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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 (δ^{37}Cl value) during evaporations of solutions containing NaCl, KCl and $MgCl_2{\cdot}6H_2O$ at 28 ± 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 Cs_2Cl^+ ion measurement. The results are as follows: the mean fractionation factors of the three solutions are $\alpha_{Na} = 1.00055$, $\alpha_K = 1.00025$, and $\alpha_{Mg} = 1.00012$, respectively, where α_{Na}, α_K and α_{Mg} are the fractionation factors between salts (NaCl, KCl and $MgCl_2{\cdot}6H_2O$) and saturated solutions. The results showed that the δ^{37}Cl values of precipitate and coexisting brine samples decrease during the precipitation of single chloride minerals. The residual brine was a ^{35}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, δ^{37}Cl decreased continuously, and the most important thing is that this trend continues during the final stages when Mg–salts begin to precipitate.

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).

δ^{37}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 δ^{37}Cl values. Chiaradia et al. (2006) used δ^{37}Cl values for tracing the origin of mixed magmatic–basinal brine. Nahnybida et al. (2009) obtained the δ^{37}Cl values for Bingham Canyon samples ranged from −0.9‰ to −4.1‰, 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 δ^{37}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 α between precipitate and coexisting brine. The chlorine isotope fractionations (^{37}Cl/^{35}Cl) between NaCl, KCl, and $MgCl_2 \cdot 6H_2O$ and their saturated solutions are as follows:

$$10^3 \ln \alpha(\mathrm{NaCl - solution}) = +0.26 \pm 0.07(1\sigma),$$
$$10^3 \ln \alpha(\mathrm{KCl - solution}) = -0.09 \pm 0.09(1\sigma),$$
$$10^3 \ln \alpha(\mathrm{MgCl_2 \cdot 6H_2O - solution}) = -0.06 \pm 0.10(1\sigma).$$

For NaCl precipitate, α is higher than unity; for KCl and $MgCl_2 \cdot 6H_2O$ 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 δ^{37}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 δ^{37}Cl values, which is inconsistent with the results of Eggenkamp et al. (1995). Eastoe et al. (2007) reported the potash facies salt (mean δ^{37}Cl −0.30 ± 0.04‰) that was isotopically lighter than the halite facies salt (mean 0.06 ± 0.04‰) in the Zechstein; in Siberia, the potash facies salt (mean −0.32 ± 0.06‰) was lighter than the halite facies salt (mean 0.06 ± 0.05‰). 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 δ^{37}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 sylvinite deposit.[a]

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

[a] These are data reported by Sun et al. (1998).

[b] 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 $MgCl_2$ 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 $MgCl_2$. The Cl^- amount in the three solutions was 1.744 mol for NaCl, 1.140 mol for KCl, and 2.000 mol for $MgCl_2$.

3.2. Equipment

The thermal-ionisation mass spectrometer used was a Triton (with a 90° 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 ±1 °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 $MgCl_2$ 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 ± 2 °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