

Aqueous Mineral Speciation And Geochemical Processes Within The Keana-Awe-Azara Brine Fields Of The Central Benue Trough, Nigeria

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ABSTRACT: Nineteen (19) groundwater samples were collected and analysed for a wide range of elements. The study aimed at determining the mineral saturation index and hydrogeochemical characteristics of the groundwaters within the study area. Geochemical processes were elucidated using PHREEQC software. Oxidation of Fe-bearing sulfide minerals, Silicate & Carbonate weathering are the most dominant hydrogeochemical processes influencing the groundwater chemistry in the study area.

KEYWORDS; *Aqueous mineral speciation, Mineral saturation index, Carbonate and Sulphide minerals oxidation.*

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I. INTRODUCTION

The study area is defined by longitudes $8^{\circ}30'E - 9^{\circ}30'E$ and latitudes $8^{\circ}N - 8^{\circ}30'N$, which falls within the Central Benue Trough of Nigeria. This covers Keana-Awe-Azara towns and environs, all in the present day Nasarawa state of Nigeria.

The Benue Trough of Nigeria consists of a series of rift basins which form a part of the Central West African Rift System [1], [15], [23], [24]. Basement fragmentation, block faulting, subsidence and rifting accompanied the opening of the South Atlantic Ocean which led to the deposition and accumulation of sediments ranging between 4000 m to 6000 m in the Trough along the 800 km axis over a width of 120 km. Localized geological factors controlled the basin's development and are reflected in the lithostratigraphy and ages of the facies' associations. The zipper - like separation of the South American and African plates was consequent to crustal uplift, doming, subsidence and development of rift valleys flanked by stable cratons in the Late Jurassic to Early Cretaceous [1], [15], [16], [23], [24]. This Mesozoic event led to the initial opening of the South Atlantic Ocean with the associated basins dominated by extensional processes.

The occurrence of saline groundwaters (brines) has been known for a long time in parts of the Benue Trough, Nigeria [15], [16],[23], [24]. Prominent occurrences have long supported local salt production at Uburu-Okposi, Enyigba-Abakaliki and in the Ogoja-Okpoma area, in the Lower Benue; Awe, Azara, Ribbi, Akiri and in the Kanje area in the Middle Benue Trough.

PHREEQC and WATEQ4F, geochemical modeling softwares which are based on ion-association were used as a speciation program to calculate saturation indices (SI) and the distribution of aqueous species within the study area. This uses temperature, pH, Eh, TDS and alkalinity of water parameters, in addition to the chemical analysis computing the distribution of aqueous species, ion activities, and mineral saturation indices that specify the propensity of a water to dissolve or precipitate a set of minerals. Understanding the distribution of elements in precipitated mineral phases is important for the interpretation of aqueous geochemical data. These results are used primarily to examine the tendency of water to reach mineral solubility equilibrium as a constraint on interpreting the chemistry of the waters within the study area. The SI indicates if a solution is in equilibrium with the solid phase or if it is undersaturated or supersaturated. Equilibrium was defined as Zero (0). If SI is below 0, the solution is undersaturated on the corresponding mineral and waters still have the ability to dissolve that mineral phase. When SI exceeds 0, then the solution is oversaturated in that mineral and has the tendency to precipitate the mineral phase.

The hydrogeochemical processes in the study area are noted to be dominated by the oxidation of Fe-bearing sulfide minerals. The main sulfide minerals which have significant acid generating capacity in the study area are arsenopyrite (FeAsS), Pyrite (FeS₂), and Chalcopyrite (CuFeS₂), producing H⁺, SO₄²⁻ and metals/metalloids. The generation and discharge of acids with low pH and containing high concentrations of

dissolved metals may seriously disturb the hydrogeochemical characteristics in an environment [5]. Most of the groundwater samples in the study area are seen to be undersaturated with respect to carbonate (calcite and dolomite) and Sulfate (gypsum and anhydrite) minerals. Undersaturation with respect to carbonate bearing minerals suggest that the groundwater has short residence time and natural equilibrium with these minerals is not reached [5], [6], [8], [9], [10]. Calcium (Ca) and Sulphate (SO_4^{2-}) concentrations, however, are not limited by the precipitation of gypsum and calcite, since all water samples have increased Ca and SO_4^{2-} . The source of Ca, Fe, Mg, K, Na and metal(loid)s could be attributed to the silicate weathering, calcite dissolution and sulfide-mineral oxidation. This therefore, could be the prominent processes that contributed to the observed geochemical characteristics within these areas.

II. GEOLOGY OF THE STUDY AREA

The Benue Trough of Nigeria is a linear NE-SW trending rift system whose development is closely associated with the separation of Africa from South America and the opening of the South Atlantic Ocean during the Cretaceous period [1], [15], [19], [20]. The origin and evolution of the Benue Trough are fairly well documented [15], [16], [23], [24].

The Trough consist of a long stretch of sedimentary basin running from about the northern tip of the Niger Delta Basin and terminates under the Chad Basin and sandwiched by the Basement Complex areas in the north and south of river Benue. It is filled by sediments that are Middle-Late Albian in age [1], [15], [23], [24]. The oldest sediments belong to the Asu River Group and consist of shales and siltstones of marine origin, representing the first Middle Albian transgression into the Benue Trough. This formation is found at the crest of the Keana anticline to the east of Keana town. The Asu River Formation is overlain by the transitional beds of the Awe Formation, which consist of flaggy, whitish, and medium to coarse-grained sandstones which are interbedded with carbonaceous shales or clays from which brine springs issue continuously. The Awe formation marks the beginning of the regressive phase of the Albian sea and is overlain by continental fluviatile sands of the Keana Formation, which is of late Cenomanian to Early Turonian. The Eze-aku, Agwu and Lafia Formations are also found within the study area, which are of Turonian to Early Maestriachian. The Eze-aku Formation consists essentially of calcareous shales, micaceous fine to medium grained friable sandstones and occasional beds of limestones. The Agwu Formation, which is Coniacian in age, consists mainly of black shales, sandstones and some coal seams. The Lafia Formation is the youngest formation in the Benue Trough, Maestriachian in age, consists of coarse grained ferruginous sandstones, red loose sand, flaggy mudstones and clays.

Sedimentation and stratigraphic settings are characterized by transgressive and regressive cycles, starting in the pre-Albian or mid-Albian times with the Asu-River Group, which lies directly over the Precambrian Basement and is followed by subsequent Cretaceous sediments up to the Maestriachian. These sedimentary fills range from predominantly shale to various degrees of interlayering of moderate to well-indurated shale, mudstone, sandstone and even limestone and have been affected by two main (major) tectonic episodes during the pre-Turonian and Santonian periods [1], [15], [23], [24].

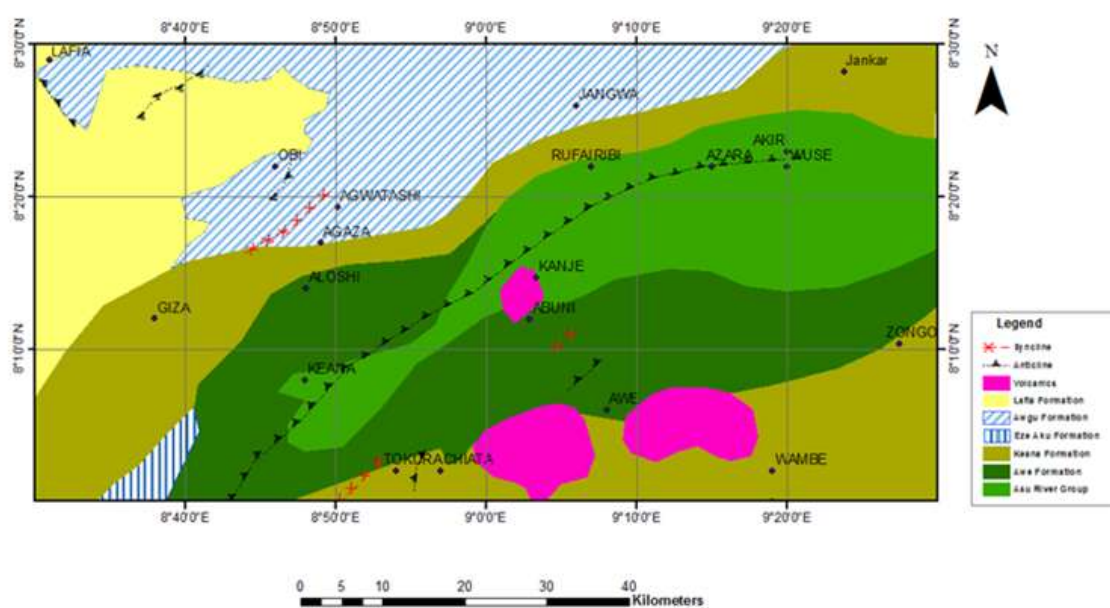


Fig. 1: Geological Map of the Study Area [13].

III. METHODOLOGY

A total of nineteen (19) water samples were considered for this study. The water sample positions were determined using the Global Positioning System (GPS). Physical parameters such as temperature, pH, conductivity and total dissolved solid (TDS) were measured in the field using TDS/conductivity meter (HACK KIT, Optima 2000 DV PerkinElmer model). Major cations and trace elements were analysed through Inductively Coupled Plasma Mass-Spectrometry using direct current plasma Optical Emission Spectrometry (ICP-OES) at the Geology Laboratory of the University of Jos-Nigeria. The major anions (HCO_3 , Cl, Br, F, SO_4 , and NO_3) were analyzed through Ion Chromatography at Activation Laboratories, Ontario, Canada. Hydrogeochemical characterization of the groundwater samples were evaluated from the physico-chemical analysis results. Geochemical processes were studied using PHREEQC software, from WATE4QF database to compute aqueous speciation and fluid-mineral equilibrium on the groundwater samples.

IV. RESULTS

Table 1: Physico-Chemical Parameters and Results

S/No	Samples Location	pH	eH	Tempt.	TDS (ppm)	Elev. (M)	Ca (mg/l)	Fe (mg/l)	Mg (mg/l)	K (mg/l)	Na (mg/l)	P (mg/l)	S (mg/l)	Sr (mg/l)	Cl (mg/l)	F (mg/l)	Br (mg/l)	SO_4 (mg/l)	H_2CO_3 (mg/l)	^{18}O (per mL)	D (per MIL)
1	ZC's House, Keana	5.48	0.56	30.8	376	138	26.45	<DL	62.16	0.014	41.82	0.073	33.7	0.114	10	0.07	0.06	6.14	255		
2	Akyana Gbogbo, Keana	5.64	0.77	29.9	480	134	63.82	<DL	11.22	28.74	231.2	0.248		<DL	81.6	0.1	0.06	3.33	426	-4.8	-23.1
3	Fed. Govt. Girls Coll. Keana	10.8	0.32	33.6	172	153	3.045	0.392	0.247	1.126	34.23	0.052	19.25	<DL	5.23	0.32	0.03	16.7	149		
4	Aloshi Water Works	10.5	0.41	29.3	237	197	0.987	0.672	0.126	4.089	38.85	0.048	9.259	0.001	1.85	0.17	0.03	33.5	206		
5	Obi Town	6.7	-	29.4	183	174	4.705	0.2	0.39	<DL	5.623	1.711	49.24	0.015	34.4	0.07	0.03	17.9	84		
6	Ribi Town	6.39	0.12	32.1	870	156	331.3	21.9	77.33	168	6463	0.142	2.232	1.048	589	0.14	0.46	58.3	214		
7	Azara Town	5.96	0.72	31.5	410	118	548	<DL	121	306	7622	<DL	<DL	44.8	22.1	0.11	4.53	22.3	341		
8	Akiri Hot Brine Spring	4.76	6.76	46.7	598	115	200	97610	8738	3749	11700	2875	6392	<DL	3300	0.98	1.8	1.81	371		
9	Akiri Town	4.66	0.2	34.6	120	120	103	<DL	20.2	82.9	2381	<DL	<DL	8.3	11.2	0.11	2.4	8.67	83		
10	Wuse Town	4.91	0.38	32.3	222	120	68.16	0.029	28.56	4.087	103.1	<DL	<DL	0.763	8.58	0.16	0.03	6.1	188		
11	Ribi Health Center	5.52	9.01	35.6	480	163	122.3	0.664	24.44	4.036	4142	0.109	326.3	<DL	4550	0.81	6.13	14.3	238	-6.13	-35.5
12	Adudu Town	5.7	0.61	31.7	356	188	90.74	0.001	0.02	<DL	0.166	<DL	<DL	<DL	8.5	1.41	0.06	17.3	267		
13	Kanje town	6.3	0.91	30.2	536	178	69.61	1.317	29.49	103.4	2357	0.119	10.19	0.497	68.8	0.08	0.1	4.73	404		
14	Abuni town	5.85	0.79	31.8	531	163	36.62	0.794	32.06	4.412	78.45	0.088	12.97	<DL	161	0.4	0.1	0.94	256		
15	New Awe Town	7.03	0.37	31	334	144	10.32	0.01	4.48	8.9	22.83	<DL	<DL	<DL	13.7	0.18	0.06	34.6	207		
16	Old Awe Town	6.85	-	41.3	951	104	134	<DL	40.25	53.99	30360	0.05	35.49	<DL	5430	0.62	3.57	13.6	431	-5.98	-34.4
17	Agwatashi, Obi	6.26	0.5	29.6	500	190	221.6	0.742	10.59	<DL	26.83	0.322	124.1	0.015	70.6	0.2	0.18	33.6	110		
18	ERCC P College, Obi	6.23	0.32	29.8	360	203	2.994	0.055	0.404	<DL	6.931	<DL	39.51	0.015	3.56	0.01	0.03	3.02	9		
19	Agaza Town	9.18	0.66	30	365	156	69.61	1.317	29.49	103.4	2357	0.119	10.19	0.824	9.77	0.27	0.06	27.5	264		

Table 2: Ion Activation Product of prominent minerals in the study area

S/No	Samples Location	Aragonite	Barite	Calcite	Dolomite	Gypsum	Halite
1	ZC's House, Keana	-10.604	-9.822	-10.604	-20.616	-7.874	-6.379
2	Akyana Gbogbo, Keana	-9.888	-9.946	-9.888	-20.308	-7.77	-4.741
3	Fed. Govt. Girls Coll. Keana	-7.889	-9.145	-7.889	-16.691	-8.298	-6.717
4	Aloshi	-8.313	0	-8.313	-17.264	-8.521	-7.119
5	Obi	-10.508	-9.331	-10.508	-21.882	-7.856	-6.668
6	Wuse	-11.946	-9.514	-11.946	-24.024	-8.496	-6.283
7	Adudu	-9.802	0	-9.802	-23.043	-6.809	-8.842
8	Abuni	-10.089	-11.297	-10.089	-20.015	-8.522	-4.903
9	New Awe	-9.496	0	-9.496	-19.139	-7.337	-6.481
10	Agwatashi, Obi	-9.323	-9.816	-9.323	-19.747	-6.309	-5.74
11	ERCC P College, Obi	-12.081	-11.285	-12.081	-24.816	-8.736	-7.543

Table 3: Aqueous Mineral Species (Solubility-Equilibrium) within the study area

S/No	Samples Location	Supersaturated	Equilibrium	Undersaturated
		SI = > 0	SI = 0	SI = < 0
1	ZC's House, Keana	None	Barite	Anglesite, Anhydrite, Aragonite, Calcite, Cerrusite, Dolomite, Fluorite.

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2	Akyana Gbogbo, Keana	None	None	Anglesite, Aragonite, Cerrusite, BaCrO ₄ , Fluorite, Magnesite, Therite,	Anhydrite, Calcite, PbCrO ₄ , Dolomite, Gypsum, Otavite
3	Fed. Govt. Girl's Coll. Keana	Goethite, Manganite, Pyrolusite, Zincite, ZnO	Aragonite, Barite, Calcite, Dolomite, Ferrihydrite,	Anhydrite, Bunsenite, BaCrO ₄ , Hydcerrusite, Smithsonian, Witherite,	Brucite, Cerrusite, Fluorite, Malachite, Tenorite,
4	Aloshi	Goethite, Manganite, Pyrolusite, Zincite, ZnO	Aragonite, Calcite, Ferrihydrite, Smithsonian	Anhydrite, Bunsenite, Dolomite, Gypsum, Tenorite,	Brucite, Celestine, Fluorite, Strontianite,
5	Obi	Cr ₂ O ₃ , FeCr ₂ O ₄ , Goethite, Se metal, Cuprite	Barite,	Anglesite, Aragonite, Celestine, Cr(OH) ₃ , Ferrihydrite, Gypsum, Otavite, Strontianite, Witherite,	Anhydrite, Calcite, Cerrusite, Dolomite, Fluorite, Magnesite, Siderite, Tenorite,
6	Wuse	Cr ₂ O ₃ , Goethite,	Barite, FeCr ₂ O ₄ , Smithsonian,	Anglesite, Aragonite, Celestine, Cr(OH) ₃ , Fluorite, Magnesite, Otavite, Smithsonian, Tenorite, Zincite, ZnO.	Anhydrite, Calcite, Cerrusite, Ferrihydrite, Gypsum, Malachite, Siderite, Strontianite, Witherite,
7	Adudu	Cr ₂ O ₃ , Goethite,	Fluorite, Otavite,	Anhydrite, Azurite, Cerrusite, FeCr ₂ O ₄ , Dolomite, Gypsum, Manganite, Scorodite, Tenorite, Zincite,	Aragonite, Calcite, Cr(OH) ₃ , PbCrO ₄ , Ferrihydrite, Malachite, Pyrolusite, Smithsonian,
8	Abuni	Ferrihydrite, Goethite, Pyrolusite,	Manganite,	Anglesite, Aragonite, Cerrusite, BaCrO ₄ , Fluorite, Magnesite, Otavite, Witherite,	Anhydrite, Barite, Calcite, PbCrO ₄ , Dolomite, Gypsum, Malachite, Tenorite,
9	New Awe	Cr(OH) ₃ , FeCr ₂ O ₄ , Otavite, Cr ₂ O ₃ , Goethite,	Azurite, Calcite, Ferrihydrite, Malachite, Tenorite	Anglesite, Antlerite, Atacamite, Bunsenite, PbCrO ₄ , Dolomite, Fluorite, Magnesite, Smithsonian, ZnO.	Anhydrite, Aragonite, Brochantite, Cerrusite, Cuprite, Epsomite, Gypsum, Manganite, Siderite, Zincite,

10	Agwatashi	Cr ₂ O ₃ , Ferrihydrite, Goethite,	FeCr ₂ O ₄ , Aragonite, Barite, Calcite,	Anglesite, Celestine, Cr(OH) ₃ , BaCrO ₄ , Epsomite, Gypsum, Malachite, Otavite, Scorodite, Strontianite, Witherite.	Anhydrite, Cerrusite, PbCrO ₄ , Dolomite, Fluorite, Magnesite, Manganite, Pyrolusite, Siderite, Tenorite,
11	ERCC Pastor's College, Obi	Cr ₂ O ₃ , Goethite,	Cr(OH) ₃ , Ferrihydrite,	Anglesite, Aragonite, Barite, Calcite, Celestine, Cerrusite, Gypsum, Malachite, Siderite, Tenorite.	Anhydrite, Barite, Calcite, Cerrusite, Magnesite, Scorodite, Strontianite,

Fig. 3: Groundwater Classification using Piper-Trilinear diagram

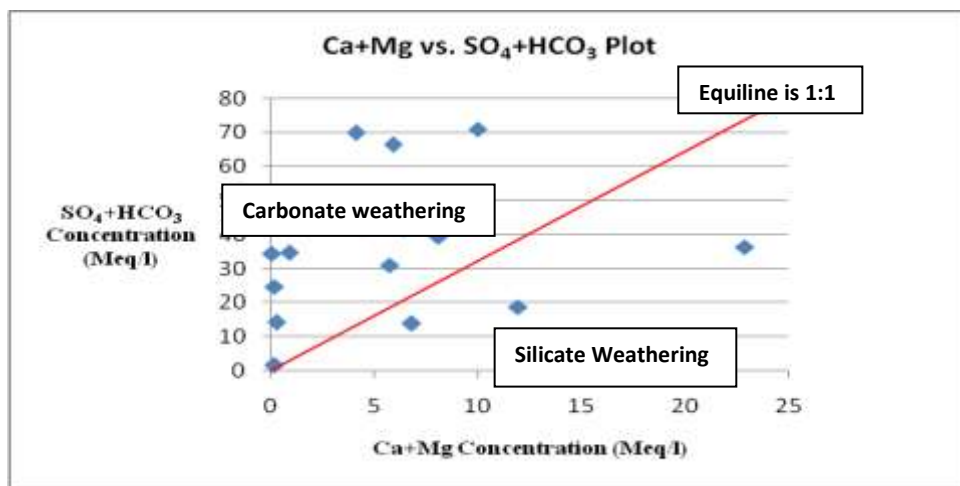
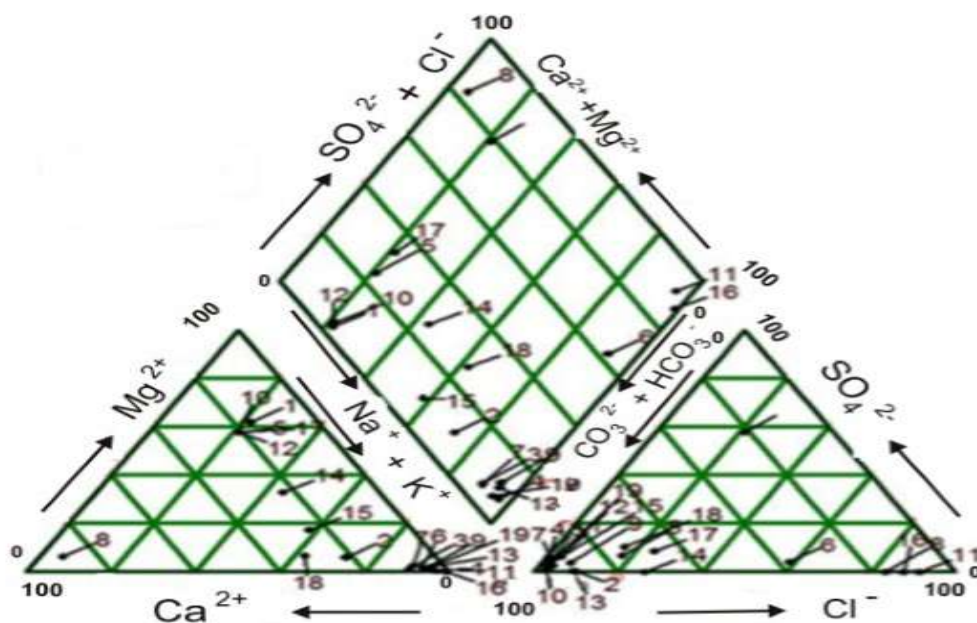


Fig. 4: Scatter diagram of (Ca + Mg) vs (SO₄ + HCO₃)

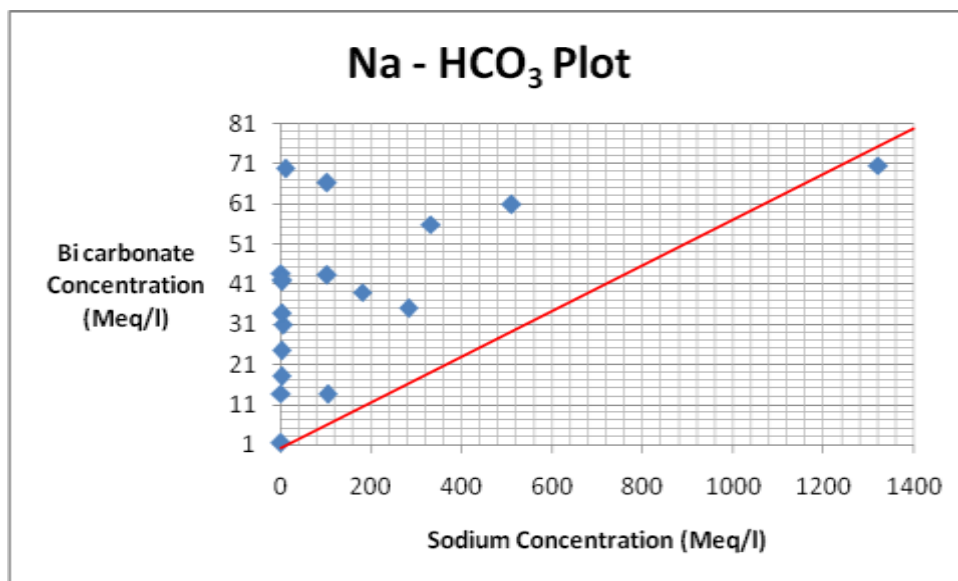


Fig. 5 Sodium-Bicarbonate plot

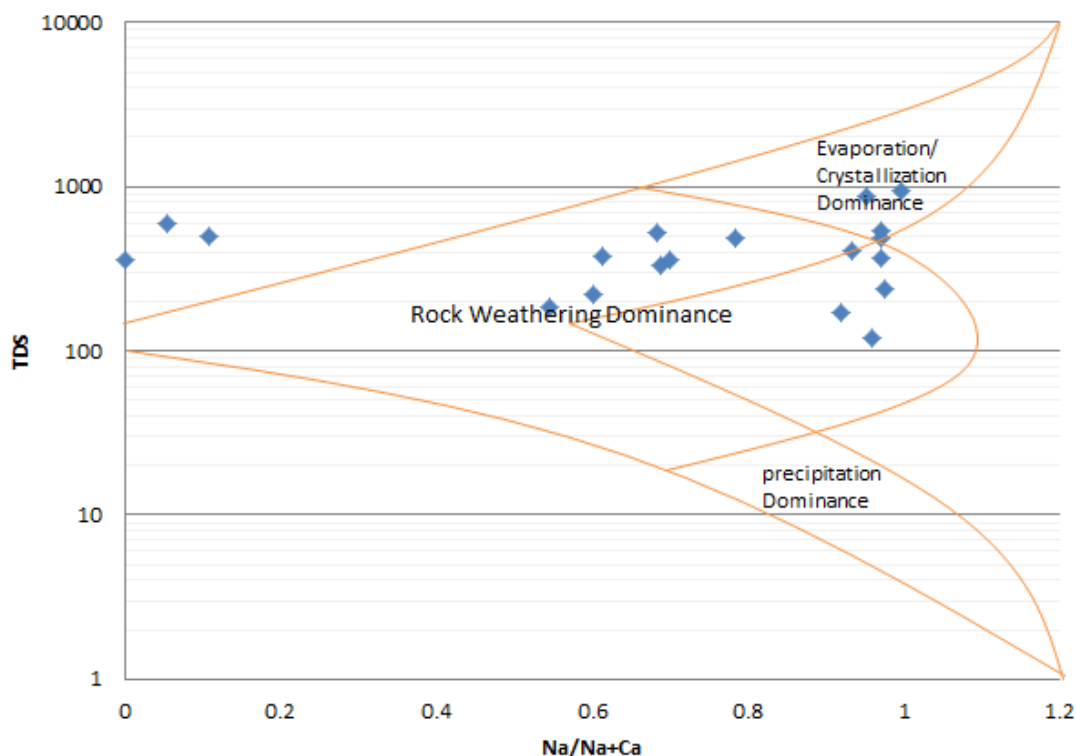


Fig. 6: Groundwater sample plots on Reaction Dominance Diagram (After Gibbs, 1970)

V. INTERPRETATION AND DISCUSSION

The chemical composition of the analyzed groundwater samples within the study area are thus: Eh ranges from 0.12-9.01us/cm, The results shows an order of abundance for the cations as $\text{Na}^+ > \text{Mg}^{2+} > \text{K}^+ > \text{Ca}^{2+}$, with Na^+ constituting more than 75% in most cases while for the anions the order is $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^- > \text{NO}_3^-$ with Cl^- forming at least 80% in all cases, Calcium constituents vary between 0.987mg/l-90.74mg/l, Sodium concentration vary from 0.166mg/l-30360mg/l, Chloride concentration ranges from 1.85mg/l-5430mg/l, Sulphate concentration ranges from 0.94mg/l-58.3mg/l, Bromide concentration ranges from 0.03mg/l-6.13mg/l. From the Ternary and Piper diagrams (Figs.3,4.), the water samples within the study area are seen to display relative high percentage of major cations of Mg^{2+} and Na^+ and the prominent anions displayed are Cl^- and HCO_3^- Temperature range of the water samples within the study area span from 29.3^o C to 41.3^o C in Aloshi

and Old Awe town spring, respectively. The Total Dissolved Solids (TDS), range between 120ppm -951ppm in Akiri and Old Awe town spring, respectively.

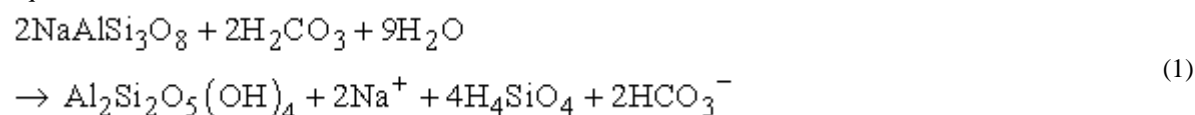
The classification of the groundwater was studied by plotting cations and anions in the Piper diagram (Figs 2&3) [8], [9], [10], [11]. The trilinear plots suggest that among the anions, Cl⁻ is most abundant with Na⁺ cations more abundant in the groundwaters.

From the Piper-Trilinear plot, the distribution of hydrochemical facies of groundwater within the study area could be classified into three groups:

- (i) Magnesium-Bicarbonate Type (Adudu Town, Zc's House, Keana, Obi Town, Abuni Town)
- (ii) Sodium-Bicarbonate Type (New Awe Town, Akyana Gbogbo, Alosi, Agaza Town, Kanje town)
- (iii) Mixed Type (ERCC Pastors College, Obi premises).

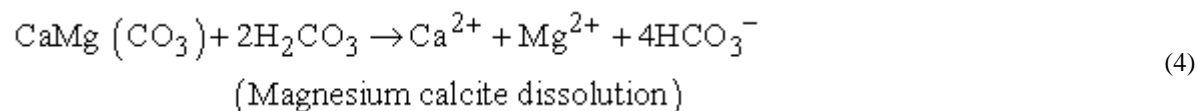
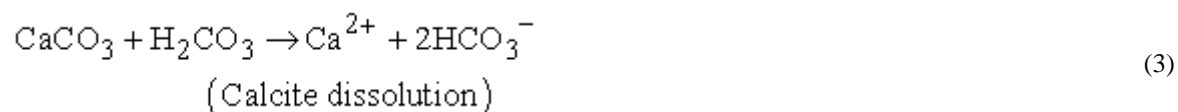
The Sodium Bicarbonate type of saline groundwater therefore stood out to be the most prominent. Its occurrence in the aquifers within the study area may be due to the interactions between groundwater and different rocks with mineralogical compositions along the groundwater flow paths.

The High concentration of Ca²⁺, Na⁺, and HCO₃³⁻ in the groundwater could be due to the dissolution of plagioclase feldspars, magmatic activity and carbonate weathering in the rocks resulting in the release of the elements responsible for the various hydrochemical facies. These elements, (Ca, Na and K, and Mg, HCO₃, SO₄ and Cl) are therefore the major ions in groundwaters within the study area which are derived from water rock interaction [6], [7], [9], [10], [11], [13]. This is better elucidated through the Na vs HCO₃⁻ scatter diagram (Fig. 5). From this diagram, most points plot above the equiline of 1:1, thus indicating increased HCO₃⁻ compared to Na which could have resulted from silicate weathering. The weathering process is given by the following equation:



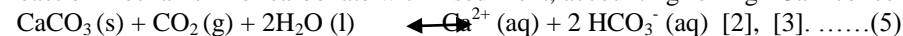
In the scatter diagram of Ca + Mg Vs. SO₄ + HCO₄ (Fig. 4), about 70% of the samples plotted above the 1:1 equiline, thus representing carbonate weathering. Carbonate weathering may be caused by atmospheric water charged with CO₂ which further results in the formation of carbonic acid. This accelerates the dissolution of carbonate rocks such as dolomite, limestone and gypsum along groundwater flow path. The result is the release of Ca²⁺ and Mg²⁺ from the carbonate weathering into groundwater system through recharge. Carbonate weathering is prominently found to have operated within the study area, usually caused by atmospheric water charged with carbon dioxide (CO₂) which further results in the formation of carbonic acid. The result is the release of Ca²⁺ and Mg²⁺ from the carbonate weathering into groundwater system through recharge. The weathering of carbonate minerals which is responsible for the release of the ions is expressed in equations 2, 3, 4.

The weathering of calcite minerals which is responsible for the release of the ions is expressed through the following equations:



Gibbs [12] indicated a close relationship between water composition and the hydrochemical processes involving precipitation, water interaction and evaporation. From Fig. 6 most points of the samples plotted in the region of rock dominance and weathering.

Since the dissolution of carbonates and other related minerals are determined by the acidity of the environment, and having pH of 4.6 to 10.8 in the study area, it means that the acidity is moderately low. The reaction mechanism for carbonate within sediment, accounting for high Ca²⁺ concentration could be thus;



At low acid concentration, CaCO₃ + H⁺ ⇌ Ca²⁺ + HCO₃⁻, showing that H⁺ takes CO₃ away from Ca²⁺ to form the weak acid HCO₃⁻.

Also the solubility of CaCO_3 , to an extent is determined in large part by the pH of the environment. When these carbonates dissolve in carbonic acid, eg Limestone, it equally accounts for the high Ca^{2+} concentration within the study area, thus: $\text{CaCO}_3 + \text{H}_2\text{CO}_3 \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^- \dots\dots(6)$

The study area is also characterized by widespread sulphide, sulphate and coal mineralizations with mainly mineral ores like Galena (PbS), Sphalerite (ZnS), Chalcopyrite (CuFeS_2) [12], [17], [19], [20]. This is with particular reference to the Awe, Alosi and Keana areas where sulfide minerals are mined and waste dumps, tailings, low-grade ore, overburden and run-off mill stockpiles, and are disposed off without any consideration for its potential for pollution. Polluted or acid rich waters released from the mines is a consequence of the oxidation of sulfide minerals mainly pyrite (FeS_2), but also galena (PbS), sphalerite (ZnS), pyrrhotite (FeS), marcasite (FeS_2), arseno-pyrite (FeAsS), and chalcopyrite (CuFeS_2). FeS_2 . When these minerals (like FeS_2) are exposed to water and oxygen, they become oxidized in the presence of water to sulphuric acid and ferrous hydroxide as follows;



It is the sulphuric acid that gives the strong acidic property [14], [20], [22]. This sulphuric acid further attacks other sulphide minerals and thus breaks them down to release trace elements/metals such as Pb, As, Cd, Cu, Zn, Cr, Co, Ni, others. The stronger the acid solution, the more the metals become soluble and this continues to lower the pH.

The concentration of dissolved ions in groundwater depends on the hydrogeochemical processes that take place in the aquifer [5], [6], [7], [9], [19], [20]. The hydrogeochemical processes in the study area are known to be dominated by the oxidation of Fe-bearing sulfide minerals and Carbonate weathering which is usually caused by atmospheric water charged with carbon dioxide (CO_2) resulting in the formation of carbonic acid. It then releases Ca^{2+} and Mg^{2+} into groundwater system through recharge [20]. The main sulfide minerals which have significant acid generating capacity in the study area are arsenopyrite (FeAsS), Pyrite (FeS_2), and Chalcopyrite (CuFeS_2), producing H^+ , SO_4^{2-} and metals/metalloids [20], [22]. The generation and discharge of acids with low pH and containing high concentrations of dissolved metals may seriously disturb the hydrogeochemical characteristics in an environment [5], [6]. Most of the groundwater samples in the study area were carbonate (calcite and dolomite) and Sulfate (gypsum and anhydrite) minerals. Ca^{2+} and SO_4^{2-} concentrations, however, are noted not to be limited by the precipitation of gypsum and calcite, since all water samples have increased Ca^{2+} and SO_4^{2-} [12], [14], [20], [22].

PHREEQC and WATEQ4F (geochemical modeling softwares), which are based on the ion-association were used as a speciation program to calculate saturation indices (SI) and the distribution of aqueous species within the study area. This uses tempt, pH, Eh, TDS and alkalinity water parameters, in addition to the chemical analysis computing the distribution of aqueous species, ion activities, and mineral saturation indices that specify the propensity of a water to dissolve or precipitate a set of minerals. Understanding the distribution of elements in precipitated mineral phases is important for the interpretation of aqueous geochemical data. Goethite, Manganite, Pyrolusite, Zincite, Cr_2O_3 , FeCr_2O_4 , Cuprite are the mineral phases that are supersaturated within the study area where they precipitate within the environment with Aragonite, Barite, Calcite, Dolomite, Ferrihydrite being in equilibrium. Anglesite, Anhydrite, Aragonite, Calcite, Celestine, Cerrusite, $\text{Cr}(\text{OH})_3$, Dolomite, Ferrihydrite, Fluorite, Gypsum, Magnesite, Otavite, Siderite, Strontianite, Tenorite, Witherite appear undersaturated in most of the locations, thereby dissolved in the environment. Aqueous Cu, Zn and Mn concentrations might have been reduced by Goethite, Manganite, Pyrolusite, Zincite, ZnO and or ferrihydrite precipitation in the oxidation zone through adsorption processes [3], [4].

The Aqueous Mineral Speciation result suggests that most waters within the study area are undersaturated with respect to gypsum and calcite and as a result, calcium concentrations are not limited by the precipitation of gypsum and calcite, being all water samples have elevated Ca. This could be attributed to silicate weathering, calcite dissolution and sulfide-mineral oxidation [3], [4]. This indicates that most areas in this study are dominantly influenced by rock weathering. It could therefore, be concluded that Ion Exchange Reactions, Pyrite Oxidation, Plagioclase and Carbonate Weathering Processes could have influenced the chemistry of the groundwater within the study area.

VI. SUMMARY AND CONCLUSION

An assessment of the groundwaters within Keana-Awe-Azara brine fields was carried out. Hydrogeochemical characteristics of the groundwaters were evaluated in terms of Magnesium-Bicarbonate, Calcium-Chloride, Sodium-Chloride, Sodium-Bicarbonate and Mixed Types, with Sodium-Bicarbonate Type being most prevalent within the study area. Calculated saturation indexes for selected minerals are presented, which suggests different mineral-solution interactions as precipitation-dissolution and adsorption-desorption processes within the study area. The hydrogeochemical processes in the study area are noted to be dominated by the oxidation of Fe-bearing sulfide minerals and carbonate weathering. Most of the groundwater samples in the

study area were seen to be undersaturated with respect to carbonate (calcite and dolomite) and Sulfate (gypsum and anhydrite) minerals. Undersaturation with respect to carbonate bearing minerals suggest that the groundwater has short residence time and natural equilibrium with these minerals is not reached.

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