



## Stable isotope fractionation of chlorine during the precipitation of single chloride minerals



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### ABSTRACT

In order to better understand chlorine isotopic variations during brine evolution, experiments were designed to determine the changes in the chlorine isotope composition ( $\delta^{37}\text{Cl}$  value) during evaporations of solutions containing NaCl, KCl and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  at  $28 \pm 2$  °C. Three evaporation experiments were conducted in a clean environment. The precipitate and brine samples were collected during the evaporation, and the chlorine isotopic ratios of the samples were determined using an improved thermal ionisation mass spectrometry procedure based on  $\text{Cs}_2\text{Cl}^+$  ion measurement. The results are as follows: the mean fractionation factors of the three solutions are  $\alpha_{\text{Na}} = 1.00055$ ,  $\alpha_{\text{K}} = 1.00025$ , and  $\alpha_{\text{Mg}} = 1.00012$ , respectively, where  $\alpha_{\text{Na}}$ ,  $\alpha_{\text{K}}$  and  $\alpha_{\text{Mg}}$  are the fractionation factors between salts (NaCl, KCl and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) and saturated solutions. The results showed that the  $\delta^{37}\text{Cl}$  values of precipitate and coexisting brine samples decrease during the precipitation of single chloride minerals. The residual brine was a  $^{35}\text{Cl}$  reservoir for different single chloride solutions. New chlorine isotopic evolution curve during seawater evaporation were also calculated. The results indicated that during the primary precipitation stage of halite,  $\delta^{37}\text{Cl}$  decreased continuously, and the most important thing is that this trend continues during the final stages when Mg-salts begin to precipitate.

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### 1. Introduction

There are two reservoirs of chlorine on Earth (i.e., the surface and mantle chlorine reservoirs). The main carriers in the surface reservoir are seawater, evaporite, and brine, which is a key chlorine sink (Kaufmann, 1984; Kaufmann et al., 1984; Eggenkamp, 1994; Shirodkar et al., 2006). Isothermal evaporation experiments of seawater indicate that nearly all of the salt formation processes after gypsum precipitation involve chlorine and the production of main chloride minerals, such as halite, sylvine, carnallite, and bischofite (Chen, 1983).

$\delta^{37}\text{Cl}$  values are widely used to determine the origin of salinity in various fluids. Banks et al. (2000a,b) distinguished different

sources of magmatic fluids for mineralisation using  $\delta^{37}\text{Cl}$  values. Chiaradia et al. (2006) used  $\delta^{37}\text{Cl}$  values for tracing the origin of mixed magmatic–basinal brine. Nahnybida et al. (2009) obtained the  $\delta^{37}\text{Cl}$  values for Bingham Canyon samples ranged from  $-0.9\text{‰}$  to  $-4.1\text{‰}$ , which suggested that the porphyry system at Bingham inherited negative chlorine isotopic signatures from the subducting slab. Gleeson and Smith (2009) analysed the chlorine stable isotope composition of fluid inclusion leachates from Fe-oxide–apatite and Greenstone deposits in Norrbotten, Sweden and found that most of the isotopic data are consistent with a mantle-derived source of chlorine. Richard et al. (2011) used  $\delta^{37}\text{Cl}$  signatures to unravel the mechanisms underlying the origin of salinity of crustal fluids (Athabasca Basin, Canada). Barnes et al. (2008, 2009) used Cl isotope variations in arc-derived materials in order to track devolatilization reactions in subduction zones.

Brine evolution is crucial for studying chlorine geochemistry in the surface reservoir (Liu et al., 1997; Eastoe et al., 1999, 2001, 2007; Richard et al., 2011). Therefore, elucidating how chlorine isotopes change in the course of brine evolution is significant for understanding chlorine isotope geochemistry.

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## 2. Previous work

Eggenkamp et al. (1995) evaporated solutions with a single chloride and determined the fractionation factor  $\alpha$  between precipitate and coexisting brine. The chlorine isotope fractionations ( $^{37}\text{Cl}/^{35}\text{Cl}$ ) between NaCl, KCl, and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and their saturated solutions are as follows:

$$10^3 \ln \alpha(\text{NaCl} - \text{solution}) = +0.26 \pm 0.07(1\sigma),$$

$$10^3 \ln \alpha(\text{KCl} - \text{solution}) = -0.09 \pm 0.09(1\sigma),$$

$$10^3 \ln \alpha(\text{MgCl}_2 \cdot 6\text{H}_2\text{O} - \text{solution}) = -0.06 \pm 0.10(1\sigma).$$

For NaCl precipitate,  $\alpha$  is higher than unity; for KCl and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  precipitates, the factors are less than unity. With these fractionation factors, the isotopic evolutions of the evaporated seawater are then calculated using the Rayleigh fractionation model by Eggenkamp et al. (1995). The  $\delta^{37}\text{Cl}$  values of the precipitate systematically decreased during the main stage of halite crystallisation and then increased again at the bischofite stage of evaporation.

However, the chlorine isotopic composition in the geological samples does not support these observations (Table 1). Sun et al. (1998) studied the chlorine isotopic composition of ancient and modern salt minerals. In general, the order is halite > sylvite > carnallite according to their  $\delta^{37}\text{Cl}$  values, which is inconsistent with the results of Eggenkamp et al. (1995). Eastoe et al. (2007) reported the potash facies salt (mean  $\delta^{37}\text{Cl} -0.30 \pm 0.04\text{‰}$ ) that was isotopically lighter than the halite facies salt (mean  $0.06 \pm 0.04\text{‰}$ ) in the Zechstein; in Siberia, the potash facies salt (mean  $-0.32 \pm 0.06\text{‰}$ ) was lighter than the halite facies salt (mean  $0.06 \pm 0.05\text{‰}$ ). Xiao et al. (1994) investigated chlorine isotopic composition of brines and salts from a series of artificial ponds in the saline Qarhan Lake, and the fractionation factors between the precipitates and coexisting brines are higher than unity in most cases. Chlorine isotopic fractionation during evaporation of brine from the saline Qarhan Lake has also been studied by Luo et al. (2012). The results indicate that  $\delta^{37}\text{Cl}$  values in brines and precipitates constantly decreased with continuous salt crystallisation at different stages of brine evolution.

**Table 1**  
Chlorine isotope distribution in the world sylvinitic deposit.<sup>a</sup>

Zone	Sample	$\delta^{37}\text{Cl} \pm \text{SD}\text{‰}$
Qarhan Salt Lake, China	Halite (0.7–0.8m depth)	$-0.44 \pm 0.13$
	Modern carnallite	$-1.38 \pm 0.19$
Mengye Yunnan, China	White halite	$-0.38 \pm 0.13$
	Sage green sylvinitic	$-0.69 \pm 0.19$
	Caesious sylvinitic	$-0.88 \pm 0.13$
Navarra Basin, Spain	Pink sylvinitic	$-0.88 \pm 0.50$
	Red sylvinitic	$-2.41 \pm 0.34$
	Carmine sylvinitic	$-0.75 \pm 0.09$
Catalonia Basin, Spain	Halite (lower zone)	$1.00 \pm 0.16$
	White halite	$0.47 \pm 0.25$
	Pink halite	$0.60 \pm 0.19$
	Red sylvinitic	$-0.41 \pm 0.13$
	Carnallite	$-1.22 \pm 0.19$
Sitaluobin Belarus	Halite (S-84)	$-0.06 \pm 0.09$
	Sylvinitic (S-83)	$-1.44 \pm 0.53$
	Sylvinitic (S-80)	$-2.22 \pm 0.13$
	Carnallite (S-79)	$-2.60 \pm 0.53$
Mahai Salt Lake, China	Halite	$-0.41 \pm 0.09^b$
	Early sylvinitic deposit	$-1.10 \pm 0.09^b$
	Early carnallite deposit	$-2.07 \pm 0.06^b$

<sup>a</sup> These are data reported by Sun et al. (1998).

<sup>b</sup> These values were calculated on the basis of raw data in that paper but different from values in it.

In the single chloride experiments of Eggenkamp et al. (1995), once the mineral precipitated, it was immediately separated from the remaining liquid, and the evaporation experiments had been simultaneously terminated. Fractionation factors for a salt-solution were determined at a single point in the evolution of the evaporating system, not over the full extent of evaporation. Therefore, further experimental study of the evolution of chlorine isotopes during the evaporation of single chloride solutions is required. The primary aim of this work is to investigate the features of chlorine isotopic fractionation during single chloride solutions evaporation, especially chlorine isotopic evolution in brine throughout the entire salt crystallisation process of Na, K, and Mg with single chloride.

## 3. Materials and methods

### 3.1. Reagents

High-purity water was obtained by double sub-boiling distillation with double normal boiling of fresh water. To guarantee the same chlorine source for three single chloride solutions in the experiment, NaCl, KCl, and  $\text{MgCl}_2$  solutions were prepared by sequentially mixing liquid from the same hydrochloric acid (Guaranteed reagent, GR) with KOH (GR), NaOH (GR), and ultra-pure magnesium powder. The reaction was terminated when the solution pH values ranged between 5.0 and 7.0. Then, the prepared single chloride solutions were diluted to a certain volume as follows: 550 mL for NaCl, 400 mL for KCl, and 400 mL for  $\text{MgCl}_2$ . The  $\text{Cl}^-$  amount in the three solutions was 1.744 mol for NaCl, 1.140 mol for KCl, and 2.000 mol for  $\text{MgCl}_2$ .

### 3.2. Equipment

The thermal-ionisation mass spectrometer used was a Triton (with a  $90^\circ$  magnetic sector, 81 cm radius, and 10 kV acceleration voltage) produced by Thermo Fisher Scientific (Bremen, Germany). A VD-650 vertical desktop clean bench produced by Sujing Antai Airtech (Suzhou, China) with a vertical laminar flow supplying was also used. The cleanliness class of it was class 100 (Fed 209E). A Zhenghong DBF anti-corrosion electric hot plate with cast aluminum Teflon coating and temperature accuracy of  $\pm 1^\circ\text{C}$  simultaneously accommodated multiple samples without cross-contamination (Binhai, China).

### 3.3. Evaporation experiment

Evaporation experiments were conducted on a VD-650 clean bench. NaCl, KCl and  $\text{MgCl}_2$  solutions were placed in three 1 L graduated beakers. The beakers were placed on a DBF anti-corrosion electric hot plate and evaporated at  $28 \pm 2^\circ\text{C}$ . An appropriately sized watch glass was placed at the bottom of each beaker. The watch glass was removed from the beaker as soon as a sufficient amount of solid precipitated was formed on it; simultaneously, a little liquid sample was collected, and the change in volume of the liquid in the beaker was recorded to calculate the degree of evaporation. Then, the pH and density of the solution were measured, and 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 and rinsed with acetone to remove the remaining solution. X-ray diffraction analyses of the precipitate were conducted to determine the mineral type. The liquid and solid in the beakers were not separated, and the residual precipitate-brine mixture was evaporated until the amount left in the beaker was insufficient to continue the experiment. The samples were sealed

in 4 mL polyethylene tubes to determine the chlorine isotopic compositions.

The three groups of experiments were simultaneously and continually conducted from December 14, 2010 to January 28, 2011.

During experiments, given the rapid evaporation and salt crystallisation of  $K^+$ , the evaporation speed of single chloride (K) solution was controlled using a preservative film in the beaker mouth after collecting one sample during the single chloride evaporation experiment. Similarly, considering the relatively rapid speed of salt crystallisation for NaCl solution, the evaporation speed was also controlled after collecting two solid samples.

#### 3.4. Determination of chlorine isotopic composition

The positive thermal ionisation mass spectrometry (P-TIMS) method based on the  $Cs_2Cl^+$  with graphite load was used to measure the chlorine isotopes in all samples in this study. The P-TIMS for the measurement of stable chlorine isotopes was first proposed by Xiao and Zhang (1992) and has been widely applied for the  $^{37}Cl/^{35}Cl$  ratio measurements of various geological samples including salt lake brine and salt mineral (Xiao et al., 1994, 1997, 2000; Liu et al., 1995, 1997, 1998; Sun et al., 1998; Tan et al., 2009), sea water (Zhou et al., 1998; Shirodkar et al., 2006), marine aerosol (Volpe and Spivack, 1994; Volpe et al., 1998), chlorinated organic solvent (Numata et al., 2002), fluid (Ransom et al., 1995; Banks et al., 2000a, b; Wei et al., 2008) and meteorite and rock (Magenheim et al., 1995; Nakamura et al., 2011). A cross-comparisons of gas source dual inlet isotope ratio mass spectrometry (IRMS) and P-TIMS for chlorine isotopic measurement in various geological samples, such as seawater, pure CsCl solution, NaCl solutions and brine, were completed by Rosenbaum et al. (2000) and Godon et al. (2004). The results indicated that within error, both techniques are in good agreement.

To determine the chlorine isotopic compositions, the samples were dissolved in high-purity sub-boiling distilled water. The samples were prepared in a two-step resin method. Approximately 200–400 mesh regenerative H-cation exchange resin (resin type: Dowex 50W×8, which contains  $-SO_3H$  and is a cation exchange resin with strong acidity) was injected into a polyethylene-accompanied ion-exchange column with a diameter of 0.4 cm and resin height of 2 cm to form a H-cation exchange resin column. Then, a regenerative Cs-cation exchange resin was injected into a polyethylene-accompanied ion-exchange column with a diameter of 0.4 cm and resin height of 1.6 cm to form a Cs-cation exchange resin column. First, the samples were passed through the H-cation exchange resin column (at this time, all Cl in the liquid samples transformed to HCl solution). Then, the CsCl solution was collected after the liquid went through the Cs-cation exchange resin column. During the preparation, the sample solution was transformed into the CsCl solution. Because the guarantee reagent and double-distilled water were used to prepare the single chloride solutions for evaporation, the NaCl, KCl, and  $MgCl_2$  solutions are pure. The effects of  $SO_4^{2-}$ ,  $NO_3^-$  and  $F^-$  can be neglected (Lu and Xiao, 2001).

For the mass spectrometric measurement, a tantalum filament heated at a current of 2.5 A for 1 h in a vacuum system was treated with 2.5  $\mu$ L of graphite slurry (80% ethanol mixed with 80  $\mu$ g of graphite) to coat the centre of the filament. Then, 3  $\mu$ L of the test solution containing  $\sim 10$   $\mu$ g of chlorine as CsCl was loaded on the filament and dried using a current of 1 A for 1.5 min. The samples were placed in the mass spectrometer, and the determination was started when the ion source was under of vacuum of less than  $2.5 \times 10^{-7}$  mbar. The intensity of the  $Cs_2Cl^+$  ion was adjusted to  $4 \times 10^{-12}$  A by controlling the filament current. The data were simultaneously obtained on Faraday cup C and H1 by collecting the ion flow with mass numbers of 301 ( $^{133}Cs_2^{35}Cl^+$ ) and 303 ( $^{133}Cs_2^{37}Cl^+$ ).

The isotope standard is ISL 354 NaCl, which is a chlorine isotope reference material. The absolute  $^{37}Cl/^{35}Cl$  ratio for ISL 354 NaCl determined using the precise calibrated mass spectrometric measurement was  $0.319549 \pm 0.000044$  (Wei et al., 2012). The ISL 354 NaCl with an absolute chlorine isotopic composition was prepared from special sea water located at  $4^\circ 18'N$ ,  $101^\circ 08'E$ , and the  $\delta^{37}Cl$  difference of ISL 354 NaCl from the special sea water is 0.02‰, which is within the precision of the measurement (Xiao et al., 2002). Therefore, ISL 354 NaCl can be impartially recognised as Standard Mean Ocean Chloride (SMOC) possessing a definitive location, which was used to represent SMOC. The ISL 354 NaCl was recommended as a chlorine isotope reference material by International Atomic Energy Agency on its web site: ([http://nucleus.iaea.org/rpst/ReferenceProducts/ReferenceMaterials/Stable\\_Isotopes/37Cl35I/ISL-354.htm](http://nucleus.iaea.org/rpst/ReferenceProducts/ReferenceMaterials/Stable_Isotopes/37Cl35I/ISL-354.htm)).

The  $\delta^{37}Cl$  values were calculated by the following equation:

$$\delta^{37}Cl (\text{‰}) = \left[ \left( \frac{^{37}Cl}{^{35}Cl} \right)_{\text{sample}} - \left( \frac{^{37}Cl}{^{35}Cl} \right)_{\text{smoc}} \right] / \left( \frac{^{37}Cl}{^{35}Cl} \right)_{\text{smoc}} \times 1000, \quad (1)$$

here, the average measured  $\left( \frac{^{37}Cl}{^{35}Cl} \right)_{\text{smoc}}$  value for ISL 354 NaCl was  $0.318925 \pm 0.000053(2\sigma)$ , which was obtained from the results of 18 continuous determinations under the same conditions as those of the samples. The correction factor  $K_{37/35}$  for our Triton T1 is 0.99805 (i.e.,  $0.318925/0.319549 = 0.99805$ ), which is consistent with  $K_{37/35} = 0.99806$  for Triton T1 reported by Wei et al. (2012).

## 4. Results

Tables 2–4 list the density and pH value of the liquid, the  $\delta^{37}Cl$  values for the brines and precipitates, and the chlorine isotopic fractionation factors between the precipitates and liquid during the precipitation of the three chloride (NaCl, KCl, and  $MgCl_2$ ) solutions. Figs. 1–3 show the fractionation characteristics of the chlorine isotope. With constant evaporation and crystallisation, the pH values of the three single chloride solutions decreased significantly, but those of the  $MgCl_2$  solution initially decreased and then slightly increased. When the degree of evaporation reaches approximately 0.5, the density of all three solutions exhibit a flat zone, which is due to the solubility of the single mineral. The  $\delta^{37}Cl$  values of the three single chloride solutions significantly decreased. From the beginning to the end of the evaporation, the  $\delta^{37}Cl$  values ranged from 1.82‰ to 0.37‰ for the NaCl solution, 1.85‰ to 0.72‰ for the KCl solution, and 1.99‰ to 0.81‰ for the  $MgCl_2$  solution. For the chlorine isotopic fractionation between the brines and precipitates, no converse fractionation occurred in the NaCl and KCl solutions, and all of the precipitated samples concentrate  $^{37}Cl$  relative to the coexisting liquid samples. However, two converse fractionations were observed for the  $MgCl_2$  solution (Table 4).

## 5. Discussion

### 5.1. Chlorine isotopic evolution of single chloride solutions

The average fractionation factors between deposited minerals and solutions for these three single minerals were calculated, and the following  $\alpha$  values were obtained:  $\alpha_{Na} = 1.00055$ ,  $\alpha_K = 1.00025$ , and  $\alpha_{Mg} = 1.00012$  (Fig. 4). In contrast, Eggenkamp et al. (1995) obtained  $\alpha_{Na} = 1.00026$ ,  $\alpha_K = 0.99991$ ,  $\alpha_{Mg} = 0.99994$ . A comparison reveals that our fractionation factors are higher and all are more than unity. It seems that there is no dependence of  $\alpha$  on the degree of evaporation in each system. All the values of  $\alpha$  appear to be independent measurements of the same

**Table 2**  
Chlorine isotopic compositions of evaporation experiment for NaCl solution.

Sample	Degree of evaporation <sup>a</sup>	pH	Density (g/mL)	$\delta^{37}\text{Cl} \pm 2\sigma \text{‰}$		$\alpha_{\text{Solid/Liquid}} \pm 2\sigma$
				Liquid	Solid	
Na1	0.00	5.926	1.1545	1.82 ± 0.16	–	–
Na2	0.56	5.198	1.2016	1.10 ± 0.11	1.17 ± 0.33	1.00007 ± 0.00033
Na3	0.69	5.001	1.2010	0.84 ± 0.24	2.12 ± 0.10	1.00128 ± 0.00010
Na4	0.82	4.888	1.2020	0.32 ± 0.29	1.31 ± 0.24	1.00099 ± 0.00024
Na5	0.90	4.838	1.2012	0.27 ± 0.28	0.57 ± 0.30	1.00029 ± 0.00030
Na6	0.93	–	1.2016	0.13 ± 0.08	0.63 ± 0.07	1.00051 ± 0.00007
Na7	0.95	–	1.2013	0.60 ± 0.18	0.66 ± 0.27	1.00006 ± 0.00027
Na8	0.98	–	1.2012	0.37 ± 0.10	1.03 ± 0.34	1.00066 ± 0.00034

<sup>a</sup> Degree of evaporation (DE) was calculated from the ratio of the volume disappeared ( $V_t$ ) to the initial volume ( $V_0$ ) in the beaker,  $DE = V_t/V_0$ .

**Table 3**  
Chlorine isotopic compositions of evaporation experiment for KCl solution.

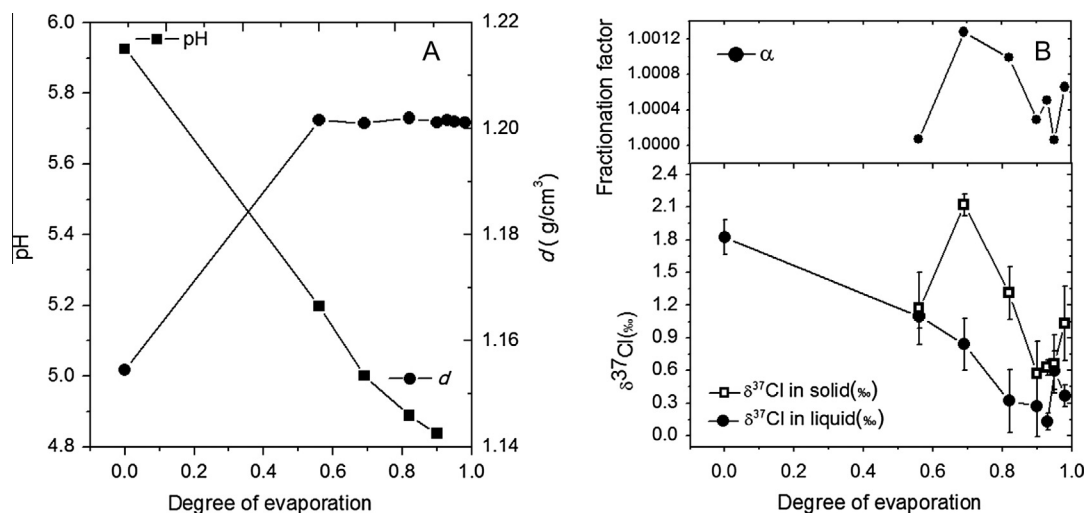
Sample	Degree of evaporation <sup>a</sup>	pH	Density (g/mL)	$\delta^{37}\text{Cl} \pm 2\sigma \text{‰}$		$\alpha_{\text{Solid/Liquid}} \pm 2\sigma$
				Liquid	Solid	
K1	0	5.452	1.1637	1.85 ± 0.19	–	–
K2	0.56	5.059	1.1779	1.00 ± 0.09	1.15 ± 0.27	1.00015 ± 0.00027
K3	0.75	5.022	1.1810	0.97 ± 0.13	1.36 ± 0.18	1.00039 ± 0.00018
K4	0.80	5.002	1.1815	0.84 ± 0.26	1.04 ± 0.29	1.00020 ± 0.00029
K5	0.90	–	1.1818	0.72 ± 0.10	0.97 ± 0.18	1.00025 ± 0.00018

<sup>a</sup> Degree of evaporation (DE) was calculated from the ratio of the volume disappeared ( $V_t$ ) to the initial volume ( $V_0$ ) in the beaker,  $DE = V_t/V_0$ .

**Table 4**  
Chlorine isotopic compositions of evaporation experiment for MgCl<sub>2</sub> solution.

Sample	Degree of evaporation <sup>a</sup>	pH	Density (g/mL)	$\delta^{37}\text{Cl} \pm 2\sigma \text{‰}$		$\alpha_{\text{Solid/Liquid}} \pm 2\sigma$
				Liquid	Solid	
Mg1	0.00	5.269	1.2171	1.99 ± 0.32	–	–
Mg2	0.59	4.450	1.3386	1.68 ± 0.03	2.18 ± 0.11	1.00050 ± 0.00011
Mg3	0.64	4.405	1.3385	1.22 ± 0.22	1.36 ± 0.29	1.00015 ± 0.00029
Mg4	0.68	4.422	1.3391	1.29 ± 0.20	0.69 ± 0.15	0.99939 ± 0.00015
Mg5	0.72	4.432	1.3389	0.91 ± 0.33	1.67 ± 0.22	1.00077 ± 0.00022
Mg6	0.76	4.720	1.3386	1.16 ± 0.17	1.22 ± 0.02	1.00005 ± 0.00002
Mg7	0.79	4.920	1.3382	1.20 ± 0.26	0.74 ± 0.12	0.99954 ± 0.00012
Mg8	0.90	–	–	0.81 ± 0.21	1.26 ± 0.20	1.00045 ± 0.00020

<sup>a</sup> Degree of evaporation (DE) was calculated from the ratio of the volume disappeared ( $V_t$ ) to the initial volume ( $V_0$ ) in the beaker,  $DE = V_t/V_0$ .



**Fig. 1.** The pH and density (A) of brine and  $\delta^{37}\text{Cl}$  values (B) in brines and precipitates during evaporation experiment of NaCl.

parameter in each system. Therefore, multiple measurements have shown a shift of the means. The order of fractionation factors for these three minerals is also consistent with those reported in the Qarhan Lake brine evaporation experiment (Luo et al., 2012).

The average differences between  $\delta^{37}\text{Cl}$  values for the solid and liquid of the three minerals were calculated. The mean value obtained for the NaCl precipitate-solution fractionation was 0.55‰. For KCl and MgCl<sub>2</sub>·6H<sub>2</sub>O, the mean differences are 0.25‰

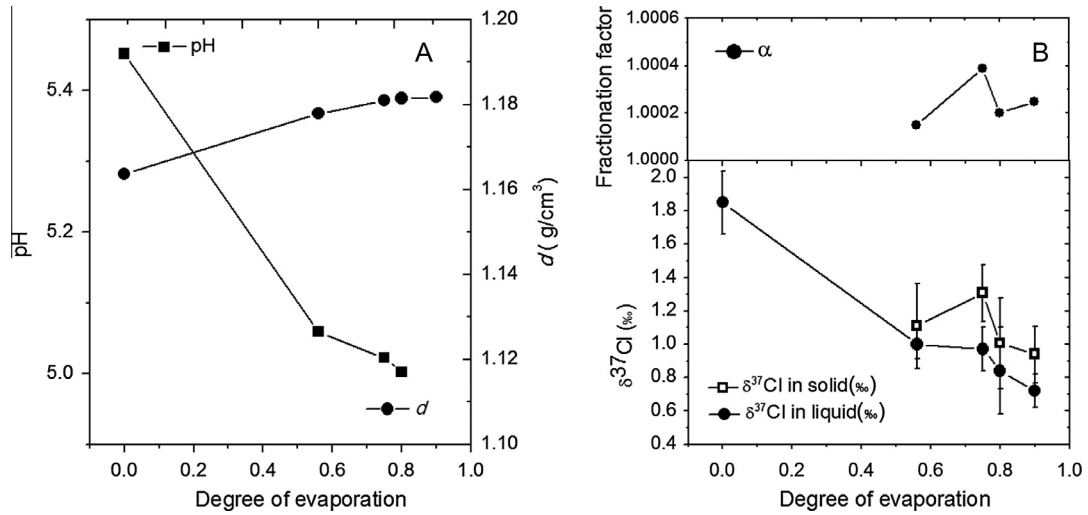


Fig. 2. The pH and density (A) of brine and  $\delta^{37}\text{Cl}$  values (B) in brines and precipitates during evaporation experiment of KCl.

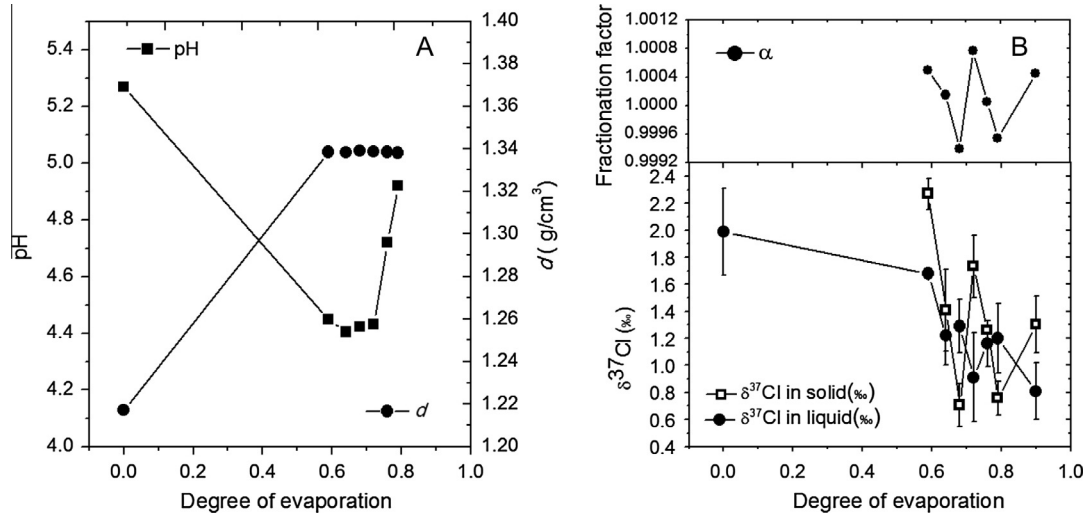


Fig. 3. The pH and density (A) of brine and  $\delta^{37}\text{Cl}$  values (B) in brines and precipitates during evaporation experiment of  $\text{MgCl}_2$ .

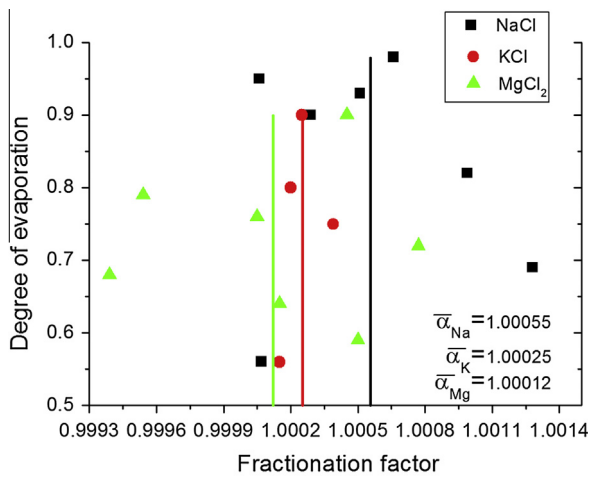


Fig. 4. Mean values of fractionation factors for NaCl, KCl, and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ .

and 0.12‰, respectively. Special attention should be paid to the capacities of  $^{37}\text{Cl}$  enrichment for NaCl and KCl where the difference between the two systems is 0.3‰, which is a slightly more than the

0.2‰ deduced from the Qarhan Salt Lake brine evaporation experiment (Luo et al., 2012) and less than the 0.8‰ predicted by Schauble et al. (2003). It is still unclear why the fractionation factors for NaCl, KCl and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  differ. These differences may be related to the crystal growth of different salts. However, among the alkali chlorides, Schauble et al. (2003) predicted a progressive decrease in the  $^{37}\text{Cl}/^{35}\text{Cl}$  ratios from NaCl to KCl and RbCl, which is consistent with the larger ionic radii and softer M–Cl bonds of the  $\text{K}^+$  and  $\text{Rb}^+$  cations relative to  $\text{Na}^+$ .

For comparison, three single chloride solutions with the same chlorine source were prepared. Initially, the  $\delta^{37}\text{Cl}$  values of NaCl, KCl, and  $\text{MgCl}_2$  were 1.82‰, 1.85‰, and 1.99‰. Therefore, the three solutions have nearly the same chlorine isotopic composition. In separate evaporation experiments, the  $\delta^{37}\text{Cl}$  values of these solutions in the last sampling were 0.37‰, 0.72‰, and 0.81‰, respectively. The evaporation experiments were only terminated when no evaporation occurred and only a small amount of brine remained. Therefore, the results of the isotopic effects for the different mineral solutions are the liquid  $\delta^{37}\text{Cl}$  values obtained in the last sampling. When evaporation stops, the  $\delta^{37}\text{Cl}$  value for NaCl, KCl, and  $\text{MgCl}_2$  decreased by 1.45‰, 1.13‰, and 1.18‰,



respectively. These results indicate that  $^{37}\text{Cl}$  will be concentrated in NaCl relative to KCl and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ .

## 5.2. Chlorine isotopic evolution during precipitation of salts from seawater

Eggenkamp et al. (1995) constructed the chlorine isotopic evolution curves during seawater evaporation. Assuming ideal Rayleigh behaviour, the  $\delta^{37}\text{Cl}$  values of the brine and precipitate from the moment the first halite precipitates can be calculated as Eqs. (2) and (3):

$$\delta^{37}\text{Cl}_{\text{liquid}} = 1000 * [(1 - m_c/m_0)^{\alpha} - 1], \quad (2)$$

$$\delta^{37}\text{Cl}_{\text{solid}} = 1000 * [(1 - m_c/m_0)^{\alpha} + \alpha - 2], \quad (3)$$

where  $m_c/m_0$  is defined as the weight fraction of chloride precipitated relative to the initial amount available. Because brine evolution is a process divided into different stages, the  $\delta^{37}\text{Cl}$  value of the brine is a piecewise continuous function, and the  $\delta^{37}\text{Cl}$  value of the precipitate is a piecewise discontinuous function. The curves of the  $\delta^{37}\text{Cl}$  values reported by Eggenkamp et al. (1995) and calculated by the new fractionation factors in this study are shown in Fig. 5.

The horizontal ordinate in Fig. 5 is  $m_c/m_0$ , and the values fall within a closed interval [0,1], among which [0,0.825] represents the halite stage, [0.825,0.869] represents the kainite stage, [0.869,0.889] represents the carnallite stage, and [0.889,1] represents the bischofite stage. From the fractionation factors obtained in this study, the Rayleigh fractionation model predicts that the  $\delta^{37}\text{Cl}$  value of the brine decreased from 0‰ to  $-0.96‰$  in the halite stage,  $-0.96‰$  to  $-1.07‰$  in the kainite stage,  $-1.07‰$  to  $-1.12‰$  in the carnallite stage and  $-1.12‰$  to  $-1000‰$  in bischofite stage. For the precipitate, the  $\delta^{37}\text{Cl}$  decreased from  $0.55‰$  to  $-0.41‰$  during the halite stage, from  $-0.56‰$  to  $-0.67‰$  in the kainite stage, from  $-0.80‰$  to  $-0.85‰$  in the carnallite stage and from  $-1.00‰$  to  $-1000‰$  in the bischofite stage.

Eggenkamp et al. (1995) reported that the  $\delta^{37}\text{Cl}$  value of the brine would decrease from 0‰ to  $-0.45‰$  during the halite stage. During the kainite and the carnallite stages, the fractionation factor is closer to unity and the decrease in  $\delta^{37}\text{Cl}$  of the brine is only 0.04‰. Because the fractionation factor in the bischofite stage is less than unity,  $\delta^{37}\text{Cl}$  must increase during the last stages of the evaporation in their study. Our results indicate that the  $\delta^{37}\text{Cl}$  of the brine decreases from 0‰ to  $-0.96‰$  during the halite stage. During the kainite and the carnallite stages, the decrease in  $\delta^{37}\text{Cl}$  of the brine is 0.16‰. If we set  $m_c/m_0$  to asymptotically approach 1, which means that nearly all of the chlorine has precipitated,

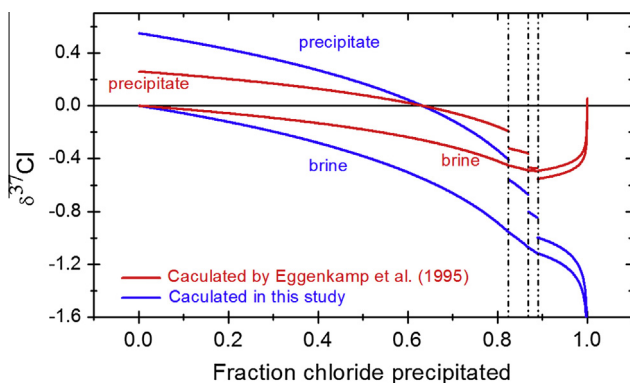


Fig. 5. Calculated  $\delta^{37}\text{Cl}$  values of the precipitate and the remaining brine during evaporation of modern seawater reported by Eggenkamp et al. (1995) and in this study.

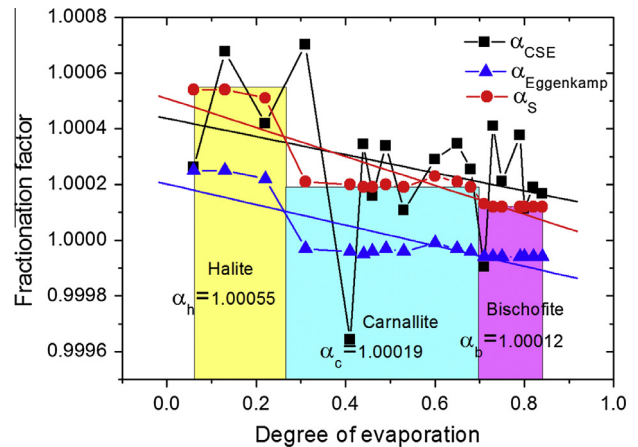


Fig. 6. Calculated fractionation factor curve in CSE experiment. CSE was the experiment that the precipitates and brines were complete separated at different stages of evaporation in Luo et al. (2012);  $\alpha_{\text{Eggenkamp}} = f_{\text{Na}} \times 1.00026 + f_{\text{K}} \times 0.99991 + f_{\text{Mg}} \times 0.99994$ ,  $\alpha_{\text{S}} = f_{\text{Na}} \times 1.00055 + f_{\text{K}} \times 1.00025 + f_{\text{Mg}} \times 1.00012$ ,  $f_{\text{Na}}$ ,  $f_{\text{K}}$  and  $f_{\text{Mg}}$  were the percentages of  $\text{Cl}^-$  precipitated as NaCl, KCl and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  reported in Luo et al. (2012);  $\alpha_{\text{CSE}}$  were the actual values determined in that paper.

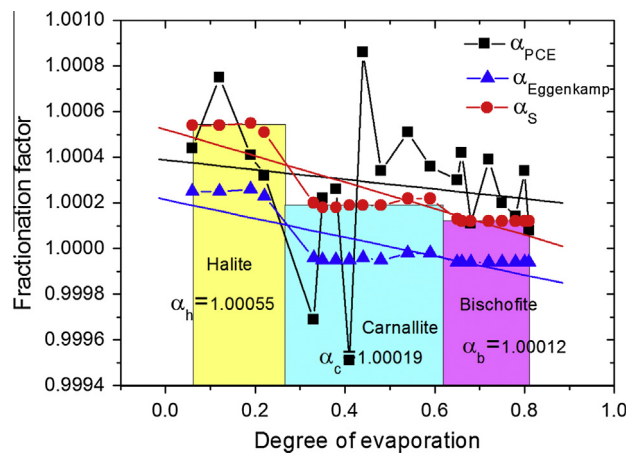
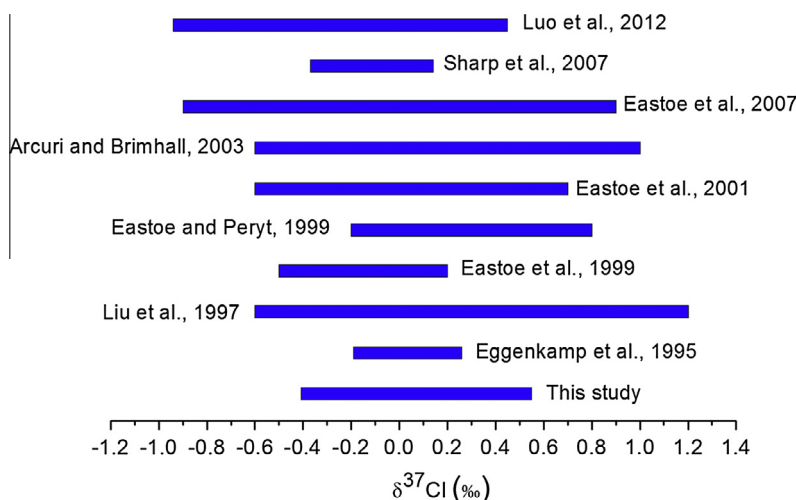


Fig. 7. Calculated fractionation factor curve in PCE experiment. PCE was the experiment that precipitation during evaporation in Luo et al. (2012);  $\alpha_{\text{Eggenkamp}} = f_{\text{Na}} \times 1.00026 + f_{\text{K}} \times 0.99991 + f_{\text{Mg}} \times 0.99994$ ,  $\alpha_{\text{S}} = f_{\text{Na}} \times 1.00055 + f_{\text{K}} \times 1.00025 + f_{\text{Mg}} \times 1.00012$ ,  $f_{\text{Na}}$ ,  $f_{\text{K}}$  and  $f_{\text{Mg}}$  were the percentages of  $\text{Cl}^-$  precipitated as NaCl, KCl and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  reported in Luo et al. (2012);  $\alpha_{\text{PCE}}$  were the actual values determined in that paper.

the existing limit for the  $\delta^{37}\text{Cl}$  values in brine is  $-1000.0‰$ . The major difference between the two studies is in the Mg and K–Mg salt stages. Therefore, the isotopic composition of the highly evaporated Mg and K–Mg salts are lighter than that of the preceding salts in the late halite stage, and their  $\delta^{37}\text{Cl}$  values vary towards a lower level.

Eggenkamp et al. (1995) also reported the  $\delta^{37}\text{Cl}$  variation of the precipitate, which decreased from  $0.26‰$  to  $-0.19‰$  during the halite stage. During the kainite stage,  $\delta^{37}\text{Cl}$  further decreased to approximately  $-0.34‰$ , and it decreased to  $-0.47‰$  during the carnallite stage. In this study, the  $\delta^{37}\text{Cl}$  of the precipitate decreased from  $0.55‰$  to  $-0.41‰$  during the halite stage. During the kainite stage,  $\delta^{37}\text{Cl}$  further decreased to approximately  $-0.67‰$ , and it decreased to  $-0.85‰$  during the carnallite stage. If we set  $m_c/m_0$  to asymptotically approach 1, the existing limit for the  $\delta^{37}\text{Cl}$  values in the solid was  $-1000.0‰$ , which is not possible in nature.



**Fig. 8.** Ranges of published  $\delta^{37}\text{Cl}$  values of various halites. References as follows: Eggenkamp et al., 1995; Liu et al., 1997; Eastoe et al., 1999, 2001, 2007; Eastoe and Peryt, 1999; Arcuri and Brimhall, 2003; Sharp et al., 2007; Luo et al., 2012.

### 5.3. Interpretation of evaporation experiments of salt lake brine (Luo et al., 2012)

There are different stages in the evaporation process for natural brine. The salts that precipitated in different stages have different capacities for enrichment of  $^{37}\text{Cl}$ , which causes differences in contributions to a low  $^{37}\text{Cl}$  in natural brine. For natural brine in Qarhan Lake, the largest contributor was NaCl, but in the later stage of the brine evolution, NaCl has undergone a large amount of precipitation (Luo et al., 2012).  $\text{Na}^+$  is no longer the dominant cation in the liquid. Chloride salts containing elements, such as Mg and K, contribute the most to changes in the isotopic compositions of chlorine in the brine. In the last stage of the brine evolution,  $\text{Mg}^{2+}$  is the major cation in the liquid, and chloride salt containing Mg contributes the most to changes in the isotopic compositions of chlorine in the brine. Regarding the trend for  $\delta^{37}\text{Cl}$ , no primary change in the chlorine isotopic evolution of brine was observed, and therefore, natural brine always has a lower  $\delta^{37}\text{Cl}$  value in the latter stage. Because NaCl has a stronger  $^{37}\text{Cl}$  collection capability compared to the other chlorides containing Mg and K, the isotopic fractionation between the precipitate and brine decreased. Therefore, in different crystallisation stages during brine evolution, the brine exhibited similar tendencies and various characteristics caused by the effects of different precipitated salts. In addition, due to the effects of the actual environment, the same salt mineral exhibited differences in chlorine isotopic fractionation in the brine.

Based on the Na/K/Mg ratios of the precipitating salts in the evaporation experiments (Luo et al., 2012), new fractionation factors ( $\alpha_S$  and  $\alpha_{\text{Eggenkamp}}$ ) were calculated through Eqs. (4) and (5). Single chlorides fractionation factors determined in this study and by Eggenkamp et al. (1995) were used.

$$\alpha_S = f_{\text{Na}} * 1.00055 + f_{\text{K}} * 1.00025 + f_{\text{Mg}} * 1.00012, \quad (4)$$

$$\alpha_{\text{Eggenkamp}} = f_{\text{Na}} * 1.00026 + f_{\text{K}} * 0.99991 + f_{\text{Mg}} * 0.99994, \quad (5)$$

where  $f_{\text{Na}}$ ,  $f_{\text{K}}$  and  $f_{\text{Mg}}$  were the percentages of  $\text{Cl}^-$  precipitated as NaCl, KCl and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , respectively. The results and actual fractionation factors are shown in Fig. 6 and 7.

The fractionation factors determined in the natural brine evaporation experiments also reflect the fractionation characteristics of single chloride solutions. Three single chloride fractionation properties can explain these changes in the natural brine evaporation (i.e., the fractionation factors ( $\alpha_h = 1.00055$ ) between halite and brine are the highest followed by that ( $\alpha_c = 1.00019$ ) between

carnallite and brine and then by that ( $\alpha_b = 1.00012$ ) between bischofite and brine). The results of the evaporation experiments for the single chloride solutions have demonstrated the reliability of the evaporation experiments for natural saline lake brine (Luo et al., 2012). The results in Figs. 5, 6 and 7 indicate that the single chloride solution curve (the red curve<sup>1</sup>) of the isotopic fractionation factor is consistent with the curve for the natural brine evaporation experiments (the black curve). Using the three single chloride fractionation factors reported by Eggenkamp et al. (1995), we calculated the fractionation factor curve (the blue curve) shown in Figs. 6 and 7. The results show that this curve is not consistent with the curve from the natural brine evaporation experiments (the black curve). The results indicate that the three single chloride fractionation factors reported by Eggenkamp et al. (1995) do not fit the interpretation of the natural brine evaporation experiments.

### 5.4. $\delta^{37}\text{Cl}$ values of halites

The ranges of the published  $\delta^{37}\text{Cl}$  values of various halites are shown in Fig. 8. Luo et al. (2012) reported the determined fractionation between crystalline NaCl and the coexisting brine (from  $-0.94\text{‰}$  to  $0.45\text{‰}$ ). In this study, the range is from  $-0.41\text{‰}$  to  $0.55\text{‰}$ , which are also larger than that reported by Eggenkamp et al. (1995) (from  $-0.19\text{‰}$  to  $0.26\text{‰}$ ). Although the  $\delta^{37}\text{Cl}$  values for the halite have a wider range due to the addition of  $\text{Cl}^-$  of non- $0.0\text{‰}$   $\delta^{37}\text{Cl}$  to the evaporite brine, our knowledge of isotopic fractionation between precipitates and brines is still insufficient.

Eastoe et al. (2007) have calculated  $\delta^{37}\text{Cl}$  for the bulk halite removed from seawater. The  $\delta^{37}\text{Cl}$  value of the accumulated halite was calculated using Eq. (6):

$$\delta_{(\Sigma\text{halite})} = \delta_0 + \varepsilon * \ln(f) - \varepsilon \ln(f)/(1 - f), \quad (6)$$

where  $\delta_0$  is the initial  $\delta^{37}\text{Cl}$  value of the brine reservoir (given the value  $0.0\text{‰}$ ),  $f$  is the residual  $\text{Cl}^-$  fraction in the brine, and  $\varepsilon$  is  $\delta^{37}\text{Cl}$  (halite)– $\delta^{37}\text{Cl}$  (brine). Given a value of  $0.26\text{‰}$  for  $\varepsilon$  (Eggenkamp et al., 1995), the range for  $\delta_{(\Sigma\text{halite})}$  is between  $0.26\text{‰}$  ( $f$  approaching 1) and  $0.13\text{‰}$  ( $f = 0.3$ , at the onset of bitter salt formation). However, given a value of  $0.55\text{‰}$  for  $\varepsilon$  obtained in this study, the range for the halite facies becomes  $0.27\text{‰}$  (between

<sup>1</sup> For interpretation of colour in Figs. 5, 6 and 7, the reader is referred to the web version of this article.

0.55‰ and 0.28‰), which is larger than that calculated using the value reported by Eggenkamp et al., but still not sufficiently large to explain the range of  $\delta^{37}\text{Cl}$  values measured in marine halite facies. There may be a difference in brines with different origins and evolutions. For example, the brines that primarily come from the bulk halite separated from the coexisting brine may possess a higher  $\delta^{37}\text{Cl}$  value.

## 6. Conclusion

- (1) With constant evaporation, the  $\delta^{37}\text{Cl}$  values for the NaCl, KCl, and  $\text{MgCl}_2$  solutions significantly decreased.
- (2) The capacities of  $^{37}\text{Cl}$  enrichment for the precipitated NaCl, KCl, and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  successively decreased. The  $\delta^{37}\text{Cl}$  values for these three minerals are 0.55‰, 0.25‰, and 0.12‰, respectively more than those of the coexisting brine, and the mean fractionation factors of the three solutions are  $\alpha_{\text{Na}} = 1.00055$ ,  $\alpha_{\text{K}} = 1.00025$ , and  $\alpha_{\text{Mg}} = 1.00012$ , respectively.
- (3) Fractionation differences for various minerals significantly influence chlorine isotope evolution for the single chloride brine. The  $\delta^{37}\text{Cl}$  values for the three solutions with the same initial chlorine isotopic composition decreased by 1.45‰, 1.13‰, and 1.18‰, respectively, when no evaporation occurred.
- (4) By combining these fractionation factors for the single chloride minerals, the chlorine isotopic evolution curves for seawater evaporation was recalculated. The  $\delta^{37}\text{Cl}$  value of the brine decreased from 0‰ to  $-0.96$ ‰ in the halite stage,  $-0.96$ ‰ to  $-1.07$ ‰ in the kainite stage,  $-1.07$ ‰ to  $-1.12$ ‰ in the carnallite stage and  $-1.12$ ‰ to  $-1000.0$ ‰ in the bischofite stage. For the precipitate,  $\delta^{37}\text{Cl}$  decreased from 0.55‰ to  $-0.41$ ‰ during the halite stage,  $-0.56$ ‰ to  $-0.67$ ‰ in the kainite stage,  $-0.80$ ‰ to  $-0.85$ ‰ in the carnallite stage and  $-1.00$ ‰ to  $-1000.0$ ‰ in the bischofite stage. However,  $-1000.0$ ‰ is the limiting value, which do not occur in natural samples.
- (5) Analysis and comparison indicated that the chlorine isotopic evolution of natural brine was controlled by single chloride fractional properties. The results of the evaporation experiments for the single chloride solutions can explain the phenomena observed in the evaporation experiments of natural saline lake brine.

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## References

- Arcuri, T., Brimhall, G., 2003. The chloride source for atacamite mineralization at the Radomiro Tomic porphyry copper deposit, Northern Chile. *Econ. Geol.* 98, 1667–1681.
- Banks, D.A., Green, R., Cliff, R.A., Yardley, B.W.D., 2000a. Chlorine isotopes in fluid inclusions: determination of the origins of salinity in magmatic fluids. *Geochim. Cosmochim. Acta* 64 (10), 1785–1789.
- Banks, D.A., Gleeson, S.A., Green, R., 2000b. Determination of the origin of salinity in granite-related fluids: evidence from chlorine isotopes in fluid inclusions. *J. Geochem. Explor.* 69–70, 309–312.
- Barnes, J.D., Sharp, Z.D., Fischer, T.P., 2008. Chlorine isotope variations across the Izu-Bonin-Mariana arc. *Geology* 36, 883–886.
- Barnes, J.D., Sharp, Z.D., Fischer, T.P., Hilton, D.R., Carr, M.J., 2009. Chlorine isotope variations along the Central American volcanic front and back arc. *Geochem. Geophys. Geosyst.* 10. <http://dx.doi.org/10.1029/2009GC002587>.
- Chen, Y.H., 1983. Sequence of salt separation and regularity of some trace elements distribution during isothermal evaporation (25°C) of the Huanghai sea water. *Acta Geol. Sin.* 57 (4), 379–390 (in Chinese with English abstract).
- Chiaradia, M., Banks, D.A., Cliff, R., Marschik, R., de Haller, A., 2006. Origin of fluids in iron oxide–copper–gold deposits: constraints from  $\delta^{37}\text{Cl}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$  and Cl/Br. *Miner. Deposita* 41 (6), 565–573.
- Eastoe, C.J., Long, A., Knauth, L.P., 1999. Stable chlorine isotopes in the Palo Duro Basin, Texas: evidence of preservation of Permian evaporite brines. *Geochim. Cosmochim. Acta* 63 (9), 1375–1382.
- Eastoe, C.J., Peryt, T., 1999. Multiple sources of chloride in Badenian evaporites, Carpathian Mountains: Stable chlorine isotope evidence. *Terra Nova* 11, 118–123.
- Eastoe, C.J., Long, A., Land, L.S., Kyle, J.R., 2001. Stable chlorine isotopes in halite and brine from the Gulf Coast Basin: brine genesis and evolution. *Chem. Geol.* 176 (1–4), 343–360.
- Eastoe, C.J., Peryt, T.M., Petrychenko, O.Y., Geisler-Cussey, D., 2007. Stable chlorine isotopes in Phanerozoic evaporites. *Appl. Geochem.* 22 (3), 575–588.
- Eggenkamp, H.G.M., 1994.  $\delta^{37}\text{Cl}$ : The Geochemistry of Chlorine Isotope. PhD Thesis, Utrecht Univ. 150 pp.
- Eggenkamp, H.G.M., Kreulen, M.R., Koster Van Groos, A.F., 1995. Chlorine stable isotope fractionation in evaporites. *Geochim. Cosmochim. Acta* 59 (24), 5169–5175.
- Gleeson, S.A., Smith, M.P., 2009. The sources and evolution of mineralising fluids in iron oxide–copper–gold systems, Norrbotten, Sweden: constraints from Br/Cl ratios and stable Cl isotopes of fluid inclusion leachates. *Geochim. Cosmochim. Acta* 73 (19), 5658–5672.
- Godon, A., Jendzejewski, N., Eggenkamp, H.G.M., Banks, D.A., Ader, M., Coleman, M.L., Pineau, F., 2004. A cross calibration of chlorine isotopic measurements and suitability of seawater as the international reference material. *Chem. Geol.* 207, 1–12.
- Kaufmann, R.S., 1984. Chlorine in Ground Water: Stable Isotope Distribution. PhD Thesis, Tucson (Arizona) Univ. 137 pp.
- Kaufmann, R., Long, A., Bentley, H., Davis, S., 1984. Natural chlorine isotope variations. *Nature* 309, 338–340.
- Liu, W.G., Xiao, Y.K., Sun, D.P., Qi, H.P., Wang, Y.H., Jin, L., Zhou, Y.M., 1995. A preliminary study of chlorine isotopic composition of salt lakes in the Qaidam Basin. *Chin. Sci. Bull.* 40 (8), 699–700.
- Liu, W.G., Xiao, Y.K., Wang, Q.Z., Qi, H.P., Wang, Y.H., Zhou, Y.M., Shirodkar, P.V., 1997. Chlorine isotopic geochemistry of salt lakes in the Qaidam Basin, China. *Chem. Geol.* 136 (3–4), 271–279.
- Liu, W.G., Xiao, Y.K., Han, F.Q., Peng, Z.C., 1998. Characteristics of chlorine isotopes in salt lakes of Kuntuyi and their significance of paleoclimate. *Oceanol. Limnol. Sin.* 29 (4), 431–435 (in Chinese with English abstract).
- Lu, H., Xiao, Y.K., 2001. The effects of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  on the isotopic measurement of chlorine and their elimination. *Salt Lake Sci.* 9, 7–12 (in Chinese with English abstract).
- Luo, C.G., Xiao, Y.K., Ma, H.Z., Ma, Y.Q., Zhang, Y.L., He, M.Y., 2012. Stable isotope fractionation of chlorine during evaporation of brine from a saline lake. *Chin. Sci. Bull.* 57 (15), 1833–1843.
- Magenheim, A.J., Spivack, A.J., Michael, P.J., Gieskes, J.M., 1995. Chlorine stable isotope composition of the oceanic crust: implications for Earth's distribution of chlorine. *Earth Planet. Sci. Lett.* 131, 427–432.
- Nahnybida, T., Gleeson, S.A., Rusk, B.G., Wassenaar, L.I., 2009. Cl/Br ratios and stable chlorine isotope analysis of magmatic-hydrothermal fluid inclusions from Butte, Montana and Bingham Canyon, Utah. *Mineral. Deposita* 44 (8), 837–848.
- Nakamura, N., Nyquist, L.E., Reese, Y., Shih, C.-Y., Fujitani, T., Okano, O., 2011. Stable chlorine isotopes and elemental chlorine by thermal ionization mass spectrometry and ion chromatography: Martian meteorites, carbonaceous chondrites, and standard rocks. *Lundar Planet. Sci. Conf.*, 42, # 2513.
- Numata, M., Nakamura, N., Koshikawa, H., Terashima, Y., 2002. Chlorine stable isotope measurements of chlorinated aliphatic hydrocarbons by thermal ionization mass spectrometry. *Anal. Chim. Acta* 455, 1–9.
- Ransom, B., Spivack, A.J., Kastner, M., 1995. Stable Cl isotopes in subduction-zone pore water: Implications for fluid-rock reactions and the cycling of chlorine. *Geology* 23, 715–718.
- Rosenbaum, J.M., Cliff, R.A., Coleman, M.L., 2000. Chlorine stable isotopes: a comparison of dual inlet and thermal ionization mass spectrometric measurements. *Anal. Chem.* 72, 2261–2264.
- Richard, A., Banks, D.A., Mercadier, J., 2011. An evaporated seawater origin for the ore-forming brines in unconformity-related uranium deposits (Athabasca Basin, Canada): Cl/Br and  $\delta^{37}\text{Cl}$  analysis of fluid inclusions. *Geochim. Cosmochim. Acta* 75 (10), 2792–2810.
- Schauble, E.A., Rossman, G.R., Taylor Jr, H.P., 2003. Theoretical estimates of equilibrium chlorine-isotope fractionations. *Geochim. Cosmochim. Acta* 67 (17), 3267–3281.
- Sharp, Z.D., Barnes, J.D., Brearley, A.J., Chaussidon, M., Fischer, T.P., Kamenetsky, V.S., 2007. Chlorine isotope homogeneity of the mantle, crust and carbonaceous chondrites. *Nature* 446, 1062–1065.
- Shirodkar, P.V., Xiao, Y.K., Sarkar, A., Dalal, S.G., Chivas, A.R., 2006. Influence of air-sea fluxes on chlorine isotopic composition of ocean water: Implications for constancy in  $\delta^{37}\text{Cl}$ —a statistical inference. *Environ. Int.* 32 (2), 235–239.
- Sun, D.P., Shuai, K.Y., Gao, J.H., Liu, W.G., Zhou, Y.M., Ma, Y.H., 1998. A preliminary investigation on stable isotopic geochemistry of chlorine for the sylvinitic



- deposits of chloride-type. *Geoscience* 12 (2), 80–85 (in Chinese with English abstract).
- Tan, H.B., Ma, H.Z., Zhang, X.Y., Xu, J.X., Xiao, Y.K., 2009. 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. *Acta Petrol Sinica* 25, 955–962 (in Chinese with English abstract).
- Volpe, C., Spivack, A.J., 1994. Stable chlorine isotopic composition of marine aerosol particles in the western Atlantic Ocean. *Geophys. Res. Lett.* 21, 1161–1164.
- Volpe, C., Wahlen, M., Pszeny, A.A.P., Spivack, A.J., 1998. Chlorine isotopic composition of marine aerosols: implications for the release of reactive chlorine and HCl cycling rates. *Geophys. Res. Lett.* 25, 3831–3834.
- Wei, H.Z., Jiang, S.Y., Xiao, Y.K., Wang, J., Lu, H., Wu, B., Wu, H.P., Li, Q., Luo, C.G., 2012. Precise determination of the absolute isotopic abundance ratio and the atomic weight of chlorine in three international reference materials by positive thermal ionization mass spectrometry  $Cs_2Cl^+$ -graphite method. *Anal. Chem.* 84 (23), 10350–10358.
- Wei, W., Kastner, M., Spivack, A., 2008. Chlorine stable isotopes and halogen concentrations in convergent margins with implications for the Cl isotopes cycle in the ocean. *Earth Planet. Sci. Lett.* 266, 90–104.
- Xiao, Y.K., Zhang, C.G., 1992. High precision isotopic measurement of chlorine by thermal ionization mass spectrometry of the  $Cs_2Cl^+$  ion. *Int. J. Mass Spectrom. Ion Processes* 116 (3), 183–192.
- Xiao, Y.K., Liu, W.G., Zhang, C.G., 1994. The preliminary investigation on chlorine isotopic fractionation during the crystallization of saline minerals in salt lake. *Salt Lake Sci.* 2 (3), 35–40 (in Chinese with English abstract).
- Xiao, Y.K., Liu, W.G., Zhou, Y.M., 1997. Isotopic compositions of chlorine in brine and saline minerals. *Chin. Sci. Bull.* 42 (6), 406–409.
- Xiao, Y.K., Liu, W.G., Zhou, Y.M., Wang, Y.H., 2000. Variations in isotopic compositions of chlorine in evaporation-controlled salt lake brines of Qaidam Basin, China. *Chin. J. Oceanol. Limnol.* 18 (2), 169–177.
- Xiao, Y.K., Zhou, Y.M., Wang, Q.Z., Wei, H.Z., Liu, W.G., Eastoe, C.J., 2002. A secondary isotopic reference material of chlorine from selected seawater. *Chem. Geol.* 182 (2–4), 655–661.
- Zhou, Y.M., Xiao, Y.K., Hong, A.S., Liu, W.G., Wang, Y.H., 1998. The variation of stable chlorine isotopic composition in ocean. *Salt Lake Sci.* 6 (1), 34–40 (in Chinese with English abstract).