VARIATIONS IN ISOTOPIC COMPOSITIONS OF CHLORINE IN EVAPORATION-CONTROLLED SALT LAKE BRINES OF QAIDAM BASIN, CHINA *

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Abstract   The variations in the isotopic compositions of chlorine in evaporation-controlled saline lake brines were determined by using an improved procedure for precise measurement of chlorine isotopes based on Cs_2Cl^+ ion by thermal ionization mass spectrometry. The results showed that variation in $\delta^{37}Cl$ values in these evaporation-controlled brines are attributable to evaporation of brine accompanied by the deposition of saline minerals. The isotopic fractionation of chlorine between the deposited saline mineral and the co-existing brine caused the variation of $\delta^{37}Cl$ values in the brine. In general the isotopic fractionation of chlorine in nature indicates enrichment of ^{37}Cl in the solid phase relative to ^{35}Cl. The reverse isotopic fractionation of chlorine in which ^{35}Cl is enriched in the solid phase, was observed to some extent during quick deposition under laboratory conditions as well as in nature. The mechanism of isotopic fractionation of chlorine during evaporation deposition was studied.

Key words: chlorine, isotopic composition, salt lakes

INTRODUCTION

Chlorine has two naturally occuring stable isotopes, ^{35}Cl and ^{37}Cl. Several studies reported the variations in the isotopic composition of chlorine in nature. However, in the early years Owen and Schaeffer (1955) reported no observable difference in the $^{37}Cl/^{35}Cl$ ratios in ten samples examined (within experimental error of 0.2%) using the procedure based on methylchloride. Hoering and Parker (1961) observed no significant variations in the $^{37}Cl/^{35}Cl$ ratio of 81 natural samples. Subsequently, variations of chlorine $\delta^{37}Cl$ values in nature were confirmed after a precision better than 0.02% had been achieved. Desaulniers et al. (1986) reported $\delta^{37}Cl$ value variations from -0.8×10^{-3} to 2.2×10^{-3} with gradual increase in ^{37}Cl, with increasing distance upward in a diffusion-controlled groundwater systems. The isotopic fractionation of chlorine in ore-forming hydrothermal system was reported by Eastoe et al. (1989). $\delta^{37}Cl$ values of chlorine from the fluid inclusions in hydrothermal minerals was found (with precision of 0.016%) to range from -1.1×10^{-3} to 0.8×10^{-3}, relative to the ocean chlorine standard collected from San Diego. Eastoe and Guibert (1992) studied (with analytical precision of 0.02%) the stable chlorine isotopes in hydrothermal

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processes and reported that relative to standard mean ocean chlorine, δ^{37}Cl values were -1.0×10^{-3} to 0.5×10^{-3} in hydrothermal fluids from ore-forming systems, -1.0×10^{-3} to 0.8×10^{-3} in formation waters from sedimentary basins and 0.3×10^{-3} to 1.7×10^{-3} in biotites. Kaufmann et al. (1988) reporting on the distribution of chlorine isotopes in formation waters, said that the δ^{37}Cl in 18 formation water samples were -1.2×10^{-3} to 0.6×10^{-3} (precision of 0.012%) relative to standard mean ocean chlorine, and that this finding indicated enrichment of ^{37}Cl with increasing concentration of chlorine.

A new procedure developed for measurement of chlorine isotopes based on positive thermal ionization mass spectrometry (PTIMS) of Cs_2Cl^+ ion (Xiao and Zhang, 1992; Magenheim et al., 1994) has precision of better than 0.02% (2σ) (Xiao et al., 1995). In the present study, a new procedure with greater precision using PTIMS was used. The PTIMS procedure described here involves simpler treatment of sample than that using CH_3Cl and the $^{37}Cl/^{35}Cl$ ratio can be directly calculated from $^{133}Cs_2{}^{37}Cl^+$ and $^{133}Cs_2{}^{35}Cl^+$ ion beams using PTIMS procedure.

Geography and geology of the studied area

The 1.21×10^5 km^2 Qaidam Basin, with elevation ranging from 2675 – 3171m a.s.l., is the largest down-fault basin in the Qinghai-Xizhang Plateau; is located in the northwestern part of Qinghai Province; and is surrounded by the Aerjing Mountains in the northwest, the Qilian Mountains in the northeast and the Kunlun Mountains in the south. The altitude of the surrounding mountains ranges from 4200 – 5000 m. This area has very dry climate and about 28 – 30 mm of precipitation and 3000 mm evaporation per year (Cheng, 1991). The evaporation is 100 times higher than the precipitation. Consequently, many contemporary salt lakes were formed in the Qaidam Basin. Most of the salt lakes have surface brine, 0.02 m to 0.5 m thick. The average TDS of the brines is 340.7 g/L, maximum 555 g/L. The Qaidam Basin brines are characterized by high salinity, have average contents of 68.4 g Na$^+$, 35.1 g Mg^{2+}, 6.00 g K$^+$, 4.24 g Ca^{2+}, 204 g Cl$^-$, 22.3 g SO$_4^{2-}$, 0.17 g CO$_3^{2-}$ and 0.13 g HCO$_3^-$ per liter (Zhang, 1987). A variety of saline mineral deposits, such as halite, gypsum, mirabilite, borate and potash deposits were found on the bottoms of these salt lakes.

The sampling locations in Qaidam Basin are shown in Fig. 1. The brine and saline mineral samples were collected in July, 1992. The pH and density of the brine samples were measured at the time of sampling. Pure crystals of NaCl were separated from the saline minerals for isotopic analyses. A classical silver nitrate titration procedure was used to estimate the chloride content of the brines (Qinghai Institute of Salt Lakes, 1988).

EXPERIMENTAL DETAILS

Sample preparation for mass spectrometry procedure

Twenty to forty mg of chloride mineral (halite) was dissolved in 0.5 – 1.0 ml of water or an amount of brine sample containing about 5 mg of chlorine in a volume of 0.5 – 1.0 ml was taken. About 0.5 g each of dry Ba-form resin and dry H-form resin were successively added to the above solutions which were then allowed to stand for 5 min. After discarding the resins, the clear solutions containing chloride were adjusted to pH 3 – 4 by adding Cs_2CO_3 solution. The resulting concentra-

tion of the test solution was 5 – 10 mg/ml of Cl.

Mass spectrometry procedure

The procedure described here is essentially the same as that reported previously by Xiao and Zhang (1992) but with slight modification (Xiao et al., 1995). The filaments were first treated with 3 μg of graphite slurry containing about 100 μg of graphite to coat the center of the filament. Next, 2 μg of the test solution containing about 10 μg of chlorine as CsCl was loaded and then dried by a current of 1.1A for 3 min.
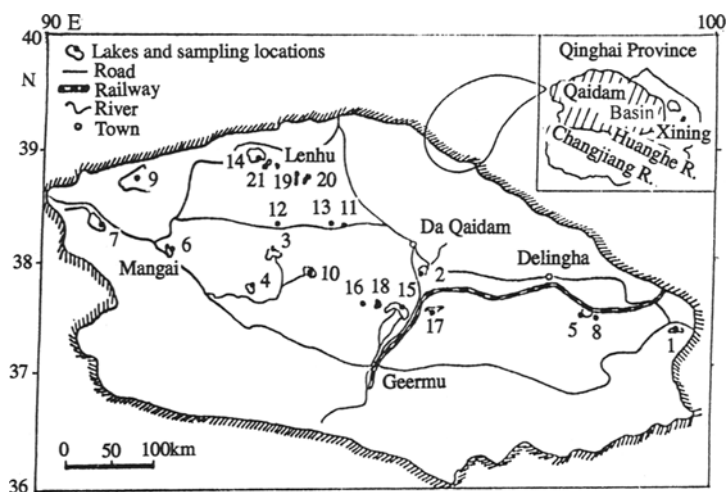

Fig.1   The sampled locations of salt lake brine in Qaidam Basin

A VG 354 mass spectrometer was used for this study. The isotopic analyses were started when the base pressure in the source section reached 3×10^{-5} Pa. The filament current was increased to 1.05 A over 10 min. The Cs_2Cl^+ ion was monitored and used to focus the instrument. The intensity of the Cs_2Cl^+ ion was adjusted to $(6-8) \times 10^{-12}$ A by controlling the filament current. The data were collected on a Faraday cup by switching magnetically between the masses $301(^{133}Cs_2{}^{35}Cl)$ and $303(^{133}Cs_2{}^{37}Cl)$. The isotopic composition of chlorine in the studied samples are expressed as $\delta^{37}Cl$ (10^{-3}) relative to standard seawater collected at 80°00'E, 63°58'S. The $^{37}Cl/^{35}Cl$ value of seawater was repeatedly measured to be $0.319084 \pm 0.000050(2\sigma)$ with a precision of 0.016% (Xiao et al., 1995). The calculation of $\delta^{37}Cl$ (10^{-3}) is shown below:

$$\delta^{37}Cl \ (10^{-3}) = [(^{37}Cl/^{35}Cl)_{sam} \div (^{37}Cl/^{35}Cl)_{sea} -1] \times 1000$$

Here $(^{37}Cl/^{35}Cl)_{sea} = 0.319084$.

RESULTS AND DISCUSSION

Distribution of the isotopic compositions of chlorine in evaporation-controlled saline lake brines

The data (Table 1) indicate the $\delta^{37}Cl$ values in the salt lakes brines ranged from $-2.05 \times$

10^{-3} to 1.01×10^{-3} (mean of -0.45×10^{-3}) relative to standard ocean water from the Indian Ocean. The variation in the isotopic composition of chlorine related to pH, density and the chloride concentrations as shown in Figs 2, 3. The $\delta^{37}Cl$ values decreased with decrease of pH and increase

Table 1   The isotopic compositions of chlorine in brine of Qaidam Basin

| Location No	Lakes	pH	Density	Contents (g/L)	$\delta^{37}Cl(10^{-3})$ Brine	Solid	Fractionation factor
1	Chaka	7.31	1.052	45	0.21	0.26	1.0001
2	Xiao Qaidam	8.14	1.126	83	1.01	–	–
3	Xitai	7.60	1.147	120	– 0.12	–	–
4	Taerding	7.37	1.255	124	– 0.22	– 0.08	1.0001
5	Qaikai	7.68	1.158	136	– 0.30	0.16	1.0005
6	Mongai	7.49	1.250	150	0.10	–	–
7	Gasikule	7.10	1.109	171	– 0.53	– 0.52	1.0000
8	Keke	7.25	1.221	185	– 0.06	– 0.08	1.0000
9	Dalangtan	7.06	1.223	186	– 0.31	0.32	1.0006
10	Dongtai	6.99	1.266	187	0.17	– 0.16	0.9997
11	Nanbaxian	7.16	1.205	190	0.43	–	–
12	Yiliping	7.03	1226	195	– 0.77	– 0.29	1.0005
13	Balen	6.50	1.207	195	0.53	1.20	1.0007
14	Kunteyi	6.65	1.212	199	– 0.47	– 0.60	0.9999
15	Dabusun	6.80	1.233		– 0.56	–	–
16	Bielie	5.84	1.282	240	– 0.98	– 0.53	1.0004
17	Xiezuo	5.63	1.263	252	– 1.38	–	–
18	Daxi	6.07	1.282		– 1.15	–	–
19	Liulang	5.34	1.284	277	– 1.50	– 0.37	1.0011
20	Zhinu	4.43	1.300		– 1.55	– 0.48	1.0011
21	Jiahu	4.62	1.300	293	– 2.05	0.02	1.0021
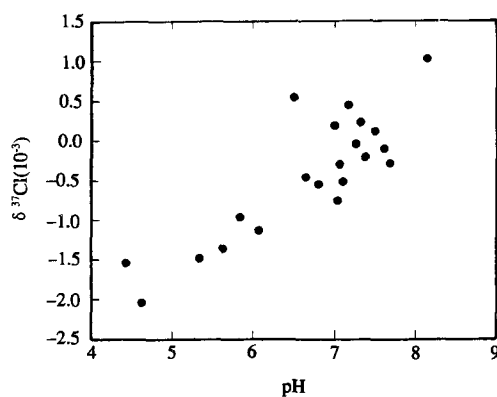
Fig.2   Variation of $\delta^{37}Cl$ vs pH in salt lake brine
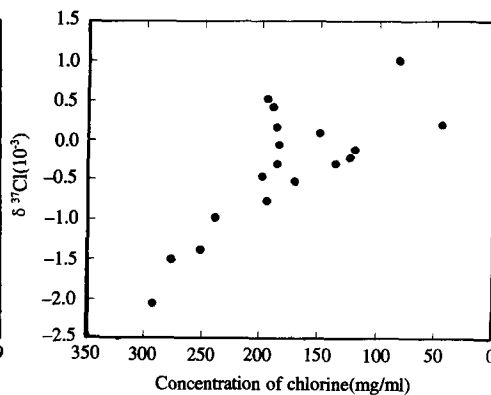
Fig.3   Variation of $\delta^{37}Cl$ vs concentration of chlorine in brine

of chloride concentrations. Zhang (1987) showed that the TDS of brine was related to evaporation and that the pH of the brines decreased with increase in density. The evaporation of brine caused decrease in pH and increase in density and chloride concentrations. Consequently, the $\delta^{37}Cl$ values decreased with the decrease of pH and increase of density during evaporation. Desaulniers et al. (1986) reported the ^{35}Cl to ^{37}Cl variations in a diffusion-controlled groundwater system. The results showed a gradual increase in ^{35}Cl relative to ^{37}Cl in ground water accompanied by decrease in Cl⁻ with distance upward from the bedrock. Upward diffusion in the transport of chlorine caused the enrichment of ^{37}Cl.

The mechanism of enrichment of ^{35}Cl in salt lake brines is very different from that in diffusion controlled groundwater systems. This enrichment of ^{35}Cl with increase of Cl⁻ was apparently caused by the deposition of saline minerals during evaporation of brine. Various investigations (Xiao et al., 1994a; Vengosh et al,, 1989) showed that the ^{37}Cl preferentially enters into the solid phase during the incorporation of dissolved chloride into chloride salts. The factor of fractionation between the liquid and the solid phase was reported to be 1.0002 by Hoering and Parker (1961). The results for Da Qaidam Lake (Xiao et al., 1994 b) indicated that the isotopic fractionation factor of chlorine in the saline minerals and chlorine in the co-existing brine was 1.0006, much higher than the 1.0002 reported above. The isotopic fractionation of chlorine in the salt and chlorine in the co-existing brine in Qaidam Basin as observed in this study (Table 1) indicated unusually higher $\delta^{37}Cl$ values in solids than in the co-existing brine. The average fractionation factor defined as $[(^{37}Cl/^{35}Cl)_{solid}/(^{37}Cl/^{35}Cl)_{liquid}]$ was 1.0005, ranging from 0.9997 to 1.0021, which indicated reverse isotopic fractionation of chlorine in some surface brines, i.e., the enrichment of ^{35}Cl in solid phase. However, the fractionation factors of chlorine in the interstitial brine and chlorine in the co-existing solid were always higher than 1.000, which indicated stable deposit environment in the interstitial brine.

Variations of chlorine isotopic composition during evaporation in laboratory experiment

A laboratory experiment was carried out with natural salt lake brine from Chaerhan Lake in Qaidam Basin. Brine(5000 ml) in a large container was evaporated at 25 – 28°C in an oven in clean environment. The rate of evaporation was about 60 ml per day at the start and gradually decreased to about 1 ml per day at the end of the three months experiment.

Table 2   The chemical compositions in residual brine and solid during evaporation
of brine under laboratory condition (w/w, %)

Step	In residual brine						In deposition					
	Na	K	Mg	Ca	Cl	SO₄	Na	K	Mg	Ca	Cl	SO₄
*	2.44	1.33	4.80	0.06	18.8	0.32						
1	1.52	1.56	5.62	0.05	20.0	0.27	32.38	0.49	1.29	0.42	54.1	1.08
2	0.39	0.68	7.05	0.04	21.6	0.24	7.41	8.55	6.88	0.38	39.1	1.13
3	0.07	0.05	7.93	0	23.2	0.20		10.6	12.0	0.46	35.9	1.11
4	0.09	0.04	8.98	0	26.2	0.25	3.54	0.31	9.27	0.03	32.7	0.08

* The original brine

The $\delta^{37}Cl$ values and chemical composition of a 10 ml portion of the brine sample taken at intervals were determined. The solid deposited at every step was separated from the solution and the

remaining brine was allowed to evaporate further till the end of the experiment. The chemical compositions of residual brine and precipitate are shown in Table 2. The test was divided into 4 steps. The original brine contained Na^+, Mg^{2+}, Cl^- and SO_4^{2-} ions. Table 2 shows that halite was mainly deposited in step one and then kainite, carnallite and bischofite were precipitated in succession in steps 2 to 4. The isotopic chlorine in residual brine(Table 3) indicated that the $\delta^{37}Cl$ values decreased with decrease of pH and increase of density. The highest isotopic fractionation occurred in step 1, when NaCl was deposited. The variation of chlorine isotopes in residual brine vs fraction brine evaporated is shown in Fig. 4.

Table 3   The variation in isotopic compositions of chlorine in residual
brine during evaporation of brine under laboratory condition

Step	pH	Density	$^{37}Cl/^{35}Cl$	$\delta^{37}Cl$ (10^{-3})	$K^{a)}$
*	6.2	1.2186	0.319117	0.10	1.00
1	–	1.2577	0.318783	– 0.94	0.76
2	5.5	1.2846	0.318710	– 1.17	0.46
3	5.0	1.3217	0.318780	– 0.95	0.28
4	4.0	1.3246	0.318660	– 1.33	0.17

* The original brine; a) K Fraction of residual brine to original brine
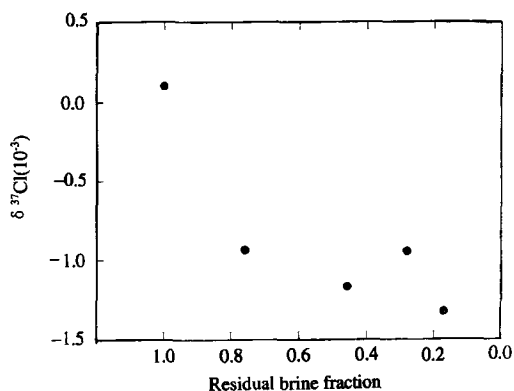

Fig. 4   The variation of $\delta^{37}Cl$ in residual brine vs fraction of residual brine

The results are consistent with Eggenkamp's data (Eggenkamp, 1995). Most of the isotopic fractionation of chlorine occurred during deposition of halite. It is therefore evident that the $\delta^{37}Cl$ values of the brine are indicators of the evaporation degree of the brine.

The isotopic fractionation of chlorine in quick deposit of salt during evaporation of brine

The isotopic fractionation of chlorine during the quick deposition of salt in laboratory environment or in some natural environment was very strange as the enrichment of ^{35}Cl in the solid phase was observed. The fractionation factor was found to be 0.9986 ± 0.0009 (Xiao et al., 1994 a).

In this study, an experiment was conducted to gain understanding of the variations in the isotopic fractionation of chlorine, as a function of equilibration time in evaporation of brine. Two samples were selected, one a saturated solution of NaCl and the other a brine from Da Qaidam Lake. These two solutions were oven heated to boiling for quick evaporation till enough salt was deposited in 5 – 7 min. The solutions with the salt, were immediately cooled to room temperature by cold water bath after they were taken out of the oven. The solutions together with salt were divided into many parts and the salt was separated from each part after keeping for different time. The measured isotopic composition of chlorine in the solutions and salt are presented in Table 4.

The results listed in Table 4 agree with those of Xiao et al. (1994a) showing ^{35}Cl was enriched in the solid phase when the salt was quickly deposited from solution. Therefore, the isotopic

fractionation factor of chlorine during quick deposition was lower than 1.00. However, the fractionation factors increased with the standing time and became greater than 1.00 when the standing time reached 3 h for NaCl solution and 3 d for brine. The values in Table 4 indicate that the equilibration time is very important for the isotopic fractionation of chlorine in nature. The isotopic exchange between chlorine in the salt and chlorine in the brine of the salt lakes may be reached in longer period. No detailed study regarding the fractionation mechanism of chlorine isotopes during rapid deposition

Table 4   The variation in isotopic compositions of chlorine in deposition of saline mineral

No	Standing time	α(Isotopic fractionation factor)	
		NaCl saturated solution	Brine of Da Qaidam Lake
1	0	0.99946	0.99957
2	3 h	1.00043	0.99996
3	5 h	1.00056	0.99985
4	10 h	1.00081	0.99984
5	24 h	1.00018	0.99977
6	3 d	1.00032	1.00034
7	5 d	1.00062	–
8	10 d	1.00044	–
9	30 d	1.00047	1.00018
10	3 months	1.00071	–
11	6 months	1.00068	1.00005
12	12 months	1.00103	1.00040
13	5 a		1.00089[a]

a) The crystal of NaCl was taken from Da Qaidam Lake brine and stored for 5 a in laboratory

was reported. Zhang (1983) indicated that the molecule with heavy isotope has a low zero point energy and that the bond of molecule with heavy isotope is not easily broken when the molecule is dissolved. So in general chemical reactions, the molecules containing lighter isotope react more easily compared to those with heavy isotopes. The isotopic equilibrium between the salt and the co-existing brine in the natural environment can be attained due to slow deposition of salt. In this case, usually the ^{37}Cl, like halite and carnallite, preferentially enters into the solid phase due to the different binding energies of ^{37}Cl and ^{35}Cl with Na^+ and K^+ ions to form NaCl and KCl. Therefore, the saline minerals tend to be enriched in ^{37}Cl. The chloride ions in solution may be present as $Cl-H_2O^-$, a hydrate ion of chlorine. These hydrated ions of chlorine react with Na^+, K^+ or other ions to form NaCl, KCl, etc. when the solution is evaporated to a saturated state. The $^{35}Cl - H_2O^-$ should preferentially react with Na^+ or K^+ ions to form solids. Therefore, ^{35}Cl is enriched in the solid phase in the salt being crystallised. The apparent isotopic fractionation factor α is equal to α_{cry}, the isotopic fractionation factor of chlorine during salt crystallization, because only salt crystallization occurs while salt dissolution, is negligible in this case. However, salt crystallization and salt dissolution, occur simultaneously when the salt is slowly crystallised. Since the $Na^{35}Cl$ or $K^{35}Cl$ should dissolve faster than $Na^{37}Cl$ or $K^{37}Cl$, which causes enrichment of ^{37}Cl in the solid phase, when the deposition is slower or the period of standing time is longer, the enrichment of ^{37}Cl in solid phase is more and the fractionation factor is higher till the isotopic equilibrium is reached. The apparent isotopic fractionation factor(α_{app}) is dependent on both α_{cry} and α_{dis}, and equals $\alpha_{cry} \times \alpha_{dis}$, where α_{dis}

is the isotopic fractionation factor of chlorine during salt dissolution. The fractionation factor of chlorine isotopes in nature being higher than 1.00 suggests that the isotopic fractionation of chlorine in dissolution of salt (α_{dis}) is higher than that in the crystallization of salt (α_{cry}). Unfortunately, the α_{dis} value was not measured in this case, but can be calculated by using the equation $\alpha_{app} = \alpha_{cry} \times \alpha_{dis}$.

CONCLUSION

The variations of isotopic compositions of chlorine in the salt lake brines of Qaidam Basin are related to pH, density and the chlorine concentration of the brine. This results from the evaporation of brine accompanied by salt deposition. The saline minerals are deposited when the brine is evaporated to a saturated state. The isotopic fractionation between chlorine in saline minerals and chlorine in the co-existing brine caused the depletion of ^{37}Cl in brine because ^{37}Cl preferentially enters into the solid phase during the deposition of saline minerals. A reverse isotopic fractionation of chlorine associated with the zero point energy of the molecule with different isotopes during rapid deposition in the laboratory was observed. The ^{35}Cl preferentially enters into the solid phase during rapid deposition and causes the reverse isotopic fractionation of chlorine in some surface samples experiencing high atmospheric temperature and strong evaporation. The experimental results are in fair agreement with the fractionation in nature.

ACKNOWLEDGEMENTS

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