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Enrichment Mechanism of Lithium in Geothermal Waters from a Bedrock Reservoir in Xiong'an New Area, China

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Abstract: The lithium concentrations in the geothermal waters of the Wumishan Formation carbonate reservoir in China Xiong'an New Area are over 1 mg/L and are even higher than those in the geothermal waters of granite reservoirs in some areas of China. It is still unknown which are the most important factors controlling the lithium concentrations in the geothermal waters in the study area. This article selected the analysis and test data of 32 geothermal water samples obtained in recent years from the study area and combined them with hydrochemical analysis and test data from granite reservoirs in other regions of China to study the enrichment mechanism of lithium in the geothermal waters in the study area. The results of the hydrochemical data analysis indicate that the lithology, pH, and water–rock interaction between geothermal water and carbonate rocks are not the main factors affecting the lithium concentrations in the study area. The mixing of paleo-seawater and the leaching of the evaporated rocks formed by it are the most important factors controlling the lithium concentrations in the study area, and temperature is also an important factor affecting the lithium concentrations. The research results are of great significance to the study of the enrichment mechanism of lithium in geothermal waters and the formation mechanism of geothermal waters in similar areas around the world.

Keywords: hydrogeochemistry; carbonatite; paleo-seawater; granite; lithium concentration

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1. Introduction

Traditional oil and gas resources have gradually declined, with new energy sources, such as geothermal and hydrate sources, gradually replacing them. It is very important to study the development and utilization of new energy sources, such as geothermal energy [1–3]. Geothermal waters have both thermal energy and valuable elements, such as lithium, which is an indispensable strategic key metal that has been widely used in many new industrial fields, such as new energy, new materials, electronic information, and aerospace. Due to the vigorous development of new energy vehicles in recent years, the demand for lithium has also increased rapidly. Seeking more lithium mineral resources is an urgent goal for many countries around the world. In addition to lithium resources of the rock, salt lake, and ground brine types, lithium resources in geothermal waters have received extensive attention in recent years [4–6]. The lithium concentration in some geothermal waters can reach industrial grade and has good production prospects, such as that in some geothermal waters in Tibet (China) and Europe [4–6]. In addition to the resource properties of lithium, geothermal waters can have good therapeutic effects when the lithium concentration is over 1 mg/L. At the same time, lithium and its isotopes are also good tracers for water–rock interactions and have been widely used in groundwater-related studies [7,8]. Therefore, it is of great significance to study the enrichment mechanism of lithium in geothermal waters.

Thus far, the geothermal waters in China Xiong'an New Area have been extensively studied, including hydrogeological and geochemical characteristics, genesis, and geothermal resources [9–16]. However, research on the enrichment mechanism of lithium in the geothermal waters in the study area is very rare, and only the lithium concentrations in the geothermal waters have been reported [17,18]. Lithium is the 30th most abundant element in the upper continental crust, and its abundance varies depending on the lithology. The average concentration of shale and granite is 5–10 times that of carbonate [7]. Normally, the lithium element concentration in the groundwater of carbonate aquifers is relatively low. However, the lithium concentration in the geothermal waters of the Wumishan Formation carbonate reservoir in Xiong'an New Area is higher than that in some granite reservoir areas in China, mostly above 1 mg/L, reaching the level for therapeutic water. For example, the concentration in the geothermal waters in some geothermal fields in Zhangzhou ranges from 0.02 to 0.17 mg/L [19], while the lithium concentration in the geothermal waters in Fengshun, Guangdong, ranges from 0.19 to 0.79 mg/L [20]. It is still unknown which factors are the main reasons for this. Therefore, studying the enrichment mechanism of lithium in geothermal waters plays an important role in the comprehensive utilization of geothermal waters and further enriches the theory on the formation mechanism of geothermal waters in Xiong'an New Area. Moreover, the research results could be used to reveal the origin and evolution of geothermal resources in similar areas.

This article selected the analysis and test data of 32 geothermal water samples from the Wumishan Formation carbonate rock reservoir in Xiong'an New Area obtained in recent years and combined them with hydrochemical analysis and test data of geothermal waters in other regions of China to explore the enrichment mechanism of lithium in the geothermal waters in the study area.

2. Geological Background

The study area is located in the central part of the China Heibei Province Jizhong Depression, with the Bohai Sea to the east and the Taihang Mountains to the west, at the intersection of Level IV structural units such as the Langgu Depression, Niutuozhen Uplift, Baoding Depression, and Gaoyang Low Uplift [21]. Xiongxian County in the east is mainly located on the Niutuo Town Uplift; Rongcheng County in the west is mainly located on the Rongcheng Uplift in the Langgu Depression; Anxin County in the south is located in the northern part of the Gaoyang Low Uplift. The main faults developed in the area are the Rongcheng Fault, Xushui Fault, Niunan Fault, Niudong Fault, and Gaoyang Fault [22] (Figure 1). These faults control the structural pattern of the region and provide migration pathways for geothermal waters [23], which is of great significance for the formation of the deep geothermal system in Xiong'an New Area.

There are two types of thermal reservoirs in the study area: Neogene pore-type thermal reservoirs and bedrock fracture-type thermal reservoirs. Pore-type thermal reservoirs include sandstone thermal reservoirs in the Minghuazhen Formation and Guantao Formation, which are widely distributed in the area. Meanwhile, fractured Jixian carbonate rock thermal reservoirs are distributed in the Niutuozhen Uplift, Rongcheng Uplift, and Gaoyang Low Uplift, with a continuous northeastern distribution The lithology mainly consists of dolomite, flint-banded dolomite, muddy dolomite, etc., with developed karst fractures and good connectivity. The minimum thickness is 570 m, and the maximum thickness is over 2000 m, as indicated by drilling investigations. The water inflow is generally between 40 and 140 m^3/h, with a unit inflow of 1.5–5.1 $m^3/h \cdot m$ and a maximum of 11.3 $m^3/h \cdot m$ [14].

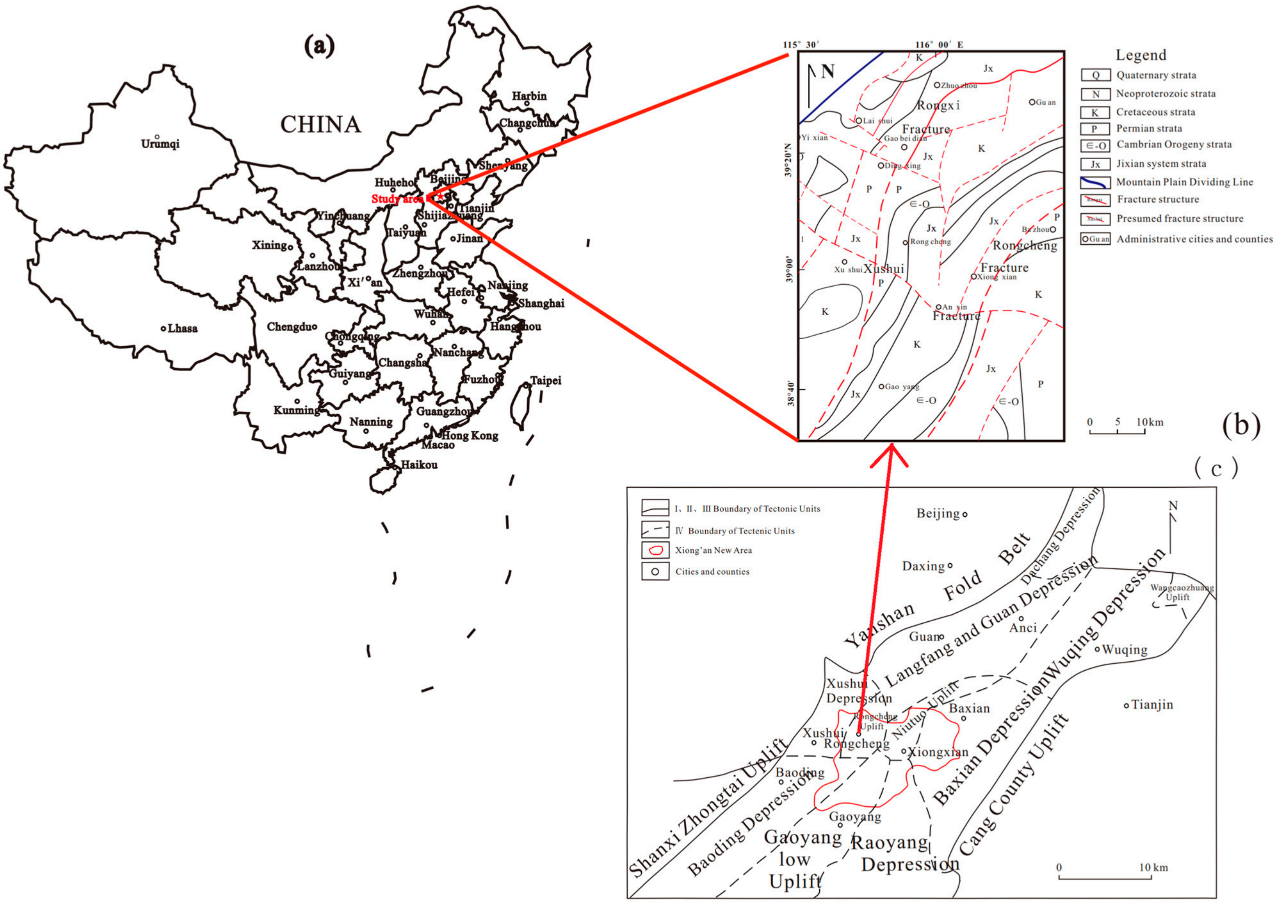

Figure 1. Geological map of the study area: (**a**) shows a map of China; (**b**) shows the regional structure; (**c**) shows the stratigraphic distribution in the study area. ((**b**,**c**) are modified from [17]).

3. Materials and Methods

Field investigation and sampling were conducted from 2013 to 2019. All of the samples in China Xiong'an New Area (XA) were stored in 550 mL polyethylene bottles that had been rinsed with the sampled spring water three times before sampling and sent to the testing laboratory immediately, and acidified to pH < 2 using 6 mol/L of purified HNO_3. All of the water samples were filtered through 0.45 μm pore size cellulose–acetate membranes in situ. The temperature and pH values were measured using the hand-held meters in situ after calibration. Chemical analyses of the elements listed in Table 1 were conducted at the laboratory of the Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences (Shijiazhuang, China) using the following methods: Na, K, and Mg were analyzed using a Dionex ICS-1100 ion chromatograph (Thermo Fisher Scientific Inc., Waltham, MA, USA) according to standard test methods for domestic drinking water (China—GB/T 5750.6-2006); Cl and SO_4 were analyzed by Inductively Coupled Plasma Emission Spectrometer-6800 (ICP-6800) (Macy (China) Instruments Inc., Shanghai, China) according to groundwater quality inspection methods (China—DZ/T 0064.51-1993); Ca and HCO_3 were analyzed by titration (China—DZ/T 0064.9-1993); lithium was analyzed by ICP-6800 (China—DZ/T 0064.80-1993). The analytical reproducibility for trace elements was less than 5%, and the charge balance was less than 5%. The test results of the geothermal waters from the Xinzhou geothermal system (XZ) in Guangzhou and the Fengshun geothermal system (FS) in Guangzhou came from [20]. The test results of the thermal spring (TS) and thermal well (TW) geothermal waters in the Zhangzhou geothermal system in Fujian came from [21].

Table 1. Hydrogeochemical data of the geothermal waters from the study area (mg/L).

ID	T (°C)	pH	K	Na	Ca	Mg	Cl	SO_4	HCO_3	Li	SiO_2
XA1	60.5	7.25	51.68	784.1	58.75	28.62	1065	16.21	674.8	1.417	35.14
XA2	50	7.08	23.5	393.1	40.02	18.73	479.3	19.08	442.7	0.631	31.224
XA3	52	6.92	43.46	777.3	49.29	26.15	1078	1.49	651.8	1.386	32.234
XA4	52	6.96	40.71	801.3	48.39	24.77	1077	5.74	645.1	1.274	51.62
XA5	57	7.06	48.74	759.8	48.67	26.88	1068	5.14	646.7	1.342	53.02
XA6	51	6.99	37.08	655.4	51.29	25.54	852.6	7.71	598	1.123	41.13
XA7	53.1	6.61	42.95	839.5	176.9	85.43	1450	42.95	699.8	1.354	45.66
XA8	52	7.11	40.46	548.7	58.41	29.01	749.3	12.33	628.1	0.998	28.86
XA9	57	7.15	59.69	913.4	66.59	32.91	1169	4.74	777.7	1.384	35.07
XA10	56.5	6.88	51.77	823.6	52.56	28.48	1103	3.63	682	1.368	36.95
XA11	55.5	6.83	46.33	819.8	46.16	26.12	1078	24.13	646.4	1.351	37.07
XA12	55.1	6.78	51.78	831.5	58.06	28.71	1092	9.15	676.6	1.436	37.15
XA13	55	7.14	51.06	830.8	68.75	34.92	1138	5.88	774.4	1.49	29.57
XA14	51.5	7.6	39.86	639.7	56.29	28.97	877.5	6.76	646.1	1.046	27.41
XA15	56	6.76	44.52	795.5	43.85	25.39	1064	2.3	640.3	1.387	33.98
XA16	59	7.06	50.99	815.7	61.33	30.15	1105	1.37	704.5	1.446	43.58
XA17	59	7.43	47.38	796.2	54.45	25.98	1071	4.01	676.6	1.382	35.67
XA18	123.4	8.48	63.99	920.6	17.01	4.3	1271	5.41	448.7	1.75	150.31
XA19	85	7.69	51.53	849.6	52.09	17.67	1185	2.81	647.5	1.572	60.25
XA20	83.2	7.21	50.5	842.4	52.49	18.63	1185	2.12	653.8	1.56	58.15
XA21	88	7.84	50.62	852.9	37.65	16.08	1185	2.64	610.2	1.605	60.15
XA22	82	8.44	51.98	856.6	48.07	16.91	1185	2.69	567.8	1.635	57.95
XA23	83	7.3	54.8	914.3	48.1	23.3	1375.6	3.9	505.2	1.235	63.68
XA24	85	7.04	43.9	862.7	47.3	22.8	1290.5	6.3	507.7	1.455	60.08
XA25	72	7.36	48.7	875	35.9	34.1	1236	4.8	491.8	1.47	52.69
XA26	74.5	8.01	48.2	900.9	68.8	31	1127.3	15.6	727.3	2.05	47.23
XA27	50	7.33	50.5	844.5	62.95	38.75	1095.4	14.05	702.43	1.32	35.92
XA28	52	8.87	41.14	800.3	62	31.52	1033	23.96	618.8	1.211	41
XA29	52	7.31	43.37	819	64.31	30.58	1103	0.96	708.3	1.228	20.86
XA30	50	7.11	41.17	766.3	64.3	31.68	1008	5.4	686.5	1.312	42.2
XA31	109.2	7.94	47.83	769.2	35.5	9.1	1041	12.77	540.7	1.325	107.38
XA32	56	7.3	41.6	788.8	57.01	27.78	1094	2	688.3	1.157	37.2

4. Results

Hydrochemical Characteristics

All of the geothermal water temperatures were above 40 °C, indicating medium–high-temperature water. The temperatures of the geothermal waters in the study area were mostly between 50 and 88 °C, and the temperatures of XA18 and XA31 (XA-Xiong'an New Aera) were very high, reaching 123.4 and 109.2 °C, respectively, with an average of 64.92 °C. The temperatures of the XZ (Xin Zhou geothermal system in Guangdong province) geothermal waters ranged from 72.4 to 94.8 °C, with an average of 83.93 °C. The temperatures of the FS (Fengshun geothermal system in Guangzhou) geothermal waters ranged from 46.6 to 92.4 °C, with an average of 75.98 °C. The temperatures of the TS (thermal springs in the Zhangzhou geothermal system in Fujian) geothermal waters were between 45 and 60.2 °C, with an average of 50.76 °C. The temperatures of the TW (thermal wells in the Zhangzhou geothermal system in Fujian) geothermal waters ranged from 42.1 to 65 °C, with an average of 53.07 °C.

All of the geothermal waters were neutral–alkaline. The pH values of the geothermal waters in the study area ranged from 6.61 to 8.87, with an average of 7.34. The pH values of the XZ geothermal waters ranged from 7.91 to 8.54, with an average of 8.18. The pH values of the FS geothermal waters were between 7.24 and 9.09, with an average of 8.47. The pH values of the TS geothermal waters were between 7.7 and 8.9, with an average of 8.56. The pH values of the TW geothermal waters ranged from 8.4 to 9.17, with an average of 8.71.

The main hydrochemical type of geothermal water in the study area was HCO3·Cl-Na/Cl-Na type (Figure 2). The HCO_3 concentrations ranged from 442.7 to 777.7 mg/L, with an average of 634.89 mg/L. The Cl concentrations ranged from 479.3 to 1375.6 mg/L, with an average of 1091.61 mg/L. The Na concentrations ranged from 393.1 to 920.6 mg/L, with an average of 796.52 mg/L (Table 1). The main hydrochemical type of XZ geothermal water was the Cl-Na type. The Cl concentrations ranged from 1725.23 to 2268.2 mg/L, with an average of 2026.6 mg/L. The Na concentrations ranged from 849.2 to 1033 mg/L, with an average of 951.52 mg/L. The main hydrochemical type of FS was HCO_3-Na or Cl·HCO_3-Na/HCO_3·Cl-Na. The highest Cl concentration was 198.92 mg/L or 193.7 mg/L, with the rest ranging from 9.13 to 21.39 mg/L. The HCO_3 concentrations ranged from 131.02 to 468.98 mg/L, with an average of 232.97 mg/L. The Na concentrations ranged from 76.15 to 216.7 mg/L, with an average of 123.61 mg/L. The main hydrochemical type of TS geothermal water was SO_4·HCO_3-Na/HCO_3·SO_4-Na, with the highest SO_4 concentration of 106.2 mg/L and the rest ranging from 35.9 to 55.61 mg/L. The HCO_3 concentrations ranged from 48.91 to 229.3 mg/L, with an average of 111.9 mg/L. The Na concentrations ranged from 68.62 to 116.4 mg/L, with an average of 89.34 mg/L. The main hydrochemical types of TW geothermal water were similar to those of TS, with SO_4 concentrations ranging from 36.44 to 135.9 mg/L, with an average of 71.04 mg/L, and HCO_3 concentrations ranging from 58.08 to 137.6 mg/L, with an average of 96.18 mg/L (Table 2). It can be seen that the Cl concentrations in the study area and XZ were significantly higher than in the other geothermal waters.

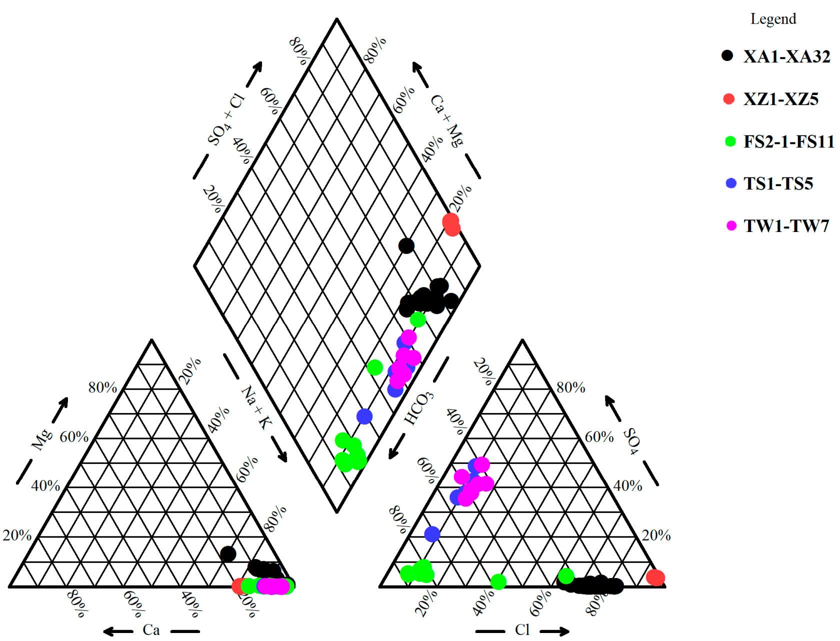

Figure 2. Piper diagram of the geothermal waters.

The lithium concentrations in the geothermal waters in the study area ranged from 0.631 to 2.05 mg/L, with an average value of 1.388 mg/L, mostly above 1 mg/L, which meets the standards of physiotherapy water and can be used for physical therapy and health care. The lithium concentrations in the XZ geothermal waters ranged from 2.81 to 3.6 mg/L, with an average of 3.192 mg/L. The lithium concentrations in the FS geothermal waters ranged from 0.19 to 0.79 mg/L, with an average of 0.346 mg/L. The lithium concentrations in the TS geothermal waters ranged from 0.02 to 0.17 mg/L, with an average of 0.076 mg/L. The lithium concentrations of the TW geothermal waters ranged from 0.04 to 0.017 mg/L, with an average of 0.084 mg/L. It can be seen that the lithium concentrations of the geothermal waters in the study area were significantly lower than those of the XZ geothermal waters, but significantly higher than the concentrations of the FS, TS, and TW geothermal waters (Figure 3).

Table 2. Hydrogeochemical data of the geothermal waters from granite reservoirs in southeast China.

ID	T (°C)	pH	K	Na	Ca	Mg	Cl	SO_4	HCO_3	Li	SiO_2
XZ1	85.8	7.91	73.08	899.5	190.3	1.17	1875.55	97.93	48.78	2.97	115.93
XZ2	/	8.54	87.47	1033	220.8	1.19	2268.2	112.1	34.96	3.6	128.36
XZ3	94.8	8.04	82.56	984.1	211.6	1.21	2082.57	105.25	49.8	3.27	122.36
XZ4	72.4	8.28	82.8	991.8	214	1.09	2154.43	107.61	42.87	3.31	121.07
XZ5	82.7	8.15	71.87	849.2	157.7	1.1	1752.23	96.07	60.35	2.81	121.82
FS2-1	52.5	7.24	16.24	216.7	37.16	0.27	193.7	13.08	468.98	0.79	93.71
FS2-2	66.3	7.88	7.59	159	16.74	0.12	198.92	18.58	175.33	0.37	75.02
FS3	85.8	8.33	5.55	90.19	5.92	0.08	9.13	9.38	190.26	0.26	87.47
FS4	74.3	8.29	6.04	88.75	7.37	0.18	9.58	8.6	190.97	0.27	83.70
FS5	88.2	8.66	5.89	76.15	5.63	0.12	10.85	10.14	131.02	0.19	80.53
FS6	71.2	8.38	6.57	87.38	10.9	0.26	15.88	9.61	196.52	0.22	90.09
FS7	46.6	8.66	6.81	114.4	4.64	0.04	21.39	10.02	213.13	0.24	76.31
FS8	89.6	8.96	9.42	132.8	3.41	0.02	18.78	16.45	245.68	0.38	92.91
FS9	87.5	8.76	9.76	128	4.83	0.16	20.53	15.6	266.22	0.36	89.44
FS10	92.4	8.96	9.52	131.9	3.43	0.02	18.96	15.89	246.99	0.39	93.51
FS11	81.4	9.09	9.57	134.4	3.36	0.02	18.99	15.92	237.54	0.339	94.26
TS1	53	8.82	1.35	70.69	2.84	0.04	7	36.42	70.31	0.06	67.26
TS2	45.5	8.9	1.11	68.62	2.97	0.05	7	35.9	48.91	0.06	68.82
TS3	45	8.79	1.64	81.8	6.14	0.0065	12.25	55.61	94.77	0.07	60.59
TS4	50.1	7.7	3.6	116.4	10.85	0.22	14.71	53.89	229.3	0.17	81.92
TS5	60.2	8.57	2.55	109.2	11.17	0.19	15.06	106.2	116.2	0.02	69.23
TW1	42.1	8.85	1.26	69.98	2.87	0.03	8.75	36.44	58.08	0.06	69.18
TW2	48.4	8.8	1.31	71.71	3.46	0.05	10.5	40.85	67.25	0.05	57.81
TW3	55.8	8.4	2.51	127	12.46	0.14	22.76	135.9	137.6	0.17	65.20
TW4	50.2	8.67	2.55	98.27	6.88	0.05	9.1	83.36	116.8	0.08	76.10
TW5	50	9.17	1.38	86.36	3.48	0.0065	15.41	52.69	67.25	0.07	62.29
TW6	65	8.45	2.08	116.2	9.25	0.07	24.51	100.4	137.6	0.12	57.16
TW7	60	8.6	1.11	74.91	3.6	0.07	12.25	47.63	88.65	0.04	46.92

Note: XZ—Xinzhou geothermal system in Guangzhou; FS—Fengshun geothermal system in Guangzhou [20]; TS and TW—thermal springs and thermal wells in the Zhangzhou geothermal system in Fujian, respectively [19]. Unit—mg/L.

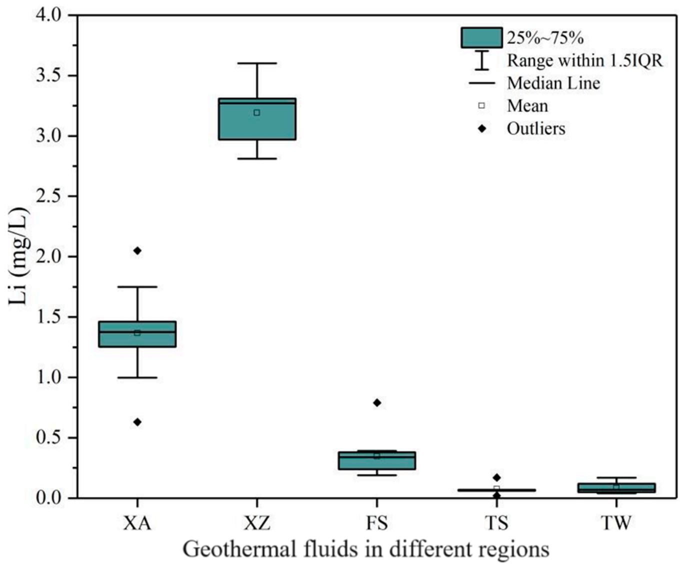

Figure 3. Lithium concentration plot of the geothermal waters.

5. Discussion

5.1. Factors Affecting the Lithium Concentration

5.1.1. Reservoir Lithology

The amount of lithium in granite is much higher than that in carbonate rock, and generally speaking, the lithium concentrations in carbonate rock aquifers are significantly lower than those in granite fissure aquifers. However, although the reservoir lithology of FS, TS, and TW geothermal systems are granite while the reservoir lithology of the study area is carbonate rocks, the lithium concentrations in the study area were much higher than those of FS, TS, and TW, with a 4.01, 18.26, and 16.52 times higher average concentration, respectively. Therefore, lithology is not the main factor controlling the lithium concentrations in the geothermal waters in the study area. The reservoir lithology of XZ is also granite, but its lithium concentrations were much higher than those of the study area, with a 2.3 times higher average content that those in the study area, which is due to other factors.

5.1.2. Temperature

Temperature is an important parameter that affects the thermodynamic properties of elements and their compounds, and can promote the dissolution of elements in host rocks, thereby increasing the concentrations of elements in geothermal waters. Therefore, it could have a significant impact on the lithium concentrations in the study area. Temperature can be divided into geothermal water temperature and reservoir temperature. As per the plot of lithium concentrations in geothermal waters vs. geothermal water temperatures (Figure 4), the lithium concentrations in the geothermal waters in the study area were positively correlated with the water temperature. As the temperature increased, the lithium concentrations in the geothermal waters gradually increased, and the magnitude of the change became smaller with increasing water temperatures. The lithium concentrations in the XZ, FS, TS, and TW geothermal waters did not correlate well with water temperature. However, for these geothermal waters, which all occur in granite, the lithium concentrations of geothermal water with a high water temperature were generally higher than those of geothermal water with a low water temperature. Both of these phenomena indicate that water temperature is one of the important factors controlling the lithium concentrations in geothermal waters.

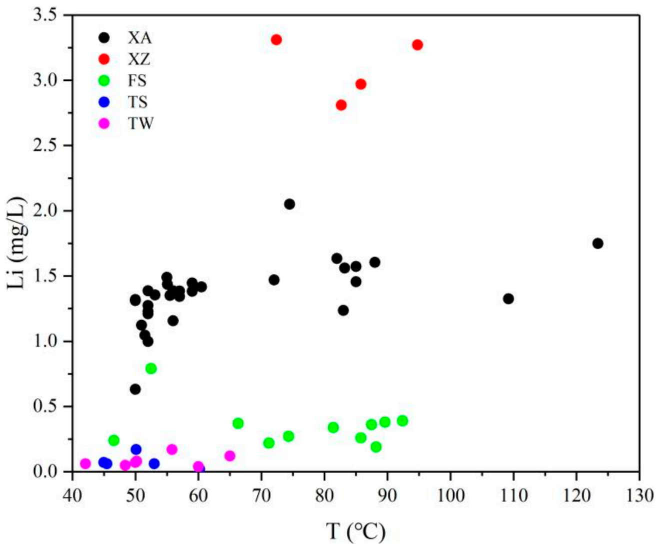

Figure 4. Plot of the lithium concentrations vs. temperature.

At present, there are various geothermometers available for estimating the temperature of reservoirs. Overall, quartz geothermometers are suitable for medium–high-temperature geothermal systems, while Na-K geothermometers are suitable for high-temperature geothermal systems, and K-Mg geothermometers are suitable for medium–low-temperature geothermal systems [6,24]. Due to the presence of high- and moderate–low-temperature geothermal systems in this study, quartz, Na-K, and K-Mg temperature scales were selected for analysis in this paper.

As per the plot of lithium concentrations in geothermal water vs. reservoir temperature calculated by quartz, Na-K, and K-Mg geothermometers (Figure 5), only the K-Mg geothermometer indicated a good positive correlation with the lithium concentrations in the geothermal waters in the study area, while there were no obvious correlations between the lithium concentrations in geothermal waters from other geothermal systems and reservoir temperatures. The reservoir temperature of the geothermal system in the study area was generally less than 150 °C, belonging to a medium–low-temperature geothermal system. The estimated reservoir temperature of XA18 using a K-Mg geothermometer (126.99 °C) was very close to its logged temperature (123.4 °C), while the estimated reservoir temperature of XA18 using other geothermometers was quite different from the actual logged temperature. Therefore, the reservoir temperature is an important factor in controlling the lithium concentrations in the geothermal waters in the study area. Although there were no significant correlations between the lithium concentrations in geothermal waters from other geothermal systems and the reservoir temperature, if they were all considered geothermal waters in a granite reservoir, the lithium concentrations of geothermal waters with a higher reservoir temperature were generally relatively high. For example, the geothermal waters from FS, which had a higher reservoir temperature, had relatively higher lithium concentrations. However, although the reservoir temperature of XZ was the highest, its lithium concentrations were much higher than those in some FS geothermal waters with a similar reservoir temperature. Therefore, this phenomenon is due to other factors.

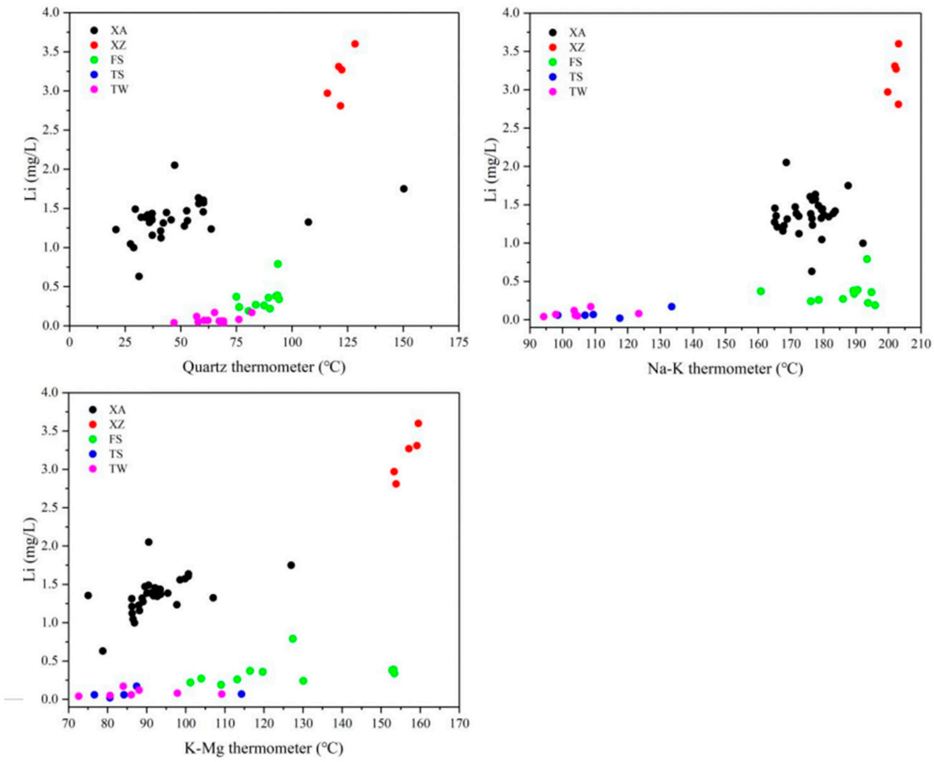

Figure 5. Plot of the lithium concentrations vs. reservoir temperature.

5.1.3. pH

A low pH can enhance the leaching of host rocks, thereby increasing the concentrations of elements in the waters [25]. By establishing a relationship plot between the pH and lithium concentrations in geothermal waters (Figure 6), no good correlations were found between the pH and lithium concentrations in the geothermal waters of different geothermal systems, indicating that pH is not the main factor affecting the lithium concentrations in geothermal waters.

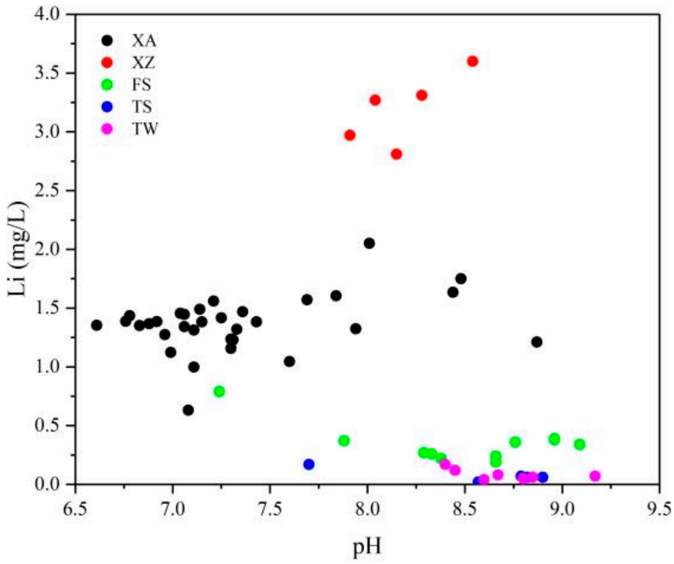

Figure 6. Plot of the lithium concentrations vs. pH.

5.1.4. Water–Rock Interaction

Water–rock interaction is an important factor affecting the element concentrations in waters. In the logarithmic relationship plot of Cl and Li (Figure 7), both the water samples in the study area and the granite water samples were distributed below the ratio line of carbonate and granite rocks, indicating preferential leaching of Cl from the host rocks into the water or other sources of Cl or adsorption of lithium by minerals. Lithium can be adsorbed by quartz, and its concentrations in waters also decreases as quartz precipitates [26]. As per the relationship diagram between the lithium and quartz saturation index (SI) (Figure 7), there was no correlation between the lithium concentrations in granite water and quartz SI, indicating that lithium in granite geothermal waters is less affected by quartz adsorption and precipitation. However, there was a certain negative correlation between the lithium concentrations in the geothermal water from the study area and quartz SI, with the quartz of most of the geothermal waters having reached saturation. This indicates that the lithium concentrations in the geothermal waters in the study area are influenced by quartz adsorption and precipitation. However, as per the logarithmic relationship plot of Cl and lithium, the water samples of the geothermal waters in the study area gradually approached the rock ratio line, indicating that there are other factors affecting the lithium and Cl concentrations in the geothermal waters of the study area. As per the logarithmic relationship diagram between lithium and K (Figure 7), the water samples were distributed below the rock ratio line, and most of the granite water samples gradually deviated from the granite rock ratio line. This indicates that in addition to surrounding rock leaching, displacement reactions occur between lithium and K, resulting in gradually higher concentrations of K compared to lithium [27]. Although the lithium concentrations of the geothermal waters in the study area are affected by quartz, the water samples did not deviate significantly from the rock ratio line, indicating that there are other factors affecting the lithium concentrations of the geothermal waters in the study area. Meanwhile, although the lithium concentrations in XZ geothermal waters are affected by a substitution reaction with K, in the logarithmic relationship between lithium and Cl, the XZ water samples did not gradually deviate from the rock ratio line, indicating that its Li concentrations are influenced by other factors.

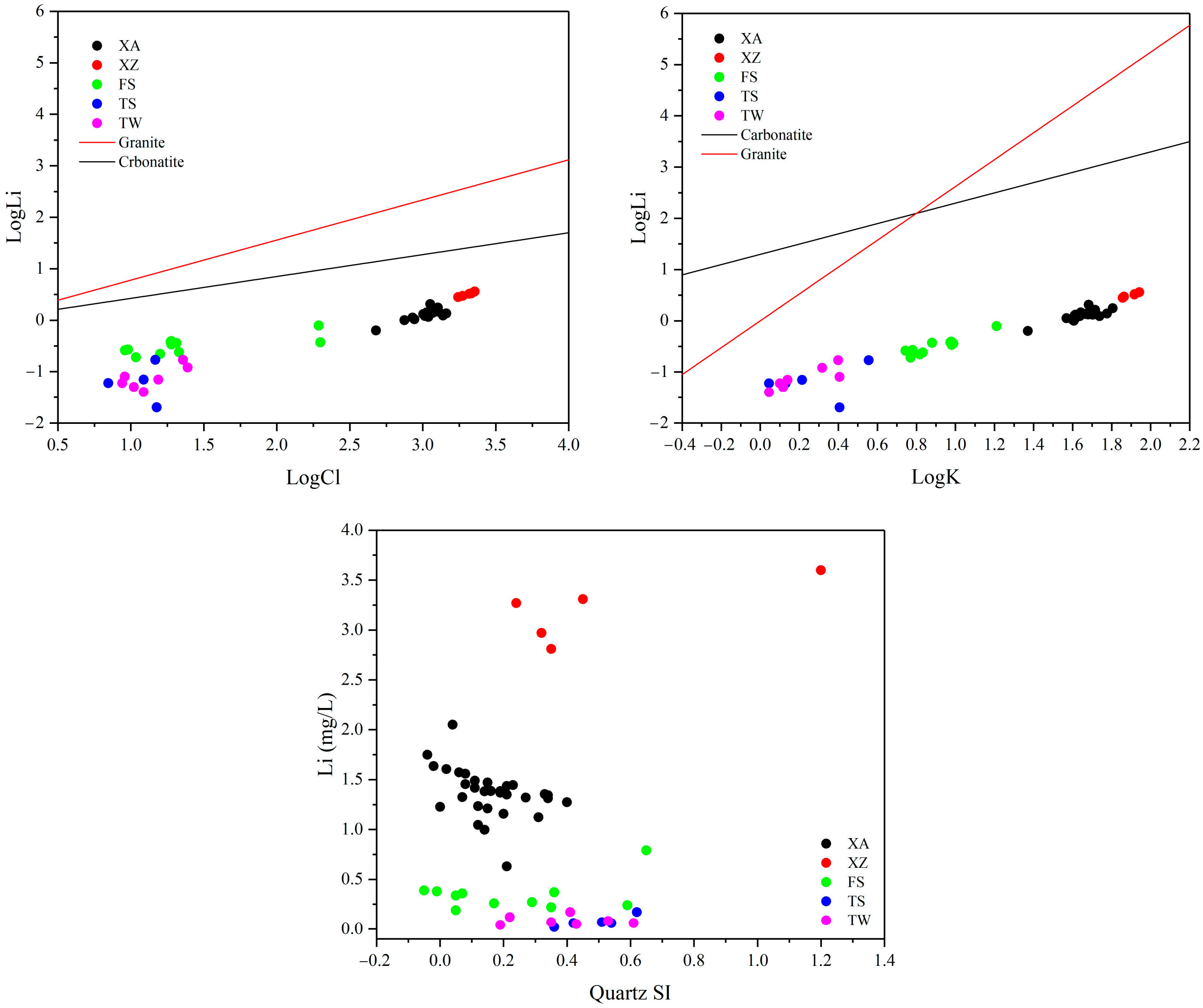

Figure 7. Logarithmic plot of the lithium concentrations vs. Cl, K, and quartz SI.

Research has shown that the mixing of seawater intrusion or sealed paleo-seawater can increase the lithium concentrations in geothermal waters, as was the case for XZ [20], so its lithium concentrations were significantly higher than those of other granite geothermal waters. Combined with the geological background of Xiong'an, its lithium concentrations are also likely to be influenced by paleo-seawater.

5.2. Evidence of the Influence of Paleo-Seawater on Li Concentrations

5.2.1. rNa/rCl

The rNa/rCl ratio is an effective indicator of whether groundwater is affected by seawater or flows through an evaporite (gypsum) [22]. Regarding the relationship between the lithium content and rNa/rCl ratio (Figure 8), the lithium concentrations of geothermal waters with a high rNa/rCl ratio were significantly lower than those of geothermal waters with a low rNa/rCl ratio. The rNa/rCl ratio of XA geothermal waters was between 0.989 and 1.27, which is close to 1, while the rNa/rCl ratio of XZ geothermal waters was between 0.7 and 0.75, which is close to the rNa/rCl ratio of average seawater—0.85. However, the rNa/rCl ratios of other granite geothermal waters were significantly greater than 0.85 and 1. This indicates that the lithium concentrations of XA are affected by paleo-seawater and the evaporite formed by it, the lithium concentrations of XZ are affected by seawater intrusion, and the lithium concentrations of other geothermal waters mainly originate from the leaching of granite.

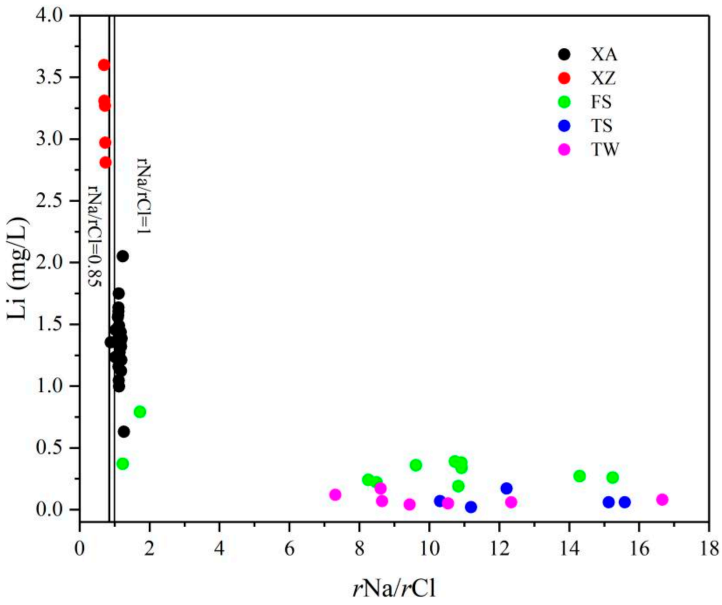

Figure 8. Plot of the lithium concentrations vs. rNa/rCl.

5.2.2. Cl/Br

The Cl/Br ratio is an important indicator of whether groundwater is affected by seawater [15]. As per the relationship diagram between the Cl concentrations and Cl/Br ratio (Figure 9), the geothermal waters in the study area were mostly distributed above the Cl/Br line (298) in seawater, with only one close to 298. Meanwhile, according to [15], the Cl/Br ratio of geothermal waters in the Xiong'an is close to 298, indicating that the geothermal waters in the study area are influenced by paleo-seawater.

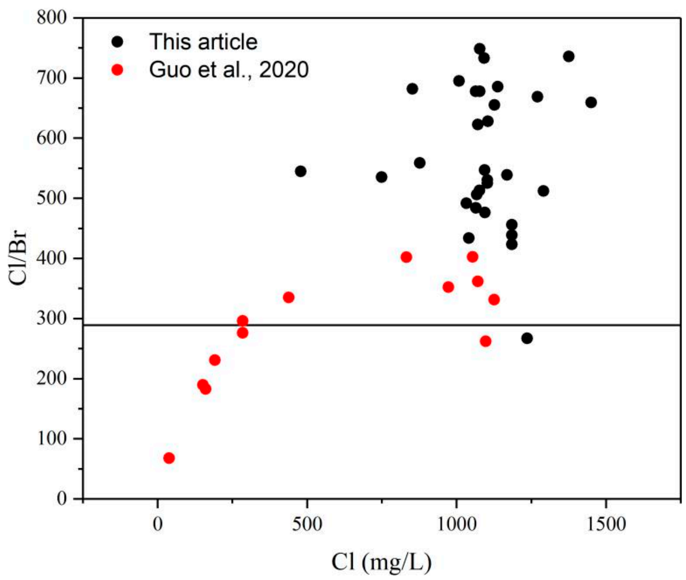

Figure 9. Plot of Cl/Br vs. Cl concentrations (the data of red filled circles are from [15]).

5.2.3. Cl Concentrations

The Cl concentrations of the XA and XZ geothermal waters were much higher than those of the other geothermal waters, with higher Cl concentrations than geothermal waters recharged by magmatic fluids [25]. These two geothermal systems do not have magma heat sources, meaning that there is no magma water providing a large amount of Cl, and the leaching of surrounding rocks cannot provide so much Cl. Therefore, based on the appeal analysis, their Cl concentrations are only affected by paleo-seawater/seawater intrusion. There was a positive correlation between Cl and Li (Figure 10), indicating that they have a common source. Therefore, paleo-seawater is an important factor affecting the lithium concentrations in the geothermal waters from the study area.

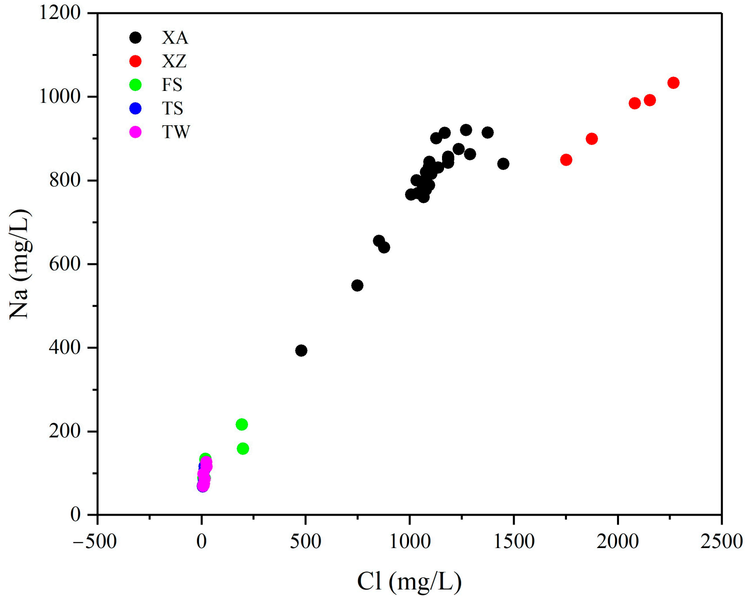

Figure 10. Plot of the lithium concentrations vs. Cl concentrations.

5.3. Enrichment Mechanism of Lithium

The study area is recharged by atmospheric precipitation and infiltrates underground [17]. During the underground runoff process, lithium leaches from the surrounding rocks and enters the groundwater. At the same time, it is heated by the terrestrial heat flow to form geothermal waters. With an increase in temperature (both reservoir and water temperature), leaching of the host rock increases, and more lithium enters the geothermal waters, but the lithium concentrations still do not reach the standard of medical water (1 mg/L). After encountering paleo-seawater left over from historic geological periods with higher lithium concentrations and leaching of the evaporated rock formations formed by paleo-seawater, the lithium concentrations in geothermal waters are significantly enriched and reach over 1 mg/L.

6. Conclusions

(1) The main hydrochemical type of geothermal waters in the study area is the HCO3·Cl-Na/Cl-Na type, while XZ has Cl-Na-type geothermal waters, FS has HCO_3-Na- or Cl·HCO_3-Na/HCO_3·Cl-Na-type geothermal waters, TS has SO_4·HCO_3-Na/HCO_3·SO_4-Na,-type geothermal waters, and TW has similar geothermal waters to TS. The Cl concentrations in the study area and XZ are significantly higher than those of the other geothermal waters.

(2) The lithium concentrations of the geothermal waters in the study area are significantly lower than those of XZ geothermal waters, but significantly higher than those of FS, TS, and TW geothermal waters.

(3) Lithology, pH, and the interaction between geothermal waters and carbonate are not the main factors controlling the lithium concentrations in the geothermal waters in the study area. Meanwhile, the mixing of paleo-seawater and the leaching of the evaporated rocks formed by it significantly increase the lithium concentrations in the study area. Temperature is also an important factor affecting lithium concentrations, which can promote the leaching of lithium from host rocks.

(4) The research results not only clarify the origin and enrichment mechanism of lithium in the geothermal waters in the study area, but also provide research methods for the study of lithium in geothermal waters. They can also enrich the knowledge of the origin and evolution of the geological background of the geothermal resources in the study area and similar areas, which is very important for the exploration and utilization of geothermal resources.

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