



Chlorine isotopes in sediments of the Qarhan Playa of China and their paleoclimatic significance



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ABSTRACT

This study presents chlorine isotopic composition of salt deposits recovered in a core from the Qarhan Saline Lake in the Qinghai Province of China. The $\delta^{37}\text{Cl}$ trend has three stages, and they correspond to the upper, middle, and lower salt-bearing groups of the entire evaporite system. The $\delta^{37}\text{Cl}$ values are between -0.22‰ and 0.13‰ with an average value of -0.02‰ in the lower salt-bearing group. It ranges between 0.14‰ and 0.76‰ ($\bar{x} = 0.36\text{‰}$) in the middle salt-bearing group, and varies between -0.35‰ to 0.35‰ ($\bar{x} = -0.04\text{‰}$) in the upper salt-bearing group. This work indicates that stratification of $\delta^{37}\text{Cl}$ values is accompanied by stratigraphic variations in Mg/Cl and K/Cl in halite. We suggest a “evaporation cycles model” and it indicates the potential of Cl isotope as a geochemical tracer in order to understand paleoclimatic conditions during different stages of evaporite deposition.

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1. Introduction

Chlorine is abundant in brines, and it provides important information about the brine evolution process. The $\delta^{37}\text{Cl}$ values are widely used to determine the origin of salinity in various fluids. Banks et al. (2000a, b) distinguished the sources of magmatic fluids, and Chiaradia et al. (2006) traced the origin of mixed magmatic-basinal brine. Nahnybida et al. (2009) used $\delta^{37}\text{Cl}$ value of the Bingham Canyon samples suggest that the porphyry system at Bingham has inherited negative chlorine isotopic signatures from the subducting slab. Gleeson and Smith (2009) found that most of the chlorine isotope data of fluid inclusion from the Fe-oxide-apatite and Greenstone deposits in Norrbotten (Sweden) are consistent with a mantle-derived source. Richard et al. (2011) used $\delta^{37}\text{Cl}$ signatures to unravel the mechanisms for acquiring the 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. Compositions of the crustal Cl reservoir and the potential mantle reservoir were

outlined by Eastoe et al. (2007), Sharp et al. (2007), Bonifacie et al. (2008) and Layne et al. (2009).

Chlorine geochemistry and especially Cl isotopes are crucial in studying brine evolution in a surface reservoir (Liu et al., 1997; Eastoe et al., 1999; Eastoe et al., 2001; Eastoe et al., 2007; Richard et al., 2011; Li et al., 2012; Chen et al., 2014). Previous studies have demonstrated that precipitates are enriched in ^{37}Cl compared to the coexisting brines during the deposition of halite (Vengosh et al., 1989; Xiao et al., 1994, 2000; Eggenkamp et al., 1995). Luo et al. (2012) determined the chlorine isotopic ratio in brines and precipitates during the process of evaporation and salt crystallization in the Qarhan Lake. The obtained results indicate decrease in $\delta^{37}\text{Cl}$ values as the entire process of brine evaporation continues. This finding is inconsistent with observation of Eggenkamp et al. (1995), indicating increase in $\delta^{37}\text{Cl}$ values of the remaining brine during the stages of carnallite and bischofite precipitation. This shows the necessity to compare the experimental results with results obtained from natural samples (Eggenkamp et al., 1995; Luo et al., 2012) should be compared with a series of natural samples. Additionally, more information about chlorine isotopes in nonmarine evaporates are required (Eggenkamp et al., 1995; Eastoe and Peryt, 1999; Eastoe et al., 2007).

Halite phase is a longer process in chloride precipitating stage of seawater, as at least 80% of the precipitated Cl is in the form of

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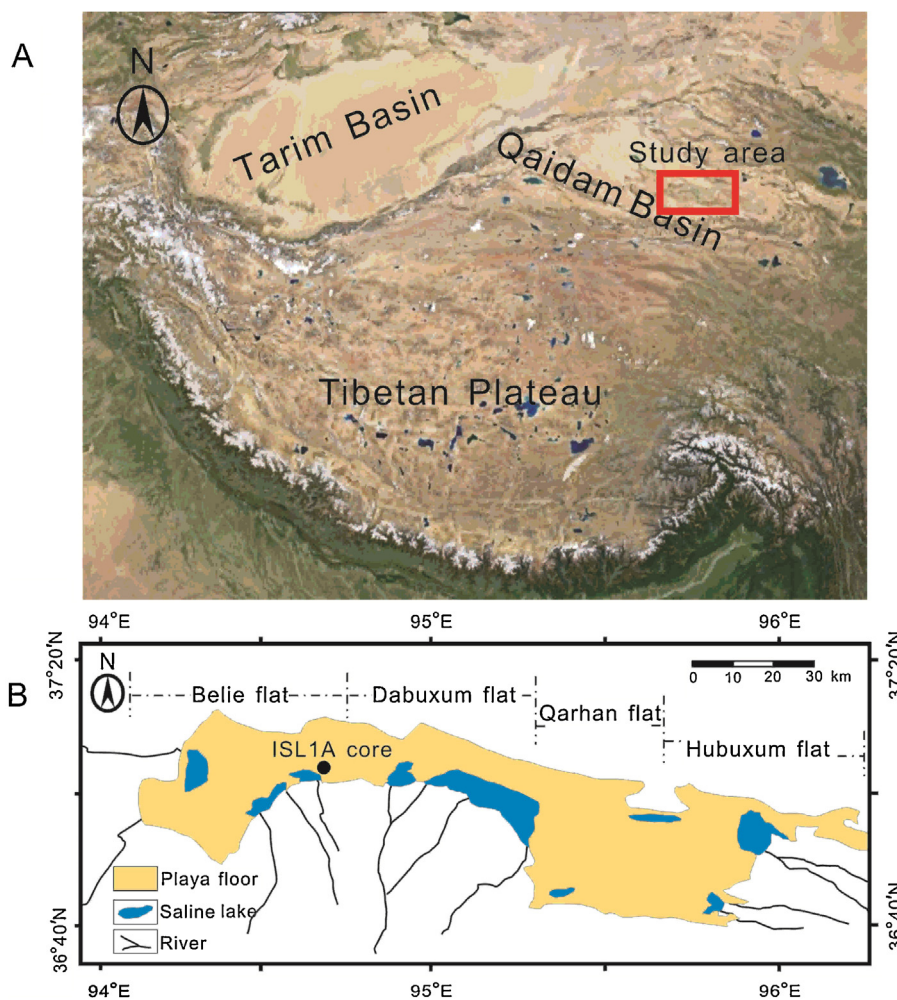


Fig 1. (a) Map showing locations of the Qarhan Saline Lake and (b) ISL 1A core.

NaCl. Halite occurs much larger in proportion compared to other chlorides. The main objective of this study is to test the possibility of using $\delta^{37}\text{Cl}$ of halites as an indicator to understand the processes involved in formation of evaporites.

2. Geological background

The Qaidam Basin is the largest intermontane basin in the Qinghai–Tibetan Plateau, covering 120,000 km² with an average elevation 2800 m asl. It is surrounded by Kunlun Mountains, Qilian Mountains and Altun Mountains, with elevation of 4500–5000 m asl (Fig. 1). Multiple saline lakes and dry salt flats distributed inside the basin have the “high mountain–deep basin” features (Yuan et al., 1983). The Qarhan Saline Lake is a huge dry saline lake with an area of 5850 km² in the central sections of the Qaidam Basin. It is the largest solid–liquid ore potash deposits found in China, with a total KCl reserve of 194×10^6 t (Cao and Wu, 2004). K⁺-rich brines are also used for the production of potash fertiliser. Lacustrine deposits of the Qarhan Playa have interbedded clastic rocks and evaporites interbeds (>70% of overall thickness) and are of the late Pleistocene in age.

Halite deposits and clastics sediments can be compared to explore the evolution history of lakes. Qarhan salt-bearing system has 5 salt stratas (bottom-up: S1–S5) and 5 corresponding clastic stratas (bottom-up: L1–L5) (Fig. 2) (Yuan et al., 1995; Yu, 2000). Some researchers considered both S4 and S5 as the same salt strata (S4). Salt strata and clastics sediments form sedimentary cycles

and each cycle starts with clastic sediments and ends with salts. The main features of Qarhan evaporites system include chloride bearing salts developed within clastic stratas. Sulfates are absent and the salt-bearing stratas are accompanied by wind-borne sediments. The western section of the Qarhan Saline Lake (Bieletan) has a 40-km long and 25–40-km wide evaporites system. It covers an area of 1500 km² with a maximum thickness above 70.2 m for the salt-bearing system (general thickness for the evaporites system is from 55 m to 65 m). The salt stratas and the potash deposits are well-developed in this region.

Lowenstein et al. (1989) analysed chemical composition of inflow waters in the Qarhan Basin and demonstrated that anomalous evaporites in this basin may have formed from nonmarine brines instead of seawater. Generally, the marine potash deposits older than Quaternary have thicker stacks than any other Quaternary potash settings (Warren, 2010). The solid potash sediments are distributed over a small area in the vertical direction, while the halite deposits are widespread in the Qarhan evaporites system. However, it is unclear which stage of brine evolution process led to halite precipitation.

3. Samples and methods

3.1. Sampling and processing procedure

A 102.03 m long core (ISL1A) was collected from western section of the Qarhan Saline Lake (37°3'50"N, 94°43'41"E; core depth:

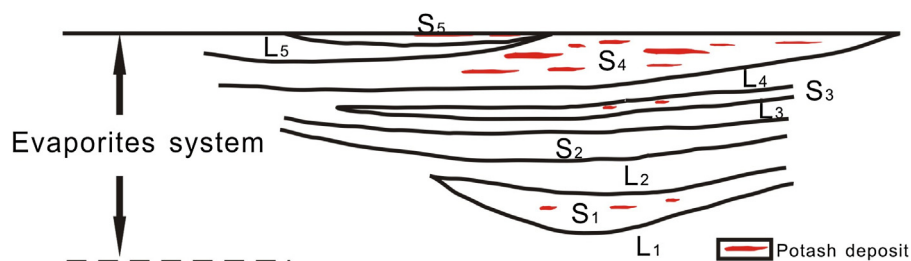


Fig. 2. Vertical distribution of salt stratums in the saline Qarhan Lake (figure is not accurate in detail and only includes the main features) (Yuan et al., 1995; Yu, 2000).

102.03 m.) (Fig. 1). The core collection was part of a Scientific Drilling Project of the Qinghai Institute of the Salt Lakes of the Chinese Academy of Sciences. Upper 50 m of the deposits correspond to the evaporites system, while the deposits below 50 m are clastic lacustrine deposits (silt and clay). A total of 26 samples in upper 50 m of the core representing the evaporites system were collected to study the chlorine isotopic geochemistry. In order to avoid potential errors, we picked fresh and primary halite crystals from the salt layers under a microscope. All the samples were picked from evaporites and the stratification is expressed as both textural and mineralogical variations. The criteria to distinguish the primary evaporites are (Hardie, 1984; Hardie et al., 1985): free crystal growth, intergrowth, cement textures (for example, hoppers and chevrons) in a low temperature (<40 °C) assemblage, abundance of fluid inclusions with low filling temperatures, settle out and wave-sorted clastic textures.

The chronology of the ISL1A core was reported by Wei (2011) and Fan et al. (2014a,b). Halite samples were used for ^{230}Th dating and clay samples containing dark organic matter (collected from the upper 54.5 m) were used for accelerator mass spectrometry (AMS) ^{14}C dating. Eight ^{230}Th ages and four AMS ^{14}C ages in stratigraphic were used to establish the age-depth framework in ISL1A (Fig. 3a)

3.2. Analysis of elemental concentration

Cl concentration was determined by chemical mercurimetry method (with precision better than 0.3%) (Qinghai Institute of Salt Lakes and Chinese Academy of Sciences, 1988). Concentration of K^+ , Mg^{2+} were measured in an atomic absorption spectrometry (with precision better than 5%).

3.3. Reagents and ion-exchange procedure

High-purity water was obtained by boiling and sub-boiling the fresh water. The isotopic standard is a reference material of NaCl (ISL 354 NaCl) (Xiao et al., 2002; Wei et al., 2012). It was prepared from special sea water collected from $4^{\circ}18'N$, $101^{\circ}08'E$, and represented Standard Mean Ocean Chloride (SMOC).

To determine the chlorine isotopic ratios, ~ 0.066 g of halite was dissolved in 4 ml high-purity distilled water. Samples were prepared by a two-step resin method (Xiao and Zhang, 1992; Magenheimer et al., 1994; Xiao et al., 1995). Approximately 200–400 mesh of reborn H-cation exchange resin (resin type: Dowex 50 W \times 8) was injected into a polyethylene-accompanied ion-exchange column with a diameter of 0.4 cm and a resin height of 2 cm. Then, reborn Cs-cation exchange resin was injected into a polyethylene-accompanied ion-exchange column with a diameter of 0.4 cm and a resin height of 1.6 cm. First, the samples were passed through the H-cation exchange resin column (at this time, all the Cl in the liquid samples transformed into HCl solution). Then, CsCl solution used for mass spectrometry analysis was collected after

the liquid went through the Cs-cation exchange resin column. The pH of the solution was between 2.5 and 6.

Concentrations of SO_4^{2-} and NO_3^- were far lower than concentration of Cl^- . As the molar ratio of $c(\text{SO}_4^{2-})/c(\text{Cl}^-)$ is lower than 2.5 and ratio of $c(\text{NO}_3^-)/c(\text{Cl}^-) < 0.5$, we did not take into consideration the interferences of SO_4^{2-} and NO_3^- (Lu and Xiao, 2001).

3.4. Mass spectrometry

Chlorine isotopes were analyzed by the P-TIMS method in a Triton mass spectrometer (Xiao and Zhang, 1992; Xiao et al., 1995). The tantalum filament was heated using current of 2.5 A for 1 h in a vacuum system and treated with 2.5 μL of graphite slurry (80% ethanol mixed with 80 μg of graphite) to coat the centre of the filament. 3 μL of the test solution containing ~ 30 μg of chlorine as CsCl was loaded onto the filament and dried using a current of 1 A for 1.5 min. The samples were placed in the mass spectrometer, and the measurement was initiated when the ion source was evacuated to a pressure lower than 2.5×10^{-7} mbar. The intensity of the Cs_2Cl^+ ion was adjusted to 4×10^{-12} A by controlling the filament current. Data were simultaneously collected on Faraday cup C and H1 by gathering the ion flow with mass numbers of 301 ($^{133}\text{Cs}_2^{35}\text{Cl}^+$) and 303 ($^{133}\text{Cs}_2^{37}\text{Cl}^+$).

$\delta^{37}\text{Cl}$ values were calculated using the following equation:

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

In the Eq. (1), the average value of SMOC was $(^{37}\text{Cl}/^{35}\text{Cl})_{\text{smoc}} = 0.318990 \pm 0.000041$ (2σ) and it was obtained from results of 6 repetitive determinations under the same conditions. The correction factor $K_{37/35}$ for our mass (Triton) is 0.99825 (Eq. (2) i.e., $0.318990/0.319549 = 0.99825$), which is consistent with $K_{37/35} = 0.99806$ for Triton TI (Wei et al., 2012).

$$K_{37/35} = \frac{R\left(\frac{^{37}\text{Cl}}{^{35}\text{Cl}}\right)_{\text{measured}}}{R\left(\frac{^{37}\text{Cl}}{^{35}\text{Cl}}\right)_{\text{absolute}}} \quad (2)$$

4. Results

$\delta^{37}\text{Cl}$ values of the primary halite minerals are presented in Table 1 and Fig. 3a. Elemental compositions of the samples are listed in Table 2. Due to low bromine content in the samples, we failed to obtain $\text{Br} \times 10^3/\text{Cl}$ ratio index.

Based on the distribution of $\delta^{37}\text{Cl}$ values, the core is divided into three parts (Fig. 4). It includes the top section (with lower $\delta^{37}\text{Cl}$ values), the middle section (with higher $\delta^{37}\text{Cl}$ values), and the lower section (with lower $\delta^{37}\text{Cl}$ values).

The lower section has bottom-up samples from Z50 to Z44 (43.31–36.73 m). $\delta^{37}\text{Cl}$ values are between -0.22% and 0.13% with

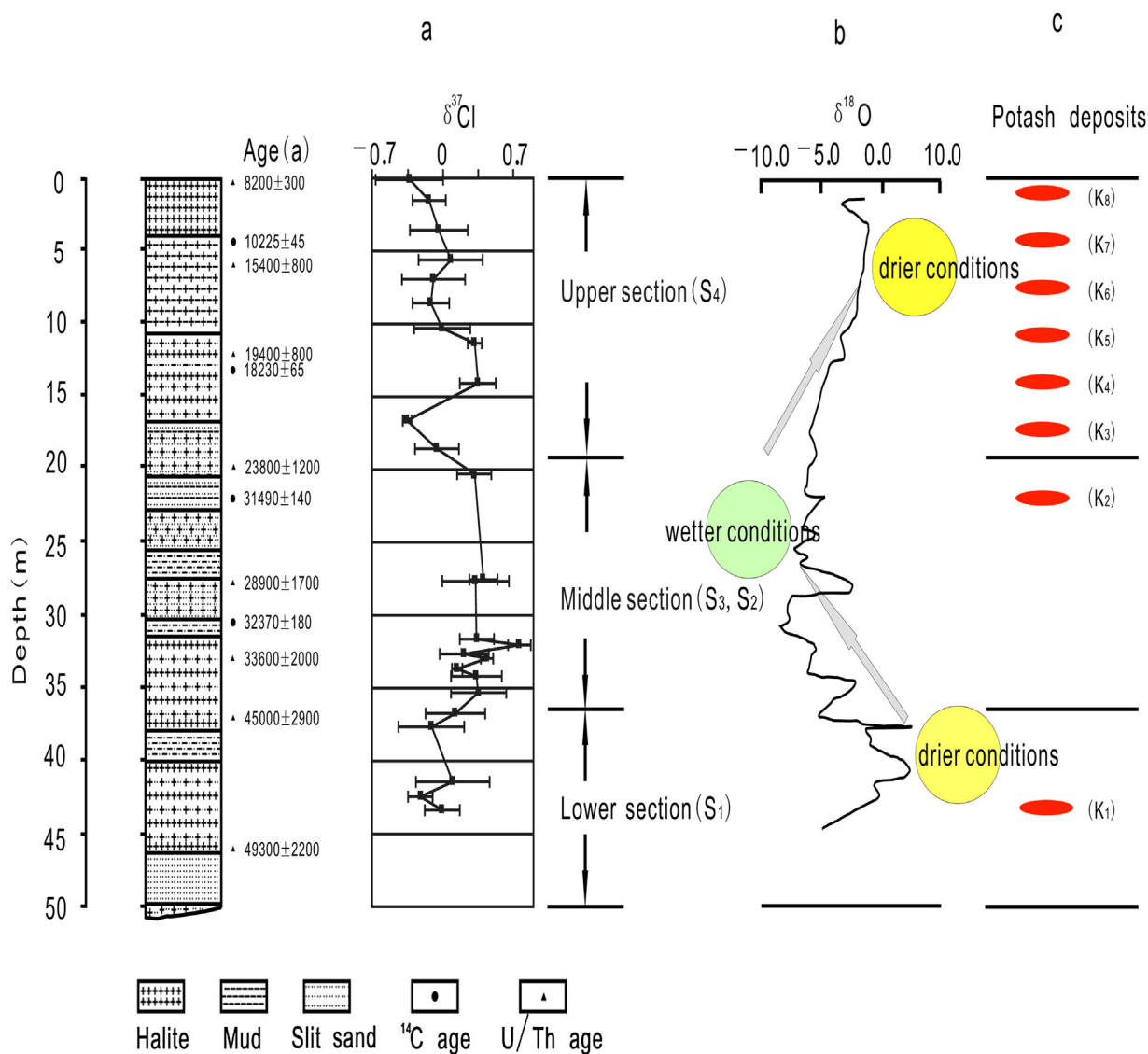


Fig. 3. Variation of $\delta^{37}\text{Cl}$ values in samples from (ISL1A) and other geochemical records. Ages are reported by [Wei \(2011\)](#) and [Fan et al. \(2014a\)](#). (a) $\delta^{37}\text{Cl}$ of halite in this study (ISL1A), (b) $\delta^{18}\text{O}$ of lacustrine carbonate from the Qarhan Salt Lake (ISL1A) ([Fan et al., 2014b](#)) and (c) distribution of sylvinite deposits of the Qarhan Saline Lake ([Yuan et al., 1995](#)).

an average value of -0.02% . Variation of the $\delta^{37}\text{Cl}$ value shows a two-time fluctuation process.

The middle section has samples from Z40 to Z30 (35.28–20.32 m). $\delta^{37}\text{Cl}$ values are significantly high, (0.14–0.76‰) with an average value of 0.36‰. Despite the small fluctuations in this section, $\delta^{37}\text{Cl}$ values for most of the samples have an average value close to 0.36‰. $\delta^{37}\text{Cl}$ value of Z36 (32.9 m depth) is 0.76‰, and it is the highest of all the samples collected from the core.

The top section has samples from Z28 to Z1 (18.5–0 m depth). Chlorine isotopic composition indicate that samples in this section have lower $\delta^{37}\text{Cl}$ values zone, (-0.35% to 0.35‰) with an average value of -0.04% . Sample Z26 (16.58 m depth) has the lowest value (-0.35%), and Z23 to Z1 (14.0–0 m depth) exhibits positive resilience.

5. Discussion

5.1. Interpretation of $\delta^{37}\text{Cl}$ of halite

Cl isotopes has received considerable attention in evaporites ([Xiao et al., 1994, 1997, 2000](#); [Eggenkamp et al., 1995](#); [Liu et al.,](#)

[1995, 1997, 1998](#); [Wang et al., 1995](#); [Sun et al., 1998](#); [Eastoe et al., 1999, 2007](#); [Luo et al., 2012, 2014](#)), but it is necessary to clarify the fundamental mechanism of chlorine isotope in fractionation that occurs during the evaporation process. In the Qaidam Basin, $^{37}\text{Cl}/^{35}\text{Cl}$ ratios in salt minerals are higher than those in modern brines. In general salt minerals are enriched in ^{37}Cl , and the chlorine isotopic composition of salt mineral varies depending upon the climatic conditions ([Xiao et al., 1994, 1997, 2000](#); [Liu et al., 1995, 1997, 1998](#); [Wang et al., 1995](#)). The chlorine isotopic fractionations during the formation of evaporite in experimental settings ([Eggenkamp et al., 1995](#); [Luo et al., 2012, 2014](#)) suggest that $\delta^{37}\text{Cl}$ decreased continuously during the early stage and hence the halites precipitating in later stages have negative $\delta^{37}\text{Cl}$ values. This trend continues even with the crystallization of K-Mg salts ([Luo et al., 2012, 2014](#)). Therefore, the evaporation process can be indicated using ^{37}Cl in halite and the $\delta^{37}\text{Cl}$ changes may be associated with the evaporation cycle of saline lake.

However, the experimental model to interpret the observed isotopic fractionation requires some extra points of explanation. Some influx of salt into this basin occurs under both the wet or dry conditions. These chlorides are sourced from the ancient salts in deep

Table 1
Chlorine isotope composition of primary halites in the ISL1A core.

Sample	Depth (m)	Age (ka) ^a	Lithology	³⁷ Cl/ ³⁵ Cl ± 2σ	δ ³⁷ Cl ± 2σ(‰)
Z1	0.05	8.5	Halite	0.318884 ± 0.00011	−0.33 ± 0.33
Z4	1.52	9.7	Halite	0.318947 ± 0.00005	−0.14 ± 0.16
Z7	3.53	11.4	Halite	0.318978 ± 0.00009	−0.04 ± 0.29
Z10	5.58	13.1	Halite	0.319016 ± 0.00010	0.08 ± 0.32
Z13	6.93	14.2	Halite with a little silt and clay	0.318960 ± 0.00010	−0.09 ± 0.32
Z16	8.50	15.5	Halite	0.318953 ± 0.00006	−0.12 ± 0.19
Z18	10.25	17.0	Clay with halite	0.318987 ± 0.00009	−0.01 ± 0.28
Z20	11.25	17.8	Halite with gray silt	0.319090 ± 0.00002	0.31 ± 0.07
Z23	14.00	20.1	Halite	0.319101 ± 0.00006	0.35 ± 0.18
Z26	16.58	22.2	Halite	0.318877 ± 0.00001	−0.35 ± 0.04
Z28	18.50	23.8	Halite	0.318972 ± 0.00007	−0.06 ± 0.22
Z30	20.32	25.3	Halite with gray silt and clay	0.319090 ± 0.00005	0.31 ± 0.17
Z31	27.56	31.3	Halite	0.319119 ± 0.00005	0.40 ± 0.14
Z32	27.66	31.4	Halite	0.319094 ± 0.00011	0.33 ± 0.33
Z33	31.57	34.6	Halite with gray silt	0.319098 ± 0.00005	0.34 ± 0.17
Z34	31.97	34.9	Halite with gray silt	0.319234 ± 0.00004	0.76 ± 0.11
Z35	32.65	35.5	Halite	0.319058 ± 0.00008	0.21 ± 0.24
Z36	32.90	35.7	Halite	0.319130 ± 0.00002	0.44 ± 0.06
Z37	33.66	36.3	Gray silt with halite crystals	0.319036 ± 0.00002	0.14 ± 0.05
Z39	34.13	36.7	Halite with silt	0.319097 ± 0.00008	0.34 ± 0.26
Z40	35.28	37.7	Halite	0.319104 ± 0.00009	0.36 ± 0.27
Z44	36.73	38.9	Halite	0.319030 ± 0.00010	0.13 ± 0.30
Z45	37.59	39.6	Silt with halite crystals	0.318954 ± 0.00011	−0.11 ± 0.33
Z48	41.37	42.7	Halite	0.319021 ± 0.00012	0.10 ± 0.37
Z49	42.41	43.6	Halite with silt	0.318920 ± 0.00004	−0.22 ± 0.12
Z50	43.31	44.3	Halite	0.318988 ± 0.00006	−0.01 ± 0.18

^a Ages are reported by Wei (2011) and Fan et al. (2014a).

Table 2
Chemical compositions of samples of the ISL1A core (concentration in, wt%).

Sample	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	SO ₄ ^{2−}	Cl [−]	Water-insoluble solid
Z1	37.49	0.24	0.45	0.24	1.03	58.73	0.32
Z4	37.77	0.23	0.48	0.070	1.08	58.68	0.56
Z7	35.69	0.25	1.07	0.26	2.53	56.03	2.72
Z10	38.79	0.24	0.15	0.065	0.33	60.22	0.40
Z13	37.00	0.29	0.62	0.20	1.44	57.91	1.43
Z16	38.06	0.48	0.14	0.22	0.63	59.54	0.61
Z18	31.43	0.31	0.60	0.37	1.40	49.84	15.23
Z20	35.63	0.26	0.39	0.22	0.78	55.90	6.08
Z23	36.78	0.32	0.68	0.18	1.58	57.52	2.27
Z26	34.60	0.21	0.36	0.09	0.80	53.82	9.91
Z28	35.38	0.24	0.24	0.21	0.42	55.48	6.44
Z30	34.87	0.19	0.15	0.18	0.24	54.53	9.09
Z31	36.94	0.21	1.03	0.05	2.35	57.34	1.20
Z32	37.38	0.20	0.75	0.04	1.66	58.00	1.21
Z33	36.46	0.23	0.61	0.06	1.42	56.60	4.13
Z34	34.90	0.18	1.45	0.14	3.45	54.36	4.05
Z35	38.83	0.16	0.16	0.03	0.33	60.10	0.40
Z36	38.16	0.20	0.72	0.02	1.69	59.08	0.11
Z37	32.70	0.17	0.34	0.15	0.75	51.04	13.96
Z39	35.88	0.14	0.62	0.075	1.40	55.71	6.39
Z40	37.72	0.14	0.067	0.080	0.03	58.60	2.42
Z44	38.10	0.14	0.54	0.033	1.28	58.96	0.14
Z45	35.50	0.13	1.59	0.14	3.64	55.38	1.99
Z48	36.08	0.18	0.51	0.18	1.20	56.31	4.52
Z49	36.69	0.12	0.52	0.11	1.17	57.05	3.05
Z50	38.61	0.13	0.12	0.055	0.26	59.81	0.75

strata and were brought into the basin by the meteoric river inflow mixed with spring inflow (Chen and Bowler, 1985; Lowenstein et al., 1989; Schubel and Lowenstein, 1997). Under wetter conditions, one source of chloride in the lake water is dissolution of halite from last drought cycle and the other source is ancient halite. Chloride obtained from the dissolution of halite has higher δ³⁷Cl compared to lake water at that moment. δ³⁷Cl of chloride obtained from ancient halite is consistent with bulk lake water when drought cycle started, which is also higher than lake water at that moment. Under drought conditions, a small amount chloride enter into the basin, and the δ³⁷Cl value of bulk lake water decreases continuously during the evaporation process. The sources of inflow water

into salt lakes are mainly fluvial water and groundwater. It also includes oil-field water and hot spring water. Liu et al. (1997) have reported δ³⁷Cl values of different waters entering into the Qaidam Basin (hot spring water δ³⁷Cl = 2.94‰; river water δ³⁷Cl = 1.35‰; oil-field brine δ³⁷Cl = −0.38‰; saline water δ³⁷Cl = −0.40‰ and salt lake brine δ³⁷Cl = −0.63‰). Sun et al. (2004) determined the Cl isotopic composition (δ³⁷Cl = 0.88‰) of rainwater in Xi'ning near the Qaidam Basin. Therefore, the bulk lake water under wetter conditions has higher δ³⁷Cl than under drought conditions. Higher δ³⁷Cl values represent the conditions of halite precipitation from saline lake with larger amount of lake water. The dry or wet cli-

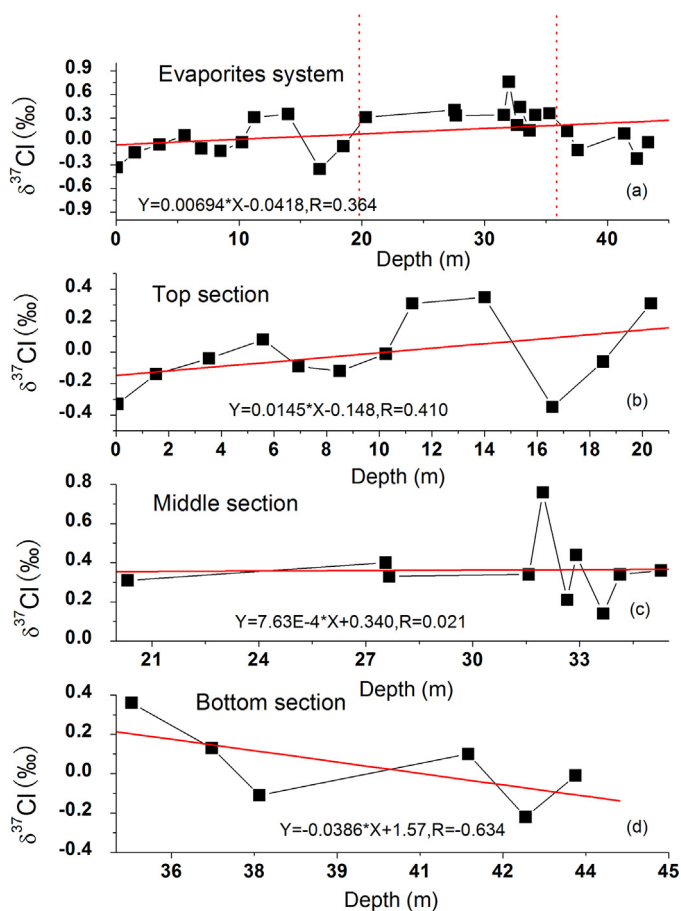


Fig. 4. $\delta^{37}\text{Cl}$ vs. depth in different salt-bearing sections of sedimentary sequence.

mates might be a factor to control the hydrology and Cl isotopic composition of surface lake brine in the Qarhan Playa.

5.2. Distribution of $\delta^{37}\text{Cl}$

Both the range (-0.22 – 0.13‰) and average (-0.02‰) values of $\delta^{37}\text{Cl}$ of the lower section is more compared to the top section but less compared to the middle. We inferred dry conditions of the lower section is wetter than that of the top section. There are two dramatic fluctuations of $\delta^{37}\text{Cl}$ values in the lower section, and they suggest that the saline lake experienced processes of concentration and dilution (Fig. 4).

In the middle section, $\delta^{37}\text{Cl}$ values are positive and they indicate addition of a large amount of fresh water occurred and as a result brine was diluted (Fig. 4). In addition to the extremely positive value 0.76‰ in the Z34 sample, range of $\delta^{37}\text{Cl}$ values exhibits no significant changes. Samples from Z40 to Z30 are distributed around average value of 0.36‰ in the high $\delta^{37}\text{Cl}$ value zone. It reveals that the lake had a slowly evaporating and stably evolving status. The lithological characteristics of samples in this section with a high $\delta^{37}\text{Cl}$ value are mainly salts containing mud or mud containing salts. The sedimentary properties show precipitation was occurring in a shallow water environment. Huang et al. (1985) reported existence of the interlayer deposits as two layers of salts and three layers of silty clay between S_2 and S_3 . A high percentage of mud and sand in the salts layers (above 10%) together with 10–20% of salts in these mud interlayers were observed. These characteristics also support findings from $\delta^{37}\text{Cl}$ value that the lake was under a relatively stable status during this stage.

Table 3

Relationship between salt stratum and sylvinite deposits of the saline Qarhan Lake (Yuan et al., 1995).

	Salt-bearing group	Salt stratum	Sylvinite deposits
Evaporite system	Fifth group	S_5 (salt strata) L_5 (clastic strata)	K_8
	Fourth group	S_4	K_7
		(salt strata)	K_6
		K_5 K_4	K_3
	Third group	L_4 (clastic strata) S_3 (salt strata)	K_2
Second group	L_3 (clastic strata)		
	S_2 (salt strata)		
First group	L_2 (clastic strata)		
	S_1 (salt strata) L_1 (clastic strata)	K_1	

In top section, the samples from Z28 to Z1 represent low $\delta^{37}\text{Cl}$ value section. Z26 has the lowest value (-0.35‰) of all samples. The positive resilience of Z23 exhibits a diluting process. During the deposition of Z13, the Qarhan Saline Lake suffered a second event of dilution and this caused positive values of $\delta^{37}\text{Cl}$ in Z10, Z13 and Z16 (Fig. 4). $\delta^{37}\text{Cl}$ exhibits a trend of decreasing values towards the lower part of the section. It indicates drought conditions and intense lake evaporation. Salt deposits continued during this period and this represented an high-temperature conditions with sylvite precipitation in the Qarhan Saline lake (Figs. 2 and 3).

5.3. Comparisons with previous work

Based on the geological data potash deposits of the Qarhan evaporites system can be divided into eight layers (top–down: K_1 – K_8) (Table 3) (Yuan et al., 1995). The relationship between spatial distribution of the potash deposits and variation of $\delta^{37}\text{Cl}$ values is shown in Fig. 3. Sylvite stratas in the three salt-bearing groups have features that include: (1) concentrated distribution (from K_3 – K_8); (2) basically no distribution (K_2 has a small area of 6 km^2 and only seven small lenticles in S_3); and (3) distribution for single layer (K_1). Chlorine isotopic composition of the core have the following features: (1) low value section (average value -0.04‰); (2) high value section (average value 0.36‰); and (3) lower value section (average value -0.02‰). In the upper salt-bearing group with five sylvite stratas, several samples were found to have $\delta^{37}\text{Cl}$ values below 0. The lowest $\delta^{37}\text{Cl}$ value of -0.35‰ was observed in joint parts of the upper and middle salt-bearing group, in which two sylvite deposit stratas (K_2 and K_3) were developed. $\delta^{37}\text{Cl}$ value for sample Z1 in the top section is -0.33‰ and it indicates the present brine evolved into a later stage. This deduction is also supported precipitation of modern carnallite in the Qarhan Lake surface.

Zhang et al. (1993) deciphered the three stages with distinct environmental conditions from the elemental compositions, $\delta^{18}\text{O}$ and δD in fluid inclusions of primary halite in the Qarhan evaporite system: (1) the first is high-temperature salt deposition stage; (2) the second is diluting stage suggesting rise of water level under damp conditions; (3) the last is high temperature salt deposition stage in the upper salt-bearing groups. These conclusions are consistent with our study.

Comparing the $\delta^{18}\text{O}$ record of lake carbonates with $\delta^{37}\text{Cl}$ values of halites in ISL1A, we found that both have similar tendencies and synchronous pattern for the large-scale variations (Fig. 3b). Fan et al. (2014b) inferred drier climate conditions from the positive $\delta^{18}\text{O}$ values. Positive $\delta^{18}\text{O}$ values of lake carbonates resulted from the strong evaporation and hence enrichment of the heavier isotope. Therefore, the interpretation of $\delta^{37}\text{Cl}$ in ISL1A is reasonable.

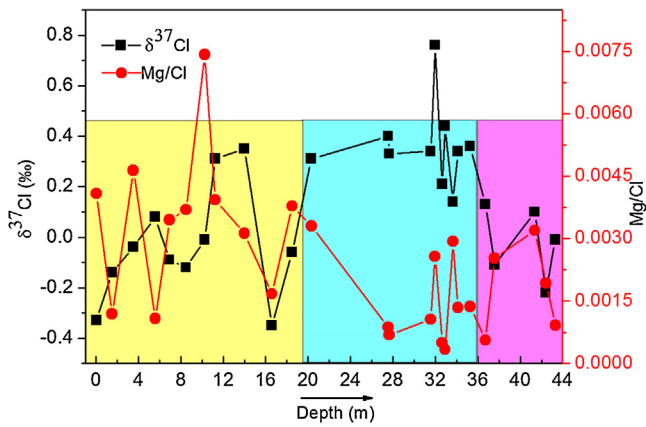


Fig. 5. Relationship between Mg/Cl in halite and $\delta^{37}\text{Cl}$.

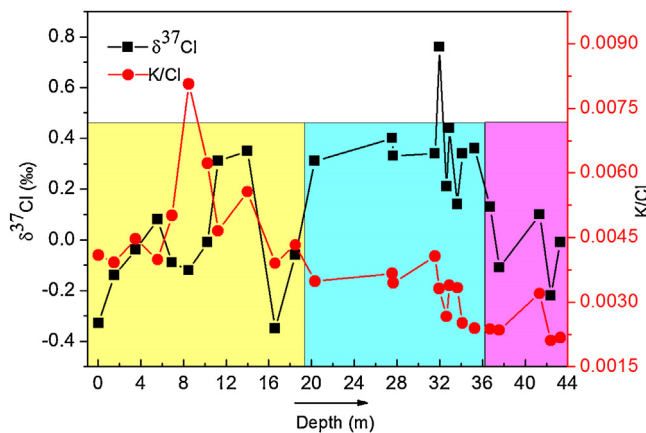


Fig. 6. Relationship between K/Cl in halite and $\delta^{37}\text{Cl}$.

5.4. Insights from Mg/Cl, K/Cl and $\delta^{37}\text{Cl}$ values

Fig. 5 indicates that $\delta^{37}\text{Cl}$ is inversely proportional to Mg/Cl ratio. Mg exhibits an increasing trend during the brine evaporation (Valyashko, 1972). In evaporites sedimentary sequences, magnesium salt usually emerges at the end. Therefore, the concentration of Mg in brine roughly reflects the stage of brine evolution. Mg/Cl ratio in halite minerals is heavily influenced by Mg content in the brine. More Mg is incorporated into the halite mineral from Mg-enriched brine. However, we do not know the concrete mechanism of changing Mg/Cl ratio in the halite minerals. $\delta^{37}\text{Cl}$ value and Mg/Cl have almost similar tendencies in the three sections. This may well be indicating a phase of re-dissolution of halite. Higher $\delta^{37}\text{Cl}$ values and lower Mg/Cl in middle section suggest that the lake was in wet climatic conditions. However, the relationship between $\delta^{37}\text{Cl}$ and K/Cl is different in lower section (Fig. 6). We assume that climatic conditions for the lower and middle sections were wetter than that for upper section. This is because the precipitation of sylvite, carnallite and bischofite occurs in the advanced stage of evaporation. Both the K and Mg have lower concentrations low in the middle and lower salt-bearing groups. However, Mg is more soluble compared to K. In a closed lake, content of K is controlled by evaporation and then other geological processes such as metasomatism. Our results add an important piece of evidence that $\delta^{37}\text{Cl}$ of halite is a better tracer of potash-bearing evaporites.

6. Conclusions

This study investigated chlorine isotopic compositions of primary halite samples in sediments (ISL1A core) of the Qarhan Saline Lake in China and compared the results with geological distribution of salt and potash deposits. The main conclusions are as follows:

1. $\delta^{37}\text{Cl}$ value in the core is closely related to evolution of the mother solution and is sensitive to the natural brine concentration and dilution processes. $\delta^{37}\text{Cl}$ is characteristically different for the upper (S_4), middle (S_3 and S_2), and lower (S_1) salt bearing groups as well as small climate cycles.
2. Stratigraphic horizons with potash deposits often have halite samples with lower $\delta^{37}\text{Cl}$ value. It indicates that $\delta^{37}\text{Cl}$ values act as an indicator to reflect different stages of the brine and can be used to track the possible sylvite-bearing horizons.
3. $\delta^{37}\text{Cl}$ is inversely proportional to Mg/Cl ratio in the entire evaporites system. An inverse relationship between K/Cl ratio and chlorine isotopic ratio is limited only to the upper salt-bearing group.

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