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

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A B S T R A C T

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 $\delta^{37}$Cl values have three stages, and they correspond to the upper, middle, and lower salt-bearing groups of the entire evaporite system. The $\delta^{37}$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\% (X$\times$=0.36\%) in the middle salt-bearing group, and varies between $-0.35\%$ to $0.35\%$ (X$\times$=0.04\%) in the upper salt-bearing group. This work indicates that stratification of $\delta^{37}$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 CI 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 $\delta^{37}$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. Nahinyida et al. (2009) used $\delta^{37}$Cl value of the Bingham Canyon samples suggest that the porphyry system at Bingham has inherited negative chlorine isotopic signatures from the subducting slab. Gleson 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 $\delta^{37}$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 CI 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 $\delta^{37}$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 $\delta^{37}$Cl values as the entire process of brine evaporation continues. This finding is inconsistent with observation of Eggenkamp et al. (1995), indicating increase in $\delta^{37}$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
NaCl. Halite occurs much larger in proportion compared to other chlorides. The main objective of this study is to test the possibility of using $\delta^{37}$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 km$^2$ with an average elevation 2800 masl. It is surrounded by Kunlun Mountains, Qilian Mountains and Altun Mountains, with elevation of 4500–5000 masl (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 km$^2$ 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 $194 \times 10^4$ 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 strata (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 (Biletan) has a 40-km long and 25–40-km wide evaporites system. It covers an area of 1500 km$^2$ 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:
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