HYDROCHEMICAL CHARACTERIZATION OF GROUNDWATER IN THE AKYEM AREA, GHANA

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The Akyem area is a small farming community located in southeastern Ghana. Groundwater samples from wells in the area were analyzed for concentrations of the major ions, silica, electrical conductivity and pH. The objective was to determine the main controls on the hydrochemistry of groundwater. Mass balance modeling was used together with multivariate R-mode hierarchical cluster analysis to determine the significant sources of variation in the hydrochemistry. Two water types exist in this area. The first is influenced most by the weathering of silicate minerals from the underlying geology, and is thus rich in silica, sodium, calcium, bicarbonate, and magnesium ions. The second is water that has been influenced by the effects of fertilizers and other anthropogenic activities in the area. Mineral speciation and silicate mineral stability diagrams suggest that montmorillonite, probably derived from the incongruent dissolution of feldspars and micas, is the most stable silicate phase in the groundwaters. The apparent incongruent weathering of silicate minerals in the groundwater system has led to the enrichment of sodium, calcium, magnesium and bicarbonate ions as well as silica, leading to the supersaturation of calcite, aragonite, dolomite and quartz. Stability in the montmorillonite field suggests restricted flow conditions and a long groundwater residence time, leading to greater exposure of the rock to weathering. Cation exchange processes appear to play minor roles in the hydrochemistry of groundwater.

INTRODUCTION

In Ghana, sustainable national economic development is tied to the proper development and management of groundwater resources in conjunction with surface water resources for use in households and irrigation as well as in industry. The proper development of groundwater resources for all uses begins with an appreciation of its quality and the various factors that control quality. Groundwater has been known to be largely safe from most surface polluting activities and has been accordingly judged better suited for drinking purposes compared to most surface water sources. The hydrochemistry of groundwater results from the combined effect of the composition of the water that enters the groundwater reservoir and reactions with minerals in the aquifers. Apart from these natural processes acting as the controlling processes in groundwater hydrochemistry, in recent times the effects of pollution, such as nitrate from fertilizers and acid rain, also influence groundwater hydrochemistry. Due to the long residence time of groundwater in the subsurface environment, the effects of pollution may first become apparent tens to hundreds of years after the pollution occurred (Appelo and Postma, 1996). The combined effects of natural and anthropogenic processes sometimes render groundwater resources unsuitable for many uses.

In the literature many different methodologies have been applied to characterize the sources of variation in surface and groundwater chemistry. Various investigators (e.g. Bowser and Jones, 2002; Garrels and Mackenzie, 1967; Holland, 1978; Sillen, 1967) have studied the relationship between groundwater geochemistry and weathering of host rock minerals. Garrels and Mackenzie (1967) calculated mass balances derived from spring water data in the Sierra Nevada, California, based on the extensive analysis of Feth et al. (1964). This work stimulated research on the contribution of silicate weathering to water composition, especially using mass balance methods. Drever (1997); Plummer et al. (1991) and Appelo and Postma (1996) have recently commented on the work of Garrels and Mackenzie (1967) and made some interpretive modifications. This mass balance approach has been modified and used in many instances to quantify reactions controlling water chemistry along groundwater flowpaths (Busby et al., 1991; Hidalgo and Cruz-Sanjulian, 2001) and quantify mixing of end-member components in a flow system (Kuells et al., 2000). Escolero et al. (2005) applied the mass balance approach to a set of hydrochemical data to describe the processes that modify groundwater composition along flowpaths and the effects of seawater on groundwater chemistry in Yucatán, Mexico. They used the PHREEQC package (Appelo and Postma, 1996) to calculate the saturation indices of minerals that were suspected to be responsible for the chemical composition of the groundwater.

PHREEQC (Parkhurst and Appelo, 1999) modeling and the thermodynamic database WATEQ4F (Ball and Nordstrom, 1991), were used by von der Heyden and New (2004) to perform speciation and saturation index computations using available geochemical data to determine the sources of groundwater pollution in the Zambian Copperbelt.

In addition to the mass balance methods, multivariate statistical tools have also been widely used to help determine the sources of the chemical components of water systems. Usually, statistical associations are established among chemical parameters to help make some useful interpretive analysis. A statistical association does not establish any cause-and-effect relationships but it frequently presents data in a way that such relationships can be deduced (Drever, 1988). Multivariate statistical methods have gained global acceptance as effective tools in interpreting hydrochemical relationships. Excellent examples of the application of multivariate statistical techniques to solve hydrochemical problems are contained in Dalton and Upchurch (1978),

Ashley and Lloyd (1978), Usunoff and Guzman-Guzman (1989), Briz-Kishore and Murali (1992), Grande et al. (1996), Huizar et al. (1998), Ceron et al. (1999), Suk and Lee (1999) and Sanchez-Martos et al. (2001). Multivariate techniques have been used to resolve hydrological factors such as aquifer boundaries, groundwater flow paths and hydrochemical parameters (e.g. Seyhan et al., 1985; Razack and Dazy, 1990; Join et al., 1997; Liedholz and Schameister 1998; Wang et al., 2001; Locsey and Cox 2003), to identify geochemical controls on the composition of water (Adams et al., 2001; Alberto et al., 2001) and to separate anomalies such as anthropogenic impacts from background concentrations (Hernandez et al., 1991; Birke and Rauch 1993; Helena et al., 2000; Pereira et al., 2003). Multivariate statistical methods can be used in much the same way as the trilinear diagram, but with the advantage of being able to include additional ions and non-chemical data (van Tonder and Hodgson, 1986). If the variables measured for each groundwater sample include those that can be expected to differentiate groundwater by source, then multivariate data analysis can be used to formulate and test hypotheses of possible segregation among groundwater sources or mixing between aquifers (Steinhorst and Williams, 1985).

In this research, mass balance methods have been used with multivariate statistical tools to explain the possible controls on the groundwater hydrochemistry at the Akyem mine area, Ghana. Silicate mineral stability diagrams are used to indicate the phase transitions possible in the groundwater system.

GEOGRAPHY AND HYDROGEOLOGY OF THE AKYEM AREA

The Akyem area (Figure 1) is located within an undulating lowland at altitudes approximately 200 m above sea level. It forms steep-sided ridges, which rise 100 m to 150 m above the surrounding terrain. The climate is tropical – humid. Rainfall occurs in a double maxima pattern from May to July peaking in June, and from September to October. The average annual rainfall in the area is 1389 mm and humidity is 47 to 80 percent. The daily temperature range is 20°C to 30°C and varies little throughout the year (Dickson and Benneh (1988). From November to April, the dust-laden Harmattan wind blows from the Sahara desert, resulting in relatively dry weather. The project location is predominantly rural and surrounded by seven small communities and settlements within 5 km of the site. The main occupation of the people is farming. Crops cultivated include palm-nut, cocoa and citrus fruits.

The project area is underlain mainly by the paleoproterozoic basement rocks of the Birimian Supergroup (2.2-2.1 Ga). The Birimian in southwestern Ghana comprises northeast trending belts principally of volcanic and volcaniclastic material, of tholeiitic and acidic composition. These are separated by broad sedimentary basins dominated by turbidites. The granitic to dioritic Dixcove suite granitoids intrude and are comagmatic with volcanics of the volcanic belts; while the biotitic Cape Coast type granites, believed to be a little younger, are more batholithic and principally associated with the sediments.

Unconformably overlying the Birimian volcanic belts are the Tarkwaian sedimentary sequences. These sequences appear to have accumulated in restricted basins in the volcanic belts of the Birimian towards the end of the depositional cycle. The Tarkwaian sedimentary sequence comprises conglomerates, sandstones, and phyllites. The local geological setting consists of underlying thinly foliated tuffaceous phyllitic rocks, greywacke and metavolcanics intruded by quartz veins. In places, these rocks are highly sheared with some shear zones swinging from NE-SW direction to ENE-WSW. The sheared metavolcanics wrap around more competent ones. The
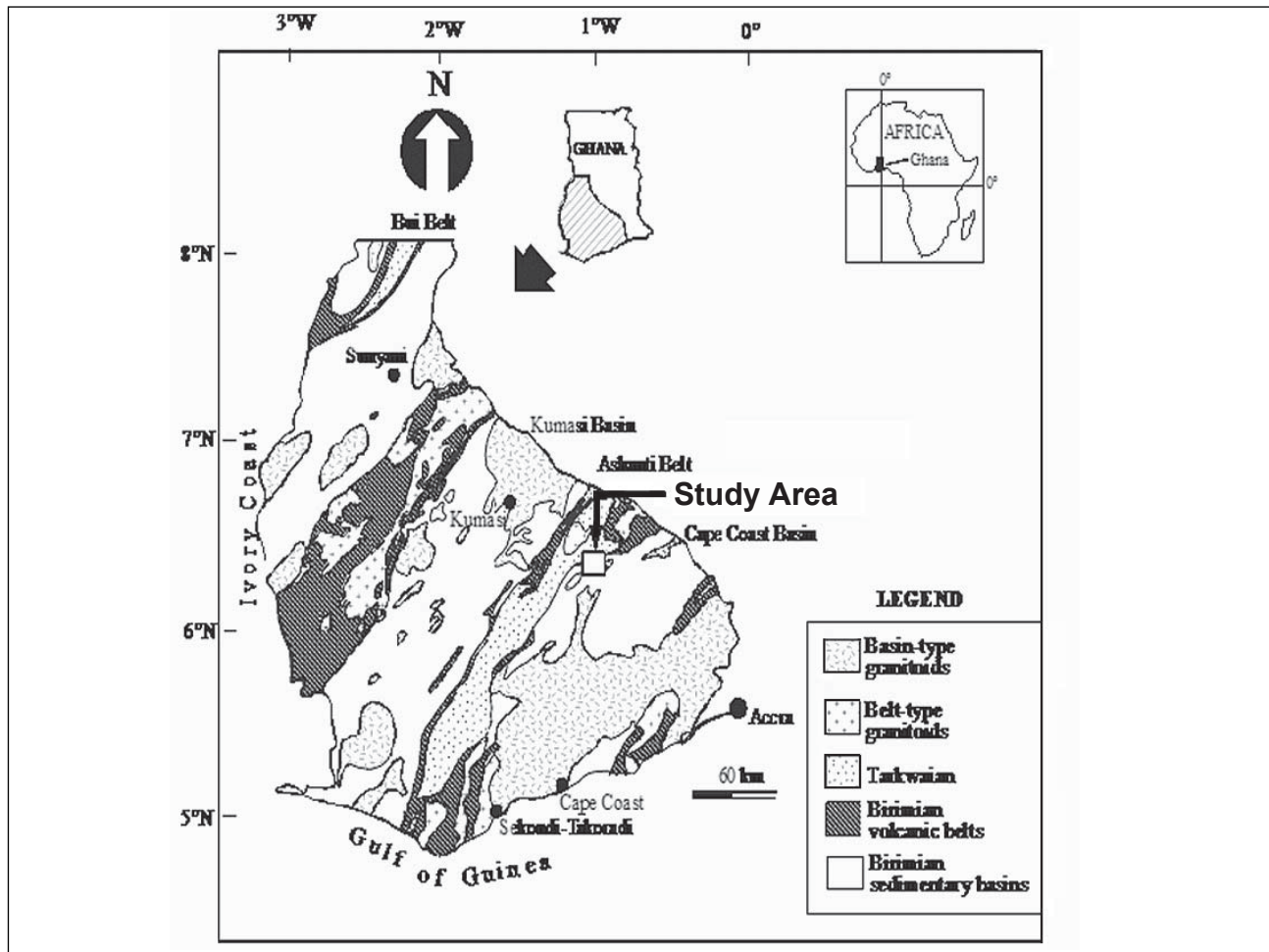
Figure 1. Map of Ghana showing the study area.

general local structural grain follows a NE-SW trend. However, joints which trend slightly discordant to the general structure are common and some are filled with quartz veins. These joints show cleavages that might have developed from a major fold and their trend appears to be sub-parallel to the foliation. Major lineaments in the area follow a NW-SE trend and these lineaments follow fracture traces.

METHODOLOGY

Groundwater samples from wells and boreholes drilled in the area were analyzed to determine the concentration of the major cations and anions. pH and electrical conductivity were measured in situ. Concentrations of the major cations (Na^+, Mg^{2+}, K^+, Ca^{2+}), anions (HCO_3^-, SO_4^{2-}, Cl^-, NO_3^-, F^-) and silica were determined in the laboratory after the samples had been treated with acid in the field to discourage bacterial action and oxidation processes. Table 1 shows the statistical summaries of the data on each of the chemical parameters measured.

Preliminary analysis on the data sought to determine the accuracy of the field and laboratory techniques. The electroneutrality (EN) ratio (Appelo and Postma, 1996) was determined using Equation 1.

$$E.N = \frac{\left(\sum cations + \sum anions\right)}{\left(\sum cations - \sum anions\right)} x100 \tag{1}$$

Table 1. Statistical summaries of the chemical data used for this research.

	Ca	Mg	Na	K	Cl	NO3	SO4	Si	Fluoride	HCO3	Fe (total)	pH (field)	Cond (field)
Mean	31.00	10.79	21.90	2.31	11.78	0.81	7.76	21.06	0.39	162.60	0.49	6.39	31.51
Max.	59.00	31.70	33.00	4.20	31.50	4.73	72.70	39.70	0.80	286.70	3.80	7.00	61.40
Min.	0.10	0.05	9.70	0.70	3.00	0.00	0.00	14.80	0.10	58.00	0.02	5.90	12.50
Std.dev	17.89	8.06	5.90	1.18	8.85	1.48	20.41	6.72	0.22	70.52	1.02	0.33	14.68

The raw data for each variable was then tested for normal distribution to fulfill the requirement for multivariate statistical modeling and facilitate detailed hydrochemical characterization. When it was seen that data for all parameters failed to fit a normal distribution, a log transformation was applied. The results of the transforms were in turn standardized to *z*-scores according to Equation 2. Data standardization is preferred in cluster analysis since it gives equal weight to each variable in the multivariate analysis. Otherwise, the Euclidean distances calculated will be influenced most strongly by the variable that has the greatest magnitude (Güler et al., 2002).

$$z = \frac{x - \mu}{s} \tag{2}$$

where x and μ respectively represent the value and mean value of each parameter, s is the standard deviation, and z is the standardized value.

The Statistical Package for Social Sciences, SPSS (SPSS Inc. 2006) was used for all the statistical analysis. The standardized z-scores were in turn used for R-mode hierarchical cluster analysis (HCA) to classify the data into groups based on similarity or dissimilarity. In the HCA, squared Euclidean distance was used as a measure of similarity/dissimilarity among the parameters in the field. The squared Euclidean distance between any two locations x and y is computed using Equation 3.

$$d_{xy} = \left[\sum_{j=1}^{p} (x_j - y_j)^2 \right] \tag{3}$$

where j represents the parameter under consideration.

The Ward's agglomeration technique was chosen as a linkage method between clusters. Squared Euclidean distance as a clustering algorithm, when combined with the Ward's linkage scheme has been determined to yield optimal results in HCA (Kuels et al., 2000; Güler and Thyne, 2004; Helsrup et al., 2007; Yidana et al., 2008a,b).

Mineral speciation was done using the PHREEQC-2 (Parkhurst and Appelo, 1999) package. Mineral saturation indices (SI) were computed from Equation 4.

$$SI = \log \frac{IAP}{K_c} \tag{4}$$

where IAP is the ion activity product and K_c is the equilibrium constant for the mineral. A mineral with SI less than 0 is said to be undersaturated in the system. When SI is 0, the mineral is saturated and the K_c just equals the IAP. With SI's higher than 0, the system is supersaturated with respect to the minerals in question.

The result of the speciation was used to construct mineral stability diagrams with thermodynamic boundary conditions taken from Tardy (1971) to explain the phase transitions occurring in the area. Stability diagrams were drawn for $CaO-H_2O-Al_2O_3-SiO_2$, $Na_2O-H_2O-Al_2O_3-SiO_2$, and $MgO-H_2O-Al_2O_3-SiO_2$ systems in the aquifers.

RESULTS AND DISCUSSIONS

The result of the HCA is illustrated by the dendrogram in Figure 2. Two main groups are discernible from the dendrogram. The first group contains Na^+, SiO_2, Ca^{2+}, Mg^{2+}, Cl^- and HCO_3^- in close association. This group represents the effect of water – rock interaction, leading to silicate mineral weathering. The second group comprises K^+, SO_4^{2-}, F^-, Fe (total) and NO_3^-, and represents the effects of anthropogenic activities including sulfate and nitrate fertilizers from agricultural activities in the area

The speciation calculations suggest that groundwater in the Akyem area is almost everywhere supersaturated with calcite, dolomite, and quartz. Table 2 summarizes the SI values of these minerals at some of the wells from which samples were taken for this analysis.

Figures 3, 4, and 5 show the phase diagrams for the $CaO-H_2O-Al_2O_3-SiO_2$, $Na_2O-H_2O-Al_2O_3-SiO_2$, and $MgO-H_2O-Al_2O_3-SiO_2$ systems respectively. Thermodynamic boundary data were taken from Tardy (1971).

All three phase diagrams indicate stability in the montmorillonite field. Montmorillonite is the solid state product of the incongruent weathering of silicate minerals. Freeze and Cherry (1979) suggest that when montmorillonite is the dominant stable phase in the weathering of silicate minerals, groundwater flow is restricted, probably due to reduced interconnection between the fractures that control the hydrogeological conditions of the aquifers in the area. Restricted flow conditions imply longer residence times of groundwater in the system, leading to higher degree of rock-water interactions. Otherwise, gibbsite would have been a preferred phase in an unrestricted flow situation where there is limited interaction time between the rock and the liquid phase. The stability diagrams indicate that silicate mineral weathering might be one of the significant sources of variation in the hydrochemistry.

A scatter plot of the $(Mg^{2+}+Ca^{2+})-HCO_3^--SO_4^{2-}$ against $(Na^++K^+)-Cl^-$ is shown in Figure 6. $(Mg^{2+}+Ca^{2+})-HCO_3^--SO_4^{2-}$ is the sum of calcium and magnesium in the system that can not be
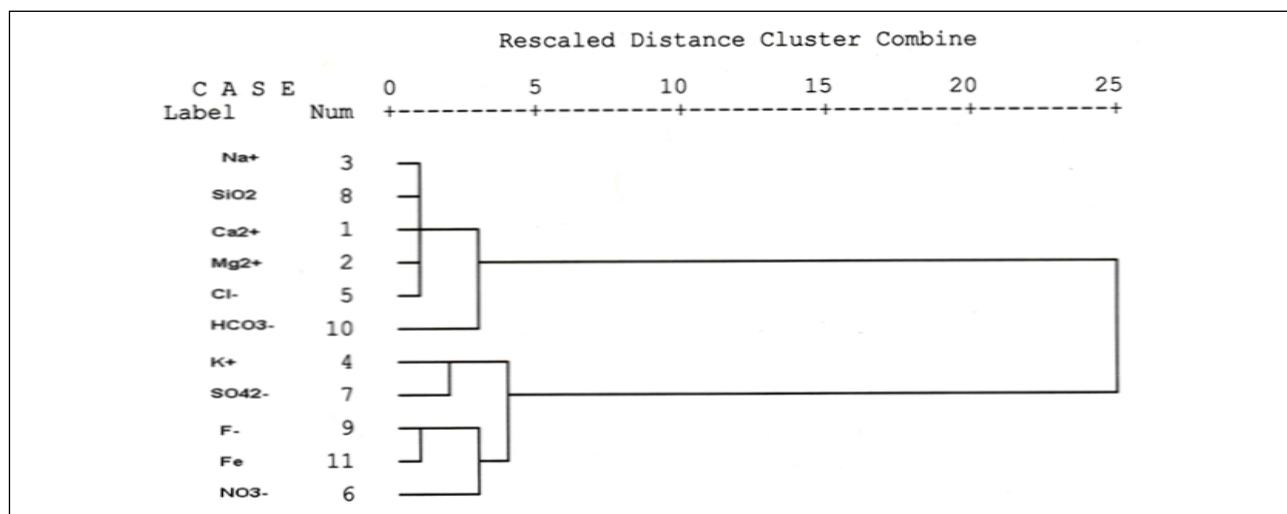

Figure 2. A dendrogram showing the different facies or water groups in the Akyem area.

Table 2. Saturation indices of selected minerals in some locations in the Akyem area.

Location	Calcite	Dolomite	Gypsum	Quartz
MW 7	0.84	1.31	-	2.27
MW 8	0.30	0.25	-2.27	2.14
AdsDBH 2	0.33	0.48	-0.20	2.33
NtDBH 1	1.54	2.77	-0.03	2.40
MnDBR 2	1.64	3.19	-0.50	2.35
YYDW	1.39	2.32	-0.35	2.29
GRCDBH	0.07	0.0	-	2.13
NADBH	1.01	1.98	-	2.19
HWKDBH 2	2.33	3.92	-1.23	2.29
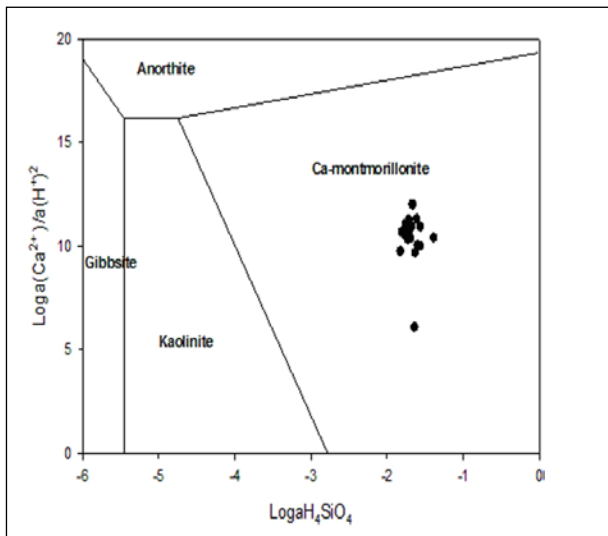
Figure 3. Stability diagram for the Ca-montmorillonite field.
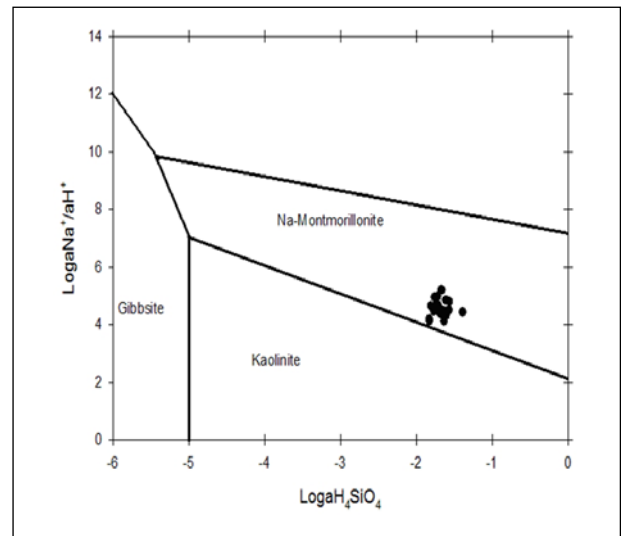
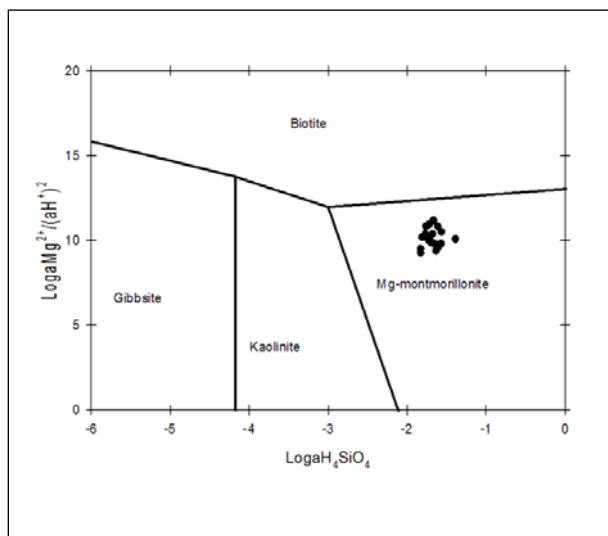Figure 4. Stability diagram for the Na-montmorillonite field.

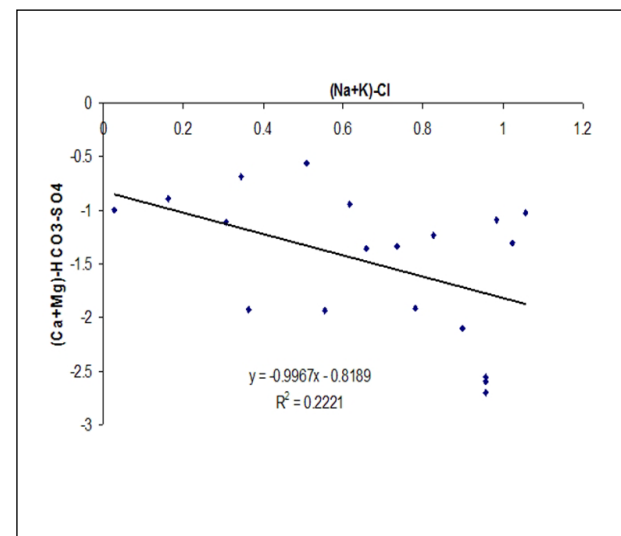Figure 5. Stability diagram for the Mg-montmorillonite field.

Figure 6. Scatter diagram showing the relationship between (Na+K)-Cl against (Ca+Mg)-HCO_3-SO_4.

accounted for by the dissolution of carbonate minerals and gypsum, while $(Na^+ + K^+) - Cl^-$ represents the total sodium and potassium in excess of the contribution of chloride salts of these cations in the system. If cation exchange plays a role in the hydrochemistry, a plot of these ions would result in a straight line of slope approximately -1 (Jalali, 2006). Otherwise all points would plot close to the origin of the axes. In Figure 6, a straight line graph of slope approximately -1 is generated for the Akyem area, which indicates that cation exchange processes may be active in the area. Drever (1988) and Appelo and Postma (1996) suggest that clay minerals act as suitable surfaces for cation exchange activity in surface and groundwater systems. The mineral speciation calculations and the corresponding mineral stability diagrams indicate that montmorillonite is the dominant silicate mineral phase which has a strong implication for cation exchange activity.

The cation contribution to groundwater by silicate weathering is also estimated by the (Na+K)/ total cation index, TC (Sarin et al., 1989; Awad and Hussein 2006). Figure 7, a scatter diagram of TC against (Na+K) shows that half of the samples fall above the (Na+K) = 0.33 TC line, the remaining points lie between the (Na+K) = 0.33 TC line and the Na+K = 0.5 TC line. The distribution of the scatter points in Figure 7 suggests that silicate mineral weathering accounts for a significant fraction of the cations in the groundwater from the Akyem area. The scatter line for $(Mg+Ca)$ against (SO_4+HCO_3) in Figure 8 supports this possibility. Most of the samples taken from the study area plot below the equiline suggesting that silicate weathering is the main contributor to the magnesium and calcium concentrations in the groundwater system in the area. The interpretation from these two figures lends credence to the results of the speciation and mineral stability diagrams, which suggest that the supersaturation of calcite, aragonite, dolomite and quartz in the area is a result of the accumulation of the cations calcium and magnesium, and the bicarbonate anion as well as silica, from the incongruent weathering of feldspars and micas in the aquifers. Supersaturation of calcite and dolomite does not, however, automatically suggest the precipitation of these minerals. The presence or absence of nucleation sites as well as the intervening influence of other cations and anions in the system are some of the factors that could impede precipitation. The preponderance of silicate mineral weathering in the hydrochemistry does not preclude the possibility of cation exchange activity. In fact, the formation of clay minerals from weathering of silicate minerals creates the rightful platform for cation exchange activity in the area. In order to conclusively determine the main controls on the hydrochemistry, Gibb's ratios were calculated for both cations and anions. Equations 5 and 6 (Gibbs, 1970) were used to compute Gibb's ratios for the anions and cations respectively.
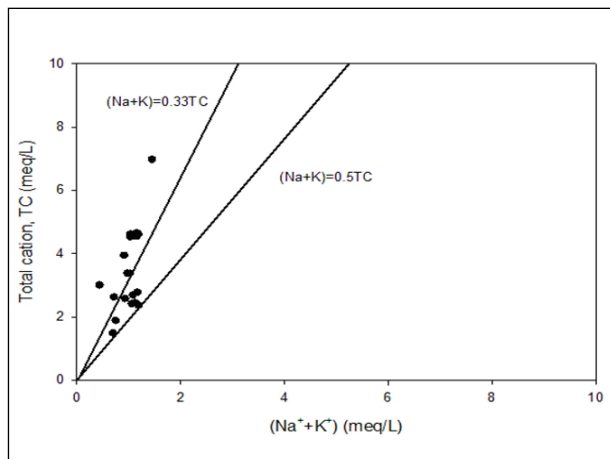

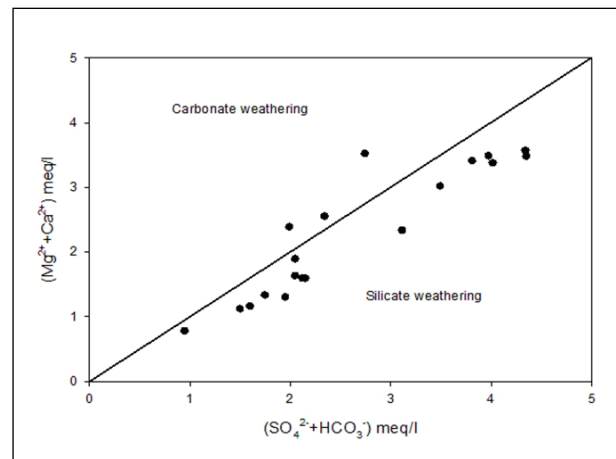Figure 7. Scatter diagram showing the relationship between total cation concentration and $Na^+ + K^+$.

Figure 8. Scatter diagram showing the relationship between $Mg^{2+} + Ca^{2+}$ against $SO_4^{2-} + HCO_3^-$.

$$\text{Gibbs Ratio I} = Cl^-/(Cl^- + HCO_3^-) \tag{5}$$

$$\text{Gibbs Ratio II} = (Na^+ + K^+)/(Na^+ + K^+ + Ca^{2+}) \tag{6}$$

where the concentrations of the ions are in meq/l.

The Gibbs ratios were plotted against TDS on semilog axes as shown in Figures 9 and 10. Both plots point to rock mineral weathering as being the main control on the hydrochemistry of groundwater in the Akyem area. This is in agreement with the results of Figures 7 and 8 and the mass balance calculations from PHREEQC. Rock – water interactions appear to be the main influence on the hydrochemistry of groundwater in the area.
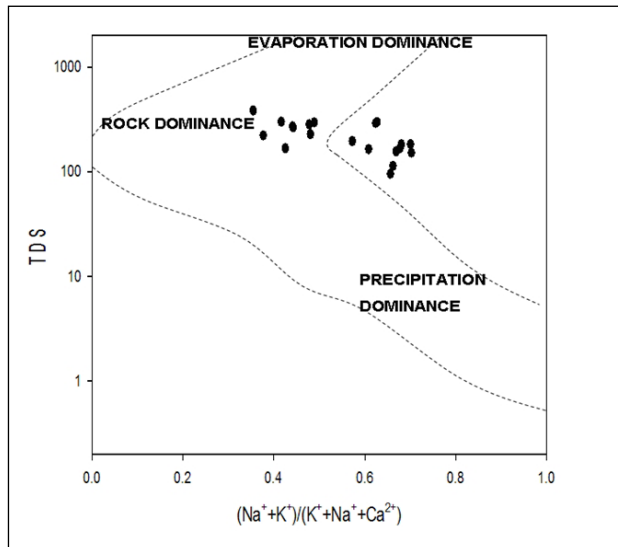
Figure 9. Gibb's diagram for cations showing the most prominent sources of variation in the hydrochemistry in groundwater at Akyem.
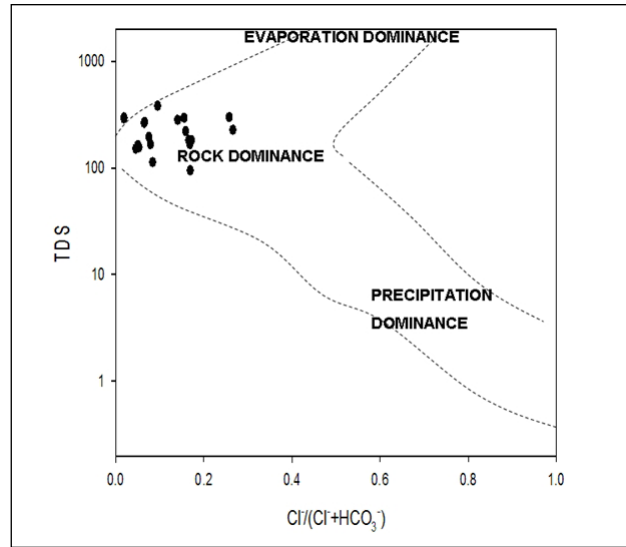
Figure 10. Gibb's diagram for anions showing the most prominent sources of variation in the hydrochemistry in groundwater at Akyem.

CONCLUSIONS

Major ion concentrations, and silica, pH and EC have been used to explain the probable sources of variation in the hydrochemistry of groundwater in the Akyem area, southeastern Ghana. Multivariate statistical methods were combined with mass balance models to account for the main factors that influence groundwater hydrochemistry. R-mode hierarchical cluster analysis performed on the dataset produced two water types: waters influenced predominantly by the weathering of silicate minerals, and those influenced significantly by anthropogenic activities such as agriculture. Mass balance modeling mineral phase diagrams indicate that incongruent weathering of silicate minerals might be the most significant factor influencing the hydrochemistry at this location. Montmorillonite appears to be the most stable silicate mineral phase in the system. Stability in the montmorillonite field indicates restricted flow conditions in which the residence time of groundwater is long enough to encourage rock-water interactions. Cation exchange also appears to play a role, albeit a much lesser role than silicate mineral weathering.

ACKNOWLEDGMENTS

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