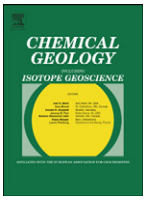
Chemical Geology 433 (2016) 46–56

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo



Experimental determination of stable chlorine and bromine isotope fractionation during precipitation of salt from a saturated solution

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ARTICLE INFO

Article history:
Received 11 May 2015
Received in revised form 30 December 2015
Accepted 9 April 2016
Available online 26 April 2016

Keywords:
Chlorine
Bromine
Stable isotopes
Fractionation
Salt

ABSTRACT

In order to better understand the chlorine and bromine stable isotope fractionation that occurs when chloride and bromide salts precipitate from their saturated solutions, we determined experimentally the equilibrium fractionation factors between precipitating pure salt minerals and their coexisting saturated brine at 22 °C. Fractionation factors (expressed as $10^3\ln\alpha^{(37Cl/35Cl)}{}_{\text{salt-brine}}$ and $10^3\ln\alpha^{81Br/79Br}{}_{\text{salt-brine}}$) obtained for 11 chloride and 7 bromide salts of geological and industrial interest show a relatively largerange of variation (from −0.31 to +0.41), with the salt that precipitates having either a lower or a higher isotope ratio than the brine from which they precipitate. A negative fractionation factor indicates that the brine has a larger isotope ratio than the precipitate, a positive factor that the precipitate has a larger isotope ratio. The results of the chlorine and bromine isotope fractionation measurements ($10^3\ln\alpha$) for the various salts at a temperature of 22 ± 2 °C are: LiCl: +0.03 ± 0.05, NaCl: +0.35 ± 0.08, KCl: −0.12 ± 0.05, NH_4Cl: +0.09 ± 0.03, RbCl: −0.31 ± 0.05, CsCl: −0.23 ± 0.02, $MgCl_2$: −0.02 ± 0.02, $CaCl_2$: +0.04 ± 0.02, $SrCl_2$: +0.15 ± 0.02, $BaCl_2$: +0.41 ± 0.03, $FeCl_3$: −0.23 ± 0.05, LiBr: −0.03 ± 0.09, NaBr: +0.07 ± 0.05, KBr: 0.00 ± 0.01, NH_4Br: +0.11 ± 0.05, $MgBr_2$: +0.06 ± 0.06, $CaBr_2$: −0.06 ± 0.04 and $SrBr_2$: +0.05 ± 0.06. In these measurements the uncertainty is defined as the 1σ standard deviation of replicate determinations. We compare the results to previous theoretical calculations based on reduced partition coefficients as well as with thermodynamic properties of precipitated salts. Though most of our experimental fractionation data qualitatively agree with theoretical predictions (e.g., larger isotope fractionation for Cl than for Br species), it remains difficult to directly and finely compare those estimations which is likely due to the complexness of the processes that take place in saturated solutions. We use the data to predict the δ^{37}Cl evolution of the Earth's oceans' through geological time under the condition that solely isotope fractionation during evaporation and salt precipitation took place, together with erosion of evaporite deposits. Under these conditions, we calculate a δ^{37}Cl decrease of at most 0.25‰ for the Earth's oceans during the last 1 billion years. Such a trend is not observed in old evaporite deposits, in part because δ^{37}Cl variations in most evaporite deposits are larger than the expected trend, and we conclude that δ^{37}Cl may also be influenced by other processes such as chloride exchange with the deep Earth. We only observed very small bromine isotope fractionation during precipitation of bromide salts from brine. This small fractionation cannot explain the large deviation of δ^{81}Br of dissolved evaporite samples from precipitation of seawater with a modern bromine isotope composition, and suggests large bromine isotope variations in the oceans through time.

1. Introduction

The number of studies on chlorine and bromine isotope variations in natural settings is growing steadily (Eggenkamp, 2014) and this increases the importance to constrain the equilibrium isotope fractionation between the different phases in chemical reactions. Both chlorine and bromine have two stable isotopes. These are ^{35}Cl and ^{37}Cl for chlorine and ^{79}Br and ^{81}Br for bromine. Variations in isotope compositions are reported in the familiar delta notation. The definition for chlorine is:

$$\delta^{37}\mathrm{Cl} = \frac{\left(^{37}\mathrm{Cl}/^{35}\mathrm{Cl}\right)_{sample} - \left(^{37}\mathrm{Cl}/^{35}\mathrm{Cl}\right)_{standard}}{\left(^{37}\mathrm{Cl}/^{35}\mathrm{Cl}\right)_{standard}} * 1000$$

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http://dx.doi.org/10.1016/j.chemgeo.2016.04.009
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and for bromine it is:

$$\delta^{81}Br = \frac{(^{81}Br/^{79}Br)_{sample} - (^{81}Br/^{79}Br)_{standard}}{(^{81}Br/^{79}Br)_{standard}} * 1000$$

For both chlorine and bromine the accepted international standard is the isotope ratio of the halide ion (Cl^- or Br^-) in ocean water which are called SMOC (Standard Mean Ocean Chloride) for chlorine (Kaufmann, 1984) and SMOB (Standard Mean Ocean Bromide) for bromine (Eggenkamp and Coleman, 2000).

Theoretical studies on the partitioning of chlorine and bromine stable isotopes between phases of different oxidation states are known since 1935 (Urey and Greiff, 1935; Urey, 1947; Richet et al., 1977; Schauble et al., 2003; Czarnacki and Hałas, 2012) and allow for predicting the equilibrium isotope fractionation between different oxidation states. These predictions have only seldom been tested (Hoering and Parker, 1961; Giunta et al., 2013). However, since chlorine and bromine species with oxidation states higher than −I are unusual in natural environments, most phase transitions found on Earth are between different occurrences of the Cl^- and Br^- ions so that this lack of experimental validation has not been an issue in Earth Sciences, at least as far as it concerns Cl (Eggenkamp, 2015a). Concerning phase transitions between different occurrences of the Cl^- and Br^- ions experimental attention has already been given to the transitions between the Cl^- ion in aqueous solution and the Cl^- ion incorporated in mineral lattices in Na, K and Mg chloride minerals (Eggenkamp et al., 1995; Luo et al., 2012, 2014) and between the HCl_g molecule and the aqueous Cl^- ion in volcanic environments (Sharp et al., 2010).

The theoretical values of equilibrium fractionation between the HCl_g molecule and the anhydrous Cl^- ion were calculated by Schauble et al. (2003) and between the HCl_g molecule and the hydrated Cl^- ion by Czarnacki and Hałas (2012). The results obtained in these theoretical studies agreed reasonably well with experimental data obtained by Sharp et al. (2010) with $10^3\ln\alpha$ values of about 1.4 to 1.7 at temperatures between 50 and 100 °C. Czarnacki and Hałas (2012) also calculated the bromine isotope fractionation between the HBr_g molecule and the hydrated Br^- ion. This fractionation seemed relatively temperature invariant with $10^3\ln\alpha$ values between 0.2 and 0.3 for temperatures between 0 and 400 °C — much smaller than the equivalent $10^3\ln\alpha$ values for chlorine, which are expected to be between 1.1 and 1.7 for the same temperature range.

The research by Schauble et al. (2003) is the only study in which chlorine isotope fractionation factors were theoretically approached for salts with different cations bound to chloride. They suggested that: (i), the reduced partition coefficients ($10^3\ln(\beta_{37-35})$ for the exchange of chlorides bound to alkaline metals (Na^+, K^+ and Rb^+) are significantly lower than the reduced partition coefficients for the exchange of chlorides bound to divalent ions (Fe^{2+} and Mn^{2+}) – at 25 °C about 3 for the alkali metals versus 6 for Fe^{2+} and Mn^{2+} – and that (ii) the reduced partition coefficients for the alkaline metal chlorides decrease with increasing ion radius. However, they did not investigate the equilibrium fractionation of these salts in equilibrium with their saturated solution.

In a few experimental studies the equilibrium fractionation between NaCl, KCl and $MgCl_2 \cdot 6H_2O$ and their saturated solutions (Eggenkamp et al., 1995; Luo et al., 2012, 2014) was determined. These studies were originally applied in order to explain chlorine isotope variations that were observed in salt deposits from the Dutch Zechstein (Eggenkamp et al., 1995) or in the Chinese Qaidam Basin (Xiao et al., 1997, 2000). The chlorine stable isotope ratios decrease in these deposits with increasing degree of evaporation. As a result, it was concluded that the $\delta^{37}Cl$ evolution during formation of evaporites from saturated solutions can provide information on the evaporation stage of these deposits. In addition, Eggenkamp et al. (1995) were the first to show that stable isotope fractionation of the chloride ion depends on the coprecipitating cation and they experimentally determined the chlorine isotope fractionation factors during precipitation of NaCl, KCl and $MgCl_2 \cdot 6H_2O$ from their saturated solution (with $10^3\ln\alpha$ values of $+0.26 \pm 0.07$, -0.09 ± 0.09 and -0.06 ± 0.10 respectively at 22 ± 2 °C). These observations were experimentally confirmed by Eastoe et al. (1999) who evaporated seawater to dryness. The results of their experiment showed that during precipitation of halite the precipitate has a larger isotope ratio than the brine indicating a decreasing $\delta^{37}Cl$ of the remaining brine. During precipitation of potassium and magnesium salts, that precipitate after halite (see e.g. Braitsch, 1962), this trend was reversed, so that it was concluded that in the last stage of salt precipitation from seawater $\delta^{37}Cl$ values of both the brine and the precipitate increase again.

In contrast, later studies on salt deposits from the Chinese Tarim and Western Qaidam Basins (Tan et al., 2005, 2006, 2009) suggested that the $\delta^{37}Cl$ values of salt deposits continue to decrease in the potassium and magnesium chloride stages. This effect seemed so strong that it is locally used as a proxy for the exploration of potassium deposits. The recent study by Luo et al. (2012) in the same basins confirmed these results. However, we believe that such $\delta^{37}Cl$ decrease during precipitation of potassium and magnesium chlorides might be the result of the specific character of these deposits, which are terrestrial rather than marine, and their original composition might not be comparable to seawater. Indeed, as suggested by Luo et al. (2012), a possible cause for this difference might be that potassium and magnesium chlorides precipitate so fast in these basins that non-equilibrium processes take place.

Luo et al. (2014) determined new data for the chlorine isotope fractionation factors of the individual salts (NaCl, KCl and $MgCl_2$) in continuous evaporation experiments and observed for all three salts significantly more positive fractionation factors ($10^3\ln\alpha$ of $+0.55 \pm 0.46$, $+0.25 \pm 0.10$ and $+0.12 \pm 0.50$ respectively) than Eggenkamp et al. (1995). Unfortunately the data presented by Luo et al. (2014) have large errors (Table 1) making it difficult to directly compare them to those presented by Eggenkamp et al. (1995). Eggenkamp (2015b) and Luo et al. (2015) discussed the possible origins of the differences between the two studies, which may be related to either the used analytical techniques or the way the different experiments have been set up.

Such discrepancies (and their possible related implications) motivated the present study, which aim is to (re)examine the fractionation factors for the Na, K and Mg salts, together with other chloride and bromide salts of geological and industrial interest. Until now published studies focussed only on chlorine isotope fractionation of the most common cations in marine and terrestrial evaporites (Na, K and Mg) while it is possible, in specific geological circumstances, that brines exist with other cations. Notably, in (terrestrial) brines with low sulphate concentrations calcium can be highly concentrated, giving rise to precipitation of calcium chloride minerals such as polyhalite and tachydrite (van 't Hoff, 1905; van 't Hoff et al., 1906). Similarly, Dubois et al. (1994) stated that LiCl concentrations can sometimes be as high as NaCl in Li rich pegmatites (London, 1985, Lagache and Sebastian, 1991; Wood and Williams-Jones, 1993) and in magmatic fluids associated with Li-rich leucogranites (Cuney et al., 1992). Even Caesium, normally a trace element, can be enriched in some fluids to such extend that minerals such as pollucite ($Cs(Si_2Al)O_6 \cdot nH_2O$, a zeolite) are formed (Carron and Lagache, 1980; Cerny, 1982). The existence of chloride-rich fluids containing other cations than Na^+, K^+ and Mg^{2+} indicate that the

Table 1
Comparison of the published fractionation factors from Eggenkamp et al. (1995) and Luo et al. (2014). Standard deviations of the fractionation factors presented by Luo et al. (2014) are calculated from the individual measurements in this publication.

	Eggenkamp et al. (1995)	Luo et al. (2014)
NaCl	$+0.26 \pm 0.07$	$+0.55 \pm 0.46$
KCl	-0.08 ± 0.10	$+0.25 \pm 0.10$
$MgCl_2.6H_2O$	-0.06 ± 0.10	$+0.12 \pm 0.50$