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Original Research

Hydrochemical Characteristics and Reverse Hydrogeochemical Modeling of Taiyuan Formation Limestone Groundwater of Sunan Mining Area in Huaibei Coalfield

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Abstract

Taiyuan Formation limestone groundwater is the main aquifer threatening the safety of exploration under deep mining in the Huaibei coalfield. Therefore, acknowledging the hydrochemical characteristics and constructing reverse hydrogeochemical modeling are crucial for predicting and preventing mine water hazards. In this study, the mathematical statistical analysis, Piper three-line diagram, Gibbs diagram, ion proportional relationship, Chlorine-Alkali index, and the reverse hydrogeochemical modeling were employed for determining the hydrochemical characteristics and the formation mechanism. The results revealed that the hydrochemical types of groundwater samples were SO_4.Cl-Ca.Mg and HCO_3.Cl-Na, respectively. The water-rock interactions were primarily influenced by the leaching and the cation exchange, with these processes being more intense in the eastern region. Through reverse hydrogeochemical modeling, the water-rock interactions in the process of groundwater runoff were quantitatively verified, viz. the calcite and the dolomite were saturated and precipitating, while the gypsum and the halite were unsaturated and still dissolving. Furthermore, the simulations of mass transfer in groundwater runoff indicated that the dissolution and the leaching of gypsum, dolomite and halite, positive ion exchange, the precipitation of calcite, and the dissolution of CO_2 gas predominantly occurred along four simulated flow paths. These results offered a scientific foundation for the prevention and controlling of mine water hazards in deep mining contexts.

Keywords: Taiyuan formation limestone groundwater, hydrochemical characteristics, reverse hydrogeochemical modeling, Huaibei coalfield, Sunan mining area

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Introduction

Coalfield mining can cause a series of mine environmental problems, such as large-scale air-mining areas, leakage of surface water, the deterioration of groundwater quality, etc., which seriously threaten the water safety of residents' living, production and industry [1-4]. The rational development and utilization of water resources, especially groundwater resources, are significant to the ecological environment protection and the sustainable development of the coalfield [5-7].

The chemical compositions of groundwater are the main elements of the hydrogeological study in the mining area, which is intimately linked with regional geochemical evolution and cycling processes. Investigating its spatial distribution is essential for delineating hydrogeochemical processes and flow paths in mines. Currently, a suite of established methodologies, including ion ratios, multivariate statistical analysis, isotopic tracing, hydrochemical modeling, geographic information systems (GIS), hierarchical clustering analysis (HCA), principal component analysis (PCA), and self-organizing maps (SOM), are extensively utilized to investigate the dominant factors and spatio-temporal variations of hydrochemical evolution within the multilayered aquifer systems [8-19]. Moreover, water-stable isotopes and tritium radioactive isotopes have been extensively employed to investigate the origin and age of the water [20-24].

The Huaibei coalfield, an important coal production zone in Eastern China, is underlain by a groundwater system composed of multiple aquifers, and these aquifers have proved that there is a certain hydraulic connectivity between different aquifers. Currently, with the development of deep mining, the original underground flow patterns have been gradually changed. This may enhance the hydraulic connections among the aquifers, thereby elevating the risk of water inrush events. Particularly, the Taiyuan Formation limestone in the Huaibei coalfield, being a deep and abundant aquifer, presents a significant threat to deep mining operations [25, 26].

In response to the hydrogeochemical evolution in the Huaibei coalfield, numerous researchers have conducted a series of hydrogeochemical studies, which focus on both single and multiple aquifer systems [27-30]. For instance, Zhang et al. (2022) used cluster analysis combined with geological conditions, water-rock interactions and mining activities to investigate the spatiotemporal variations and primary controlling factors of deep groundwater hydrogeochemistry in the Carboniferous limestone aquifer of the Huaibei coalfield [31]. Meanwhile, Cheng et al. (2022) combined hydrochemical and dual isotopic analyses of sulfate in surface water, soil water and groundwater with evaluations of the UZ to identify the groundwater sulfate source and transformation in the coal mining area [32]. Although previous studies have made certain progress in the field of hydrogeochemistry of groundwater in mining areas, regional research on the hydrochemical evolution of Taiyuan Formation limestone groundwater, particularly from the perspective of deep water-bearing system and flow system, combined with the specific characteristics of the hydrological circulation conditions of deep groundwater in mining areas, is still relatively lacking. Systematic analyses along flow paths are especially scarce. In addition, previous studies have mostly focused on qualitative analysis of hydrochemical reactions, and there is a shortage of quantitative simulation research on the hydrochemical evolution of Taiyuan Formation limestone groundwater. In fact, unlike the conditions of shallow unconsolidated groundwater circulation, deep groundwater circulation in the Taiyuan Formation is often significantly affected by regional faults and major fractures [33, 34], which is often ignored by previous studies [35, 36]. Therefore, accurately understanding the distribution of water-blocking faults in Sunan mining area and defining hydrological units, as well as conducting reverse simulation modeling, will contribute to the elaborate characterization of hydrogeochemical evolution.

Therefore, in order to master the intrinsic geochemical evolution of the Taiyuan Formation limestone groundwater in Sunan mining area of Huaibei coalfield, the Piper diagram, the Gibbs diagram, the ion ratio relationship, and the Chlorine-Alkali index are utilized. Furthermore, the reverse hydrogeochemical modeling was employed using PHREEQC software. The main objectives of this study are: 1) analyze the hydrochemical characteristics and explore the mechanism of deep water-rock interactions, 2) verify the water-rock interactions quantitatively. This provides a more systematic perspective for the study of groundwater hydrogeochemistry, and is a step forward in the knowledge of quantitative simulation of regional deep confined aquifer systems. The findings of this study would provide a scientific basis for water hazard prevention and rationalization of deep groundwater resources.

Material and Methods

Regional Geological Situation

Huaibei coalfield is an important coal production base in China, crossing three cities and seven counties in northern Anhui Province. The coalfield covers an area of 30,000 km^2, with proven reserves of 6.7 billion tons. Sunan mining area is located in the southeast of the coalfield, inside the Suxian-Guoyang depression zone. The terrain in the mining area is relatively flat, with an elevation of 20.6 to 27.3 m. The surface rivers in the mining area belong to the Huai River system, mainly including Tuo River, Xinbian River, Hui River and other seasonal rivers. The Taiyuan Formation is about 600 m deep and 105~160 m thick with an average of 130 m, the formation lithology is mainly dark gray to gray

Table 1. Development characteristics of fold structure in Sunan mining area.

Name	Development characteristics	Axial direction	Dip angle	Fold description	Cause
Shudong syncline	Asymmetric syncline structure	NW	70°	The axis is 18 km long and 1.5~5.8 km wide, the core is Permian strata.	In the early stage of Yanshan activity, the Tanlu fault moved leftward and squeezed from east to west.
Shunan syncline	Asymmetric syncline structure	NNE	25° in the north section, 18° in the south section	The axis is 12 km long and 22 km wide, the core is Permian strata.	
Sunan anticline	Asymmetric anticline structure,the west wing is cut by NE strike fault.	NE	25° on the east flank, 20°on the west flank	The core is Permian strata.	

Table 2. Characteristics of main faults in Sunan mining area, Huaibei coalfield.

Name	Property	Trend	Tendency	Dip angle	Drop	Extended length	Positive or reverse faults	Cause
Subei fracture	Boundary fault	Near EW	S	45-70°	>1000m	>200km	Positive	East-west extension in the late Indosinian movement
Banqiao-Guzhen fracture	Boundary fault	Near EW	N	60-70°	>1000m	>100km	Positive	East-west extension in the late Indosinian movement
Nanping fault	Boundary fault	NS-NNE	NW	40-70°	>1000m	40km	Positive	Extension in the middle-late Yanshan movement
Dongsanpu fault	Boundary fault	NW	NE	-	>500m	>20km	Reverse	Overthrust folding in late Yanshan movement
Xisipo fault	Major fracture	NW	NE	25-55°	>1000m	>40km	Reverse	Overthrust folding in late Yanshan movement
Xinjia fault	Major fracture	Near EW	N	-	>500m	>20km	Positive	East-west extension in the late Indosinian movement
Shuangdui fault	Major fracture	NE	NW	-	>1000m	40km	Positive	Extension in the middle-late Yanshan movement

Note: "-" indicates absence of data.

limestone, which accounts for 40% of the formation thickness, with sandstone, siltstone, mudstone and carbonaceous mudstone. The recharge of groundwater runoff is poor due to the fact that the groundwater of Taiyuan Formation limestone consists mainly of buried and confined karst groundwater, and its water richness varies greatly, from weak to very strong, specifically strong in the east and north, and weak in the south and west. Vertically, the watery is strong in the upper part and weak in the lower part. Because of its proximity to the main mineable coal seam (No. 10 coal), the groundwater of Taiyuan Formation limestone is the main aquifer which threatens mining safety.

Sunan mining area belongs to the southeast of North China plate tectonically, the structures of Sunan mining area are controlled by the superposition of Indosinian movement and Yanshan movement. The NNE structures, NW structures and near EW structures are mainly developed [37] (Tables 1, 2). With the EW extension in the late Indosinian period, regional boundary faults were formed, and in the middle and late Yanshan movement, the major fractures were formed. The low-order NW structures and NE-NNE structures were distributed in the fault blocks formed by regional faults and major fractures [38] (Fig. 1).

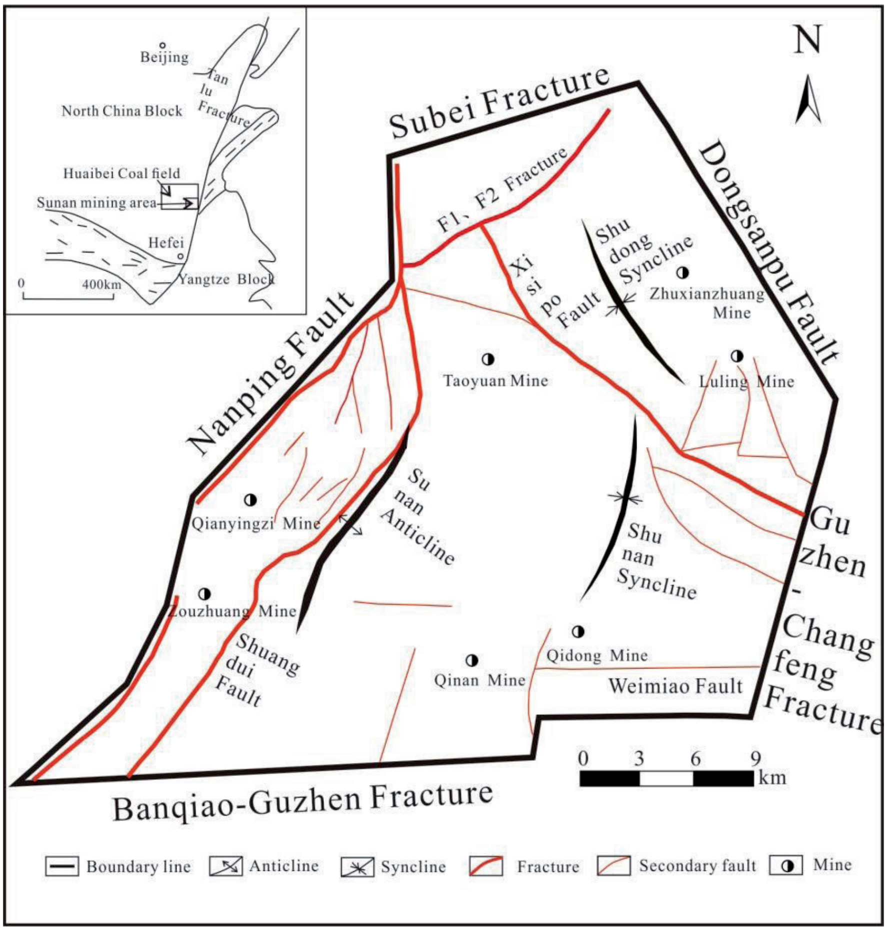

Fig. 1. Regional geology and mine distribution map of Sunan mining area in Huaibei Coalfield.

Data Collection and Processing

In this paper, the conventional hydrochemical data of limestone water of typical Taiyuan Formation in Zhu Xian Zhuang coalmine, Luling coalmine, Taoyuan coalmine, Qinan coalmine, Qidong coalmine, Zouzhuang coalmine, and the Qianyingzi coalmine in Sunan mining area were collected [28, 39, 40].The data included seven conventional ion components $K^+ + Na^+$ (replaced by Na^+ due to the low content of K^+ and its similar chemical properties to Na^+), Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, and CO_3^{2-}. The values of TDS and pH were also applied to suggest these hydrochemical characteristics.

Considering the existence of subjective and objective errors in the test process, the data were tested for anion and cation balance, and the test formula was calculated as follows:

$$E = \frac{\sum m_c - \sum m_a}{\sum m_c + \sum m_a} \times 100\% \quad (1)$$

Where E is the relative error, m_c and m_a are the milligram equivalent concentration (meq/L) of anions and cations, respectively. If K^+ and Na^+ are measured values, E values should be less than 5% positive and negative. If K^+ and Na^+ are calculated values, E values should be zero or close to zero. The tests revealed that the E-values of the groundwater samples from the Taiyuan Formation at the mine site were in a reasonable range (-2.66% to 1.81%), and the results could be used for subsequent analyses

Research Methods

Hydrological Units Division

Tectonic water control is closely related to the mechanical nature of the tectonics, tectonic morphology, generation and resurrection time, the fracture zones of regional faults and major fractures are densely cemented and tend to form water-resisting boundaries [41]. According to the structures, stratigraphic conditions, hydrogeological characteristics and boundary conditions, the hydrological unit of Huaibei coalfield can be divided into two primary hydrological units in the north and south; the southern hydrological unit is divided into three secondary hydrological units, viz. Sunan, Linhuan and Guoyang. Due to the distribution of water-blocking faults (mainly concave-controlling faults and basin-controlling faults), the tertiary hydrological unit in Sunan mining area was further divided on the basis of the division of the primary and secondary hydrological units.

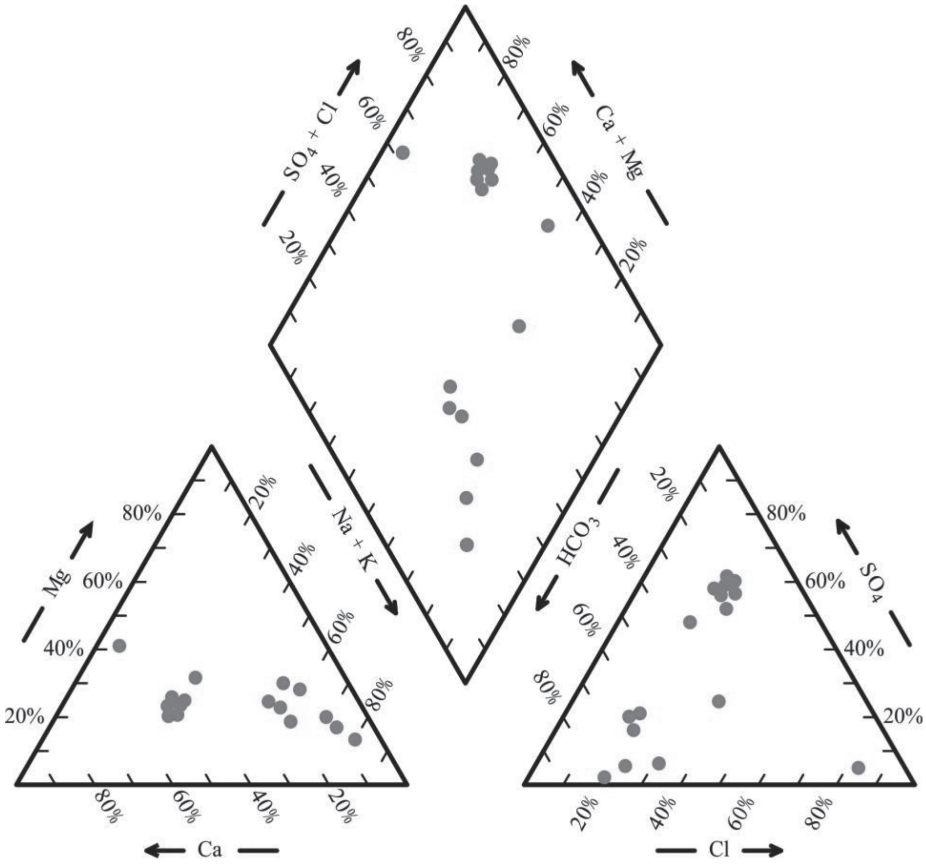

Fig. 2. Piper three-line diagram of Taiyuan Formation limestone groundwater in Sunan mining area, the Huaibei coalfield.

Reverse Simulation

Based on chemical thermodynamics and chemical kinetics, hydrogeochemical modeling has been studied since the 1960s, and WATEQ, WATEQF, EQ3/6, SOLMINEQ.88, PHREEQC, NETPATH, MT3DMS, NETPATH, PHAST and other software have been developed with the wide application of computer [42]. The PHREEQC software based on ion-association water model is the most widely used simulation program [43, 44], which can realize the simulation calculation of mineral saturation index and mass transfer of mineral or gas components in the process of groundwater runoff under different paths. The saturation index (SI) of major minerals, which represents the saturation state of minerals relative to groundwater, is a necessary parameter for reverse geochemical modeling. When the value of SI is greater than 0, it indicates that the mineral is in a saturated - oversaturated state, and the mineral tends to precipitate. When the value of SI is less than 0, it indicates that the mineral is in an unsaturated state, and the mineral tends to dissolve.

Results and Discussion

Hydrochemical Characteristics

Characteristics of Hydrochemical Components

In terms of ion concentration, the cations of groundwater samples in the mining area were mainly K^++Na^+ and Ca^{2+}, and the anions were mainly SO_4^{2-}, HCO_3^- and Cl^-. The concentration of K^++Na^+ ranged from 27.3 to 413.73 mg/L, with an average of 168.8 mg/L, and the concentration of K^++Na^+ of water sample No. 11 was the highest. The concentration of Ca^{2+} ranged from 4.45 to 385 mg/L, with an average

Table 3. Characteristics of main faults in Sunan mining area, Huaibei coalfield.

Index	K^++Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	CO_3^{2-}	TDS	PH
Maximum value	413.73	385	119	339	1180	529.1	187.71	2190	10.1
Minimum value	27.3	4.45	6.35	13.95	2.47	33.9	0	123	7.7
Average value	168.81	161.54	63.71	175.49	481.46	308.27	17.54	1043.50	8.57

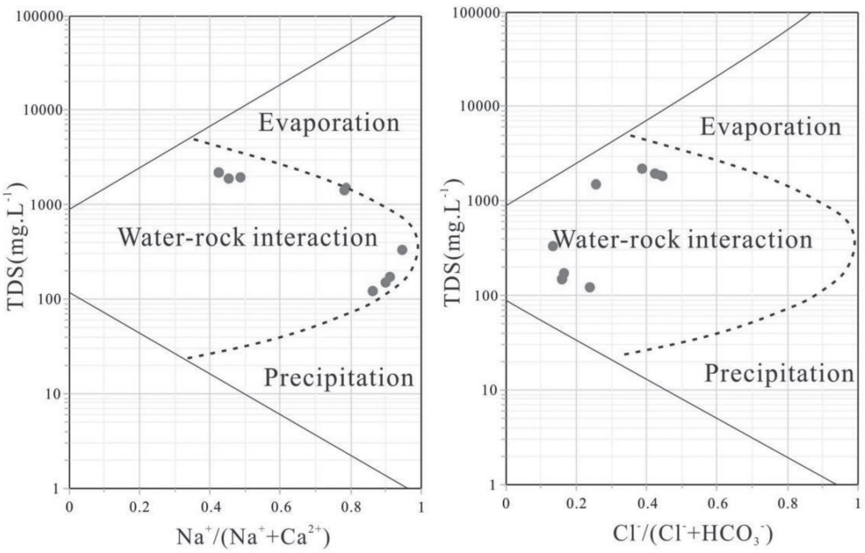

Fig. 3. Gibbs diagram of Taiyuan Formation limestone groundwater in Sunan mining area.

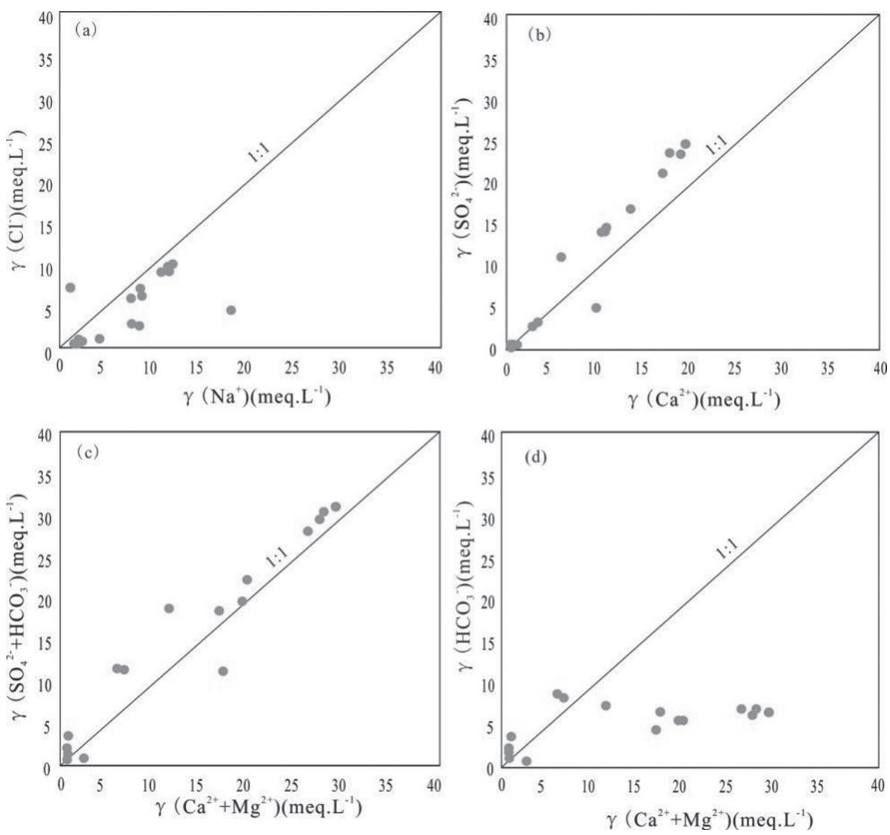

Fig. 4. Diagram of ion proportional relationship of Taiyuan Formation limestone groundwater.

of 161.5 mg/L. The concentration of SO_4^{2-} ranged from 2.47 to 1180 mg/L, with an average of 481.5 mg/L, the highest concentration of SO_4^{2-} was found in water sample No. 7. The concentration of HCO_3^- ranged from 33.9 to 529.1 mg/L, with an average of 38.3 mg/L, of which the highest concentration of HCO_3^- was found in water sample No. 2. The concentration of Cl^- ranged from 13.95 to 339 mg/L, with an average of 175.5 mg/L (Table 3).

In terms of TDS and pH, the concentration of TDS ranged from 123 to 2190 mg/L, with an average of 1043.5 mg/L. The pH value ranged from 7.7 to 10.1, indicating that the groundwater was weakly alkaline to alkaline. The pH value of water sample No. 16 from Zouzhuang coalmine was the highest, and the TDS concentration of water sample No. 6 from Taoyuan coalmine was the highest with 2190 mg/L (Table 3).

Hydrochemical Type Analysis

According to the Piper three-line diagram of Taiyuan Formation limestone water in Sunan mining area of Huaibei coalfield (Fig. 2), the hydrochemical types of Taiyuan Formation limestone water in the mining area were mainly SO_4.Cl-Ca.Mg (50%) and HCO_3.Cl -Na (43.75%). There are obvious differences in the hydrochemical types between different regions of the mining area, the HCO_3.Cl-Na type was dominated in the western and eastern parts of the Sunan mining area, and the SO_4.Cl-Ca.Mg type was dominated in the central part of the mining area.

Hydrochemical Formation Mechanism

Gibbs Diagram

The Gibbs diagram can macroscopically reflect the controlling factors of major ions in the process of groundwater formation. Generally speaking, the control factors of major ions are divided into three types: evaporation concentration-controlled, rock weathering-controlled and precipitation-controlled. As shown in Fig. 3, the water sample points of Taiyuan Formation limestone were mainly located in the water-rock action zone, far away from the evaporation zone and atmospheric precipitation zone, indicating that the water-rock action played a dominant role in the chemical composition of groundwater.

Dissolution

The difference of chemical composition of groundwater is affected by many factors, such as dissolution and precipitation of halite, carbonate minerals, sulfate minerals, weathering of silicate minerals and ion exchange, of which the strength of lixiviation depends on the solubility of rock, the development of pores, the solubility of water, and the alternating strength of water [45]. The ion ratio relationship can be used to reveal the source of chemical components in groundwater and the possible hydrogeochemical effects.

Based on the relative stability of Cl^- in groundwater [46], the relationship between Na^+ and Cl^- can be used to explore the source of Na^+ in groundwater. The Na^+-Cl^- molar ratio produced by halite dissolution was 1:1. From the Fig. 4a), it can be seen that the water samples of the Taiyuan Formation limestone aquifer were generally below the 1:1 dissolution line of Na-Cl. The relatively high Na^+ was derived from the dissolution of rock salt, and it can also be derived from the alternating adsorption of Mg^{2+} and Ca^{2+} in the water layer and Na^+ ions in the surrounding rock, resulting in the increase of Na^+ in the water layer.

The relationship between Ca^{2+} and SO_4^{2-} in groundwater can be used to explore the source of SO_4^{2-} in groundwater. The ion ratio of Ca^{2+} - SO_4^{2-} generated by gypsum dissolution was 1:1. As can be seen from the Fig. 4b), the water samples were generally close to the 1:1 dissolution line, indicating that the main source of SO_4^{2-} was the dissolution of gypsum. The water samples located above the 1:1 dissolution line may be owing to the increase of HCO_3^- caused by desulfurization, which furthermore resulted in calcite precipitation (Eq. 2, 3) and the decrease of Ca^{2+}.

$$SO_4^{2-} + 2C + 2H_2O \rightarrow H_2S\uparrow + 2HCO_3^- \quad (2)$$

$$Ca^{2+} + 2HCO_3^- \rightleftarrows CaCO_3(\text{Calcite})\downarrow + H_2O + CO_2 \quad (3)$$

The relationship between (Ca^{2+} + Mg^{2+}) and (HCO_3^- + $SO4^{2-}$) in groundwater reflected the main source of Ca^{2+} and Mg^{2+} [47]. The ratio of (Ca^{2+} + Mg^{2+}) – (HCO_3^- + $SO4^{2-}$) produced by the dissolution of carbonate and sulfate was 1:1. As shown in Fig. 4c), all water samples were generally distributed along the dissolution line 1:1 of (Ca^{2+}+Mg^{2+}) - (HCO_3^-+$SO4^{2-}$), indicating that the dissolution of gypsum, calcite and dolomite was the main source of Ca^{2+} + Mg^{2+} ions in groundwater. Most of the water samples located above the 1:1 dissolution line implied that there are other losses of Ca^{2+} and Mg^{2+}. It is highly probable that Mg^{2+} and Ca^{2+} in the limestone groundwater were alternately adsorbed with Na^+ in the surrounding rocks.

The relationship between (Ca^{2+} + Mg^{2+}) and HCO_3^- in groundwater can also be used to confirm the main source of Ca^{2+} and Mg^{2+}. The (Ca^{2+} + Mg^{2+}) – HCO_3^- ion ratio produced by carbonate dissolution was 1:1. As shown in Fig. 4d), the contents of (Ca^{2+} + Mg^{2+}) were much higher than HCO_3^- in some water samples, which proclaimed that carbonate dissolution was one source of Ca^{2+} and Mg^{2+}, and other sources may be from the sulfate dissolution.

Ion Exchange Adsorption

The Chlorine-Alkali Index (CAI) was commonly used to describe the direction and intensity of cation exchange [48]. When the values of CAI-1 and CAI-2 were negative, it indicated that the Ca^{2+} and/or Mg^{2+} in the groundwater were exchanging ions with Na+ and/or K^+ in the surrounding rock. When the values of CAI-1 and CAI-2 were positive, it demonstrated the existence of reverse ion exchange. When the absolute values of CAI-1 and CAI-2 were larger, it suggested that the strength of ion exchange was stronger, and a value of 0 indicated that there was no ion exchange during the hydrochemical evolution..

The formulas for CAI-1 and CAI-2 were as follows:

$$\text{CAI-1} = (Cl^- - (Na^+ + K^+)) / Cl^- \quad (4)$$

Table 4. Concentrations of mineralization degree of Taiyuan Formation limestone groundwater (mg / L).

Mineralization degree	Su_{II-1}	Su_{II-2}	Su_{II-3}	Sunan
Maximum value	1929.11	2685	387.88	2685
Minimum value	132.99	211.58	178.65	132.99
Average value	892.7	1808.7	283.265	1376.82

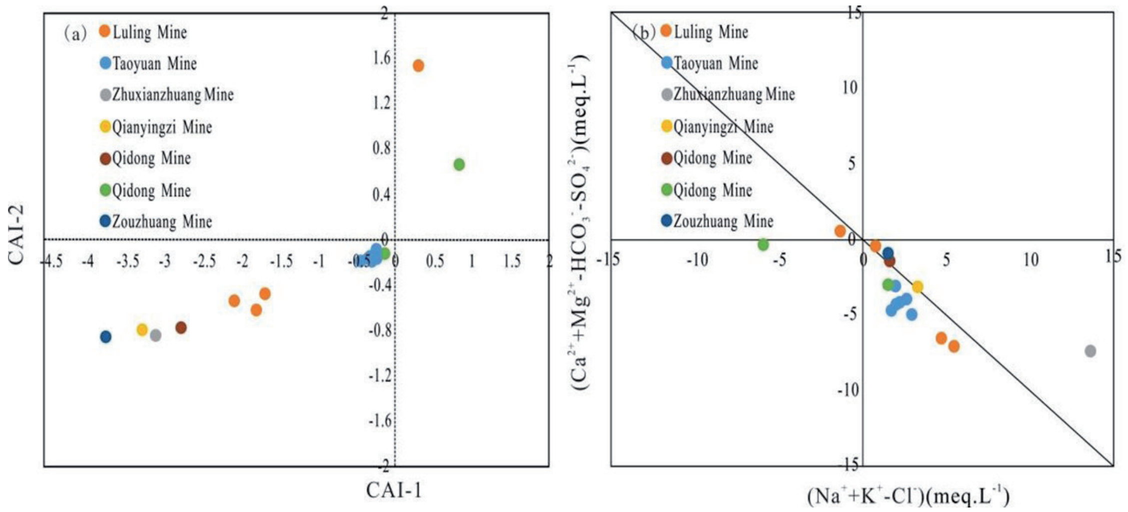

Fig. 5. Chlor-alkali index and $(Ca^{2+} + Mg^{2+} - HCO^{3-} - SO_4^{2-})/(Na^+ + K^+ - Cl^-)$ of limestone groundwater.

$$CAI\text{-}2 = (Cl^- - (Na^+ + K^+)) / (HCO_3^- + SO_4^{2-} + CO_3^{2-} + NO_3^-) \quad (5)$$

The unit of each index was meq/L.

According to the Chlorine-Alkali Index diagram of limestone groundwater in the mining area (Fig. 5a), the CAI-1 and CAI-2 values of limestone water in Taiyuan Formation ranged from -3.76 to 0.83 and -0.86 to 1.53, respectively. The values of all water samples were less than 0, except for water sample No. 3 from Luling Mine and water sample No. 15 from Qinan Mine, suggesting that the limestone water in the Taiyuan formation mainly underwent positive cation exchange (Eq. 6), resulting in Ca^{2+} and Mg^{2+} in the groundwater replacing Na^+ in the surrounding rock.

$$Ca^{2+} (Mg^{2+}) (Water) + Na^+ (K^+) (Rock) \rightarrow Na^+ (K^+) (Water) + Ca^{2+} (Mg^{2+}) (Rock) \quad (6)$$

In addition, $(Ca^{2+} + Mg^{2+} - HCO_3^- - SO_4^{2-})/(Na^+ + K^+ - Cl^-)$ can be used to analyze the influence of ion exchange on water. Specifically, $(Na^+ + K^+ - Cl^-)$ represented the increase or decrease of $Na^+ + K^+$ except for the dissolution of halite, and the $(Ca^{2+} + Mg^{2+} - HCO_3^- - SO_4^{2-})$ represented the increase or decrease of $Ca^{2+} + Mg^{2+}$except for the dissolution of calcite, dolomite and gypsum. From Fig 5b), it can be seen that the water samples in the study area were mainly distributed in the IV quadrant of the coordinate axis, and most of the water samples fell on or closed to the - 1:1 straight line, indicating that the limestone water of Taiyuan Formation was affected by ion exchange, which was in agreement with the conclusion of the Chlorine-Alkali Index (CAI). The farther the water sample point was from the coordinate origin, the stronger the ion exchange effect was. So, it can be inferred that the ion exchange effect was stronger in the mines of Zhu Xianzhuang, Luling, Qinan and Taoyuan than in the mines of Zouzhuang, Qidong and Qianyingzi.

Hydrogeochemical Reverse Simulation

Tertiary Hydrological Units Division

Taking the Xisipo reverse fault and the Shuangdui normal fault as the dividing line, which have a drop of more than 1,000 meters and are the relative watertight boundaries of the mine area, the Sunan mining area, which is a secondary hydrological unit, was divided into three tertiary hydrological geological units: Su_{II-1}, Su_{II-2} and Su_{II-3}.

The Xisipo thrust fault is located in the northeastern part of the mining area and belongs to the Xusu nappe shielding fault, which thrusts the Ordovician Cambrian limestone in the upper plate onto the Carboniferous Permian limestone in the lower plate, resulting in the interruption of the hydraulic connection between the two plates.

Table 5. Water level elevation of tertiary hydrological unit in Sunan mining area (m).

Water level elevation	S_{II-1}		S_{II-2}			S_{II-3}	
	Luling mine	Zhuxianzhuang mine	Qidong mine	Qinan mine	Taoyuan mine	Qianyingzi mine	Zouzhuang mine
	9.44~20.98	-	8.09~19.6	–93.9~–10.1	–173.4~–69	18.6~50.19	-

Note: "–" indicates absence of data.

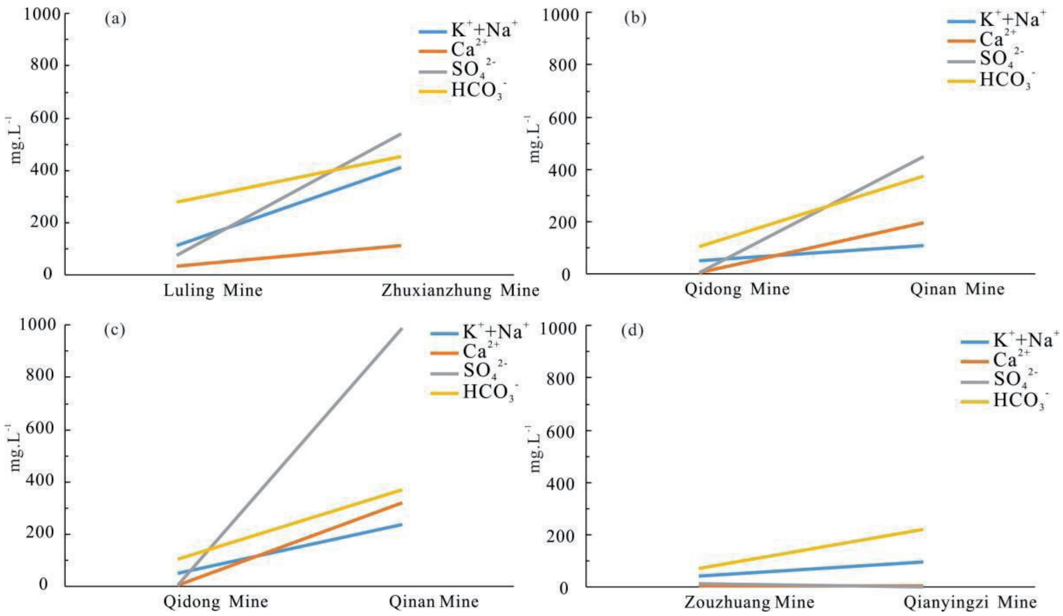

Fig. 6. The variation of main ion concentration in different runoff paths of Taiyuan Formation limestone groundwater in Sunan mining area.

The Shuangdui normal fault extends to the northeast and cuts the western flank of the Sunan anticline. The Carboniferous-Permian strata on the lower plate of the fault buttress the Ordovician-Cambrian strata on the upper plate, resulting in the interruption of the hydraulic connection of the limestone water in the Taiyuan Formation on both sides, and the Taiyuan Formation limestone water in the upper side is recharged by the Ordovician limestone water in the lower side.

The limestone aquifers of Taiyuan Formation were relatively closed among different hydrological units with very small mutual connectivity and large differences in mineralization degree and water level elevation. The mineralization degree of Taiyuan Formation limestone groundwater in the mining area ranges from 132.99 to 2685 mg/L, with the maximum value occurring in the Taoyuan mine of the Su_{II-2} hydrological unit, and the minimum value occurring in Luling mine of Su_{II-1} hydrological unit (Table 4). The difference of mineralization degree reflects the strength of karst development and groundwater runoff between the three tertiary hydrological units to some extent. Specifically, the karst development and the groundwater runoff of Su_{II-2} hydrological unit is relatively strong, the karst development and the groundwater runoff of Su_{II-1} hydrological unit is relatively weak, and Su_{II-3} hydrological unit is the weakest.

In terms of the original water level elevation, the water level elevation of the Taiyuan formation limestone groundwater in the mining area varied greatly, showing high around and low in the middle, in which Su_{II-3} water level elevation>Su_{II-1} water level elevation>Su_{II-2} water level elevation, also showing obvious blocky characteristics (Table 5).

Selection of Simulation Path

The characteristics of limestone water runoff in Taiyuan Formation are mainly controlled by the tectonic background and dominated by horizontal movement, with no overflow movement between aquifers, which means that the selection of runoff paths must be based on rational and fine-grained division of hydrological units.

According to the regional hydrogeological conditions and the division of tertiary hydrogeological units, and with reference to the spatial distribution characteristics of dominant ions and TDS (along the direction of the runoff , with the increase of the runoff path, the concentration of dominant ions and TDS increases under

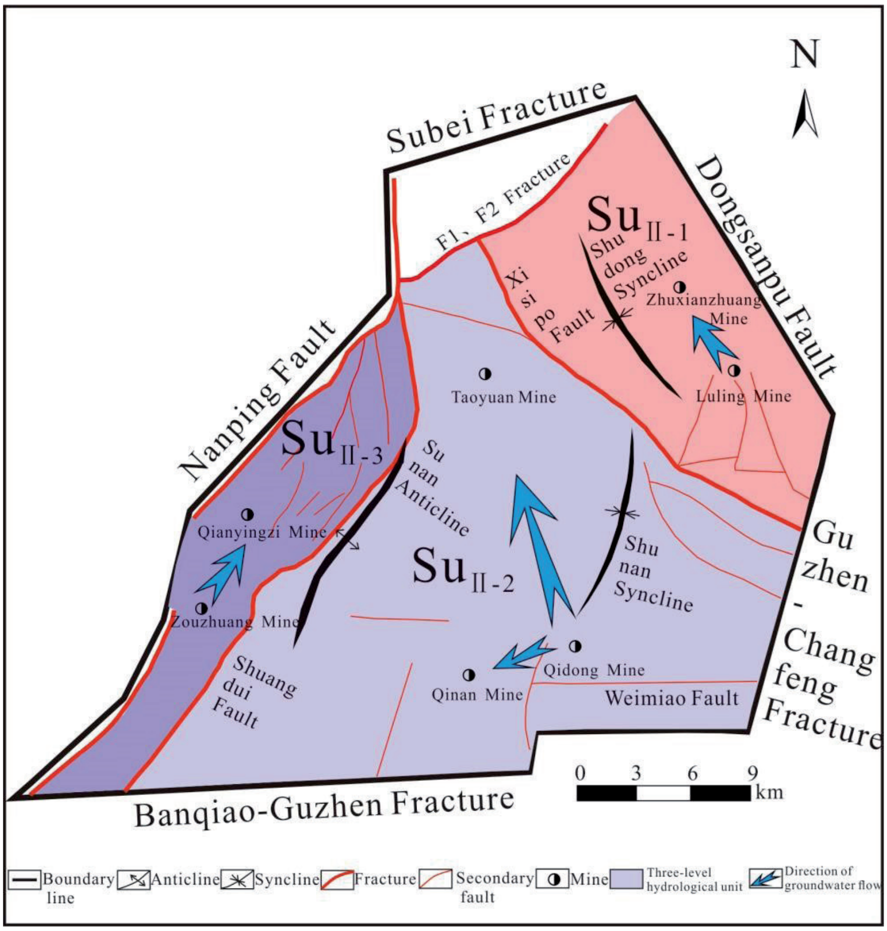

Fig. 7. Hydrogeological units division and four simulation paths in the Sunan mining area.

the effect of leaching and ion exchange, as shown in Fig. 6, the concentrations of SO_4^{2-} and HCO_3^- of the rest of the paths are significantly increased except for Zouzhuang mine → Qianyingzi mine), the simulation paths were selected. Each simulated water flow path included two water sample points: the initial water sample and the terminal water sample. Finally, four simulation paths were identified in the mining area, including Luling mine → Zhuxianzhuang mine, Qidong mine → Qinan mine, Qidong mine → Taoyuan mine, Zouzhuang mine → Qianyingzi mine, as shown in Fig. 7.

Determination of Possible Mineral Phase

The selection of possible mineral phases is fundamental and critical in determining the reactions that may occur along groundwater flow paths and is central to inverse hydrogeochemical modeling [49].

Firstly, based on the distribution characteristics of dominated ion such as K^++Na^+, Ca^{2+}, HCO_3^-, SO_4^{2-} in the Taiyuan Formation limestone groundwater in the Sunan mining area, and combining with the lithological characteristics and hydrogeochemical formation mechanism of the Taiyuan Formation, the calcite, dolomite, gypsum, and halite were selected as the main mineral phases. Secondly, considering the cation exchange adsorption, NaX, CaX_2, and MgX_2 were selected as the main mineral phases. Finally, CO_2(g) was selected as a possible mineral phase considering that CO_2(g) would continue to dissolve into groundwater, and H_2S(g)) was selected as a possible mineral phase considering desulfurization. The dissolution of albite would lead to the increase of Na^+, which was selected as a possible mineral phase, and also FeS_2 and O_2(g) were considered as possible mineral phases considering the oxidation of pyrite due to mining disturbance

The SI values of main minerals in the limestone groundwater samples from the Taiyuan Formation in the mining area were simulated by reverse hydrogeochemical simulation (Table 6). The SI values of calcite and dolomite in all mines in the Sunan mining area were greater than 0, indicating that they were in a supersaturated state and were not the main source of Ca^{2+}, Mg^{2+}, HCO_3^-. The SI values of gypsum and halite were less than 0, indicating that they were always in a dissolved state in groundwater and the leaching of gypsum and halite was continuous during the water runoff in the Taiyuan Formation, which were an important source of Ca^{2+}, Na^+, Cl^- and SO_4^{2-} in groundwater. The SI values of albite and pyrite were both 0, with no precipitation or dissolution, which could be excluded as the possible phases.

Table 6. SI values of main minerals of Taiyuan Formation limestone groundwater in Sunan mining area.

Mine	$SI_{Calcite}$	$SI_{Dolomite}$	SI_{Gypsum}	SI_{Halite}	SI_{albite}	SI_{pyrite}
Luling	0.23	0.79	-2.56	-6.78	0	0
Taoyuan	0.28	0.40	-0.43	-5.84	0	0
Zhuxianzhuang	2.22	4.58	-1.12	-5.82	0	0
Qianyingzi	0.63	1.66	-4.21	-7.03	0	0
Qidong	0.57	1.54	-3.75	-7.52	0	0
Qinan	0.19	0.42	-0.91	-6.37	0	0
Zouzhuang	0.61	1.66	-3.45	-7.76	0	0

Table 7. Simulation results of Taiyuan Formation limestone groundwater under different simulation paths (mmol / L).

Serial number	Path	Calcite	Dolomite	Gypsum	Halite	NaX	CaX_2	$H_2S(g)$	$O_2(g)$	$CO_2(g)$
1	Luling mine→Zhuxianzhuang mine	-1.98	1.70	4.83	1.83	5.26	-2.63	-	-	1.58
2	Qidong mine→ Qinan mine	-5.63	3.92	4.60	6.49	-3.88	1.94	-	-	4.71
3	Zouzhuang mine → Qianyingzi mine	-0.25	0.11	1.12	0.58	1.93	-0.97	-1.24	-2.49	-
4	Qidong Mine to Taoyuan Mine	-5.76	3.97	10.23	7.53	1.11	-0.55	-	-	4.64

Note: Positive value indicates dissolution; negative value indicates precipitation;"-"indicates no reaction.

Material Transfer under Different Runoff Paths

The complexity of the lithology, geology and the surrounding physical, chemical and biological environment of the aquifer leads to multiple solutions for the simulation results. It is necessary to determine the optimal solution based on the hydrogeological conditions of the study area, combined with the source analysis of hydrochemical components and the saturation index of minerals. When the amount of mineral transfer is greater than 0, it means that the minerals are dissolved (or gases dissolve into the groundwater), and the amount of mineral transfer is less than 0, it means that the minerals precipitate (or gases escape from the groundwater). The simulation results of hydrogeochemical reactions under different runoff paths (the uncertainty in the simulation process is 0.05) were shown in Table 7.

In runoff path 1 from Luling mine to Zhu Xian Zhuang mine, the hydrochemical type of Taiyuan Formation limestone groundwater changed from Na-HCO_3 type to Ca-SO_4 type, and the dissolution and leaching of gypsum, halite and dolomite mainly occurred, with the dissolution amounts of 4.83 mmol/L, 1.82 mmol/L and 1.7 mmol/L, which led to an increase in the content of Na^+, Ca^{2+}, Mg^{2+}, SO_4^{2-} and CL^-, respectively. The increased content of Ca^{2+} in water resulted in the precipitation of calcite with the amount of 1.98 mmol/L. Positive cation exchange occurred with Ca^{2+} and Mg^{2+} in the groundwater replacing Na^+ in the surrounding rock, and the exchange amount was 5.26 mmol/L. During the runoff process, CO_2 gas was dissolved into the water body, causing dolomite (SI>0) to continue to dissolve and precipitate with a lag, the content of HCO_3^- to increase and PH to decrease.

In runoff path 2 from Qidong mine to Qinan mine, the hydrochemical type of Taiyuan Formation limestone groundwater changed from Na-HCO_3 type to Ca-SO_4.Cl type, and the dissolution and leaching of halite, gypsum and dolomite occurred, with the dissolution amounts of 6.49 mmol/L, 4.6 mmol/L and 3.92 mmol/L, which led to an increase in the content of Na^+, Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2}, respectively. The increased content of Ca^{2+} in water resulted in the precipitation of calcite with the amount of 5.63 mmol/L. Reverse cation exchange occurred with Na^+ in groundwater replacing Ca^{2+} and Mg^{2+} in the surrounding rock, and the exchange amount was 3.88 mmol/L, resulting in a decrease in the content of Na^+. During the runoff process, a large amount of CO_2 gas was dissolved into the groundwater, resulting in partial dissolution of the dolomite (SI>0), an increase in the content of HCO_3^- and a decrease in pH..

Because the runoff path 3 from Zouzhuang mine to Qianyingzi mine was shorter than other paths, the intensity of leaching and ion exchange was lower than other paths, and the hydrochemical type had not changed, which was still Na-HCO_3 type. The dissolution and leaching of gypsum and halite mainly occurred, with the dissolution amounts of 1.12 mmol/L and 0.58 mmol/L. Positive cation exchange occurred with Ca^{2+} and Mg^{2+} in groundwater replacing Na^+ in surrounding rock, and the exchange amount was 1.93 mmol/L. The dissolution of dolomite and the precipitation of calcite were relatively weak. During the runoff process, H2S gas escaped from the groundwater and desulfurization occurred.

In runoff path 4 from Qidong Mine to Taoyuan Mine, the hydrochemical type of Taiyuan Formation limestone water changed from Na-HCO_3 type to Ca-SO_4 type, and the dissolution and leaching of gypsum, halite and dolomite occurred, with the dissolution amounts of 10.23 mmol/L, 7.53 mmol/L and 3.97 mmol/L, which led to an increase in the content of Mg^{2+}, Na^+, SO_4^{2-} and Cl^-. The increased content of Ca^{2+} in water resulted in the precipitation of calcite with the amount of 5.76 mmol/L. Ca^{2+} and Mg^{2+} in groundwater replaced Na^+ in surrounding rock with the exchange capacity was 1.11 mmol/L. During the runoff process, CO_2 gas was dissolved into the water body, causing dolomite (SI > 0) to continue to dissolve, the content of HCO_3^- to increase and PH to decrease.

Overall, the dissolution and leaching of gypsum, halite and dolomite and the precipitation of calcite occurred in all simulated paths, showing approximately the same dissolution and precipitation pattern, with Path 4>Path 2>Path 1>Path 3 in terms of the intensity of action. Positive cation exchange occurred in all paths except path 2, with path 1>path 3>path 4 in terms of the intensity of action, where desulfurization occurred in path 3.

Conclusion

This study delves into the hydrochemical characteristics and formation mechanism of the Taiyuan Formation limestone groundwater by using Piper three-line diagram, Gibbs diagram, ion proportional relationship, and Chlorine-alkali index. The water-rock interactions were quantitatively verified by the PHREEQC software at the regional scale. The results provided scientific basis for reasonable utilization and protection for deep groundwater resources, and the following key findings were established:

1. The cations in groundwater were mainly $K^+ + Na^+$, Ca^{2+}, and the anions were mainly SO_4^{2-}, HCO_3^- and Cl^-. The hydrochemical types mainly contained the SO_4.Cl-Ca.Mg type and the HCO_3.Cl-Na type.

2. The dissolution of halite, gypsum, calcite, dolomite, and the ion exchange played a dominant role in the chemical composition of groundwater. The ion exchange was dominated by positive cation exchange, and the ion exchange intensity in the mining areas of Zhuxianzhuang, Luling, Qinan and Taoyuan were stronger than that in the mining areas of Zouzhuang, Qidong, and Qianyingzi.

3. Taking the Xisipo reverse fault and Shuangdui normal fault as the dividing line, the Sunan mining area can be divided into three tertiary hydrogeological units: Su_{II-1}, Su_{II-2} and Su_{II-3}. The block characteristics of each hydrological unit were significant, which controlled the runoff of Taiyuan Formation limestone groundwater.

4. The SI values of calcite and dolomite in the Sunan mining area were greater than 0, indicating a tendency to precipitate. The SI values of gypsum and Halite were less than 0, indicating that they still dissolved in groundwater, which were important sources of ions such as Ca^{2+}, Na^+, Cl^- and SO_4^{2-} in groundwater.

5. In the four simulated runoff paths, the dissolution and leaching of gypsum, halite and dolomite, the precipitation of calcite, dissolution of CO_2 gas and positive ion exchange with different intensities mainly occurred, and reverse cation exchange and desulfurization partially occurred, which can jointly prove the hydrochemical evolution process of limestone water in Taiyuan Formation in the study area.

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Conflict of Interest

The authors declare no conflict of interest.

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