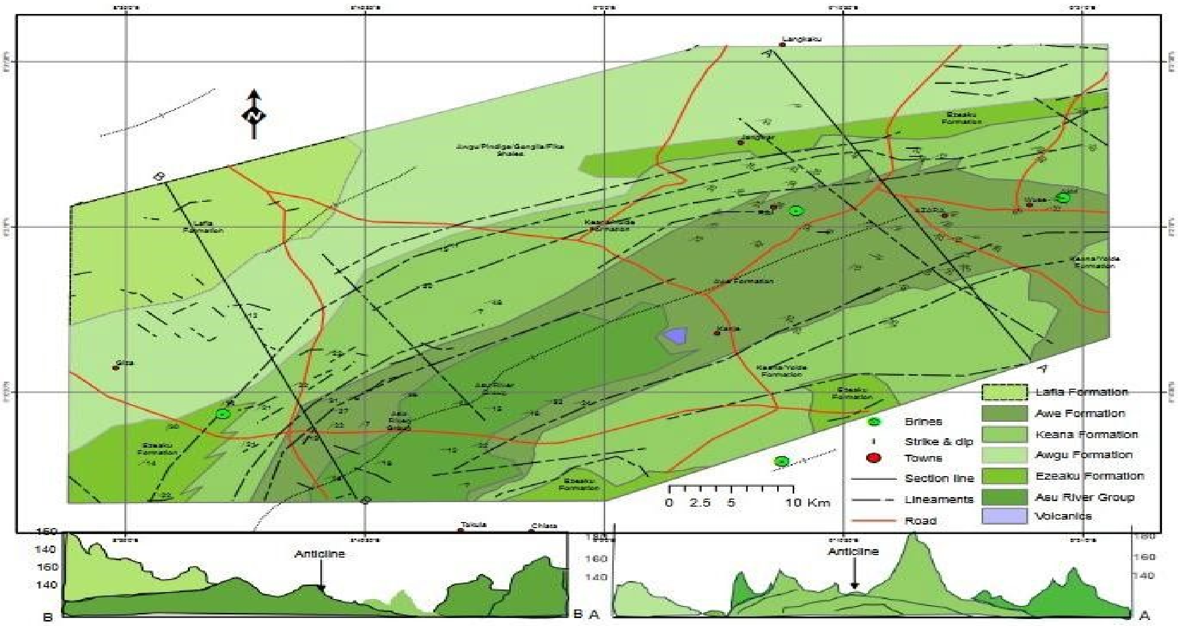

Figure 4.1: Geologic Map of the Study Area.

Table 4.1 shows the result of isotope studies on the six brines samples

Table 4.1: Summary of Isotope Results

LAB ID	Sample ID	δ2H	Std Dev	δ18O	Std Dev
NG-461	Akuri pond salt (hot)	-32.83	0.75	-4.84	0.16
NG-462	Ribi cold salt pond	-28.88	0.72	-3.99	0.10
NG-463	Awe pond 1cold saltwater	-33.72	0.72	-5.48	0.16
NG-464	Awe hot pond saltwater	-34.92	0.78	-5.28	0.14
NG-465	Keana saltwater	10.91	0.37	2.43	0.06
NG-466	Akiri pond salt	-32.58	0.60	-5.13	0.11

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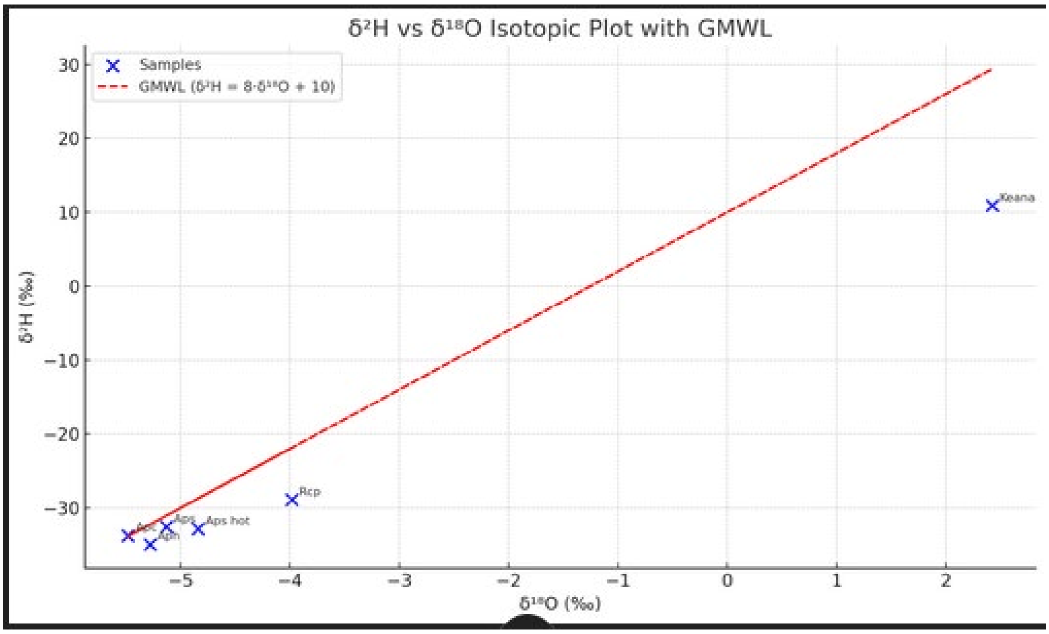

Figure 4.2: Plot of δ^2H vs $\delta^{18}O$ with Global Meteoric Water Line (GMWL)
(Craig, 1961).*Note: APC (Akiri Pond Cold), APH (Awe Pond Hot), APS hot (Awe Pond Salt).*

The Global Meteoric Water Line (GMWL) (Figure 4.2), which serves as a global reference for evaluating the isotopic composition of natural waters. Water derived from meteoric sources—such as precipitation from rainfall or snow - typically plots along or near this line. Four samples, including Akiri Pond Cold Awe Pond Hot, and Hot Awe Pond Salt, plot below the GMWL, indicating isotopic enrichment due to evaporation or mixing with isotopically heavier fluids such as brine. In contrast, the Keana sample exhibits highly enriched δ^2H and $\delta^{18}O$ values and deviates significantly from the GMWL, which is uncharacteristic of typical meteoric water. This marked deviation suggests that the Keana water sample may have undergone intense evaporation or has interacted with deep-seated, saline, or geothermal fluids. The presence of positive isotopic values, such as those recorded in the Keana sample, strongly implies a dominant influence from non-meteoric sources, highlighting significant external geochemical processes involving brine or geothermal contributions.

Below is the d-excess versus $\delta^{18}O$ Plot; d-excess plot (Figure 4.3), which is used to differentiate between meteoric origins, evaporation, and mixing processes in water samples.

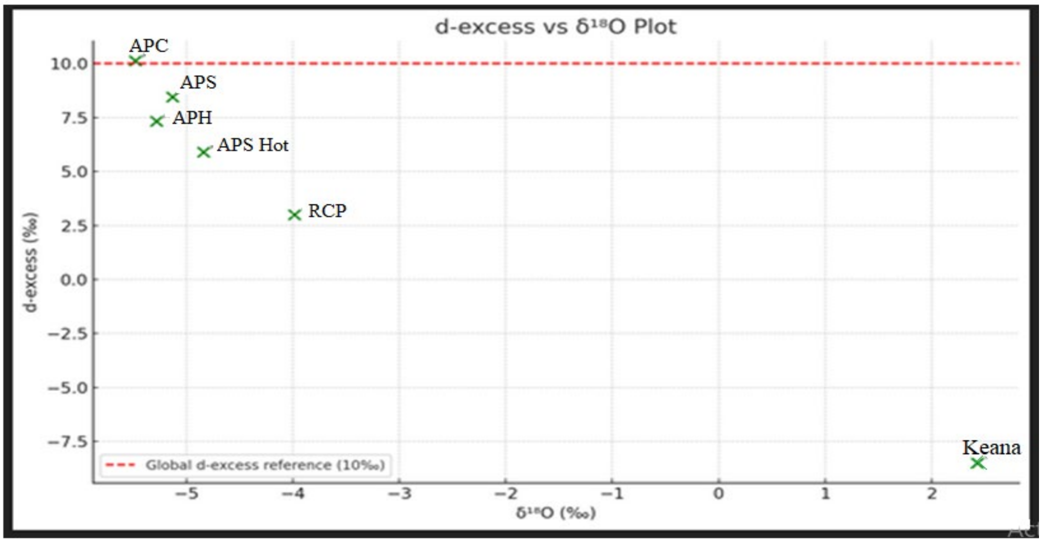

Figure 4.3: d-excess versus $\delta^{18}O$ plot

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Significant deviations from this benchmark suggest non-equilibrium processes, such as evaporation or interaction with saline (brine) water, which alter the isotopic signature of the samples.

Key observations from the d-excess versus $\delta^{18}O$ plot reveal important isotopic trends: Keana exhibits a notably low d-excess value (\~ -8.49‰), strongly suggesting significant brine influence or intense evaporation.

Samples from Awe Pond hot Akiri pond cold and Awe Pond salt show d-excess values below the typical meteoric threshold of 10‰, indicating enrichment through evaporative processes. In contrast, Ribi cold pond aligns more closely with the meteoric water range, pointing to a potentially less altered or fresh water source. These isotopic patterns are consistent with brine infiltration or geothermal mixing, particularly evident in the distinct behavior of the Keana sample. Results of the cluster analysis of the isotope data as shown in figure 4.4.

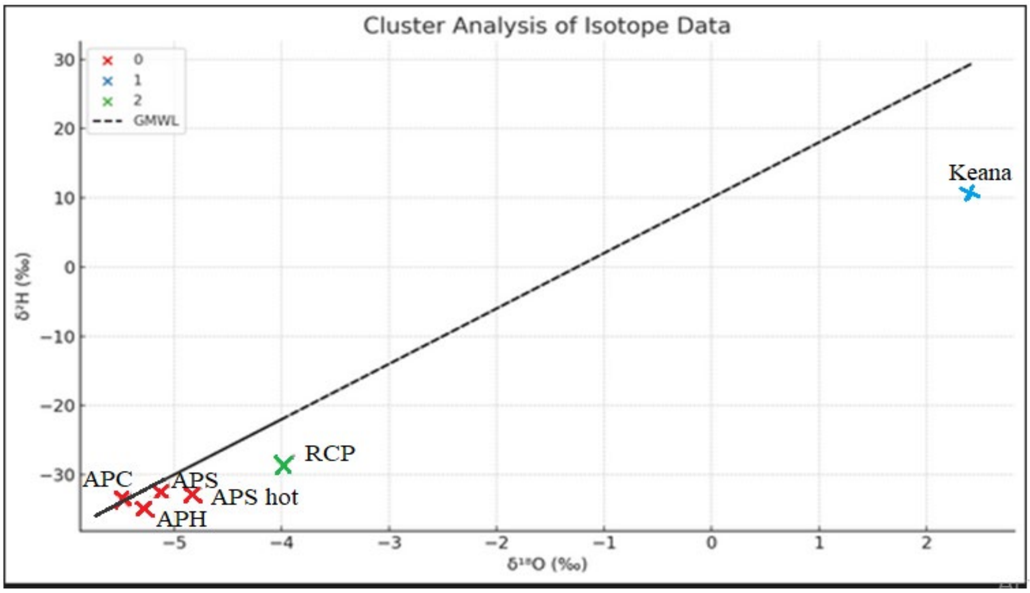

Figure 4.4: Plot of Plot of δ^2H Vs $\delta^{18}O$ for cluster analysis.

The cluster analysis (Figure 4.4) revealed three distinct groups based on the isotopic composition of the water samples, providing valuable insights into their origin and evolution. The clustering effectively differentiates between brine-impacted waters—such as Keana, which displays highly enriched isotopic values and low d-excess, indicating influence from deep-seated brine or geothermal fluids—evaporated meteoric waters (e.g., APH, APC, and APS hot), and relatively fresh water with signatures closer to meteoric origin (e.g., RCP). Specifically,

Cluster 0 comprises samples isotopically depleted, representing meteoric waters with minor evaporation;

Cluster 1 includes isotopically enriched samples, such as Keana, indicative of brine or geothermal influence; and Cluster 2 exhibits intermediate characteristics, suggesting possible mixing zones between meteoric and saline sources. This clustering pattern supports the interpretation that Keana's water sample originates from a distinctly different source, impacted by brine infiltration or geothermal processes.

Stable isotopes of hydrogen (^2H, deuterium) and oxygen (^{18}O) are essential tools in hydrogeology for tracing the origin, movement, and mixing processes of groundwater. These isotopes help distinguish between different water sources and assess modifications due to environmental or geochemical processes. The Global Meteoric Water Line (GMWL), expressed as $\delta^2H = 8 \times \delta^{18}O + 10‰$ (Craig, 1961), serves as a global reference for identifying meteoric water, which originates from precipitation. Groundwater samples that plot significantly below or above this line typically indicate the influence of non-meteoric processes such as evaporation, water–rock interaction or mixing with saline or brine-rich fluids. Such deviations are critical in identifying and understanding the presence of brine or geothermal inputs in aquifer systems.

The deuterium excess (d-excess), calculated as d-excess = $\delta^2H - 8 \times \delta^{18}O$, serves as a valuable parameter for identifying isotopic deviations from typical meteoric water. Values significantly lower than the global average of approximately +10‰ are indicative of non-equilibrium processes, such as evaporative enrichment (Gat & Gonfiantini, 1981) or mixing with brine and geothermal waters

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(Clark & Fritz, 1997). In this study, the Keana sample exhibits notably enriched δ-values and a low d-excess, characteristics that are consistent with isotopic signatures influenced by brine infiltration or geothermal input.

Cluster analysis effectively classified the water samples into three distinct groups: fresh meteoric waters evaporated meteoric waters, and brine-influenced waters. This statistical grouping supports and reinforces interpretations derived from isotopic plots and d-excess values, providing a coherent framework for distinguishing between different hydro chemical processes and sources influencing the water samples.

According to Rollinson (1993), the diagram provides insight into the source of hydrogen in natural waters, offering a comparative framework for interpreting hydrogen isotopic compositions. The supporting diagram that follows illustrates this relationship.

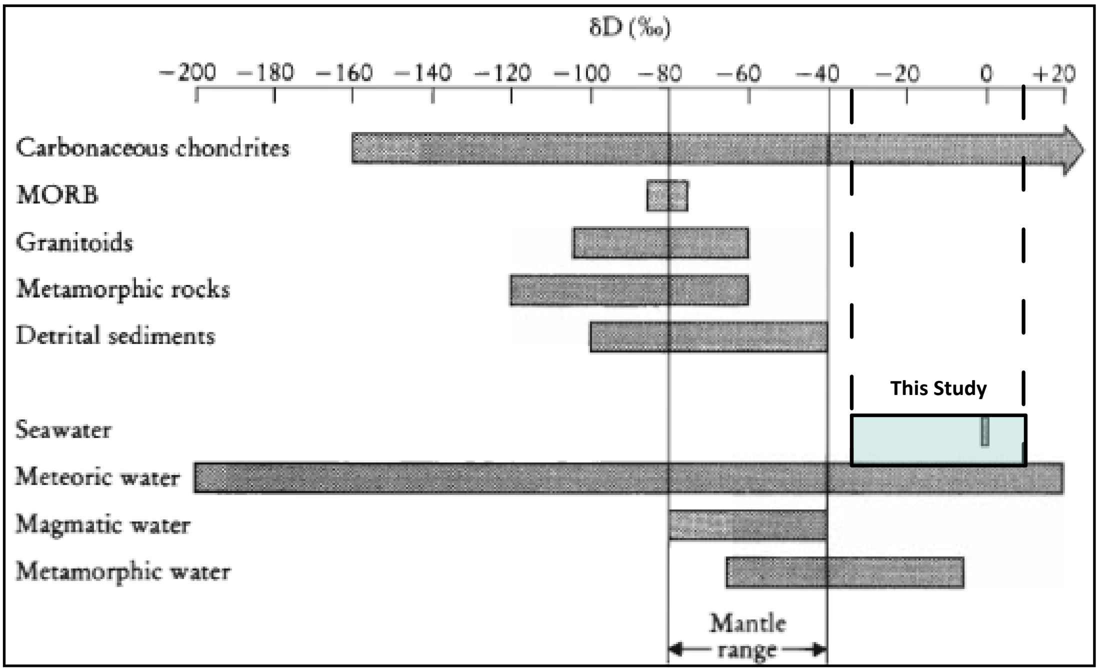

Figure 4.5: Natural Hydrogen isotope reservoirs for samples of the study area sub- System (modified from Rollinson, 1993)

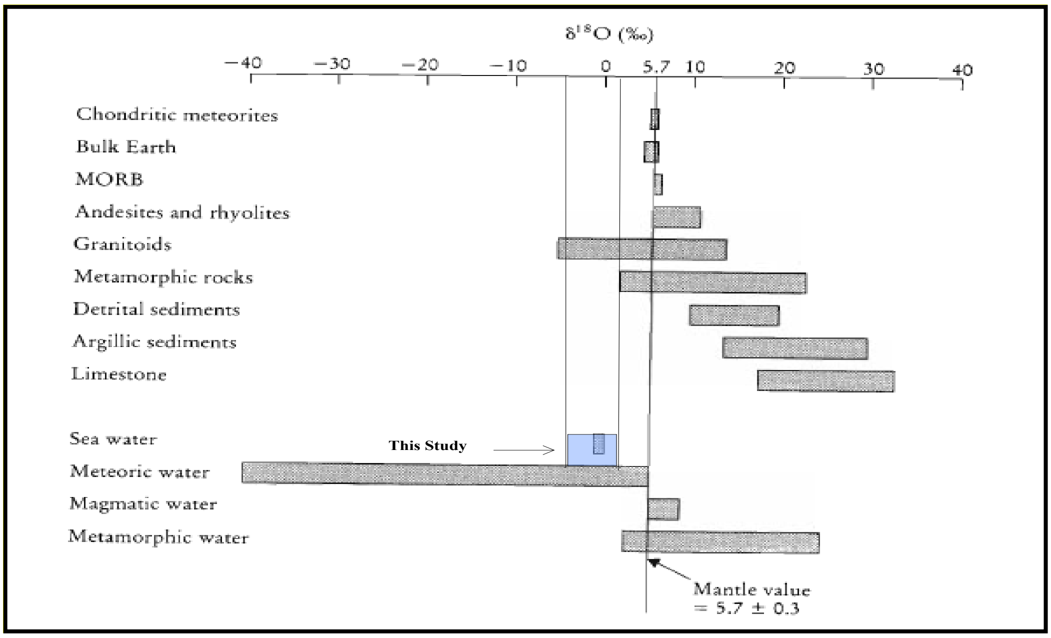

Figure 4.6: Natural Oxygen isotope reservoirs for samples of the study area sub-system (modified from Rollinson, 1993)

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The hydrogen isotopic composition of the samples studied indicates a meteoric origin, reflecting input from precipitation (Figure 4.5). Similarly, the oxygen isotopic signatures align with characteristics typical of meteoric water sources (Figure 4.6).

Isotopic Insights on Brine Genesis suggests that stable isotope data ($\delta^{18}O$ and $\delta^{2}H$) provide crucial evidence for fluid provenance and mixing. Samples plot below the Global Meteoric Water Line (GMWL), with Keana brine exhibiting a low d-excess (~–8.49‰), a signature of pronounced evaporative enrichment and deep-seated brine input.

Such isotopic characteristics, displayed in standard diagrams (Figure 4.7), indicate that MBT brines are hybrids of meteoric water, fossil connate fluids, and geothermal inputs. The brine's distinctive δ-values and d-excess suggest substantial mixing below the surface, while structural traps and permeability barriers facilitate storage and further concentration through repeated fluid cycle

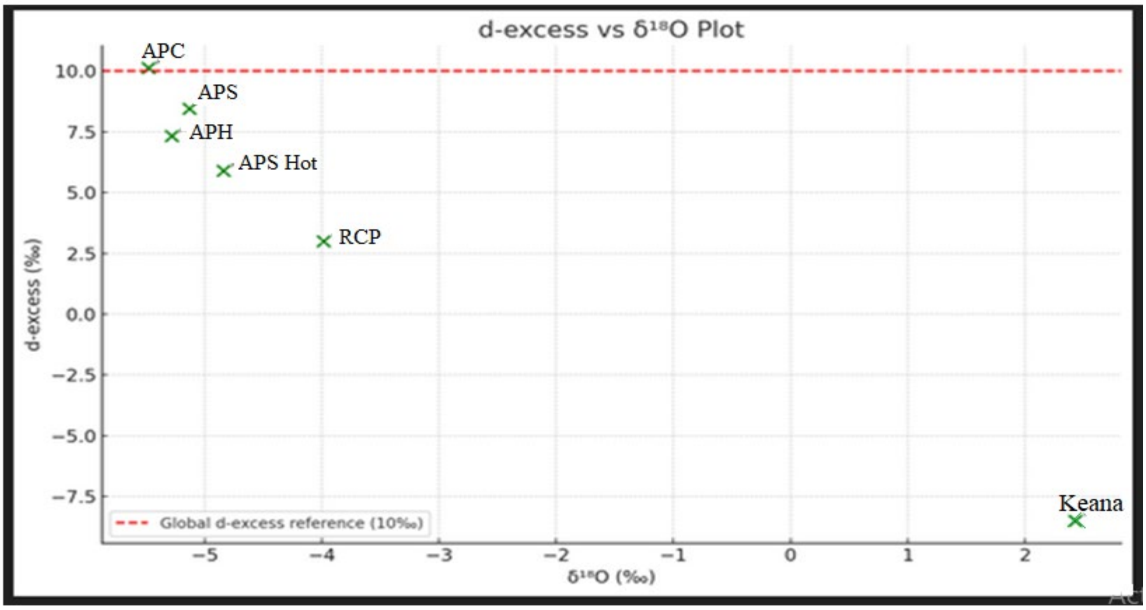

Figure 4.7: D-Excess versus $\Delta^{18}O$ Plot. APC (Akiri Pond Cold), APH (Awe Pond Hot), APS Hot (Awe Pond Salt).

A hydrothermal-evaporative model may best explain a conceptual model for brine migration synthesizing geological, geochemical, and isotopic data, and for the MBT brine system, thus; connate and geothermal fluids ascend through fault-controlled pathways, mingled with meteoric inputs and dissolve evaporite minerals, leading to the formation of highly saline brines. Recurrent cycles of fluid migration and surface evaporation result in significant halite and gypsum accumulations, structurally trapped along fault corridors. This model is best visualized using the below conceptual diagrams figure 4.8.

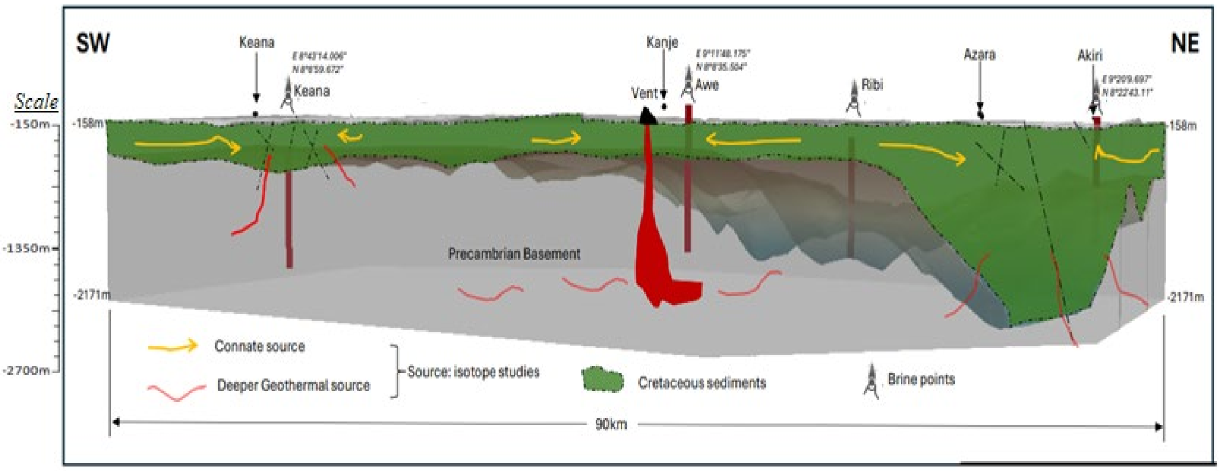

Figure 4.8: Conceptual Model of Brine Emergence in the Middle Benue Trough.

5.0 CONCLUSION

Although the isotopic data for most brine samples indicate a meteoric origin, the Keana sample exhibits a pronounced deviation from typical meteoric signatures, with highly enriched δ^2H and $\delta^{18}O$ values and a markedly low d-excess. This suggests that, while the brines initially derive from meteoric waters, they have undergone significant modification through processes such as intense evaporation, water–rock interaction, and mixing with non-meteoric fluids, including deeper saline or geothermal contributions. Therefore, the brines should be considered to have a primary meteoric origin that has been substantially altered by secondary geochemical processes.

The conceptual hydrothermal-evaporative model proposed in this study invokes contributions from both connate and geothermal fluids. Although direct evidence of high temperatures is limited, the isotopic enrichment and low d-excess values observed in the Keana brines are consistent with interaction with deep-seated or saline fluids, as also supported by regional studies of the Middle Benue Trough. In this context, *connate fluids* refer to waters trapped within the sediments during deposition that were later mobilized, whereas *hydrothermal fluids* represent deeper, crustally derived waters that migrate upward through fracture networks. The isotopic patterns, therefore, provide a rational basis for including these fluid types in the model.

The presence of both hot and cold brines in the study area can be interpreted within the framework of fault-controlled fluid pathways. Isotopic data show that hot brines, such as those from Awe Pond Hot, are more enriched in δ^2H and $\delta^{18}O$ and exhibit lower d-excess compared to cooler brines like Akiri Pond Cold and Ribi Cold. This pattern indicates that deeper, warmer fluids ascend along permeable fractures, while cooler meteoric waters follow shallower pathways. These observations underscore the critical role of structural features in directing the movement and distribution of brines, supporting the integrated hydrothermal-evaporative model and explaining the coexistence of hot and cold brine zones within the Middle Benue Trough.

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