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Hydrogeochemistry and Netpath Modeling of Groundwater in Taklimakan Desert, China†

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The eco-environment is highly dependent on groundwater in arid areas, especially in desert. Because of the scarcity of surface water resources within the Taklimakan desert, a groundwater-fed water supply system was constructed by Shelter-forest ecological engineering and oilfield engineering in the hinterland of the desert. The groundwater's TDS concentrations were relatively high in the north and lower in the south. A continuous evaporation and leached effects lead to the downstream ion concentration increased. Natural rock salt was dissolved always and the calcite was at precipitation state, resulting in a decrease of the HCO_3^- concentration. Due to the fewer amounts of orthoclase and the precipitation state of muscovite in chemical reaction, the potassium content was low in groundwater solution. The above processes may ultimately results in a groundwater of Cl-SO_4-Na type that resulting in the formation of brine in the downstream.

Keywords: Hydrogeochemistry, Simulation, Netpath, Groundwater, Desert.

INTRODUCTION

Intense human activities and climatic changes have had negative influences on much environmental chemical process within arid areas. This has aggravated the salinization of groundwater and induced the problem of ecological environmental degradation, such as water quality deterioration, vegetation deterioration and desertification[1,2]. Groundwater plays a very important role in the maintenance of ecological balance in desert. Taklimakan desert is the largest sand dune in China and the world's second largest shifting sand desert, occupied area about 337,000 km^2 in the Tarim Basin of northwest China[3]. Although the study of groundwater chemistry was a focus and hotspot in the groundwater science fields, they have not yet been fully involved in the Taklimakan Desert.

Mondal *et al.*[4] believe that by studying the chemical composition of groundwater may reflect the interaction between groundwater and seawater. Malcolm and Soulsby[5] explored hydro geochemical of coastal wetlands in different hydrogeological unit of the Scottish and simulate the water-rock interaction model using NETPATH. However, knowledge about the evolution process of groundwater chemical composition in the Taklimakan desert is still quite limited. Tarim Basin is located in the arid areas of northwest China. Taklimakan desert located in the central of the basin has rich oil-gas resources. The objective of this paper is to present the zonality of hydrochemistry of groundwater in the unconsolidated sediment aquifer in the Taklimakan Desert. An inverse hydrogeochemical simulation was realized and applied to the desert using the program NETPATH. This is especially true for research focusing on chemical characters and formation mechanisms.

EXPERIMENTAL

Study area: Taklimakan Desert is the second largest mobile desert in the world which is located in the central region of the Tarim Basin. The ground landscape are mainly mobile dunes and large complex dune chains. The annual mean temperature is 12.4 ºC, with the highest temperature of 45.6 ºC and the lowest temperature of -22.2 ºC. The annual precipitation of the central desert region is 10.7 mm and annual potential evaporation is up to 3 806.4 mm[6]. Tarim basin is surrounded by a series of tall and large mountains which make the climate to be drought and rainless. The terrain nearby the piedmont is higher and nearby the desert is lower. The terrain slopes from west-east and the slope is generally among 1-3 ‰. The south edge of the basin is the Kunlun mountains and the north edge of the basin is the Tianshan mountains. The central part of the basin is the Tarim platform which is composed of a series of uplifts and depression basins. Mesozoic and tertiary age geology are mainly exposed in the surrounding hills and plain uplifts and most of the ancient bedrock is exposed as outcrops. Quaternary geology is widely distributed

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in the piedmont and desert plains. Thick loose materials of tertiary and quaternary age deposit and become the vehicle of groundwater storage and flow space. In the central part of the basin, Taklimakan desert becomes the surface water and groundwater collection, runoff and evaporation discharge area. The Lop Nor, located at the east of the Tarim basin is the catchment center of the basin convergence[7,8]. The shallow groundwater aquifers along the sampling section mainly contain fine sand. Sediment particles found in these aquifers are mostly very fine sand, with very low content of clay particle[9].

Observation wells: The groundwater observation sections were set up along the Luntai-Tazhong-Kalamilan hydrogeological profile that traversed north-south through the Taklimakan desert (Fig. 1). The overall trend of shallow groundwater flowed from south to north. Tarim river is the lowest point of the terrain on the north and south sides. A numbers of wells selected for groundwater observation wells. Numbers GY 1 to GY 9 were vertically into the River. Numbers GR 1 to GR 3 were springs water points. Total five numbers represented surface water sampling points.

Water samples: Sampling point position were measured used the GPS measurement system (Model X90, Huace Ltd., China) in conjunction with the water level contour map (Fig. 1). EC of samples was measured using a TLC meter (107, Solinst Ltd., Canada). Subsequently, The measurement of ions in the water samples was performed by using ion chromatography (Model DX-100, Dionex Ltd., US). The $CO_3^{2-}$and HCO_3^- concentrations were measured by Titrino Automatic Potentiometric Titrator (Model 702 SM, Metrohm, Switzerland) and c = 0.1017 mol L^{-1} HCl. TDS were tested for by using the 180 ºC drying weight method[10]. Measurement of pH was performed using a pH meter (Model PHS-3C, Shanghai Lici Ltd., China). Water chemistry data were analyzed using SAS statistical software (version 9.1, sas institute inc.).

Hydrological chemical model: The hydrological chemical models were used to explain the evolution of the components of the groundwater and reveal the chemistry evolution rules of regional groundwater. NetpathXL is a revised version of NETPATH that runs under Windows operating systems. NETPATH is a computer program that uses inverse geochemical modeling techniques to calculate net geochemical reactions that can account for changes in water composition between initial and final evolutionary waters in hydrologic systems[11,12]. The mineral saturation indices and solution distribution were calculated by inputting the water chemistry data and selecting a set of constraints and phase state. The possible hydrogeochemical evolution process can be determined by NETPATH. Three reaction simulated paths (AB, CD and EF) were chosen.

RESULTS AND DISCUSSION

Groundwater chemical characteristics: The highest value of the groundwater TDS was up to 30.246 mg L^{-1} and the lowest value was 3.093 mg L^{-1}. Fig. 2 showed the TDS values in north were larger than the south. The central section showed small TDS variations and compared with the spatial distribution of TDS along the groundwater levels which were along the groundwater flow directions. The TDS of the upstream groundwater were slightly above that of the midstream, but far more lower than that of the downstream. The possible reason was that most soluble minerals dissolved slowly in water and the longer time water contacted soluble minerals resulted in higher TDS, which was the reason that high salinity levels were evident in the north of the desert[13]. On the other aspect, there was a trend of diminishing mineral composition from upstream to downstream within the rivers originated from the northern foot of the Kunlun mountains[14]. The southern part of the desert is an upstream area where groundwater actively recharges. Here, soluble mineral content in the stratum is higher than that of the middle and lower reaches. However, the TDS values found in the upstream were slightly higher than the midstream. The pH values were mostly alkaline of 7.35-8.38. The characteristics of the water were spatially random and had no obvious regularity. Among the soluble ions, HCO_3^- showed the opposite spatial distribution trend to TDS, decreased from the groundwater recharge area at the piedmont of the Kunlun Mountains to the desert runoff process. Potassium ion was most stable and contrary to the

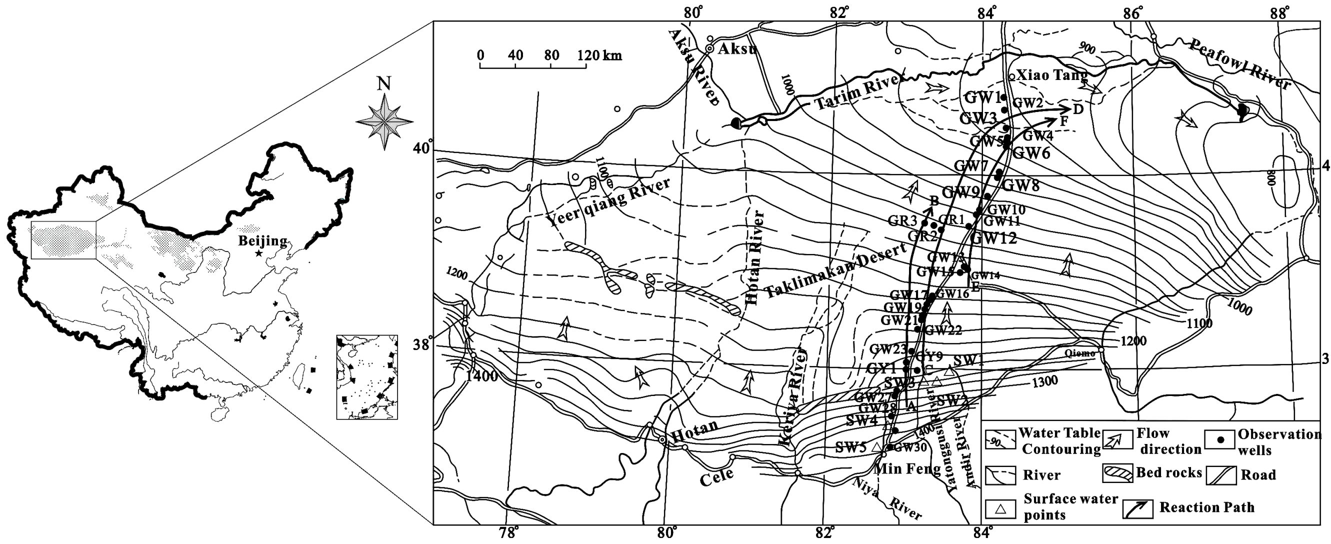

Fig. 1. Location of the study area, black dots indicate the location of the observation wells

spatial distribution trend of TDS and showed no obvious spatial distribution rule. The spatial distribution of other soluble ions showed an increasing concentration trend in the groundwater runoff process and was consistent with the spatial distribution of the TDS values of groundwater (Fig. 2).

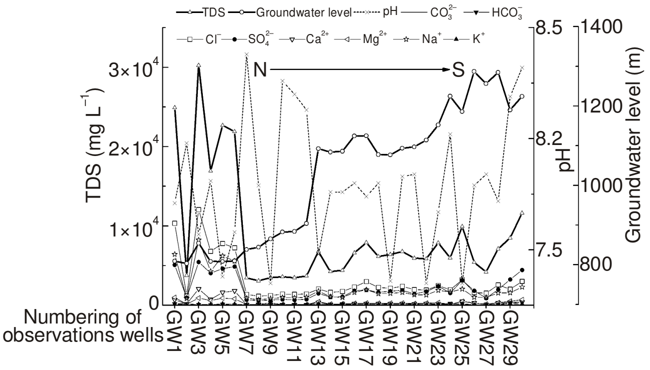

Fig. 2. Spatial difference of groundwater chemical characteristics and water level

Based on the descriptive statistics of the major ions of the cross-section of groundwater as well as the TDS and pH values of the water chemistry data, it is evident that the groundwater chemistry shows a large spatial variability. This is due to the effect of aquifer media, topography, hydrogeological conditions, human activities and other factors. The mean values and standard deviation of Cl^-, SO_4^{2-}, Na^+, Ca^{2+} were larger, indicating higher absolute levels. It is the variability of ions that plays a decisive role controlling TDS and the typical ion could be representative of the features of water samples. The concentration of CO_3^{2-} in all the samples was almost zero, with CO_3^{2-} detected in only one sample with a concentration of 23 mg L^{-1}. This single occurrence resulted in a larger coefficient of variation, but was not representative. The remaining ions had a larger coefficient of variation, reflecting the high spatial dispersion and indicating that they are sensitive to changes in environmental factors. The pH value of each statistic was very small and reflected the relative stability of pH. Climate change and Water-rock interaction in a long historical period resulted in transformation of Cl-SO_4-Na-Mg into the Cl-SO_4-Na and Cl-SO_4-Na-Ca along the groundwater flow direction.

Statistical characteristics of main ions: The correlation matrix of water chemical composition is shown in Table-1. TDS and Cl^- were significantly correlated with Na^+, with the correlation coefficients being 0.986 and 0.993, respectively. The correlations between SO_4^{2-}, Ca^{2+} and Mg^{2+} were significant with the correlation coefficients reaching more than 0.9. The correlation between pH, CO_3^{2-} and HCO_3^- was poor. Due to the absolute contents of CO_3^{2-} and HCO_3^- being small, the correlation of CO_3^{2-} and HCO_3^- with the other ions were weak. HCO_3^- showed a negative correlation with Cl^-, Ca^{2+} and Na^+. The relationship between Ca^{2+}, Mg^{2+} and Na^+ and Cl^- and SO_4^{2-} show a strong correlation, with the correlation coefficients being greater than 0.8. The content of K^+ was relatively low, resulting in the correlation between K^+ and SO_4^{2-} and Mg^{2+} being 0.65 and 0.685, respectively. The correlation between K^+ and other ions was weak, with the correlation coefficients < 0.5. The Taklimakan desert was a phreatic runoff discharge area, where evaporation played a dominant role. Within the groundwater flowed from the upstream region to desert, there was a gradual increase in Na^+ content and TDS of groundwater, while HCO_3^- had a gradually decreasing trend.

Factor analysis of ion ratio: The contributing factor coefficient of groundwater, also known as the rNa^+/rCl^- coefficient, reflects a hydro-geochemical parameter that was characterized by the sodium ion concentration in the groundwater. The functional relationship between Na^+ and Cl^- within the groundwater samples is shown in Fig. 3. Rock salt dissolved in the aqueous solution and released Na^+ and Cl^- of similar amounts. Data analysis showed that the value of the scale factor for rNa^+/rCl^- was being close to 1:1 and its function was as follows:

$$Y = 0.9271X + 0.4946 \ (R^2 = 0.9794) \qquad (7)$$

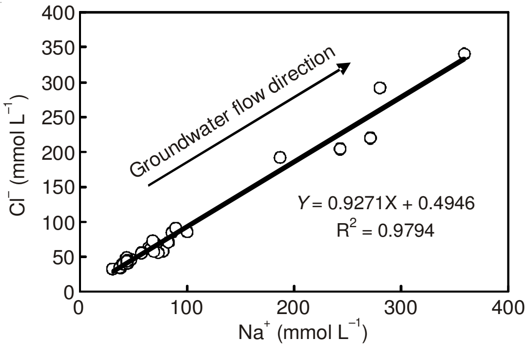

Fig. 3. rNa^+ *versus* rCl^- values and their correlation

It was shown that the chemical composition of groundwater was mainly formed with rock salt stratum by weathering and lixiviation. Fig. 4 shows that within the region of groundwater TDS < 4,000 mg L^{-1}, the rNa^+/rCl^- coefficient presented an upward trend and essentially increased with increasing TDS. This indicates that in the low salinity water within the

TABLE-1
CORRELATION COEFFICIENTS MATRICES OF GROUNDWATER HYDROCHEMICAL PARAMETERS, N = 30

	HCO_3^-	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+	TDS	pH
HCO_3^-	1	–	–	–	–	–	–	–	–
Cl^-	-0.079	1	–	–	–	–	–	–	–
SO_4^{2-}	0.203	0.882^{**}	1	–	–	–	–	–	–
Ca^{2+}	-0.121	0.878^{**}	0.831^{**}	1	–	–	–	–	–
Mg^{2+}	0.157	0.892^{**}	0.973^{**}	0.840^{**}	1	–	–	–	–
Na^+	-0.059	0.990^{**}	0.895^{**}	0.922^{**}	0.909^{**}	1	–	–	–
K^+	0.378^{*}	0.428^{*}	0.650^{**}	0.468^{**}	0.685^{**}	0.473^{**}	1	–	–
TDS	0.001	0.986^{**}	0.937^{**}	0.917^{**}	0.943^{**}	0.993^{**}	0.521^{**}	1	–
pH	0.175	-0.309	-0.243	-0.367^{*}	-0.304	-0.320	-0.142	-0.313	1

Note: The ** indicated the correlation is significant at 0.01 level. The * indicated the correlation is significant at 0.05 level.

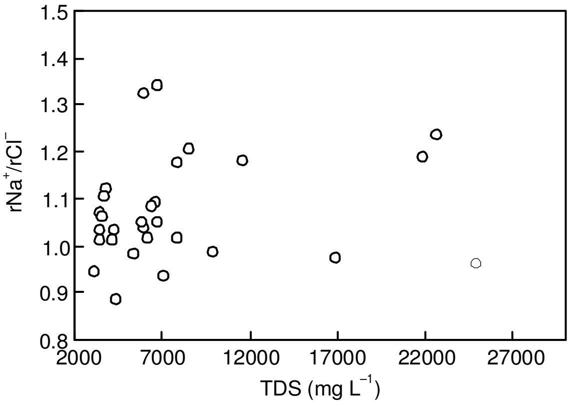

Fig. 4. Change of rNa^+/rCl^- *versus* TDS

groundwater flow path and an increasing retention time, the concentration of Na^+ increased due to the weathering of minerals. In addition to the trend evident, when the groundwater TDS > 4,000 mg L^{-1}, rNa^+/rCl^- presented a declining trend. Na^+ carried out ion exchange with Ca^{2+} and Mg^{2+} that was adsorbed by clay minerals in the water content layer. In contrast, HCO_3^- and SO_4^{2-} precipitation occurred, causing an enrichment of Cl^-.

Groundwater chemical evolution model: In order to further understand the groundwater evolution characteristics from upstream to downstream, the simulation modeling approach was adopted. Taklimakan desert climate is extremely dry with very little rainfall. The surface leaching process is weak and controlled by the centripetal terrain. Salt generally accumulates in the basin, thereby increasing sources of soluble salts to rivers and underground runoff, which is one of the most important factors that affect the chemical composition of groundwater. The formation and evolution of groundwater was analyzed using NETPATH. Within the analysis, there was first a need to identify constraints and possible reaction phase states. According to the test results of groundwater quality, the constraints were identified as carbon, calcium, magnesium, sodium, potassium, sulfur and chlorine. According to analysis of current data, the light mineral composition (specific gravity < 2.84) in sedimentary mineral had a high level generally > 90 % in the desert areas and flood plains of southern slope of the Kunlun Mountains[15,16]. The amphibole minerals dominate the heavy minerals (specific gravity > 2.84) with a range of 30-72 % content, but mostly around 40-55 %.

Desert groundwater depth was very shallow (about 2-4 m[17]) between low-lying sand dunes, it can be affected by the strong evaporation. In study area, the precipitation was very rare or ignored because of almost 10 months without rain but evaporation potential was unusually huge. Thus, the evaporation factor was a very important parameter. Other than, ion exchange (Ca/Na exchange) was the important factors to effect the concentration of sodium, calcium and magnesium. When pH > 7.4 and TDS > 600 mg/L $Ca^{2+}$and HCO_3^- generated calcium carbonate precipitation. In the absence of excessive alkalinity, the dolomitization could occur, calcium was released and settle down in the form of gypsum. The important reactions were $Ca^{2+} + 2HCO_3^- = CaCO_3 + CO_2 + H_2O$ and $Ca^{2+} + 2H_2O + SO_4^{2-} \rightarrow CaSO_4{\cdot}2H_2O$. At the same time, Na^+ in the water could carry out ion exchange with Ca^{2+}, Mg^{2+} in the soil and resulting in Na^+ accumulation in the soil. These important reactions were $2Na^{+(water)} + Ca^{2+(soil)} = Ca^{2+(water)} + 2Na^{+(soil)}$ and $2Na^{+(water)} + Mg^{2+(soil)} = Mg^{2+(Water)} + 2Na^{+(soil)}$.

Based on the above analysis, the constraint of the model was determined to C, Ca, Cl, K, Mg, Na and S. The Phases was determined to augite, calcite, chlorite, halite, hornblende, mirabili, muscovite, orthoclase and plagioclase. The Parameter was determined to Ca/Na exchange and evaporation. Only the dissolution reactions of igneous rocks are apparent in study area. All mineral saturation indexes (MSI) of response models were calculated by netpath program and shown in Fig. 5.

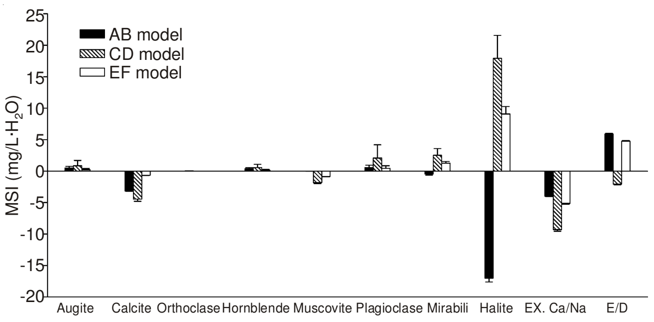

Fig. 5. Simulation of the evolution of groundwater chemistry with NETPATH, a positive MSI value indicated the mineral dissolution, sodium ions coming into the solution and evaporation. A negative MSI value indicated the mineral precipitation, leaving groundwater, calcium ions coming into the solution and dilution

The Netpath simulation results for the flow path AB showed that the chemical compositions satisfied the mass-balance reaction model, shown in Fig. 5. These models are in line with the laws of thermodynamics. The MSI values of augite, orthoclase, hornblende and plagioclase were positive 0.5, 0.01, 0.39 and 0.54, respectively. It indicated these above minerals dissolution into the groundwater. The MSI values of calcite, muscovite, mirabili, halite and EX. Ca/Na (ion exchange) were negative -3.16, -0.02, -0.46, -16.99 and -3.97, respectively. It indicated a lot of Halite dissolved into the groundwater as the main characteristics, these above minerals precipitation in the groundwater. At the same time, an action occurred with calcium-sodium ion exchange and the strong evaporation, although the chemical reaction has experienced a long period of geological history. But seen from the outcomes of the research of the groundwater chemical characteristics, if Na^+ was completely precipitated and all Na^+ was out of solution, adequate Na^+ needed to be provide from solution, in fact in addition to ground water TDS was high at the end, the remaining points were not high. Therefore, this reaction path represented the exposed areas or shallow areas of groundwater; it was water quality evolution results under the strong influence of the natural evaporation.

The simulation results for the flow path CD showed that the MSI values of augite, hornblende, plagioclase, mirabili and halite were positive 0.85, 0.54, 2.09, 2.51 and 17.91, respectively. It indicated that these above minerals dissolution into the groundwater. The MSI values of calcite, muscovite, EX. Ca/Na and E/D (evaporation or dilution) were negative -4.45, -1.83, -9.29 and -2.07, respectively, which indicated the mineral precipitation and Na^{2+} leaving solution. The MSI values also suggested that mirabilite and halite was the provider of sodium, chloride and sulfate. These processes led to a large amount of rock salt being dissolved, with their water type was Cl-SO_4-Na. In conjunction, relative to other water flow path models, there was a special reason to exist for some ancient lenticular freshwater aquifer to dilute the groundwater when the high salinity brine flow through here.

The simulation results for the flow path EF showed that the MSI values of augite, hornblende, plagioclase, mirabili, halite and E/D were positive 0.21, 0.13, 0.43, 1.25, 9.06 and 4.75, respectively, it indicated these above minerals dissolution into the groundwater. The MSI values of calcite, muscovite and EX. Ca/Na were negative -0.66, -0.87 and -5.12, respectively, it indicated the mineral precipitation or leaving groundwater. As well as the evaporation was strong in EF model and Ca^{2+} exchanged Na^+, their water type became to Cl-SO_4-Na and Cl-SO_4-Na-Ca.

Mica was mainly in the precipitated state as it was visible in the water samples. Orthoclase was close to saturation in the all the flow paths, indicating that the orthoclase in the basin and groundwater aquifers had reached equilibrium, which was the reason that the content of K^+ in groundwater was lower. Calcite and Ca^{2+} were present in the precipitated state, resulting in the water containing very low amounts of HCO_3^-. Much of the rock salt and Glauber's salt was dissolved. The solution was consistently in a weakly alkaline state.

It is clear from the overall simulation results of three different paths, with the source minerals gradually decreasing, rock salt was always in dissolved state within groundwater and calcite was always in the precipitated state, causing a decrease in the HCO_3^- concentration. The dissolution of mirabilite provided sufficient SO_4^{2-}. Orthoclase was close to saturation in all the flow paths while muscovite mainly appeared as a precipitate. Because of this reaction, the content of K^+ in the groundwater was extremely rare. The groundwater has ultimately evolved into the Cl-SO_4-Na type because of these processes and gradually formed highly mineralized ground water.

Conclusion

The most abundant anion and cation were chlorine ion and sodium ion, respectively. The types of groundwater were Cl-SO_4-Na-Mg and Cl-SO_4-Na. There were no significant differences between groundwater chemical types in the spatial distribution. The northern groundwater TDS values were greater than in south significantly and southern TDS values larger than the middle.

The water-rock reaction product volumes were decreased from upstream to downstream. Thus, ion concentration of downstream was significantly higher than the upstream region under the dual influence of leaching and evaporation, which is one of the main reasons for the formation of brine.

The research on groundwater chemical characteristics and its formation evolution has only contributed to the development of the sustainable utilization of water resources in arid areas, but also had a positive effect on the fields of crossover study between desert eco-hydrology and eco-hydrogeology. Analysis of the chemical interaction between groundwater and sandstone will provide significant guidance to environmental engineering and construction within the Taklimakan desert.

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