Pol. J. Environ. Stud. Vol. XX, No. X (XXXX), 1-16
DOI: *10.15244/pjoes/220228* ONLINE PUBLICATION DATE: 2026-08-03

Original Research

Coupled Hydrochemical Controls on Fluoride Enrichment in Ca-Rich Mine Water: Insights from Saturation Indices and PMF

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Received: 16 January 2026
Accepted: 31 March 2026

Abstract

Fluoride enrichment in mine water is an emerging environmental concern in carbonate-hosted mining regions, yet its controlling mechanisms remain insufficiently constrained. This study investigates fluoride enrichment in 106 mine water samples from the Huaibei Coalfield, eastern China, using integrated hydrochemical analysis, mineral saturation indices, and positive matrix factorization (PMF). High-fluoride mine water is characterized by the coexistence of elevated Ca^{2+} and F^{-}, deviating from the conventional Ca-F antagonistic model typical of low-Ca groundwater. Saturation index results show that most samples remain undersaturated with respect to fluorite, and fluorite saturation is reached only after substantial fluoride accumulation, indicating that fluorite precipitation does not effectively limit fluoride levels. Weakly alkaline, bicarbonate-buffered conditions combined with prolonged water-rock interaction and evaporative concentration create favorable environments for fluoride persistence. PMF results reveal that fluorine-bearing mineral dissolution is the dominant contributor to fluoride enrichment (31.80%), followed by reverse cation exchange (28.75%), evaporative concentration (20.24%), and competitive adsorption (19.22%). These findings demonstrate that fluoride accumulation in Ca-rich mine water is driven by multiple coupled hydrochemical processes rather than a single mechanism, and they provide a quantitative framework for assessing fluoride contamination in similar mining environments.

Keywords: high-fluoride mine water, hydrochemical processes, fluoride enrichment, positive matrix factorization (PMF)

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Introduction

Fluoride contamination in groundwater and mine water has become a widespread environmental concern due to its well-documented impacts on human health and aquatic ecosystems. Long-term exposure to excessive fluoride through drinking water is widely recognized as a primary cause of dental and skeletal fluorosis, posing persistent risks to public health and water security [1, 2]. At the global scale, elevated fluoride concentrations in groundwater have been reported across a wide range of geological and climatic settings, indicating that fluoride enrichment is a common geochemical phenomenon rather than a regionally isolated issue [3, 4]. Previous studies have demonstrated that the occurrence and spatial distribution of fluoride in groundwater are closely controlled by lithology, hydrochemical conditions, and groundwater residence time [5].

In mining regions, fluoride-related problems are often further intensified by large-scale underground excavation and long-term coal extraction activities. Mining operations can substantially disturb natural hydrogeological conditions, enhance water-rock interactions, and accelerate the release of fluoride from fluorine-bearing minerals into mine water [6-8]. As a result, elevated fluoride concentrations have frequently been reported in coal mining areas, particularly in deep or confined aquifers with prolonged circulation and limited recharge [6, 9]. High-fluoride mine water not only restricts its direct utilization for industrial and domestic purposes but also poses potential environmental risks when discharged into surrounding surface water and groundwater systems [7, 9]. Untreated high-fluoride mine water poses severe environmental risks upon discharge: it bioaccumulates in aquatic organisms, impairing their growth and disrupting aquatic community stability; infiltrates soil to enrich fluoride in crops and plants, threatening the safety of agricultural products and terrestrial food chains; and contaminates regional groundwater aquifers, endangering the quality of critical drinking water sources for mining and surrounding communities. These characteristics make fluoride enrichment in mine water a critical issue for both mine water management and regional environmental protection.

Previous studies on fluoride enrichment have predominantly focused on natural groundwater systems. In these systems, fluoride accumulation is commonly associated with low-calcium, Na-HCO_3-type hydrochemical facies and is primarily controlled by fluorite solubility, alkaline pH conditions, and evaporative concentration [10-12]. Numerous hydrogeochemical investigations have further demonstrated that the dissolution of fluorine-bearing minerals provides the fundamental source of fluoride, while processes such as ion exchange, adsorption-desorption, and prolonged water-rock interaction can significantly influence fluoride mobility and distribution [11, 13]. At broader spatial scales, statistical and modeling approaches have also been applied to identify the key geological and hydrochemical factors governing fluoride enrichment [3, 10]. However, hydrogeochemical conditions in mining-affected aquifers are often more complex, and most existing studies have examined these processes independently or qualitatively, limiting a comprehensive understanding of their combined effects on fluoride enrichment [14, 15].

Moreover, field observations from several coal mining areas indicate that high-fluoride mine water does not always conform to the conventional Ca-F antagonistic model established for groundwater systems. The coexistence of elevated Ca^{2+} and F^- concentrations has been reported in multiple mining-affected aquifers, suggesting that additional hydrogeochemical processes may modify traditional fluoride controls [6, 7, 16]. Nevertheless, integrated investigations that simultaneously consider mineral equilibrium constraints, hydrochemical evolution, and quantitative source apportionment remain scarce, particularly for carbonate-hosted mine water systems [14, 17].

In this study, the Huaibei Coalfield was selected as a representative mining area to investigate fluoride enrichment in mine water derived from carbonate-dominated strata. By integrating conventional hydrochemical analysis, saturation index evaluation using PHREEQC [18], and positive matrix factorization (PMF) techniques [19-21], this study quantitatively identifies the relative contributions of fluorine-bearing mineral dissolution, reverse cation exchange, evaporative concentration, and competitive adsorption to fluoride enrichment. The results aim to improve the understanding of coupled hydrochemical processes governing fluoride accumulation in Ca-rich mine water systems and to provide a scientific basis for mine water management and environmental protection in similar mining regions.

Materials and Methods

Study Area

The Huaibei Coalfield is located at the southeastern margin of the North China Block and represents one of the major coal-producing regions in eastern China. The coalfield extends approximately 40-150 km in length and about 110 km in width, covering a total area of ~11,350 km^2. Structurally, it is bounded by the Bengbu Uplift to the south and the Yongxia Coalfield to the north. Proven coal reserves in the Huaibei Coalfield reach 12.736 billion tons, accounting for approximately 37.5% of the total coal reserves in Anhui Province. At present, more than 20 mines are in operation, with an annual coal production of nearly 40 million tons.

From a hydrogeological perspective, the Taiyuan Formation constitutes the principal aquifer system in the coalfield and is the main source of mine water inflow. The Taiyuan Formation is composed predominantly of

limestone interbedded with clastic strata and coal seams, and it is characterized by well-developed fractures and karst features. Locally, groundwater from this formation is referred to as "Taihui Water". With the progressive exploitation of deeper coal seams, particularly the No. 6 and No. 10 seams, the regional hydrogeological regime has been substantially altered, resulting in changes in groundwater flow patterns and water-rock interaction conditions within the Taiyuan Formation aquifer.

In recent years, mine water derived from the Taiyuan Formation aquifer has shown elevated fluoride concentrations that exceed the limits specified by the national water quality standards. Most mine water samples collected from the coalfield exhibit fluoride concentrations above acceptable thresholds for surface water and groundwater, indicating a widespread fluoride contamination problem. This issue poses potential risks to drinking water safety and may lead to cumulative ecological and environmental impacts if mine water is discharged without adequate treatment.

In this study, mine water samples were collected from ten active production mines distributed across the Huaibei Coalfield to ensure representative coverage of regional hydrochemical conditions. Sampling points included mining drainage outlets, observation wells in goaf areas, surface hydrological wells, seepage points, and roof water from coal seams. A total of 106 mine water samples were collected and analyzed. The spatial distribution of the sampling locations is shown in Fig. 1.

Sampling and Testing

Mine water samples were collected from ten active production mines across the Huaibei Coalfield to ensure representative coverage of regional hydrochemical conditions, following standard hydrogeochemical sampling procedures commonly adopted in mining-affected aquifers [22, 23]. Sampling was conducted at multiple types of mine-water outlets, including mining drainage holes, observation wells in goaf areas, surface hydrological wells, seepage points, and roof water from coal seams. Prior to sample collection, each outlet was purged for an adequate period to remove stagnant water and to obtain representative samples of the aquifer system.

All water samples were filtered on-site through 0.45 μm membrane filters and stored in pre-cleaned polyethylene bottles. Samples intended for cation analysis were acidified to pH<2 using 65-68% (v/v) ultrapure nitric acid, whereas samples for anion analysis were left unacidified. All samples were stored at 4ºC and transported to the laboratory for analysis as soon as possible.

Major cations (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}) and anions (Cl^{-}, SO_4^{2-}, and F^{-}) were analyzed using an ion chromatograph (ICS-2100, Thermo Fisher Scientific, Waltham, USA) in accordance with GB/T 8538-2022; fluoride concentration was additionally verified by the ion-selective electrode method following GB/T 7484-2019. Bicarbonate (HCO_3^{-}) concentrations were determined by acid titration in compliance with GB/T 8538-2022.

A strict quality control (QC) protocol was implemented throughout the analytical process to ensure data reliability. The ion chromatograph was calibrated prior to sample analysis using certified national standard reference materials (GBW series) for cations and anions, with calibration verification conducted at regular intervals to ensure analytical precision. In addition, duplicate samples and blank samples were run at a frequency of 10% alongside the test samples to

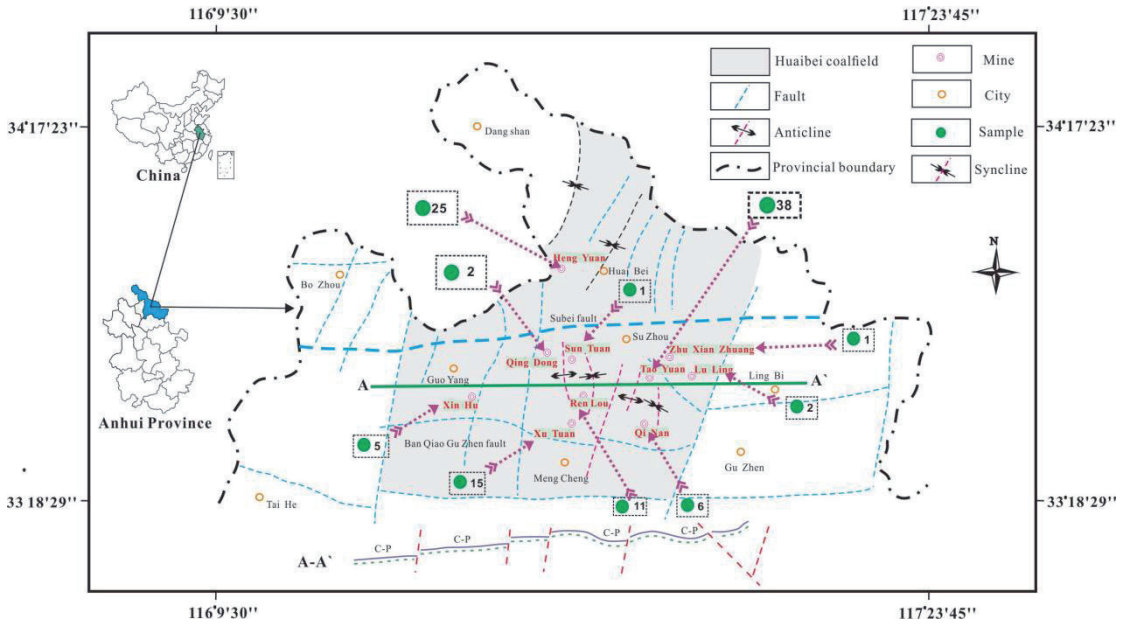

Fig. 1. Location of the study area and distribution of mine water sampling sites in the Huaibei Coalfield.

monitor analytical repeatability and eliminate potential contamination. Analytical accuracy was further evaluated using charge balance errors, all of which were maintained within ±5%, consistent with commonly accepted hydrochemical quality control criteria [23, 24].

Data Processing

Saturation Index and Hydrochemical Indicators

Mineral saturation indices (SI) were calculated using the geochemical modeling software, PHREEQC (version 3), based on measured major ion concentrations, pH, and temperature data [25]. The thermodynamic database was selected to ensure consistency with carbonate and fluoride mineral equilibria. The calculated SI values were used to evaluate the dissolution and precipitation tendencies of major minerals, including fluorite, calcite, dolomite, gypsum, and halite, which are commonly involved in fluoride enrichment processes in groundwater and mine water systems [26, 27].

Hydrochemical facies were classified using Piper trilinear diagrams to characterize the overall chemical composition of mine water and to distinguish between high- and low-fluoride water types [28]. To further assess cation exchange processes between groundwater and aquifer materials, chloro-alkaline indices (CAI1 and CAI2) were calculated following classical hydrogeochemical formulations [29]. Positive CAI values indicate reverse cation exchange, whereas negative values suggest direct ion exchange between groundwater and the surrounding geological media.

PMF Analysis

Positive matrix factorization (PMF) was applied to quantitatively apportion the relative contributions of different hydrogeochemical processes controlling fluoride enrichment in mine water. PMF decomposes the original concentration matrix into factor profiles and their corresponding contributions under non-negativity constraints, minimizing the weighted residuals between observed and modeled concentrations [19, 30, 31]. In this study, the PMF model was implemented using EPA PMF version 5.0, and uncertainty estimates were derived from analytical errors and method detection limits [32].

The optimal number of factors was determined by evaluating Q values, residual distributions, and the physical interpretability of factor profiles. To assess the robustness and stability of the PMF solution, bootstrap and displacement (BS-DISP) analyses were performed following recommended procedures for groundwater PMF applications [33, 34].

Statistical Analysis

Descriptive statistics, including mean, standard deviation, and range, were calculated for the chemical parameters. Pearson correlation analysis was conducted to assess the relationships between fluoride and other major ions in the samples, providing additional support for interpreting the PMF results. All statistical analyses were performed using R (version 4.1.0) and SPSS (version 26.0).

Results

Hydrochemical Characteristics of High- and Low-Fluoride Mine Water

Descriptive Statistics of Major Ions

Based on commonly adopted fluoride concentration thresholds in groundwater quality standards, the mine water samples were classified into low-fluoride (F^- <1.0 mg/L) and high-fluoride (F^- >1.0 mg/L) groups. A total of 106 mine water samples were analyzed,

Table 1. Descriptive statistics of major hydrochemical parameters in low- and high-fluoride mine water.

Type and Quantity	Parameters	pH	TDS	F^-	Cl^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}	HCO_3^-	CO_3^-	NO_3^-
		-	mg/L										
Low fluoride samples n = 11	Maximum	7.31	396.38	0.30	64.66	53.82	97.40	3.66	1.47	11.20	0.00	0.00	0.49
	Minimum	8.60	4472.02	0.96	971.93	2382.25	1389.50	59.17	123.09	276.12	1244.74	65.09	15.05
	Average	8.00	1804.23	0.66	232.76	742.39	442.38	12.89	46.74	94.13	432.49	17.75	7.06
	Coefficient of variation	0.06	0.79	0.35	1.09	1.13	1.01	1.21	0.77	0.96	0.79	1.31	0.76
High fluoride samples n = 95	Maximum	7.00	408.37	1.03	17.64	8.67	107.00	1.89	5.55	8.24	207.70	0.00	0.00
	Minimum	8.57	3778.50	3.33	1144.10	2097.54	1269.36	110.91	136.53	534.13	1040.82	71.66	3.27
	Average	7.62	1911.49	1.92	307.37	775.21	310.88	25.90	66.67	221.03	399.95	2.13	0.92
	Coefficient of variation	0.04	0.34	0.30	0.86	0.63	0.48	0.75	0.36	0.60	0.32	5.17	1.18

among which 11 samples (10.38%) were identified as low-fluoride mine water and 95 samples (89.62%) were classified as high-fluoride mine water. The descriptive statistics of major hydrochemical parameters for both groups are summarized in Table 1.

The pH values of low-fluoride mine water ranged from 7.31 to 8.60, with a mean value of 8.00, indicating a weakly alkaline environment. High-fluoride mine water exhibited pH values between 7.00 and 8.57, with a lower average value of 7.62. Although both groups were characterized by neutral to weakly alkaline conditions, the mean pH of high-fluoride mine water was slightly lower than that of the low-fluoride group.

Total dissolved solids (TDS) showed substantial variability in both groups. Low-fluoride samples exhibited TDS values ranging from 396.38 to 4472.02 mg/L, with an average of 1804.23 mg/L, whereas high-fluoride samples ranged from 408.37 to 3778.50 mg/L, with a comparable mean value of 1911.49 mg/L. The relatively high coefficients of variation observed in both groups indicate pronounced spatial heterogeneity in dissolved solute concentrations within the aquifer system.

Fluoride concentrations in low-fluoride mine water ranged from 0.30 to 0.96 mg/L, with a mean concentration of 0.66 mg/L. In contrast, fluoride concentrations in high-fluoride mine water varied from 1.03 to 3.33 mg/L, with an average value of 1.92 mg/L, clearly exceeding commonly referenced drinking water guideline limits. Overall, the statistical results highlight a clear differentiation between high- and low-fluoride mine water in terms of fluoride levels, while pH and TDS exhibit overlapping but variable ranges across the two groups.

Comparison of Hydrochemical Components Based on Box Plots

Fig. 2 presents box plots of major hydrochemical parameters for low- and high-fluoride mine water, providing a visual comparison of their distribution characteristics.

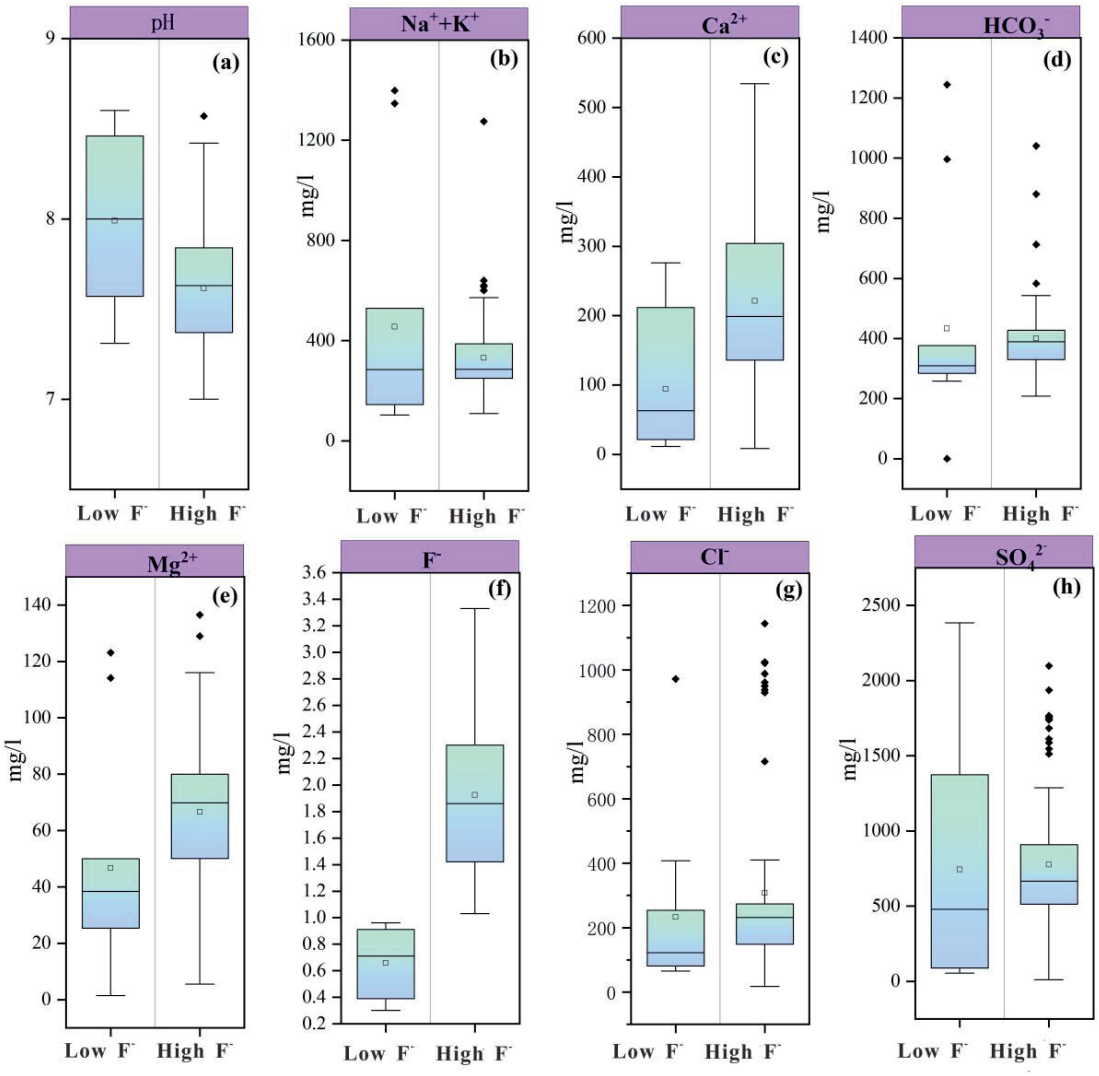

Fig. 2. Box plots of major hydrochemical parameters in low- and high-fluoride mine water.

As shown in Fig. 2, the pH distributions of the two groups largely overlap. However, the median pH value of low-fluoride mine water is slightly higher than that of the high-fluoride group. The interquartile ranges of pH are relatively narrow for both groups, indicating limited variability in acid-base conditions across the study area.

The box plots of total dissolved solids (TDS) reveal substantial dispersion in both low- and high-fluoride mine water. Several samples extend toward the upper range of TDS values, reflecting considerable variability in solute concentrations. Overall, high-fluoride mine water exhibits a slightly higher median TDS compared with low-fluoride samples.

For major cations, Ca^{2+} shows a distinctly higher median value and upper quartile in the high-fluoride group than in the low-fluoride group, indicating a higher calcium content in high-fluoride mine water. In contrast, Na^{+} displays a slightly higher median concentration in low-fluoride samples, although the overall distributions of Na^{+} overlap considerably between the two groups. Mg^{2+} concentrations also tend to be higher in high-fluoride mine water, but the difference between groups is less pronounced than that observed for Ca^{2+}.

Regarding major anions, SO_4^{2-}, HCO_3^{-}, and Cl^{-} exhibit broadly similar distribution patterns in both low- and high-fluoride mine water. Their median values and interquartile ranges largely overlap, suggesting that differences in fluoride concentration are not accompanied by systematic changes in dominant anion composition. Nitrate concentrations are generally low in both groups and show limited variability.

Overall, the box plot comparison indicates that high-fluoride mine water is characterized by relatively higher Ca^{2+} concentrations and slightly elevated TDS, whereas the distributions of major anions remain broadly comparable between the high- and low-fluoride groups.

Correlation between Fluoride and other Hydrochemical Parameters

The relationships between fluoride (F^{-}) and other hydrochemical parameters were evaluated using correlation analysis, and the results are illustrated in Fig. 3.

As shown in Fig. 3, fluoride exhibits a positive correlation with Ca^{2+} in mine water samples. Higher fluoride concentrations are generally associated with elevated Ca^{2+} levels, indicating that fluoride enrichment occurs over a wide range of calcium concentrations. This correlation is observed consistently across the dataset and is particularly evident in high-fluoride mine water.

Fluoride also shows a moderate positive correlation with total dissolved solids (TDS), suggesting that higher fluoride concentrations tend to occur in waters with relatively higher overall mineralization. In contrast, the correlation between fluoride and pH is relatively weak, although fluoride concentrations are predominantly distributed within a neutral to weakly alkaline pH range.

Regarding other major ions, fluoride displays weak to moderate correlations with Mg^{2+} and SO_4^{2-}, while its relationships with Na^{+}, Cl^{-}, and HCO_3^{-} are less pronounced. These parameters exhibit substantial scatter in relation to fluoride concentration, indicating that their variations are not directly proportional to fluoride levels.

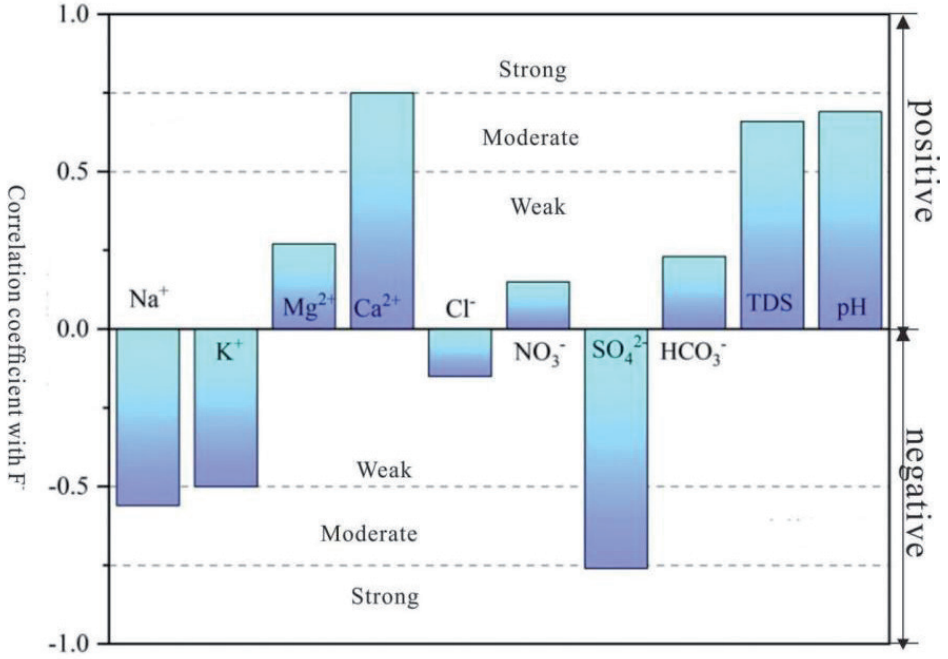

Fig. 3. Correlation coefficients between fluoride (F^{-}) and major hydrochemical parameters in mine water.

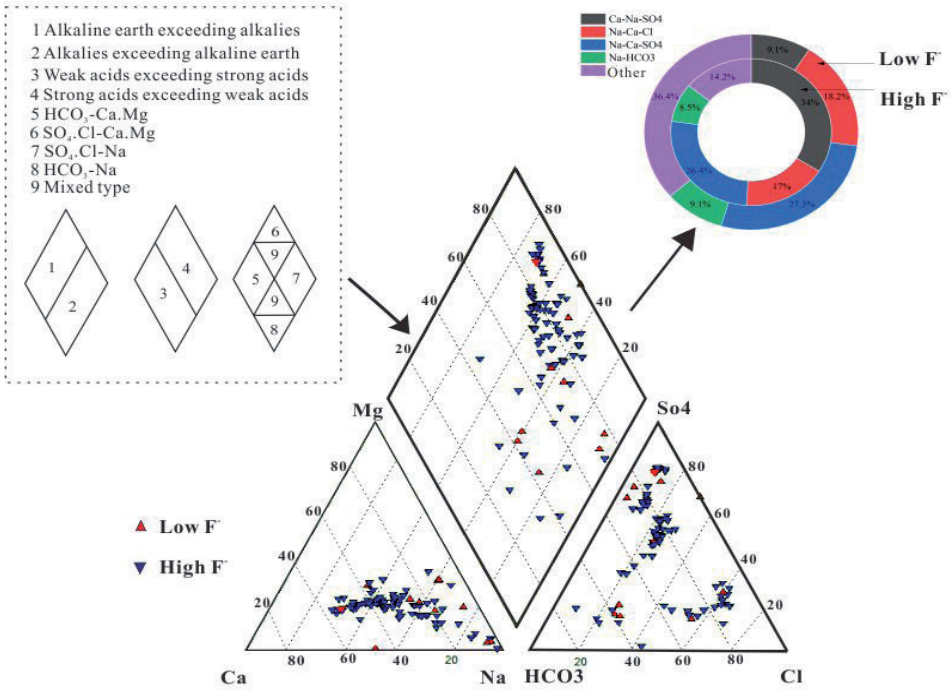

Fig. 4. a) Piper diagram showing hydrochemical facies of low- and high-fluoride mine water; b) Statistical distribution of hydrochemical types.

Overall, the correlation analysis highlights distinct associations between fluoride and selected hydrochemical parameters, particularly Ca^{2+} and TDS, whereas relationships with other major ions are comparatively weak. These patterns provide a quantitative basis for further examination of fluoride enrichment processes in mine water.

Hydrochemical Types of High- and Low-Fluoride Mine Water

The hydrochemical characteristics of mine water were further examined using Piper diagrams, and the distribution of hydrochemical types for low- and high-fluoride mine water is shown in Fig. 4.

As illustrated in Fig. 4, most mine water samples plot within the Ca-HCO_3 and Ca-Mg-HCO_3 fields, indicating a predominance of alkaline earth cations and bicarbonate anions. This pattern is observed in both low- and high-fluoride groups, suggesting broadly similar hydrochemical facies across the study area.

Low-fluoride mine water samples are mainly distributed in the Ca-HCO_3-type field, with a limited spread toward mixed Ca-Mg-HCO_3 compositions. In contrast, high-fluoride mine water exhibits a wider distribution in the cation triangle, extending from Ca-dominated compositions toward Ca-Mg and mixed alkaline earth types. Despite this broader variability, Ca^{2+} remains the dominant cation in most high-fluoride samples.

In the anion triangle, both low- and high-fluoride mine water samples are predominantly characterized by HCO_3^- dominance, with subordinate contributions from SO_4^{2-} and Cl^-. The anion compositions of the two groups largely overlap, indicating that fluoride enrichment is not accompanied by a distinct shift in dominant anion types.

Taken together, the Piper diagram results indicate that both low- and high-fluoride mine water are mainly of Ca-HCO_3 and Ca-Mg-HCO_3 types. Compared with low-fluoride mine water, high-fluoride samples display greater dispersion in cation composition, while maintaining similar anion characteristics.

Discussion

Hydrochemical Anomaly of High-Fluoride Mine Water: Coexistence of High Ca^{2+} and F^-

High-fluoride groundwater is commonly characterized by low Ca^{2+} concentrations and Na^+-dominated hydrochemical facies, as Ca^{2+} is generally considered to inhibit fluoride enrichment through fluorite precipitation [26, 27]. However, the hydrochemical results of the present study reveal a distinctly different pattern in high-fluoride mine water.

As shown in Fig. 3, fluoride exhibits a clear positive correlation with Ca^{2+} in high-fluoride mine water, indicating that elevated fluoride concentrations coexist with relatively high Ca^{2+} levels. This relationship contrasts with the conventional Ca-F antagonistic behavior widely reported for Na-HCO_3-type high-fluoride groundwater systems. In addition, fluoride also shows

moderate positive correlations with TDS and pH, suggesting that high-fluoride mine water is associated with a relatively evolved hydrochemical environment rather than a simple dilution-controlled system.

The Piper diagram further highlights the anomalous hydrochemical facies of high-fluoride mine water (Fig. 4). Most high-fluoride samples are characterized by Ca-Na-SO_4-type compositions, whereas low-fluoride mine water exhibits a higher proportion of Na-dominated facies. The dominance of alkaline earth metals in high-fluoride samples indicates that fluoride enrichment in the study area does not occur under Ca-depleted conditions. Instead, Ca^{2+} remains an important component of the major cation assemblage.

The statistical distribution of hydrochemical types (Fig. 4) reinforces this distinction. High-fluoride mine water is primarily composed of Ca-Na-SO_4 and Na-Ca-SO_4 types, while low-fluoride mine water shows greater diversity and a higher proportion of Na-Ca-SO_4 and Na-Ca-Cl facies. This systematic difference in hydrochemical facies provides additional support for the coexistence of elevated Ca^{2+} and fluoride concentrations in high-fluoride mine water [35, 36].

On this basis, the hydrochemical characteristics of high-fluoride mine water in the study area deviate markedly from the traditional low-Ca, Na-rich fluoride groundwater model. The persistent coexistence of elevated Ca^{2+} and F^- therefore represents a notable hydrochemical anomaly, which points to the involvement of additional mineralogical and water-rock interaction processes that are explored in the following sections.

Mineral Dissolution and Saturation Constraints on Fluoride Enrichment

The coexistence of elevated Ca^{2+} and F^- in mine water (Fig. 5a)) indicates that fluoride enrichment in the study area does not follow the classical Ca-F antagonistic pattern typically observed in low-Ca, Na-HCO_3 groundwater systems. In conventional models, increasing F^- concentrations are accompanied by decreasing Ca^{2+} due to fluorite (CaF_2) precipitation. However, the broad distribution of sample points in Fig. 5a) shows that high F^- concentrations occur across a wide range of Ca^{2+} levels, including Ca-rich conditions, implying that fluorite precipitation does not exert a strong regulatory control on fluoride concentrations.

To further examine mineral equilibrium constraints, saturation index (SI) values for fluorite, calcite, dolomite, and gypsum were evaluated. Fig. 6a) shows that SI values of all four minerals are predominantly negative, demonstrating that both high- and low-fluoride mine water generally remain undersaturated with respect to these minerals. Fluorite, in particular, exhibits consistently negative SI values for the majority of samples, confirming that fluorite precipitation is thermodynamically unfavorable under current hydrochemical conditions. This finding is consistent with numerous studies reporting persistent fluorite undersaturation in fluoride-rich groundwater and mine water systems [26, 34, 35].

The relationships between fluoride concentration and mineral SI values (Fig. 6(b-e)) provide additional insights into mineral-water interactions. Fluorite SI values (Fig. 6b)) increase gradually with rising F^- concentration but remain below saturation for most samples. Only a small subset of the highest-fluoride samples approaches or slightly exceeds fluorite saturation. This trend indicates that saturation is reached only after substantial fluoride accumulation has already occurred, suggesting that fluorite precipitation is a secondary response to fluoride enrichment rather than a primary limiting mechanism [31, 35].

Calcite and dolomite exhibit similar patterns (Fig. 6(c-d)), showing undersaturation across much of the dataset. Their SI values increase slightly with fluoride concentration, reflecting enhanced water-rock interaction in chemically evolved, bicarbonate-rich groundwater. Gypsum SI values (Fig. 6e)) remain negative throughout the entire fluoride range, indicating

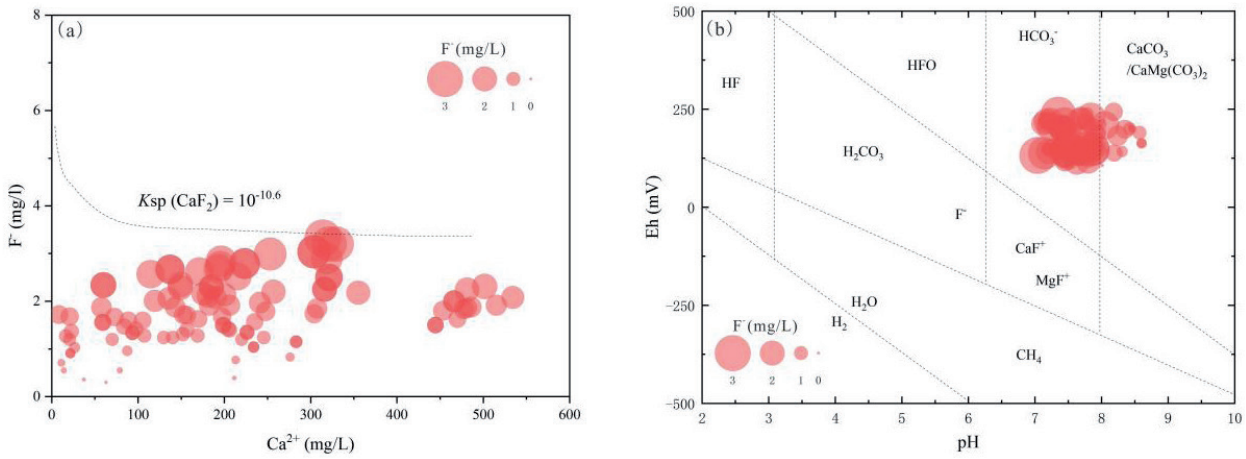

Fig. 5. a) Relationship between Ca^{2+} and F^- concentrations in mine water; b) Eh-pH diagram of F^- species.

no tendency for sulfate minerals to precipitate and no significant control on fluoride mobility.

Fluoride speciation results (Fig. 5b)) further support the predominance of dissolved free F^- under the observed hydrochemical conditions. Most samples fall within pH-Eh fields where fluoride remains stable in solution, consistent with carbonate-buffered, Ca-rich settings [33, 36].

In summary, the combined evidence from the Ca^{2+}-F^- relationship (Fig. 5a)), mineral saturation indices (Fig. 6(a-e)), and fluoride speciation (Fig. 5b)) demonstrates that fluoride enrichment in the study area is primarily governed by the dissolution of fluorine-bearing minerals, while fluorite precipitation does not effectively limit dissolved fluoride. Fluoride accumulates in mine water under hydrochemical conditions that remain

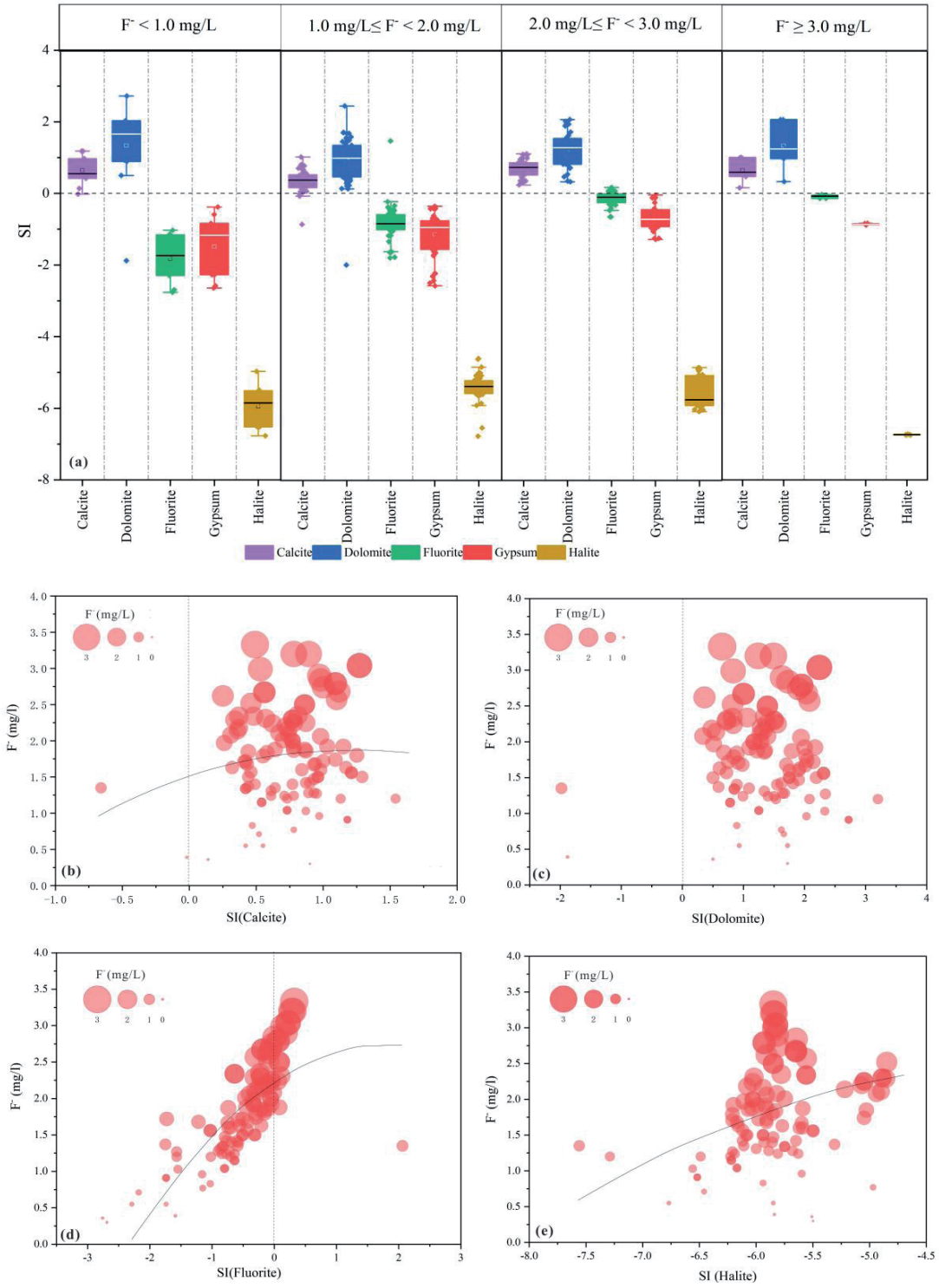

Fig. 6. a) Box plots of saturation indices (SI) for fluorite, calcite, dolomite, and gypsum in low- and high-fluoride mine water; (b-e) Relationships between fluoride concentration and saturation indices of b) fluorite, c) calcite, d) dolomite, and e) gypsum.

persistently undersaturated with respect to fluorite, supporting the conclusion that fluoride enrichment occurs in Ca-rich, carbonate-hosted systems through mineral dissolution processes rather than by mineral precipitation.

Role of Hydrochemical Conditions in Promoting Fluoride Persistence and Accumulation

Influence of pH and Fluoride Speciation

The Eh-pH distribution of mine water samples shows that most samples, particularly those with high fluoride concentrations, fall within a weakly alkaline pH range (Fig. 5b)). Under such conditions, fluoride predominantly exists as free F^-, which favors its thermodynamic stability and persistence in aqueous solution [36]. The absence of pronounced redox-driven speciation changes or complexation reactions indicates that pH conditions support fluoride stability rather than restricting its availability.

Similar pH-controlled fluoride behavior has been widely reported in carbonate-hosted aquifers and mining-affected groundwater systems, where weak alkalinity promotes the retention of fluoride in solution over extended timescales [33, 36]. Therefore, the relatively narrow and stable pH range observed in high-fluoride mine water represents a hydrochemical setting conducive to sustained fluoride accumulation.

Role of Bicarbonate in Fluoride Mobility

Most high-fluoride mine water samples are located within the HCO_3^--dominated field, reflecting carbonate-buffered hydrochemical conditions. Such environments typically develop during prolonged water-rock interaction in carbonate-bearing strata and are characteristic of chemically evolved groundwater systems. Under bicarbonate-rich conditions, competitive interactions at mineral-water interfaces may suppress fluoride adsorption onto solid phases, thereby enhancing fluoride mobility and retention in solution [37, 38].

In the study area, the predominance of HCO_3^- in high-fluoride mine water indicates that carbonate equilibria play an important role in maintaining elevated fluoride concentrations. Comparable associations between bicarbonate enrichment and

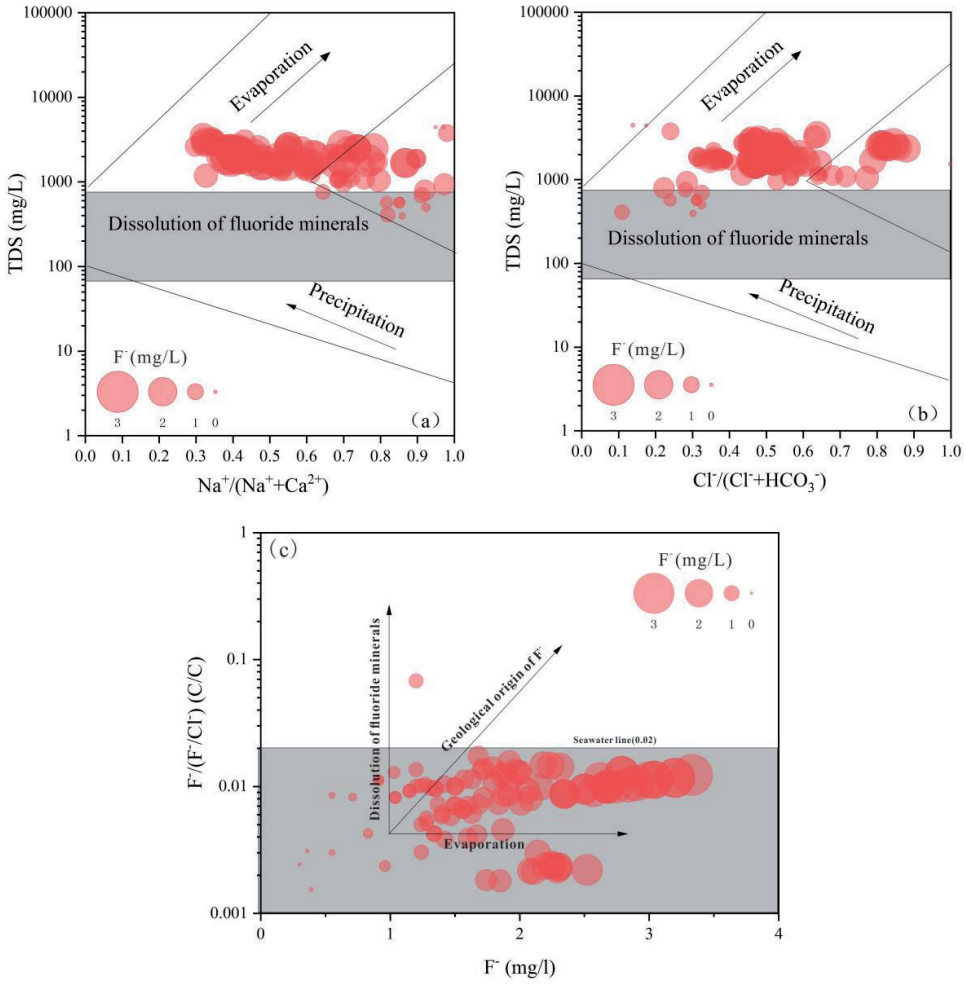

Fig. 7. Gibbs diagram showing dominant hydrochemical processes controlling mine water chemistry.

fluoride accumulation have been documented in both natural groundwater and mining-influenced aquifers, underscoring the significance of bicarbonate buffering in controlling fluoride behavior [31, 35].

Water-Rock Interaction and Evaporative Concentration Effects

The Gibbs diagrams (Fig. 7) show that both low- and high-fluoride mine water samples plot mainly within

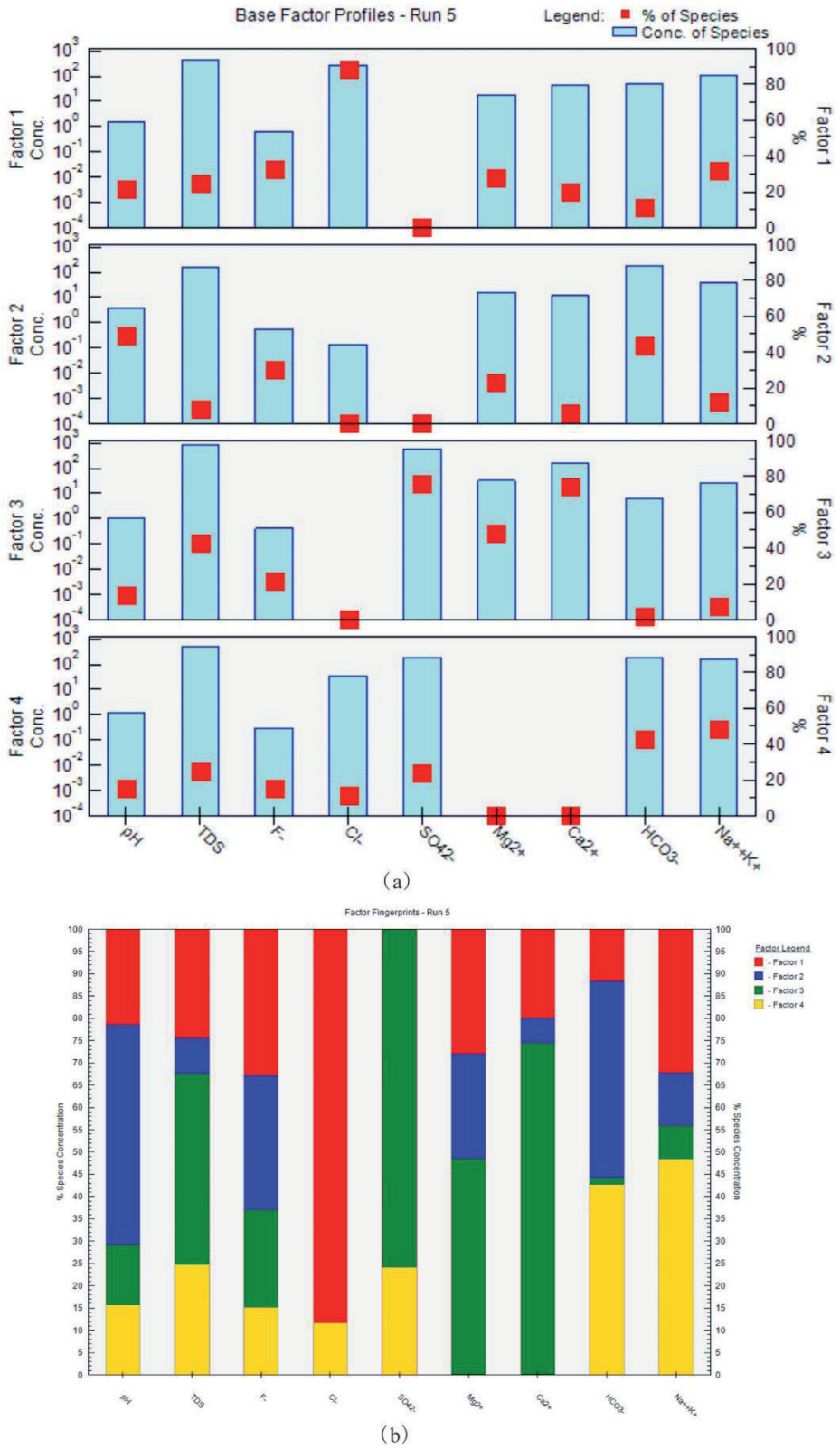

Fig. 8. a) Contribution of PMF factors to fluoride; b) PMF factor profiles of major hydrochemical parameters.

the water-rock interaction and evaporation dominance fields. This distribution indicates that mine water chemistry is primarily controlled by prolonged water-rock interaction rather than direct precipitation inputs. High-fluoride samples are generally associated with higher total dissolved solids (TDS), suggesting a more advanced stage of hydrochemical evolution.

As groundwater evolves along water-rock interaction pathways, dissolved solute concentrations increase progressively, creating favorable conditions for fluoride accumulation. Evaporative concentration further intensifies this process by increasing ionic strength and concentrating dissolved constituents, thereby amplifying fluoride enrichment. These observations indicate that fluoride accumulation in mine water reflects the cumulative effects of long-term hydrochemical evolution rather than a transient geochemical process [35, 36].

Quantitative Source Apportionment of Fluoride Based on PMF Analysis

To quantitatively identify the relative contributions of different hydrogeochemical processes to fluoride enrichment in mine water, positive matrix factorization (PMF) was applied to the conventional hydrochemical dataset [30, 33, 39]. The PMF results provide a quantitative extension of the qualitative hydrogeochemical interpretations presented earlier, enabling the dominant and secondary processes controlling fluoride enrichment to be clearly distinguished.

PMF Model Configuration and Factor Determination

The PMF model was constructed using major ions and physicochemical parameters, including F^-, Ca^{2+}, Mg^{2+}, Na^++K^+, SO_4^{2-}, Cl^-, HCO_3^-, pH, and TDS. After multiple model runs and diagnostic evaluations, a four-factor solution was identified as the optimal configuration, yielding stable factor profiles, physically interpretable hydrochemical signatures, and minimal residuals. The resolved factor fingerprints and their corresponding contribution proportions are presented in Fig. 8.

Hydrochemical Interpretation of PMF Factors

Factor 1 is characterized by very high loadings of Cl^- (88.3%), accompanied by substantial contributions of F^- (32.8%) and Na^++K^+ (32.2%) in the PMF fingerprint (Fig. 8b)). The dominance of Cl^+ and Na^+ indicates a strong evaporite influence, consistent with the widespread undersaturation of halite observed in the saturation index analysis.

The relatively high F^- loading reflects the occurrence of fluorine-bearing minerals in the Taiyuan Formation, including fluorite, fluorapatite, and fluorine-bearing silicates. Accordingly, Factor 1 represents the primary fluoride source associated with the dissolution of fluorine-bearing minerals under a high-TDS, evaporite-influenced hydrochemical background.

Factor 2 exhibits high loadings of HCO_3^- (44.0%), pH (49.5%), and F^- (30.2%), indicating a close association between fluoride behavior and carbonate-buffered hydrochemical conditions (Fig. 9). This factor reflects environments characterized by elevated bicarbonate concentrations and weakly alkaline pH.

Under such conditions, competitive adsorption between F^- and carbonate-related species at mineral-water interfaces becomes increasingly important. Elevated HCO_3^- and OH^- concentrations reduce fluoride adsorption onto mineral surfaces, thereby enhancing fluoride mobility and persistence in solution. Consequently, Factor 2 is interpreted as a competitive adsorption process operating under chemically evolved, carbonate-buffered conditions.

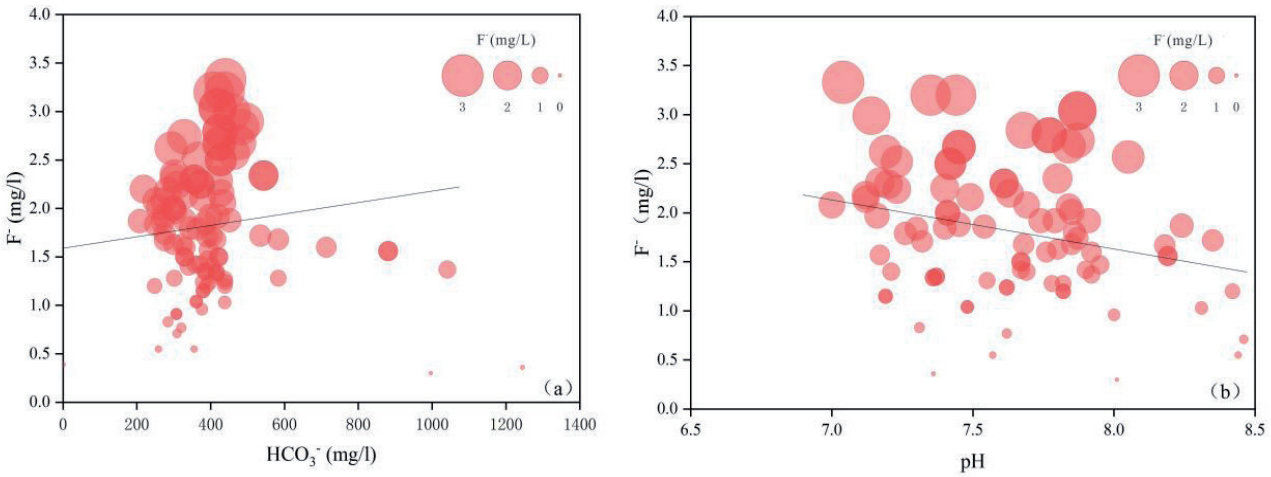

Fig. 9. Relationships of fluoride with a) HCO_3^- and b) pH.

Factor 3 is distinguished by high loadings of Ca^{2+} (74.4%) and SO_4^{2-} (76.0%), together with notable contributions from Mg^{2+} (48.6%) and TDS (42.9%), while Na^++K^+ display relatively low loadings (7.4%) (Fig. 10b)). This hydrochemical signature is characteristic of reverse cation exchange, whereby Ca^{2+} and Mg^{2+} released from exchange sites replace Na^+ and K^+ in groundwater.

This interpretation is further supported by chloro-alkaline indices (CAI1 and CAI2) and ion balance relationships (Fig. 10). Low-fluoride samples show negative CAI values, indicating normal cation exchange, whereas high-fluoride samples predominantly exhibit positive CAI values, consistent with reverse cation exchange. In addition, the linear relationship between (Ca^{2+}+Mg^{2+}-SO_4^{2-}-HCO_3^-) and (Na^++K^+-Cl^-) with a slope close to -1 confirms the occurrence of active cation exchange processes.

Reverse cation exchange increases Ca^{2+} availability in mine water, indirectly promoting further dissolution of fluorine-bearing minerals and reinforcing the characteristic Ca-rich, high-fluoride hydrochemical signature.

Factor 4 is dominated by Na^++K^+ (48.4%) and HCO_3^- (42.6%), reflecting the influence of evaporative concentration and progressive solute accumulation (Fig. 8b)). This factor corresponds closely with the evaporation-dominated field identified in the Gibbs diagrams.

Although evaporation does not introduce fluoride directly, it enhances fluoride concentrations by concentrating dissolved constituents during groundwater evolution. Therefore, Factor 4 represents an evaporative concentration process that amplifies fluoride enrichment in mine water.

Quantitative Contribution of Different Factors to Fluoride Enrichment

Based on the PMF contribution results (Fig. 8a)), fluorine-bearing mineral dissolution (Factor 1) constitutes the dominant fluoride source, accounting for 31.80% of the total fluoride load. Reverse cation exchange (Factor 3) contributes 28.75%, highlighting its important role in modifying cation composition and facilitating fluoride accumulation. Evaporative concentration (Factor 4) accounts for 20.24%, while competitive adsorption under carbonate-buffered conditions (Factor 2) contributes 19.22%.

Taken as a whole, secondary hydrochemical processes account for more than two-thirds of the total fluoride enrichment, demonstrating that fluoride accumulation in mine water arises from the combined effects of mineral sources and hydrochemical evolution rather than from a single controlling mechanism [34, 39].

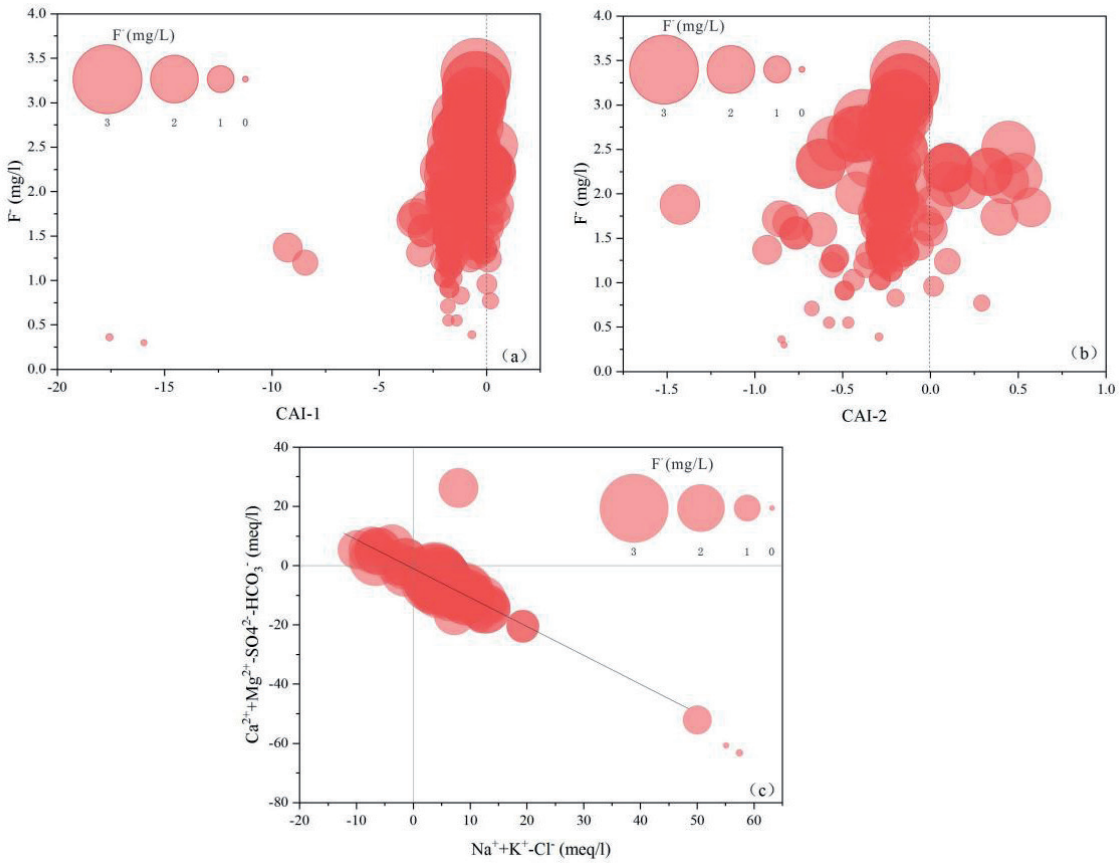

Fig. 10. Relationships of fluoride with CAI1, CAI2, and ion balance indicators.

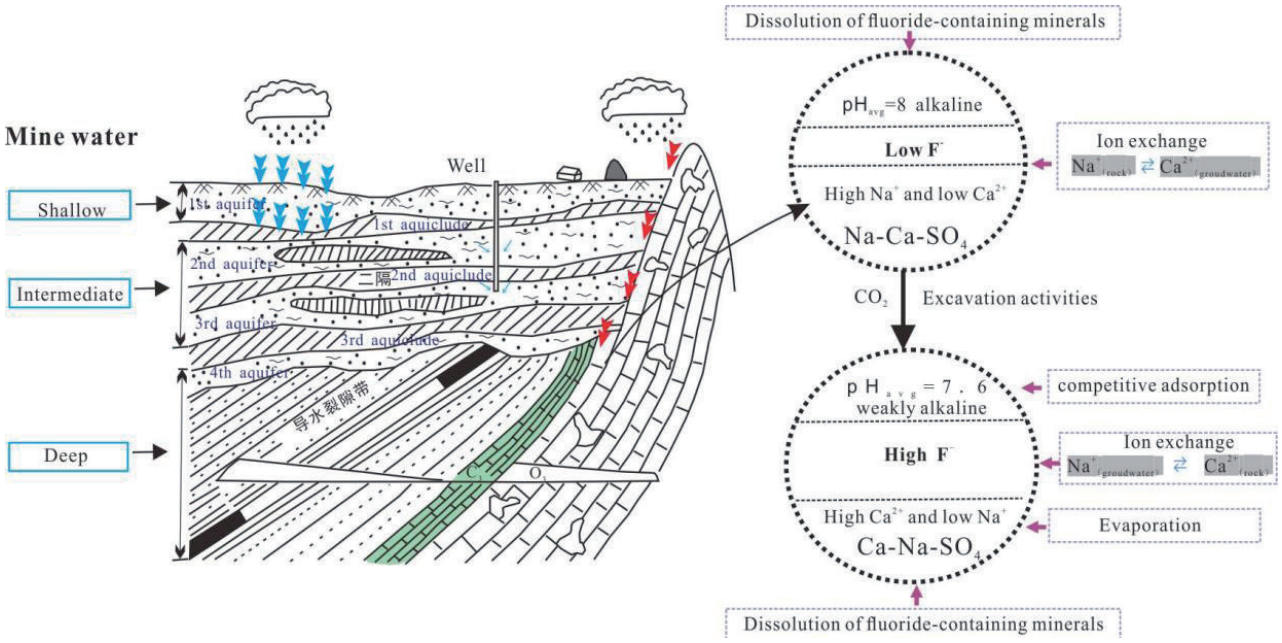

Fig. 11. Conceptual model illustrating fluoride enrichment in Ca-rich mine water.

Conceptual Model and Implications for High-Fluoride Mine Water Systems

Based on the integrated hydrochemical analysis, mineral equilibrium evaluation, and PMF-based quantitative source apportionment, a conceptual model is proposed to illustrate the coupled processes governing fluoride enrichment in high-fluoride mine water (Fig. 11). The model synthesizes the primary fluoride sources, controlling hydrochemical conditions, and reinforcing mechanisms identified in this study.

In this framework, fluoride is initially released into mine water through the dissolution of fluorine-bearing minerals hosted in carbonate-dominated strata. Under fluorite-undersaturated conditions, fluoride can be liberated without being effectively constrained by Ca-F precipitation, providing the fundamental material basis for fluoride enrichment. This process explains the widespread occurrence of elevated fluoride concentrations under Ca-rich conditions observed in the study area.

Subsequent hydrochemical evolution plays a critical role in sustaining and amplifying fluoride enrichment. Weakly alkaline pH, bicarbonate-buffered conditions, prolonged water-rock interaction, and evaporative concentration jointly favor fluoride stability and progressive accumulation in solution. Secondary processes, including reverse cation exchange and competitive adsorption, further modify the ionic composition of mine water, indirectly enhancing fluoride persistence and reinforcing the characteristic Ca-rich, high-fluoride hydrochemical signature.

The conceptual model highlights that high-fluoride mine water does not necessarily develop under Ca-depleted, Na-dominated conditions traditionally associated with fluoride-rich groundwater. Instead, fluoride enrichment can occur in carbonate-hosted, Ca-rich systems when mineral dissolution and hydrochemical evolution operate in concert. This finding extends the conventional understanding of fluoride enrichment mechanisms in groundwater systems.

From an applied perspective, the proposed model provides a transferable framework for interpreting fluoride behavior in mine water systems developed in carbonate aquifers. It emphasizes that fluoride risk assessment and management should consider both mineral sources and long-term hydrochemical evolution rather than relying solely on simplified hydrochemical indicators. This integrated perspective is essential for predicting fluoride evolution and for guiding mine water utilization and mitigation strategies in similar mining environments.

Conclusions

This study systematically investigated the hydrochemical characteristics and fluoride enrichment mechanisms of high-fluoride mine water using integrated hydrochemical analysis and positive matrix factorization (PMF). The main conclusions are as follows:

(1) High-fluoride mine water exhibits a distinctive hydrochemical pattern characterized by the coexistence of elevated Ca^{2+} and F^-. High fluoride concentrations occur across a wide range of Ca^{2+} levels, including Ca-rich conditions, indicating that fluoride enrichment in mine water does not conform to the conventional Ca-F antagonistic model commonly reported for groundwater systems.

(2) Fluoride enrichment is not effectively constrained by fluorite precipitation under the prevailing

hydrochemical conditions. Most mine water samples remain undersaturated with respect to fluorite, and fluorite saturation is generally approached only after substantial fluoride accumulation. This demonstrates that fluorite precipitation represents a geochemical response to fluoride enrichment rather than a primary controlling mechanism.

(3) Hydrochemical evolution provides favorable conditions for the persistence and accumulation of fluoride in mine water. Weakly alkaline pH, bicarbonate-buffered conditions, prolonged water-rock interaction, and evaporative concentration collectively promote fluoride stability and progressive accumulation during groundwater evolution.

(4) PMF analysis quantitatively confirms that fluoride enrichment results from multiple coupled processes. Fluorine-bearing mineral dissolution constitutes the dominant fluoride source (31.80%), while reverse cation exchange (28.75%), evaporation (20.24%), and competitive adsorption (19.22%) act as important reinforcing processes, highlighting the multifactorial nature of fluoride enrichment in mine water systems.

Acknowledgments

This research was supported by the Open Fund of the Coal Industry Engineering Research Center for Exploration and Early Warning of Mine Water Disaster (Grant No. 2024-CIERC-07). The authors also acknowledge financial support from the Excellent Young Teachers Training Program of Anhui Province (Grant No. YQYB2024075), the Academic and Technical Leader Reserve Program of Suzhou University (Grant No. 2024XJHB08), the Postdoctoral Research Start-up Fund of Suzhou University (2025BSH001) , and the Drilling Engineering Technology Research Center of Suzhou University (2024PT04). The authors also acknowledge additional financial support from the Anhui Provincial Department of Education Research Project (2023AH052224), the Anhui Provincial Department of Education Quality Engineering Projects (2024zygzts115; 2024jsqygz117), and the Suzhou University Institutional Quality Engineering Project (szxy2023xxhz01), which provided important assistance for the completion of this study.

AI Usage Disclosure Statement

During manuscript preparation, the authors used DeepSeek (an AI-assisted language tool) solely for English grammar and fluency improvement. No AI tools were used for data analysis, modeling, figure preparation, or interpretation. All AI-generated suggestions were critically reviewed and verified by the authors, who assume full responsibility for the final content.

Conflict of Interest

The authors declare no conflict of interest.

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