

Stable isotope fractionation of chlorine during evaporation of brine from a saline lake

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Brine from the saline Qarhan Lake was evaporated at $28\pm 2^\circ\text{C}$ in a clean environment. Two groups of experiments were conducted; one with complete separation of precipitate and brine at different stages of evaporation, and the other with continuous precipitation during the evaporation. Seventy-nine precipitate and brine samples were collected during the experiments, and the $\delta^{37}\text{Cl}$ values were determined using an improved thermal ionization mass spectrometry procedure for precise measurement of chlorine isotopes based on Cs_2Cl^+ ions. Based on the concentrations of Na^+ , K^+ , and Mg^{2+} , evaporation was divided into three main precipitation stages as follows: halite dominant, carnallite dominant, and bischofite dominant. The $\delta^{37}\text{Cl}_{\text{solid}}$ and $\delta^{37}\text{Cl}_{\text{liquid}}$ values of the precipitate and coexisting brine samples at different stages showed the following characteristics. The precipitates were enriched with ^{37}Cl relative to the coexisting brine samples, and the $\delta^{37}\text{Cl}$ of both the precipitate and brine samples decreased gradually during evaporation. The fractionation factors (α_{b}) between halite and brine were the highest, followed by that (α_{c}) between carnallite and brine, and then that (α_{b}) between bischofite and brine. The α_{c} and α_{b} values of less than one, which indicate the precipitate is enriched in ^{35}Cl , were found when the evaporation process entered a new stage. However, the $\delta^{37}\text{Cl}$ values of carnallite, bischofite, and the coexisting brine samples decreased during evaporation. The residual brine is a ^{35}Cl reservoir. The experimental phenomena were consistent with the $\delta^{37}\text{Cl}$ values in saline deposits in the literature. $\delta^{37}\text{Cl}$ can be used as an indicator of brine evaporation processes, which is important in the exploration of sylvinite deposits.

saline lake, brine, evaporation, chlorine stable isotope, fractionation

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Chlorine is involved in many geochemical processes. It has two stable isotopes in nature, ^{37}Cl and ^{35}Cl , which have average relative abundances of 75.78% and 24.22% [1], respectively. Since the 1980s, with the development of mass spectrometry techniques and the improvement of measurement precision, several studies have been conducted on the fractionation mechanisms of chlorine stable isotopes, analytical methods, and the applications in the geochemistry [2–8]. Richard et al. [9] summarized the published $\delta^{37}\text{Cl}$

values of various liquids, rocks, and minerals important for the interpretation of $\delta^{37}\text{Cl}$ values of Athabasca brines. The lowest $\delta^{37}\text{Cl}$ value was -4.69‰ [10] and the highest was 7‰ [11]. The $\delta^{37}\text{Cl}$ values in brine from saline lakes range from -2.05‰ to 1.01‰ [12]. Chlorine ions are abundant in saline lakes because of its high solubility in water. Chlorine, in electrovalent bonds with metals, forms several halogenides found in evaporites. However, ^{37}Cl and ^{35}Cl have the same valency and chemical properties, and the simple geochemical behavior of chlorine isotopes leads to limited fractionation with narrow variation. Therefore, high-precision

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measurement is necessary to avoid errors in reporting geological information.

Previous interpretations of the physicochemical type of chlorine isotopic fractionation during evaporation crystallization have varied. Eggenkamp et al. [13] thought it was by Rayleigh fractionation, which is a dynamic fractionation, but they ignored the equilibrium condition of the Rayleigh fractionation model in their experiments. Whereas, Tan et al. [14] thought it was by equilibrium fractionation. Dynamic fractionation is different from equilibrium fractionation in that isotope distribution between the two phases in the former is related to time and the evaporation process [15]. The evaporation process of brine is extremely short compared with the long geological time at which the isotopes equilibrate between the precipitates and coexisting brines. Therefore, it is a transient equilibrium. Crystallization occurs for a long time when the crystallized mineral is separated from the system, so the stable isotope compositions of the brine and precipitate continuously change. Therefore, the Rayleigh fractionation model is more appropriate to describe this process.

According to an evaporation experiment of modern seawater, chloride precipitates as halite, kainite, carnallite, and bischofite after the gypsum stage [16]. Eggenkamp et al. [13] carried out evaporation of solutions with a single mineral, and determined the fractionation factor, α , between the NaCl precipitate and the coexisting brine was greater than one. For the KCl and MgCl₂·6H₂O precipitates, α was less than one. These experiments indicated that KCl is the least likely to be enriched in ³⁷Cl. Combining the fractionation factors, evolution of the isotope fractionation of the evaporating brine and the precipitating salt was calculated using

the Rayleigh fractionation model by Eggenkamp et al. The $\delta^{37}\text{Cl}$ values of the precipitate decreased systematically during the main phase of halite crystallization, and then increased again at the bischofite stage of evaporation. However, chlorine stable isotope ratios in geological samples did not support these observations (Table 1). Sun et al. [17] studied the chlorine stable isotope ratios of ancient and modern salt minerals, and found there was a clear difference in the chlorine isotope fractionation among the different stages of evaporites. Generally, the order was halite > sylvite > carnallite according to their $\delta^{37}\text{Cl}$ values. The $\delta^{37}\text{Cl}$ values of the evaporites decreased as the Mg concentration increased, which is inconsistent with the results from the study of Eggenkamp et al. [13]. Negative thermal-ionization mass spectrometry [4] and positive thermal-ionization mass spectrometry [18] were used to measure the chlorine stable isotope ratios of brine and salt samples, respectively, from a series of artificial ponds in Qarhan Lake, China (Table 2). The samples in the two studies were collected from the same places but at different times. The fractionation factors between each precipitate and the coexisting brine were higher than one in most cases, the $\delta^{37}\text{Cl}$ values of the precipitates were higher than those of brines. Vengosh et al. [4] found that carnallite is more likely to be enriched in ³⁷Cl than other minerals, with the $\delta^{37}\text{Cl}$ value of the precipitate 24‰ higher than that of coexisting brine. However, it is not known if the $\delta^{37}\text{Cl}$ values increased during the bischofite stage, or if the fractionation factor during this stage was greater than one. Therefore, it is necessary to carry out an evaporation experiment of brine from a saline lake to study the isotope fractionation behavior of chlorine in the evaporation stages. These results could be used to

Table 1 Chlorine stable isotope ratios in sylvinitic deposits around the world

Zone	Sample	$\delta^{37}\text{Cl} \pm \text{SD} \text{‰}^{\text{a}}$
Qarhan Salt Lake, China	salt (0.7–0.8 m depth)	-0.44±0.13
	modern carnallite	-1.38±0.19
Mengye Yunnan, China	white salt	-0.38±0.13
	sage green sylvinitic	-0.69±0.19
	caesious sylvinitic	-0.88±0.13
Navarra Basin, Spain	pink sylvinitic	-0.88±0.50
	red sylvinitic	-2.41±0.34
	carmine sylvinitic	-0.75±0.09
Catalonia Basin, Spain	salt (lower zone)	1.00±0.16
	white salt	0.47±0.25
	pink salt	0.60±0.19
	red sylvinitic	-0.41±0.13
	carnallite	-1.22±0.19
Sitaluobin, Belarus	salt (S-84)	-0.06±0.09
	sylvinitic (S-83)	-1.44±0.53
	sylvinitic (S-80)	-2.22±0.13
	carnallite (S-79)	-2.60±0.53
Mahai Salt Lake, China	salt	-0.41±0.09 ^b
	early sylvinitic deposit	-1.10±0.09 ^b
	early carnallite deposit	-2.07±0.06 ^b

a) Standard deviations (SD) were calculated from the raw data in [17]. b) These values were also calculated from the raw data in [17] but are different to the values in the reference.

Table 2 Chlorine stable isotope ratios in brine and salt samples from a series of artificial ponds in the saline Qarhan Lake (China) reported by Xiao et al. [18] and Vengosh et al. [4]

Sample location and description	pH [18]	Temperature of brine (°C) [18]	$\delta^{37}\text{Cl}$ (‰)		$\alpha_{\text{solid/liquid}}$	
			[18]	[4]	[18]	[4]
Inlet brine to the artificial ponds	6.7	13.0	-0.03	-3.5		
Brine of first artificial pond	6.3	17.6	-1.00		1.0021	
Halite in first artificial pond			-1.10	2.7		
Brine of second pond	6.2	15.5	-0.82	-7.2	1.0080	1.0109
Halite in second pond			-0.03	3.6		
Brine of third pond	5.7	18.2	-1.79	-2.0	1.0022	0.9971
Sylvite+carnallite in third pond			0.37	-4.9		
Brine of fourth pond	5.6	25.2	-1.35	-0.6	1.0014	1.0253
Carnallite in fourth pond			0.06	24.7		
Brine of fifth pond	5.1	20.8	-1.28	9.1	1.0010	
Bischofite in fifth pond			-0.28			

evaluate the use of $\delta^{37}\text{Cl}$ as a valid index to identify sylvinite deposits.

The objectives of the present study were: (1) to measure the chlorine stable isotope ratios of precipitate and brine samples during evaporation; (2) to check whether significant changes occurred through the consecutive stages of evaporation, especially in the carnallite and bischofite precipitation stages; (3) to clarify the isotopic relationship between the brine and precipitate in the different stages; and (4) to test the possibility of using the chlorine stable isotope ratios of evaporites in the geological record as an indicator of the degree of evaporation.

1 Materials and methods

1.1 Reagents and equipment

The secondary isotopic reference material NaCl (ISL 354 NaCl) [19] was used as the isotope standard for chlorine. High-purity water was obtained using double sub-boiling distillation with double normal boiling of fresh water.

A VG 354 single magnetic sector (90°, 27 cm radius) (made in VG Isotopes Limited, Winsford, Cheshire, UK) thermal ionization mass spectrometer controlled by a Legend LX-386/33S dedicated computer was used. The experiments were performed using a Suzhou Antai VD-650 desktop clean bench (Suzhou, China) with vertical laminar flow supply cleanliness of class 100 (Fed 209E). A Zhenghong DBF anti-corrosion electric hot plate (Binhai, China) with cast aluminum Teflon coating and a temperature accuracy of $\pm 1^\circ\text{C}$ was used to accommodate multiple samples simultaneously without cross-contamination.

1.2 Evaporation experiment

Brine used for the evaporation experiments was collected on May 14, 2010 from Qarhan Lake (China). This brine contains mainly chloride (Table 3) and is simpler than other brines in the salt lakes of Qaidam Basin (China). Carnallite was produced by natural evaporation. The chemical compositions of the brines and precipitates during the evaporation varied regularly, with the Na^+ content gradually decreasing, the Mg^{2+} content increasing, and the K^+ content alternating from low to high, then from high to low. The initial precipitate was mainly halite with a small amount of carnallite, this then changed to a precipitate containing mainly carnallite, and finally to a precipitate that was primarily composed of bischofite.

The following evaporation experiments were carried out in the Suzhou Antai VD-650 desktop clean bench. The first experiments involved complete separation of the precipitates and brines at different stages of evaporation (CSE). In these experiments, a 2 L beaker with scale was filled with 2000 mL of brine. The beaker was placed on the DBF anti-corrosion electric hot plate with Teflon coating. The brine was slowly evaporated at $28\pm 2^\circ\text{C}$. A watch glass was placed at the bottom of the beaker, and removed as soon as a sufficient quantity of solid had precipitated on it. A small liquid (2 mL) sample was collected, and the scale of the beaker was recorded to calculate the degree of evaporation (DE). The pH and density of the solution were measured, and then a new watch glass was placed at the bottom of the beaker. The precipitate on the watch glass was collected and filtered from the solution. The precipitate was rinsed with acetone to remove any remaining solution. X-ray diffraction (XRD) analyses were conducted on the precipitate to

Table 3 Chemical composition of Qarhan brine (g/L)

Na^+	Li^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-	B_2O_3	SO_4^{2-}	NO_3^-	Total salt content
15.6	0.242	15.7	73.0	0.452	247	1.21	0.657	5.98	0.0437	360

determine the type of mineral. As soon as a new type of mineral precipitated, which indicated that the brine was in a new evaporation stage, all the precipitates were filtered, and the residual brine was evaporated until the volume left in the beaker was not sufficient to continue the experiment. Thirty-nine precipitate and brine samples were collected during these experiments. The samples were sealed in 4 mL polyethylene tubes. Their elemental compositions and chlorine stable isotope ratios were determined. This precipitation process ensured that isotopic equilibrium was attained between the brine and precipitate present at that stage, and not the precipitate from previous stages. Thus, the chlorine stable isotope fractionation characteristics in each evaporation stage are described more accurately.

In a second set of experiments, precipitation was continuous during evaporation (PCE). This evaporation experiment differed from CSE because there is no precipitate-brine separation throughout the evaporation. However, the other operations were the same. As soon as sufficient solid had precipitated on the watch glass, the solid on the watch glass and a small volume (2 mL) of the coexisting brine were collected simultaneously. The residual precipitate-brine mixture was evaporated until the volume remaining was too small for the experiment to continue. This process simulates natural salt deposition, so it is representative of the isotopic fractionation process during natural evaporation.

The two groups of experiments were conducted simultaneously and continually between the middle of July 2010 and November 2010. The samples were dissolved in chlorine-free distilled water for elemental composition and chlorine isotope ratio analyses.

1.3 Analysis of elemental composition

According to the Qinghai Institute of Salt Lakes, Chinese Academy of Sciences [20] analytical techniques for chemical analysis of the composition of brine, the chlorine concentration was determined by the mercurimetric method, the potassium concentration by gravimetry, and the magnesium concentration by EDTA volumetric analysis (precision is better than 0.3%). If the Na⁺, K⁺, and Mg²⁺ concentrations were too low, atomic absorption spectrometry was used (precision is better than 5%).

1.4 Chlorine stable isotope ratio analysis

Sample pretreatment and mass spectrometry analyses were similar to those reported by Xiao et al. [5,21].

The concentrations of SO₄²⁻ and NO₃⁻ in the samples were far lower than the Cl⁻ concentration. If the molar concentrations are such that c(SO₄²⁻)/c(Cl⁻) < 2.5 and c(NO₃⁻)/c(Cl⁻) < 0.5, then SO₄²⁻ and NO₃⁻ will have no effect on chlorine stable isotope ratio determination [22]. For analysis, each precipitate was dissolved in high-purity water, and the

Cl⁻ concentration was about 10 mg/mL. The sample solution was passed through a ion exchange column (filled with H⁺ type ion exchanger) to remove cations while converting Cl⁻ to HCl. The pure HCl solution was then passed through a ion exchange column filled with Cs⁺ type ion exchanger to produce a CsCl solution. This CsCl solution was used for mass spectrometry analysis. The pH of the solution was between 2.5 and 6.

A Ta filament, heated with a 2.5 A for 1 h in a vacuum system, was first treated with 3.5 μL of graphite slurry (80% ethanol, with 100 μg of graphite) to coat the center of the filament. Next, 3 μL of a test solution containing approximately 30 μg of chlorine as CsCl was loaded on the filament and then dried using a 1 A for 2.5 min. The sample was then analyzed with the mass spectrometer. The intensity of the Cs₂Cl⁺ ion was adjusted to 4 × 10⁻¹² A by controlling the filament current. Data were collected by switching magnetically between the masses 301 (¹³³Cs₂³⁵Cl⁺) and 303 (¹³³Cs₂³⁷Cl⁺). The δ³⁷Cl values were calculated using the following formula:

$$\delta^{37}\text{Cl}(\%) = \left\{ \left[\frac{(^{37}\text{Cl}/^{35}\text{Cl})_{\text{sample}} - (^{37}\text{Cl}/^{35}\text{Cl})_{\text{standard}}}{(^{37}\text{Cl}/^{35}\text{Cl})_{\text{standard}}} \right] \times 1000 \right\}$$

The average (³⁷Cl/³⁵Cl)_{standard} ratio obtained through repeated analysis of ISL 354 NaCl, an isotopic reference material was 0.319030 ± 0.000071 (2σ).

2 Results and discussion

The elemental compositions of the precipitates, and the chlorine stable isotope ratios of the precipitates and brines are listed in Tables 4 and 5.

2.1 Precipitation stages during brine evaporation

Figures 1(a) and 2(a), and the data in Tables 4 and 5 show the concentration changes for the elements in the precipitates obtained from the CSE and PCE experiments. The trends in Figures 1(a) and 2(a) clearly show three evaporation phases. In the precipitates, the Cl⁻ concentration gradually decreased and reaches a minimum in the third phase of evaporation. The Na⁺ concentration was highest in the first evaporation phase, and then declined sharply until it reached a constant level. The K⁺ concentration was highest in the second phase, and was low in the other two phases. The Mg²⁺ concentration gradually increased to a maximum in the third phase. Based on the above trends, the three phases can be identified as the precipitation phases of halite, carnallite, and bischofite, which confirm the values in Table 6. In the halite zone, the experimental concentrations of Cl⁻ and Na⁺ were close to the theoretical values, which suggests that the solid precipitated as halite. Because of the small amount of KCl and MgCl₂ in the precipitates, the experimental values are slightly lower than the theoretical values, especially in the later stages of evaporation when carnallite

Table 4 Chemical compositions of the precipitates and $\delta^{37}\text{Cl}$ values of the brines and precipitates from the CSE experiment

Sample	Degree of evaporation ^{a)}	pH of brine	Density (g/mL)	Precipitates (w/w, %)				Compositions of minerals (results of XRD and microscopic identification)	$\delta^{37}\text{Cl}\pm 2\text{SE}\%_o$ (2σ)		$\alpha_{\text{solid/liquid}}\pm 2\text{SE}$ (2σ)
				Cl	Na	K	Mg		Brines	Precipitates	
CSE1	0.00	6.407	1.2432	–	–	–	–	–	–0.21±0.29	–	–
CSE2	0.06	5.985	1.2483	59.15	37.56	0.13	0.38	halite	–0.31±0.28	–0.05±0.05	1.00026±0.00005
CSE3	0.13	5.941	1.2542	59.39	37.75	0.14	0.35	halite	–0.31±0.21	0.37±0.30	1.00068±0.00030
CSE4	0.22	5.753	1.2803	56.32	32.43	1.92	1.47	halite, carnallite ^{b)}	–0.27±0.17	0.15±0.22	1.00042±0.00022
CSE5	0.31	5.654	1.2916	38.72	3.30	12.09	7.93	carnallite, halite ^{b)}	–0.43±0.48	0.27±0.31	1.00070±0.00031
CSE6	0.41	5.637	1.2906	38.72	2.36	12.66	8.21	carnallite, halite ^{b)}	–0.41±0.21	–0.77±0.15	0.99964±0.00015
CSE7	0.44	5.576	1.2933	38.32	1.85	12.69	8.32	carnallite, halite ^{b)}	–0.49±0.20	–0.14±0.43	1.00035±0.00043
CSE8	0.46	5.597	1.2952	39.16	2.12	13.00	8.33	carnallite, halite ^{b)}	–0.44±0.37	–0.28±0.17	1.00016±0.00017
CSE9	0.49	5.505	1.3053	39.12	2.77	12.26	8.20	carnallite, halite ^{b)}	–0.59±0.21	–0.25±0.29	1.00034±0.00029
CSE10	0.53	5.424	1.3081	38.29	1.94	12.43	8.31	carnallite, halite ^{b)}	–0.54±0.19	–0.43±0.34	1.00011±0.00034
CSE11	0.60	5.325	1.3238	40.11	4.49	11.79	7.79	carnallite, halite ^{b)}	–0.59±0.22	–0.31±0.24	1.00028±0.00024
CSE12	0.65	5.324	1.3395	39.37	3.48	12.17	8.05	carnallite, halite ^{b)}	–0.42±0.32	–0.08±0.27	1.00034±0.00027
CSE13	0.68	5.278	1.3465	39.15	2.22	11.75	8.49	carnallite, halite ^{b)}	–0.43±0.15	–0.17±0.42	1.00026±0.00042
CSE14	0.71	5.296	1.3477	34.69	0.24	0.55	11.73	bischofite	–0.82±0.38	–0.92±0.07	0.99990±0.00007
CSE15	0.73	5.223	1.3494	34.00	0.11	0.02	11.74	bischofite	–0.93±0.51	–0.52±0.24	1.00041±0.00024
CSE16	0.75	5.354	1.3507	34.05	0.12	0.05	11.69	bischofite	–0.78±0.13	–0.56±0.18	1.00022±0.00018
CSE17	0.79	5.307	1.3514	34.61	0.17	0.11	11.87	bischofite	–0.90±0.16	–0.53±0.24	1.00037±0.00024
CSE18	0.80	5.431	1.3533	34.65	0.17	0.10	11.89	bischofite	–0.92±0.31	–0.81±0.60	1.00011±0.00060
CSE19	0.82	5.494	1.3546	34.32	0.11	0.07	11.81	bischofite	–0.88±0.13	–0.69±0.06	1.00019±0.00006
CSE20	0.84	5.382	1.3557	34.70	0.26	0.03	12.24	bischofite	–0.85±0.16	–0.68±0.29	1.00017±0.00029

a) Degree of evaporation (DE) was calculated from the ratio of the evaporated volume (V_i) to the initial volume (V_0) in the beaker, $\text{DE}=V_i/V_0$; b) minor component.

Table 5 Chemical compositions of the precipitates and $\delta^{37}\text{Cl}$ values of the brines and precipitates from the PCE experiment

Sample	Degree of evaporation ^{a)}	pH	Density (g/mL)	Precipitates (w/w, %)				Compositions of minerals (results of XRD and microscopic identification)	$\delta^{37}\text{Cl}\pm 2\text{SE}\%_o$ (2σ)		$\alpha_{\text{solid/liquid}}\pm 2\text{SE}$ (2σ)
				Cl	Na	K	Mg		Brines	Precipitates	
PCE1	0.00	6.407	1.2432	–	–	–	–	–	–0.21±0.29	–	–
PCE2	0.06	5.983	1.2591	58.38	36.53	0.20	0.62	halite	–0.26±0.23	0.18±0.45	1.00044±0.00045
PCE3	0.12	5.908	1.2647	59.23	37.68	0.09	0.34	halite	–0.30±0.23	0.45±0.29	1.00075±0.00029
PCE4	0.19	5.829	1.2636	58.05	36.43	0.06	0.16	halite	–0.23±0.16	0.18±0.21	1.00041±0.00021
PCE5	0.22	5.765	1.2686	56.43	33.21	1.49	1.25	halite, carnallite ^{b)}	–0.41±0.47	–0.09±0.10	1.00032±0.00010
PCE6	0.33	5.665	1.2743	39.06	2.59	12.28	8.17	carnallite, halite ^{b)}	–0.44±0.32	–0.75±0.16	0.99969±0.00016
PCE7	0.35	5.624	1.2755	38.73	1.46	13.08	8.43	carnallite, halite ^{b)}	–0.54±0.38	–0.32±0.26	1.00022±0.00026
PCE8	0.38	5.590	1.2804	38.49	1.23	12.92	8.52	carnallite, halite ^{b)}	–0.51±0.37	–0.25±0.21	1.00026±0.00021
PCE9	0.41	5.595	1.2813	38.71	1.74	12.91	8.33	carnallite, halite ^{b)}	–0.45±0.08	–0.94±0.26	0.99951±0.00026
PCE10	0.44	5.490	1.2860	39.02	2.13	12.39	8.39	carnallite, halite ^{b)}	–0.62±0.22	0.24±0.29	1.00086±0.00029
PCE11	0.48	5.404	1.3091	38.58	1.79	12.47	8.40	carnallite, halite ^{b)}	–0.70±0.11	–0.36±0.11	1.00034±0.00011
PCE12	0.54	5.326	1.3233	39.88	3.94	11.98	7.85	carnallite, halite ^{b)}	–0.65±0.13	–0.14±0.27	1.00051±0.00027
PCE13	0.59	5.342	1.3374	40.41	4.11	12.18	7.85	carnallite, halite ^{b)}	–0.58±0.14	–0.22±0.19	1.00036±0.00019
PCE14	0.65	5.319	1.3457	34.72	0.27	0.51	11.70	bischofite	–0.66±0.20	–0.36±0.37	1.00030±0.00037
PCE15	0.66	5.292	1.3468	34.16	0.20	0.10	11.68	bischofite	–0.88±0.18	–0.46±0.32	1.00042±0.00032
PCE16	0.68	5.265	1.3475	34.13	0.07	0.02	11.68	bischofite	–0.78±0.08	–0.67±0.28	1.00011±0.00028
PCE17	0.72	5.391	1.3491	34.51	0.11	0.05	11.79	bischofite	–0.82±0.16	–0.43±0.13	1.00039±0.00013
PCE18	0.75	5.369	1.3507	34.28	0.09	0.03	11.78	bischofite	–0.85±0.09	–0.65±0.33	1.00020±0.00033
PCE19	0.78	5.542	1.3531	34.52	0.09	0.04	11.99	bischofite	–0.71±0.03	–0.57±0.07	1.00014±0.00007
PCE20	0.80	5.533	1.3539	34.27	0.12	0.12	11.74	bischofite	–0.86±0.17	–0.52±0.12	1.00034±0.00012
PCE21	0.81	5.479	1.3541	34.42	0.08	0.03	11.82	bischofite	–0.91±0.15	–0.83±0.03	1.00008±0.00003

a) Degree of evaporation (DE) was calculated from the ratio of the evaporated volume (V_i) to the initial volume (V_0) in the beaker, $\text{DE}=V_i/V_0$; b) minor component.

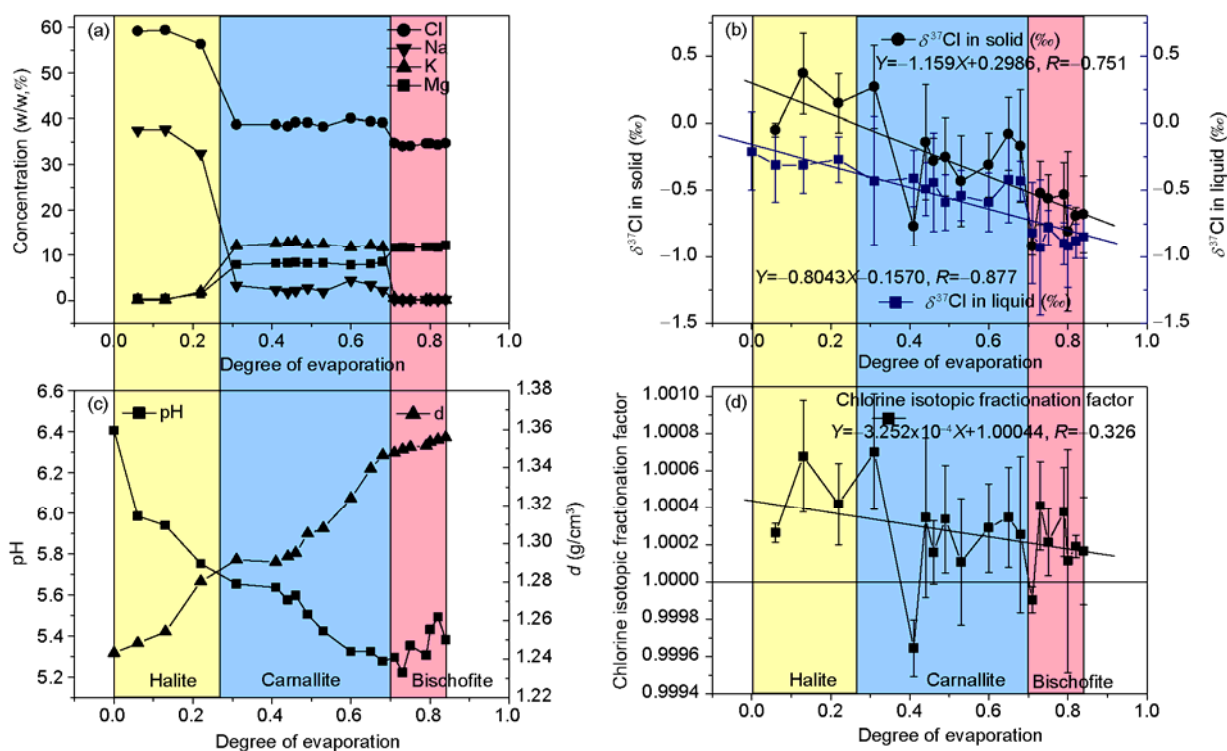


Figure 1 Concentrations of the main elements in the precipitates (a), chlorine stable isotope ratios for the precipitate and brine samples (b), density and pH of brine (c) and chlorine stable isotope fractionation factors (d) for the CSE experiment.

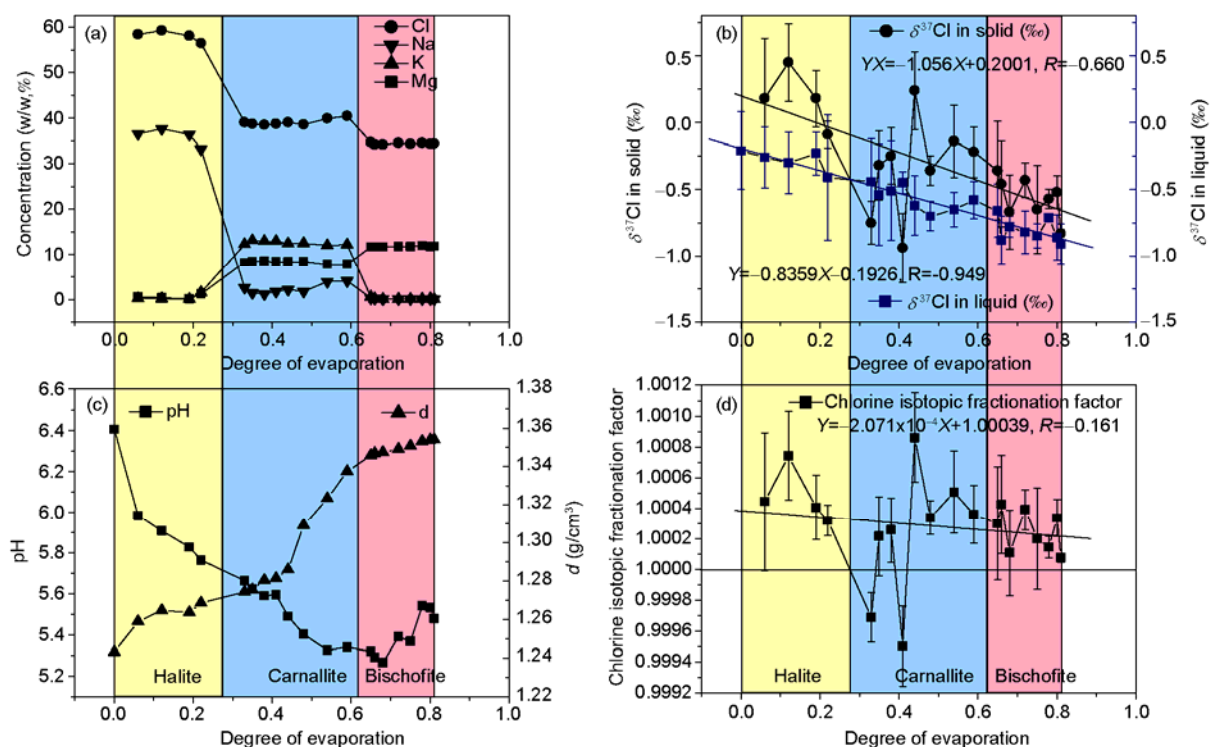


Figure 2 Concentrations of the main elements in the precipitates (a), chlorine stable isotope ratios in the precipitates and brine samples (b), density and pH of brine (c) and chlorine stable isotope fractionation factors (d) for the PCE experiment.

Table 6 Theoretical and experimental chemical compositions of the main minerals formed during brine evaporation

Mineral	Molecular formula (molecular weight)	Cl (w/w, %)		Na (w/w, %)		K (w/w, %)		Mg (w/w, %)	
		Theoretical value	Experimental value	Theoretical value	Experimental value	Theoretical value	Experimental value	Theoretical value	Experimental value
Halite	NaCl (58.44)	60.7	56.32–59.39 ^{a)}	39.3	32.43–37.75 ^{a)}	0	0.13–1.92 ^{a)}	0	0.35–1.47 ^{a)}
			56.43–59.23 ^{b)}		33.21–37.68 ^{b)}		0.06–1.49 ^{b)}		0.16–1.25 ^{b)}
Carnallite	KCl·MgCl ₂ ·6H ₂ O (277.85)	38.3	38.29–40.11 ^{a)}	0	1.85–4.49 ^{a)}	14.07	11.75–13.00 ^{a)}	8.75	7.79–8.33 ^{a)}
			38.47–39.88 ^{b)}		1.23–3.94 ^{b)}		11.98–13.08 ^{b)}		7.85–8.52 ^{b)}
Bischofite	MgCl ₂ ·6H ₂ O (203.30)	34.88	34.00–34.70 ^{a)}	0	0.11–0.26 ^{a)}	0	0.02–0.55 ^{a)}	11.96	11.69–12.24 ^{a)}
			34.13–34.72 ^{b)}		0.07–0.27 ^{b)}		0.03–0.51 ^{b)}		11.68–11.99 ^{b)}

a) Data from the CSE experiment; b) data from the PCE experiment.

precipitation increases. Compared with the halite stage, the Cl⁻ concentration was lower in the carnallite stage. Because of a small amount of NaCl in the precipitates, the experimental concentrations of Cl⁻ were close to or slightly higher than the theoretical values for carnallite. By contrast, the Na⁺ sharply declined at this stage, but was still higher than that in the bischofite stage. The main feature of the carnallite phase was that the concentrations of K⁺ and Mg²⁺ sharply increased, but the maximum experimental concentrations for K⁺ and Mg²⁺ were still lower than the theoretical values because of the small amount of halite present in the precipitate. In the bischofite phase, the Cl⁻ and Mg²⁺ concentrations were close to the theoretical values. The concentration of Mg²⁺ reached its maximum value with small amounts of NaCl and KCl present in the precipitate.

2.2 Stable isotope fractionation characteristics of chlorine in the brine evaporation process

Figures 1(b), (d) and 2(b), (d) present the fractionation characteristics of the chlorine stable isotopes during brine evaporation. These figures show that the $\delta^{37}\text{Cl}_{\text{solid}}\text{-DE}$ regression curve for the precipitate samples is always higher than that for the brine samples in both the CSE and PCE experiments. This indicates stable isotope fractionation of chlorine occurs between the precipitate and coexisting brine, with an apparent ³⁷Cl enrichment in the precipitate. The slopes of the $\delta^{37}\text{Cl}_{\text{solid}}\text{-DE}$ and $\delta^{37}\text{Cl}_{\text{liquid}}\text{-DE}$ regression curves were -1.159 and -1.056 for the precipitate samples (s_{solid}), respectively. The corresponding values for the brine samples (s_{liquid}) were -0.8043 and -0.8359, respectively. Because of the different slopes of these two regression curves, the regression curves gradually approach each other as the DE increases. This indicates that the stable isotope fractionation of chlorine between the precipitate and the brine gradually reduces as the evaporation progresses. This is clearly shown in Figures 1(d) and 2(d), where the chlorine isotope fractionation factor $\alpha_{\text{solid/liquid}}$ between the precipitate and brine samples reduces with the evaporation. When this is correlated with the results from the analysis of the precipitation stage, we can see that $\alpha_{\text{solid/liquid}}$ gradually decreases from halite, to carnallite, to bischofite precipita-

tion stage. This indicates that the halite precipitation stage has the largest chlorine isotope fractionation. The average values of $\alpha_{\text{solid/liquid}}$ in the halite precipitation stage for the CSE and PCE experiments were $\alpha_{\text{h/CSE}}=1.00045\pm 0.00024(2\sigma)$ and $\alpha_{\text{h/PCE}}=1.00048\pm 0.00018(2\sigma)$, respectively. These isotope fractionation factors were clearly higher than the average values of $\alpha_{\text{c/CSE}}=1.00032\pm 0.00013(2\sigma)$ and $\alpha_{\text{c/PCE}}=1.00042\pm 0.00019(2\sigma)$ in the carnallite stage, and $\alpha_{\text{b/CSE}}=1.00024\pm 0.00010(2\sigma)$ and $\alpha_{\text{b/PCE}}=1.00025\pm 0.00009(2\sigma)$ (four data points with $\alpha<1$ were excluded) in the bischofite stage (Figures 1 and 2). This finding confirms the prediction of Schauble et al. [23] that a progressive decrease in the ³⁷Cl/³⁵Cl ratios will occur from NaCl to KCl and RbCl because of the larger ionic radii, and consequently, the weaker M-Cl bonds of the K⁺ and Rb⁺ cations relative to Na⁺. Schauble et al. predicted that NaCl would be approximately 0.8‰ heavier than coexisting KCl at 295 K. In the present study, the NaCl deposited in the CSE and PCE experiments was 0.47‰ heavier than the coexisting NaCl saturated brine, whereas KCl·MgCl₂·6H₂O was approximately 0.23‰ heavier than coexisting brine, and MgCl₂·6H₂O was approximately 0.22‰ heavier than the coexisting MgCl₂ saturated brine. If KCl and MgCl₂·6H₂O are considered as the components of the KCl·MgCl₂·6H₂O precipitate, and we assume the fractionation factors for these components are not affected by other components, then KCl should be approximately 0.24‰ heavier than the coexisting brine. These results suggest chlorine stable isotope fractionation of approximately 0.2‰ occurs between crystalline NaCl and KCl, which is much lower than the approximately 0.8‰ fractionation predicted by Schauble et al. [23]. This difference may be caused by the precipitation of multiple minerals in our study, which should reduce the isotope composition differences among the main minerals. The chlorine isotope of MgCl₂·6H₂O was approximately 0.22‰ heavier than the coexisting MgCl₂ saturated brine, which is lower than that of NaCl. This finding is inconsistent with the prediction of Schauble et al. [23], which states that among chlorides, ³⁷Cl is enriched more in compounds where Cl is bonded to +2 cations (i.e. FeCl₂, MnCl₂) than in compounds where Cl is bonded to +1 cations (i.e. NaCl) by approximately 2‰–3‰ at 298 K. This finding implies that the fractionation charac-

teristics of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ may be different from those of FeCl_2 and MnCl_2 .

The slopes $s_{d/\text{CSE}}$ and $s_{d/\text{PCE}}$ of the regression curves (Figures 1(d) and 2(d)) were -3.252×10^{-4} and -2.071×10^{-4} , respectively. The fractionation factor α_{CSE} showed larger variations in the CSE experiment than in the PCE experiment. This was because complete separation of the precipitate and brine during the evaporation meant the fractionation factor curve more accurately represented the isotope fractionation in the different stages than in the continuous precipitation.

The $\delta^{37}\text{Cl}$ values of the brine and precipitate samples in the carnallite phase decreased regardless of whether the precipitated halite from the first stage was separated from the brine or not. In the bischofite stage, each $\delta^{37}\text{Cl}$ value was lower than that in the previous sample, which shows the decreasing trend was still present. However, this was not reflected in the fractionation factor as much at this stage as in the earlier precipitation stages.

Figures 1 and 2 show the chlorine stable isotope ratios and the chlorine stable isotope fractionation characteristics for halite precipitation in the halite stage in the CSE and PCE experiments. The $\delta^{37}\text{Cl}$ values of the brine and the halite precipitate decreased, but the fractionation factor did not change markedly. This suggests that if the chemical conditions of the solution do not change, the isotope fractionation factor for chlorine will be constant during halite precipitation. Therefore, halite precipitation will cause the $\delta^{37}\text{Cl}$ values of the brine and the halite precipitate to decrease monotonically. However, the small amount of halite present in the carnallite and bischofite precipitates could not be collected, which meant that the $\delta^{37}\text{Cl}$ of the halite in these precipitates could not be determined. Using the fractionation factors for the halite stage precipitate (1.00045 in CSE, 1.00048 in PCE) and the average $\delta^{37}\text{Cl}$ values of the brine samples from the carnallite and bischofite stages (-0.48‰ and -0.87‰ in CSE, -0.56‰ and -0.81‰ in PCE), we can calculate the average $\delta^{37}\text{Cl}$ value for halite in the carnallite (-0.03‰ in CSE, -0.08‰ in PCE) and bischofite (-0.42‰ in CSE, -0.33‰ in PCE) stage precipitates. Compared to average $\delta^{37}\text{Cl}$ values of the halite stage precipitates (0.16‰ in CSE, 0.18‰ in PCE) the average $\delta^{37}\text{Cl}$ values of halite in the carnallite and bischofite stage precipitates are lower.

In Figures 1 and 2, four data points have fractionation factors $\alpha < 1$, which indicates that ^{35}Cl is enriched in the precipitate. After careful analysis, two points (CSE6, CSE14) in the CSE experiment were found to be at the transition of the brine precipitation from one stage to a new stage, which indicates that these data points are relevant to the speed of crystallization. The result reported by Xiao et al. [24] showed the converse isotopic fractionations of chlorine, in which ^{35}Cl enriched in the solid phase during a quick crystallization of chloride salts under laboratory conditions is observed. In the present study, when the concentrations of the K^+ and Mg^{2+} in the solution reach saturation and the system nears eutectic crystallization in the metastable state,

new phase carnallite or bischofite will swiftly crystallize. Isotope exchange between the precipitate and brine do not reach equilibrium during the sampling time, and dynamics factors causing ^{35}Cl enrichment in the precipitate may play a role in isotope fractionation of chlorine between the precipitate and brine. Then, the crystallization gradually stabilizes, and saline minerals become enriched in the heavy isotopes because of their slow growth. The isotope fractionation trend at the beginning of the carnallite and bischofite stages is the opposite, and implies that the crystallization at the beginning of these stages is fast.

In contrast to the conclusion of Eggenkamp et al. [13], the $\delta^{37}\text{Cl}$ value of the remaining brine consistently decreased in the halite, carnallite, and bischofite precipitation stages during brine evaporation. Therefore, the residual brine is a reservoir of ^{35}Cl .

Although a positive thermal-ionization mass spectrometry method with high precision was used, a smooth curve such as that calculated by Eggenkamp et al. [13] was not obtained because Cl isotope fractionation during evaporation was small.

The present study explains the $\delta^{37}\text{Cl}$ trends in continuously deposited saline minerals in the core samples from Mahai, Kuntanyi, and Charhan lakes (China) [25–28]. Continuous reduction of the $\delta^{37}\text{Cl}$ value in these core samples is a result of a drought that caused long-term stable evaporation of the closed salt lakes. This decreasing trend appears not only in the halite stage, but also throughout the entire process of brine evaporation.

In the experiments of Eggenkamp et al. [13], once the mineral precipitated, it was separated from the remaining liquid immediately. Chlorine isotope ratios for the precipitate and coexisting liquid were obtained, and surprisingly showed the opposite isotope fractionation when chlorine isotopes evaporated to the potassium and magnesium salt stage, which is similar to the fractionation of sulfur isotopes during seawater evaporation [29]. However, in the saline lake brine system, chlorine exists in compounds with electrovalent bonds, and ^{37}Cl and ^{35}Cl have the same valency and chemical properties. Therefore, the geochemical behavior of chlorine is completely different from that of sulfur. When the single mineral salts of KCl and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ crystallize, the crystal growth is very fast, and in this case, the precipitate is initially enriched in ^{35}Cl . Eggenkamp et al. did not continuously determine the chlorine stable isotope ratios for the solution system, so their conclusions may not be convincing. In the natural brine system, even if the mineral crystallizes rapidly, it is impossible to achieve immediate and complete separation of the precipitate from the brine system to stop isotope exchange. So in both natural and laboratory evaporation processes, we can observe the decreasing trend in the $\delta^{37}\text{Cl}$ value. In fact, we found that the chlorine stable isotope ratio in the precipitate was equal to or higher than that in the solution in the single mineral evaporation experiments of KCl and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ of Eg-

genkamp et al. [13].

2.3 Concentrations of the main elements in the precipitate and chlorine isotope fractionation

The fractionation factors in the CSE and PCE experiments showed the same trends for the changes in the concentrations of the elements in the precipitates. This was a downward trend for the increase in Mg^{2+} , an upward trend for the increase in Na^+ and Cl^- , and no obvious trend for the change in the concentration of K^+ . The fractionation factor was closer to one at high K^+ concentrations than at low K^+ concentrations. The concentrations of Mg^{2+} and Cl^- showed obvious phase characteristics. The experimental Mg^{2+} and Cl^- concentrations were very close to the theoretical values in halite (0% for Mg^{2+} , 60.7% for Cl^-), carnallite (8.75% for Mg^{2+} , 38.3% for Cl^-), and bischofite (11.96% for Mg^{2+} , 34.88% for Cl^-) (Table 6). The different concentrations of Mg^{2+} and Cl^- represent the precipitation phase that is the dominant chlorinated mineral. Excluding the four data points in which the fractionation factors are less than 1, the fractionation factors between the three chloride minerals and the mother liquor are in the following order: halite > carnallite > bischofite. That is, halite is the most likely to be enriched in ^{37}Cl with its theoretical Mg^{2+} concentration of 0. The concentration of Mg^{2+} in the solid shows an upward trend, whereas the concentration of Cl^- shows a downward trend. The trend for the fractionation factor with the changes in the Mg^{2+} and Cl^- concentrations reflects the trend for the fractionation factor in brine evaporation because the fractionation characteristics of the chlorine isotopes are different for different chloride minerals and coexisting brines (Figures 3 and 4).

2.4 Geological significance

From a practical viewpoint, chlorine isotope geochemistry methods are very important for the identification of sylvinitic deposits. Tan et al. [30] obtained good results by combining geochemical methods that use chlorine isotopes and bromine to explore sylvinitic deposits in the halite region. They found that the $\delta^{37}Cl$ values of mineral samples in the Shaqa sub-basin were all negative, whereas those in the Kupa sub-basin were all positive. In addition, the $Br \times 10^3 / Cl$ ratio, which is a common geochemical index that is used to detect sylvinitic deposits, was higher in the Shaqa sub-basin than in the Kuqa sub-basin. Consequently, the Shaqa sub-basin was chosen as a regional sylvinitic deposit forecast area. In this study, there was a clear correlation between low $\delta^{37}Cl$ values and high $Br \times 10^3 / Cl$ ratios.

Reviewing the study history of the classic indicators of halite $Br \times 10^3 / Cl$, it tells us that the development of measurement techniques has already promoted chlorine isotope to be a promising exploration indicator. Bromine will be-

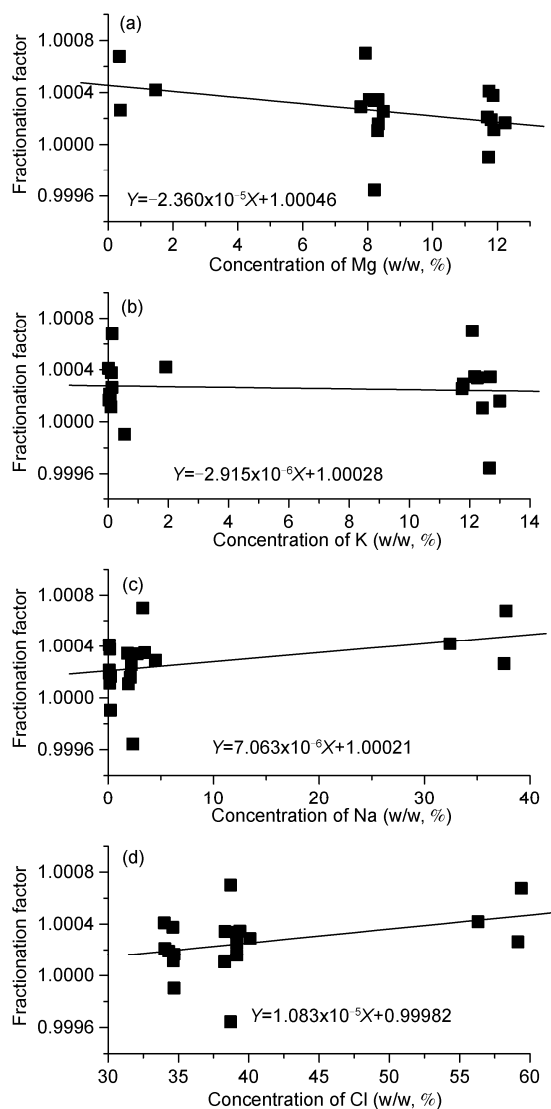


Figure 3 Relationship between the chlorine isotope fractionation factor and the concentrations of the main elements in the CSE experiment.

come concentrated when seawater evaporates, and $Br \times 10^3 / Cl$ in the chloride minerals will steadily increase as seawater evaporation progresses. For the chlorine stable isotope ratio, a similar trend will be observed in saline deposits in closed basins under stable evaporation to that observed in the above evaporation experiments. Chlorine stable isotope ratios have been used successfully in paleoclimatic studies [25–28], such as the dilution and concentration of brine in core drilling studies. Therefore, introduction of chlorine stable isotope ratios in the analysis of salt basins could enhance our knowledge of the historical and future salt basin evolution. The chemical data we obtained for precipitation in the evaporation experiments corresponds to the composition data for salt deposits. Chlorine isotope geochemistry information may help to clarify the salts in the salt basin and the liquid (that is, the mother liquor which salts precipitate in turn).

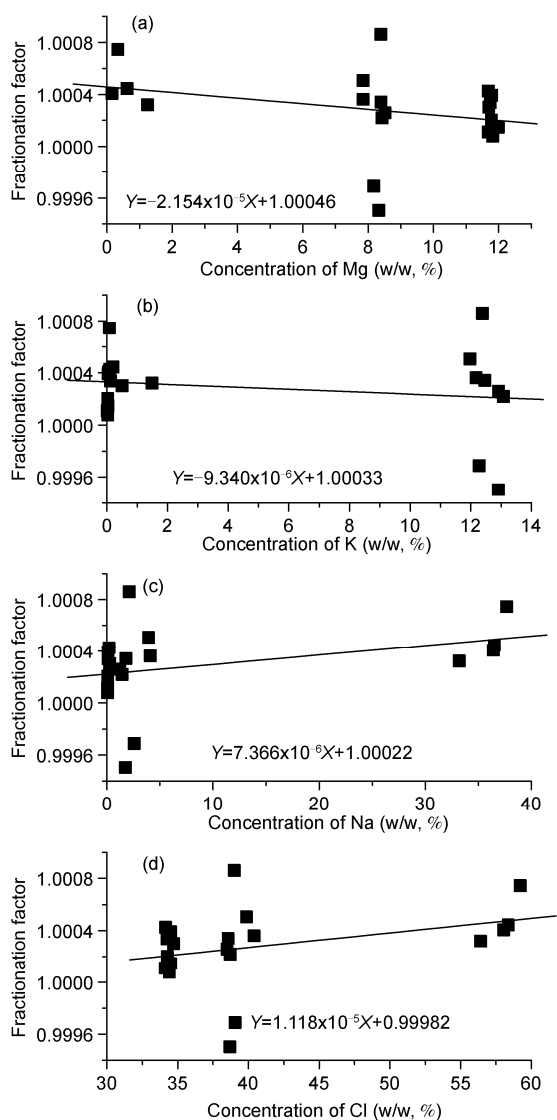


Figure 4 Relationship between the chlorine isotope fractionation factor and the concentrations of the main elements in the PCE experiment.

3 Conclusions

(1) There was significant positive isotope fractionation of chlorine in the halite stage during brine evaporation, and the $\delta^{37}\text{Cl}$ value of the remaining brine showed a downward trend in the halite phase both in the CSE and PCE experiments. The average fractionation factors in the halite phases in the CSE and PCE experiments were $\alpha_{\text{h/CSE}} = 1.00045 \pm 0.00024(2\sigma)$ and $\alpha_{\text{h/PCE}} = 1.00048 \pm 0.00018(2\sigma)$, respectively. These were higher than the fractionation factors $\alpha_{\text{c/CSE}} = 1.00032 \pm 0.00013(2\sigma)$, $\alpha_{\text{b/CSE}} = 1.00024 \pm 0.00010(2\sigma)$, $\alpha_{\text{c/PCE}} = 1.00042 \pm 0.00019(2\sigma)$, and $\alpha_{\text{b/PCE}} = 1.00025 \pm 0.00009(2\sigma)$ (four data points with $\alpha < 1$ were excluded) in the carnallite and bischofite stages. They were also higher than the fractionation factor, $\alpha_{\text{h}} = 1.00026$, in the halite stage obtained by Eggenkamp et al. [13].

(2) In the CSE and PCE experiments, two opposing frac-

tionation trends were observed in the carnallite and bischofite stages, and these were associated with the rapid crystallization of saline minerals.

(3) Compared with the isotopic fractionation factors in the halite phase, those in the carnallite and bischofite phases in the CSE and PCE experiments were lower. The average values were $\alpha_{\text{c/CSE}} = 1.00032 \pm 0.00013(2\sigma)$ and $\alpha_{\text{c/PCE}} = 1.00042 \pm 0.00019(2\sigma)$ in the carnallite phase, and $\alpha_{\text{b/CSE}} = 1.00024 \pm 0.00010(2\sigma)$ and $\alpha_{\text{b/PCE}} = 1.00025 \pm 0.00009(2\sigma)$ in the bischofite phase. Compared with the fractionation factors of the same phase, the values in the present study were much higher than those calculated by Eggenkamp et al., which were $\alpha_{\text{c}} = 1.00002$ in the carnallite phase and $\alpha_{\text{b}} = 0.99994$ in the bischofite phase. According to our analysis, the observed opposite fractionation is because Eggenkamp et al. neglected the fact that isotope exchange equilibrium was not reached after the rapid crystallization of salts.

(4) Comparing the results obtained in the CSE and PCE experiments, the saline mineral separation from brine had little effect on the $\delta^{37}\text{Cl}_{\text{brine}}$ trends in brine. The slope, $s_{\text{d/CSE}}$, of the α -DE regression curve in the CSE experiment showed more significant variations than that in the PCE experiment. Complete separation of the precipitate and brine (CSE experiments) in each evaporation stage means the results reflect the chlorine isotope fractionation in the different stages more accurately.

(5) The fractionation factor shows a downward trend with the increase in the Mg^{2+} concentration and an upward trend with the increase in the Na^+ and Cl^- concentrations, but did not exhibit any obvious change with the increase in the K^+ concentration. The isotope fractionation factors of chlorine for the precipitation stages represented by different concentrations of Mg^{2+} and Cl^- in the precipitate were in the order $\alpha_{\text{h}} > \alpha_{\text{c}} > \alpha_{\text{b}}$.

(6) Throughout the evaporation, the $\delta^{37}\text{Cl}$ values in the brine and precipitate samples show decreasing trends simultaneously. The residual brine is a reservoir of ^{35}Cl . The continuing low trend of the $\delta^{37}\text{Cl}$ value suggests it could be used to detect sylvinite deposits. If the $\delta^{37}\text{Cl}$ value correlates with the traditional halite $\text{Br} \times 10^3 / \text{Cl}$ coefficient, it will be important in the exploration of sylvinite deposits.

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- 1 Rosman K J R, Taylor P D P. Isotopic compositions of the elements 1997. Pure Appl Chem, 1998, 70: 217–235
- 2 Kaufmann R, Long A, Bentley H, et al. Natural chlorine isotope variations. Nature, 1984, 309: 338–340
- 3 Kaufmann R S, Long A, Campbell D J. Chlorine isotope distribution in formation waters, Texas and Louisiana. AAPG Bull, 1988, 72: 839–844
- 4 Vengosh A, Chivas A R, McCulloch M T. Direct determination of boron and chlorine isotopic compositions in geological materials by

- negative thermal-ionization mass spectrometry. *Chem Geol*, 1989, 79: 333–343
- 5 Xiao Y K, Zhang C G. High precision isotopic measurement of chlorine by thermal ionization mass spectrometry of the Cs_2Cl^+ ion. *Int J Mass Spec Ion Proc*, 1992, 116: 183–192
 - 6 Long A, Eastoe C J, Kaufmann R S, et al. High-precision measurement of chlorine stable isotope ratios. *Geochim Cosmochim Acta*, 1993, 57: 2907–2912
 - 7 Magenheimer A J, Spivack A J, Volpe C, et al. Precise determination of stable chlorine isotopic ratios in low-concentration natural samples. *Geochim Cosmochim Acta*, 1994, 58: 3117–3121
 - 8 Volpe C, Spivack A J. Stable chlorine isotopic composition of marine aerosol particles in the western Atlantic Ocean. *Geophys Res Lett*, 1994, 21: 1161–1164
 - 9 Richard A, Banks D A, Mercadier J, et al. An evaporated seawater origin for the ore-forming brines in unconformity-related uranium deposits (Athabasca Basin, Canada): Cl/Br and $\delta^{37}Cl$ analysis of fluid inclusions. *Geochim Cosmochim Acta*, 2011, 75: 2792–2810
 - 10 Stewart M A, Spivack A J. The stable-chlorine isotope compositions of natural and anthropogenic materials. *Rev Mineral Geochem*, 2004, 55: 231–254
 - 11 Willmore C C, Boudreau A E, Spivack A, et al. Halogens of Bushveld Complex, South Africa: $\delta^{37}Cl$ and Cl/F evidence for hydration melting of the source region in a back-arc setting. *Chem Geol*, 2002, 182: 503–511
 - 12 Liu W G, Xiao Y K, Wang Q Z, et al. Chlorine isotopic geochemistry of salt lakes in the Qaidam Basin, China. *Chem Geol*, 1997, 136: 271–279
 - 13 Eggenkamp H G M, Kreulen M R, Koster Van Groos A F. Chlorine stable isotope fractionation in evaporites. *Geochim Cosmochim Acta*, 1995, 59: 5169–5175
 - 14 Tan H B, Ma H Z, Zhang X Y, et al. Fractionation of chlorine isotope in salt mineral sequences and application: Research on sedimentary stage of ancient salt rock deposit in Tarim Basin and western Qaidam Basin (in Chinese). *Acta Petrol Sin*, 2009, 25: 955–962
 - 15 Zheng Y F, Chen J F. *Stable Isotope Geochemistry* (in Chinese). Beijing: Science Press, 2000. 10–12
 - 16 Chen Y H. Sequence of salt separation and regularity of some trace elements distribution during isothermal evaporation (25°C) of the Huanghai sea water (in Chinese). *Acta Geol Sin*, 1983, 57: 379–390
 - 17 Sun D P, Shuai K Y, Gao J H, et al. A preliminary investigation on stable isotopic geochemistry of chlorine for the sylvinitic deposits of chloride-type (in Chinese). *Geoscience*, 1998, 12: 80–85
 - 18 Xiao Y K, Liu W G, Zhang C G. The preliminary investigation on chlorine isotopic fractionation during the crystallization of saline minerals in salt lake (in Chinese). *Salt Lake Sci*, 1994, 2: 35–40
 - 19 Xiao Y K, Zhou Y M, Wang Q Z, et al. A secondary isotopic reference material of chlorine from selected seawater. *Chem Geol*, 2002, 182: 655–661
 - 20 Qinghai Institute of Salt Lakes, Chinese Academy of Sciences. *The Analytical Method for Brine and Salt* (in Chinese). Beijing: Science Press, 1988. 35–67
 - 21 Xiao Y K, Zhou Y M, Liu W G. Precise measurement of chlorine isotopes based on Cs_2Cl^+ by thermal ionization mass spectrometry. *Anal Lett*, 1995, 28: 1295–1304
 - 22 Lu H, Xiao Y K. The effects of SO_4^{2-} and NO_3^- on the Isotopic Measurement of Chlorine and Their Elimination (in Chinese). *Salt Lake Sci*, 2001, 9: 7–12
 - 23 Schauble E A, Rossman G R, Taylor Jr H P. Theoretical estimates of equilibrium chlorine-isotope fractionations. *Geochim Cosmochim Acta*, 2003, 67: 3267–3281
 - 24 Xiao Y K, Liu W G, Zhou Y M, et al. Variations in isotopic compositions of chlorine in evaporation-controlled salt lake brines of Qaidam Basin, China. *Chin J Oceanol Limnol*, 2000, 18: 169–177
 - 25 Liu W G, Xiao Y K, Sun D P, et al. Characteristics and significance of chlorine isotope of brine and deposits in the Mahai salt lakes (in Chinese). *Salt Lake Sci*, 1995, 3: 29–33
 - 26 Wang Q Z, Xiao Y K, Liu W G, et al. The stable chlorine isotopes in quaternary halite deposits of Charhan area (in Chinese). *Salt Lake Sci*, 1995, 3: 40–44
 - 27 Liu W G, Xiao Y K, Sun D P, et al. Chlorine isotopic composition in Qaidam Basin (in Chinese). *Geochimica*, 1996, 25: 296–303
 - 28 Liu W G, Xiao Y K, Han F Q, et al. Characteristics of chlorine isotopes in salt lakes of Kuntzei and their significance of paleoclimate (in Chinese). *Oceanol Limnol Sin*, 1998, 29: 431–435
 - 29 Raab M, Spiro B. Sulfur isotopic variations during seawater evaporation with fractional crystallization. *Chem Geol: Isot Geosci Sect*, 1991, 86: 323–333
 - 30 Tan H B, Ma H Z, Xiao Y K, et al. Characteristics of chlorine isotope distribution and analysis on sylvinitic deposit formation based on ancient salt rock in the western Tarim Basin. *Sci China Ser D-Earth Sci*, 2005, 48: 1913–1920

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