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Hydrochemical framework of groundwater in the Ankobra Basin, Ghana

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Abstract Hydrochemical and stable isotope $(^{18}O$ and ²H) analyses of groundwater samples were used to establish the hydrochemistry of groundwater in the Ankobra Basin. The groundwater was generally mildly acidic, low in conductivity and undersaturated with respect to carbonate phases. Major ions except bicarbonate were low and dissolved silica was moderately high. Silicate minerals weathering is probably the main process through which major ions enter the groundwater. Groundwater samples clustered tightly along the Global Meteoric Water Line suggesting integrative, smooth and rapid recharge from meteoric origin. The majority of the boreholes and a few hand dug wells cluster towards the Ca–Mg–HCO₃ dominant section of the phase diagram, in conformity with the active recharge and short residence time shown by the isotope data. Aluminium, arsenic, manganese, iron and mercury were the only trace metals analysed with concentrations significantly above their respective detection limits. Approximately 20%, 5%, 40% and 25% respectively of boreholes had aluminium, arsenic, iron and manganese concentrations exceeding the respective WHO maximum acceptable limits for drinking water. The relatively large percentage of boreholes with high concentration of aluminium reflects the acidic nature of the groundwater.

Keywords Ghana Groundwater quality Hydrochemistry \cdot Maximum acceptable limit \cdot Silicate weathering

1 Introduction

Ankobra Basin lies between latitudes 4.8° N and 6.5° N, and longitudes 1.75° W and 2.5° W respectively, and occupies approximately 8,400 km². The location map for the Ankobra Basin is presented in Fig. [1.](#page-1-0) It is one of the most important river basins in Ghana, in that it has some of the richest gold and manganese mines in the country.

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Fig. 1 Location map of the Ankobra Basin

Diamonds are also known to occur within the Ankobra Basin (Appiah et al. [1993\)](#page-32-0). Minerals are not the only commodities produced. Large volumes of timber, palm-oil and coconut as well as rubber are also produced in this Basin.

Ghana government's policy of trade liberalization and amendment of mining laws to attract foreign investments into the mining industry area have resulted in intensified and uncontrolled mining (particularly gold mining) activities in the Ankobra Basin with the subsequent degradation of the environment, putting water resources, particularly surface water, at high risk of pollution (Acquah [1993\)](#page-32-0).

Realising that most of the surface water resources are polluted, the government of Ghana has shifted attention from developing surface water resources to groundwater

resource development and supply to the communities in the Basin because of the anticipated high cost of treating polluted surface water resources. Consequently, groundwater has become the principal source of potable water supply for the communities within the Ankobra Basin.

Groundwater in hard rock aquifers, particularly in mining areas, are known to be vulnerable to quality problems as rocks are often carbonate-deficient and give rise to poorly buffered groundwater (Smedley et al. [1995](#page-33-0)). Gold ores in the Ankobra Basin are partly sulphidic ores (Acquah [1993](#page-32-0)), and exposure of the sulphides to the atmosphere either through natural processes of weathering, or anthropogenic processes such as mining, road cutting results in oxidation that often leads to generation of acid mine drainage. Acid mine drainage may eventually infiltrate into aquifers and lower the pH of the groundwater, depending on the buffering capacity of the aquifer. Additionally, acidic groundwater may encourage dissolution of minor and trace elements such as Al, As, Mn, Be and Fe from most minerals if they are present in the rock matrix and render the groundwater unsafe for drinking. Thus, there is a need to examine the hydrochemical composition and quality of groundwater in the Basin.

In spite of the importance of groundwater to this Basin, there is hardly any baseline information on hydrochemical composition of the groundwater or water quality data on which the present and future groundwater quality assessment could be based. The main objective of this paper is to determine the hydrochemistry and assess the groundwater quality in relation to drinking water.

2 Physiography and climate

Geomorphologically, the Ankobra Basin consists of a series of ridges separated by steep-sided, flat-bottomed valleys varying in altitude from 46 m in the south to 76 m in the north that are parallel to one another and to the strike of the rocks. The ridges at some places reach a height of 200 m. Due to the heavy rainfall and forest vegetation that prevent sheet erosion, the whole area is highly dissected and reduced to uniformly moderate relief with a gentle slope to the south (Service [1938;](#page-33-0) Dickson and Benneh [1980\)](#page-32-0). Erosion is mainly restricted to river channels that cut up the plateau surfaces and the hills are usually capped with iron-pan (laterite) and bauxite (Dickson and Benneh [1980\)](#page-32-0).

The climate of the Ankobra Basin falls partly under the wet semi-equatorial and partly under south-western equatorial climatic zones of Ghana (Dickson and Benneh [1980\)](#page-32-0). It is thus characterised by double rainfall maxima. The first peak occurs in June whilst the second peak occurs in October. The mean annual rainfall values in the northern part of the Basin (wet semi-equatorial climatic zone) and in the southern part (equatorial climatic zone) are approximately 1600 mm and 2000 mm, respectively. The highest mean monthly temperature for the two climatic zones is 30° C and occurs between March and April and the lowest temperature is approximately 26° C and occurs in August (Dickson and Benneh [1980](#page-32-0)).

3 Hydrogeological setting

The geology of the Ankobra Basin consists mainly of lower Proterozoic rocks divided into the Birimian (Lower and Upper) system, unconformably overlain by the

Tarkwaian system. Sills and dykes of igneous rocks ranging from felsite and quartz porphyry to meta-dolerite, gabbro and norite intrude into the Birimian and the Tarkwaian Systems at several places. The Lower Birimian rocks underlie approximately 60% of the Basin and are mainly pelitic in origin and consist of great thicknesses of alternating shales, phyllites, greywacke and argillaceous beds with tuffs and lavas. The Upper Birimian system covers approximately 8% of the Ankobra Basin and is dominated by rocks of volcanic and pyroclastic origin. The rocks consist of a bedded group of green lavas (greenstones), tuffs and sediments with minor bands of phyllite that include a zone of manganiferous phyllites containing manganese ore (Junner et al. [1942](#page-32-0); Kesse [1985](#page-32-0)).

The Tarkwaian system that forms nearly 15% of the rock cover occupies an elongated and narrow geosyncline about 16 km wide that stretches in a northeastern to south-western direction. It consists of an overall thick clastic sequence of arenaceous and argillaceous sediments with two well-defined zones of pebbly beds and conglomerate in the lower members of the system (Kesse [1985](#page-32-0)). The Granitoid occupies about 10% of the Ankobra Basin while the Eocene and Cretaceous Deposits occupy approximately 3% of the Basin. The Eocene and Cretaceous Deposits occur along the coast. A geological map of the Ankobra Basin is presented in Fig. [2](#page-4-0).

Groundwater occurrence in the Ankobra Basin is associated with the development of secondary porosities as a result of fissuring and weathering. Tectonic lines of weakness created by the orogenic regimes have facilitated extensive and deep weathering and thick regolith development under the highly humid tropical climate with distinct wet and dry seasons. The weathering depth is greatest in the Birimian rock areas, where it has reached between 90 m and 120 m. The depth of the weathering in the granites, porphyries, felsites and other intrusive igneous rocks is between 20 m and 80 m. However, in the Tarkwaian system, the weathered depth rarely exceeds 20 m (Junner et al. [1942;](#page-32-0) Kesse [1985](#page-32-0)). Aquifers are mostly either semi-confined or confined due to the high argillite content of the regolith and occur mainly in the transition zone between weathered zones and the fresh rock or in the fractured or fissured zone normally at some depth below the weathered zone. Borehole yields are highly variable and in the range of 0.3–36.0 m^3 h⁻¹ with a mean 2.5 m³ h⁻¹ while static water levels vary from 0.0 (flowing well) to 26.5 m below ground level (Nii Consult [1998](#page-33-0)).

4 Sampling and analytical techniques

Water samples were collected from 64 boreholes, 12 hand-dug, 3 major rivers and 2 streams that drain mining concession in January 2005 for physico-chemical analysis. Additionally 4 rainwater samples were also collected. At each sampling point, two samples were collected for major ions and trace elements analyses. Each sample was collected in acid-washed high-density linear polyethylene (HPDE) 100 ml bottle with strict adherence to the sampling protocol as described by Claasen [1982;](#page-32-0) Barcelona et al. [1985](#page-32-0); Gale and Robins [1989](#page-32-0). Samples were filtered using Sartorius polycarbonate filtering apparatus and a $0.45 \mu m$ cellulose acetate filter membrane. Sample for metal analyses were acidified to a pH < 2 after filtration using reagent grade nitric acid. Samples for anion analyses were without preservation. In this case, unfiltered sample was collected in 100 ml polyethylene bottles. The bottles

Fig. 2 Geological map of the Ankobra Basin

were tightly capped to protect samples from atmospheric $CO₂$ and stored in ice chest (with temperature variation between 4° C and 8° C). Precaution was also taken to avoid sample agitation during transfer to the laboratory. Furthermore, 39 water samples were collected from selected boreholes and hand dug wells, rivers and rainwater for deuterium and Oxygen-18 analyses. These consisted of 25 borehole, 4 hand dug well, 4 river and 6 rainwater samples. The isotope samples were collected unfiltered in 30 ml glass bottles with poly-sealed lids.

On-site analyses of temperature, redox potential (Eh), pH and electrical conductivity (EC) were conducted using a WTW-Multiline P4 Universal Meter in flow-through cell attached in line to the borehole pump outlet. Before taking readings, pumping was carried out until the meter readings were stable for each

parameter. Since the boreholes were already being used, the pumping time before stable meter readings were achieved was, on average, 5 min. Hand-dug wells were not pumped, so measurements were carried out at the wellhead or water point as soon as the samples were taken. Alkalinity titrations were carried out at the wellhead or water point using a HACH Digital Titrator Model 16900. All major ions [sodium (Na⁺), potassium (K⁺), calcium (Ca²⁺), magnesium (Mg²⁺), bicarbonate (HCO $_3^-$), chloride (Cl⁻), sulphate (SO $_4^{2-}$)] and minor elements such as nitrate (NO \overline{z}) fluoride (F⁻) etc. were analysed using double column Dionex DX-120 ion $\overline{3}$), fluoride (F⁻) etc. were analysed using double column Dionex DX-120 ion chromatograph. Trace metals analyses were carried out using ICP-MS. ICP-MS and stable isotope analysis of deuterium and oxygen –18 analyses were performed at the Geological Institute of the University of Copenhagen, Denmark. The ionic balances for the analyses varied from –5.9% to 10.1%, though more than 85% of the samples had an ionic balance within $\pm 5\%$. An ionic balance outside $\pm 5\%$ was largely associated with samples with very low total dissolved solids (TDS).

5 Results and discussions

5.1 Summary statistics

A statistical summary of chemical parameters measured in the groundwater samples is presented in Table [1](#page-6-0) and actual results are put in appendices 1 and 2. Minimum, maximum, median are non-parametric statistics, which may be used to summarise non-normally distributed water quality data (Caritat et al. [1998](#page-32-0); UNESCO/WHO/ UNEP [1996\)](#page-33-0).

The groundwater pH is typically low, in the range 3.89–6.78 with mean and median values of 5.70 and 5.72, respectively. However, the majority of the samples (>95%) falls within the pH range 4.5 to 6.9. Natural water pH values generally lie between 4.5 and 9.0 (Langmuir [1997\)](#page-32-0). Electrical conductivity values are generally low. Maximum and minimum values are 780 μ S cm⁻¹ and 37 μ S cm⁻¹ respectively (Table [1\)](#page-6-0).

Major cations $(Ca^{2+}, Mg^{2+}, Na^{+}$ and $K^{+})$ are generally low. In the majority of the cases (>60%) no particular cation shows a clear dominance but in a few cases, either Na⁺ or Ca²⁺ appears to be the dominant cation. Apart from bicarbonate $(HCO₃)$, which is by far the dominant anion and forms approximately 40% of the TDS content, the concentrations of other major anions are generally low. Sulphate and nitrate occur only in trace concentrations in the groundwater. Dissolved silica concentration is moderately high and on average accounts for 15% of the TDS load.

5.2 Saturation indices

The saturation state of the groundwater was assessed with respect to the major carbonate minerals in order to investigate the thermodynamic controls on the composition of the groundwater and the approximate degree to which the groundwater has equilibrated with the various carbonate mineral phases since HCO_3^- is the dominant anion. The saturation indices were determined using the hydrogeochemical equilibrium model, Phreeqc for Windows (Parkhurst and Appelo [1999](#page-33-0)). The saturation index (SI) of a given mineral is defined in Eq. 1

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No.	Method detection limit	Min.	Max.	Mean	Median	Std.	WHO (1993) guideline limit
Temp		25.7	30.3	27.2	27	0.8	
pH		3.89	6.8	5.7	5.715	0.5	$6.5 - 8.5$
EC		37	780.0	253.0	230	144.9	
Alk.		0.0	284.0	86.4	82	53.9	
Eh		52	201.0	114.9	106.5	36.5	
Ca	0.01	0.1	74.8	17.8	13.2	15.2	
Mg	0.01	0.2	19.4	6.5	5.80	4.6	
Na	0.1	0.3	68.9	17.4	16.3	9.5	200.0
K	0.01	0.1	25.5	2.4	1.30	3.5	
HCO ₃	0.1	< 0.1	346.5	105.4	100.1	65.8	
Cl	0.1	0.5	121.0	23.8	15.5	24.6	250.0
SO ₄	0.2	< 0.2	54.9	10.3	5.4	11.8	250.0
NO ₃	0.2	${<}0.2$	4.8	1.2	0.8	1.2	50.0
SiO ₂	0.1	0.6	56.9	30.4	31.70	14.6	
Al	0.1	< 0.1	2510.5	105.0	0.10	320.7	200.0
As	0.05	< 0.05	491.09	6.5	0.05	38.5	10.0
B	0.5	< 0.5	1056	13.9	8.50	14.6	300.0
Ba	0.04	27	8676.6	113.8	88.05	87.9	700.0
Cd	0.02	< 0.02	7.2	0.1	0.02	0.2	3.0
Cr	0.2	< 0.2	205.4	2.7	2.7	1.2	50.0
Cu	0.04	< 0.04	1120.6	14.7	3.455	30.3	2000.0
Fe	10	<10	12100.0	1300.0	150.0	2600.0	300.0
Hg	0.05	< 0.05	3.85	0.18	0.05	0.0	1.0
Mo	0.03	< 0.03	4.6	0.1	0.03	0.1	
Mn	0.02	1.0	1300.0	300.0	247.0	300.0	500.0
Ni	0.06	< 0.06	746.1	9.8	7.28	10.3	
Pb	0.03	0.56	167.5	2.2	1.33	3.2	
Rb	0.01	< 0.01	47.4	$0.6\,$	0.33	0.9	
Sb	0.025	${<}0.05$	7.2	0.1	0.05	0.3	5.0
Se	0.5	< 0.5	254.6	3.4	1.00	4.2	10.0
Sn	0.05	< 0.05	3.9	< 0.05	0.05	0.0	
Th	0.02	< 0.02	1.5	< 0.02	0.02	0.0	
U	0.01	< 0.01	0.8	< 0.01	0.01	0.0	
Zn	0.1	10.0	8496.0	111.7	32.0	342.6	3000.0

Table 1 Statistical summary of the parameters determined in the 76 groundwater samples

Temp. in °C, pH in pH-units, EC in μ S cm⁻¹, Ca to SiO₂ in mg l⁻¹, Al to Zn in μ g l⁻¹, Eh in mV

$$
SI = \log_{10}(IAP/K_{sp})
$$
 (1)

where IAP is the ion activity product and $K_{\rm{sp}}$ is the solubility product at a given temperature (the thermodynamic equilibrium constant adjusted to the temperature of the given sample).

The thermodynamic data used in this computation were those contained in the default database of the 'Phreeqc for Windows'. Supersaturation $(SI > 0)$ indicates that precipitation is thermodynamically favourable in spite of the fact that slow rates of reaction can inhibit precipitation. On the other hand, undersaturation $(SI < 0)$ signifies that dissolution is favoured. The summary statistics of saturated indices of some of the common mineral phases is presented in Table [2.](#page-7-0)

A plot of the computed saturation indices for calcite and dolomite (the commonest carbonate phases) based on the analytical results and measured field temperatures and pH for groundwater samples is shown in Fig. [3](#page-7-0) (data for the plot is presented in appendix 3). In the diagram, calcite saturation is indicated on the

Parameter	Min.	Max.	Mean	Median	Std.
pH	3.89	6.79	5.7	5.7	0.6
si Calcite	-6.1	-0.6	-2.7	-2.7	1.2
si Dolomite	-2.0	-0.6	-5.5	-5.5	2.3
si_Gypsum	-4.6	-2.0	-3.3	-3.3	0.7
si Anhydrite	-4.8	-2.2	-3.5	-3.5	0.6
si Goethite	-3.0	9.0	2.3	2.4	2.7
si Hematite	-3.9	16.5	6.2	6.9	4.6
si_Fe (OH) ₃ (a)	-8.9	3.1	-3.6	-3.5	2.7
Si $SiO2$ (a)	-5.1	-0.3	-0.8	-0.6	0.8
si Ouartz	0.1	0.9	0.6	0.7	0.3
$Fe/SO4$ (molar ratio)	0.03	21.6	0.8	0.05	2.7
H_4SiO_4/Na^+	0.02	2.3	0.8	0.8	4.8
H_4SiO_4/HCO_3^-	0.01	2.8	0.5	0.4	0.4

Table 2 Summary statistics of saturation indices for carbonate, iron bearing minerals, gypsum, anhydrite, amorphous silicate and quartz

ordinate and dolomite on the abscissa. A central band, of 0.4 units wide along each axis, represents essential equilibrium with respect to either mineral to account for the possible errors that may occur in the measurement pH, Mg^{2+} and Ca^{2+} . The four quadrants of the plotting field, I–IV, outside the equilibrium area represents different kinds of equilibrium conditions with respect to calcite and dolomite. Quadrant I represents supersaturation with respect to both carbonates. This condition represents water brought to equilibrium with respect to these carbonates and subsequently transported into a different environment where a higher pH or an apparent

Fig. 3 Plot of calcite versus dolomite saturation indices ² Springer

condition caused by the failure of the measured pH to accurately represent the actual equilibrium pH of the water in the aquifer (Langmuir [1971](#page-32-0)). Quadrant II represents super-saturation with respect to calcite but undersaturation with respect to dolomite. Water undergoing incongruent dissolution of dolomite or precipitation of calcite would plot in this quadrant. Quadrant III represents undersaturation with respect to both calcite and dolomite. A sample plotting in this quadrant represents water that has come from an environment where carbonates are impoverished. Water that has not reached equilibrium with the carbonates due to the short residence time would also plot in this quadrant (Langmuir [1971](#page-32-0)). Quadrant IV represents supersaturation with respect to dolomite and undersaturation with respect to calcite.

All the groundwater samples plotted in quadrant III, is an indication that the groundwater is undersaturated with respect to the major carbonate species. Thus, either the groundwater originates from an environment where calcite and dolomite are impoverished or the residence time is short and the groundwater has inadequate time for the mineral phases to react to equilibrium. Petrographic evidence, however, indicates the presence of significant proportion of carbonates in some of the rock types that have underlain the Basin. Various researchers (Jacobson and Langmuir [1970;](#page-32-0) Back and Hanshaw [1970](#page-32-0); Kenoyer and Bowser [1992](#page-32-0)) observed that vast majority of groundwater samples approach saturation with respect to calcite and dolomite even in fractured bedrock aquifers, if these carbonates are present to significant degree in an aquifer. Thus, the undersaturation of the groundwater with respect to calcite and dolomite can be attributed to short residence time of the groundwater in the aquifer or the carbonates may have occurred in some insoluble form. The groundwater is also undersaturated with respect to gypsum and anhydrite due to their absence from the rocks. The groundwater is uniformly supersaturated with respect to quartz but undersaturated with respect to amorphous silica (Table [2\)](#page-7-0) suggesting that amorphous silica possibly controls the silica concentration in the groundwater.

5.3 Hydrochemical facies

The chemical composition of groundwater (borehole samples) from the Ankobra Basin is shown on the phase diagrams in Fig. [4](#page-9-0). The majority of the boreholes and a few hand dug wells cluster towards the Ca–Mg–HCO₃ dominant Section (A) of the diamond field, in conformity with the active recharge and short residence time shown by the isotope data. A few of the boreholes (Section B) also show $Na-HCO₃$ characteristic reminiscent of aggressive recharging water reacting with silicate rocks mainly containing albite. Other processes that can lead to $Na-HCO₃$ water type include cation exchange, anaerobic degradation of organic matter and proton exchange. However, as can be seen later, albite weathering is the main process. The $Na-HCO₃$ water type does not appear to be associated with any particular geology or area. The remaining hand dug wells and few boreholes are Na–Cl in character (Section C). Less than 10% of the groundwater show Na–Cl water type. Hand dug wells in the Aboso area and low pH and conductivity boreholes in Tamso area (please refer to Fig. [1\)](#page-1-0) show this character. This water type may, therefore, be due to the influence of the local rain and illustrates the importance of local recharge conditions in this Basin. The rivers and springs plot mainly in section D. This is mixed water type where there is neither dominant cation nor anion.

Fig. 4 Phase diagrams for water samples from the Ankobra Basin

5.4 Sources of major ions

Figure [5](#page-10-0) shows the relationship between Ca + Mg (meg 1^{-1}) vs. $SO_4 + HCO_3$ (meq 1^{-1}) for the groundwater. A 1:1 relationship would indicate gypsum, anhydrite, calcite and dolomite dissolution as the predominant processes controlling solution composition while groundwater falling below the 1:1 dissolution line signifies ion exchange, in which case $Ca^{2+} + Mg^{2+}$ are being depleted with respect to $SO_4^{2-} + HCO_3^-$ (McLean and Jankowski [2000\)](#page-33-0). Several samples fall on the 1:1 line. Gypsum and anhydrite have not been detected in the rocks within the Ankobra Basin, thus the 1:1 ratio probably implies the dissolution of calcite or dolomite or both. In spite of petrographic evidence that the rocks in the study area contain carbonates, the groundwater is largely undersaturated with respect to the common carbonates (calcite and dolomite) suggesting the carbonates dissolution is not enough to explain the 1:1 relationship. The $HCO₃/SiO₂$ ratio for about 80% of the water samples is relatively low, varying between 1 and 5, while the Mg^{2+} / $(Mg²⁺ + Ca²⁺)$ equivalent ratio for approximately 46% of the samples is greater than 0.5, suggesting silicate (mainly, ferromagnesian mineral) weathering is likely Hounslow ([1995\)](#page-32-0). Thus, silicate weathering may have contributed significantly to the

Fig. 5 Relationship between Ca + Mg versus $HCO₃ + SO₄$ of the groundwaters in the Ankobra Basin

concentrations of the Ca²⁺ and Mg²⁺. Approximately 50% of the water samples have $Na^+(Na^+ + Cl^-)$ ratio within the range 0.5 ± 0.1 or plot along or close to 1:1 line in $Na⁺$ vs. Cl[–] graph (Fig. 6) suggesting that either sea aerosols or halite dissolution is partially responsible for $Na⁺$ in the groundwater. However, halite is not known to be associated with the rocks in this area implying sea aerosols is partially the likely source of sodium in the groundwater. A few (8%) of the samples plot below and away from the 1:1 line suggesting reverse ion exchange also occurs but is not a major process responsible for chemical evolution of groundwater in this Basin. Approximately 32% of the water samples, however, have $Na^+/(Na^+ + Cl^-)$ ratios significantly greater than 0.5 (samples falling above the 1:1 line in Na vs. Cl graph indicating other sodium sources than sea spray; perhaps cation exchange or alumino-silicate (Na-plagioclase or albite) dissolution). Figure [7](#page-11-0) is a plot of

Fig. 6 Plot of Na versus Cl for representative groundwater samples from the Ankobra Basin

Fig. 7 Relationship between Ca + Mg – $(HCO₃ + SO₄)$ versus Na – Cl for the groundwaters of the Ankobra Basin

 $Ca^{2+} + Mg^{2+} - SO_4^{2-} - HCO_3^-$ (meq l⁻¹) vs. Na⁺-Cl⁻ (meq l⁻¹) for groundwater samples that show $Na^+/(Na^+ + Cl) > 0.5$. Waters undergoing ion exchange would plot along a line whose slope is –1 while waters plotting close to the zero value on the x-axis are not influenced by ion exchange (Jankowski et al. [1998\)](#page-32-0). A closer look at Fig. 7 reveals that the samples plot away from the zero value of the x-axis with a slope of -2 . This slope is twice as steep as the slope of -1 expected if cation exchange were the dominant process through which $Na⁺$ enters the groundwater system. Ion exchange can, therefore, not explain the observed excess of Na⁺ over Cl⁻. Therefore, if ion exchange is taking place, other processes like Na-plagioclase(albite) weathering may be masked.

5.5 Silicate weathering

The predominant mineralogy of the igneous rocks and the low-grade metamorphic rocks of the Ankobra Basin consists of plagioclase feldspars (mainly albite), hornblende and pyroxenes. The groundwater composition is influenced by the reaction between these mineral phases and the groundwater. The degree to which the mineral phases react with the groundwater depends on the availability of protons $(H⁺)$, the contact time and the surface area per unit volume of water (Hem [1985\)](#page-32-0). The forest vegetation and the humid climatic conditions of the Ankobra Basin provide avenues for the decay of leaves and other organic matter as well as root respiration that produce substantial amount of $CO₂$ in the soil zone and hence the H⁺ availability for circulation in the groundwater. Dissolution of sodium feldspars (albite (NaAl $Si₃O₈$) or intermediate plagioclase $(Na_{0.62}Ca_{0.38}Al_{1.38}Si_{2.62}O_8)$ is probably the source of $Na-HCO₃$ water type and produces the secondary mineral products kaolinite and/or gibbsite. Meteoric water dissolving $Na⁺$ from Na-bearing silicates results in Na– $HCO₃$ waters having Na⁺/Cl[–] ratios greater than one (Garrels and Mackenzie [1967\)](#page-32-0). The alteration of albite and intermediate plagioclase to kaolinite is given by Eqs. 2 and 3, respectively.

$$
2NaAlSi3O8 + 2CO2 + 11H2O = Al2Si2O5(OH)4 + 2Na+ + 2HCO3- + 4H4SiO4 (2)
$$

$$
1.45Na_{0.62}Ca_{0.38}Al_{1.38}Si_{2.62}O_8 + 2CO_3 + 6.6H_2O
$$

= Al_2Si_2O_5(OH)₄ + 0.9Na⁺ + 0.55Ca²⁺ + 2HCO₃⁻ + 1.8H_4SiO₄ (3)

Theoretically, the H_4SiO_4/Na^+ molar ratio is 2.0 for the reactions in both Eqs. 2 and 3. Similarly the H_4SiO_4/HCO_3^- ratio is 2 for albite Eq. 2 and 0.9 for intermediate plagioclase dissolution Eq. 3. Molar ratios of H₄SiO₄/HCO₃ and H₄SiO₄/Na⁺ for the groundwater are in the ranges 0.01–2.80 and 0.02–2.30 with median values of 0.40 and 0.80 respectively (Table [2\)](#page-7-0). These ratios are within the limits of the theoretical values, suggesting the plausibility of albite and intermediate plagioclase weathering to kaolinite and contributing Na^+ , HCO $_3^-$ and H₄SiO₄ to the groundwater and the possible source of excess of Na^+ over Cl⁻. The evolution of Na–HCO₃ water type in some of the wells can, therefore, be explained by dissolution of albite by $CO₂$ charged meteoric recharging waters. The stability diagram of albite and its possible weathering products gibbsite, kaolinite and Na-montmorillonite (Tardy [1971](#page-33-0)) for the groundwaters in the Ankobra Basin is shown in Fig. 8. All the groundwater samples plotted in the kaolinite field as would be expected for a system controlled by reactions in Eqs. 2 and 3. Similar to the dissolution of albite and intermediate plagioclase, the dissolution hornblende $(NaCa_2(Mg,Fe,A1)_5Si_8O_{22}(OH)_2)$ and other ferromagnesian silicates probably resulted in the Ca–Mg–Na–HCO₃ or Na–Ca–Mg– $HCO₃$ water types.

Fig. 8 The stability of albite and its possible weathering products gibbsite, kaolinite and Namontmorillonite with respect to the groundwaters in the Ankobra Basin (modified after Tardy [1971\)](#page-33-0)

5.6 Stable isotopes

The results of the oxygen-18 ($\delta^{18}O_{\gamma o}^{\gamma}$) and deuterium ($\delta^{2}H_{\gamma o}^{\gamma}$) analyses are presented in Table [3](#page-14-0). The variation in δ^{18} O was from -2.65% to -0.99% with mean and median values of -2.12% and -2.21% respectively. Deuterium values varied between -11.7% and -2.2% with mean and median values of -6.99% and -7.3% , respectively. The relationship between δ^2 H $\%$ and δ^{18} O $\%$ of the samples is shown in Fig. [9](#page-16-0). The groundwater samples were relatively tightly clustered along the Global Meteoric Water Line $(\delta^2 H = 8\delta^{18}O + 10$ (Craig [1961\)](#page-32-0)) suggesting an integrative, smooth and rapid recharge from meteoric origin. Consequently recharge to the aquifer system within the Ankobra Basin is mainly meteoric water with little or no isotopic modification. A few groundwater samples (e.g. the open hand-dug wells at Huni Valley and Aboso, with $(\delta^{18}O, \delta D)$ values of (–1.16, –2.2) and (–0.99, –2.2), respectively), showed evidence of some degree of isotopic enrichment by evaporative processes. Since evaporation may have taken place in these open wells under the humid climatic conditions of the Ankobra Basin, the deviation from the Global Meteoric Water Line has not been as much pronounced as may have occurred under less humid climatic conditions (IAEA [1983\)](#page-32-0). Two of the surface water samples with isotopic composition ($\delta^{18}O$, δD) of (-1.54% , 8%) and (-1.54% , 7.5%) respectively, plot relatively far below the Global Meteoric Water Line indicating a degree of isotopic enrichment as a result of surface evaporation. The samples were taken in the dry season when the rivers were at their lowest stage and flow was comparatively slow and sluggish and thus there was adequate time for the almost stagnant water to be subjected to intense evaporation. It is therefore not surprising that these two surface water bodies show isotopic enrichment typical of surface evaporation. Alternatively, the isotope enrichment could be reflecting the integration of the isotopic composition of the various tributaries that take their sources from a relatively drier part of Ghana than the Ankobra Basin.

5.7 Minor and trace ions

Contrary to expectation from a mining area, the analytical results did not indicate high levels of trace metal loading. Nonetheless, aluminium, arsenic, iron and manganese showed concentrations significantly above their detection levels in a considerable number of wells. The spatial distributions and the histograms of the concentrations of aluminium, arsenic, iron and manganese are shown in Figs. [10a](#page-17-0)–d, [11](#page-18-0)a–d, respectively.

5.7.1 Aluminium (Al^{3+})

The Al^{3+} ion concentration in the groundwater varies from <0.1 µg l^{-1} (below detection limit) to 2,510 μ g l⁻¹ with median value 0.10 μ g l⁻¹. Approximately 20% of the boreholes have Al^{3+} concentrations exceeding the WHO maximum acceptable limit of 200 μ g l⁻¹ for drinking water (WHO [1993](#page-33-0)) and thus pose the risk of significant aesthetic problems to groundwater usage. As expected, higher Al ion concentrations are associated with the boreholes with lower pH (3.89–4.2) water. The very low pH boreholes, nonetheless, constitute only 5% of the total number of boreholes. Dissolution of kaolinite or alunite, to provide extra acid neutralisation capacity to the groundwater, and appears to be the main source of Al^{3+} in the low

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Fig. 9 Isotopic composition of groundwaters and major rivers from the Ankobra Basin

pH waters. The typical kaolinite dissolution reaction in low pH water is given by Eq. 4

$$
Al_2Si_2O_5(OH)_4 + 6H^+ = 2Al^{3+} + 2H_2SiO_4 + H_2O
$$
 (4)

5.7.2 Arsenic (As)

The concentration of arsenic is generally low varying from <0.05 μ g l⁻¹ to 491 μ g l⁻¹ with a median value of 0.05 μ g l⁻¹. Relatively high As concentrations (>5 μ g l⁻¹) occur in the western and the northwestern part of the study area, where the Birimian rocks contains significant amount of pyrite and arsenopyrites (Fig. [2](#page-4-0)). However, only 5% of the wells and boreholes have arsenic concentrations slightly in excess of the WHO guideline limit of 10 μ g l⁻¹ (WHO [1993](#page-33-0)). Arsenic therefore does not potentially pose any significant physiological problem for groundwater usage in the Ankobra Basin. On the contrary, the surface waters (creeks) draining mining concessions have relatively high levels of arsenic concentrations (130–2,700 μ g l⁻¹) and high sulphate levels (190.0–1,840 mg l^{-1}). This indicates pyrite and arsenopyrite oxidation. Low concentrations of arsenic in the shallow groundwater (boreholes) regardless of the high presence of arsenopyrite in association with the gold ore, suggest a level of co-precipitation of arsenic with ferric oxyhydroxide or adsorption onto the ferric oxyhydroxide masses in the creeks before possible infiltration into the aquifer. Nevertheless, arsenopyrite oxidation can take place to produce a measurable arsenic concentration, even with only a small quantity of arsenopyrite. The reaction involving arsenopyrite oxidation is given in Eq. 5.

$$
4FeAsS + 13O2 + 6H2O = 4Fe2+ + 4AsO43- + 4SO42- + 12H+(aq)
$$
 (5)

If complete and congruent reactions were assumed, the highest measured arsenic concentration in the boreholes within the Ankobra Basin of 49 μ g l⁻¹ would require the oxidation of 10,749 μ g l⁻¹ of arsenopyrite. This would also produce corresponding concentrations of only 36 μ g l⁻¹ and 63 μ g l⁻¹ of Fe and SO₄⁻ respectively.

Fig. 10 (a–d) Spatial distribution of selected trace metals in the groundwaters of the Ankobra Basin

Thus, arsenopyrite oxidation appears to be the main source of arsenic concentration in the groundwater in spite of the generally low sulphate concentrations.

5.7.3 Iron

The minimum and maximum concentrations of iron in the groundwater are \leq 10 µg l⁻¹ and 12,100 µg l⁻¹ respectively with a mean and median values of 1,300 μ g l⁻¹ and 150 μ g l⁻¹ respectively. The WHO guideline maximum for iron in drinking water is 300 μ g l⁻¹ but an upper limit of 1,000 μ g l⁻¹ should suffice for most purposes (WHO [1993\)](#page-33-0). Approximately 40% of boreholes in the Ankobra Basin have

Fig. 11 (a–d) Histogram of the distribution of selected trace metals in the groundwaters of the Ankobra Basin

 Fe^{2+} greater than 1,000 µg l⁻¹. This poses major aesthetic quality problems to groundwater usage for domestic purposes in the Basin as it may lead to consumer complaints and indeed a significant number of boreholes has already been abandoned due to the iron problem. It has been mentioned earlier that iron minerals, particularly pyrites and arsenopyrite are common in the rocks that have underlain the Ankobra Basin. Oxidation and dissolution of pyrites and arsenopyrite should naturally be a major source of iron and sulphate (SO_4^{2-}) in the groundwaters. However, SO_4^{2-} concentration in the boreholes is generally low, 0.002–0.57 mmol 1^{-1} with a median value of 0.06 mmol 1^{-1} and only a few samples satisfy the iron to sulphate (Fe^{2+}/SO_4^{2-}) molar ratios of 0.5 and 1 for the stoichiometry of pyrite and arsenopyrite oxidation respectively. Median (Fe^{2+}/SO_4^{2-}) (Fe^{2+}/SO_4^{2-}) (Fe^{2+}/SO_4^{2-}) is 0.05 (Table 2). Additionally, boreholes with high iron concentration also have $(Fe^{2+}/SO_4^{2-} > 1)$ suggesting that unless SO_4^{2-} reduction or gypsum precipitation had taken place, which has not been evident, pyrite and/or arsenopyrite oxidation cannot exclusively explain the high iron concentration in some of the boreholes. The calculated saturation indices of the iron species indicate that the waters are highly supersaturated with respect to goethite, hematite and magnetite. The supersaturation of the groundwater with respect to these iron-bearing minerals suggests that the groundwater has reacted with these minerals for long enough time to reach equilibrium and should be thermodynamically incapable of dissolving more of these iron species unless

equilibrium conditions are changed. In other words, the groundwater should be precipitating these iron minerals if it is oxygenated as in the case of phreatic aquifers and therefore, reducing the iron concentration in the boreholes. However, this does not seems to be the case. As indicated by White and Yee [\(1985](#page-33-0)), Fe^{3+} is reduced to $Fe²⁺$ at the mineral surface. Goethite, hematite and magnetite are the main iron species present in the rock matrix within the study area. Iron may, therefore, have been derived from the reductive dissolution of hematite and goethite and to a limited extent magnetite in the presence of organic matter. The reduction is likely microbially mediated. Hematite dissolution in the presence of protons (acid) is extremely slow. However, in the presence of organic ligands the reaction can be fast (Appelo and Postma [1999\)](#page-32-0). The presence of organic matter in the soil zone of the study area is indicated by the brown colouration of rivers and streams throughout the year. An additional source of iron could be the leaching from ferromagnesian silicates, such as hornblende and pyroxenes.

5.7.4 Manganese

Manganese occurs in the rocks mainly as manganese and manganiferrous oxides, particularly in areas underlain by Birimian rocks (Kesse [1985](#page-32-0)). Reaction between these oxides and the mildly acidic groundwater results in the production of manganous ions (Mn²⁺). Mn²⁺ concentration varies from 1.0 µg l⁻¹ to 1,300 µg l⁻¹ and is greater than 500 μ g l⁻¹ (WHO permissible limit for potable water) in approximately 25% of the boreholes and wells within the Ankobra Basin. Similar to iron, the manganese concentration in the groundwater also poses major quality problems in the Ankobra Basin.

5.7.5 Mercury

The concentration of mercury (Hg) in the groundwaters varies from <0.05 µg l⁻¹to 36.8 µg l⁻¹. The maximum acceptable limit for mercury in drinking water is 1.0 μ g l⁻¹. The occurrence of mercury in water is mainly due to leaching from rocks and sometimes from release into the water in the form of wastewater effluents from industrial plants that use mercury (Holden [1972\)](#page-32-0). Mercury has not been detected in any of the rocks within the Ankobra Basin. Neither are there industries in the area, apart from mining, that can release mercury in significant quantities to the environment. Mercury amalgamation used to be the main method for the processing of gold ores in the Ankobra Basin. Currently, the major goldmining companies use the more efficient cyanide leaching method. However, because mercury amalgamation requires little capital investment in equipment, it is still popular and widely used by small-scale miners and the galamsey (illegal gold miners) operators in the Ankobra Basin. The occurrence of mercury in the groundwater bodies is, therefore, suspected to be largely due to contamination from surface sources, perhaps resulting from indiscriminate use of mercury for gold processing. The concentration of mercury exceeds the WHO permissible limit for drinking water in approximately 10% of the boreholes in the Ankobra Basin. Because mercury toxicity can lead to kidney damage, brain and nervous system disorder (WHO 1980; Carlos et al. [1997\)](#page-32-0) therefore, it potentially poses the greatest physiological problem for using the groundwater for drinking purposes in the Ankobra Basin.

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5.8 Groundwater acidity

Acidity in groundwater could be due to natural biogeochemical or anthropogenic processes. Natural acidification is obvious in areas with weathering-resistant soils and rocks, where the climate is humid and the dominating water movement as well as the transport of chemical components is downward, resulting in run off of base cations as in the Ankobra Basin (Knutsson [1994](#page-32-0)). Figure 12 illustrates the relationship between total hardness and alkalinity of groundwater in the Ankobra Basin. The non-marine total hardness-alkalinity plot is usually used to evaluate the status of ground and surface waters (Von Brömssen [1989](#page-33-0); Caritat 1995). The total hardness values are assumed to be non-marine because chlorine which is conservative and originates exclusively from marine source is very low in concentration and also there is no petrographic evidence to suggest the existence of marine carbonate in most part of the Ankobra Basin, particularly areas where relatively low pH values were obtained. Figure 12 shows that most of the groundwater samples plot along the 1:1 line suggesting that acidification is principally due to natural biogeochemical processes $(CO₂$ generation in the soil zone through root respiration and decay of organic matter). The presence of organic matter in the soil zone is supported by the brown colouration of surface waters through out the year. The few samples that plot along or above the 2:1 line probably resulted from sulphide (pyrite or arsenopyrite) oxidation enhanced by mining.

Groundwater acidification (Aci.) can also be defined as loss of alkalinity and computed using Eq. 6.

$$
Aci. = 0.93 (Ca^* + Mg^*) - 14 - Alk + Al
$$
 (6)

where all concentrations are expressed in meq l^{-1} (Henriksen and Kirkhusmo [1986](#page-32-0); Caritat et al. [1998](#page-32-0)). Similarly, the acid neutralising capacity of the groundwater can be computed using Eq. 7.

$$
ANC = (Ca2+ + Mg2+ + Na+ + K+) - (NO3- + SO42- + Cl-)
$$
 (7)

where all concentrations are expressed in meq I^{-1} (Stumm [1992](#page-33-0); Caritat [1998\)](#page-32-0)

The relationships between ANC, NANC (net acid neutralising capacity) and Aci are presented in Fig. [13.](#page-21-0) The groundwaters are low in acid neutralising capacity with

Fig. 12 Relationship between total hardness and alkalinity

Fig. 13 Relationship between ANC, NANC and Aci

ANC varying from -1.7 meq 1^{-1} to 4.26 meq 1^{-1} with a mean value of 1.15 meq 1^{-1} confirming buffering agents other than carbonates. Nonetheless, the Aci of the groundwaters is also very low varying between -15.1 meq 1^{-1} and -10.7 meq 1^{-1} with a mean value of -14.1 meq 1^{-1} . It is obvious from Fig. 13 that though the ANC is low it remains positive for most samples while Aci remains negative. The net acid neutralising capacity is thus positive for all the groundwater samples. This gives an indication that, notwithstanding the moderately low pH, the groundwaters still have the potential to neutralise acids probably due to the presence of alumino-silicates and some mafic rocks.

6 Summary and conclusions

Analysis of the hydrochemical survey data from the Ankobra Basin has revealed that the groundwater is generally mildly acidic (pH 4.5–6.9) with a few of the boreholes showing strong acidic character ($pH < 4.5$). Major cations are generally low and in about 60% of the wells no clear-cut dominant cation emerged. Bicarbonate is by far the most dominant anion and in a large number of wells forms approximately 40% of the TDS.

Three major water types have been delineated using the phase diagrams. These are Ca–Mg–HCO₃, Na–HCO₃ and Na–Cl waters. The Ca-Mg-HCO₃ water type represents over 60% of the groundwater in the Ankobra Basin and it is not associated with any particular rock type. The Na–Cl water-type comprises less than 10% of the groundwater and is mainly associated with boreholes with very low pH. The groundwater is generally undersaturated with respect to major carbonate species namely calcite, dolomite and ankerite. Dissolution of alumino-silicate minerals particularly plagioclase, amphiboles and pyroxenes by mildly acidic groundwater is responsible for the major ions in the groundwater.

The trace metal loading of the groundwater is not high. Only aluminium, arsenic, manganese, iron and mercury show significant concentrations in the boreholes.

Approximately 20% of the boreholes have Al^{3+} concentration exceeding the WHO maximum acceptable limit of 0.2 mg I^{-1} for drinking water. The elevated concentration of aluminium in the groundwater reflects the acidic nature of the groundwater and aluminium probably entered the groundwater as result of dissolution of kaolinite and alunite to provide extra acid neutralisation. Approximately 5% of the boreholes have arsenic concentrations slightly in excess of the WHO [\(1993](#page-33-0)) guideline limit of 10 μ g l⁻¹. Relatively high arsenic concentrations occur in the western and the north-western part of the study area where the Birimian rocks contain significant amounts of pyrite and arsenopyrites. Nearly 40% of boreholes in the Ankobra Basin have Fe^{2+} greater than 1.0 mg l⁻¹. Unless iron is removed through the use of aerators or iron removal plants, it poses significant water quality problems for domestic purposes in the Ankobra Basin. Sources of iron in the groundwater include oxidation of pyrite and arsenopyrite, the reductive dissolution of hematite and goethite and, to a limited extent, magnetite in the presence of organic matter and leaching from ferromagnesian silicates, such as hornblende and pyroxenes. All these iron minerals are common in the Ankobra Basin. Manganese occurs in greater concentrations than 0.5 mg I^{-1} (WHO permissible limit for potable water) in approximately 25% of the boreholes within the Ankobra Basin and thus also poses the risk of major aesthetic quality problems.

Mercury potentially poses the greatest physiological problem for using the groundwater for drinking purposes in the Ankobra Basin. Its concentration exceeded the WHO [\(1993](#page-33-0)) permissible limit for drinking water in 10% of the boreholes. It originates from anthropogenic sources since it has not been detected in any of the rocks in the Ankobra Basin. Mercury amalgamation, which is widely used by small-scale miners for gold extraction is suspected to be the source.

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Appendix 1 continued

Computation of electrical balance and charge balance error carried out using Phreeqc for Windows (Parkhurst and Appelo 1999) Computation of electrical balance and charge balance error carried out using Phreeqc for Windows (Parkhurst and Appelo [1999\)](#page-33-0)

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Appendix 2 continued

Appendix 3 Saturation indices for carbonate iron bearing minerals, gypsum, anhydrite, amorphous silicate and quartz Appendix 3 Saturation indices for carbonate, iron bearing minerals, gypsum, anhydrite, amorphous silicate and quartz

75 Tarkwa Hospital HDW2 26.7 5.7 –2.9 –5.6 –3.6 7.3 –2.4 –3.8 –5.1 1.4 76 Tarkwa (W. Univ.) HDW 26.8 5.8 –3.1 –5.5 –3.4 7.1 –0.5 0.7 –0.6 1.2 77 Aboso Spring 28.2 5.2 –0.8 –0.6 –2.3 7.1 –3.0 0.6 –0.6 1.2 9.27 Natural Spring 1 26.1 1 26.1 1 26.1 1 26.1 26.2 – 1 26.2 – 1 26.2 – 1 26.2 – 1 26.2 – 1 26.2 – 1 26.2 – 1 80 Th 20 20 21.0 – 20 21.0 – 20 21.0 – 20 21.0 – 20 21.0 – 20 21.0 – 20 21.0 – 20 21.0 – 20 21.0 – 20 21.0 – 2 81 Spring 27.8 – 5.5 – 5.3 – 5.3 – 5.3 – 5.5 – 5.5 – 1.2 – 1.2 – 1.3 – 1.3 – 1.3 – 4.3 – 4.3 – 4.3 – 4.3 – 4.3 – 5.5 – 5.5 – 1.2 – 1.2 – 1.2 – 1.2 – 1.2 – 1.2 – 1.2 – 1.2 – 1.2 – 1.2 – 1.2 – 1.2 – 1.2 – 1.2 – 1.2 – 1.2 – 1 82 Teberebe Stream 1 27.1 –1.7 –1.7 –1.7 –1.7 –4.7 –4.7 –4.7 –4.2 –1.6 –6.6 –5.3 – 1.2 – 1.2 – 1.2 – 1.4.7 – 1 83 Teberebe Tebeream 2 3.5 – 3.4 – 3.4 – 3.5 – 4.5 – 4.5 – 4.5 – 4.5 – 4.5 – 4.5 – 4.5 – 4.5 – 4.5 – 4.5 – 4.5 84 Pestea River Ankobra 26.8 6.5 –3.4 –6.6 –3.8 4.7 –2.0 0.9 –0.3 –1.1 85 Wassa Nkran River Bonsa 24.7 –2.5 –3.3 5.1 –2.4 0.3 –1.0 –0.8

 -8.2 -2.5
 -1.1 -0.8

 $\begin{array}{c} \circ \\ \circ \\ \circ \end{array}$ -0.9

 3374

 -5.5
 -5.5

 2.3

 -1.0 -1.7

 -4.6

 -8.8 -11.0 -6.0

Spring 1
Spring 2

Tarkwa Tarkwa

Aboso

Spring HDW

Tarkwa (W. Univ.)

Spring

Tarkwa (Bobobo)

Teberebe Teberebe

 -4.7

 -0.6 -0.6 -0.9 -1.2 -0.4 -0.3 -1.0 -0.7

 0.7

 -3.4 -3.3 -4.3 -3.3

 -5.5
-0.6 -10.2

> -0.8 -4.5

 -3.1 -5.1 0.2

 89996

 4.040
 4.040

 3471

 -6.6 -6.7

 -3.4 -3.6

 $\begin{array}{c} 0.7 \\ 0.7 \\ 0.8 \\ 0.9 \end{array}$

26.8
26.8
24.7 26.4

> River Ankobra River Bonsa **Xiver Manse**

> > Wassa Nkran

Pestea

Stream₂ Stream₁

 -3.7

 $\ddot{4}$ $-3.\overline{3}$

 -2.9

 -11.2

 -5.0

6.6

 -51

Si-Cal, saturation index for calcite; Si-Dol, saturation index for dolomite; Si-Gyp, saturation index for gypsum; Si-Goe, saturation index for goethite; Si-Sid, saturation index for siderite, Si-Quartz, saturation index for quartz; Si-SiO₂ (a), saturation index for amorphous silica; Si-Fe(OH)₃, saturation index for Si-Cal, saturation index for calcite; Si-Dol, saturation index for dolomite; Si-Gyp, saturation index for gypsum; Si-Goe, saturation index for goethite; Si-Sid, saturation index for siderite, Si-Quartz, saturation index for quartz; Si-SiO2 (a), saturation index for amorphous silica; Si-Fe(OH)3, saturation index for 86 Beposo River Manse 26.4 6.0 – 3.7 – 3.7 – 3.7 – 3.7 pm – 3.7 pm – 3.7 pm – 3.7 – 3.7 pm – 3.7 – 3.7 pm amorphous ferric hydroxide amorphous ferric hydroxide Beposo

 $Si_Fe(OH)_3$

 $iO₂$ (a)

 -1.8

 $\ddot{0}$

 1.9

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