



Research article

Investigation into factors controlling groundwater evolution in mining areas with an integrated approach

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ABSTRACT

The study of groundwater evolution is of great significance for water resource protection and management, groundwater pollution control, and ecological environment protection. Experts and scholars have found that the hydrochemical processes and evolutionary patterns of groundwater are determined by both natural processes and human activities. However, there is relatively little research on the evolution of groundwater in mining areas where human activities have a significant impact. Therefore, to study the main controlling factors affecting the hydrogeochemical evolution of groundwater in mining areas, this paper proposes a method combining mixed ratio calculation and multivariate statistical analysis. Firstly, a total of 40 groundwater samples are classified into six clusters via hierarchical cluster analysis. By comprehensively analyzing the spatial location of the samples, it was found that there was no obvious distribution pattern of groundwater in space. Furthermore, the rationality of the cluster analysis is evaluated via principal component analysis. Next, hydrochemical and isotopic analyses were conducted to determine the source of groundwater in the mining area, and a three terminal element mixing model was established to identify the source of pollutants and calculate the terminal element mixing ratio. The research results indicate that groundwater in mining areas is formed by a mixture of shallow bedrock fissure water, deep bedrock fissure water, and rainwater, and the mixing effect is the main factor affecting the evolution of groundwater in mining areas, with a more significant impact than the depth of groundwater circulation. In addition, different types and degrees of water–rock interaction in different regions have altered the hydrochemical characteristics of groundwater in mining areas, such as the dissolution of multiple minerals, cation exchange, and common ion effects. Based on the above analysis results, a water circulation model for the mining area has been established. The findings of this study not only contribute to the protection of shallow fissure groundwater in the study area, but also provide a basis for investigating the groundwater evolution patterns in other metal mines.

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1. Introduction

Groundwater constitutes approximately 99 % of all available freshwater resources [1]. Meanwhile, billions of people rely on groundwater as a source of domestic water, and approximately 40 % of agricultural irrigation water comes from groundwater and groundwater is becoming increasingly important in mitigating water scarcity [2]. In the past few decades, climate change has substantially altered groundwater recharge, discharge, flow, storage, and distribution. In addition, anthropogenic activities, such as mining, may affect groundwater quality in several ways. Blasting, unloading of surrounding rocks, and the presence of a goaf can result in the emergence and expansion of cracks, as well as the closure of primary cracks [2–4]. When secondary fractures establish hydraulic connections with aquifers, they can alter the original groundwater circulation patterns and result in groundwater pollution [5–7]. Therefore, water circulation models must be established under mining conditions for the orderly management of water resources. Groundwater quality is constrained by various factors, and its deterioration is typically associated with human activity [3]. Owing to the different sources of recharge from aquifers, determining the hydrogeochemical processes of groundwater is challenging and fragmented. Furthermore, mining activities exacerbate the problem. In recent years, the groundwater evolution characteristics in mining areas has been investigated extensively [8–11]. In most cases, the interaction between water, air, and rock are the key mechanisms in the evolution of groundwater. Various methods such as field investigation and analysis, multivariate statistical analysis, geochemical modeling, and Geographic Information System, have been applied to study the evolutionary characteristics that occur in regional and local groundwater systems [12–22]. Argamasilla performed multivariate statistical analysis and discovered that coastal aquifers in southern Spain are affected by Atlantic rainfall and cation exchange [23]. Multivariate statistical analyses and boxplots have been to be promising for evaluating the spatiotemporal evolution patterns of groundwater in karst aquifers [24]. Douglas, who performed multiple isotope analysis, provided evidence that mining activities resulted in a deep circulation of atmospheric precipitation, which increased from less than 30 %–70 % at a Canadian Shield mine [25]. An analysis of the gold-mineralized zone in Central Burkina Faso finds that the hydrogeochemical processes of groundwater are governed by silicate and carbonate weathering [22]. Studies pertaining to groundwater in the Huaibei Coalfield in China showed that mineral dissolution and cation exchange govern its hydrogeochemical evolution. Long-term mining activities disrupt the original groundwater evolution law and circulation patterns [26], whereas mining activities and auxiliary engineering can damage the upper aquiclude and create new water channels that form new hydraulic connections. By conducting hydrogeochemical inversion of groundwater in mining cities, three main reaction transport pathways were identified in the mining area [27]. In addition, temporal machine learning methods have been used for predicting groundwater levels in mining areas, and the research results are of great significance for preventing and controlling water damage in coal fields [28,29]. Therefore, the sources and evolutionary patterns of groundwater affected by mining activities must be understood to protect and utilize regional groundwater resources effectively.

Previous studies have predominantly focused on groundwater in coal mining regions, whereas steeply inclined metal mines are rarely investigated. Compared with coal mines, metal mines feature a larger mining depth, which communicates with deep groundwater and renders the hydrogeological conditions of the mining area more complex. Additionally, the morphology of metal mines is irregular and rock formations are susceptible to uneven subsidence, which results in the expansion of water-bearing fractures. In addition, previous scholars focused on studying the controlling factors of groundwater evolution, without analyzing the sources of groundwater. This study focused on a typical metal mine, i.e., the Jinchuan copper-nickel mine, to investigate factors that affect groundwater evolution in mining areas. Previously, investigations into groundwater in mining areas has mainly focused on hydrogeological surveys, the identification of water inflows, the calculation of mixing ratios, and hydrochemical reactions. However, comprehensive investigations into the hydrogeochemical groundwater processes in mining areas are few. Therefore, regional researches are crucial for gaining deeper understanding of the spatial differences and underlying causes of groundwater hydrogeochemical processes in mining areas [30]. The evolution trend of groundwater in mining areas are mainly influenced by human interference and natural processes, such as pumping and drainage, changes in water channels, and water–rock interaction [31–35]. The dissolution and precipitation of carbonates minerals significantly alter the chemistry of groundwater such as the alkalinity of groundwater and the contents of primary cations [22,23,36,37]. Previous studies have estimated the source of groundwater based on the concentration of $\delta^2\text{H}$ (δD) and $\delta^{18}\text{O}$ in different water sources [38]. This methodology provides valuable insights and contributes to the development of comprehensive conceptual models for regional groundwater evolution [39,40]. Therefore, the combination of isotopic analysis and water chemistry is an effective method for unraveling the sources of groundwater and elucidating the complex hydrogeochemical processes that occur along flow paths.

Herein, multivariate statistical analysis methods are often used to study the evolution laws of groundwater, but they cannot determine the source of groundwater. The author believes that the evolution of groundwater includes two processes: the formation of groundwater and changes in hydrochemical composition. Therefore, in order to study the sources and evolution control factors of groundwater in mining areas, this paper proposes a method combining multivariate statistical analysis and mixed ratio calculation. This method can be used to identify the composition and source of groundwater in mining areas, analyze the hydraulic connections between different aquifers, identify potential sources of groundwater pollution, and provide recommendations for groundwater management and protection in mining areas. Meanwhile, it can also determine the evolution law and main influencing factors of groundwater in mining areas, which can be used to predict the trend of changes in groundwater composition and formulate corresponding prevention and control measures to reduce the impact of human activities on groundwater. To study the above content, this article selects Jinchuan Nickel Mine as the research area. The main purpose of this study is to determine the source of groundwater in mining areas and identify potential sources of pollution based on the hydraulic connections between different aquifers. In addition, identifying the main factors affecting the evolution of groundwater provides a theoretical basis for the management of groundwater resources in mines and ensures the safety of mining production.

2. Background

The Jinchuan mining area is located at the northern foot of the Qilian Mountains and the southern edge of the Alxa Plateau (Fig. 1a), belonging to an inland arid region. Through detailed hydrogeological investigation of the research area, the potential recharge sources of the mining area have been determined, including Quaternary pore water, Jinchuan River water, Jinchuan Gorge reservoir water, atmospheric precipitation, shallow bedrock fissure water, deep bedrock fissure water, and filling wastewater.

The average annual precipitation is 122 mm in study area. And the average annual evaporation is 2382 mm, thus resulting in a low humidity coefficient of only 0.043. Therefore, atmospheric precipitation minimally affects groundwater recharge. However, owing to the development of weathered fractures, rainfall infiltrates rapidly into the ground after rain, which is one of the main sources of groundwater recharge, despite the low amount of precipitation. The groundwater level increases annually from July to September, with a maximum annual fluctuation of approximately 4m. The dynamic changes in groundwater are closely related to precipitation. The mining area is located downstream of the northern slope of Longshoushan Valley. Regional bedrock fissure water supplemented by the melting water of ice and snow in the Qilian Mountains flows through the mining area and is discharged into the tidal basin. Therefore, regardless of the terrain or hydrogeological conditions, the supply of regional bedrock fissure water should be the important source of groundwater in the mining area. Meanwhile, the Quaternary pore rock formation in the mining area contains pore water, and its pore water flow is mainly affected by the surface runoff of the Jinchuan River, but the Jinchuan River only has runoff during flood periods. In addition, the mining area has formed a huge volume of filling material, which generates filling wastewater during the consolidation process. So Quaternary pore water and filling wastewater can serve as secondary sources of groundwater recharge in mining areas.

The lithology of the mining area is mainly metamorphic rocks, among which marble is distributed throughout the entire mining area. The mineral composition of marble is calcite, and previous research has shown that the dissolution of calcite is an important factor affecting the evolution of groundwater [26]. In addition, there are multiple faults distributed in the mining area, which greatly communicate the hydraulic connections between multiple aquifers (Fig. 1c).

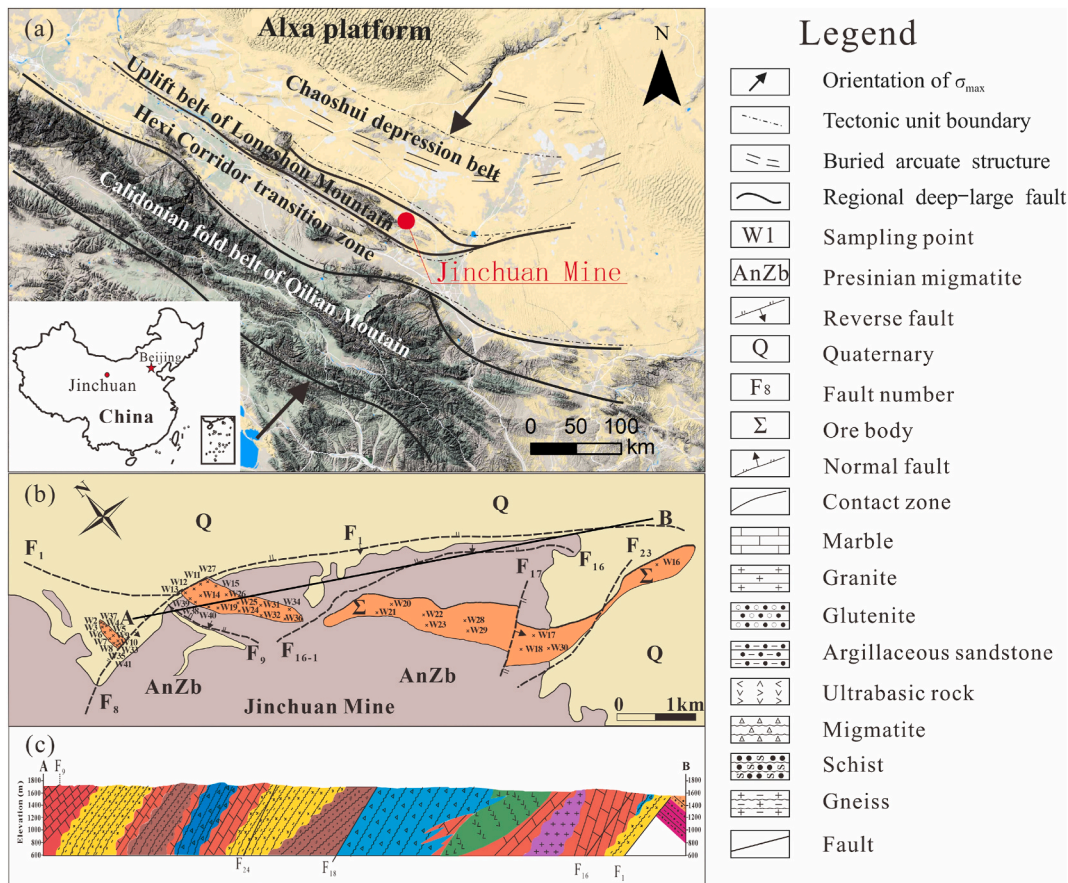


Fig. 1. (a) Geotectonic map of the study area. (b) Geological map and sample sampling location map. (c) A-B profile of Fig. 1b.

3. Materials and methods

3.1. Sampling and analytical procedures

To achieve the research objectives mentioned above, 50 samples of surface water, atmospheric precipitation, and groundwater were obtained from the study areas since 2021. Specifically, the samples comprised 2 surface water samples (taken from two reservoirs in the study area), 3 atmospheric precipitation samples (taken from different locations in the study area), and 45 groundwater samples. The groundwater samples included Quaternary pore water, bedrock fissure water, and mine water, and all samples were obtained from fractures in the surrounding rock or from continuous water drilling holes, with one sample taken from each sampling point. The shallow bedrock fissure water is taken from natural spring water in the study area, while the deep bedrock fissure water is taken from a long-term water inrush point in the deep subsection of the mining area. The filling wastewater is the effluent from the filling body, which is taken from a completed filling subsection of the mining area. The sampling personnel put the water sample into two bottles and examine the ions (including K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , HCO_3^- , CO_3^{2-} , and NO_3^-) (unit mg/L), hydrogen and oxygen isotopes (δD and $\delta^{18}O$), pH, and TDS. And the 3H content of potential end members and water inflow points with high water output will be measured. In addition, each sample was stored in 400 mL brown polyethylene plastic bottles, and tested at the Institute of Geology and Geophysics, Chinese Academy of Sciences. Anions and cations were tested in accordance with the national standards of the People's Republic of China using an ICS-1500 ion chromatograph. The hydrogen and oxygen isotopes were measured using a PICARRO L2140-i isotope analyzer. The original isotopic composition was corrected to avoid instrument drift and referenced to the Vienna Standard Mean Ocean Water in per mil (‰) units. The measurement accuracies for the δD and $\delta^{18}O$ were ± 1 ‰ and ± 0.1 ‰, respectively.

To ensure the accuracy of testing data, the water sample test results were evaluated using the PHREEQC software developed by the United States Geological Survey. Most of the samples were in a complete state of charge balance, with an error percentage of less than ± 5 %, and two samples with a percentage error exceeding 6 % were excluded; So the final dataset for further analysis comprised 40 samples, with the sampling locations shown in Fig. 1b. The presence of numerous chemical and physical parameters in each sample renders regional hydrogeochemical research a multivariate problem. For the 13 hydrochemical parameters mentioned above, NO_3^- and δD are unstable; thus, they may adversely affect the classification results. Therefore, eight parameters $Na^+ + K^+$, Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , HCO_3^- , CO_3^{2-} , and $\delta^{18}O$ were selected for multivariate statistical analysis. Before conducting multivariate statistical analysis, variables that could not provide important information were eliminated based on the Pearson correlation coefficient and the coefficient of variation to reduce the data size. Because highly correlated variables can affect the results of principal component analysis (PCA). Therefore, only one variable should be retained when the correlation coefficient exceeds 90 %. Additionally, when the temporal and spatial coefficients of variation of a variable are extremely low, irrelevant variables must be eliminated. Subsequently, the remaining variables in the dataset should be standardized (between 0 and 1) to ensure equal weighting for each parameter.

3.2. Statistical analysis

To reduce the dimensionality of hydrochemical data, extract key indicators, and simplify the analysis process, the SPSS Statistics and Mix software was utilized in this study. And multivariate analysis methods (hierarchical clustering analysis and principal component analysis) were applied, and mixed ratio calculations were performed to analyze the factors affecting groundwater evolution in the mining area. The paper analysis process is shown in Fig. 1S.

3.2.1. Hierarchical clustering analysis

Water samples have been classified successfully in several studies using this technique [41–45]. However, many clustering methods present limitations in terms of classification. Ward's method, which is proposed by Cloutier [17], yields more balanced clustering results and is more suitable for situations involving significant amounts of data. For the first time in the field of hydrochemistry, this study adopted a hierarchical clustering method based on Pearson's correlation, which is more suitable for small data volumes. The reasonableness of the clustering can be validated using other methods. Woocay and Walton used a biplot to demonstrate the validity of number of clusters [46]. In this study, the number of clusters was determined based on experience, and biplot and mixture ratio methods were used to validate the clustering accuracy.

3.2.2. Principal component analysis

Principal component analysis extracts principal components that represent most of the variable information. As the main objective of PCA is to determine the number of clusters, we used the first three principal components to plot a biplot. The principal component scores in biplot are shown as scatter plots; and the loadings are shown as scaled arrows from the origin.

3.2.3. End-member mixing analysis

Determine the source of mine water based on stable hydrochemical indicators, and calculate the end element mixing ratio of mine water on this basis. Comparing the results of multiple methods for calculating the mixing ratio, it was found that the results of the mass conservation method, least squares method, and maximum likelihood method were basically similar. Therefore, this study uses the mass conservation method to calculate the end element mixing ratio.

4. Results

4.1. Water chemistry and water isotopes

Table 1 summarizes the statistical results of the hydrogeochemical composition of groundwater in the Jinchuan mining area. The wide range of changes in the chemical composition of groundwater in the mining areas indicates that they have undergone complex hydrogeochemical reactions, thus resulting in significant spatial variability in the groundwater composition.

Fig. 2 shows the correlation between $\delta^{18}\text{O}$ and δD in the mine water. The global meteoric water line (GMWL, $\delta\text{D} = 8 * \delta^{18}\text{O} + 10$) and the local meteoric water line (LMWL, $\delta\text{D} = 6.89 * \delta^{18}\text{O} + 7.67$) are plotted on the graph, along with the results of local rainfall samples [47]. Fig. 2a shows that the groundwater in the mining area were on the lower left side of the LMWL and rainfall samples. Combined with the 13-line diagram, one can infer that the groundwater in the mining areas originated from paleo-meteoric water (Fig. 2b).

Compared with modern precipitation, the δD values of ancient meteoric water were lower, thus indicating the occurrence of water–rock interaction. The significant variations in the $\delta^{18}\text{O}$ and δD values of mine water in the study area suggest that regional major faults and small karst fissures may serve as priority flow pathways;

The ^3H content was measured for typical potential recharge sources and high flow water inflow points (as shown in Table S1), and the measurement results showed that the TU value of atmospheric precipitation was 30.33. The Quaternary pore water has a relatively deep burial depth, a long infiltration path, and a tritium value of 19.82TU, which is groundwater replenished in the past 10–20 years; The TU value of shallow bedrock fissure water is 31.68, which is relatively close to atmospheric precipitation, indicating a close connection with atmospheric precipitation. The TU value of deep bedrock fissure water is 44.891, mainly supplied from the 1960s–1970s. Among the 8 sampling points in the mine water, 4 have tritium values greater than 30TU, with an average value of 36.15TU, which should mainly be water replenished in the 1960s or 1970s. The tritium value of the water sample confirms our hypothesis that the mine water originated from ancient atmospheric precipitation or was mixed in by deep bedrock fissure water. There are 4 mine water samples with abnormally high TU values, due to the presence of radioactive anomaly zones and variant crystalline uranium anomaly zones on the east and west sides of the Jinchuan mining area.

4.2. Multivariate statistical analysis

In this study, hierarchical cluster analysis was performed to classify mine waters into different categories. Box plots, Stiff diagrams, and Piper diagrams were used to determine the hydrochemical characteristics of each cluster. Fig. 3 shows a dendrogram of the cluster analysis of groundwater in the mining area. Using a group between-linkage distance of 8 as the criterion for classifying different categories, the dendrogram was segmented into six clusters. To compare the hydrochemical parameters among the different clusters, Fig. 2S presents box plots of the hydrogeochemical parameters for each cluster. This enables a direct comparison of the different hydrochemical indicators among the six clusters. The median concentrations of $\text{Na}^+ + \text{K}^+$ increased gradually from C1 to C6, which is consistent with the TDS trend. However, the trend of TDS development did not show a clear correlation with the median concentrations of Cl^- . Thus, we can infer that the $\text{Na}^+ + \text{K}^+$ have other sources in the study area.

Additionally, Fig. 3 also shows the Stiff diagram for the six clusters, which is plotted based on the median concentrations of groundwater hydrochemical parameters. The analysis results of the Stiff plot are basically consistent with the box plot, showing the similarities and differences between the six clusters. For example, the stiff diagram of cluster C5 differs significantly from those of the other clusters because of the higher median concentrations of $\text{Na}^+ + \text{K}^+$ and $\text{CO}_3^{2-} + \text{HCO}_3^-$. The differences in the Stiff diagrams reflect the rationality of the clustering analysis from a different perspective.

Fig. 4 shows the Piper diagram for 40 mine water samples, with different clusters represented by different colors. The lower-left and lower-right triangles indicate that Mg^{2+} and $\text{Na}^+ + \text{K}^+$ are the dominant cations, respectively. Based on the differences in the concentrations of these cations, C1, C2, and C3 can be clearly distinguished. The anions exhibit scattering characteristics. Cations in C4, C5, and C6 overlapped each other, whereas distinct differences are indicated in the anions. C4 and C5 are primarily composed of Cl^- and SO_4^{2-} , respectively, and the concentration of $\text{CO}_3^{2-} + \text{HCO}_3^-$ in C6 is low. This once again proves the rationality of the clustering results.

As shown in Fig. 5, although the different clusters overlapped, the six clusters differed significantly from each other, thus indicating that the clustering results are reasonable. To validate the results of the clustering analysis, they were visualized as a dual plot via PCA,

Table 1
Statistics of 40 deep groundwater samples in Jinchuan mining area.

Items	Anions(mmol/L)				Cations (mmol/L)			pH	TDS
	Cl^-	SO_4^{2-}	CO_3^{2-}	HCO_3^-	$\text{Na}^+ + \text{k}^+$	Ca^{2+}	Mg^{2+}		
Min	8.06	7.65	0.00	0.00	14.82	0.00	0.00	6.74	2.45
Mean	21.85	16.14	3.50	2.70	49.04	3.59	2.88	9.41	4.49
Max	53.13	32.57	29.24	10.72	150.43	10.11	12.52	13.28	10.99
Variance	121.63	47.49	56.85	6.96	1091.79	10.84	12.85	4.28	3.95
SD	11.02	6.89	7.54	2.63	33.042	3.29	3.58	2.07	1.98

SD, standard deviation.

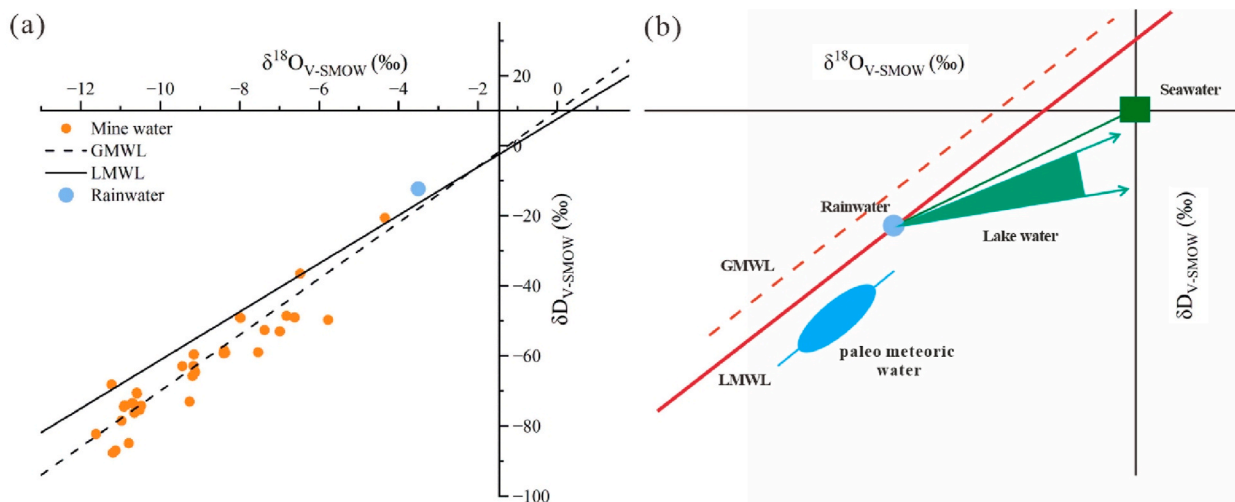


Fig. 2. (a) Relationship between $\delta^{18}\text{O}$ and δD in mine water samples in Jinchuan mining area. GMWL: global meteoric water line, expressed as $\delta\text{D} = 8 \times \delta^{18}\text{O} + 10$ (Craig, 1961); LMWL: local meteoric water line, expressed as $\delta\text{D} = 6.89 \times \delta^{18}\text{O} + 7.67$. (b) Stable isotope relationship diagram.

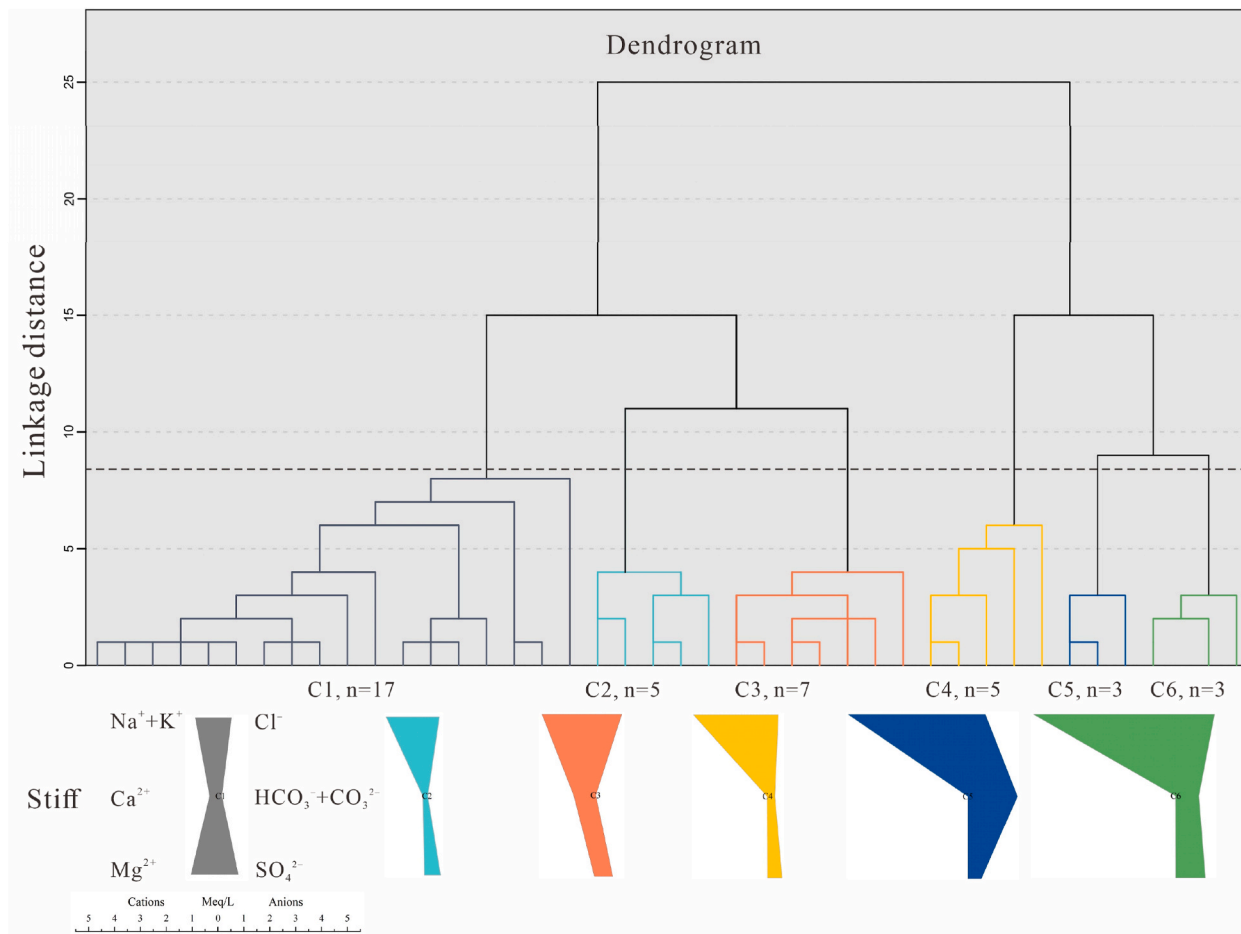


Fig. 3. Dendrogram and Stiff diagrams of cluster analysis for 40 groundwater samples. Dashed line segregates all samples into six clusters.

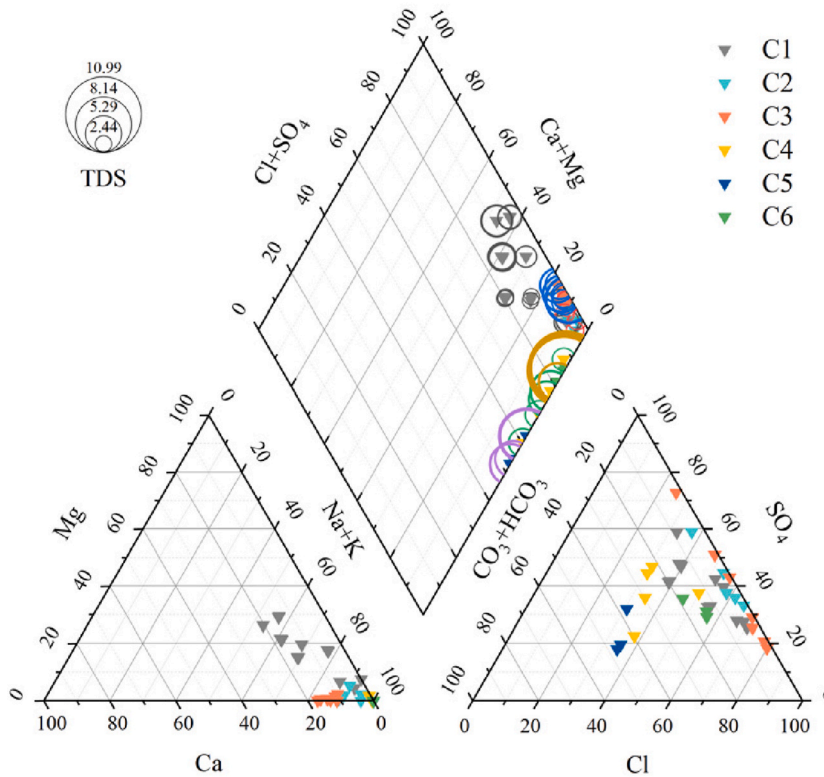


Fig. 4. Piper diagram of 40 groundwater samples for six clusters.

as shown in Fig. 5a. Although the data corresponding to C1 – C3 in Fig. 5b overlapped, the three clusters exhibited distinct differences, as shown in Fig. 5c. Therefore, the three principal components are sufficient to validate the clustering analysis results.

In order to analyze the spatial distribution characteristics of mine water, the clustering results were projected onto a plane map (Fig. 6). As shown in Fig. 6, each cluster of mine water is distributed throughout the entire mining area, indicating the need to analyze the study area as a whole because it has the same source of recharge. At the same time, some mine water has a certain degree of aggregation in local areas, indicating the existence of local dominant water conducting cracks.

4.3. Water source identification

The investigation results of hydrogeological conditions in the study area indicate six potential sources of groundwater recharge in the mining area: atmospheric precipitation, Quaternary pore water, shallow bedrock fissure water, deep bedrock fissure water, backfilling waste water, and surface water reservoir water (Fig. 7). The triangles in the figure represent potential end elements, and the red dots represent groundwater in the mining area. Oxygen 18 and chloride ions are conserved and do not react with other ions. Therefore, based on these two indicators, two possible mixing modes have been established in the mining area. The first is a ternary mixing model comprising rainwater, shallow bedrock fissure water, and deep bedrock fissure water. The other is a ternary mixing model comprising rainwater, shallow bedrock fissure water, and backfilling waste water. However, the leachate from the fill sewage is released during the consolidation of the fill material and does not replenish the underground water in the mining area after solidification. Consequently, it can supply groundwater for a certain period, but cannot serve as a continuous water supply source. Rainwater can directly replenish groundwater through faults and other pathways for water flow, and both Quaternary pore water and surface water reservoirs are replenished by atmospheric precipitation and the melting of ice and snow. However, they are not located at extreme points in the region; therefore, they cannot be regarded as end members in the mixing model. Based on the Euclidean distance between different water samples, the groundwater mixing model was determined to be a ternary mixture model comprising shallow bedrock fissure water, rainwater, and deep bedrock fissure water.

Based on the results of water-source identification, the conservation of mass method can be used to calculate the end-member mixing ratios of groundwater. The calculation of mixing ratios not only verifies the results of the cluster analysis, but also allows one to analyze the main controlling factors of mine water evolution.

4.4. Mixing ratio

Based on the water-source identification results, a three-end-member mixing ratio model was used to determine the end-member

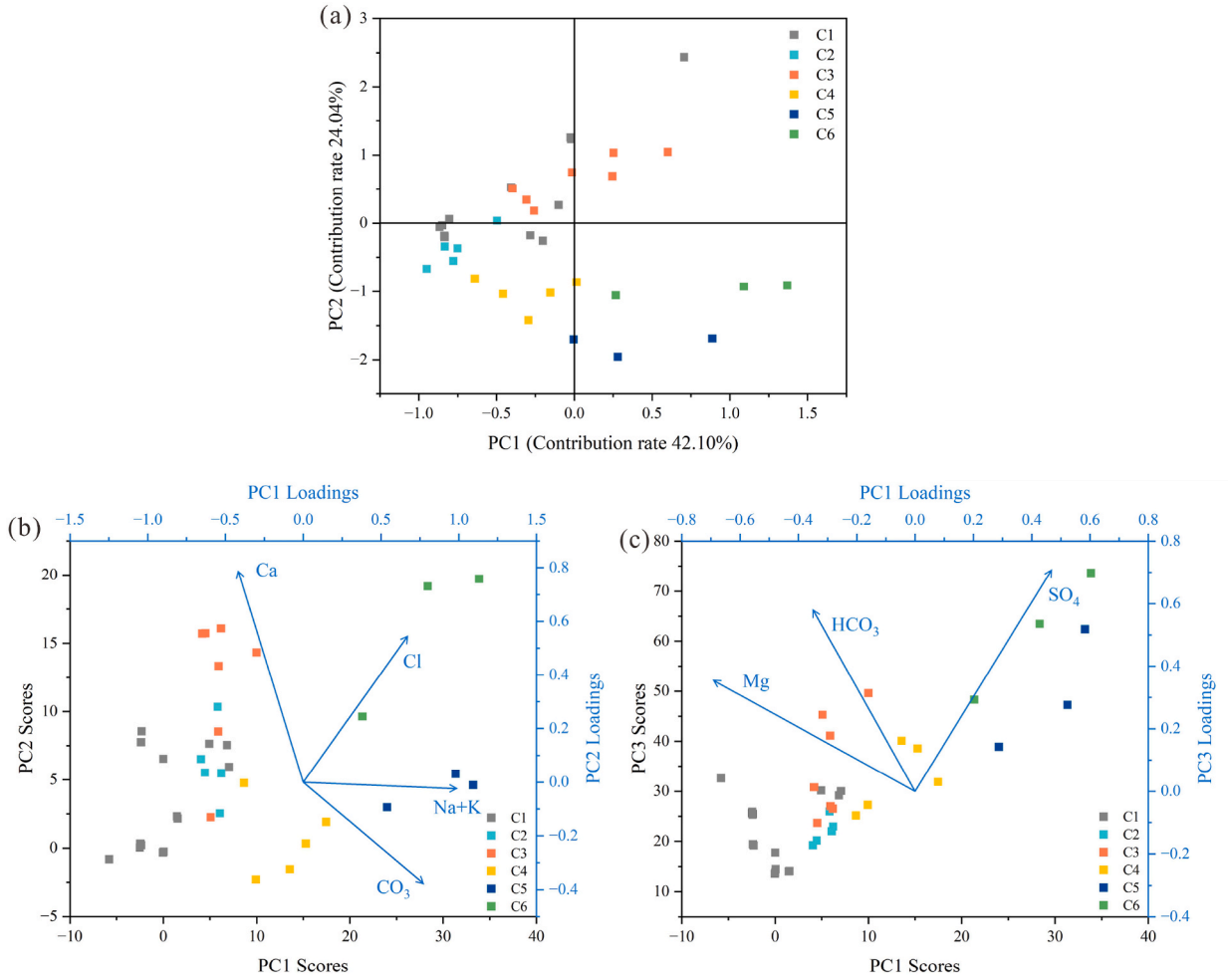


Fig. 5. (a) Scatter plots of PC1 vs. PC2; (b) PC 1 vs. PC 2 biplot; (c) PC 1 vs. PC 3 biplot (see text for explanation).

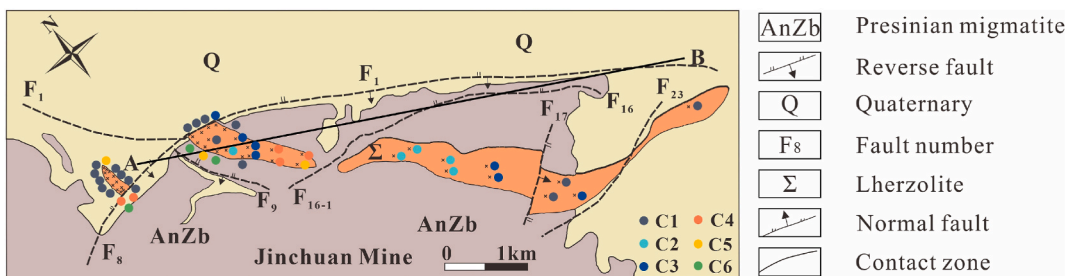


Fig. 6. The spatial distribution of clustering results of 40 groundwater samples.

mixing ratios of the groundwater samples in the mining area. This ternary mixing ratio calculation model based on mass conservation adopted in this article considers that the mine water inflow is composed of three types of end elements and assumes that the concentration of the three end elements is constant. The calculation formula is as follows:

$$\begin{bmatrix} a_1 & a_2 & a_3 \\ b_1 & b_2 & b_3 \\ 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} \delta_{1p} \\ \delta_{2p} \\ \delta_{3p} \end{bmatrix} = \begin{bmatrix} a_{sp} \\ b_{sp} \\ 1 \end{bmatrix} \quad (1)$$

Among them, $[a_1, a_2, a_3]$ are the concentrations of analytical indicators a for end-member 1, end-member 2, and end-member 3, respectively; Among them, $[b_1, b_2, b_3]$ are the concentrations of analytical indicators b for end-member 1, end-member 2, and end-

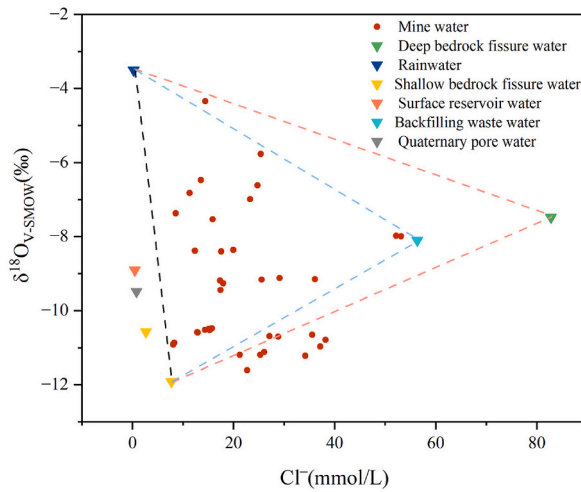


Fig. 7. Correlation diagram between Cl⁻ ions and δ¹⁸O in all water samples. Dashed lines represent possible mixed lines.

member 3, respectively; a_{sp} and b_{sp} are the concentrations of indicator a and b for the p-th tunnel water inflow sample, respectively; $[\delta_{1p} \delta_{2p} \delta_{3p}]$ are the mixing ratios of the p-th tunnel water inflow sample, respectively.

The average end-member mixing ratios for each groundwater type are shown in Fig. 8. The results of the mixing ratio calculations indicated the proportion of rainfall in clusters C2, C4, and C5 was approximately 40%. But the fact that these three types of water samples were obtained at greater depths suggests the presence of flow pathways that allowed the infiltration of rainfall.

Fig. 9a shows the correlation between different clusters and TDS, and it can be seen from the figure that TDS shows a gradually increasing trend. In the absence of sedimentation, the depth of groundwater circulation directly affects the groundwater's TDS, but this is inconsistent with the actual sampling depth for each type (Fig. 9b). And Fig. 9c indicates that its TDS is mainly influenced by the proportion of deep bedrock fissure water in the mine water. The analysis above suggests that the evolution of groundwater in the mining area is primarily affected by mixing processes. Due to the high TDS of deep bedrock fissure water and its distribution in groundwater at different depths in mining areas, it may serve as a source of pollution to the shallow bedrock fissure water and pore water in the study area.

4.5. Water-rock interactions

To quantify the differences in isotope fractionation, Dansgaard proposed the d-excess (d) parameter in 1964, which is defined as $d = \delta D - 8 * \delta^{18}O$ [48]. When atmospheric precipitation infiltrates into groundwater aquifers, water-rock interactions can result in

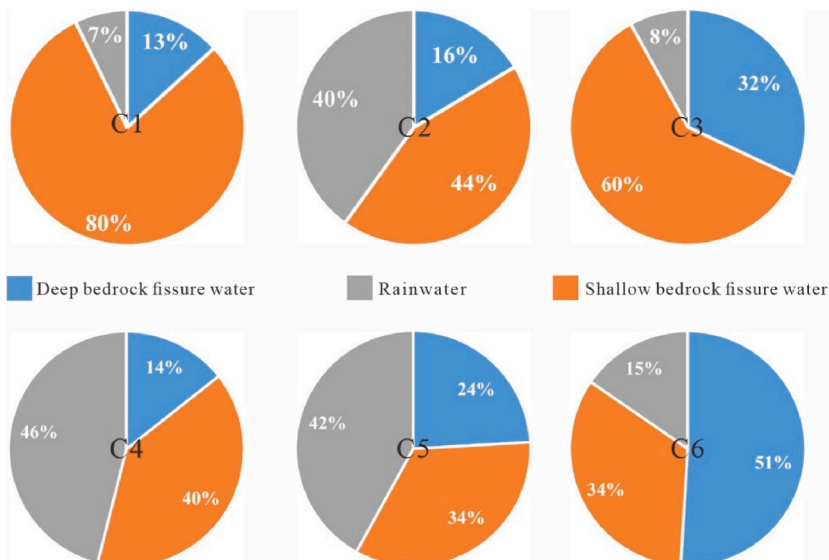


Fig. 8. End element mixing ratio of six clusters.

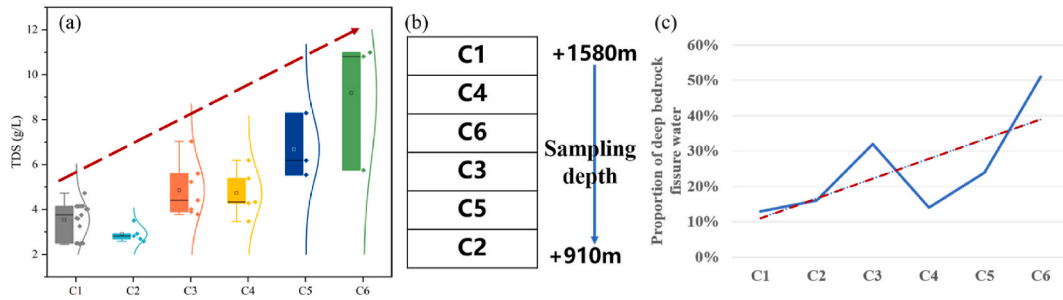


Fig. 9. (a) the correlation between categories and TDS; (b) sampling depth for different categories; (c) the correlation between categories and proportion of deep bedrock fissure water.

isotopic exchanges between water and rocks. The D content in rocks may be relatively low and insufficient to significantly affect the D content in water. However, the $\delta^{18}\text{O}$ content in groundwater can increase significantly owing to isotopic exchange processes. Water–rock reactions increase $\delta^{18}\text{O}$, where stronger reactions result in a more significant increase. The d-excess parameter can effectively eliminate the effects of seasonality and variations in water sources on the degree of isotopic exchange in groundwater aquifers. Based on the above formula and isotopic detection results of groundwater samples, the d value of groundwater samples was calculated. Because Cl^- is typically considered a conservative ion, the d-Cl correlation (Fig. 10) can be used to define a polygon that represents ideal mixing. The samples within the polygon are considered mixed and thus isotopic exchange is negligible, whereas the samples outside the polygon are assumed to have undergone isotopic exchange. From Fig. 3, it can be seen that most of the mine water falls outside the mixing boundary, indicating that the mine water has undergone a strong water–rock interaction.

In this study, PCA was performed to derive and interpret the hydrogeochemical characteristics of 40 groundwater samples obtained from mining areas. Table 2 presents the relevant results of principal component analysis. The first three principal components (PC1, PC2, and PC3) explain 81.59 % of the total variance. PC1 constituted 42.10 % of the variance and is characterized by high loadings of $\text{Na}^+ + \text{K}^+$ and CO_3^{2-} as well as a significant negative loading of $\text{Mg}^{2+} + \text{Ca}^{2+}$. This suggests that PC1 is probably affected by the cation exchange. PC2 explains 24.04 % of the total variance and is mainly determined by high loadings of $\text{Ca}^{2+} + \text{SO}_4^{2-}$ and negative loadings of HCO_3^- . This indicates the occurrence of mineral dissolution and cation exchange.

Although the analysis of end-member mixing ratios in the mining area groundwater suggests that mixing is the primary factor in groundwater evolution, the d-excess analysis and PCA confirmed that strong water–rock interactions occurred in the mining area groundwater. In this section, we analyze the ion ratios to understand the types and intensities of water–rock reactions in the groundwater of the mining area. The potential minerals involved in water–rock interactions in mining areas primarily include carbonate minerals (e.g., calcite and dolomite) and crystalline minerals (e.g., gypsum and halite) (Fig. 1c). Fig. 11a and b shows the correlation between the primary ions and saturation index (SI) of related minerals, calculated using the PHREEQC software. These graphs provide insights into the relationships between different ions and specific minerals, including their tendencies for dissolution, precipitation, and exchange. The SI of calcite ranges from -3.7 to 2.8 , and most of the samples have SI values greater than 0. Similarly, for groundwater in most mining areas, the SI of dolomite exceeds 0 and ranges from -6.8 to 4.89 . Additionally, no significant correlation was indicated between the concentrations of primary ions in the groundwater samples from the mining areas and the SI of the

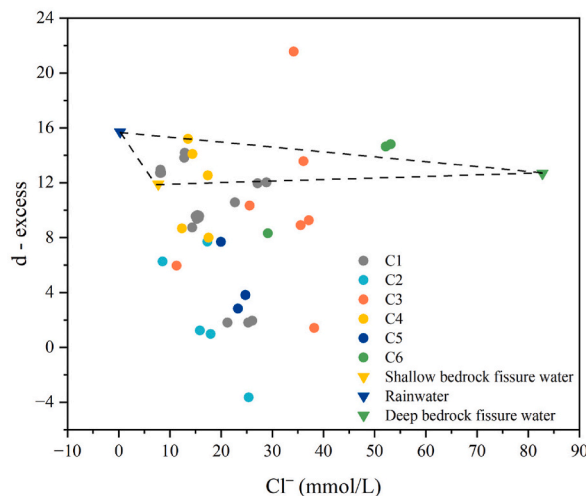


Fig. 10. Correlation diagram between Cl^- ions and d-excess in groundwater samples.

Table 2
Basic information of the three principal components.

Parameters	Component 1	Component 2	Component 3
Eigenvalue	2.947	1.682	1.082
Contribution rates (%)	42.096	24.035	15.454
Na ⁺ +K ⁺ (mmol/L)	0.974	-0.024	0.210
CO ₃ ²⁻ (mmol/L)	0.763	-0.372	0.147
Mg ²⁺ (mmol/L)	-0.685	0.213	0.351
Cl ⁻ (mmol/L)	0.663	0.538	-0.189
Ca ²⁺ (mmol/L)	-0.416	0.784	0.186
HCO ₃ ⁻ (mmol/L)	-0.346	-0.636	0.574
SO ₄ ²⁻ (mmol/L)	0.464	0.436	0.702

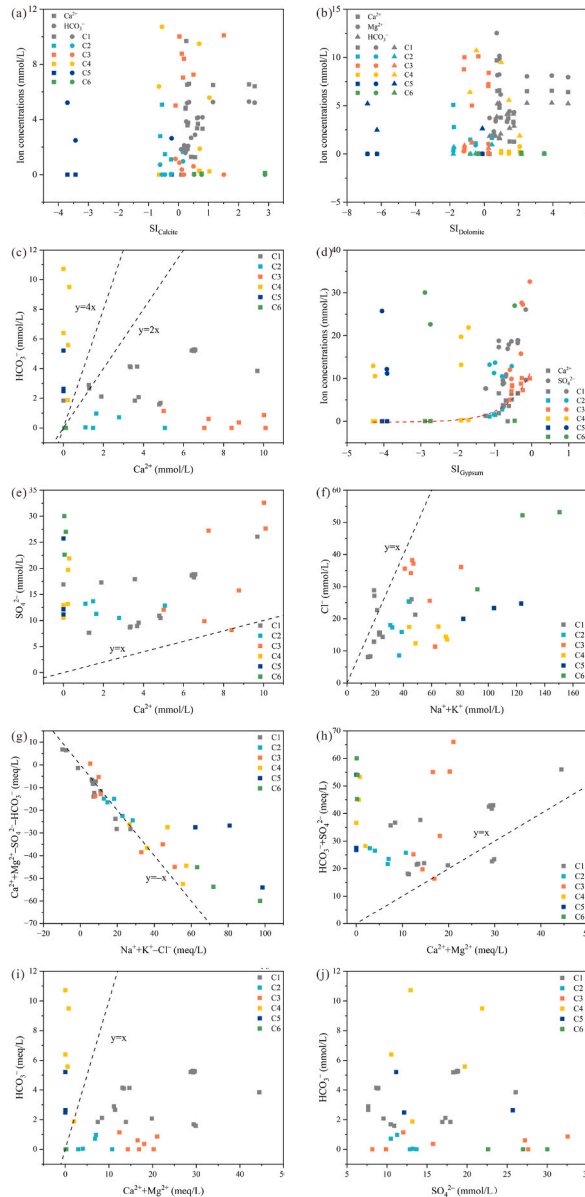


Fig. 11. Diagrams showing relationships of primary ions: (a) correlations between SI_{calcite} and related ions; (b) correlations between SI_{dolomite} and related ions; (c) Ca²⁺ vs. HCO₃⁻; (d) correlations of SI_{gypsum} and related ions; (e) Ca²⁺ vs. SO₄²⁻; (f) Na⁺ + K⁺ vs. Cl⁻; (g) Na⁺ + K⁺ - Cl⁻ vs. Ca²⁺ + Mg²⁺ - SO₄²⁻ - HCO₃⁻ in meq/L; (h) Ca²⁺ + Mg²⁺ vs. HCO₃⁻ + SO₄²⁻ in meq/L; (i) Ca²⁺ + Mg²⁺ vs. HCO₃⁻ in meq/L; (j) SO₄²⁻ vs. HCO₃⁻.

carbonate minerals. This suggests that the SI does not change significantly as the ion concentration increases, thus indicating that these minerals do not undergo significant dissolution under the current conditions. The primary source of Ca^{2+} and HCO_3^- in groundwater is the dissolution of carbonate minerals, as shown in Equations (1) and (2). Therefore, if the groundwater is formed by the dissolution of complete dolomite or calcite, then the ratio of $[\text{HCO}_3^-]/[\text{Ca}^{2+}]$ should be 4 or 2, respectively; Fig. 11c shows the relationship between these two ions, where all data points are classified into three sections by two thin lines representing fixed ratios. The upper section indicates a decrease in the Ca^{2+} concentration due to cation exchange—samples C4 and C5 belonged to this region. The middle section represents a transitional zone that indicates the coexistence of calcite and dolomite dissolution, with minimal distribution of groundwater samples. The lithological formations in this zone are predominantly composed of marble, with calcite as the main component. Therefore, most of the groundwater in the mining area is expected to be distributed in the lower section, as described previously. The Ca^{2+} concentrations are higher in the lower region, thus indicating the presence of other sources of Ca^{2+} , such as the dissolution of gypsum. All the samples from C1, C2, and C3 are located in this area, thus suggesting that the dissolution of gypsum affects the hydrochemical composition of these water samples. Fig. 11d shows that the SI of Gypsum are basically all negative values. Additionally, a clear exponential relationship is indicated between the concentration of Ca^{2+} and the SI of gypsum.

If only gypsum is dissolved in groundwater, then based on Equation (3), the theoretical Ca^{2+} to SO_4^{2-} concentration ratio should be equal to 1. In Fig. 11e, all the points are located above the dashed line ($y = x$), thus indicating that the Ca^{2+} concentration is lower than the theoretical value. This deviation suggests the possibility of cation exchange between $\text{Na}^+ + \text{K}^+$ and Ca^{2+} , thus resulting in a higher concentration of SO_4^{2-} than that of Ca^{2+} .

Cl^- is generally considered a conserved ion with high solubility and good stability. Therefore, in this study, the molar ratio of $[\text{Na}^+ + \text{K}^+]/[\text{Cl}^-]$ was used to identify the sources of Na^+ and K^+ . If the ions originate only from the dissolution of sodium chloride and potassium chloride, then this ratio should be 1. In Fig. 11f, the $\text{Na}^+ + \text{K}^+$ concentrations in almost all the water samples are higher than that of Cl^- , and the Cl^- concentrations do not change significantly with the increase in the $\text{Na}^+ + \text{K}^+$ concentration. This indicates that cation exchange governing the hydrochemical properties of groundwater as the primary process. In Fig. 11g, the $\text{Na}^+ + \text{K}^+$ concentrations in samples C2, C3, C4, and C5 are higher than the theoretical dashed line ($y = -x$), thus showing that the Na^+ and SO_4^{2-} in the groundwater originated from other sources. Considering that the study area is located in an arid region of western China, where the soil contains high levels of sodium carbonate and sulfate, mineral dissolution is an important factor governing the evolution of groundwater. Fig. 11h shows that the concentrations of $\text{Ca}^{2+} + \text{Mg}^{2+}$ are lower than $\text{SO}_4^{2-} + \text{HCO}_3^-$, thus reconfirming the occurrence of cation exchange. Based on the differences in the affinity of cations, in most cases, cation exchange tends to absorb Ca^{2+} and release $\text{Na}^+ + \text{K}^+$, as shown in Equation (4).

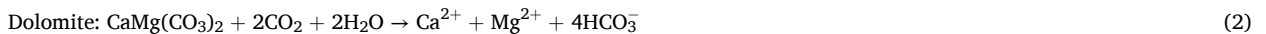


Fig. 11i shows a scatter plot depicting the relationship between the concentrations of $\text{Ca}^{2+} + \text{Mg}^{2+}$ and HCO_3^- . As shown in Equations (1) and (2), the milligram equivalent concentration ratios of the two species should be 1: However, relative to HCO_3^- , the $\text{Ca}^{2+} + \text{Mg}^{2+}$ concentrations in C1, C2, C3, and C6 are higher than the theoretical values. Based on Fig. 11h, one can deduce that the electrical charge balance of the anions is primarily governed by the dissolved SO_4^{2-} concentration. According to the above analysis, it can be concluded that SO_4^{2-} in groundwater mainly comes from the dissolution of gypsum. Furthermore, in Fig. 11h, the concentration of HCO_3^- decreases with the increase in Ca^{2+} and Mg^{2+} . This phenomenon can be explained by the typical common ion effect, in which the dissolution of gypsum causes the precipitation of calcite (Equation (5)). No apparent correlation is indicated between HCO_3^- and SO_4^{2-} in Fig. 11j, but the distribution law of sample C1 indicate the presence of typical common ion effects in some water samples. In general, mineral dissolution and cation exchange are important factors that govern the evolution of groundwater in mining areas. Additional, typical common ion effects influenced the hydrochemical processes of groundwater in mining areas.

According to the comprehensive analysis of Fig. 11, the saturation coefficient of calcium sulfate shows an exponential increase with the increase of Ca^{2+} , but there is no obvious correlation between it and SO_4^{2-} . Although the above analysis confirms the cation exchange between $\text{Na}^+ + \text{K}^+$ and Ca^{2+} in C1 – C6, Fig. 11e shows that the concentration of SO_4^{2-} in C4, C5, and C6 is much higher than that of Ca^{2+} , and Fig. 11f shows that the concentration of $\text{Na}^+ + \text{K}^+$ in C4, C5, and C6 is much higher than that of Cl^- , indicating that there is another source of $\text{Na}^+ + \text{K}^+$ in C4, C5, and C6. Considering the climatic and geological conditions of the study area, it may be that rainwater dissolves sodium sulfate in the soil during the infiltration process, which once again indicates that rainwater has a special water channel.

5. Discussion

This study proposes a combined approach involving multivariate statistical analysis and mixing ratio calculations to investigate the evolution control factors of groundwater in mining areas. It improves upon the traditional hierarchical clustering method and for the first time employs the Pearson correlation to classify groundwater samples. Clustering accuracy is evaluated based on the principal component biplot, piper plot and results of mixing ratio calculation. On this basis, hydrogeochemical analysis and mixing ratio

calculation were carried out on groundwater samples to determine the main controlling factors of groundwater evolution in the mining area.

5.1. Water circulation model

A typical water circulation model for the mountain-front mining area was established based on the results of mixing ratio calculations and analysis of water–rock interaction (Fig. 12). Part of the atmospheric precipitation and snowmelt replenish surface runoff, while another part replenishes shallow groundwater along fractures. Both undergo a certain degree of water–rock interaction during the downward infiltration process. Additionally, under the disturbance of mining activities, the fault changes from a non-water-conducting fault to a water-conducting fault. The presence of goafs causes compression deformation of the surrounding rock, leading to the expansion and connection of water-conducting fractures, providing conditions for the movement of atmospheric precipitation and shallow bedrock fissure water towards deeper layers. This establishes a hydraulic connection between shallow bedrock fissure water, deep bedrock fissure water, and atmospheric precipitation, and results in water–rock interaction with the surrounding rock during the migration process, such as mineral dissolution, cation exchange, and common ion effects. Due to the high TDS value of deep bedrock fissure water, it may pollute shallow bedrock fissure water and Quaternary pore water, affecting the groundwater quality in the study area. Therefore, it is necessary to strengthen the monitoring of shallow fractured water and Quaternary pore water in the study area.

5.2. Comprehensive analysis results

The analysis results of stable isotopes and radioactive isotopes indicate that the groundwater in the mining area originated from ancient atmospheric precipitation, and the mixing ratio calculation results also confirm this conclusion, that a large amount of deep bedrock fissure water is mixed into the groundwater in the mining area. Deep bedrock fissure water and shallow bedrock fissure water are the ancient atmospheric precipitation trapped in the formation. The groundwater in the mining area is formed by the mixed action of shallow bedrock fissure water, deep bedrock fissure water, and rainwater. However, deep bedrock fissure water has a high TDS, so there is a risk of contamination in shallow groundwater. Therefore, we need to establish the water cycle process in the mining area under the influence of mining. D-excess analysis and ion correlation analysis both indicate the existence of severe water–rock interaction in the mining area, including mineral dissolution, cation exchange, and common ion effects. C1 – C3 has a lower TDS and cation exchange degree, while C4 – C6 has a higher TDS and cation exchange degree. This is because C4 – C6 dissolves more sodium sulfate, which promotes cation exchange.

A comprehensive analysis of the groundwater classification results, mixing ratios, and sampling depths confirmed that mixing is the primary factor affecting the evolution of groundwater in the mining area. Mixing is a fundamental hydrochemical process in groundwater that typically results in transitional water quality compositions between two source components involved in mixing. As pointed out by Laura Scheiber et al. (2023), the quality of groundwater is the result of geological origin and mixing, and secondary fractures caused by mining can change the mixing mode of mining areas. Therefore, the research results of this article are of great significance for establishing a water cycle model and protecting water resources in mining areas. Research results on groundwater in the Huaibei coalfield pointed out that mineral dissolution and cation exchange control the evolution of, which is somewhat different from the research results in this paper [49]. This may be influenced by different research methods and concerns. An analysis of the ion ratios between different clusters shows that mineral dissolution and cation exchange are important factors that govern the evolution of groundwater in the mining area. Additionally, the hydrochemical processes of groundwater in mining areas are influenced by the typical common ion effect. However, this study is influenced by the breadth of time. In the future, groundwater samples from different years and seasons should be taken to analyze the evolution of groundwater in the mining area over time, and should be combined with the geological background of the mining area. The author found through research on groundwater in different mining areas that the generation of secondary water conducting cracks is mainly influenced by primary water conducting cracks. The circulation mode of groundwater in mining areas is closely related to primary water conducting cracks in mining areas. Through studying the groundwater in deep winter coal mining areas, it was found that the disturbance caused by mining formed a local groundwater circulation pattern

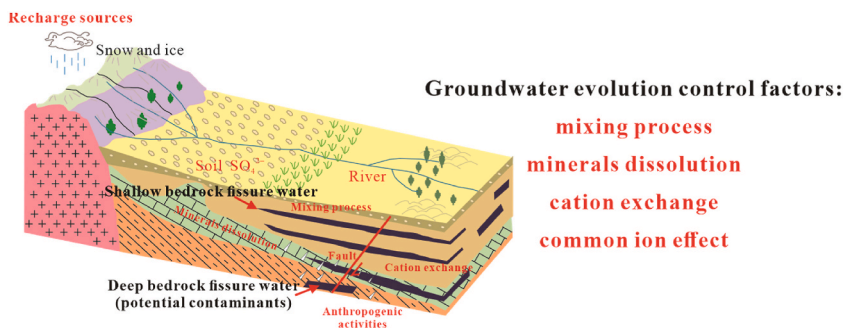


Fig. 12. A typical water circulation model for the mountain-front mining area.

centered on the mining area, which resulted in mixing of groundwater in the mining area and enhanced water–rock interaction [29]. Therefore, the author will focus on studying the impact of primary water conducting cracks in the future.

Nonetheless, the study findings provide theoretical support for the prevention of mine water inrush disasters and shallow groundwater pollution in the study area. Furthermore, the findings can serve as a reference for investigating groundwater evolution in other metal mining areas in China.

6. Conclusion

This article presents a method that integrates multivariate statistical analysis, mixing ratio calculations, and ion correlation analysis. This approach addresses the challenges faced in previous research regarding the identification of groundwater sources, analyzes the hydraulic connections between different aquifers, and identifies the primary controlling factors influencing groundwater evolution in mining areas.

The study offers valuable insights into the factors that govern groundwater evolution in the mining regions of western China. A cluster analysis was conducted to categorize the 40 groundwater samples collected from the study area into six distinct clusters. The results of this clustering analysis were validated through PCA. Additionally, hydrogeochemical analysis, along with box plots, Piper plots, and Stiff plots, highlighted both the differences and commonalities among the various clusters.

The chemical composition of groundwater is intrinsically linked to its origin and is influenced by factors such as dynamic variations, mixing between different water bodies, and the intensity of water–rock interactions. The analysis of stable ions and stable isotopes indicates that the groundwater in the mining area consists of deep bedrock fissure water, shallow fissure water, and rainwater, leading to the establishment of a three-terminal element mixing model. The results of the mixing ratio calculations reveal a positive correlation between the TDS of groundwater in the mining area and the proportion of deep bedrock fissure water, while no correlation was found with sampling depth. This suggests that mixing is the primary controlling factor for groundwater evolution in the mining area. Furthermore, the high TDS and distribution of deep fissure water may pose a risk of pollution to the shallow fissure water in the study area. Based on this, d-excess analysis was performed, demonstrating a strong water–rock interaction within the groundwater of the mining area. Ion correlation analysis indicates that the predominant types of water–rock interaction include the dissolution of minerals and cation exchange processes. Additionally, a typical common ion effect was observed in certain regions. The diversity and extent of water–rock interactions significantly altered the concentrations of primary ions, which were crucial in determining the direction of groundwater evolution.

Long-term mining activities have led to uneven subsidence of rock formations, resulting in the expansion of fractures in the study area. This disruption has compromised the original circulation pattern of groundwater and established hydraulic connections between multiple aquifers, thereby intensifying the interactions between groundwater and rock. The combination of multiple methodologies offers a more comprehensive perspective for investigating the hydrogeochemistry of groundwater in mining areas. Moreover, this article establishes a typical water circulation model for the mining area, providing theoretical support for preventing groundwater pollution. Additionally, the findings of this study serve as a foundation for future research on the hydrogeochemistry evolution of groundwater in other metal mining areas throughout western China.

Data availability

All the relevant data are included in the manuscript and the supplementary document. No separate repository is attached.

CRediT authorship contribution statement

Yewei Song: Writing – review & editing, Writing – original draft, Investigation, Data curation, Conceptualization. **Jie Guo:** Software, Methodology, Investigation, Funding acquisition. **Fangrui Li:** Writing – original draft, Software, Investigation, Data curation. **Junchao Wang:** Validation, Investigation, Data curation. **Fengshan Ma:** Software, Methodology, Investigation, Funding acquisition. **Gaofeng Wu:** Writing – original draft, Methodology, Investigation. **Guang Li:** Writing – original draft, Investigation, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.heliyon.2024.e38860>.

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