

HYDROCHEMICAL CHARACTERISTICS AND FORMATION MECHANISM OF GROUNDWATER IN THE LIULIN KARST SYSTEM

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Abstract

The Liulin karst system is typical of hydrogeological systems in northwestern China, with a group of springs as the dominant mechanism for regional groundwater discharge. To reveal the hydrochemical formation mechanism of the Liulin karst groundwater system, we studied the hydrogeochemical processes of karst groundwater in aquifers at the base of the hydrogeological investigation. Then starting from the chemical composition of karst groundwater together with the recharge-runoff-discharge process of groundwater systems, we analyzed the solutes origin and the dissolved mineral facies of the groundwater chemical composition. The results showed that the anionic and cationic compositions of karst water were different in recharge, runoff and discharge areas, with the main anions of HCO_3^- and SO_4^{2-} in recharge areas, and HCO_3^- and Cl^- in runoff and discharge areas, as well as the main cationic for Ca^{2+} and Na^+ , of which the molar concentrations of Ca^{2+} was greater than Na^+ in recharge areas and contrary to the runoff and discharge areas. Karst water was influenced by carbonate and evaporite dissolution while flowing through the aquifers, of which carbonate rock dissolution dominated in recharge areas, and evaporite rock dissolution increased to be the dominate lithology in runoff and discharge areas. Based on analysis of water-rock interaction, the main dissolved

mineral facies included dolomite, calcite, gypsum and halite. Dolomite is the most important dissolved mineral, followed by calcite and gypsum in recharge area, as well as calcite, gypsum and halite in runoff and discharge areas.

Introduction

The forming conditions of groundwater chemical composition are obviously different from those in surface water, which are often controlled by the geological and hydrogeological factors (Shen, 1993). Groundwater interacts with surrounding media and converts the chemical composition through geologic time. By the study of groundwater chemical characteristics, we can better understand the interaction mechanism of groundwater and the environment (Zhang et al., 2000), as well as the mineral rock facies in the water-rock interaction (Pu et al., 2013; Wang et al., 2006). Previous studies in this area include analysis of the model of karst water systems from the macro perspectives of time and space (Gao et al., 2008), resources development and protection (Li, 2010), as well as the evolution of water chemical characteristics and recharge source (Pei and Liang, 2005; Wei et al., 2012). Few studies have been done on the solute source and dissolved mineral facies of karst water in the Liulin karst system (Zang et al., 2013). This paper seeks to apply the relationship of cations and anions

of karst water in accordance with the recharge-runoff-discharge process to reveal the chemical characteristics and discuss the solute source and dissolved mineral facies of Liulin karst groundwater, aiming at providing a certain theoretical basis for reasonable development and protection of the karst water.

Study Area

The Liulin karst system is hydrogeologically typical of karst systems in northern China. A group of springs act as the predominant mechanism for regional groundwater discharge where carbonate rocks are widely distributed. They represent relatively independent karst systems. A distance of about 3 km along the Sanchuan River valley outcrop exists more than 100 springs with annual average discharge of 2.63m³/s. These springs outcrop in five groups and are collectively called the Liulin springs. Liulin springs discharge from the Cambro - Ordovician carbonate karst fracture, and are mainly supplied by precipitation via a carbonate fissure within a bare area of about 1,400 km². Secondly, the springs are recharged by river leakage from Sanhe valley via six 33km long fissures. Related subsurface flow runs from northeast to southwest controlled by geological structures. Water discharges from scattered springs on both sides of the Sanchuan from Ordovician Fengfeng Group.

Sampling and Analysis

In September 2011 and May 2013, fourteen groundwater samples were collected from central region. Electrical conductivity (EC), dissolved oxygen (DO), pH and temperature measurements were taken immediately after sampling. Then Atomic absorption spectroscopy (AAS) (PE - 601) was used for the cation content (Na⁺, K⁺, Ca²⁺, Mg²⁺) measurement, and high-performance liquid chromatography (HP1100) was used for the anion content (Cl⁻, SO₄²⁻, HCO₃⁻, NO₃⁻) measurement. Trace elements were measured by inductively coupled plasma mass spectrometry (ICP-MS).

Results

Major Ions of Karst Groundwater

As shown in Table 1, the pH values varied from 7.30 to 7.74. HCO₃⁻ is the dominant anion with the concentration ranging from 4.34mmol/L to 5.19mmol/L, and accounts for more than 70% of the total anion content. The concentration of secondary anion SO₄²⁻ and Cl⁻ range from 0.21mmol/L to 2.35mmol/L and 0.25mmol/L to 2.31mmol/L, separately. In the recharge, runoff and discharge areas, HCO₃⁻ is always the dominant anion in chemical composition of karst water. While there are differences in the secondary anion: the average concentration of

Time	Location	pH	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	TDS mg/L
Wet period 2011.9	Wucheng	7.56	0.03	0.41	1.77	0.66	4.42	0.27	0.23	0.16	286.5
	Chemingyu west	7.34	0.14	1.33	3.36	1.31	5.19	0.54	2.35	0.27	636.0
	Guankou Spring	7.57	0.04	0.43	1.94	0.67	4.44	0.25	0.48	0.09	315.5
	Tianjiahui	7.65	0.04	1.81	1.60	0.80	4.44	1.03	0.47	0.12	365.8
	Jinluo	7.49	0.04	1.27	2.07	1.03	4.34	0.64	1.07	0.16	417.6
	Yangjiagang Springs	7.30	0.07	3.85	1.81	1.13	4.44	2.31	1.41	0.21	571.9
	NO.1 Liulin water plant	7.31	0.04	2.49	1.82	0.95	4.34	1.62	0.94	0.16	458.4
Shangqinglong Springs	7.37	0.05	2.62	1.78	0.98	4.36	1.44	0.93	0.17	454.7	
Dry period 2013.5	Wucheng	7.74	0.03	0.36	1.76	0.66	4.46	0.25	0.21	0.17	282.2
	Chemingyu west	7.58	0.07	0.35	2.05	0.85	4.85	0.33	0.59	0.07	344.5
	Guankou Spring	7.64	0.03	0.35	1.88	0.66	4.51	0.25	0.41	0.09	304.1
	Tianjiahui	7.72	0.04	1.74	1.57	0.81	4.56	1.12	0.42	0.12	364.2
	Jinluo	7.55	0.04	1.29	2.02	1.01	4.44	0.82	0.97	0.20	420.5
	NO.1 Liulin water plant	7.50	0.04	2.31	1.76	0.93	4.53	1.52	0.84	0.17	444.1

Table 1. The chemical composition of major ions in Liulin springs (Unit: mmol/L).

SO_4^{2-} is greater than that of Cl^- in recharge areas, and it is opposite in runoff and discharge areas. Therefore, the concentration of SO_4^{2-} decreases and Cl^- increases along the recharge-runoff- discharge pathway. Karst groundwater contains relatively high levels of Ca^{2+} and Na^+ as the major cations, accounting for more than 75% of the total. The concentration of Ca^{2+} and Na^+ vary from 1.57 mmol/L to 3.36 mmol/L and 0.35 mmol/L to 1.82mmol/L, separately, which also shows a certain difference among the zonings. The average concentration of Ca^{2+} is greater than Na^+ in the recharge area, and it is opposite in runoff area and discharge areas.

As was shown in Figure 1, whether a wet or dry period, the cations of karst groundwater mainly plot on Ca^{2+} - Na^+ line with close to the Ca^{2+} end in recharge areas, and close to the Na^+ end in runoff and discharge areas. The anions mostly plot at the end of HCO_3^- , while scatter to the end of SO_4^{2-} and Cl^- in runoff and discharge areas.

Stoichiometry of Karst Groundwater

This paper referred to the Gibbs diagram to establish the relationship between total dissolved solids (TDS) and $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ as well as $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ (Figure 2) to reveal the relationship of the chemical composition and the lithology of aquifer correlation (Gibbs, 1970).

The results show that karst groundwater in Liulin springs had lower values of TDS and $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$, as well as $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$, which reflects that river leakage is the

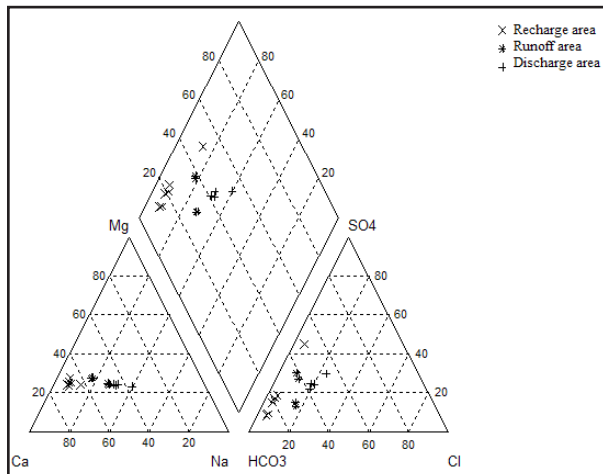


Figure 1. Major cations and anions triangle of karst groundwater chemical compositions in Liulin springs.

main groundwater source of Liulin springs, including the Yukou upstream section of Beichuan river and Yancun upstream section of Dongchuan river. There is an increasing $\text{Na}^+ / \text{Ca}^{2+}$ and $\text{Cl}^- / \text{HCO}_3^-$ concentration trend along the recharge- runoff - discharge pathway.

Groundwater in karst aquifer will react differently depending on the mineral content (calcite, dolomite and gypsum, etc.). To further explore the dissolution effect of these mineral facies and karst groundwater, calcium in groundwater could be divided into two types: calcium from non-gypsum and calcium from non-carbonate rocks. Assuming that all the SO_4^{2-} in the groundwater of the study area is derived from gypsum dissolution, calcium from non-gypsum sources are equal to $[\text{Ca}^{2+}] - [\text{SO}_4^{2-}]$ mmol/L, which is the total concentration of Ca^{2+} minus the part of Ca^{2+} balanced out by SO_4^{2-} . Similarly, calcium from non-carbonate rocks is equal to the total Ca^{2+} minus the part of Ca^{2+} balanced out by HCO_3^- , namely $[\text{Ca}^{2+}] -$

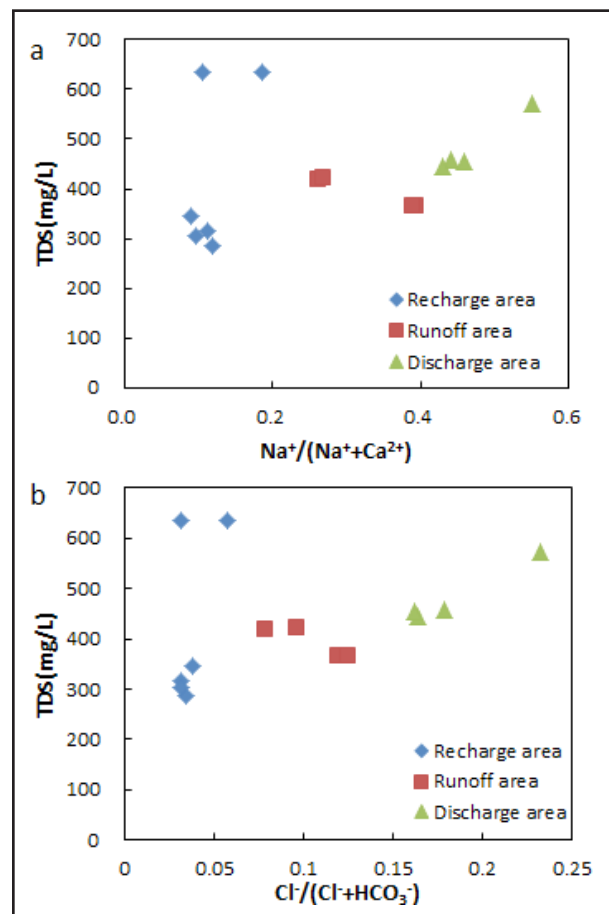


Figure 2. The relationship of TDS and ion concentration of karst groundwater in Liulin springs.

0.33[HCO₃⁻] mmol/L. The chemical reaction equation is as follows: CaCO₃+CaMg(CO₃)₂+3CO₂+3H₂O=2Ca²⁺+Mg²⁺+6HCO₃⁻.

Figure 3a shows that samples from the recharge area generally plot between the relationship line of 1:2 and 1:4, samples from the runoff area plot near the

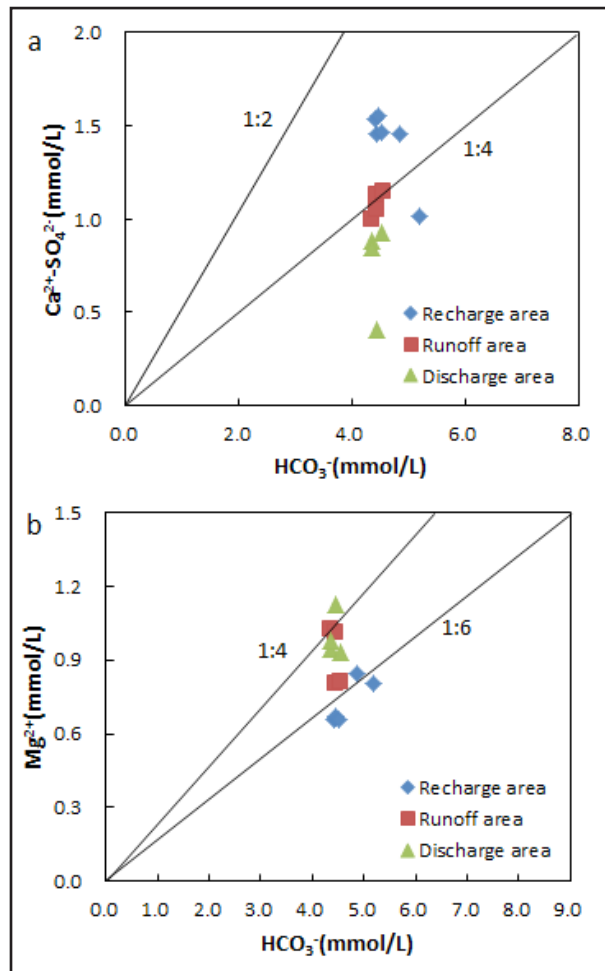


Figure 3. The relationship of bicarbonate ions and calcium from non-gypsum. Description: a. the relationship line of 1:2 means the ratio of calcium from non-gypsum and HCO₃⁻ in congruent dissolution of calcite, and the relationship line of 1:4 means the ratio of calcium from non-gypsum and HCO₃⁻ in congruent dissolution of dolomite; b. the relationship line of 1:4 refers to the ratio of Mg²⁺ and HCO₃⁻ in congruent dissolution of dolomite, and the relationship line of 1:6 refers to the ratio of Mg²⁺ and HCO₃⁻ in the dissolution equilibrium of dolomite and calcite (Wang et al., 2006).

relationship line of 1:4, and samples from the discharge area plot below the relationship line of 1:4. In Figure 3b, we can see samples from the recharge area plot near the relationship line of 1:6, samples from the runoff area plot between the relationship line of 1:4 and 1:6, and samples from the discharge area plot near the relationship line of 1:4. It can be seen from Figure 4 that samples from the recharge area plot on the relationship line of 1:1, and samples from the runoff and discharge areas plot below the relationship line of 1:1 but do not deviate far.

Discussion

The Solute Source of Karst Groundwater

The solute source and the processes that generated the observed composition of water can be revealed by the dissolved species and their relationships with each other (Hussein, 2004; Su et al., 2009). The main ion component of karst water in Liulin springs shows that HCO₃⁻ and Ca²⁺ are the dominant ions in all the areas, which indicates the control effect of carbonate minerals (such as limestone and dolomite) dissolution. Along the flow path, SO₄²⁻ and Na⁺ increase in the runoff and discharge areas. The increase of SO₄²⁻ may come from sulfate evaporite mineral dissolution (such as gypsum), sulfuric acid from sulfide oxidation, or atmospheric acid deposition. The latter two may be involved in the process of carbonate mineral dissolution by carbonic acid (Lang et al., 2005). The chemical reaction is as follows:

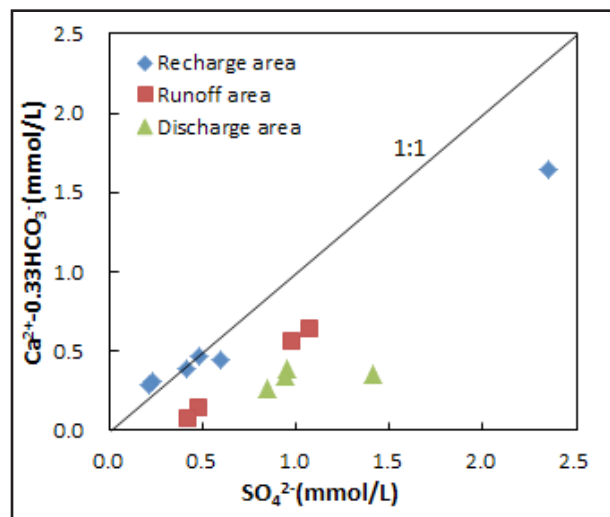
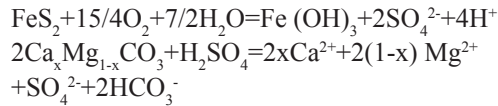


Figure 4. The relationship of sulfate ions and calcium from non-carbonate. Description: the relationship line of 1:1 refers to the ratio of SO₄²⁻ and calcium from non-carbonate in congruent dissolution of gypsum (Wang et al., 2006).



Ratio of $[\text{Ca}^{2+} + \text{Mg}^{2+}]$ and HCO_3^- of the study area is between 1.05 and 1.80, which can't be explained by pure carbonate dissolution. At the same time, the concentrations of SO_4^{2-} and $[\text{Mg}^{2+} + \text{Ca}^{2+} - \text{HCO}_3^-]$ are highly correlated with correlation coefficient of 0.901 (Figure 5b). Therefore, part of the Mg^{2+} and Ca^{2+} dissolved in the groundwater in the form of sulfate indicates that karst groundwater in Liulin springs was influenced by sulfate evaporite mineral dissolution. The positive correlation of SO_4^{2-} and Ca^{2+} as well as Mg^{2+} demonstrates that the dissolution of sulfate evaporite minerals, such as gypsum or anhydrite contributes greatly to the origin of solutes of karst groundwater. A large amount of Ca^{2+} and SO_4^{2-} ions produced by gypsum dissolution is likely due to the ion effect in the gypsum or anhydrite dissolution ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \leftrightarrow$

$\text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$), which brought about the increase of Mg^{2+} concentration with that of SO_4^{2-} increase. The Na^+ concentration increased rapidly and even exceeded the Ca^{2+} concentration indicating that the chemical composition of karst groundwater is not only influenced by carbonate dissolution, but also affected by evaporite (halite) dissolution.

The water chemistry triangle is a common means to explore the relationship of conventional ions and lithology of groundwater. Generally, when using the cation triangle, products of evaporite mineral dissolution plot at the end of $\text{Na}^+ + \text{K}^+$ line. Limestone leachates plot at the Ca^{2+} end, and dolomite leachates plot in the middle of the Mg^{2+} and Ca^{2+} line. When using the anion triangle, dissolved pure carbonate substances plot near HCO_3^- . Products of evaporite mineral dissolution should plot between Cl^- and SO_4^{2-} (Pu et al., 2011). Chemical composition of groundwater is controlled by lithology (Li et al., 2006). Plotting chemical analysis resulting on the water chemistry triangle shows that groundwater flowing through aquifers is affected by carbonate and evaporite dissolution. Cations representing recharge areas distribute along the Ca^{2+} and Mg^{2+} line, closest to Ca^{2+} , while anions mainly plot near HCO_3^- . Therefore, pure carbonate dissolution is the dominant influence on the chemical composition of karst groundwater in Liulin springs, including limestone and dolomite minerals. Runoff and discharge samples scatter resulting in cations plotting along the $\text{Ca}^{2+} - \text{Na}^+$ line and anions distributing along $\text{HCO}_3^- - \text{SO}_4^{2-}$ line. Consequently, the influence of evaporite minerals including sulfate and halite can't be ignored except for carbonate minerals.

The relationship of $\text{Mg}^{2+}/\text{Ca}^{2+}$ and $\text{Na}^+/\text{Ca}^{2+}$ molar ratios for the groundwater are illustrated in Figure 5a. The $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratios vary from 0.35 to 0.62, with all the values less than 1, while $\text{Na}^+/\text{Ca}^{2+}$ ratios range from 0.19 to 2.12, with most of the values less than 1. This indicates an abundant Ca^{2+} in groundwater. The equilibration of groundwater simultaneously with calcite and dolomite under room temperature gives an ideal molar $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio of about 0.8 (Appelo and Postma, 1993). Thus, maybe the solubility disequilibrium resulted in a high degree of variability with respect to $\text{Mg}^{2+}/\text{Ca}^{2+}$ molar ratios. It is then reasonable to consider that limestone with low $\text{Mg}^{2+}/\text{Ca}^{2+}$ and $\text{Na}^+/\text{Ca}^{2+}$ ratios, and dolomite with a high $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio and a low $\text{Na}^+/\text{Ca}^{2+}$ ratio are the main end-members controlling the variations

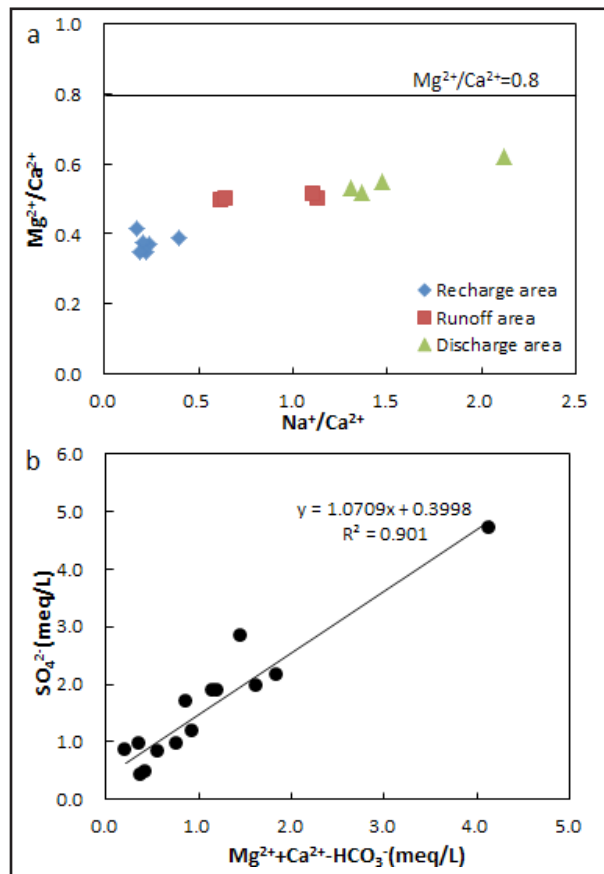


Figure 5. The relationships among ions in Liulin springs.

in chemical composition of these spring waters. Molar Mg^{2+}/Ca^{2+} ratio of karst water is below the 0.8 ratio line. Thus, it likely was related with the exchange reaction among calcite, dolomite and sulfate minerals. Molar Mg^{2+}/Ca^{2+} ratio is low in groundwater influenced by limestone dissolution, and high Mg^{2+}/Ca^{2+} molar ratio of groundwater may dissolve from dolomite aquifers. The sulfate mineral has much higher solubility than calcium, and gypsum is far from saturated. So, water has a strong leaching effect on gypsum rock, in which large amounts of Ca^{2+} and relatively few Mg^{2+} are produced making the Mg^{2+}/Ca^{2+} molar ratio decrease. Coming down to the partition of waters, Na^+/Ca^{2+} molar ratio of karst water in recharge areas is substantially less than 1, and Na^+/Ca^{2+} molar ratios of karst water in runoff and discharge areas are mostly greater than 1. According to Mg^{2+}/Ca^{2+} and Na^+/Ca^{2+} molar ratios of different dissolution media, karst aquifers in recharge areas are mainly controlled by carbonate minerals (such as limestone and dolomite) dissolution, while runoff and discharge areas are mainly influenced by evaporite minerals.

Dissolved Mineral Facies of Karst Groundwater

Chemical composition of the groundwater reflects regional hydro geochemical processes and geological history (Shen, 1993; Pu et al., 2013), which ultimately boils down to the water-rock interaction between groundwater and the mineral facies of aquifers it flows through. Therefore, the dissolved mineral facies of groundwater can be explored by analyzing the chemical composition of groundwater.

Although the dynamics factors and common ion effect wasn't considered, dissolution between mineral facies and groundwater could be proven to some extent. If $[Ca^{2+}-SO_4^{2-}]/HCO_3^- = 1:2$, it indicates congruent dissolution of calcite; if $[Ca^{2+}-SO_4^{2-}]/HCO_3^- = 1:4$, it shows congruent dissolution of dolomite (Wang et al., 2006). Samples from recharge areas plot basically along the relationship line near 1:4 and 1:6, indicating a common dissolved effect of calcite and dolomite. Most samples from runoff areas plot near the relationship line of 1:4, indicating that Ca^{2+} and HCO_3^- provided by dolomite dissolution are dominant. Samples from discharge areas basically plot below the relationship line of 1:4, indicating gypsum source of Ca^{2+} in addition to calcite and dolomite according to the hydrogeological conditions of Liulin springs. If $Mg^{2+}/HCO_3^- = 1:4$, the HCO_3^- is completely provided by dolomite dissolution (Wang et al., 2006.); If $Mg^{2+}/HCO_3^- = 1:6$, the molar ratio of calcite and

dolomite is 1: 1 ($CaCO_3 + CaMg(CO_3)_2 + 3CO_2 + 3H_2O = 2Ca^{2+} + Mg^{2+} + 6HCO_3^-$). Samples from recharge areas plot near the 1: 6 relationship line, indicating HCO_3^- ion is provided jointly by dolomite and calcite dissolution. Samples from runoff areas plot between the 1:4 and 1:6 relationship lines, indicating HCO_3^- ion content is provided by dolomite and calcite together, but dolomite contributed more. Samples from discharge areas plot mainly on the 1:4 relationship line, indicating the lead role dolomite dissolution plays. Above all, dolomite and calcite are the main dissolved minerals influencing chemical components of karst groundwater in Liulin springs, and the dissolution effect of dolomite is more pronounced than that of calcite.

The dissolution effect of gypsum can be obtained from Figure 4. Samples from recharge areas plot on the relationship line of 1:1 and most samples from runoff and discharge areas fall below the relationship line of 1:1. Therefore, it can be inferred that gypsum is involved in water-rock interaction of recharge areas and also dissolved in runoff and discharge areas, but contributed little.

In summary, the main dissolved mineral facies of karst groundwater in Liulin springs include dolomite, calcite and gypsum. Dolomite has become the most important dissolved mineral facie, followed by calcite and gypsum.

Conclusions

1. Stoichiometry showed that HCO_3^- is always the dominant anion in chemical composition of karst groundwater, while there are differences in the secondary anion. The average concentration of SO_4^{2-} is greater than that of Cl^- in recharge areas, and it is opposite in runoff and discharge areas. Karst groundwater had the highest Ca^{2+} and Na^+ as the major cations, accounting for more than 75% of the total cations, which also shows a certain difference among the zoning. The average concentration of Ca^{2+} is greater than Na^+ in recharge areas, and it is opposite in runoff and discharge areas.
2. Karst groundwater in Liulin springs flowing through the aquifers was affected by dissolved carbonates and evaporites, of which carbonates dominate in recharge areas and both carbonates and evaporites dominate in runoff and discharge areas.
3. The main mineral facies of karst groundwater in Liulin springs include dolomite, calcite, gypsum and halite. Dolomite is the most important dissolved mineral, followed by calcite and gypsum

in recharge areas as well as calcite, gypsum and halite in runoff and discharge areas.

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