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Original Research

Characteristics of Rare Earth Elements in Groundwater of Multiple Aquifers and Their Implications in the Panxie Mine Area, Huainan Coalfield, China

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Abstract

This study investigates the characteristics and distribution of rare earth elements (REEs) within the multi-aquifer groundwater system of the Panxie mining area in the Huainan coalfield, China. By analyzing groundwater samples from various aquifers, including sandstone, limestone, and shale, the research provides a comprehensive assessment of REE content, fractionation patterns, and anomalies, with a particular focus on Ce and Eu. The results show that, except for the sandstone aquifer, the REE concentrations in other aquifers are generally lower than the global average for river waters, with notable Ce negative anomalies and Eu positive anomalies observed across the samples. Additionally, the study employs Visual MINTEQ software to model the inorganic complexation of REEs, revealing that carbonate complexes, such as $Ln(CO_3)^{2-}$ and $LnCO_3^+$, dominate in these groundwater systems. Finally, the research constructs a Fisher discriminant model for groundwater source identification, using the concentrations of 14 REEs as variables. The model demonstrates high accuracy, particularly in distinguishing between sandstone and limestone aquifers, offering valuable insights for groundwater management and protection in mining areas. The study not only enhances the understanding of REE geochemical behavior in groundwater but also provides a scientific basis for the development of more effective groundwater resource management strategies in the Panxie mining area and similar environments.

Keywords: rare earth elements, groundwater geochemistry, Panxie mining area, fisher discriminant analysis, inorganic complexation

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Introduction

The Panxie mining area in the Huainan coalfield is a significant coal mining region in eastern China, where the groundwater system exhibits complex hydrogeological characteristics influenced by both mining activities and natural conditions. The rational utilization and protection of groundwater resources are among the key issues in regional environmental management. Rare earth elements (REEs), as trace elements with significant geochemical information, have unique applications in groundwater research. By studying the content characteristics, distribution patterns, and inorganic complex forms of REEs in groundwater, we can gain deeper insights into groundwater sources, evolution processes, and interactions with the surrounding environment [1-4].

In the field of groundwater resource quality prediction, the DRASTIC model is one of the most widely applied assessment methods at present. By integrating the improved DRASTIC method with machine learning models, it can predict the quality of groundwater resources more accurately, providing valuable tools for policymakers and resource managers, and promoting sustainable water resource management. However, this model only considers intrinsic vulnerability but ignores the impact of human activities on groundwater vulnerability [5-6]. By using data-driven models to evaluate the reliability of groundwater quality indices, the scientificity and accuracy of groundwater quality assessment can be enhanced, providing strong support for the rational development, protection, and management of groundwater resources. However, data-driven models have several drawbacks, including high requirements for data quality, poor model interpretability, limited generalization ability, insufficient handling capacity for extreme events, and ignoring physical mechanisms [7].

In China, the main standard used to classify the quality status of groundwater is the "Groundwater Quality Standard" (GB/T 14848-2017), which divides groundwater quality into five categories. This standard also stipulates contents such as groundwater quality investigation and monitoring, groundwater quality evaluation, etc., and is applicable to groundwater quality investigation, monitoring, evaluation, and management. In recent years, research on REEs in mining area groundwater has gradually increased, but most studies have focused on single aquifer analysis, with limited exploration of the indicative significance of REEs [8-10]. The multi-aquifer structure of the Panxie mining area offers a unique opportunity to study the characteristics of REEs across different aquifers and their environmental implications [11-13]. By systematically investigating the distribution patterns, partitioning characteristics of REEs in groundwater from different aquifers, and their relationships with other hydrochemical parameters, we can reveal the spatial and temporal evolution of hydrogeological conditions in the mining area and the potential impacts of mining activities on the groundwater system [14].

The geochemical behavior of REEs is influenced by various factors, including rock weathering, mineral dissolution, hydrological conditions, and redox environments. These factors collectively determine the distribution characteristics and partitioning patterns of REEs in groundwater [15-17]. The multi-aquifer structure of the Panxie mining area provides a rich source of samples for REE research, allowing for systematic analysis of REE content and distribution patterns across different aquifers [18]. Studying the inorganic complex forms of REEs can reveal their migration behavior in groundwater and their relationships with other hydrochemical parameters, thus deepening our understanding of hydrogeochemical processes in groundwater [19-21].

Additionally, to more accurately identify groundwater sources and hydrogeological conditions, this study employs the Fisher model to construct a source identification model [22-23]. The Fisher model, known for its superior classification ability and sensitivity to data patterns, can effectively distinguish and identify groundwater from different sources [24-25]. By combining data on REE content characteristics, distribution patterns, and inorganic complex forms with the Fisher model, we can establish an efficient source identification model, providing a scientific basis for the protection and management of groundwater in the mining area [26-27].

In summary, this study systematically measured the content, distribution patterns, and inorganic complex forms of REEs in groundwater samples from different aquifers in the Panxie mining area and constructed a source identification model using the Fisher model. The research results will provide important data support for the characteristics of the groundwater system and water source identification in mining areas, and promote the scientific management and protection of local groundwater resources. This study not only helps to optimize the management strategy of groundwater resources in mining areas, but also provides a reference for other similar mining area groundwater research.

Geological Setting

Study Area

The Panxie mining area is located in the central-northern part of Anhui Province, spanning Huainan and Fuyang cities (Fig. 1). The study area lies on the southern edge of the Huaibei Plain, in the middle reaches of the Huai River, and is part of the Huai River alluvial plain, with an elevation generally ranging from +20 to +30 meters. In the northeast, there are remnants of low hills at Minglong Mountain, with an elevation of up to 126 meters. The overall topography slopes from northwest to southeast. The Huainan mining area experiences

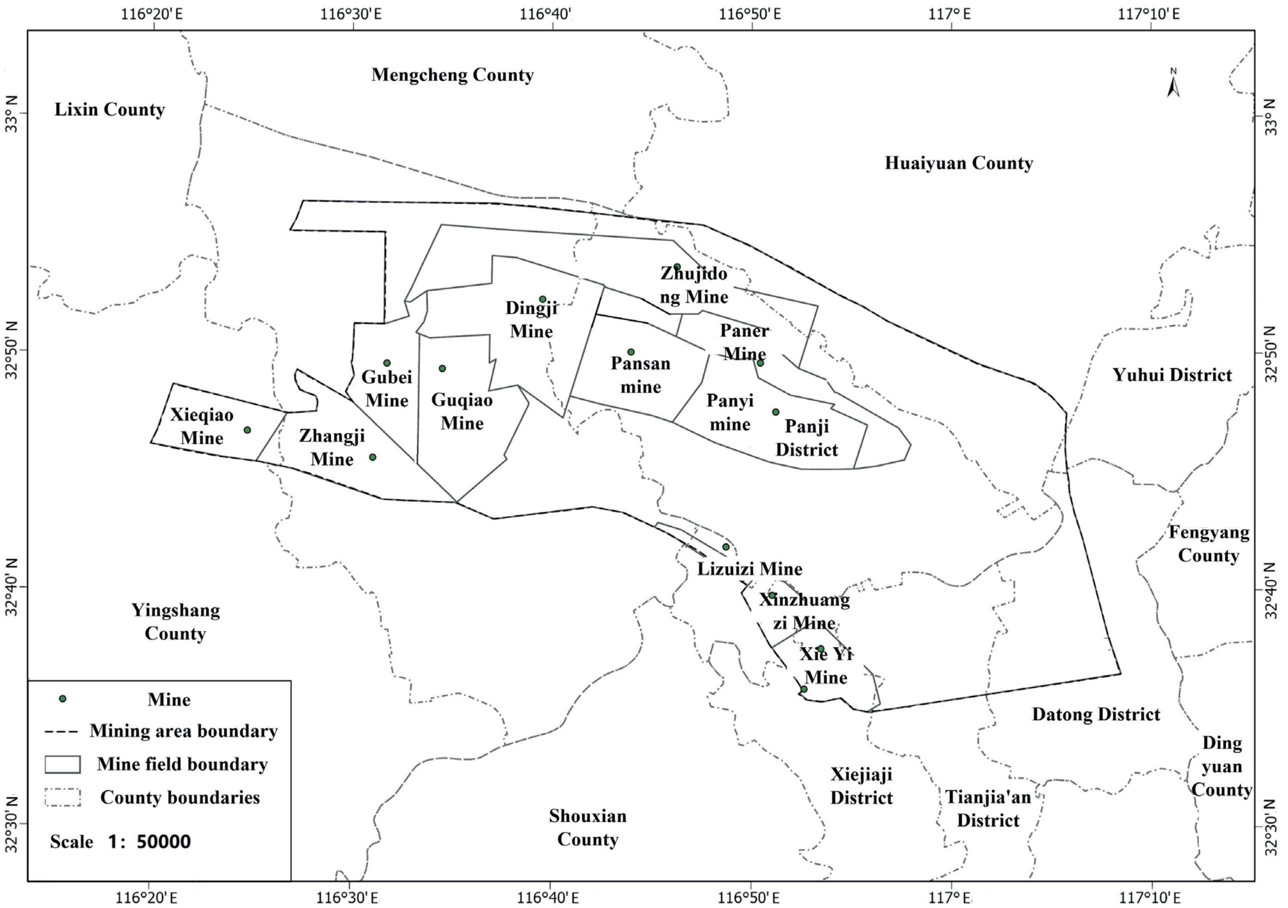

Fig. 1. Mine distribution map of Panxie mining area.

a transitional climate with distinct seasons, characterized by hot summers and cold winters, with an average annual temperature of 15.1ºC. The main water system in the area is the Huai River, followed by the Xifei River, Dongfei River, Ni River, Ying River, and various coal mining subsidence lakes.

Stratigraphy

The main aquifers in the study area include the Quaternary loose layer pore aquifer (group), the Permian sandstone fissure aquifer (group), the Carboniferous Taiyuan Formation limestone fissure karst aquifer, and the Ordovician limestone fissure karst aquifer (Fig. 2). The detailed characteristics of each aquifer are as follows:

Quaternary Loose Layer Pore Aquifer (Group)

The thickness of the Quaternary loose layer in the Huainan coalfield ranges from 0 to 860 meters. Within the coalfield's mines and exploration areas, boreholes reveal loose layer thicknesses between 52.45 and 800.90 meters, with an average thickness of 378.20 meters and a maximum thickness of 800.90 meters. Generally, the thickness increases from east to west and from south to north. This aquifer can be further divided into two secondary aquifers: the upper part (hereinafter referred to as SH) and the lower part. This aquifer is hereinafter referred to as ZX.

Permian Sandstone Fissure Aquifer (Group)

This aquifer is mainly composed of medium to fine sandstone, with local occurrences of coarse sandstone and quartz sandstone, distributed between coal seams, siltstone, and mudstone layers. The lithological thickness varies significantly. Based on its relationship with the major mineable coal seams and the degree of influence on mine water inflow, the aquifer can be divided into three sections: the bedrock weathering zone and the 13-1, 11-2, and 8-5 coal seam roof and floor aquifers. These sandstone fissure aquifers are separated by mudstone and sandy mudstone, resulting in no hydraulic connection between them. The coal-bearing strata have very low water yield and are characterized by uneven distribution, predominantly as static storage aquifers with weak water-bearing capacity. This aquifer is hereinafter referred to as SY.

Taiyuan Formation Limestone Fissure Karst Aquifer

The Taiyuan Formation is primarily composed of thin-layered limestone, mudstone, and sandy mudstone, with a total thickness ranging from 89.90 to 140.79 meters, averaging 117.82 meters. It contains 11 to 13 limestone layers, with a limestone thickness of 39.1 to 59.8 meters, averaging 44.19 meters, and weak water-bearing capacity. Fissures and karst caves are relatively developed, with cave diameters typically ranging from 0.15 to 0.7 meters. Fissures are more developed in shallow sections and diminish with depth. The unit inflow ranges from 0.047 to 3.43 L/s•m, with the third and fourth limestone layers exhibiting relatively strong water-bearing capacity. This aquifer is hereinafter referred to as TH.

Ordovician Limestone Aquifer

The Ordovician limestone is mainly composed of thick-layered limestone intercalated with thin mudstone layers. Local fissures are well developed and show signs of water erosion, primarily forming a network of fissures, often filled with calcite. The water-bearing capacity is uneven. This aquifer is hereinafter referred to as AH.

The Quaternary Loose Layer Pore Aquifer (Group) in the Panxi Coalfield primarily consists of coarse gravel and sand, characterized by large grain sizes, high porosity, and strong permeability. Geochemically, the water contains relatively high concentrations of calcium, magnesium, and sodium ions, with generally good water quality and low hardness. The predominant geochemical type is HCO_3-Ca·Mg. In contrast, Permian Sandstone Fissure Aquifer (Group) is predominantly composed of sandstone, exhibiting strong resistance to weathering, underdeveloped fractures, and weak water-bearing capacity. Its geochemical features include low concentrations of iron and aluminum ions, with similarly good water quality and low hardness. The geochemical type is predominantly Cl-Na or Cl•HCO_3-Na. The Taiyuan Formation Limestone Fissure Karst Aquifer mainly comprises limestone with fine-to-coarse crystalline structures, often filled with calcite veins and occasionally containing pyrite crystals. Geochemically, the water has relatively high levels of calcium and magnesium ions, and the oxidation of pyrite releases sulfate ions. The geochemical type is predominantly Cl•HCO_3-Na. Lastly, the Ordovician Limestone Aquifer consists primarily of limestone with a dense rock structure, featuring some pores and fractures that enable groundwater storage and flow. Geochemically, the water contains relatively high concentrations of calcium and magnesium ions, with the geochemical type being predominantly HCO_3-Ca or HCO_3-Ca·Mg.

Materials and Methods

Sampling and Testing

In this study, a total of 67 groundwater samples were collected (6 from SH, 20 from XH, 2 from SY, 25 from TH, and 14 from AH). The samples were stored in 2.5 L high-density polyethylene plastic bottles. Before sampling, the bottles were thoroughly rinsed with the native water. At each sampling point, 12 liters of water were collected. After filtering through a 0.45 µm membrane, the samples were stored at 0 to 4°C.

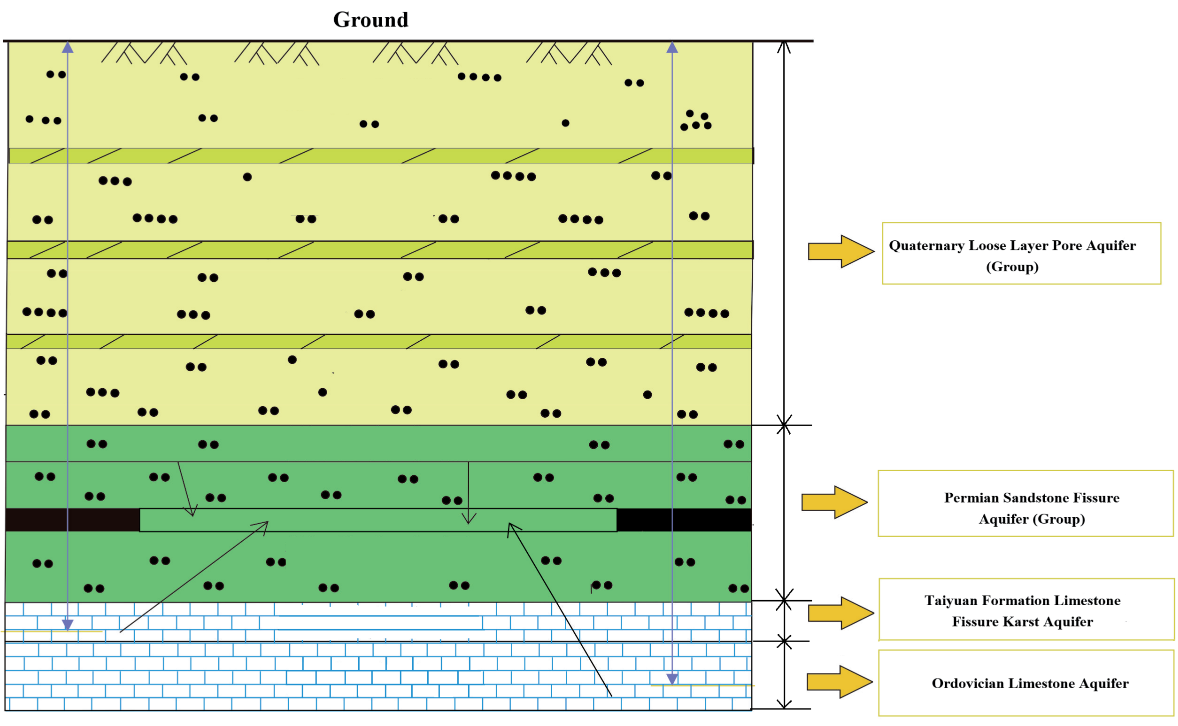

Fig. 2. Aquifer division and type of mine water-filled aquifer in Panxie mining area.

The samples were acidified to a pH of less than 2 using ultrapure HNO_3, which was distilled by sub-boiling to prevent metal ions from precipitating or being adsorbed by the containers. The rare earth elements were analyzed using an inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7500). The instrument was calibrated using standard solutions and a 1% HNO_3 sample blank, with an analytical precision better than 6%.

Results and Discussion

Characteristics of Rare Earth Element Content

The summary of rare earth element (REE) concentrations in groundwater from different aquifers within the Panxie mining area is presented in Table 1. Overall, the concentrations of REEs are low across the aquifers, with the exception of the sandstone aquifer. Notably, the REE concentrations in all other aquifers fall below the global average for river waters, which is estimated to be 0.7450 μg/L. This suggests limited mobilization and dissolution of REEs within the local hydrogeological environment, likely influenced by the specific geochemical conditions that prevail within each aquifer.

A detailed examination of the anomalies reveals that the groundwater from different aquifers exhibits systematic Ce depletion (negative Ce anomaly) and Eu enrichment (positive Eu anomaly). This trend is particularly pronounced in the SY aquifer, where Ce depletion is more marked, and Eu enrichment reaches

Table 1. Statistics of rare earth elements content in groundwater from each aquifer (μg/L).

Parameters	SH	ZX	SY	AH	TH
La	0.0165	0.0092	0.0684	0.0117	0.0127
Ce	0.0194	0.0109	0.0306	0.0144	0.0114
Pr	0.0165	0.0122	0.0275	0.0120	0.0122
Nd	0.0168	0.0108	0.0351	0.0121	0.0109
Sm	0.0220	0.0176	0.1763	0.0149	0.0300
Eu	0.0571	0.0442	1.2666	0.0247	0.1423
Gd	0.0213	0.0178	0.0343	0.0169	0.0167
Tb	0.0205	0.0176	0.0311	0.0157	0.0164
Dy	0.0243	0.0190	0.0402	0.0190	0.0188
Ho	0.0203	0.0187	0.0343	0.0168	0.0170
Er	0.0222	0.0205	0.0406	0.0207	0.0191
Tm	0.0207	0.0191	0.0334	0.0174	0.0178
Yb	0.0210	0.0193	0.0394	0.0204	0.0177
Lu	0.0217	0.0212	0.0352	0.0187	0.0193
∑REE	0.3202	0.2579	1.8925	0.2353	0.3623
LREE	0.1482	0.1049	1.6044	0.0897	0.2194
HREE	0.1719	0.1529	0.2882	0.1455	0.1428
LREE/HREE	0.8621	0.6860	5.5678	0.6167	1.5363
La_N/Yb_N	0.4662	0.2824	1.0313	0.3410	0.4268
La_N/Sm_N	0.4673	0.3245	0.2423	0.4905	0.2656
Gd_N/Yb_N	0.6231	0.5664	0.5335	0.5095	0.5788
Eu/Eu*	8.7499	8.3234	34.9804	5.2366	19.1398
Ce/Ce*	0.2410	0.1593	0.0656	0.2372	0.1186

Note: ΣREE, ΣLREE, ΣHREE represent the total amount of rare earth elements, light rare earth elements content and heavy rare earth elements content, respectively; LaN/YbN, LaN/SmN, and GdN/YbN respectively reflects the enrichment or deficiency degree of light and heavy rare earth elements, light and medium rare earth elements, and medium and heavy rare earth elements; Ce/Ce* and Eu/Eu* respectively represent the anomalies of Ce and Eu, where Ce/Ce* = CeN/(LaN•NdN)1/2 and Eu/Eu* = EuN/(SmN•GdN)1/2, EuN, SmN and GdN are the shale normalized values of Eu, Sm, Gd.

its highest values. The SH, ZX, and AH aquifers display a relative depletion of light rare earth elements (LREEs), coupled with an enrichment of heavy rare earth elements (HREEs), implying that fractionation processes favor the preferential retention of LREEs in the solid phase or their removal from the aqueous phase via adsorption or co-precipitation mechanisms. Conversely, the SY and TH aquifers show an opposite fractionation pattern, where LREEs are enriched and HREEs are depleted. This suggests varying redox conditions, water-rock interaction intensities, and possibly differences in the complexation of REEs between these aquifers, all of which influence REE mobility and distribution.

Rare Earth Element Partitioning Model

The REE distribution patterns provide critical insights into the geochemical processes governing REE behavior in the groundwater system. To better understand these patterns, the REE concentrations are often normalized against standard reference materials. Commonly used standards include chondrites (which reflect primitive solar system material), North American Shale Composite (NASC), Post-Archean Australian Shale (PAAS), and the Upper Continental Crust (UCC). These standards enable researchers to compare REE distributions across different environmental settings and

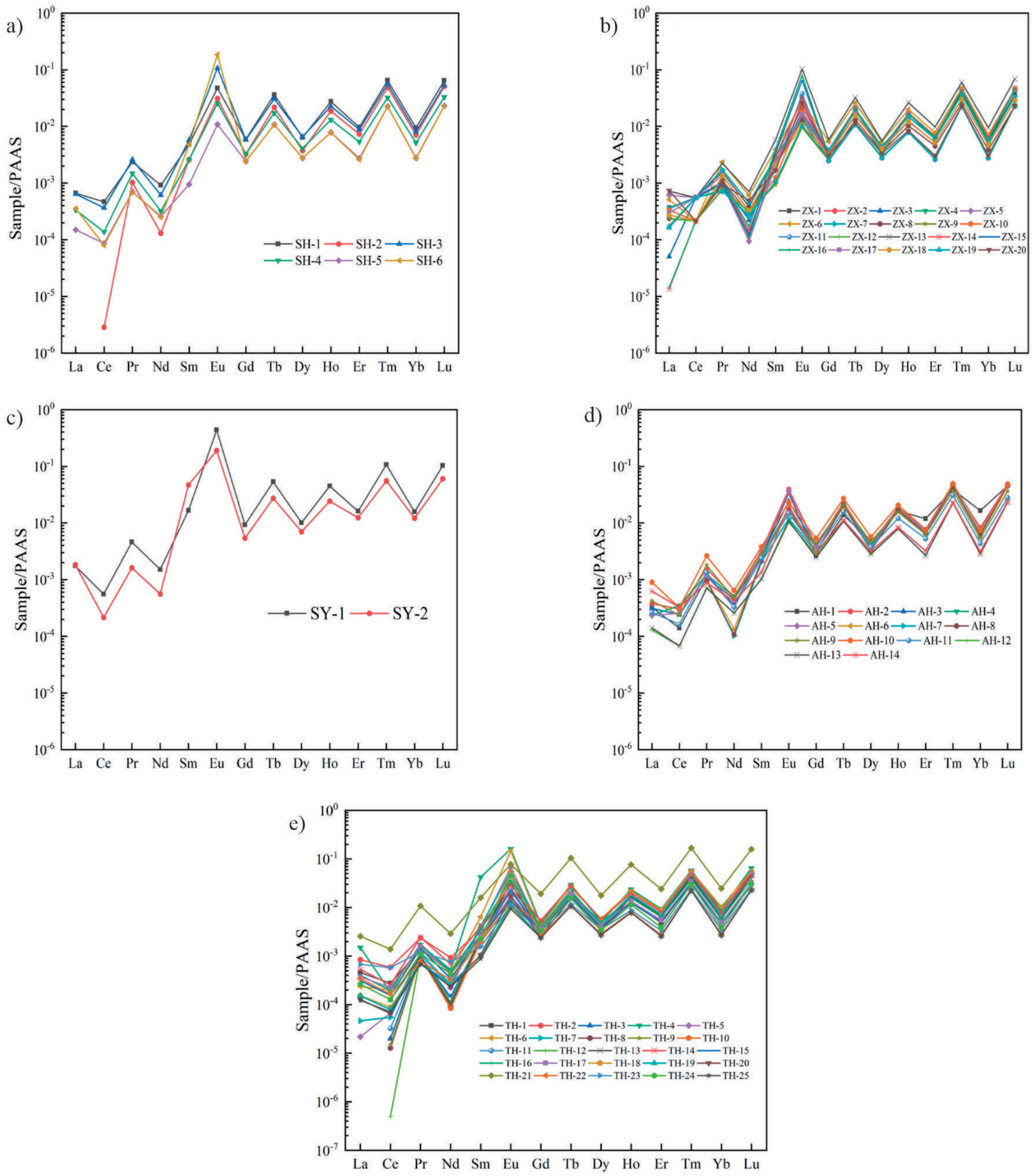

Fig. 3. Rare earth element partitioning patterns in different aquifers.

to detect potential anomalies that might indicate specific geochemical processes.

The REE distribution patterns of groundwater from various aquifers in the study area were normalized using PAAS, as shown in Fig. 3. The general uniformity in the patterns across aquifers indicates a common geochemical control on REE behavior, although the magnitude of variation differs. The flat distribution pattern in the TH aquifer suggests minimal differentiation between LREEs and HREEs, likely reflecting equilibrium conditions where REE fractionation is suppressed. In contrast, the sandstone aquifer (SY) shows a more pronounced variation in REE concentrations, particularly for LREEs, indicative of active fractionation processes, possibly driven by differences in mineral dissolution rates or complexation with organic matter. The limestone aquifer (AH) exhibits a highly consistent REE distribution, with minimal deviation among samples, reflecting a homogenous hydrogeochemical regime within this aquifer. The flatness of the REE distribution curves in some aquifers may also suggest that secondary processes such as adsorption onto mineral surfaces or co-precipitation with secondary minerals are playing a dominant role in controlling REE concentrations, rather than primary dissolution processes.

REE Anomalies

Among the rare earth elements, Ce and Eu anomalies have garnered significant attention due to their heightened sensitivity to redox conditions. Cerium, in particular, tends to form insoluble Ce (IV) in oxidizing environments, leading to its preferential removal from solution through precipitation. This redox-driven fractionation process typically results in a negative Ce anomaly in oxidized waters, as observed in the groundwater samples from the Panxie mining area. Europium, on the other hand, is known to exhibit a positive anomaly under reducing conditions due to the relative mobility of Eu (II) compared to Eu (III). The formation of Eu (II) requires strong reducing conditions, which are less frequently encountered under typical near-surface conditions.

In the SY aquifer, the Ce anomaly is notably weak, indicating that the groundwater in this aquifer has not been subject to extensive oxidation. This is consistent with the unconsolidated nature of the aquifer, which is often exposed to open, oxidizing conditions. By contrast, the limestone aquifers, such as those in the AH formation, are typically more confined and are dominated by reducing conditions, which can limit the oxidation of Ce. The Ce anomaly in these confined aquifers could also be inherited from the parent rock through prolonged water-rock interactions. Limestone, in particular, is known to exhibit prominent Ce depletion, and this characteristic can be transferred to groundwater through the dissolution of Ce-depleted mineral phases. This hypothesis is supported by the observed negative Ce anomaly in the AH aquifer, which is stronger than that in the SY aquifer, indicating that both redox conditions and lithological inheritance play a role in the development of the Ce anomaly.

Europium behaves differently from cerium due to the difficulty in reducing Eu (III) to Eu (II) under normal conditions. The positive Eu anomaly observed in the study area suggests that water-rock interactions, particularly the dissolution of feldspar minerals, play a crucial role in the enrichment of Eu in groundwater. Feldspars, such as plagioclase and albite, are common components of aquifer lithologies and are known to release significant amounts of Eu during dissolution. This process is facilitated by the relatively high solubility of feldspar compared to other minerals, and the dissolution of feldspar can be accompanied by the formation of secondary minerals such as quartz. The strong Eu anomaly in the SY aquifer, combined with the relatively weak Ce anomaly, suggests that this aquifer may be subject to active water-rock interaction, particularly involving feldspar dissolution, which enriches the groundwater in Eu.

Inorganic Complexation of REEs

The chemical speciation of REEs in groundwater is primarily governed by the formation of inorganic complexes with various anions present in the water. The software Visual MINTEQ, developed by the U.S. Environmental Protection Agency (EPA), is widely used for simulating aqueous chemical equilibria and determining the speciation of dissolved species. By inputting the concentrations of major cations, anions, trace metals (e.g., Fe, Mn), and REEs, the inorganic complex forms of REEs in groundwater from different aquifers in the study area were simulated (Fig. 4).

The results show that the inorganic speciation of REEs in the SH, ZX, TH, and AH aquifers is relatively similar, with the majority of REEs existing as carbonate complexes ($Ln(CO_3)^{2-}$ and $LnCO_3^+$). In contrast, the SY aquifer exhibits fewer types of REE complexes, suggesting simpler geochemical conditions or lower REE concentrations. The predominance of carbonate complexes, especially $Ln(CO_3)^{2-}$ for HREEs and $LnCO_3^+$ for LREEs, is consistent with the high pH and alkaline nature of the groundwater, which favors the formation of stable carbonate complexes. Carbonate complexation plays a key role in maintaining REEs in solution, as these complexes are highly stable under alkaline conditions and prevent the precipitation of REEs as insoluble hydroxides or oxides.

As shown in Fig. 4, carbonate complexes account for over 97% of the total REE speciation in all aquifers, indicating that carbonate complexation dominates the geochemistry of REEs in the study area. The higher proportion of $Ln(CO_3)^{2-}$ for HREEs compared to LREEs reflects the stronger complexation ability of HREEs with carbonate ions, which enhances their mobility in groundwater. In contrast, LREEs tend to form weaker complexes with carbonate ions, resulting in a higher proportion of $LnCO_3^+$. The stability of these complexes is influenced by the ionic strength of the groundwater, the concentration of dissolved inorganic carbon, and the presence of competing ligands such as sulfate and phosphate.

The high pH (7.87-9.11) and elevated concentrations of major cations (Na^+, Ca^{2+}, Mg^{2+}) in the groundwater of the Panxie mining area contribute to the formation of colloidal particles, which can further reduce the concentration of dissolved REEs by adsorbing REEs onto their surfaces. This is particularly relevant for HREEs, which have a stronger affinity for colloidal particles compared to LREEs, resulting in preferential removal of HREEs from solution. The differential behavior of LREEs and HREEs during adsorption and complexation processes leads to the observed fractionation patterns, where LREEs are more mobile under alkaline conditions, while HREEs are preferentially retained in the solid phase.

Studies have shown that the complexation of REEs with bicarbonate ions (HCO_3^-) plays a critical role in their mobility in groundwater. LREEs form stronger complexes with HCO_3^- compared to HREEs, resulting in the preferential formation of $LnCO_3^+$ for LREEs, while HREEs are more commonly found as $Ln(CO_3)^{2-}$. This difference in complexation behavior is a key factor

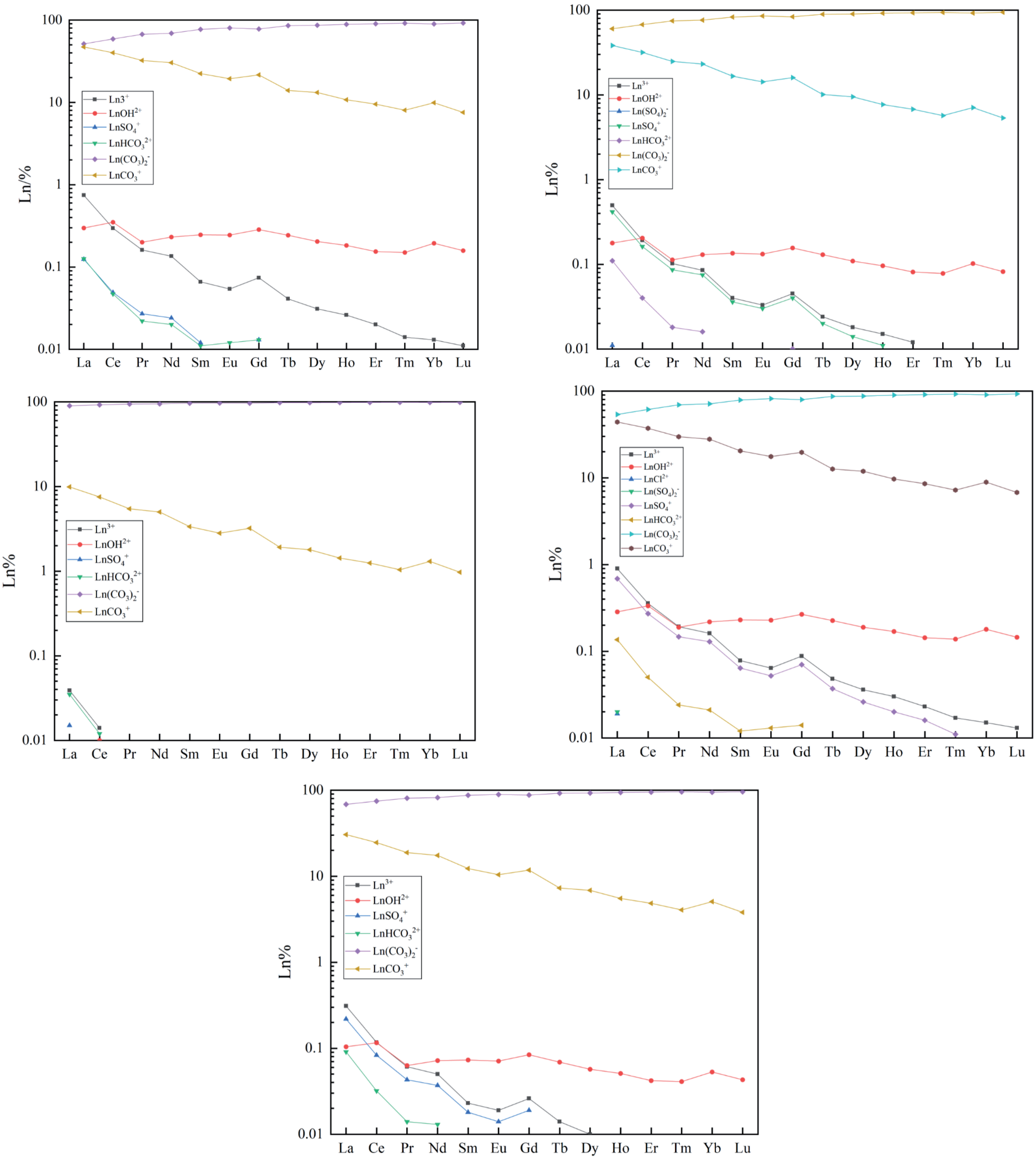

Fig. 4. Percentage of each inorganic complex form of rare earth elements in different types of water samples.

controlling the distribution and speciation of REEs in the groundwater of the Panxie mining area.

REE-Based Water Source Identification Model

Selection of Standard Samples and Model Construction

With advancements in trace element testing technologies, analyzing the rare earth element (REE) composition in groundwater to identify hydrogeochemical characteristics has become increasingly feasible, offering a robust method for water source identification. In this study, 14 REEs, including La, Ce, Pr, and Nd, were selected as the primary objects of investigation to ensure accurate prediction results.

To guarantee the accuracy of the predictive model, it is crucial to screen outliers at the beginning of the model establishment process. Outliers can introduce significant biases into the model, leading to incorrect conclusions. Therefore, outlier detection was performed using boxplot analysis in SPSS software, focusing on eliminating samples that could potentially distort the model's accuracy. The results of rare earth element outliers in ZX and AH are shown in Fig. 5 and Fig. 6.

Taking the Taihui (TH) water as an example, Fig. 7 illustrates the boxplot analysis. In the TH water, sample number 21 exhibited outlier effects across all elements except for Gd. Given that the study considers the 14 REEs as a collective group, an anomaly in even a single element within a sample could adversely affect

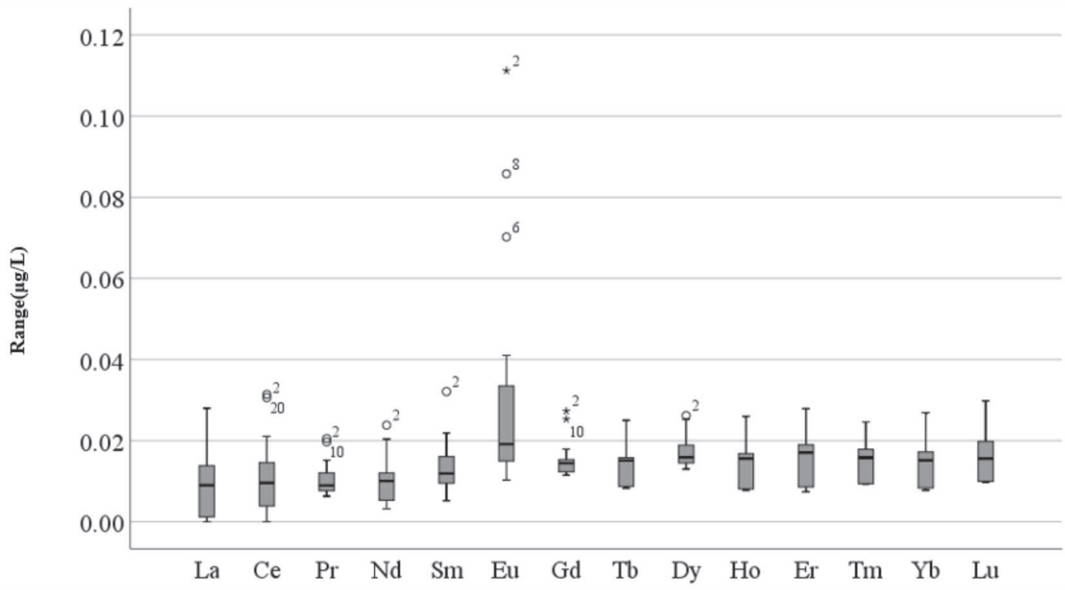

Fig. 5. Results of rare earth element outliers in ZX.

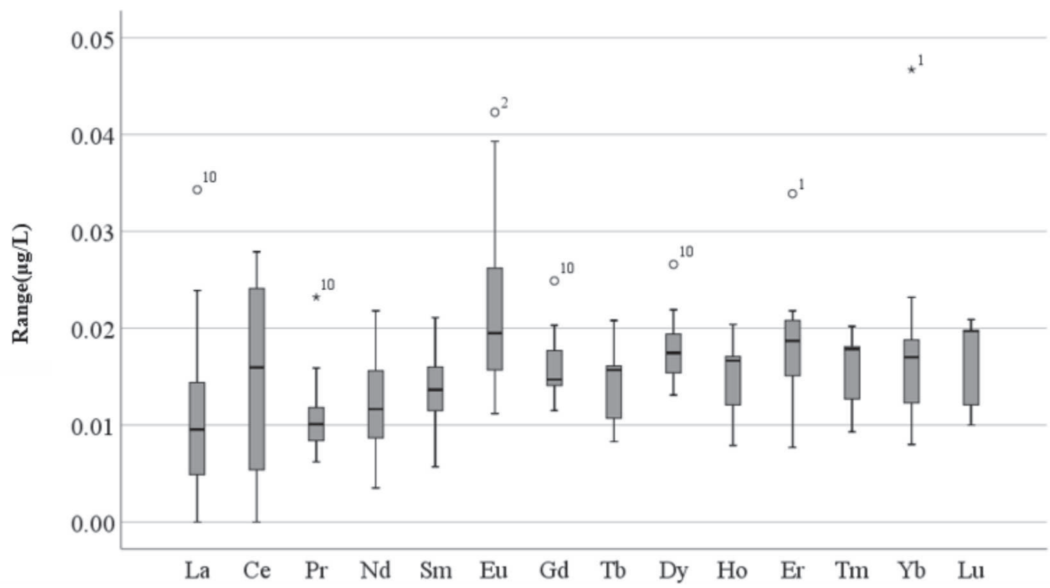

Fig. 6. Results of rare earth element outliers in AH.

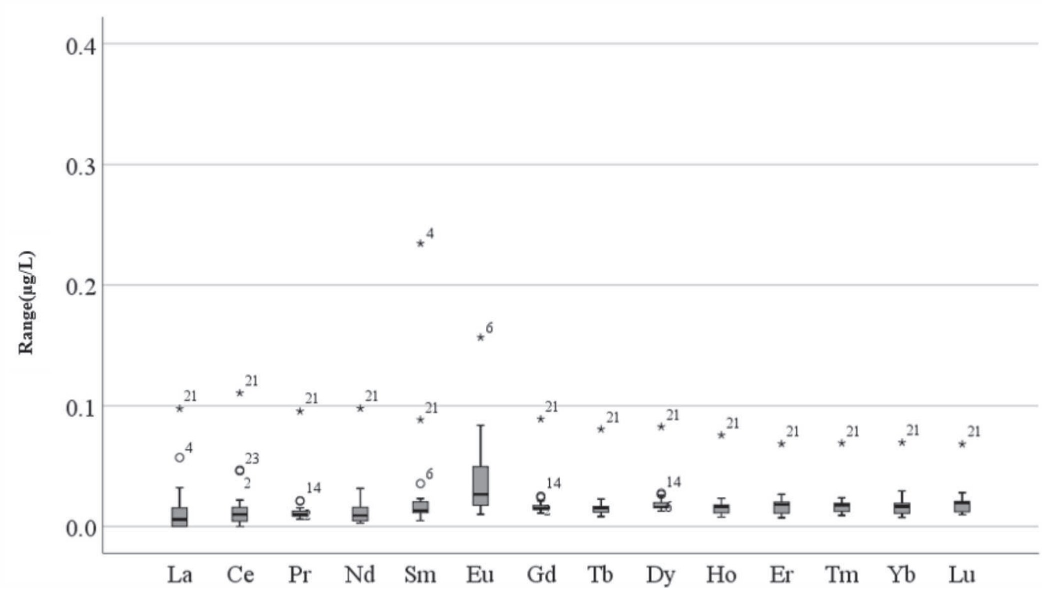

Fig. 7. Results of rare earth element outliers in TH.

the overall model accuracy. Consequently, all samples identified as outliers (both extreme and mild) were excluded to ensure the reliability of the results. For the TH water, samples 2, 4, 6, 14, 21, and 23 were removed.

Similar outlier screening was applied to the ZX, SY, AH, and TH water samples in the Panxie mining area, resulting in the exclusion of 14 outlier samples. From the remaining 47 standard samples, 7 were randomly selected as validation samples, including 1 sample from the sandstone aquifer and 2 samples from each of the other aquifers.

Currently, analyzing the chemical composition of groundwater is a common method for identifying the source of mine water inrush. The basic principle is to determine the water source location based on the differences in ionic composition between aquifers – the greater the difference, the easier the identification. At present, there are numerous methods for identifying groundwater sources, and each method has its own characteristics. The neural network method is adaptable and has strong learning ability, but its parameter adjustment is complex, and its interpretability is poor. The clustering analysis method can discover clusters of any shape and is insensitive to noise, but it performs poorly on high-dimensional data with large density variations. The logistic regression method is simple and efficient, but it performs poorly on nonlinear problems and is sensitive to outliers. The advantage of the Fisher discriminant model lies in its ability to project high-dimensional data into a low-dimensional space through dimensionality reduction, while retaining the category information, making classification easier and with lower computational complexity. It can effectively handle multivariate data in groundwater source identification and improve the accuracy of source identification. The goal of discriminant analysis is to identify indicators with strong discriminative power in a known classification dataset and to establish a discriminant function model. This model can then be applied to new samples for classification.

In this study, a Fisher discriminant model was constructed to classify and identify water sources in the Panxie mining area. The four aquifers (ZX, SY, AH, TH) were categorized into four groups, with ZX water marked as 1, SY as 2, AH as 3, and TH as 4. The 14 selected REEs served as explanatory variables, denoted as X1 to X14. According to the principles of Fisher's multivariate linear discriminant analysis, three effective discriminant equations were derived (Table 2), with a total explained variance of 100%, meeting the necessary requirements for model validation.

Validation and Application of the Identification Model

To accurately determine the source of inrushwater, the Fisher discriminant analysis was applied to selected samples from each aquifer. Classification variables were assigned values of 1, 2, 3, and 4, corresponding to ZX, SY, AH, and TH, respectively. The concentrations of the 14 REEs were used as explanatory variables, represented by X1 to X14. By applying the Fisher linear discriminant analysis principle, three effective discriminant functions were obtained, achieving a total explained variance of 100%, which satisfies the model's requirements (Table 2).

The discriminant function values for each sample were calculated using the concentrations of REEs and the coefficients of the classification functions presented in Table 3. The function with the highest value determined the classification of the sample. The accuracy of the established hydrochemical discriminant model was validated using the results shown in Table 3. The model's accuracy for identifying sandstone water and TH water reached 100%, while the accuracy for middle aquifer water and AH water was 84.6% and 77.8%, respectively. The overall accuracy of the model, based on 40 samples, was 90% (Table 4).

When examining the performance of the model across individual aquifers, it was found that the model performed exceptionally well in identifying sandstone water and TH water, whereas the accuracy for the middle aquifer and AH water was relatively lower.

To further test the model's validity, 7 randomly selected validation samples were subjected to the

Table 2. Information table of rare earth element discriminant function in aquifer water.

Function	Eigenvalue	Percentage of variance	Cumulative percentage	Typical correlation
1	55.048	94.2	94.2	0.991
2	2.075	3.6	97.8	0.821
3	1.034	2.2	100	0.752

Table 3. Coefficients of Fisher's linear discriminant function for trace elements in each aquifer.

Classification function coefficients				
Variables	1	2	3	4
La	600.85	1526.323	465.449	360.809
Ce	3532.298	7574.577	3890.864	4245.393
Pr	11960.09	65019.83	8891.748	13187.88
Nd	-8357.965	-12009	-7549.032	-8751.312
Sm	-5455.323	-21707.83	-2689.804	-3424.443
Eu	244.762	5416.285	-90.909	146.794
Gd	-7147.14	-61761.51	-6230.185	-12075.2
Tb	-7295.157	53049.764	-4476.687	2230.919
Dy	22252.012	37086.999	21354.694	23399.802
Ho	-65899.9	-234987.4	-64202.21	-73399.44
Er	-27418.96	-38065.74	-23744.77	-27693.7
Tm	107219.73	251310.07	104328.1	108424
Yb	15565.628	11828.613	7024.817	8617.805
Lu	-17955.55	-11330.07	-15186.82	-12631.9
Constants	-184.967	-1575.122	-188.431	-189.255

Table 4. Fisher's multi-class linear joint discriminant model test results.

	ZX	SY	AH	TH	Total
Number of samples	13	1	9	17	40
Number of correct identifications	11	1	7	17	36
Correct rate/%	84.6	100	77.8	100	90

Table 5. Fisher's sample test results for the multi-class linear joint discriminant test.

	ZX	SY	AH	TH	Total
Number of samples	2	1	2	2	7
Number of correct identifications	2	1	1	2	6
Correct rate/%	100	100	50	100	85.7

identification model. The results, presented in Table 5, show that 6 out of 7 samples were correctly classified, yielding an accuracy of 85.7%. This indicates that the model possesses a reasonable degree of accuracy and applicability, making it a valuable tool for water source identification in the Panxie mining area. Number of samples.

Conclusions

(1) This research provides a detailed analysis of the rare earth element (REE) content, distribution patterns, and geochemical behavior in the groundwater of the Panxie mining area. The study reveals that REE concentrations in the groundwater are generally low, with significant Ce negative anomalies and Eu positive anomalies indicating specific geochemical processes. The distribution patterns of REEs, standardized against Post-Archean Australian Shale (PAAS), show consistent fractionation across different aquifers, with the sandstone aquifer displaying more pronounced variations. The modeling of inorganic complexation forms using Visual MINTEQ software indicates that carbonate complexes dominate, with distinct differences between light and heavy REEs.

(2) The Fisher discriminant model based on rare earth element concentration was established, and the overall accuracy reached 90%, which solved the difficult problem of groundwater source identification. The model is particularly effective in distinguishing between sandstone and limestone aquifers. The successful application of this model shows that it can improve groundwater management in mining areas, and provide scientific basis for distinguishing different water sources in mining areas and understanding the impact of mining activities on groundwater systems.

In summary, the results of this study help to broaden the understanding of groundwater rare earth element geochemistry, highlight the complex interaction between rare earth elements and aquifer matrix, and provide technical support for groundwater resource management in Panxie Mine and other similar mine areas.

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Conflict of Interest

The authors declare no conflict of interest.

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