

Original Research

Hydrogeochemical Characteristics and Evolution of Groundwater Quality of an Abandoned Coal Mine in Huaibei Coalfield, Eastern China

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Abstract

In this study, major ions, isotopes and rare earth elements (REEs) were tested in groundwater from the coal-bearing sandstone aquifer of the Wolonghu coal mine in northern Anhui Province, and the elemental geochemical behavior and controlling factors in groundwater were discussed. The results indicate that the overall sandstone water is weakly alkaline, and the hydrochemical type is $\text{SO}_4\text{-Na}$. The relationship between δD and $\delta^{18}\text{O}$ suggests a hydraulic connection between the sandstone aquifer and the limestone aquifer. The composition characteristics of $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ indicate that the high concentration of SO_4^{2-} in groundwater mainly comes from the dissolution of sulfate minerals. The content of rare earth elements (ΣREEs) in groundwater is controlled by pH value and carbonate complexation reaction, and it shows a relative enrichment feature of heavy rare earth elements (HREEs) after standardization with Post-Archean Australian Shales. Ce shows a slight negative anomaly and is mainly influenced by the redox environment, while the Eu anomaly is attributed to the dissolution of silicate minerals. Compared to groundwater quality before the mine closure, the weakening of hydraulic conditions led to an increase in ΣREEs , Ca^{2+} , Mg^{2+} , SO_4^{2-} , and TDS concentrations accompanied by a significant decrease in HCO_3^- concentration. In addition, the difference between light rare earth elements (LREEs) decreased, whereas the differentiation between LREEs and HREEs gradually increased. Our findings provide valuable insights into the evolution of groundwater quality in abandoned mines and its genesis mechanism. The results could guide the utilization of groundwater resources in abandoned mines.

Keywords: rare earth elements, water resources, hydrogeochemistry, Huaibei coalfield

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Introduction

As the Chinese economy burgeons, there is an increasing awareness of the safety requirements and environmental aspects among coal mine practitioners. Many coal mines have been closed as they reach the end of their viability or in response to the policy of reducing capacity, and the number of abandoned coal mines continues to increase [1]. Abandoned coal mines are rich in groundwater resources and have great potential for development and use, which is particularly important in areas where water resources are scarce [2]. Compared with the conditions before mine closure, the hydrodynamic conditions, redox environment, and reaction conditions between water and coal rocks in aquifers have changed, which inevitably leads to a series of changes in the chemical components of water. Studies have shown that coal mine groundwater can cause a range of environmental problems, and remediation of ecological impacts is often difficult [3, 4]. Therefore, it is important to clarify the hydrogeochemical processes and circulation patterns of aquifers in abandoned mines for the exploitation of groundwater resources.

Rare Earth Elements (REEs) have stable and similar geochemical properties, and their unique geochemical behavior is widely used to trace the origin and evolution of materials during weathering, denudation, transport, deposition, and diagenesis, such as crustal evolution, magmatic origin, and paleoenvironmental reconstructions [5, 6]. In recent years, with the advancement of testing technology, the study of REEs has been gradually extended from the lithosphere to water systems, and a series of results have been obtained. Studies have shown that REEs in natural waters mainly originate from the weathering and dissolution of rock minerals, and their enrichment and partitioning characteristics are influenced by various physicochemical factors such as pH, redox conditions, and dissolution-adsorption processes [7]. Therefore, in the study of hydrogeochemistry, REEs are considered to be good tracers of water-rock interactions and water circulation [8].

In recent years, scholars have investigated the REEs in coal influenced by seawater invasions in areas such as the Sangrud coal mine, Alborz coalfield, Iran, and the Antaibao mining district, Shanxi, China [9, 10]. Σ REEs are positively correlated with fluoride complex concentrations in groundwater in the Bear Lodge carbonatites, Wyoming, USA [11] and the Datanhao mine, Daqingshan Coalfield, northern China [12]; other studies have elucidated that the presence of sulfate can significantly fertilize the REE-mineralizing fluids [13]. At present, geochemical studies on REEs in water bodies are concentrated in coal mine drainage (CMD) and acidic mine drainage (AMD), while studies related to REEs in deep groundwater are obviously insufficient [14-16].

In the north of Anhui Province, the development of the concealed coalfields has facilitated the collection of deep groundwater. Numerous previous studies have

been conducted on the characterization and sources of major ions in mine water, which have shown that the water chemistry components in groundwater are related to water-rock interactions, such as the dissolution of saline rocks, carbonate minerals, and sulfate minerals, and the weathering of silicate minerals, which have effectively guided the water hazards of producing mines [17]. However, to date, no study has conducted an in-depth exploration of the geochemical behavior of rare earth elements in the groundwater of an abandoned coal mine. As a potential source of water supply for the area, it is important to identify the sources of groundwater recharge and water quality characteristics in the abandoned mine sandstone aquifer. Based on this, this paper explores the migration patterns and partitioning patterns of REEs in sandstone aquifers before and after mine closure, using the Wolong Lake mine in the Huaibei coalfield as a research model, and combines conventional ionic and isotopic characteristics to gain insight into the evolution of water quality and influence mechanisms before and after mine closure, with a view to providing theoretical supports for the conservation and utilization of water resources in abandoned mines.

Materials and Methods

Study Area

Wolonghu coal Mine is located in the Huaibei coalfield, in the north of Anhui Province, China (Fig. 1). The elevation of the mine ranges from 20 to 50 m, with a length of 8-9 km from north to south and a width of 3.5-4 km from east to west, and a total area of 28.9 km². Wolonghu coal mine started to production in June 2008 and has ceased mining in July 2018 in response to the national capacity withdrawal plan. I, and it is currently the only unclosed abandoned mine in the Huaibei coalfield. The study area belongs to the southern part of the North China Plate, and the surface is generally covered by loose sediments of the Quaternary System, and is tectonically at the intersection of the Fengxian-Guoyang Fault and the Subei Fault. Except for the Silurian and Devonian, strata in this area have been developed in different degrees from the Neoproterozoic to the Cenozoic. According to the characteristics of surrounding rocks and void types, the aquifers can be divided from shallow to deep into the Quaternary loose layer pore aquifer (LA), Permian coal-bearing sandstone fissure aquifer (CA), and Carboniferous Taiyuan limestone karst fissure aquifer (TA). Among them, the composition of the surrounding rocks in the CA is dominated by medium and fine-grained sandstone, followed by mudstone, siltstone, and magmatic rocks.

Sample Collection and Analysis

A total of five groundwater samples were collected from the roadway in the coal-bearing sandstone aquifer

at Wolonghu coal mine, and each sample was filled with two pre-cleaned 1L polyethylene bottles, one of which was acidified to $\text{pH}<2$ to prevent precipitation of trace elements or adsorption by the container. The pH values of water samples were tested on site using a portable water quality detector, and laboratory tests included conventional water chemical ions ($\text{Na}^+\text{+K}^+$, Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , HCO_3^- and CO_3^{2-}), isotopes (D, ^{18}O , $^{18}\text{O}\text{-SO}_4^{2-}$ and $^{34}\text{S}\text{-SO}_4^{2-}$) and REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu). HCO_3^- and CO_3^{2-} concentrations were tested by acid-base titration (the concentration of hydrochloric acid used was 0.05 mol/L), and the remaining conventional ion concentrations were tested using inductively coupled plasma spectrometry (ICP-OES, Thermo Fisher Scientific). D and ^{18}O were tested using stable gas isotope mass spectrometry (Nu perspective), and $^{18}\text{O}\text{-SO}_4^{2-}$ and $^{34}\text{S}\text{-SO}_4^{2-}$ were tested by Thermo Fisher 253 Plus, USA. Among them, D, $^{18}\text{O}\text{-SO}_4^{2-}$ and $^{34}\text{S}\text{-SO}_4^{2-}$ results were expressed as relative Vienna Standard Average Seawater (δ , V-SMOW) thousandths, and $^{34}\text{S}\text{-SO}_4^{2-}$ was expressed as relative International Sulfur Isotope Standard (δ , V-CDT) thousandths. REEs were tested by inductively coupled plasma mass spectrometry (ICPMS), instrument model Jena Plasma Quant MS, Germany. In addition, seven sandstone water samples from the preclosure mine were collected from the mine's historical ledger.

Results and Discussion

Major Ion Concentrations

The concentrations of conventional chemical components in groundwater before and after the closure of the Wolonghu coal mine are shown in (Table 1). The pH and TDS in the water samples after mine closure ranged from 8.12~8.9 (mean 8.6) and 2276~3241.7 mg/L (mean 2610 mg/L), respectively, reflecting the weakly alkaline and highly mineralized environment of groundwater. Among the cations, $\text{K}^+\text{+Na}^+$ concentration dominated significantly with a mean value of 759.3 mg/L, followed by Ca^{2+} and Mg^{2+} with mean values of 103.3 mg/L and 42.9 mg/L, respectively. Among the anions, SO_4^{2-} had the highest content with a mean value of 1205.1 mg/L, HCO_3^- , and Cl^- followed by mean concentrations of 491.2 mg/L and 231.7 mg/L, respectively, and CO_3^{2-} had the lowest mean concentration of 21.9 mg/L. Overall, the mean concentrations of conventional ions in the abandoned mine water samples were ranked from the highest to the lowest: $\text{SO}_4^{2-}>\text{K}^+\text{+Na}^+>\text{HCO}_3^->\text{Cl}^->\text{Ca}^{2+}>\text{Mg}^{2+}>\text{CO}_3^{2-}$. Compared with the pre-mine closure, the concentrations of conventional chemical components in the groundwater after closure changed significantly, which was mainly characterized by the significant increase in Ca^{2+} , Mg^{2+} , SO_4^{2-} , and TDS concentrations accompanied by the significant decrease in HCO_3^- concentration.

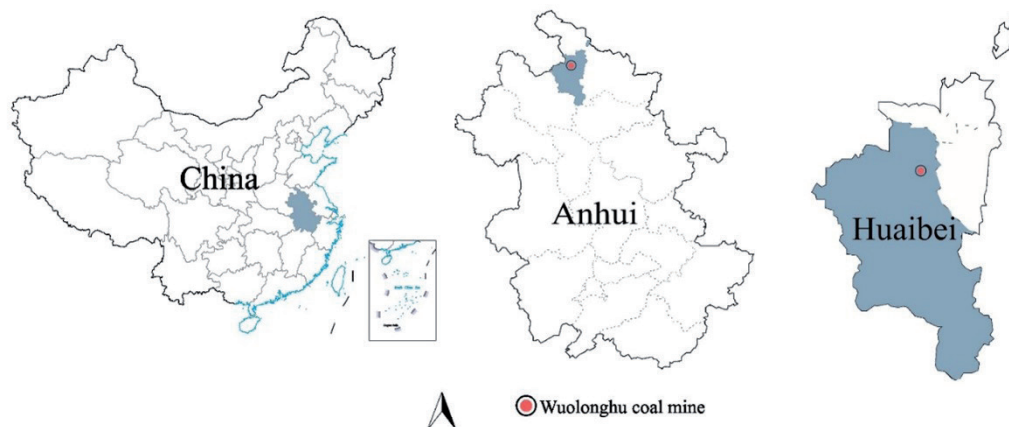


Fig. 1. Location of the Wolonghu coal mine.

Table 1. Comparison of major ion concentrations in groundwater before and after the closure of the Wolonghu coal mine (mg/L).

Sampling time	Statistics	$\text{K}^+\text{+Na}^+$	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	CO_3^{2-}	TDS	pH
After closure (2022)	Min	662.7	9.1	1.7	153.5	926.8	332.0	0.0	2276.0	8.12
	Mean	759.3	103.3	42.9	231.7	1205.1	491.2	21.9	2610.0	8.60
	Max	826.3	267.2	112.7	355.0	1643.4	629.6	41.0	3241.7	8.90
Before closure (2012)	Min	537.7	4.0	1.4	169.5	2.5	959.0	80.4	1348.5	/
	Mean	640.2	5.4	3.3	185.6	8.3	1203.3	123.4	1567.9	/
	Max	783.3	7.8	5.6	195.8	21.0	1499.2	179.4	1876.0	/

To further explore the evolution of water chemistry in abandoned mines, a Piper trilinear diagram was drawn (Fig. 2). It can be seen that all samples are located in the “D” zone for cations, indicating that Na⁺ is the dominant cation in groundwater before and after mine closure, but WLH1 and WLH2 have a tendency to shift to the “B” zone. In the anion trilinear diagram, the water samples were located in zone “F” before closure, but in zone “E” after closure, and the samples before and after closure were located in the diamond-shaped zones “IV” and “III”, respectively. The samples before and after closure were located in the diamond-shaped areas “IV” and “III”, indicating that the transition trend from HCO₃⁻ dominated to SO₄²⁻ dominated anion formation in groundwater. It was shown that the dominant anion in water shifts from HCO₃⁻ to SO₄²⁻ and Cl⁻ from the recharge area to the discharge area [18]. In this study, the groundwater water chemistry type transitioned from HCO₃-Na type to SO₄-Na type before and after mine closure. A large amount of pumping and draining was required at the working face before mine mining, and groundwater recharge in the aquifer was frequently renewed with a short retention time, while the groundwater runoff environment became worse after mine closure and water-rock interaction was more adequate, which may be the main reason for the formation of highly mineralized groundwater dominated by SO₄²⁻ in the aquifer.

Isotopic Composition Characteristics

δD and δ¹⁸O

Hydrogen and oxygen stable isotopes (D and ¹⁸O) are relatively stable in groundwater when not subjected to high temperature water-rock interaction and strong evaporation conditions, so their direct relationship is often used in studies related to the water cycle patterns and evolution of groundwater [17, 18]. In this study, δD varied from -74.15~-71.07‰ with a mean value of -72.79‰, while δ¹⁸O varied from -9.99~-9.42‰ with a mean value of -9.74‰ (Table 1). Comparing the fitted lines of D and ¹⁸O in groundwater with the global Precipitation line (GMWL) and China’s atmospheric Precipitation line (NMWL) equations can better reveal the recharge and transport mechanisms of groundwater [19]. If the groundwater sample points are located near the atmospheric precipitation line, it indicates that the aquifer is directly recharged by rainfall. As can be seen from Fig. 3a, the δD and δ¹⁸O of the seven groups of groundwater samples have a good linear fit (R² = 0.97) [20], but significantly deviate from the GMWL and NWML, indicating that the sandstone water is less likely to be recharged directly by atmospheric rainfall.

It can be found that the δ¹⁸O content is significantly enriched relative to δD. In general, this characteristic may be caused by the following two situations:

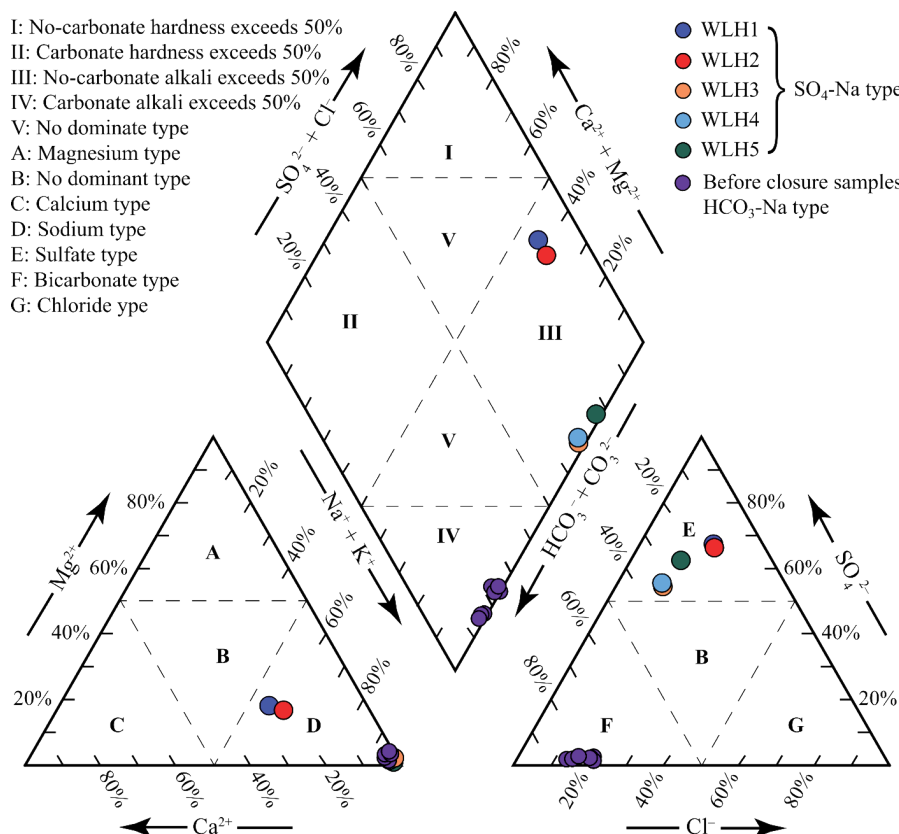


Fig. 2. Piper diagram of groundwater samples before and after closure of the Wolonghu coal mine.

Table 2. Characterization of multiple isotope compositions in groundwater from abandoned mine (‰).

Sample	$\delta^{18}\text{D}$	$\delta^{18}\text{O}$	$\delta^{18}\text{O}\text{-SO}_4^{2-}$	$\delta^{34}\text{S}\text{-SO}_4^{2-}$
WLH1	-71.33	-9.70	13.03	33.25
WLH2	-71.07	-9.42	13.37	33.73
WLH3	-73.42	-9.73	14.79	30.67
WLH4	-73.98	-9.87	15.39	31.20
WLH5	-74.15	-9.99	15.00	29.77

(1) affected by infiltration evaporation, since the preferential escape of light isotopes (δD) in water under evaporation will lead to the relative enrichment of heavy isotopes ($\delta^{18}\text{O}$), but such a situation usually occurs in surface water and shallow groundwater, and in this study, the depth of the sample collection is located in the depth of less than 500 m, and there are multiple water traps in the upper part of the coal sandstone aquifer in this area, basically denying the contribution to the hydroxide stable isotope content; (2) Influenced by the recharge of other water sources, through the analysis of the literature in the previous study area (Fig. 3a), it is found that the limestone aquifer water samples in this area are located in the fitted line equation of the $\delta^{18}\text{O}$ and δD of sandstone water of the present study ($y = 5.98x - 14.53$) nearby, indicating that the two aquifers in this mine may be hydraulically connected.

$$\delta^{18}\text{O}\text{-SO}_4^{2-} \text{ and } \delta^{34}\text{S}\text{-SO}_4^{2-}$$

Sulfate is a common inorganic component of groundwater, and its content is influenced by a combination of factors that may be anthropogenic (e.g., agricultural activities, domestic sewage, and discharge of sulfur-containing industrial effluents) and natural (mainly dissolution of evaporites and oxidation of

sulfides in aquifers) [21]. Despite the complexity of the sources, physicochemical effects, except for the action of sulfate-reducing bacteria under anaerobic conditions, do not usually cause significant fractionation of sulfur isotopes in groundwater. Numerous studies have confirmed that different sources of sulfate have different ranges of sulfur and oxygen isotope end-members, and thus the relationship between $\delta^{18}\text{O}\text{-SO}_4^{2-}$ and $\delta^{34}\text{S}\text{-SO}_4^{2-}$ is commonly used to indicate the source of sulfate in water bodies [22, 23]. In this study, $\delta^{18}\text{O}\text{-SO}_4^{2-}$ and $\delta^{34}\text{S}\text{-SO}_4^{2-}$ contents in groundwater samples from abandoned mines were relatively stable, with variations ranging from 13.03 to 15.39‰ and 29.76 to 33.73‰, respectively, and mean values of 14.32‰ and 31.72‰, respectively (Table 2.). As can be seen in Fig. 3b), all samples are located within the evaporite mineral dissolution region, implying that the dissolution of evaporite (e.g. gypsum) is the main source of high sulfate concentration in groundwater in the study area.

Rare Earth Element Content Characteristics and Partitioning Patterns

ΣREEs in groundwater before and after the closure of the Wolonghu coal mine are shown in Table 3. The variation of ΣREEs concentration in groundwater

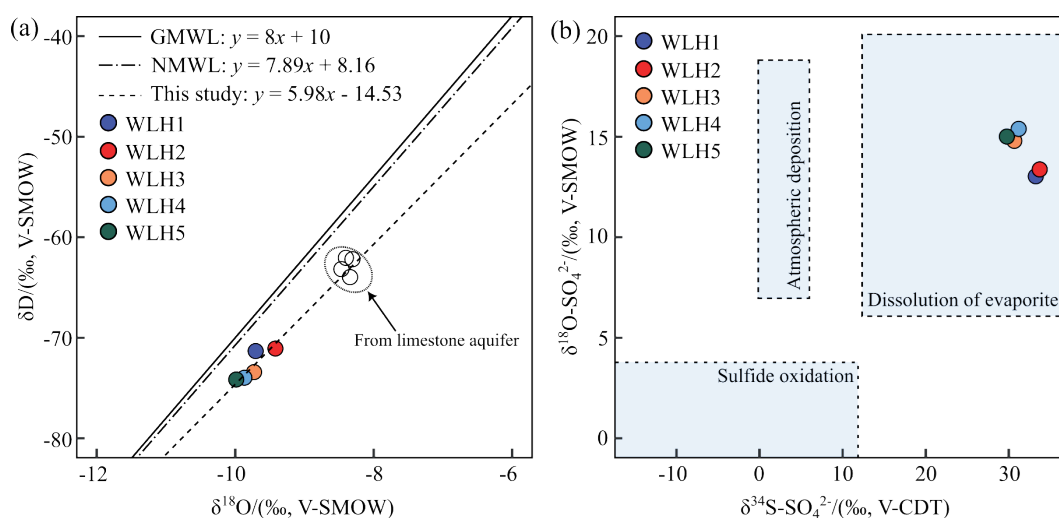


Fig. 3. Isotope composition relationships in groundwater from the abandoned mine. a) Relationship between δD and $\delta^{18}\text{O}$, b) Relationship between $\delta^{18}\text{O}\text{-SO}_4^{2-}$ and $\delta^{34}\text{S}\text{-SO}_4^{2-}$.

after closure ranged from 0.153~0.36 $\mu\text{g/L}$, with a mean value of 0.251 $\mu\text{g/L}$, which was lower than the mean value of World River (0.754 $\mu\text{g/L}$), but significantly higher than that before closure (0.08 $\mu\text{g/L}$). Compared to other studies on REEs in coal-based sandstone water in the Huabei coalfield, the mean value of ΣREEs after closure of the Wolonghu mine coal was found to be higher than that of Renlou mine coal (0.1035 $\mu\text{g/L}$) [24] and Xutong mine coal (0.1785 $\mu\text{g/L}$) [25]. Generally, the ΣREEs content in water is mainly related to pH, complexation pattern, and dissolution-adsorption interaction. As can be seen in Fig. 4a), the fitting coefficient of ΣREEs with pH reached 0.87, showing a good negative correlation. In an alkaline environment, the inorganic complexation form of REEs is mainly the carbonate complexation state, so the relationship between ΣREEs and HCO_3^- is plotted in Fig. 4b). It can be seen that the ΣREEs content shows a significant decrease with the increase in HCO_3^- content, and the two also show a negative correlation at the significance level of $\rho < 0.01$. This phenomenon indicates that the complexation of carbonate in an alkaline environment is an important controlling factor of ΣREEs in groundwater in the study area. In addition, the adsorption/desorption of Fe-Mn oxides/hydroxides with REEs under oxidizing/reducing conditions can affect the decrease/increase of ΣREEs in water [26].

The correlation between ΣREEs and Fe+Mn content is not reflected in Fig. 4c), indicating that the adsorption/desorption has a small effect on the REEs content in groundwater in the study area.

The partitioning patterns of REEs in groundwater normalized by Post-Archean Australian Shales (PAAS) are shown in Fig. 5. It can be seen that the PAAS partitioning curves of REEs in different water samples differ somewhat, but generally show an upward trend to the right. The parameters $(\text{La}/\text{Sm})_N$ and $(\text{La}/\text{Yb})_N$ reflect the partitioning of REEs in groundwater, where $(\text{La}/\text{Sm})_N$ varies from 0.85 to 1.03 with a mean value of 0.98, indicating that the partitioning between LREEs in groundwater is not obvious, while $(\text{La}/\text{Yb})_N$ of all water samples is less than 1 (mean value of 0.71), indicating that the groundwater as a whole is lightly in an alkaline environment, the HREEs are more abundant than the LREEs. In an alkaline environment, the solubility of heavy rare earths is greater, and the preferential precipitation of LREEs relative to HREEs may be the main reason for the relative enrichment of HREEs. Compared with before mine closure, $(\text{La}/\text{Sm})_N$ in groundwater increased after closure, reflecting the gradual decrease of the differentiation between LREEs. $(\text{La}/\text{Yb})_N$ usually increases with weakening hydrodynamic conditions, and the significant increase of

Table 3. Comparison of rare earth element contents in groundwater before and after closure of Wolonghu coal mine ($\mu\text{g/L}$).

Sampling time	Statistics	ΣREEs	$(\text{La}/\text{Sm})_N$	$(\text{La}/\text{Yb})_N$	δCe	δEu
After closure (2022)	Min	0.153	0.85	0.59	0.91	0.84
	Mean	0.251	0.98	0.71	0.95	0.98
	Max	0.360	1.03	0.87	0.99	1.21
Before closure (2014) [27]	Min	0.056	0.45	0.03	0.31	1.12
	Mean	0.080	0.71	0.09	0.94	5.83
	Max	0.111	1.01	0.14	2.28	11.36

** ΣREEs represents the sum of all rare earth element contents, $(\text{La}/\text{Yb})_N$ represents the ratio of La to Yb normalized by Post-Archean Australian Shales, δCe represents abnormality of Ce, which was calculated as $\delta\text{Ce} = \text{Ce}_N/(\text{La}_N \cdot \text{Pr}_N)^{1/2}$, and δEu represents abnormality of Eu, which was calculated as $\delta\text{Eu} = \text{Eu}_N/(\text{Sm}_N \cdot \text{Gd}_N)^{1/2}$.

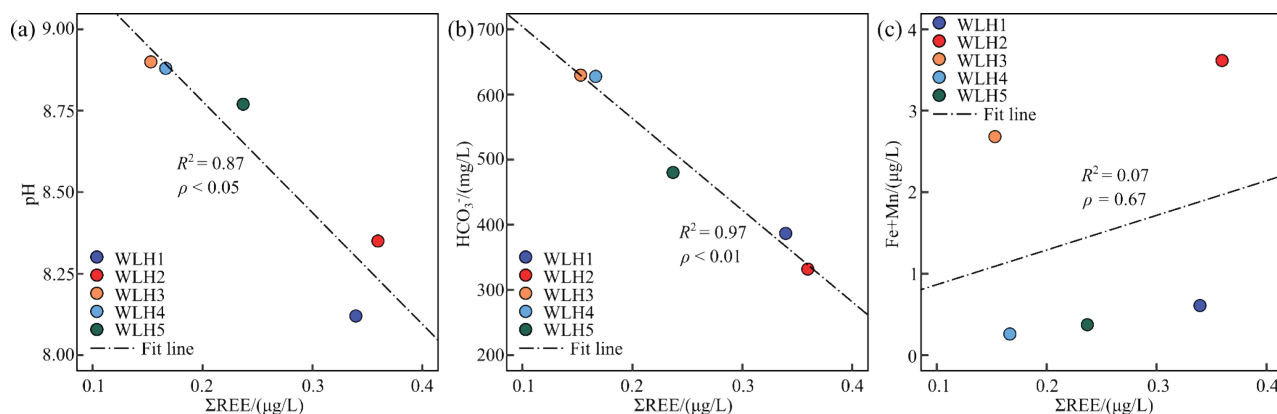


Fig. 4. Relationship between ΣREEs and pH a), HCO_3^- b) and Fe+Mn c) in groundwater from the abandoned mine.

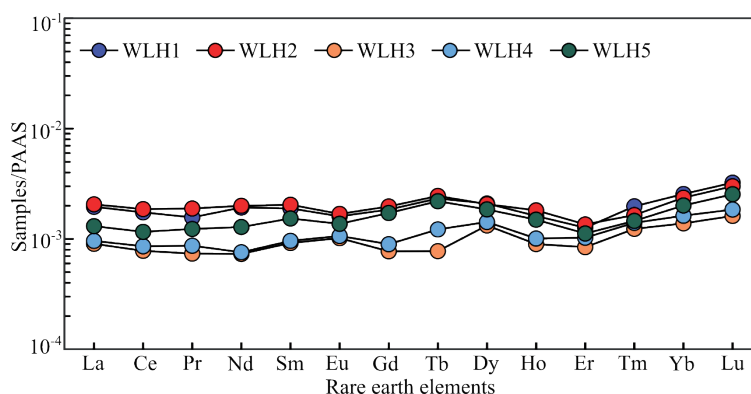


Fig. 5. Distribution patterns of PAAS-standardized rare earth element content in groundwater samples.

$(La/Yb)_N$ in groundwater after the closure of Wolonghu mine indicates that the differentiation between light and heavy rare-earth elements is related to the shift of the runoff environment caused by mine mining and decommissioning.

Rare Earth Element Anomalies and Influencing Factors

Ce anomaly (δCe) and Eu anomaly (δEu) are important features of REEs, because the hydrogeochemical behaviors of Ce and Eu are more sensitive compared with other REEs and are susceptible to redox environments during migration [28]. Among them, Ce anomalies are mainly related to pH and redox conditions. The variation of δCe in groundwater after the closure of Wolong Lake mine ranged from 0.91~0.99, with a mean value of 0.96, and all samples showed a slight negative anomaly of Ce. If Ce anomalies in groundwater were controlled by pH, both of them would show a better correlation, which was not found in Fig. 6a. In an oxidizing environment, trivalent Ce in water can be oxidized to tetravalent Ce (e.g. CeO_2 and $Ca(OH)_4$) resulting in a Ce deficit. Therefore, the negative Ce anomaly in groundwater in the study area can be considered an effect of the redox environment.

Compared with before closure, δEu in the groundwater of the mine after closure was significantly lower, with variations ranging from 0.84~1.21 and a mean value of 0.98. Among them, WLH3 and WLH4 showed positive Eu anomalies, while the rest of the samples were characterized by negative Eu anomalies. Negative anomalies of Eu in deep groundwater are more common, while positive anomalies are generally considered the exchange of Eu^{2+} with Sr^{2+} and the dissolution of Eu-rich minerals (e.g., plagioclase) under redox conditions. It was pointed out that Eu exists as Eu^{2+} under reducing conditions, and due to the similar chemical properties of Eu and Sr elements, if groundwater is enriched with large amounts of Sr^{2+} , the exchange between the two will cause Sr^{2+} to precipitate while Eu^{2+} continues to be enriched in water, resulting in positive Eu anomalies. Fig. 6b) shows the relationship between δEu and Sr in groundwater, and it can be found that the correlation between the two is not significant, implying that the exchange interaction between Eu^{2+} and Sr^{2+} has no effect or a small effect on the positive Eu anomaly in groundwater in this area. In addition, the supersaturation of carbonate phase water and the weathering dissolution of silicate minerals are also important influencing factors for the positive Eu anomaly. As shown in Fig. 6c), there is a significant positive correlation between Na^+

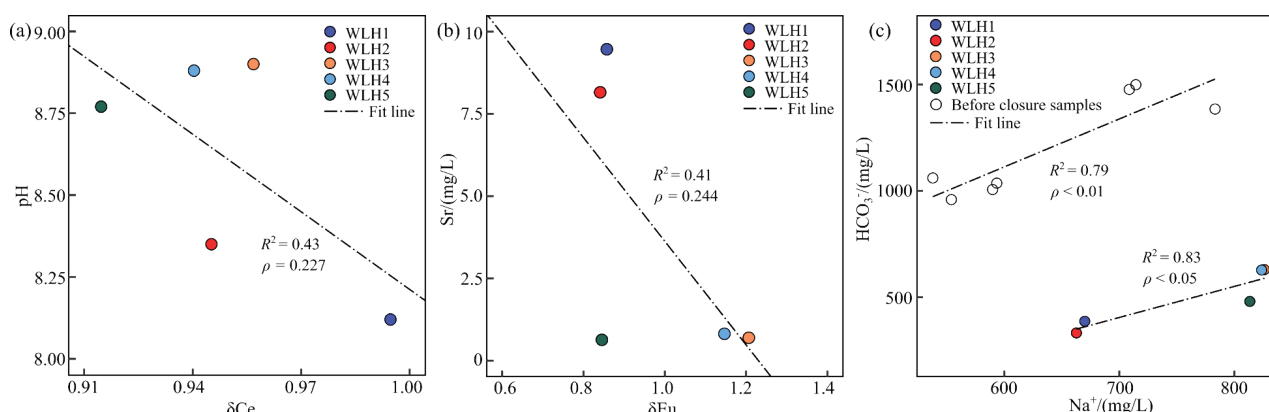


Fig. 6. Relationships between δCe and pH a), δEu and Sr b) and Na^+ and HCO_3^- c) in groundwater from the abandoned mine.

and HCO_3^- in the groundwater of the mine before and after closure, and this feature usually indicates the dissolution of feldspar-like minerals with the following chemical equation: $2\text{Na}(\text{AlSi}_3\text{O}_8) + 2\text{CO}_2 + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{Si}_5\text{O}_5(\text{OH})_4 + 2\text{Na}^+ + 4\text{SiO}_2$. Combined with the actual hydrogeological situation, the coal aquifer enclosing rocks are characterized by clastic rock types composed of feldspar-like minerals [29]; therefore, the positive Eu anomalies in samples WLH3 and WLH4 can be considered to be caused by the dissolution of high Eu minerals (feldspar-like minerals).

In general, the quality of groundwater in the aquifer after mine closure has changed significantly due to oxidation-reduction and hydrodynamic conditions, and in the subsequent use of water resources, attention should be focused on the health risks to human beings from SO_4^{2-} -dominated highly mineralized groundwater, and further remediation work can be carried out in the future to address the quality of groundwater in abandoned mines.

Conclusions

(1) The overall sandstone water is weakly alkaline after the closure of Wolong Lake mine. Compared with the pre-closing period, the groundwater concentrations of Ca^{2+} , Mg^{2+} , SO_4^{2-} and TDS are significantly higher while the HCO_3^- concentration is significantly lower. The water chemistry type transitions from HCO_3^- -Na type to SO_4^{2-} -Na type, and the dissolution of evaporite in the aquifer results in the formation of SO_4^{2-} dominant high mineralization water.

(2) The average values of δD and $\delta^{18}\text{O}$ in sandstone water are -72.79% and -9.74% , respectively, which are significantly drifted compared with the atmospheric precipitation line, reflecting the recharge trace of the bottom limestone aquifer.

(3) The ΣREEs in groundwater increased after closure relative to that before closure, with ΣREEs variation ranging from $0.153\sim 0.36 \mu\text{g/L}$, which was mainly controlled by the combination of pH and carbonate complexation reaction. It showed a relative enrichment of HREEs after normalization by PAAS. All samples show a slight negative anomaly for Ce, which is mainly influenced by the redox environment, while the Eu anomaly can be attributed to the weathering dissolution of silicate minerals. The weakening of hydrodynamic conditions in the aquifer after mine closure may lead to a decrease in the differentiation between LREEs and an increase in the differentiation between LREEs and HREEs.

The findings of this study provide valuable insights into the changes in the water chemistry of sandstone aquifers after mine closure. Future research in this field could focus on the impact of these changes on the local ecosystem and the effectiveness of remediation measures to mitigate the adverse effects of mining activities on the environment.

Acknowledgments

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Conflict of Interest

The authors declare no conflict of interest.

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