

Chapter 11

Rock–water interaction and its control on chemical composition of groundwater

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11.1. General

Groundwater chemistry is largely a function of mineral composition, the formation through which it flows due to rock–water interaction. Evaporation and concentration, dilution due to precipitation also can change the chemical composition of groundwater but rock–water interaction is the major process because solid phases (inorganic and organic matter) are the primary sources and sinks of dissolved constituents of groundwater. During groundwater movement along its path from recharge to discharge areas, a variety of chemical reactions with solid phases take place. These chemical reactions will vary spatially and temporally, depending on the chemical nature of the initial water, geological formations and residence time. The resulting concentrations of major ions of groundwater can be used to identify the intensity of rock–water interaction and chemical reactions. [Elango et al. \(2003\)](#) have inferred that carbonate weathering and dissolution, silicate weathering and ion exchange processes are responsible for groundwater chemistry in Lower Palar River Basin, India. [Apodaca et al. \(2002\)](#) have inferred that hydrogeochemical processes such as dissolution, ion exchange processes and the residence time along the flow path control the chemical composition of groundwater in the shallow alluvial aquifers of the Upper Colorado River, USA. [Martinez and Bocanegra \(2002\)](#) have identified that cation exchange processes and calcite equilibrium are the important hydrogeochemical processes that control groundwater composition in the Mar del Plata aquifer, Argentina. [Sami \(1992\)](#) demonstrated that leaching of surficial salts, ion exchange processes and residential time cause hydrogeochemical variations of groundwater from a semiarid sedimentary basin, Eastern Cape, South Africa. Hence, knowledge on rock–water interaction that control groundwater chemical

evolution will lead to improved understanding of hydrogeochemical characteristics of an aquifer. This would contribute in the effective management and utilization of groundwater resources.

11.2. Rock–water interaction

Generally different chemical processes occur during rock-water interaction, which include dissolution/precipitation, ion exchange processes, oxidation and reduction. Rock types are broadly classified as igneous, metamorphic and sedimentary. Minerals present in these rocks will completely or partially dissolve in water according to the resistance of chemical weathering (Table 11.1). Occurrence and intensity of these chemical reactions depend on the initial water's disequilibrium with rocks in contact. During rock–water interaction a variety of chemical processes occur such as weathering and dissolution, ion exchange processes, oxidation and reduction (Table 11.2). During these chemical processes the following changes may occur in the system

1. Concentration of ions in groundwater may increase or decrease
2. Mobility of the dissolved constituents may be affected
3. pH of groundwater may change

according to the chemical processes.

Table 11.1. Common rock types and its resistance to chemical weathering

Type of rock	Dominant minerals present in rock	Resistance to chemical weathering
Quartz-cemented sandstone	Quartz and k-feldspar	High
Calcite-cemented sandstone	Quartz, K-feldspar and clays	Low
Siltstone	Quartz, K-feldspar and clays	High
Shale	Quartz and clays	High
Limestone	Calcite	Low
Rock salt	Halite	Low
Rock gypsum	Gypsum	Low
Slate	Quartz, biotite and muscovite	High
Phyllite, schist	Quartz, K-feldspar, biotite and/or muscovite and amphibole	High
Gneiss	Quartz, K-feldspar, plagioclase, biotite and amphibole	High
Marble	Calcite	Moderate
Quartzite	Quartz	Very high
Granite	Quartz and K-feldspar	High
Basalt	Olivine, pyroxene	Moderate

Table 11.2. Common minerals and chemical processes during rock–water interaction

Mineral	Chemical formula	Relative resistance	Chemical weathering processes
Halite	NaCl	Very low	Dissolution
Gypsum	CasO ₄ · 2H ₂ O	Very low	Dissolution
Pyrite	FeS ₂	Low	Dissolution and oxidation
Calcite	CaCO ₃	Low	Dissolution
Dolomite	CaMg(CO ₃) ₂	Low	Dissolution
Olivine	(Fe, Mg)SiO ₄	Moderately low	Oxidation, hydrolysis
Pyroxene	Ca, Mg, Fe, Al silicates	Moderate	Oxidation, hydrolysis
Plagioclase	CaAl ₂ Si ₂ O ₈ ; NaAlSi ₃ O ₈	Moderate	Hydrolysis
Hornblende (Amphibole)	Na, Ca, Mg, Fe, Al silicates	Moderate	Oxidation, hydrolysis
Biotite	K, Fe, Mg, Al silicate	Moderate	Oxidation, hydrolysis
K-feldspar	KAlSi ₃ O ₈	Moderately high	Hydrolysis
Muscovite	K, Al silicate	High	Hydrolysis
Quartz	SiO ₂	Very high	Dissolves very slowly
Clays	Al silicates	Very high	Hydrolysis

The chemical composition of groundwater is the imprints of the rock–water interaction and chemical processes. So, groundwater chemistry can be used to identify the rock–water interaction or chemical processes. Generally, presence of rock–water interaction was identified using TDS vs. Na/(Na + Ca) and TDS vs. Cl/(Cl + HCO₃) scatter diagrams as reported by Gibbs (1970) (Fig. 11.1). In these diagrams samples falling in the center of the curve are derived from rock–water interaction. Before studying the rock–water interaction, these diagrams will give a broad idea about the intensity of rock–water interaction. The samples falling along the rock–water interaction zone can be further interpreted with various techniques to identify the exact chemical reactions that control the chemical composition of groundwater.

11.2.1. Dissolution/precipitation of minerals

Mineral dissolution and precipitation involves transfer of mass to a phase or from a phase (Deutsch, 1997). Here, in this context mass transfer takes place between rock types and groundwater, which is called as dissolution and precipitation. Dissolution starts when groundwater tends to move toward equilibrium. This process continues until groundwater is saturated

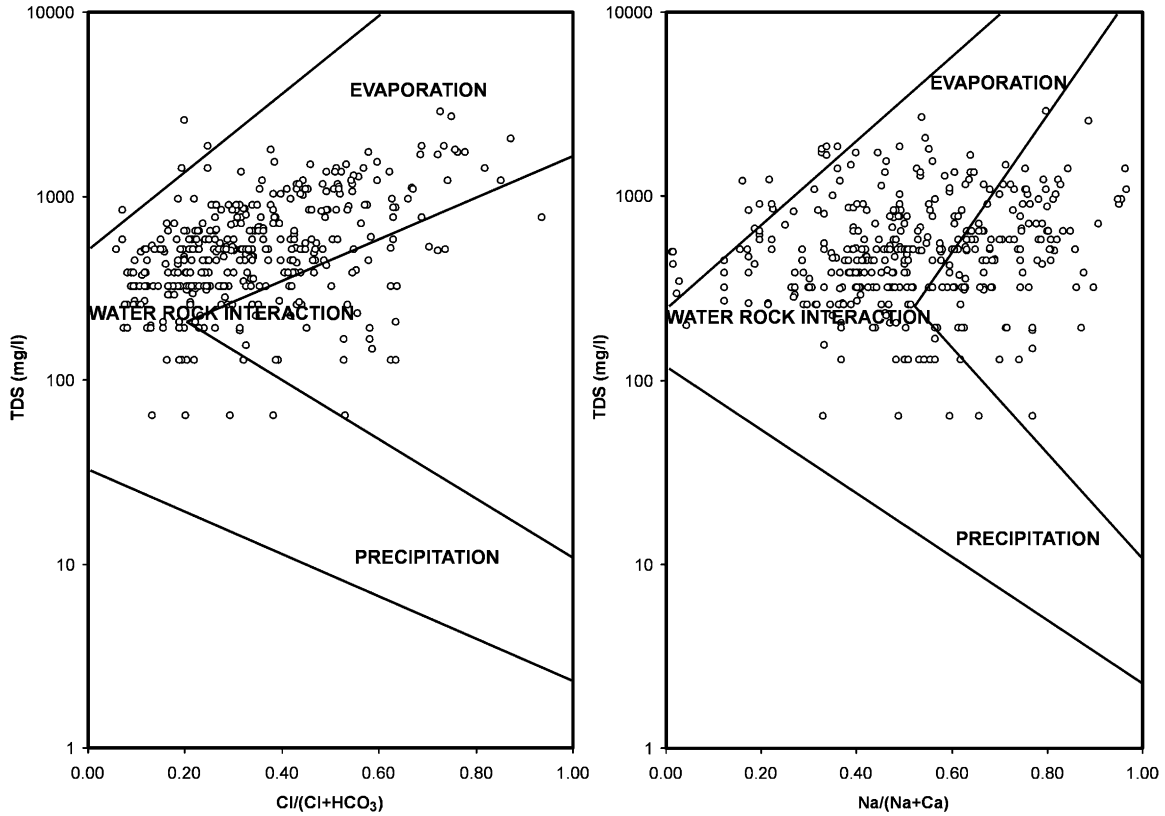


Figure 11.1. Rock–water interaction diagrams.

with those particular mineral components. At equilibrium concentration values, the mineral may continue to dissolve, that excess mineral components may combine in the solution to form precipitates of that particular mineral, and this reaction is called precipitation (Deutsch, 1997). Chemical equilibrium of groundwater for a particular mineral can be identified by calculating saturation indices. If the SI values are less than zero it will take more mineral into the solution, which is called dissolution

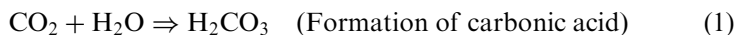
$$SI = \frac{\log IAP}{K_s}$$

where IAP is ion activity product, and K_s is solubility product of the mineral. (The use of SI is best limited to soluble simple salts like carbonate minerals.)

Carbonate weathering, silicate weathering, halite, gypsum dissolution and precipitation are common in an aquifer system. Rajmohan and Elango (2004) reported that the concentrations of the major ions increases mainly due to dissolution of minerals deposited during the preceding dry season in a part of Palar and Cheyyar River Basins. Similar kind of results was reported by Senthil Kumar (2004).

11.2.1.1. Carbonate weathering and dissolution

If calcium and magnesium are the dominant ions found in groundwater it reveals that dissolution of carbonate minerals is responsible for them. During infiltration or along the flow, groundwater may dissolve the CaCO_3 , and $\text{CaMg}(\text{CO}_3)_2$ present in the rocks will increase the concentration of calcium ions in groundwater. Datta and Tyagi (1996) explained that in the $(\text{Ca} + \text{Mg})$ vs. $(\text{HCO}_3 + \text{SO}_4)$ scatter diagram, the ionic concentrations falling above the equiline result from carbonate weathering, while those falling along the equiline are due to both carbonate weathering (Eqs. (1) and (2) and (3)) and silicate weathering (Eq. (4)). Such a $(\text{Ca} + \text{Mg})$ vs. $(\text{HCO}_3 + \text{SO}_4)$ scatter diagram of the Lower Palar River Basin was given in Fig. 11.2 (Kannan, 2005), in this most of the sample points lie above the equiline with few along the equiline and below. This indicates that carbonate weathering is the main source for calcium ions in groundwater; whereas the few points below the equiline indicate silicate weathering. In this reaction, carbonic acid (CO_2 and water) and calcium carbonate in soil react to form bicarbonate and calcium ion as given below (Eqs. (1) and (2)):



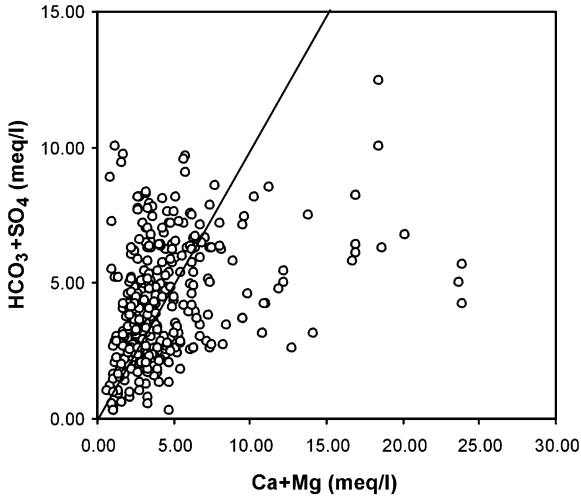
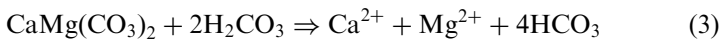


Figure 11.2. (Ca + Mg) vs. (HCO₃ + SO₄) scatter diagram of the lower Palar River Basin shows carbonate dissolution and silicate weathering.

Carbonate weathering by carbonic acid and water saturated with CO₂ is an intensive process. This water can easily dissolve the carbonate minerals available in its flow path. This process has increased the calcium, magnesium and bicarbonate ion contents in groundwater of the study area. Na vs. Ca scatter diagram (Fig. 11.3) shows that Ca/Na ion exchange also increases the concentration of Ca in groundwater. Magnesium may have come from the dissolution of magnesium calcite (Eq. (3)), gypsum and/or dolomite, as reported by Garrels (1976).



(Magnesium calcite dissolution)

If carbonate weathering and silicate weathering takes place, bicarbonate is generally dominant among anions in groundwater. During infiltration of rainwater and irrigated water, the carbonate minerals available along the path will be dissolved depending on the availability of dissolved CO₂ and carbonic acid (Eq. (1)). During the recharge process HCO₃ and Ca will be released to groundwater. Similarly, silicate weathering also increases the concentration of HCO₃ in groundwater. The Na vs. HCO₃ (Fig. 11.4) scatter diagram shows that HCO₃ also comes from silicate weathering (Eq. (4)).

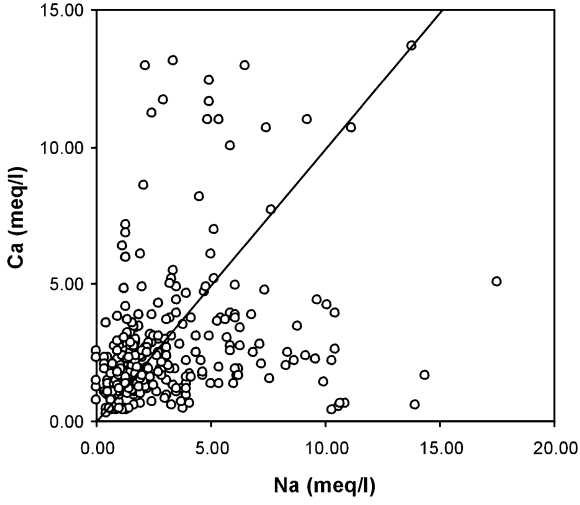


Figure 11.3. Na vs. Ca scatter diagram shows that Ca/Na ion exchange also increases the concentration of Ca in groundwater.

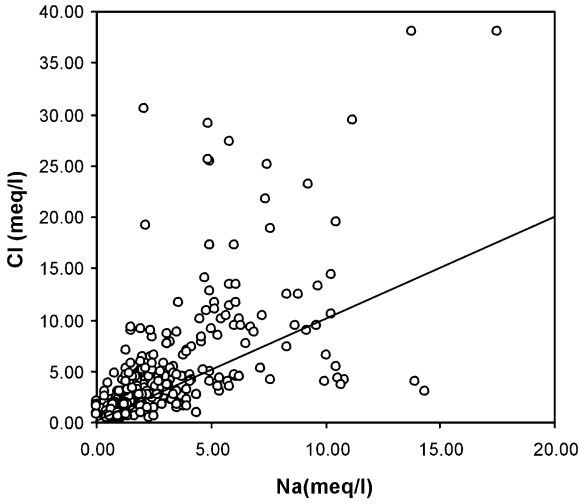
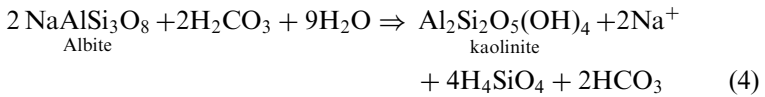


Figure 11.4. Na vs. HCO₃ diagram shows increased concentration of bicarbonate due to silicate weathering.

11.2.1.2. Silicate weathering processes

If bicarbonate and sulfate ions are dominant than calcium and magnesium that means silicate weathering is dominant (Elango et al., 2003). In Ca + Mg vs. HCO₃ + SO₄ diagram (Fig. 11.2) points falling along the bicarbonate side indicates the silicate weathering. Similarly, sodium is also high in groundwater. In general, 1:1 relationship between Na and Cl implies halite dissolution, whereas increased concentration of Na than Cl is typically interpreted as Na released from silicate weathering (Mayback, 1987). In the Lower Palar River Basin considerable amount of groundwater samples falling below the 1:1 line in the Na vs. Cl scatter diagram (Fig. 11.5) indicates silicate weathering. Samples falling all along the 1:1 comes from halite dissolution. But in the study area annual average rainfall is over 1000 mm, in this situation it is not possible for availability of free halite for dissolution in the soil zone, but the wind driven aerosol of sodium chloride from Bay of Bengal which is just 20 km from eastern side of the study area might have increased the concentration of Na and Cl in groundwater.



(Silicate weathering)

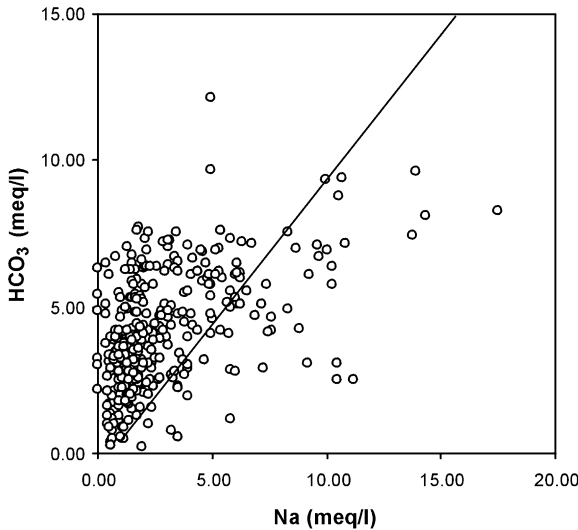


Figure 11.5. Na vs. Cl diagram shows that suggesting no halite dissolution it may be derived from silicate weathering.

The cation contribution to groundwater by silicate weathering can also be estimated by the (Na + K)/Total cations index (Stallard and Edmond, 1983; Sarin et al., 1989). The (Na + K) vs. TZ^+ (total cations) scatter diagram (Fig. 11.6) of the study area shows sample points falling both along and above the $(Na + K) = 0.5 TZ^+$ line. This suggests that the cations in groundwater might have been derived from silicate weathering. Datta and Tyagi (1996) observed that the contribution of cations may be derived from silicate weathering when $(Na + K) = 0.5 TZ^+$. In this case, however, the concentration of (Na + K) is about 50% of the total cations. The slightly lower concentration of (Na + K) is likely due to the Ca/Na exchange process as explained above, which might have reduced the amount of Na in groundwater. Potassium might have come from the illite present in the Lower Palar River Basin (Table 11.3).

11.2.2. Ion exchange processes

Ion exchange is a type of adsorption/desorption phenomenon. Clay minerals are the most common ion exchangers in soil and aquifer system. Cations present in the clay and groundwater are easily exchangeable than anion. pH of a solution also controls the exchange processes.

If huge amount of Na content is reduced from groundwater, it is attributed to ion exchange process. The Na vs. Ca (Fig. 11.3) scatter

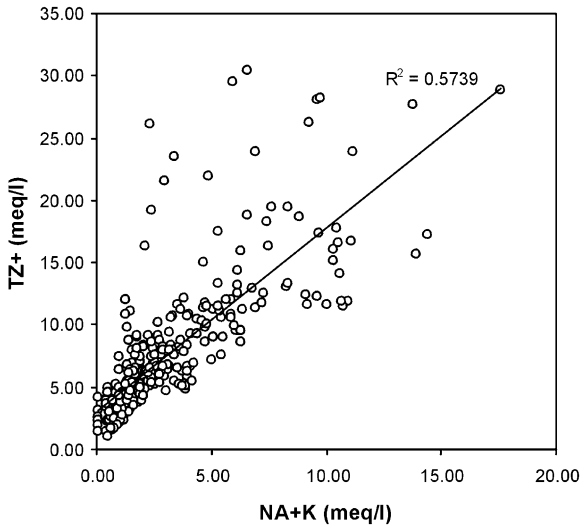
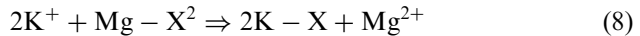
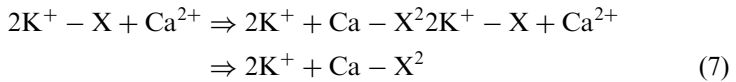
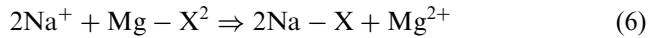
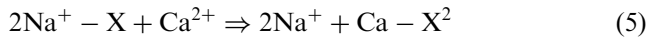


Figure 11.6. Na + K vs. Total cations diagram shows that 50 percent of Na and K comes from silicate weathering.

Table 11.3. Calculated cation exchange capacity of the clay present in the Lower Palar River Basin (after Elango et al., 2003)

Depth (m)	Sediment description	Clay %	Organic carbon %	CEC meq/100 g
1	Sand clay loam	28.4	0.12	20.30
1	Clay loam	35.9	0.30	26.18
1	Loam	23.4	3.00	26.88

diagram supports this process. Slightly elevated levels of calcium compared to sodium also confirm this, as reported by Lavitt et al. (1997). The adsorption of Ca ion and/or the release of Na to groundwater can reflect the same. Similarly, the calculated cation exchange capacity (CEC (meq/100 g) = 0.7 (%clay) + 3.5 (%OC)) value of selected well samples of the study area ranges from 20–27 meq/100 g (Table 11.1 of Chapter 5), which suggests that mixed type of clay is present in the study area. Various authors have reported CEC values for mixed clay minerals. Chapelle (1983) recorded 20–30 meq/100 g for the Aqua aquifer in Maryland, USA. Martinez and Bocanegra (2002) observed CEC values to vary from 20 to 40 meq/100 g for mixed clay sediments of The Mar del Plata aquifer. This type of mixed clay content is probably responsible for the ion exchange process. The following equations explain the ion exchange processes (Eqs. (5)–(8)).

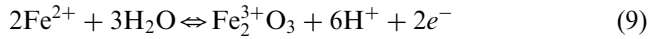


where X stands for matrix.

11.2.3. Oxidation/reduction processes

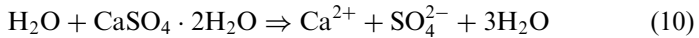
Lot of reactions in groundwater involves the transfer of electrons between dissolved and solid constituents. Electron loss results in oxidation and electron gain results in reduction. The most important oxidizing agents in groundwater are dissolved oxygen, oxo-anions such as nitrate and sulfate and water itself. Reducing agents include a wide variety of organic compounds, inorganic sulfides such as pyrite and iron silicates. At least one of the following groups will be available in groundwater. Sulfate and iron

are common constituents in soils and groundwater that participates in the oxidation and reduction reaction. These reactions readily reflect changes in surrounding Eh/pH conditions. In groundwater systems iron occurs in one of two oxidation states: reduced soluble divalent ferrous iron (Fe^{2+}) or oxidized insoluble trivalent ferric iron (Fe^{3+}) (Eq. (9)). Similarly, the sulfate ions present in water may get reduced due to reduction process (Eq. (10)). If the concentrations of sulfate and iron in groundwater are very low and Eh of the groundwater samples are also in reduced condition then the ions might have reduced due to reduction. However, in some areas the lack of source or least occurrence of source of sulfate and iron might be the reason for the low concentration. (Dissolution of gypsum as in Eq. (10), which can supply sulfate to the groundwater.)



→ Oxidation

← Reduction



Very low SO_4/Cl ratios (low concentration of SO_4) (Fig. 11.7) suggest that sulfate is being depleted, possibly by sulfate reduction (Lavitt et al., 1997). Earlier, Datta and Tyagi (1996) had observed that groundwater

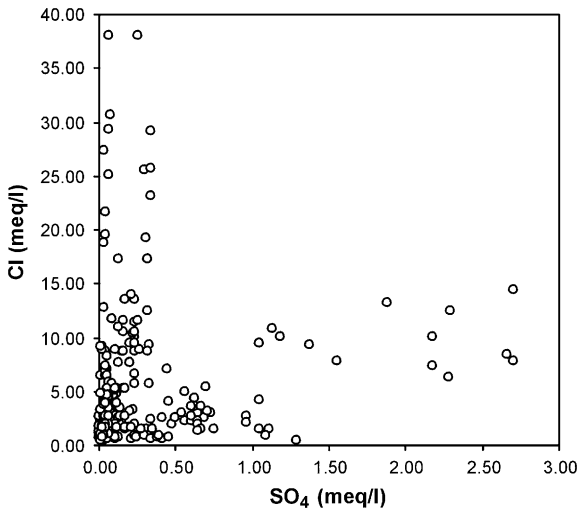
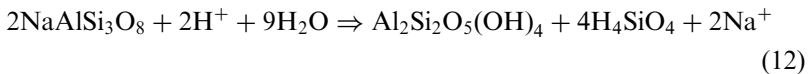
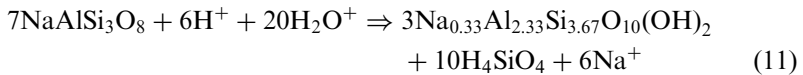


Figure 11.7. Cl vs. SO_4 scatter diagram shows that reduced amount of SO_4 is due to reduction process or lack of sulfate source.

with high Cl and low SO₄ probably indicates reduction. Thus, the low sulfate concentration in the groundwater of this area may be due to sulfate reduction and perhaps lack of natural sources in the area.

11.2.4. Hydrolysis

Hydrolysis is a chemical process in which a molecule is cleaved into two parts by the addition of a molecule of water. This is distinct from a hydration reaction, in which water molecules are added to a substance, but no cleavage occurs. Due to hydrolysis, rock and soil materials are decomposed into different products. Malov (2004) had reported that the principal role in the removal of Ca from rocks was probably played by the hydrolysis of calcium aluminosilicates that are in nonequilibrium state with all types of groundwaters present in Vendian sandy-clayey rocks aquifer. Zverev (1982) had reported that the most characteristic process is the hydrolysis of sodium aluminosilicates as follows Eqs. (11)–(13).



11.3. Rock–water interaction and hydrochemical patterns

Groundwater is classified into different types according to the percentage of chemical constituents present in it. This difference in groundwater rose mainly from different kinds of rock–water interaction. Generally, Ca–HCO₃, Ca–Mg–HCO₃, Ca–Cl, Na–HCO₃, Na–Cl, Ca–SO₄ and Na–SO₄ are the important groundwater types found throughout the world. A piper triplot (Piper, 1944) helps us to classify groundwater simply as in Fig. 11.8. Dissolution of calcite, dolomite, gypsum and halite will give rise to Ca–HCO₃, Ca–Mg–HCO₃, Ca–SO₄ and Na–Cl type of groundwaters, respectively. Huge amount of Ca and HCO₃ ions from calcite is responsible for Ca–HCO₃; Ca, Mg and HCO₃ ions that come from dolomite is responsible for Ca–Mg–HCO₃; Ca and SO₄ ions that come from gypsum is responsible for Ca–SO₄; Na and Cl that come from halite is responsible for Na–Cl. Further due to cation exchange process Na–HCO₃, Ca–Cl and Na–SO₄ groundwater types may form according

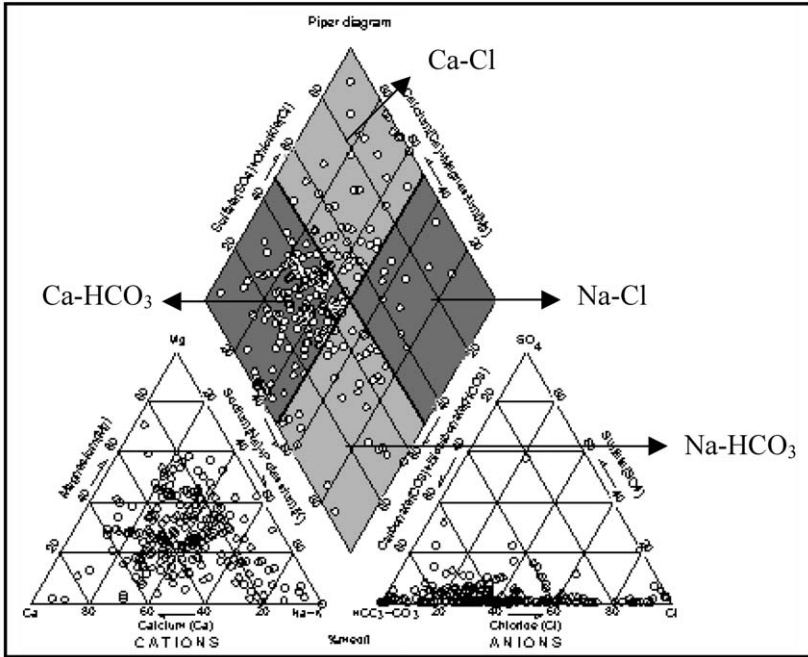


Figure 11.8. Piper triplot indicates different groundwater types.

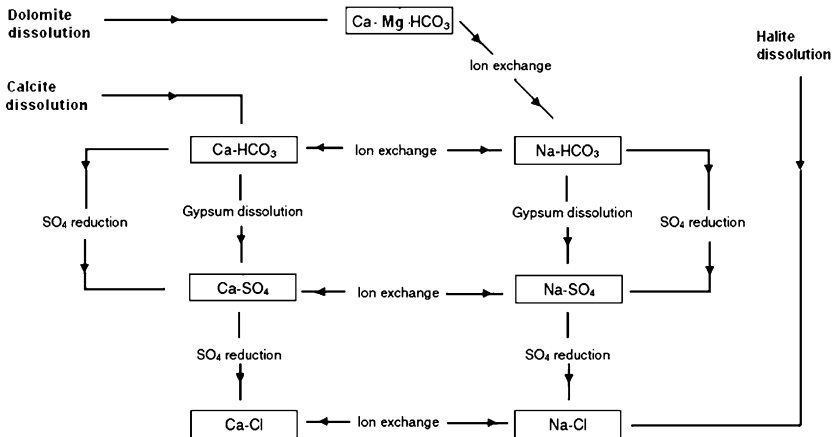


Figure 11.9. Rock–water interaction and resultant groundwater types.

to the cation exchange capacity of the matrix; this is a vice versa reaction. Sulfate reduction may also happen and it will give rise to Na–Cl, Ca–Cl, Ca–HCO₃ and Na–HCO₃ types of groundwater (Fig. 11.9). Thus, various chemical processes of rock–water interaction lead to groundwater chemical composition.

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