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ORIGINAL ARTICLE

Evaluation of hydrogeochemical characteristics and the impact of weathering in seepage water collected within the sedimentary formation

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Abstract A study was conducted by collecting eight seepage water samples that drain through the sedimentary rocks, mainly sandstone and shale, to evaluate the hydrogeochemical characteristics. The collected samples were analyzed for physico-chemical parameters using standard procedures. Three water types were identified in the Piper plot and the hydrogeochemical evolution starts from a Ca–Cl facies (type 1) via mixed Ca–Mg–Cl and Ca–Na–HCO$_3$ facies (type 2) to Na–Cl facies (type 3). Increasing trend of electrical conductivity (EC) values were observed from type 1 water to type 3 water. Lower ionic concentrations with an average EC value of 35.7 μs/cm in Ca–Cl facies indicate the recharge water by monsoonal rainfall, and ion exchange/weathering process is reflected in the mixing zone. Higher ionic concentration with an average EC value of 399 μs/cm is noted in Na–Cl facies, which indicates the ion exchange during water–rock interaction. Higher log pCO$_2$ values are also found in this facies, revealing the longer residence time of seepage water in the rock matrix, which release more ions into the water. The relative mobility of elements during weathering suggest that the order of mobility in both sandstone and shale is Na > Ca > Mg > K. It was observed that the hydrogeochemistry of seepage water is mainly controlled by the bedrock geology.

Keywords Hydrogeochemistry · Seepage water · Water–rock interaction · Weathering · Mobility of elements

1 Introduction

Geochemical behaviors and the distribution of ions during weathering of different parent rocks have been studied intensively by various researchers (Aubert et al. 2001; Duzgoren-Aydin and Aydin 2003; Krishnaswami et al. 2004; Caspari et al. 2006; Braun et al. 2009). Significant studies have discussed the relationship between chemical weathering of bedrock and stream-water chemistry (Rand and Drever 1977; Drever and Hurcomb 1986; Rochette et al. 1988; Blum et al. 1994; Edmond et al. 1995). Many of these studies were conducted within watersheds underlain by a single bedrock type, which reflects the stream chemistry on various lithologies (Driscoll et al. 1989).

The chemistry of groundwater usually indicates the mineral composition of the aquifer through which the water flows and various anthropogenic pollutants are also influence the hydrochemistry (Nordstrom et al. 1989; Banks et al. 1995; Marini et al. 2000). Chemical weathering is an important mechanism deriving elemental fractionation signatures from the parental bedrock (Nesbitt and Young 1982). During chemical weathering of silicate rocks, the larger cations (Rb, Cs and Ba) remain fixed in the weathered residue and the smaller cations (Na, Ca and Sr) are selectively leached (Nesbitt et al. 1980). The amount of aqueous Ca^{2+} and Na$^+$ derived from the weathering of granitoid rock reflects the approximate ratio found in plagioclase feldspar (Garrels 1968). However, few recent

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studies demonstrate that excess Ca found in many surface and ground waters relative to this plagioclase stoichiometry (Stauffer 1990). Cation exchange reactions exert an important control on the chemistry of water in clay-rich rocks as well (Turrero et al. 2006). The dissolved elements in the pore water are transferred from the sediment solid-phases to overlying surface water (Sherman et al. 1998; Tovar-Sanchez et al. 2006).

The relative mobility of an element during weathering moves from the parent rock to the stable environment of a sedimentary basin (Anderson and Hawkes 1958). Mobility is controlled by many factors like releasing of elements during weathering of parent rocks, contact between solutions and adsorptive media, pH and Eh of the environment and chemical reaction with organic matter.

The outcrop seepage water in this study site is a good opportunity to understand the relationship between bedrock geology and hydrochemistry of seepage water. The hydrochemistry of seepage water is largely explained the water–rock interaction process. Hence, the main objective of this study is to elucidate the relationship between the bedrock geology and the hydrogeochemical characteristics of seepage water. This study also addresses the evolution of various hydrochemical facies, controlling factors for major geochemical processes and the relative mobility of elements during water–rock interaction.

2 Study site

The study site is located near Miri, Sarawak State, East Malaysia of North West Borneo. All the seepage water samples were collected from the sedimentary rock outcrops mainly composed of sandstone and shale located along Tusan Beach. The sedimentary rocks in the study site belong to Lambir Formation of Middle Miocene, which were deposited under shallow marine environment (Hutchinson 2005). The Middle Miocene Formation consists of sandstones, shale and some limestone. The Lower Lambir Formation has thick bedded sandstones with sharp erosive base overlying medium dark-grey mudstone and calcareous mudstone. The basal sandstone is well sorted, made up of a number of sandstone cycles with hummocky cross-bedding. The top sandstone shows low-angle planar cross bedding and may be beach deposit. Structures like cross-bedding, cross-lamination, turbidite beds, flaser bedding, fractures and joints are common in several outcrops. The average annual rainfall in and around the study site is about 2813 mm per year. Higher rainfall is expected from November to February and the dry period from June to August. The rainwater seeps into the outcrops and out flowing through the bedding planes, permeable fractures and joints of the bedrocks.

3 Methodology

A total of eight seepage water samples were collected, draining through the bedding planes and permeable fractures of the sedimentary rocks. The collected samples were analyzed for various chemical parameters using standard methods described in APHA (1995). pH, electrical conductivity (EC) and total dissolved solids (TDS) were measured in the field using portable pH and conductivity meter (Thermo Scientific Orion Star, 4 Star Plus Meter). Bicarbonate (HCO_3^-) and chloride (Cl^-) were measured using titrimetric method. Sulfate (SO_4^{2-}) were analyzed using Hack Test Kits (SulfaVer 4 method). The collected samples were preserved by acidifying to pH 2 with HNO_3 for Calcium (Ca^{2+}), Magnesium (Mg^{2+}), Sodium (Na^+) and Potassium (K^+) analysis using atomic absorption spectrophotometer (Perkin Elmer Analyst 400). The precision of analysis was checked by the following error percentage calculation and it is found to vary between $\pm 1\%$ and $\pm 10\%$ (Hem 1985).

$$Error \% = \frac{(TA - TC)}{(TA + TC)} \times 100$$

where TA total anions and TC total cations.

Major oxides of two rock samples (sandstone and shale) were analyzed using Axios PANalytical X-ray fluorescence machine and the mineral constituents in the rocks were determined by X-ray diffraction (XRD) method using Panalytical X'Pert Pro diffractometer (Nagarajan et al. 2016). Saturation index (SI) of carbonate minerals, carbon dioxide partial pressure (log pCO_2) and ionic strength (IS) were computed using WATEQ4F program (Ball and Nordstrom 1992).

4 Results and discussion

4.1 Distribution of major oxides and minerals in bedrocks

In the studied outcrops, the host rocks are mainly sandstone and shale. Since the rocks are chemically homogeneous, two rock samples (each one in sandstone and shale) were analysed chemically for the determination of their major oxides (Al_2O_3, CaO, Fe_2O_3, K_2O, MgO, MnO, Na_2O, P_2O_5, SiO_2 and TiO_2). The relative variation trends of various major oxides are shown in Fig. 1. The concentration of oxides is in the following order of $SiO_2 > Al_2O_3 > Fe_2O_3 > K_2O > TiO_2 > MgO > MnO > CaO > Na_2O > P_2O_5$ in sandstone and $SiO_2 > Al_2O_3 > Fe_2O_3 > K_2O > MgO > CaO > Na_2O > TiO_2 > P_2O_5 > MnO$ in shale. It indicates that both the rocks are enriched in SiO_2 respectively. Mineral constituents of rock types collected in the study site were examined by XRD. Sandstone is mainly consists
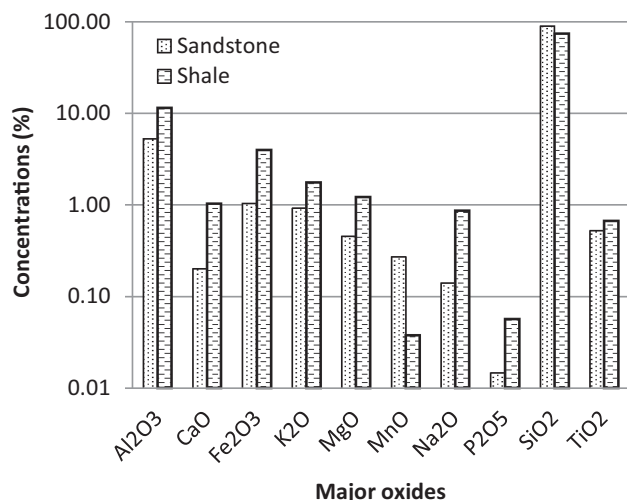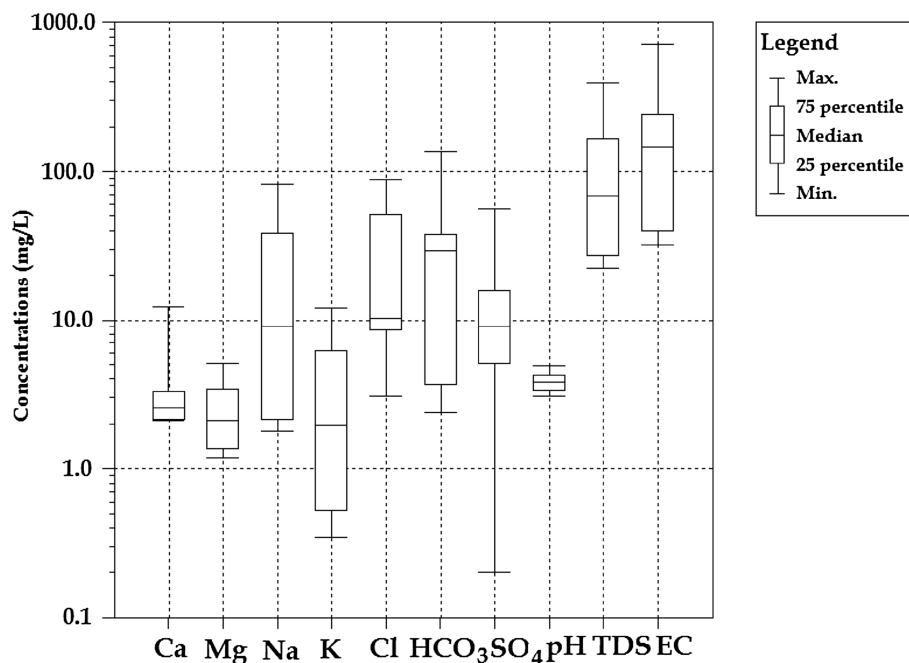
Fig. 1 Major elements concentrations in sandstone and shale

of Quartz (50.6 %), Illite/Muscovite (16.9 %), Chlorite (4.5 %) and Plagioclase (0.5 %); whereas Shale is chiefly composed of Quartz (31.7 %), Illite/Muscovite (23.4 %), Chlorite (7.9 %), Plagioclase (6.8 %) and Calcite (3.3 %).

4.2 Hydrochemistry of seepage water

The chemical composition of seepage water is shown in box plot (Fig. 2). The order of dominance of cation is $Na^+ > K^+ > Ca^{2+} > Mg^{2+}$ and the order of dominance of anion is $HCO_3^- > Cl^- > SO_4^{2-}$. The pH ranges from 3.1 to 4.9 with an average of 4.0 indicate acidic condition in nature which leads to possible dissolution of minerals from

the surrounding bedrocks. EC ranges from 32 to 712 μs/cm with an average of 206.9 μs/cm. Higher EC values are observed in samples L1, L2 and L4 indicates high ionic concentration among the other samples. TDS varies between 22.2 and 391.5 mg/L with an average of 120.8 mg/L and it follows the same trend of EC values. Na^+ is the dominant cation ranges from 1.8 to 81.4 mg/L with an average of 24 mg/L. K^+ ranges between 0.3 and 12.1 mg/L with an average of 4.1 mg/L. Clay minerals and plagioclase feldspar present in the rock types acts as the major source of Na^+ and K^+ in the water (Thivya et al. 2015). Ca^{2+} ranges from 2.1 to 12.4 mg/L with an average of 3.9 mg/L and the Mg^{2+} ranges between 1.2 and 5.1 mg/L with an average of 2.8 mg/L. Ca^{2+} is probably derived from the dissolution of calcite that identified from the rock composition (Chae et al. 2001; Prasanna et al. 2010). HCO_3^- is the dominant anion ranges from 2.4 to 136.3 mg/L with an average of 39.2 mg/L and it release during the process of weathering (Panigrahy and Raymahashay 2005). Cl^- ranges from 3.1 to 88.6 mg/L with an average of 30.9 mg/L might have derived from the atmospheric input (Mayer 1999). SO_4^{2-} ranges from 0.2 to 56 mg/L with an average of 15.9 mg/L, probably derived from the ion-exchange in soils and clastic rock units (Mayer 1999).

4.3 Hydrogeochemical evolution of seepage water

The hydrochemistry of seepage water is possibly controlled by the water–rock interaction in an open system, where the water mainly draining through the bedding surfaces and permeable fractures of the rocks. All the sample

Fig. 2 Box plot for the maximum, minimum and average values of the chemical constituents in seepage water (all values in mg/L, except pH and EC in μs/cm)

concentrations are plotted in the Piper diagram and it shows that the hydrogeochemical evolution is chiefly controlled by the bedrock geology. Three major water types were identified in the plot, based on the hydrogeochemical characteristics of seepage water (Fig. 3); Ca–Cl facies (type 1), mixed Ca–Mg–Cl and Ca–Na–HCO$_3$ facies (type 2) and Na–Cl facies (type 3). The average values of EC (µs/cm) of each water type are: type 1 = 35.7; type 2 = 128.7; type 3 = 399.1. It clearly shows that the hydrogeochemical evolution of seepage water starts from a Ca–Cl facies via mixed water facies to Na–Cl facies. The samples in the Ca–Cl facies indicate the recharge water by monsoonal rainfall with low ionic concentrations. Mixed water type, Ca–Mg–Cl and Ca–Na–HCO$_3$ reflects ion exchange/weathering process may be due to the influence of monsoon (Thivya et al. 2016). The samples in Na–Cl facies shows higher ionic concentrations, where the concentrations of Ca^{2+} in water decreases as the concentration of Na$^+$ increases during the interactions with the surrounding lithologies. This indicates that the Ca^{2+} ions are substituted by Na$^+$ ions on the solid surface, as explained in the equation below (Bundschuh and Zilberbrand 2011; Thilagavathi et al. 2012; Thivya et al. 2014; Blume et al. 2015):

$$NaX + 1/2\,Ca^{2+} \leftrightarrow Na^+ + 1/2\,CaX_2$$
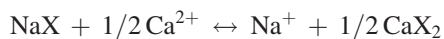
where the X is considered to be a soil/rock exchanger. The water comes into contact with Na$^+$, as a source from plagioclase feldspar that precipitated on the rock surface. Then the Na$^+$ ion pushes away the Ca^{2+} ion, and becomes dominant in the water through cation exchange process. This process is inferred by the following reaction of

plagioclase feldspar weathering (Garrels and Mackenzie 1967).

$$2NaAlSi_3O_8 + 2H^+ + 9H_2O \longrightarrow Al_2Si_8O_5(OH)_4$$
$$+ 2Na^+ + 4H_4SiO_4$$
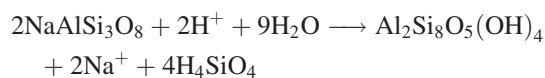
In the final stage, Na$^+$ and K$^+$ ions are released into the water by ion exchange reactions among cations as indicated from Indices of Base Exchange (IBE) (Schoeller 1965). It describes the reactions between water and rock matrix. Chloro-alkaline indices i.e. CAI1 and CAI2 are used to measure the extent of base exchange during water–rock interaction, and calculated by the following expression;

$$CAI1 = [Cl - (Na + K)/Cl]$$

$$CAI2 = [Cl - (Na + K)/(SO_4 + HCO_3 + CO_3 + NO_3)]$$

where all the ions are expressed in epm. When there is an exchange of Ca^{2+} or Mg^{2+} in water with Na$^+$ and K$^+$ in the rock matrix, both the above indices are negative, and if there is a reverse ion exchange, then both these indices will be positive (Schoeller 1965 and 1967). All the samples calculated show exchange of Na$^+$+K$^+$ in the rock to Ca^{2+}+Mg^{2+} in water, which results in the enrichment of Na$^+$ and K$^+$ ions in the water. So, it is clearly observed that Ca–Cl water type is changed to Na–Cl water type due to the ion exchange reactions.

Log pCO$_2$ versus IS plot was also used to evaluate the residence time of water with the rock matrix. Three distinct zones were identified as same as in Piper plot. Zone 1, with the samples of L7 and L8 have low pCO$_2$ and IS values indicate lesser residence time of recharge water into the rock matrix reflects low ionic concentrations in these water (Fig. 4). Zone 3 (L1, L2 and L4) has higher pCO$_2$ and IS values suggests longer residence time of water in the rock matrix leads to the intense water–rock interaction (Prasanna et al. 2015), that release more ions into the seepage water. Zone 2 (L3, L5 and L9) water act as a mixing zone due to ion exchange during weathering process.

4.4 Relative mobility of elements

The relative abundance of individual elements in the rock and in the water offers a means of determining the relative mobility of the common elements (Smyth 1913). So, the relative mobility is used as an index of redistribution of elements during the alteration of parent rock and it gives an idea about the release of cations from rock to water. The relative mobility of the cations were calculated to understand the possible water–rock reactions. For each element considered, the percentage in the rock is divided into the equivalent percentage in water draining from the rock. The greater the resulting ratio, the greater the assumed mobility
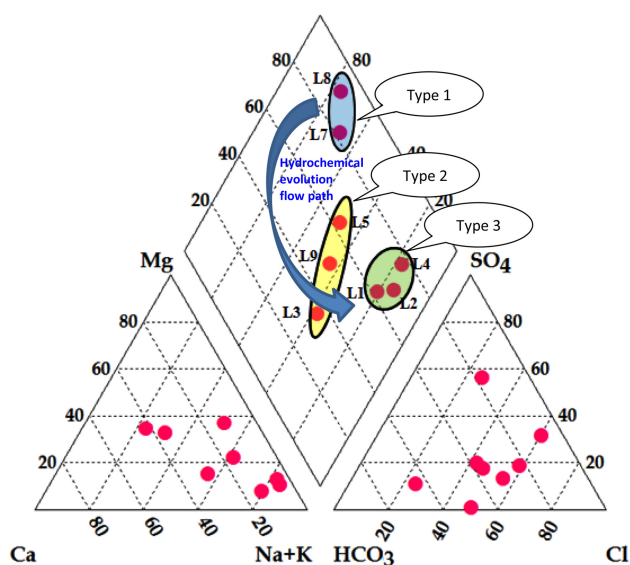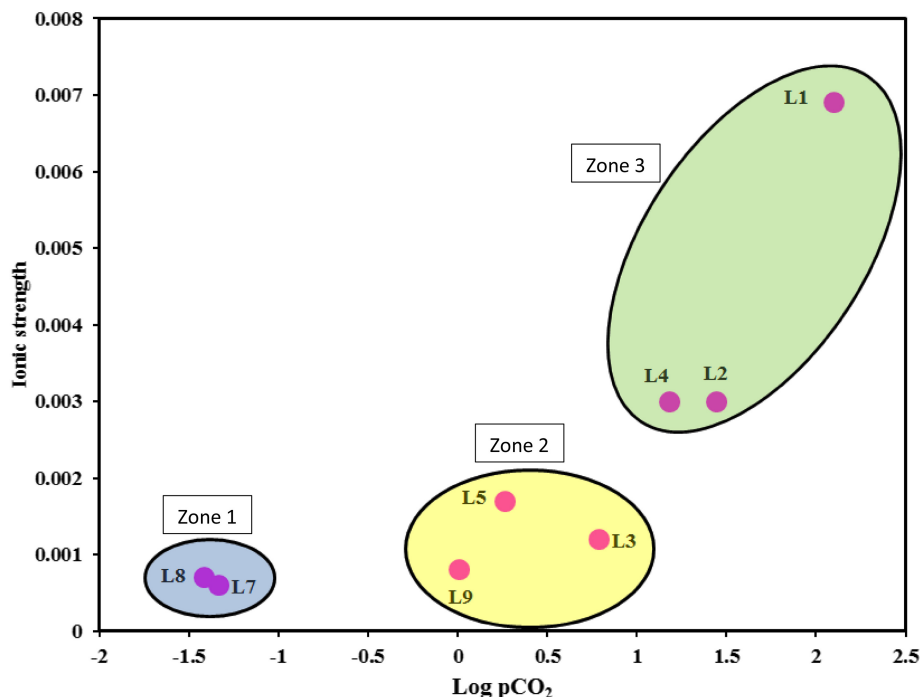

Fig. 3 Piper plot for the seepage water samples

Fig. 4 Relationship between log pCO_2 and IS

of the element. Relative mobility of cations in seepage waters of sandstone and shale is calculated as:

$$\text{Relative mobility} = \frac{\% \text{ of cation in water}}{\% \text{ of cation in rock}}$$

Calculated relative mobility of the elements suggest that the order of mobility in both sandstone and shale is $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ (Fig. 5). Sodium and calcium are the most mobile elements than the magnesium and potassium. Sodium and potassium are mainly released by the weathering of clay minerals (Illite) present in the rock composition. It was evident that the clay minerals are the second dominant consti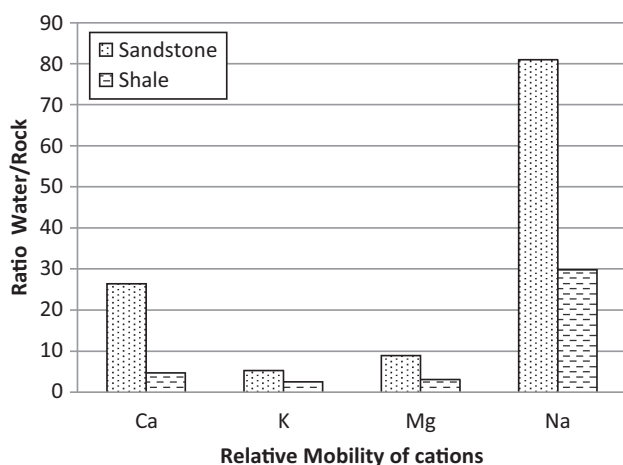tuents in the rocks. The bedrocks consists of minor quantity of plagioclase minerals, the solubility and rate of dissolution of plagioclase feldspar also makes a minor contributor of Na^+ and K^+ ions to weathering condition (Drever 2005). Since the studied outcrops are located along the coastal area, the sea salt particles from marine aerosols containing Na^+ deposited in the rock surfaces and pore spaces might be leached by the seepage water (Chesselet et al. 1972). Calcium and magnesium in the water is mainly derived from dissolution of carbonate minerals or reverse ion exchange process (Subramani et al. 2009; Prasanna et al. 2015). However, the low percentage (3.3 %) of carbonate mineral (i.e. calcite) in the rocks indicating the lesser contribution of Ca^{2+} and Mg^{2+} through rock weathering. So, it might be due to the ion exchange reactions as reflected by IBE, where the Na^+ and K^+ is enhanced and Ca^{2+} and Mg^{2+} are removed from the water. However, there is a clear variation in the percentage of mobility of cations among the samples. Samples L1, L2 and L4 shows higher mobility of elements compared to others, due to the longer residence of water in the rock matrix gives intense water–rock interaction that released more elements from the rocks. The low pH values of these samples are also supports for more dissolution of ions in the rocks.

The saturation indices of carbonate minerals like calcite, aragonite, magnesite and dolomite were calculated using WATEQ4F and studied for the dissociation factors in the seepage water. The saturation state of carbonate minerals are in the following order: SI(calcite) > SI(aragonite) > SI (magnesite) > SI(dolomite). The calcite and aragonite

Fig. 5 Relative mobility of cations from sandstone and shale

Fig. 6 SI of carbonate minerals
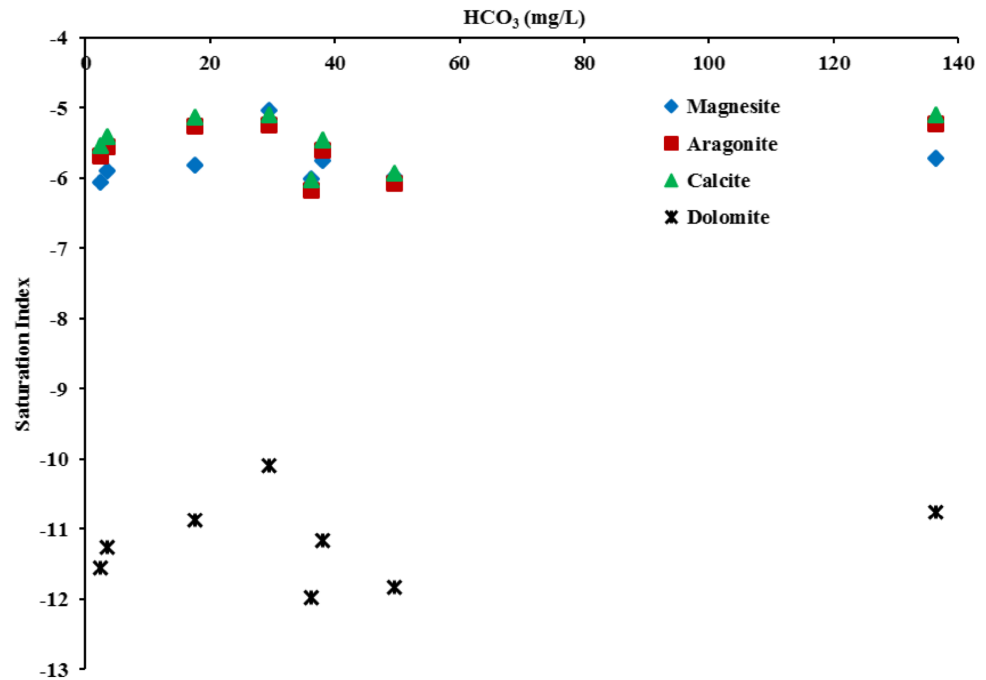
minerals are near equilibrium (Fig. 6). But overall, the SI of all carbonate minerals are under-saturation condition, indicate the dissolution of minerals (Prasanna et al. 2010).

4.5 Limitations of the study

The overall interpretation of the geochemical data reveals that the weathering of bedrocks is the main factor, which controls the hydrogeochemistry of seepage waters. However, there may be other controlling factors for the hydrogeochemistry of seepage water, which need to be studied in detail by increasing the number of chemical parameters analyzed (e.g., trace metals and isotopes) and number of sampling locations at different seasons.

5 Conclusions

This study reveals that the pH of the seepage water governs the dissolution of the minerals present in the bed rock. Na^+ and HCO_3^- are the dominant cation and anion in the seepage waters. The highest average value of EC was observed in Na–Cl facies, whereas the lowest average value was observed in Ca–Cl facies. The hydrogeochemical evolution of seepage water indicates that the Ca–Cl facies has altered to Na–Cl facies due to cation ion exchange between water and the rock matrix. Higher log pCO_2 values in Na–Cl facies indicate the longer residence time of water in the bedrock leads to the intensive water–rock interaction process. Calculation of SI of carbonate minerals explains that all the samples represent the state of

under-saturation, where the calcite shows comparatively near saturation state. Calculated relative mobility of elements in the rocks is in the following trend of $Na^+ > Ca^{2+} > Mg^{2+} > K^+$. It is inferred that Na^+ and K^+ are mainly released by the weathering of clay minerals and plagioclase feldspar and the Ca^{2+} and Mg^{2+} are derived from the dissolution of calcite and reverse ion exchange process. Na–Cl water type samples show high mobility of elements due to the longer residence of water in the rock matrix that released more cations from the bedrock. Overall, this study reveals that the weathering of rock-forming minerals in the bedrocks is the dominant controlling factor for the hydrogeochemistry of seepage waters.

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