

Supplementary captions:

Figure S1. Gibbs diagrams of groundwater samples in the study area, (a) and (b) denote TDS VS. $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ and TDS VS. $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ in SG samples, respectively and (c) and (d) denote TDS VS. $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ and TDS VS. $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ in DG samples.

Figure S2. Scatterplots of major ions to explain the formation of groundwater, (a) denotes Na^+ -normalized Ca^{2+} VS. Mg^{2+} , (b) denotes Na^+ -normalized Ca^{2+} VS. HCO_3^- in SG samples, (c) denotes Na^+ -normalized Ca^{2+} VS. Mg^{2+} , and (d) denotes Na^+ -normalized Ca^{2+} VS. HCO_3^- in DG samples, respectively.

Figure S3. Scatterplots (a) and (d) show $(\text{HCO}_3^- + \text{SO}_4^{2-})$ VS. $(\text{Ca}^{2+} + \text{Mg}^{2+})$ to verify the contribution of carbonate and dolomite dissolution in shallow and DG samples, respectively; (b) and (e) show $(\text{Ca}^{2+} + \text{Mg}^{2+} - \text{HCO}_3^-)$ VS. SO_4^{2-} to illustrate gypsum dissolution in shallow and DG samples, respectively; and (c) and (f) show Na^+ VS. Cl^- to explore halite dissolution in shallow and DG samples, respectively.

Figure. S4. The results of Spearman correlation analysis for typical hydrogeochemical parameters in shallow and DG samples are shown in (a) and (d) respectively. The asterisk marks represent the $p < 0.05$.

Figure S5. Scatterplots for evaluating fluorite dissolution and other minerals hydrolysis in SG samples. Scatterplots of (a) and (b) denote $\text{SI}_{\text{calcite}}$ VS. $\text{SI}_{\text{fluorite}}$ and $\text{SI}_{\text{dolomite}}$, respectively; (c) and (d) denote $\text{SI}_{\text{gypsum}}$ VS. $\text{SI}_{\text{calcite}}$ and $\text{SI}_{\text{dolomite}}$, respectively; (e) denotes Ca^{2+} VS. Mg^{2+} ; and (f) denotes $\text{SI}_{\text{fluorite}}$ VS. $[\text{F}]$.

Figure S6. Scatterplots for evaluating fluorite dissolution and other minerals hydrolysis in DG samples. Scatterplots of (a) and (b) denote $\text{SI}_{\text{calcite}}$ VS. $\text{SI}_{\text{fluorite}}$ and $\text{SI}_{\text{dolomite}}$, respectively; (c) and (d) denote $\text{SI}_{\text{gypsum}}$ VS. $\text{SI}_{\text{calcite}}$ and $\text{SI}_{\text{dolomite}}$, respectively; (e) denotes Ca^{2+} VS. Mg^{2+} ; and (f) denotes $\text{SI}_{\text{fluorite}}$ VS. $[\text{F}]$.

Figure S7. Evaluation of the impacts of evaporation on F^- by the scatterplots for F/Cl ratio VS. $[\text{F}]$.

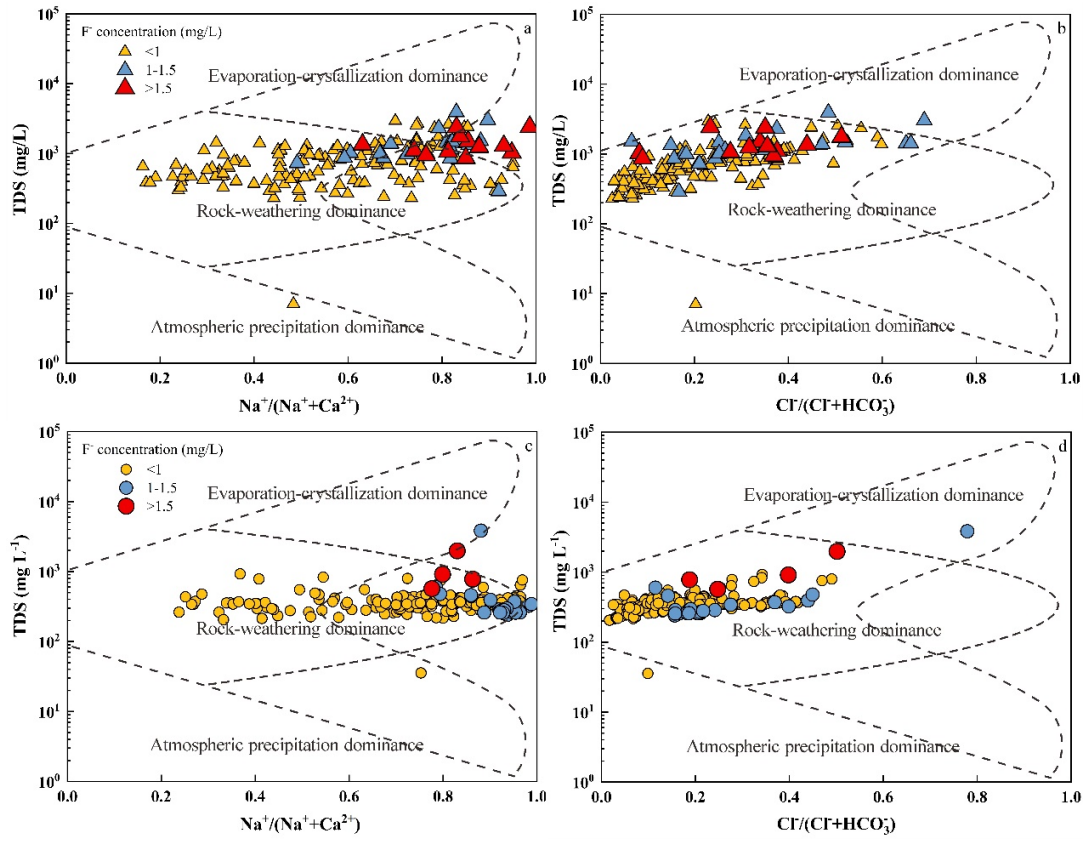


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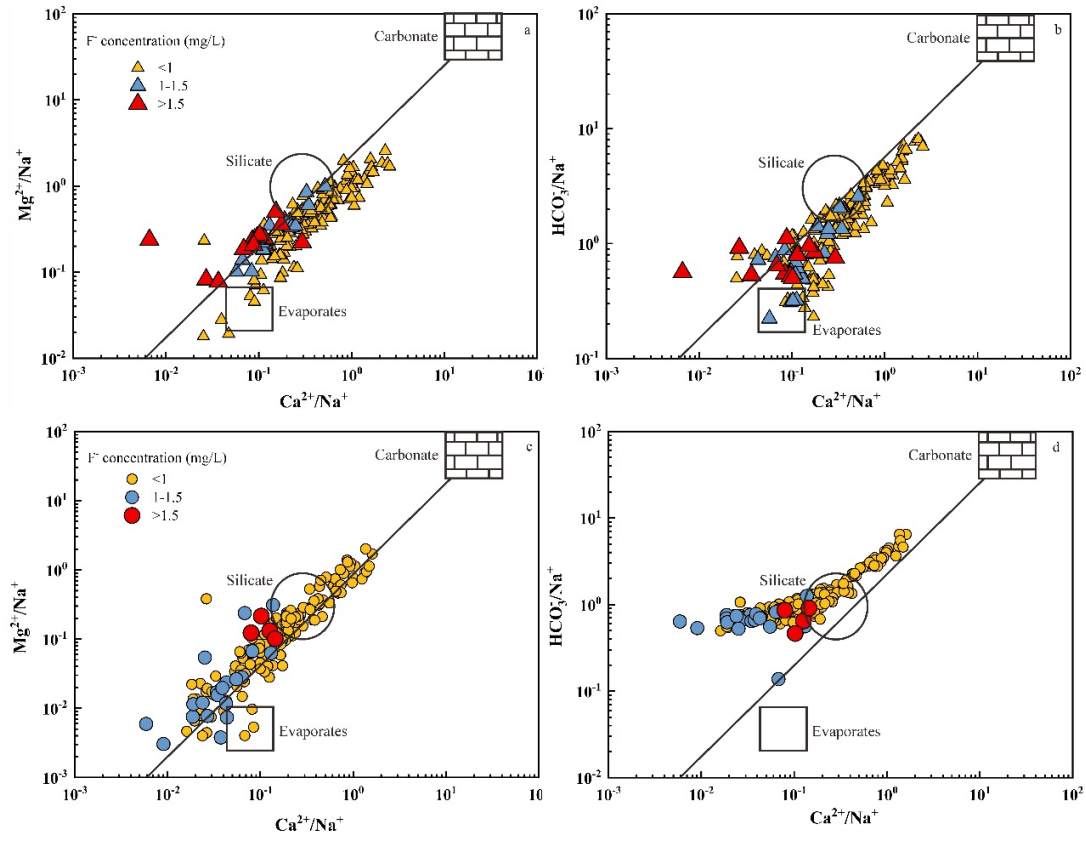


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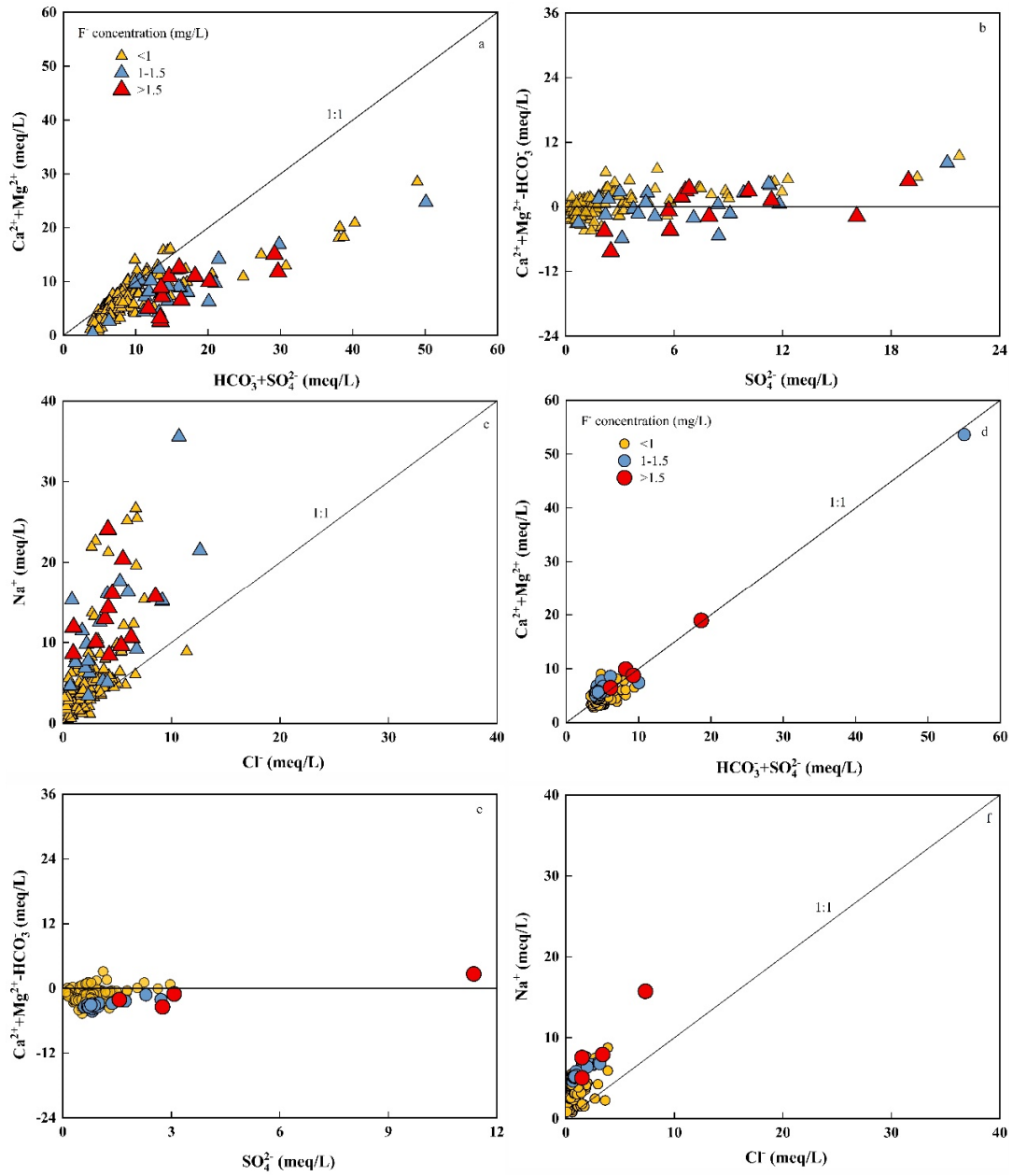


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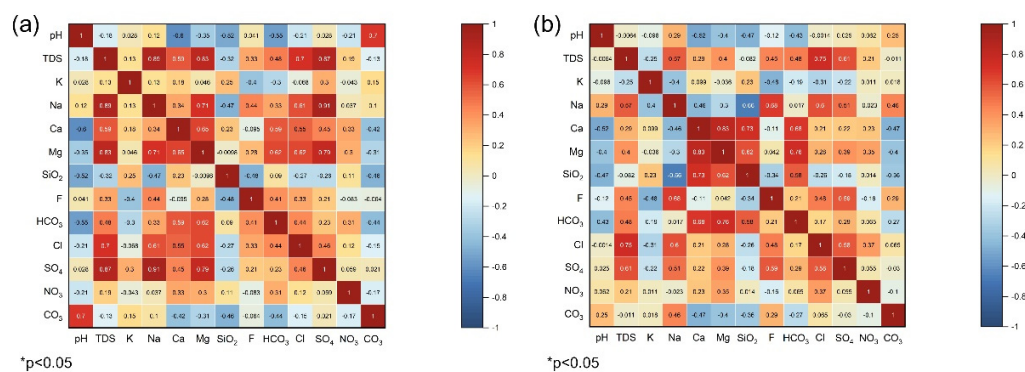


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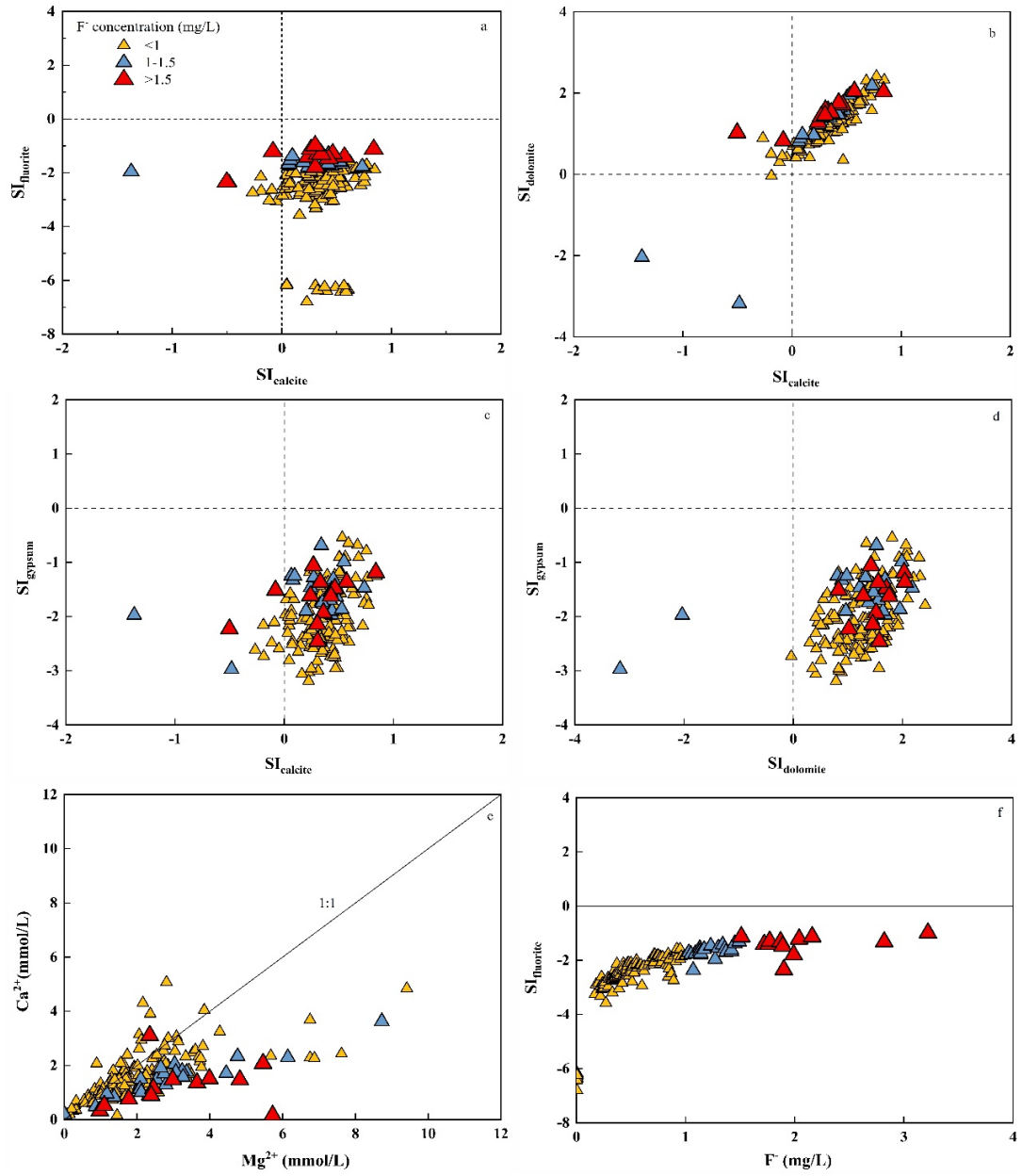


Figure S5. Scatterplots for evaluating fluorite dissolution and other minerals hydrolysis in SG samples. Scatterplots of (a) and (b) denote $SI_{calcite}$ VS. $SI_{fluorite}$ and $SI_{dolomite}$, respectively; (c) and (d) denote SI_{gypsum} VS. $SI_{calcite}$ and $SI_{dolomite}$, respectively; (e) denotes Ca^{2+} VS. Mg^{2+} ; and (f) denotes $SI_{fluorite}$ VS. $[F^-]$.

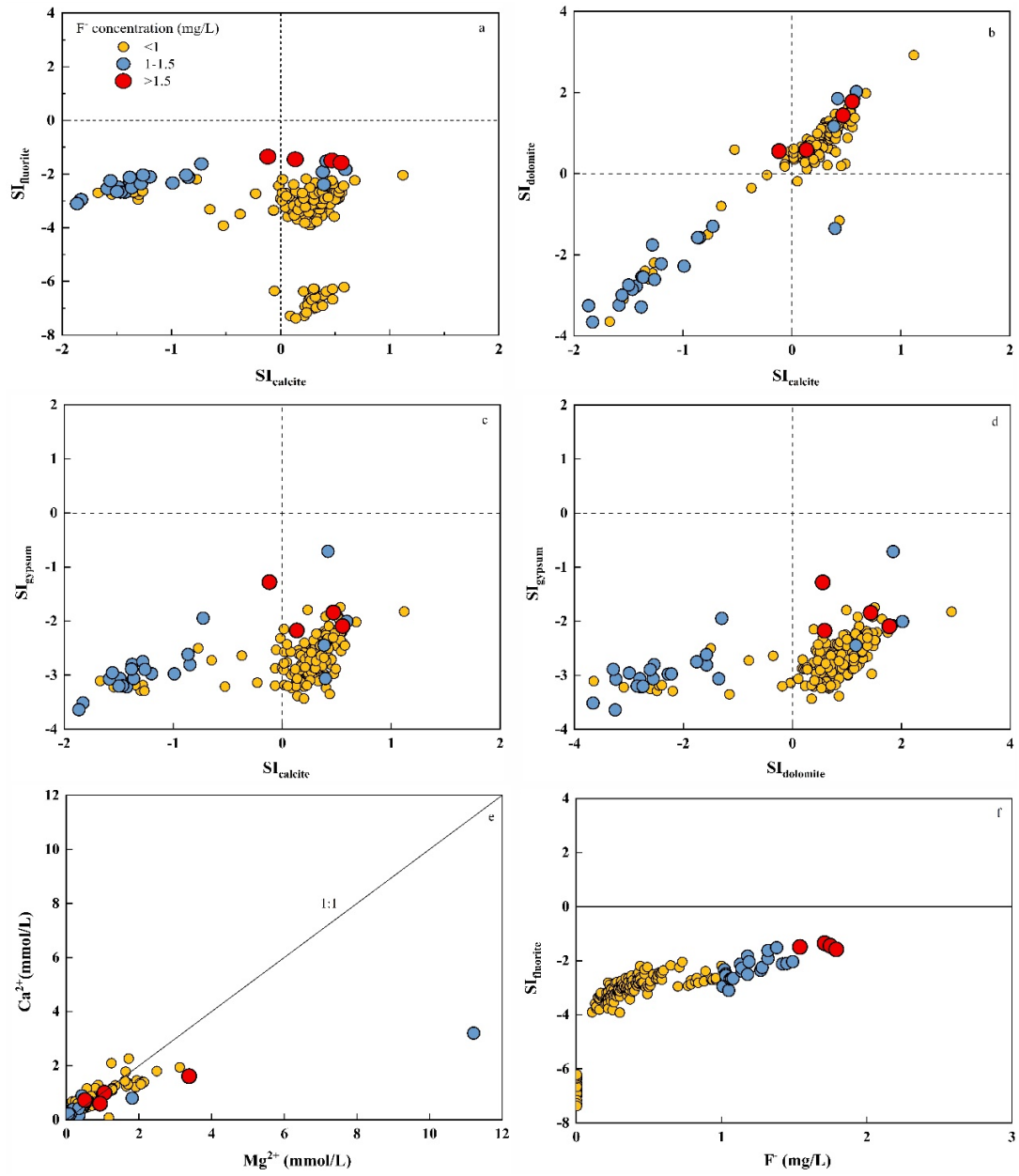


Figure S6. Scatterplots for evaluating fluorite dissolution and other minerals hydrolysis in DG samples. Scatterplots of (a) and (b) denote $SI_{calcite}$ VS. $SI_{fluorite}$ and $SI_{dolomite}$, respectively; (c) and (d) denote SI_{gypsum} VS. $SI_{calcite}$ and $SI_{dolomite}$, respectively; (e) denotes Ca^{2+} VS. Mg^{2+} ; and (f) denotes $SI_{fluorite}$ VS. $[F]$.

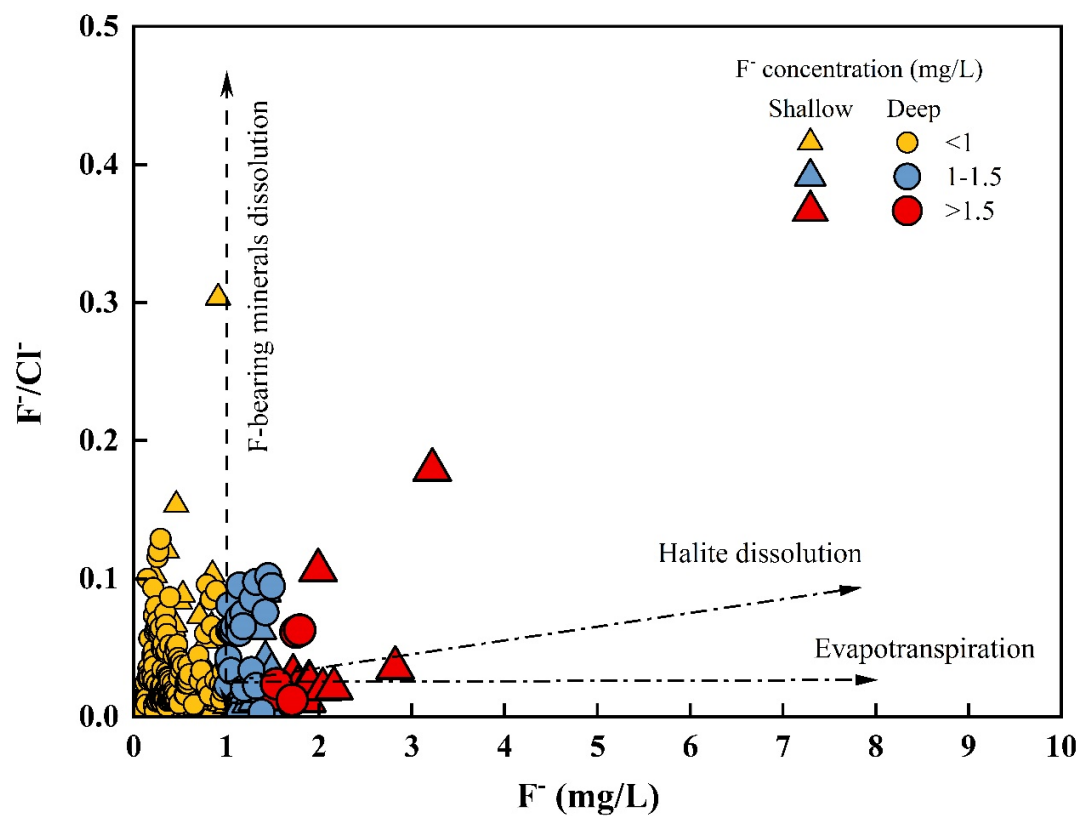


Figure S7. Evaluation of the impacts of evaporation on F^- by the scatterplots for F^-/Cl^- ratio VS. $[F^-]$.

Supplementary captions:

Text S1. Quality control (QC) and quality assurance (QA).

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The quality assurance and quality control (QA/QC) of the ion determinations were conducted according to the national standard [1]. During the analysis, analytical precision was assessed using three replicate samples for water and the average value was included in the results. The ionic charge balance error (ICBE) was calculated to identify precision and accuracy using the method of Matthess [2] (Equation (S1)):

$$\text{ICBE} = \frac{\Sigma C - \Sigma A}{\Sigma C + \Sigma A} \times 100\% \quad (\text{S1})$$

where ICBE indicates the ionic charge balance error, ΣC and ΣA denote the value of all cations and all anions, respectively (meq L^{-1}). To guarantee the accurate analysis, the values of ICBE should not exceed $\pm 5\%$ [3], whereas values greater than $\pm 10\%$ are unacceptable. In this study, the ICBE values were all within $\pm 5\%$, which means that the quality of the groundwater data was found to be acceptable [4].

Table S1. Summary of measurement methods and detection limits for the groundwater samples.

Table S2. Minimum, maximum and average values of the chemical composition of low-, moderate- and high-F⁻ shallow groundwater in Xiong'an new area.

Table S3. Minimum, maximum and average values of the chemical compositions of low-, moderate- and high-F⁻ deep groundwater in Xiong'an New Area.

Table S1. Summary of measurement methods and detection limits for the groundwater samples.

Parameters	Instruments	Detection limits
pH	pH meter	0.01
TDS	50 mL acid burette	1 mg L ⁻¹
K ⁺	Atomic absorption spectrophotometer (AAS)	0.05 mg L ⁻¹
Ca ²⁺	Inductively coupled plasma optical emission spectrometer (ICP-OES)	0.01 mg L ⁻¹
Na ⁺		0.01 mg L ⁻¹
Mg ²⁺		0.01 mg L ⁻¹
SiO ₂		0.02 mg L ⁻¹
F ⁻		0.01 mg L ⁻¹
HCO ₃ ⁻	50 mL acid burette	5 mg L ⁻¹
Cl ⁻	Ion chromatography (IC)	0.01 mg L ⁻¹
NO ₃ ⁻		0.01 mg L ⁻¹
SO ₄ ²⁻		0.01 mg L ⁻¹
CO ₃ ²⁻		0.01 mg L ⁻¹

Table S2. Minimum, maximum and average values of the chemical composition of low-, moderate- and high-F⁻ shallow groundwater in Xiong'an New Area.

Parameters	Unit	Shallow groundwater								
		Low-F ⁻ groundwater			Moderate-F ⁻ groundwater			High-F ⁻ groundwater		
		Min	Max	Avg	Min	Max	Avg	Min	Max	Avg
pH	--	6.90	8.60	7.59	6.88	7.87	7.46	7.07	7.96	7.61
TDS	mg/L	7.06	2941.50	801.39	288.91	3913.60	1427.50	862.30	2419.40	1409.66
K ⁺	mg/L	0.07	2.99	0.81	0.07	1.54	0.51	0.17	0.94	0.47
Na ⁺	mg/L	12.54	614.62	120.04	77.97	818.32	274.73	193.68	554.15	311.85
Ca ²⁺	mg/L	6.50	203.00	64.50	8.00	145.20	62.64	6.40	124.40	49.31
Mg ²⁺	mg/L	0.50	225.90	49.09	0.01	209.40	72.55	23.40	137.40	75.33
SiO ₂	mg/L	16.41	37.26	25.87	2.38	27.83	21.58	16.98	24.82	20.31
F ⁻	mg/L	0.17	1.00	0.50	1.03	1.49	1.25	1.51	3.22	2.05
HCO ₃ ⁻	mg/L	181.60	759.60	393.55	115.00	709.40	501.22	431.50	827.60	555.72
Cl ⁻	mg/L	7.20	1864.50	176.68	34.10	1861.00	393.17	103.10	910.00	402.00
SO ₄ ²⁻	mg/L	0.01	188.17	13.34	0.01	80.36	10.26	0.01	26.57	3.90
NO ₃ ⁻	mg/L	0.96	404.80	77.35	23.80	448.20	160.28	33.60	302.60	152.81
CO ₃ ²⁻	mg/L	0.00	8.70	1.36	0.00	11.90	1.40	0.00	6.00	1.00
SI _{fluorite}	--	-6.80	-1.57	-2.72	-1.96	-1.31	-1.62	-2.35	-0.99	-1.40
SI _{calcite}	--	-0.27	0.85	0.36	-1.37	0.73	0.24	-0.50	0.84	0.29
SI _{gypsum}	--	-3.19	-0.54	-2.02	-2.97	-0.68	-1.58	-2.46	-1.06	-1.66
SI _{dolomite}	--	-0.03	2.42	1.25	-3.17	2.18	1.09	0.83	2.05	1.52
SI _{halite}	--	-8.39	-5.50	-6.95	-7.13	-5.19	-6.15	-6.75	-5.58	-6.02

Table S3. Minimum, maximum and average values of the chemical composition of low-, moderate- and high-F⁻ deep groundwater in Xiong'an New Area.

Parameters	Unit	Deep groundwater								
		Low-F ⁻ groundwater			Moderate-F ⁻ groundwater			High-F ⁻ groundwater		
		Min	Max	Avg	Min	Max	Avg	Min	Max	Avg
pH	--	6.87	8.90	8.01	6.79	8.67	7.19	7.12	8.10	7.71
TDS	mg/L	35.70	926.39	370.88	241.00	3836.43	480.14	570.24	1980.00	1060.69
K ⁺	mg/L	0.23	2.64	0.99	0.19	1.15	0.37	0.28	0.60	0.42
Na ⁺	mg/L	18.25	201.51	78.75	106.99	1085.89	171.94	115.65	362.15	208.42
Ca ²⁺	mg/L	3.20	90.50	24.26	1.60	128.10	15.35	23.90	64.40	39.30
Mg ²⁺	mg/L	0.01	74.90	12.78	0.01	269.20	16.69	12.20	81.10	35.18
SiO ₂	mg/L	14.23	36.94	22.41	15.83	22.60	17.91	18.89	23.62	20.41
F ⁻	mg/L	0.11	1.00	0.33	1.01	1.49	1.19	1.54	1.79	1.70
HCO ₃ ⁻	mg/L	154.30	438.80	234.66	202.80	446.30	246.37	278.40	444.90	358.18
Cl ⁻	mg/L	4.10	142.50	37.44	28.90	2328.70	153.28	75.10	545.30	225.13
SO ₄ ²⁻	mg/L	0.01	49.15	8.71	0.01	1.00	0.25	0.01	1.61	0.83
NO ₃ ⁻	mg/L	2.80	137.30	31.71	22.40	812.40	78.75	53.20	260.50	121.85
CO ₃ ²⁻	mg/L	0.01	29.80	4.07	0.01	14.90	7.44	0.00	3.00	2.23
SI _{fluorite}	--	-7.37	-2.04	-3.60	-3.10	-1.52	-2.30	-1.58	-1.35	-1.47
SI _{calcite}	--	-1.87	0.59	-1.01	-1.67	1.12	0.21	-0.12	0.55	0.26
SI _{gypsum}	--	-3.43	-1.75	-2.68	-3.64	-0.71	-2.81	-2.17	-1.28	-1.85
SI _{dolomite}	--	-3.66	2.02	-1.92	-3.65	2.92	0.71	0.56	1.78	1.09
SI _{halite}	--	-8.70	-6.11	-7.32	-7.16	-4.75	-6.76	-6.77	-5.64	-6.31

References

1. HJ/T 164-2020; The Technical Specification for Environmental Monitoring of Groundwater. China Environmental Science Press: Beijing, China, 2020.
2. Matthess, G. *The Properties of Groundwater*; John Wiley: New York, NY, USA, 1982.
3. Singhal, B.B.S.; Gupta, R.P. *Applied Hydrogeology of Fractured Rocks*; Springer: Dordrecht, The Netherland, 2010.
4. Rashid, A.; Farooqi, A.; Gao, X.; Zahir, S.; Noor, S.; Khattak, J.A. Geochemical modeling, source apportionment, health risk exposure and control of higher fluoride in groundwater of sub-district Dargai, Pakistan. *Chemosphere* **2020**, *243*, 125409.