



Identifying the origin and geochemical evolution of groundwater

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Identifying the origin and geochemical evolution of groundwater using hydrochemistry and stable isotopes in Subei Lake Basin, Ordos energy base, Northwestern China

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Abstract

A hydrochemical and isotopic study was conducted in Subei Lake Basin, northwestern China, to identify the origin and geochemical evolution of groundwater. Water samples were collected, major ions and stable isotopes ($\delta^{18}\text{O}$, δD) were analyzed. In terms of hydrogeological conditions in study area, groundwater can be classified into three types: the Quaternary groundwater, the shallow Cretaceous groundwater, the deep Cretaceous groundwater. Piper diagram and correlation analysis were used to reveal the hydrochemical characteristics of water resources. The dominant water type of lake water was Na-Cl type, which was controlled by strong evaporation and recharge from overland flow and groundwater; the predominant hydrochemical types for groundwater were Ca-HCO₃, Na-HCO₃, and mixed Ca·Na·Mg-HCO₃ types, the groundwater chemistry is mainly controlled by dissolution/precipitation of anhydrite, gypsum, halite and calcite. The dedolomitization and cation exchange are also important factors. Rock weathering is confirmed to play a leading role in the mechanisms responsible for the chemical compositions of groundwater. The stable isotopic values of oxygen and hydrogen in groundwater are close to the local meteoric water line, showing that groundwater is of meteoric origin. The deep Cretaceous groundwater is depleted in heavy isotopes, compared to shallow Cretaceous groundwater. The hydrogen and oxygen isotopes signatures in deep Cretaceous groundwater may show a paleorecharge effect that the deep Cretaceous groundwater was recharged during a geologic period when the climate was wetter and colder than today. Due to strong evaporation effect and dry climatic conditions, heavy isotopes are more enriched in lake water than groundwater. The hydrochemical and isotopic information of utmost importance has been provided to decision-makers by the present study so that a sustainable water resources management policy could be designed for the Ordos energy base.

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5 may not provide much accurate information on the groundwater flow characteristics in small basin (Toth, 1963). Hence, it is also significant to implement local groundwater resources investigations. As Winter (1999) concluded that lakes in different part of groundwater flow systems have different flow characteristics. Data on hydrochemistry and stable isotopes of water were used to study the origin and geochemical evolution of groundwater in the Habor Lake Basin (Yin et al., 2009), which is located in recharge zone. But other lakes in the runoff and discharge area still have not been studied so far. Due to the particularity of discharge area, a variety of hydrochemical effects such as evaporation, decarbonation, strong mixing action, etc., take place and result in extremely complicated hydrochemical and isotopic characteristics of discharge area. Therefore, it is essential to conduct hydrochemical and isotopic study of Subei Lake Basin, which is located in discharge area. The present study is also the first time to study a specific lake basin in discharge zone of Ordos basin.

15 The Dongsheng-shenfu Coalfield, situated in Inner Mongolia Autonomous Region, is an important component of the Ordos energy base. It is the largest explored coalfield with an enormous potential for future development. The coal reserves explored is 230 billion tons. The coal is exploited from Jurassic strata and subsurface mining is common. Local residents there mostly depend on groundwater on account of the serious shortage of surface water. Water resources support the exploitation of coal and development of related industries. Haolebaoji well field of Subei Lake Basin is a typical, large well field and acts as an important source of water-supply in this coalfield. However, large-scale and intensive groundwater exploitation could remarkably influence water supply and hydrogeochemistry in the study area. The aim of the research is to recognize geochemical evolution of groundwater in the Subei Lake Basin by analyzing hydrochemical and stable isotopic data. The main objectives are to (1) ascertain the origin of groundwater, (2) determine the geochemical factors and mechanisms controlling the chemical composition of groundwater. The results will be valuable in obtaining a deeper insight into the hydrogeologic setting of the area, and providing significant information such as water quality situation and geochemical

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with elevations between 1290 and 1300 m. The topography of the center area is flat and low-lying, where Subei lake exists. There are no large rivers within the study area; the only surface water body is Subei lake and Kuisheng lake. Subei lake is located in the low-lying center of the study area (Fig. 1), which is an inland lake characterized by high alkalinity. In addition, Kuisheng lake is also a perennial water body and it is located in northeastern corner of the study area, only covering 2 km² (Fig. 1).

2.2 Geologic and hydrogeologic setting

Subei Lake basin is a relatively closed hydrogeological unit. The Quaternary sediments and Cretaceous formation can be observed in the study area. The Quaternary sediments are mainly distributed in the surrounding of Subei lake with relatively smaller thickness, generally the thickness of Quaternary sediments is below 20 m. The Quaternary layer is chiefly composed of the interlaced layers of sand and mud. The Cretaceous formations mainly consist of sedimentary sandstones and generally outcrop in the regions with relatively higher elevation. Calcite, dolomite, anhydrite, aragonite, gypsum, halite, and feldspar are major minerals in the Quaternary and Cretaceous aquifers (Hou et al., 2006).

Groundwater resources are very abundant in the investigated area and phreatic aquifer and confined aquifer could be observed in this region. The phreatic aquifer is composed of Quaternary and Cretaceous sandstones, with its thickness ranging from 10.52 to 63.54 m. In terms of borehole data, the similar groundwater levels in the Quaternary and Cretaceous phreatic aquifers indicate a very close hydraulic connection between the Quaternary layer and Cretaceous phreatic aquifer, which could be viewed as an integrated unconfined aquifer in the area. The depth to water table in unconfined aquifer is influenced by the terrain change, of which, the minimum value is below 1 m in low-lying region and the maximum value could be up to 13.24 m. The hydraulic conductivity of the aquifer changes between 0.16 and 17.86 m d⁻¹. The recharge source of groundwater in unconfined aquifer is mainly the infiltration recharge of precipitation, it can be also recharged by lateral inflow from groundwater

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outside the study area. Besides the above recharge terms, leakage recharge from the underlying confined aquifer and infiltration recharge of irrigation water can also provide a small percentage of groundwater recharge. Evaporation is the main discharge way of the unconfined groundwater. In addition, lateral outflow, artificial exploitation and leakage discharge are also included in the main discharge patterns. Unconfined groundwater levels were contoured to illustrate the general flow field in the area (Fig. 3). Groundwater levels were monitored during September 2003. The groundwater flows predominantly from surrounding uplands to low lands, which is under the control of topography. On the whole, groundwater in phreatic aquifer flows toward Subei lake and recharges lake water (Fig. 3).

The unconfined and confined aquifers are separated by an uncontinuous aquitard. Generally speaking, permeable layers and aquitards intervein in the vertical profile of the aquifer system. Nevertheless, aquitards may pinch out in many places, so the aquifer system acts as a single hydrogeologic unit. In the present study, the covering aquitard is composed of the mudstone layer, which is mainly distributed in the second sand layer (Fig. 4). The phreatic aquifer is underlain by confined aquifer composed of Cretaceous rocks. The maximum thickness of Cretaceous rocks could be nearly 1000 m in the Ordos Plateau (Yin et al., 2009), so the cretaceous formation composed of mainly sandstone is the major water-supply aquifer of the investigated area, and discontinued mudstone lens also could be observed in Cretaceous strata (Fig. 4). Due to its huge thickness and high permeability, it is regarded as the most promising water-supply aquifer for domestic and industrial uses. The confined aquifer primarily receives leakage recharge from the unconfined groundwater. The flow direction of confined groundwater is similar to that of unconfined groundwater (Fig. 3). Artificial exploitation is the major drainage way of confined groundwater.

In the present study, the depth of sampling wells is used to classify Quaternary groundwater, shallow Cretaceous groundwater and deep Cretaceous groundwater in combination with hydrogeological map of the study area. As a research on an adjacent, specific shallow groundwater system of Ordos Basin shows that the circulation depth

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is 120 m (Yin et al., 2009). It is difficult to determine the circulation depth of shallow groundwater in fact because the circulation depth of local flow systems is changeable dependent on the topography and the permeability of local systems (Yin et al., 2009). In this study, Quaternary groundwater was defined on the basis of the distribution of Quaternary sediments thickness and depth of sampling wells. 120 m is chosen as the maximum circulation depth of local system and is used to divide the Cretaceous groundwater samples into two groups, samples taken in wells shallower than 120 m were classified into shallow Cretaceous groundwater, while samples taken in wells deeper than 120 m were deep Cretaceous groundwater.

3 Methods

3.1 Water sampling

Two important sampling actions were conducted in the study area during August and December 2013, respectively. A total of ninety-five groundwater samples and seven lake water samples were collected. The first sampling action was during rainy season, the other was during dry season. The sampling locations are shown in Fig. 5. The water samples were taken from wells for domestic and agricultural purposes ranging in depth from 2 to 300 m. The samples from the wells were mostly taken using pumps installed in these wells and after removing several well volumes prior to sampling. The 100 and 50 mL polyethylene bottles were pre-rinsed with water sample three times before the final water sample was collected. Lake water samples were collected at Subei lake, Kuisheng lake and Shahaizi. Cellulose membrane filters (0.45 μm) were used to filter samples for cations and anions analysis. All samples were sealed with adhesive tape so as to prevent evaporation. The global positioning system (GPS) was applied to locate the sampling locations.

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3.2 Analytical techniques

Electrical conductivity (EC), pH value and water temperature of each sample were measured in situ using an EC/pH meter (WM-22EP, Toadkk, Japan), which was previously calibrated. Dissolved oxygen concentration and oxidation–reduction potential were also determined using a HACH HQ30d Single-Input Multi-Parameter Digital Meter. In situ hydrochemical parameters were monitored until these values reached a steady state.

The hydrochemical parameters were analyzed at the Center for Physical and Chemical Analysis of Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences (IGSNRR, CAS). Major ion compositions were measured for each sample, K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} and NO_3^- included. An inductively coupled plasma optical emission spectrometer (ICP-OES) (Perkin-Elmer Optima 5300 DV, USA) was applied to analyze major cations. Major anions were measured on ion chromatography (ICS-2100, Dionex, USA). HCO_3^- concentration of all groundwater samples was determined by the diluted vitriol-methylic titration method using 0.0048 M H_2SO_4 on the day of sampling, methyl orange endpoint titration was adopted with the final pH being 4.2–4.4. Due to extremely high alkalinity of lake water samples, HCO_3^- concentration of all lake water samples was analyzed by titration using 0.1667 M H_2SO_4 .

Hydrogen (δD) and oxygen ($\delta^{18}O$) composition of the water samples were analyzed using Liquid Water Isotope Analyzer (LGR, USA) at the Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences (IGSNRR, CAS). Results were expressed in the standard δ -notation as per mil (‰) difference from Vienna standard mean ocean water (VSMOW, 0‰) with analytical precisions of $\pm 1\%$ (δD) and $\pm 0.1\%$ ($\delta^{18}O$).

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4 Results

4.1 Hydrochemical characteristics

In situ water-quality parameters such as pH, electrical conductivity (EC), temperature, dissolved oxygen concentration (DO), oxidation–reduction potential (ORP) and total dissolved solids (TDS) as well as analytical data of the major ions composition in groundwater, lake water samples are shown in Table 1 and Supplementary Table S1. Based on the chemical data, hydrochemical characteristics of groundwater and lake water are discussed.

The chemical composition for lake water shows that Na^+ and Cl^- are the dominant elements (Fig. 6), which is in accordance with hydrochemical characteristics of inland salt lake. The pH is relatively stable and is always more than 8.4 without obvious seasonal variation, which indicates the dissolved carbonates are in the HCO_3^- and CO_3^{2-} forms simultaneously. The temperatures of lake water range from -6.1 to 24.3°C with a large seasonal variation, which reflects that surface water body is mainly influenced by hydrometeorological factors. Dissolved oxygen concentration of lake water shows an upward tendency from August to December, because the relationship between water temperature and DO is inverse when oxygen content in the air stays relatively stable. With the decreasing water temperature, dissolved oxygen value rises. ORP value is relatively stable over the study period. The average values of major ions show a downward trend except Ca^{2+} , Mg^{2+} from August to December. Before August, the strong evaporation capacity of lake water exceeded the finite recharge amount, which caused lake water to be enriched. After August, lake water was recharged and diluted by groundwater and a plenty of fresh overland flow in answer to precipitation. The EC values vary between 1017 and $229\,000\ \mu\text{S cm}^{-1}$. This relatively large range of variation is closely related to the oscillation of the TDS values, which range from 0.56 to $302.5\ \text{g L}^{-1}$. The results show that lake water chemistry is controlled by strong evaporation and recharge from overland flow and groundwater.

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The hydrochemical data of groundwater were plotted on a Piper triangular diagram (Piper, 1953), which is perhaps the most commonly used method for identifying hydrochemical patterns in major ion composition (Fig. 6). With respect to cations, most of samples are scattered in zones A, B, and D of the lower left triangle, indicating that some are calcium-type, some are sodium-type water, but most of all are mixed-type, as regards anions, most groundwater samples are plotted in zone E of the lower right triangle (Fig. 6), showing that bicarbonate-type water is predominant. The carbonate hardness of most samples exceeds 50 % (Fig. 6, area 5), which is calculated by the sum of Ca^{2+} and Mg^{2+} that could be coupled with HCO_3^- , CO_3^{2-} in solution. As is shown in Fig. 6, the phenomenon that alkaline earths and weak acids exceeded the alkalis and strong acids is common in most groundwater samples. The predominant hydrochemical types are Ca-HCO_3 , Na-HCO_3 and mixed $\text{Ca} \cdot \text{Na} \cdot \text{Mg-HCO}_3$ types.

With respect to the Quaternary groundwater, the pH varies from 7.64 to 9.04 with an average of 8.09 in August and changes from 7.49 to 9.26 with an average of 8.08 in December, indicating an alkaline nature. The TDS varies from 396 to 1202 mg L^{-1} , from 314 to 1108 mg L^{-1} with averages 677 and 625 mg L^{-1} , respectively in August and December. The major cations are Na^+ , Ca^{2+} and Mg^{2+} , while the major anions are HCO_3^- and SO_4^{2-} .

As for the shallow Cretaceous groundwater (< 120 m), the pH varies from 7.37 to 8.3 with an average of 7.77 in August and oscillates from 7.49 to 9.37 with an average of 8.14 in December. The TDS varies from 249 to 1383 mg L^{-1} , from 217 to 1239 mg L^{-1} with averages 506 and 400 mg L^{-1} , respectively in August and December.

For the deep Cretaceous groundwater (> 120 m), the pH varies from 7.75 to 8.09 with an average of 7.85 in August and fluctuates from 7.99 to 8.82 with an average of 8.23 in December. The TDS varies from 266 to 727 mg L^{-1} , from 215 to 464 mg L^{-1} with averages 377 and 296 mg L^{-1} , respectively in August and December.

4.2 Stable isotopic composition of groundwater and surface water

The technique of stable isotopes as excellent tracers, has been widely used by many scholars in the study of hydrological cycle (Chen et al., 2011; Hamed and Dhahri, 2013; Kamdee et al., 2013; Yang et al., 2012a; Cervi et al., 2012; Garvelmann et al., 2012). In the present study, the results of the stable isotope analysis for groundwater and lake water are plotted in Fig. 7. In previous study, the local meteoric water line (LMWL) in the northern Ordos Basin had been developed by Yin et al. (2010). The LMWL is $\delta D = 6.45\delta^{18}O - 6.51$ ($r^2 = 0.87$), which is similar to that developed by Hou et al. (2007) ($\delta D = 6.35\delta^{18}O - 4.69$). In addition, it is very clear in the plot that the LMWL is located below the global meteoric water line (GMWL) defined by Craig (1961) $\delta D = 8\delta^{18}O + 10.56$, which suggests the occurrence of secondary evaporation during rainfall. The LMWL is controlled by local hydrometeorological factors, including the origin of the vapor mass, re-evaporation during rainfall and the seasonality of precipitation (Clark and Fritz, 1997).

In general, δD and $\delta^{18}O$ range from -47 to -87‰ and from -6.2 to -10.8‰ , respectively. The linear regression curve equation of $\delta^{18}O$ and δD in groundwater can be defined as $\delta D = 6.3\delta^{18}O - 13.0$ ($r^2 = 0.62$). Groundwater follows the LMWL in study area, indicating that it is of meteoric origin. In August, the stable isotope values for the Quaternary groundwater were found to range from -9.24 to -7.95‰ in ^{18}O with an average of -8.8‰ and from -74.4 to -61.9‰ in 2H with an average of -70.8‰ ; the shallow Cretaceous groundwater has $\delta^{18}O$ ranging from -9.31 to -7.45‰ and δD varying from -75.0 to -57.4‰ . The average values of $\delta^{18}O$ and δD of the shallow Cretaceous groundwater are -8.3 and -65.6‰ , respectively. The mean values of $\delta^{18}O$ and δD of the shallow Cretaceous groundwater are heavier than those of Quaternary groundwater, showing that the stable isotopic composition of the shallow Cretaceous groundwater was enriched by evaporation. $\delta^{18}O$ and δD of the deep Cretaceous groundwater range from -9.30 to -7.82‰ and from -74.0 to -60.8‰ , respectively. The average values of $\delta^{18}O$ and δD are -8.4 and -66.5‰ , respectively. In December,

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the stable isotope values for the Quaternary groundwater range from -8.93 to -7.16 ‰ in ^{18}O with an average of -8.21 ‰ and from -74.14 to -57.14 ‰ in ^2H with an average of -64.64 ‰; $\delta^{18}\text{O}$ and δD of the shallow Cretaceous groundwater range from -9.65 to -6.53 ‰ and from -73.01 to -57.69 ‰, respectively. The average values of $\delta^{18}\text{O}$ and δD are -8.21 and -64.23 ‰, respectively. The deep Cretaceous groundwater has $\delta^{18}\text{O}$ varying from -10.01 to -7.53 ‰ and δD varying from -75.19 to -59.54 ‰. The average values of $\delta^{18}\text{O}$ and δD of the deep Cretaceous groundwater are -8.54 and -65.51 ‰, respectively.

The regression curve equation of $\delta^{18}\text{O}$ and δD in lake water could be defined as $\delta\text{D} = 1.47\delta^{18}\text{O} - 29.09$ ($r^2 = 0.95$), where $\delta^{18}\text{O}$ ranges from -5.83 to 29.40 ‰ and δD ranges from -45.5 to 14.95 ‰ with averages 14.3 and -10.49 ‰ in August; while in December, $\delta^{18}\text{O}$ and δD of lake water range from -2.61 to 16.2 ‰ and from -28.46 to -9.43 ‰, respectively. The average values of $\delta^{18}\text{O}$ and δD are 4.37 and -20.89 ‰, respectively in December.

5 Discussion

Generally speaking, water-rock interactions are the most important factors of influencing the observed geochemical composition of groundwater (Appelo and Willemsen, 1987), the geochemical and isotopic results of this work are no exceptions. In terms of dissolved minerals and the correlation of geochemical parameters, the dominant geochemical processes could be found (Su et al., 2009). The weathering and dissolution of minerals in the host rocks and ion exchange are generally the main source of ions in groundwater on a basis of available researches. The stable isotopes signatures in lake water can reveal the predominant mechanism controlling the chemical composition of lake water.

5.1 Correlation of geochemical parameters

Correlations among groundwater-quality parameters are shown in Fig. 8 and Table 2. All of the major cations and anions are significantly correlated with TDS (Table 2), which shows that these ions have been dissolved into groundwater continuously, and then resulted in the rise of TDS.

A good correlation between Mg^{2+} and HCO_3^- could be seen in Table 2, indicating that the weathering of dolomite release ions to the groundwater. Ca^{2+} has a good correlation with SO_4^{2-} , implying that the dissolution of gypsum and anhydrite may be the key processes controlling the chemical composition. Just as the achievements obtained by Hou et al. (2006), gypsum and anhydrite are present in these strata, so it is reasonable to consider that gypsum and anhydrite are the source of the SO_4^{2-} . There is no good correlation between Na^+ and SO_4^{2-} , suggesting that weathering of Glauber's salt ($Na_2SO_4 \cdot 10H_2O$) may not be the major sources of such ions in groundwater. Although there is no obvious correlation between Ca^{2+} and HCO_3^- , it is reasonable to regard the dissolution of carbonate minerals as a source of Ca^{2+} and HCO_3^- due to widespread occurrence of carbonate rocks in the study area. The concentration of Mg^{2+} is well correlated with SO_4^{2-} , suggesting the potential, possible dissolution of gypsum, followed by cation exchange. The pH is negatively correlated with Ca^{2+} , it is likely that the dissolution of carbonate minerals is constrained due to the reduction of hydrogen ion concentration in water at higher pH.

In order to explore the mechanism of salinity in semi-arid regions, the plot of Na^+ vs. Cl^- is widely used (Dixon and Chiswell, 1992; Magaritz et al., 1981; Sami, 1992). The concentration of Cl^- is well correlated with Na^+ , with correlation coefficient of 0.824, suggesting that the dissolution of halite may be the major source of Na^+ and Cl^- . Theoretically, the dissolution of halite will release equal amounts of Na^+ and Cl^- into the solution. Nevertheless, the results deviate from the anticipated 1 : 1 relation. Almost all samples have more Na^+ than Cl^- . The molar Na/Cl ratios vary from 0.68 to 16.00 with an average value of 3.48. Greater Na/Cl ratios may be ascribed to the feldspar

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5.2 Cation exchange

Cation exchange is an important process of water-rock interaction that obviously influences the major ion composition of groundwater (Xiao et al., 2012). Molar Na/Ca ratios change between 0.5 and 106.09 with an average of 3.80, suggesting the presence of Na⁺ and Ca²⁺ exchange. It could be conveyed as the following reaction:



where X is sites of cation exchange.

Schoeller proposed that chloro-alkaline indices could be used to study the ion exchange (Marghade et al., 2012; Schoeller, 1965; Li et al., 2013). The Schoeller indices, such as CAI-I and CAI-II, are calculated by the following equations:

$$\text{CAI-I} = \frac{\text{Cl}^- - (\text{Na}^+ + \text{K}^+)}{\text{Cl}^-} \quad (1)$$

$$\text{CAI-II} = \frac{\text{Cl}^- - (\text{Na}^+ + \text{K}^+)}{\text{HCO}_3^- + \text{SO}_4^{2-} + \text{CO}_3^{2-} + \text{NO}_3^-} \quad (2)$$

Where all ions are expressed in meq L⁻¹. If the Schoeller indices are negative values, Ca²⁺ will be removed from solution, and Na⁺ will be released into the groundwater. If the positive values are obtained, then the inverse reactions possibly occur. In the present study, almost all groundwater samples had negative Schoeller index values (Supplement Table S1). The results show clearly that Na⁺ is released by Ca²⁺ exchange indeed, which is a common form of cation-exchange in the study area.

5.3 The chemistry formation mechanisms of groundwater and surface water

The saturation index is one of vital geochemical parameters in hydrogeology and geochemistry field, which is usually useful for identifying the existence of some

common minerals in the groundwater system (Deutsch, 1997). In this present study, saturation indices (SI) with respect to gypsum, anhydrite, calcite, dolomite, aragonite and halite were calculated in terms of the following equation (Lloyd and Heathcote, 1985):

$$5 \quad SI = \log \left(\frac{IAP}{k_s(T)} \right) \quad (3)$$

Where IAP is the relevant ion activity product, which could be calculated by multiplying the ion activity coefficient γ_i and the composition concentration m_i , and $k_s(T)$ is the equilibrium constant of the reaction considered at the sample temperature. The geochemical computer model PHREEQC (Parkhurst and Appelo, 2004) was used to
10 calculate the saturation indices. When the groundwater is saturated with some mineral, SI equals zero; positive values of SI represent oversaturation, and negative values show undersaturation (Appelo and Postma, 1994; Drever, 1997).

Figure 10 indicates the plots of SI vs. the total dissolved solids (TDS) for all the groundwater samples. The modeled values of SI for anhydrite, gypsum and halite oscillate between -5.27 and -1.11 , -4.8 and -0.65 , -8.61 and -5.9 with averages -2.62 , -2.16 , -7.49 , respectively. It shows that the groundwater in study area was
15 below the equilibrium with anhydrite, gypsum and halite, indicating that these minerals are anticipated to dissolve. However, the SI of aragonite, calcite, and dolomite range from -0.74 to 1.09 , -0.59 to 1.25 , and -1.16 to 2.64 with averages 0.32 , 0.48 , and
20 0.81 , respectively. On the whole, the groundwater samples were dynamically saturated to oversaturated with aragonite, calcite and dolomite, representing that the three major carbonate minerals may have affected the chemical composition of groundwater in Subei Lake Basin. The results show that the groundwater may well produce the precipitation of aragonite, calcite and dolomite. Saturation of aragonite, calcite and
25 dolomite could be attained quickly due to the existence of abundant carbonate minerals in the groundwater system.

The soluble ions in natural waters mainly derive from the rock and soil weathering (Lasaga et al., 1994), anthropogenic input, and partly from the precipitation input.

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In order to make an analysis of the formation mechanisms of hydrochemistry, Gibbs diagrams have been widely used in hydrogeochemical studies (Feth and Gibbs, 1971; Marghade et al., 2012; Naseem et al., 2010; Xing et al., 2013; Yang et al., 2012b). Gibbs (1970) recommended two diagrams to assess dominant effects of precipitation, rock weathering, or evaporation on geochemical evolution of groundwater in semi-arid and arid regions. The diagrams show the weight ratios of $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ and $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ against TDS, and precipitation dominance, rock dominance, and evaporation dominance are included in the controlling mechanisms (Gibbs, 1970). The distributed characteristic of samples in Fig. 11 shows that rock weathering is the dominant mechanism in the geochemical evolution of the groundwater in the study area. The ratios of $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ were mostly less than 0.5 in shallow and deep Cretaceous groundwater, with low TDS values (Fig. 11). It shows that rock weathering was the main mechanism controlling the chemical compositions of shallow and deep Cretaceous groundwater. In the Quaternary groundwater, about 2/3 of samples had the ratios of $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ greater than 0.5 and higher TDS between 314 and 1202 mg L^{-1} , which indicated that the Quaternary groundwater was not only controlled by rock weathering, but also by evaporation-crystallization process. It is obvious that the weight ratios of cations $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ spread from low to high without great variation of TDS, which indicated that cation exchange also played a role by increasing Na^+ and decreasing Ca^{2+} under the background of rock dominance. During the cation exchange process, the TDS values do not change obviously because 2 mmol L^{-1} of Na^+ is released by 1 mmol L^{-1} Ca^{2+} exchange, and the weight of 1 mmol L^{-1} of Ca^{2+} (40 mg L^{-1}) is nearly equal to that of 2 mmol L^{-1} of Na^+ (46 mg L^{-1}).

As is shown in isotopic results of the present study, no matter in August or December, the deep Cretaceous groundwater is depleted in heavy isotopes, compared to the shallow Cretaceous groundwater. The relatively depleted characteristics of the deep Cretaceous groundwater indicate a paleorecharge effect (Clark and Fritz, 1997) and Therefore, the hydrogen and oxygen isotopes signatures in deep Cretaceous groundwater may reflect that the renewability of deep Cretaceous groundwater is

low and it was recharged during a geologic period when the climate was wetter and colder than today. The hydrogen and oxygen isotopes signatures in lake water show that lake water contains abnormally high levels of heavy isotopic composition. Compared with the stable isotopic values of groundwater, it is evident that lake water undergoes a greater degree of enrichment in heavy isotopes, which further illustrates that fractionation by strong evaporation is occurring predominantly in the lake water. This also proves to be in accordance with the unique hydrochemical characteristics of lake water.

6 Conclusions

The present study examines the hydrochemical and isotopic composition of the groundwater and surface water in the Subei Lake Basin with various methods such as correlation analysis, saturation index, Piper diagram and Gibbs diagrams. The combination of major elements geochemistry and stable isotopes ($\delta^{18}\text{O}$, δD) has provided a comprehensive understanding of the hydrodynamic functioning and the processes of mineralization that underpin the geochemical evolution of the whole water system within the study area. The hydrochemical data of the present study clarifies that the dominant water type of lake water was Na-Cl type, which was controlled by strong evaporation and recharge from overland flow and groundwater; the predominant hydrochemical types for groundwater are Ca-HCO₃, Na-HCO₃, and mixed Ca·Na·Mg-HCO₃ types, which are the results of the water-rock interaction such as dissolution/precipitation of anhydrite, gypsum, halite and calcite, the dedolomitization, etc. Furthermore, the cation exchange has also played an extremely vital role in the groundwater evolution. The absolute predominance of rock weathering in the geochemical evolution of the groundwater of the study area is confirmed by the analytical results of Gibbs diagrams. The stable isotopic data indicate that groundwater is of meteoric origin. The deep Cretaceous groundwater is depleted in heavy isotopes, compared to the shallow Cretaceous groundwater. The hydrogen and oxygen isotopes

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signatures in deep Cretaceous groundwater may reflect that the deep Cretaceous groundwater was recharged during a geologic period when the climate was wetter and colder than today. Due to strong evaporation effect and dry climatic conditions, heavy isotopes are extremely enriched in lake water.

5 With the fast development of coal-mining and related industries, groundwater over-exploitation has taken place. If it continues, it may cause a series of negative impacts on the groundwater-dependent ecosystem around Subei lake. As a result, a scientifically reasonable groundwater resources management policy should be designed so as to minimize the negative impacts of anthropogenic activities on the water system, and in
10 the future more eco-hydrological studies in Subei Lake Basin are urgently needed to do from the view of sustainable development of natural resources environment.

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doi:10.5194/hessd-11-5709-2014-supplement.**

15 *Acknowledgements.* This research was supported by the State Basic Research Development Program (973 Program) of China (Grant No. 2010CB428805) and the International Green Peace Organization. The authors are grateful for our colleagues for their assistance in sample collection and analysis.

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Table 1. The chemical composition and isotopic data of lake water in August and December 2013.

ID	Date	EC ($\mu\text{S cm}^{-1}$)	T ($^{\circ}\text{C}$)	pH	DO (mg L^{-1})	ORP (mV)	K^{+} (mg L^{-1})	Na^{+} (mg L^{-1})	Ca^{2+} (mg L^{-1})	Mg^{2+} (mg L^{-1})
EEDS08	29 Aug 2013	130 400	22.5	10.11	11.06	-1.8	1956	42 020	2.28	3.01
EEDS09	29 Aug 2013	190 100	24.3	10.25	15.8	-14.8	6475	96 530	0.00	2.4
EEDS38	30 Aug 2013	1017	23.7	8.86	7.65	61.8	10.63	97.59	17.21	70.03
EEDS08	6 Dec 2013	120 400	-3.8	8.9		17.6	1997.73	36 617.7	11.52	3.7
EEDS09	6 Dec 2013	229 000	-6.1	8.49		39.5	7567	77 840	36.34	11.39
EEDS38	4 Dec 2013	4200	1.1	10.47	17.96	26.3	38.88	602	9.06	352.2
EEDS60	4 Dec 2013	14 080	2.7	9.04	10.58	23.6	56.154	3393.74	4.27	41.49
		Cl^{-} (mg L^{-1})	SO_4^{2-} (mg L^{-1})	HCO_3^{-} (mg L^{-1})	CO_3^{2-} (mg L^{-1})	NO_3^{-} (mg L^{-1})	TDS (mg L^{-1})	δD (‰)	$\delta^{18}\text{O}$ (‰)	
EEDS08	29 Aug 2013	37 440.28	22 066.83	6000.3	19 356.45	98.93	125 943.93	-0.97	19.35	
EEDS09	29 Aug 2013	108 517.4	37 581.86	12 661.65	46 565.53	511.48	302 514.49	14.95	29.4	
EEDS38	30 Aug 2013	32.71	92.85	480.68	0	1.07	562.43	-45.46	-5.83	
EEDS08	6 Dec 2013	30 787.74	7513.4	5186.7	19 406.47	87.48	99 019.09	-17.55	5.78	
EEDS09	6 Dec 2013	113 003.44	5276.76	11 593.8	13 754.59	207.99	223 494.4	-9.43	16.2	
EEDS38	4 Dec 2013	164.54	448.23	1423.8	900.3	9.53	3236.64	-28.11	-2.61	
EEDS60	4 Dec 2013	1418.76	386.04	1067.85	2600.87	11.77	8447.02	-28.46	-1.87	

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Table 2. Correlation coefficient of major parameters in groundwater.

	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	TDS	pH
K ⁺	1.000	0.538	0.309	0.560	0.553	0.300	0.572	0.534	-0.063
Na ⁺		1.000	0.217	0.651	0.824	0.485	0.602	0.728	-0.072
Ca ²⁺			1.000	0.754	0.375	0.665	0.478	0.796	-0.600
Mg ²⁺				1.000	0.655	0.819	0.582	0.939	-0.382
Cl ⁻					1.000	0.375	0.576	0.776	-0.144
SO ₄ ²⁻						1.000	0.160	0.770	-0.226
HCO ₃ ⁻							1.000	0.625	-0.398
TDS								1.000	-0.378
pH									1.000

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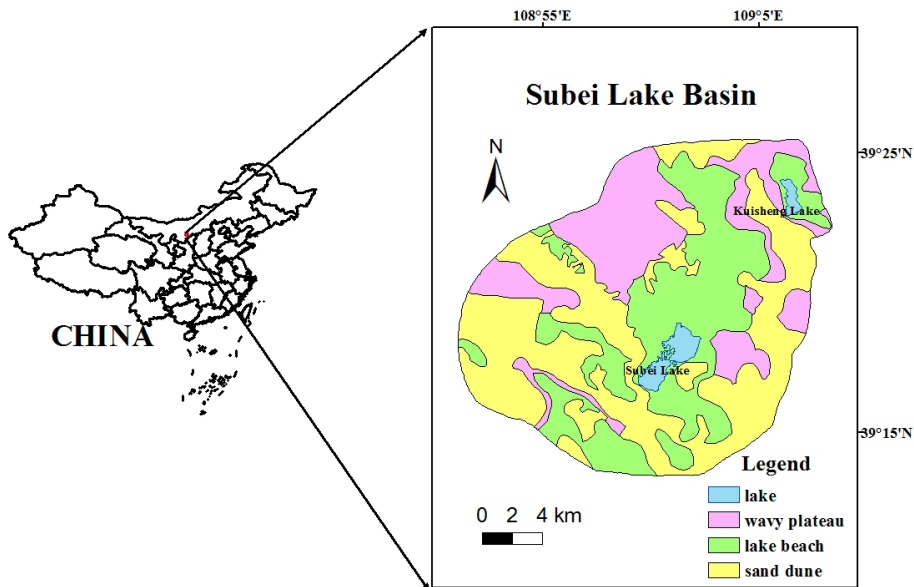


Figure 1. Location of the study area and geomorphic map.

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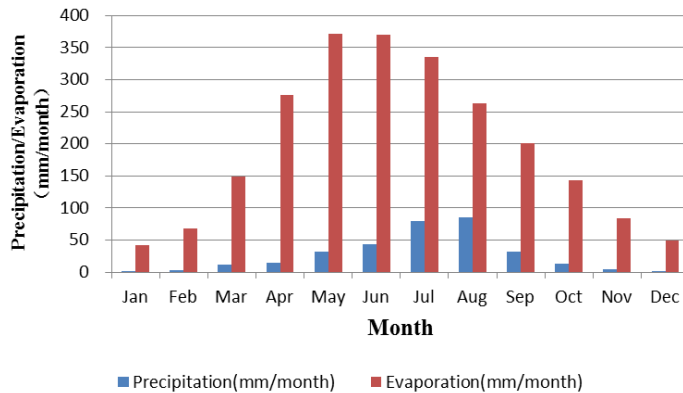


Figure 2. Average monthly precipitation and evaporation in the study area.

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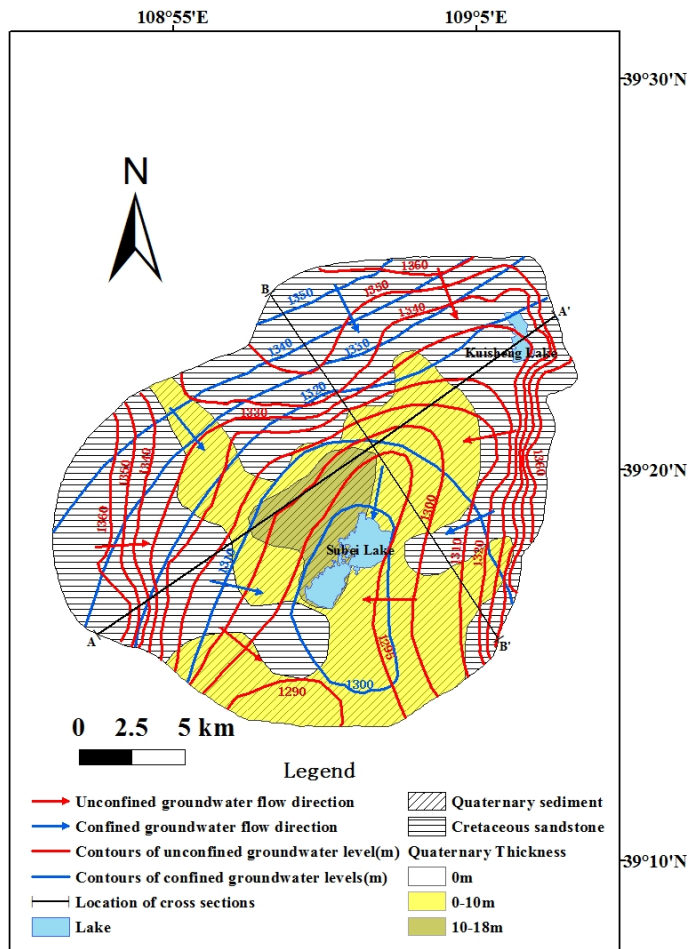


Figure 3. Hydrogeological map of the study area. Data source: revised from original source (Inner Mongolia Second Hydrogeology Engineering Geological Prospecting Institute, 2010).

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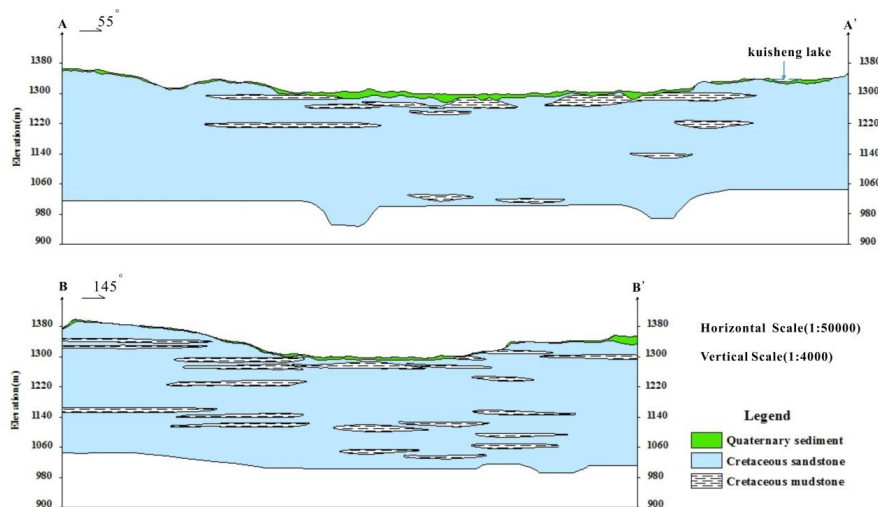


Figure 4. Geologic sections of the study area. Data source: revised from original source (Inner Mongolia Second Hydrogeology Engineering Geological Prospecting Institute, 2010).

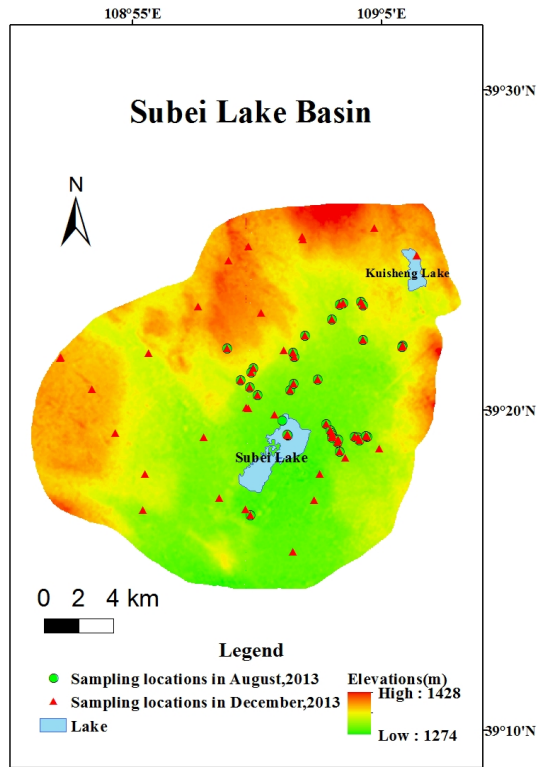


Figure 5. Sampling locations in August and December 2013.

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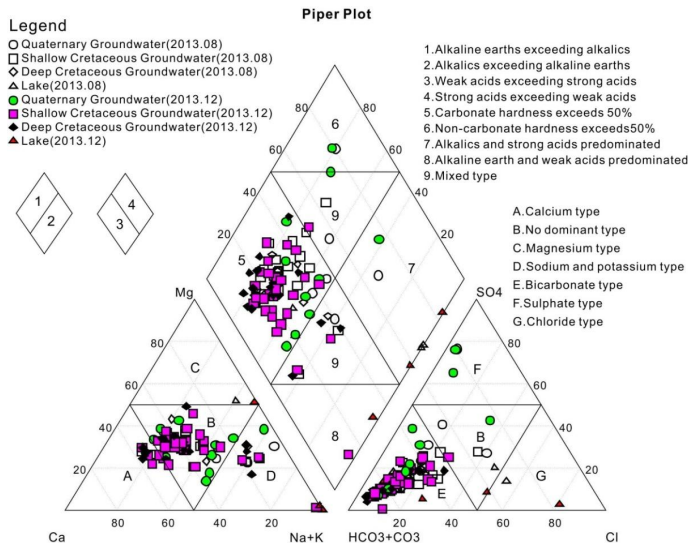


Figure 6. Piper diagram of groundwater and lake water in August and December 2013.

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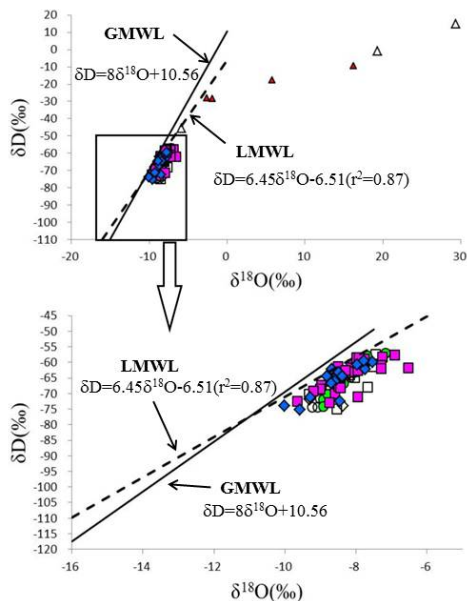
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Legend

- Quaternary Groundwater(2013.8)
- Shallow Cretaceous Groundwater(2013.8)
- ◇ Deep Cretaceous Groundwater(2013.8)
- △ Lake(2013.8)
- Quaternary Groundwater(2013.12)
- Shallow Cretaceous Groundwater(2013.12)
- ◆ Deep Cretaceous Groundwater(2013.12)
- ▲ Lake(2013.12)

Figure 7. Relationship between hydrogen and oxygen isotopes in groundwater and lake water in August and December 2013.

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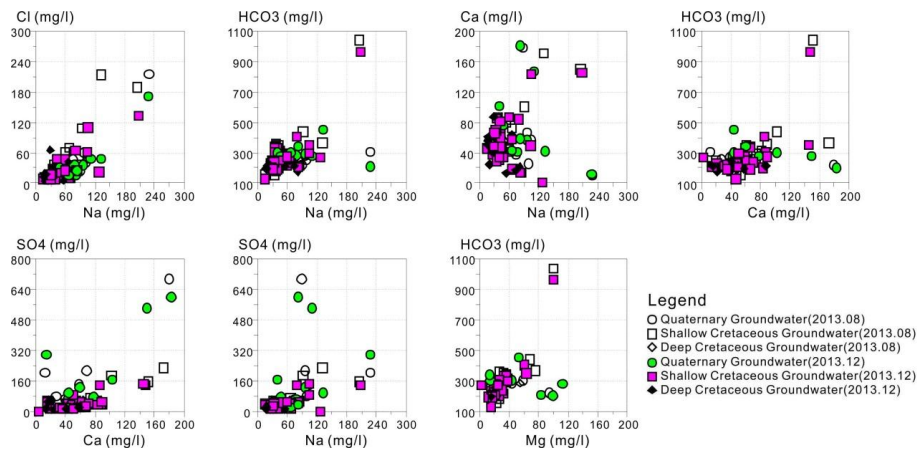


Figure 8. Inter-ionic relationships between ions in groundwater.

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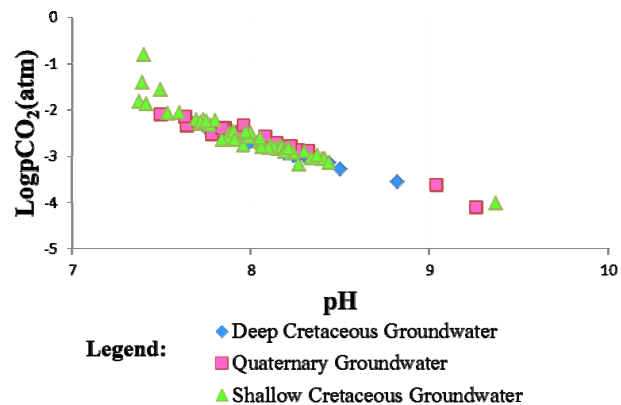
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**Figure 9.** Geochemical relationship of pH vs. Log ($p\text{CO}_2$) in groundwater.[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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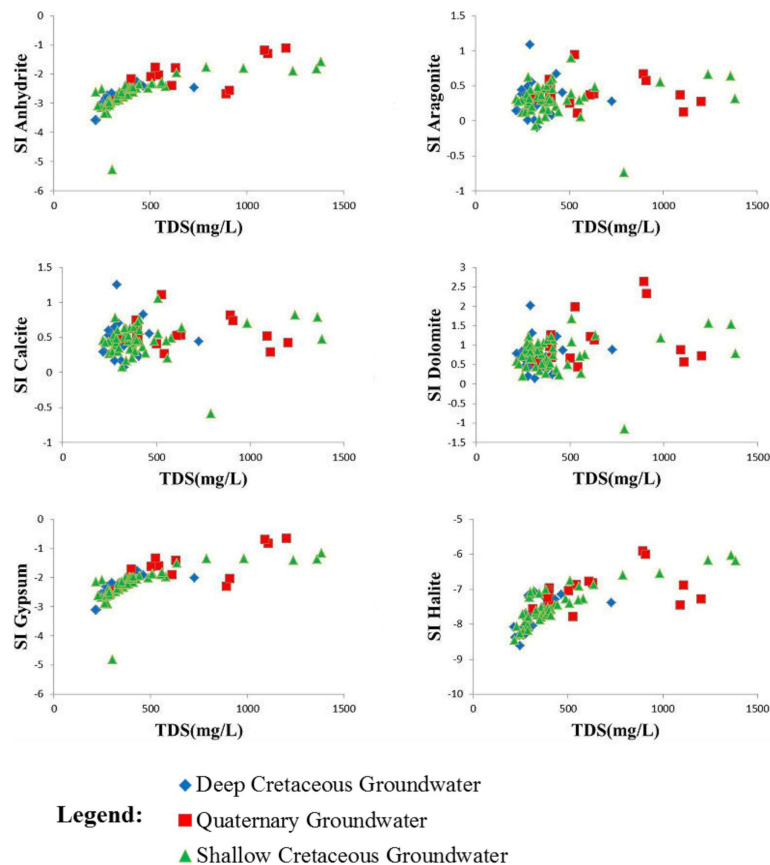


Figure 10. Plots of saturation indices with respect to some minerals in groundwater.

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Interactive Discussion



Identifying the origin and geochemical evolution of groundwater

F. Liu et al.

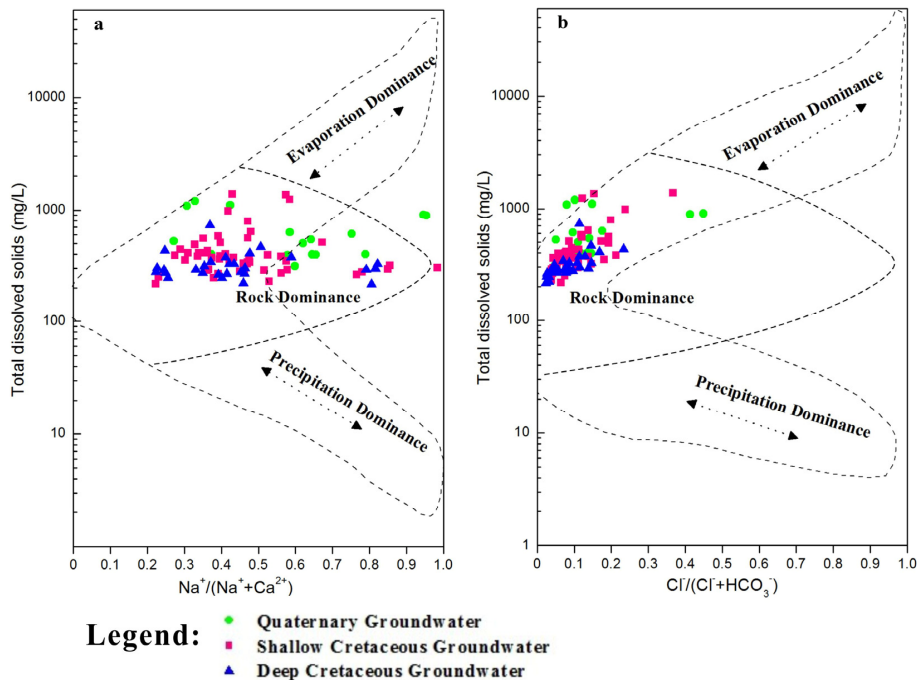


Figure 11. Gibbs diagram of groundwater samples in the Subei Lake Basin: **(a)** TDS vs. $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$, **(b)** TDS vs. $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$.