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Reply

Reply to the comment on the paper "Stable isotope fractionation of chlorine during the precipitation of single chloride minerals"

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1. Introduction

There are some conflicting findings about the fractionation between salts and the brine at present (Xiao et al., 1994, 2000; Eggenkamp et al., 1995; Sun et al., 1998; Eastoe et al., 1999, 2007; Tan et al., 2005, 2009; Luo et al., 2012, 2014). In Eggenkamp et al. (1995), the fractionation factors for the precipitation of NaCl, KCl and $MgCl_2 \cdot 6H_2O$ from their saturated solutions were 1.00026, 0.99991 and 0.99994 respectively, the last two factors were lower than one. However, δ^{37}Cl values in other studies did not support this study (Xiao et al., 1994; Sun et al., 1998; Tan et al., 2005, 2009; Eastoe et al., 2007; Luo et al., 2012, 2014). Whether the fractionation factors between salts and brines were greater than one? Whether the δ^{37}Cl value of seawater decreased over the evaporation process with progressive evaporation? These questions were points addressed in Luo et al. (2012, 2014), in Luo et al. (2014) we also constructed the chlorine isotopic evolution curves during seawater evaporation as curves in Eggenkamp et al. (1995) based on these fractionation factors.

2. Discussion

2.1. Analytical techniques have no influence on determination the sign of the fractionation

Studies on Cl isotope in evaporite deposits were divided into two groups by Eggenkamp. One the isotope composition is determined by gas source isotope ratio mass spectrometry (IRMS), the other is determined by thermal ionization mass spectrometry (TIMS). He noted the results of the chlorine isotope measurements for salt deposits appear not to agree between the two methods. However, Godon et al. (2004) noted that δ^{37}Cl values measured on natural fluid samples either by IRMS or TIMS will agree within less than ±0.10‰ near 0‰, while values as far as 10‰ (either positive or negative) from SMOC, will show agreement between both techniques within less than ±0.30‰. As mentioned in Eggenkamp's comment, Eastoe et al. (2007) reported chlorine isotopic compositions of 236 evaporite samples (using IRMS measurements). The data is distributed close to the mean value and considered to have better quality. The results in that paper show: the potash facies salt (mean δ^{37}Cl -0.30 ± 0.04‰) was isotopically lighter than the halite facies salt (mean δ^{37}Cl 0.06 ± 0.04‰) in the Zechstein; in Siberia, the potash facies salt (mean δ^{37}Cl -0.32 ± 0.06‰) was also lighter than the halite facies salt (mean δ^{37}Cl 0.06 ± 0.05‰) (Eastoe et al., 2007), therefore, data sets in different places have the same law. One important conclusion in Eastoe et al. (2007) is: potash facies salt is in general (but not in detail in all cases) of lower δ^{37}Cl than halite facies salt. This is consistent with our experiments in Luo et al. (2012, 2014) (using TIMS measurements). Results using the two techniques were in good agreement.

It is nearly 20 years since Eggenkamp et al. (1995) predicted that chlorine isotope values in evaporating seawater decrease during halite precipitation and increase again during the precipitation of magnesium salts, but it is difficult to find other studies to support this viewpoint. In Eggenkamp's comment, he cited an evaporation experiment conducted by Eastoe et al. (1999) to support it. The δ^{37}Cl value of the last sample increase again during the evaporating process, but this sample is solid–liquid mixture, it was not possible to separate salt and brine for the last three samples, the authors stated clearly in this paper (Eastoe et al., 1999), so it was improper to consider that δ^{37}Cl value of the brine increase again at the end in that experiment.

Eggenkamp noted that the errors reported by Luo et al. (2012) are on average 0.24‰, they are about three times as large as errors from IRMS measurements of simple chlorides. In fact, there are 16 solid–liquid samples collected during later stages in CSE and PCE experiments respectively in that study, although the average error is 0.24‰, it is difficult to say the δ^{37}Cl values of these samples did not show decreasing trend. If Eggenkamp's viewpoint is true, there would have to be a fractionation mechanism that causes ^{37}Cl to be highly partitioned into the brine phase, but no such mechanism

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has been identified. Schauble et al. (2003) calculated the fractionation between precipitates and brines, all chloride minerals seem to be higher than brines.

2.2. An important experimental curve during progressive evaporation

Why we have different conclusions about these fractionation factors from Eggenkamp et al. (1995)? We think it has to do with the method which we conducted the evaporation experiments. In Eggenkamp et al. (1995), 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, but the method of experiments in our studies is progressive evaporation Luo et al. (2012, 2014).

The evolution of the δ^{37}Cl of modern seawater is a basic work for Cl isotopic application. However, the curve reported in Eggenkamp et al. (1995) is not experimental curve but calculated with three fractionation factors, even the error curves in Eggenkamp et al. (1995) or this comment was calculated rather than determined in experiments. An reliable curve should be investigated in experiments of progressive evaporation, which is the subject of Luo et al. (2012, 2014).

Eggenkamp added the theoretical curves with the experimental curves determined in Luo et al. (2012, 2014) in the same *X*–*Y* plane, then he concluded that measured curves are roughly follow the expected Rayleigh fractionation curves. If we pay more attention to the evaporation process, obviously that it was improper to add these two curves in the same *X*–*Y* plane.

First, in Rayleigh fractionation model, the horizontal axis *X* (content coordinate) is the weight fraction of chloride precipitated relative to the initial amount available, but in experiment it is hard to obtain the weight that the chloride is precipitated as chloride minerals, especially in progressive evaporation experiments. Therefore, a new parameter DE (Degree of evaporation) was applied in evaluating evaporation state of solution, which was calculated from the ratio of the volume disappeared (V_t) to the initial volume (V_0) in the beaker, DE = V_t/V_0; Other parameters such as pH, density were also measured (Luo et al., 2012, 2014). In one word, due to lacking of the data for the weight fraction of chloride precipitated, all parameters for the evaporated brine should be recorded. Eggenkamp et al. (2011) presented research on the fractionation during precipitation of halite from the nearly pure halite brine well in Rio Maior, but in their preliminary results, as shown in Fig. 8 in Eggenkamp's comment, there are few parameters recorded for the evaporated brine in that experiments, the horizontal axis *X* is evaporation order, but the solution chemistry condition should not be ignored for more detailed experiment.

Second, the salt-water system in Luo et al. (2012, 2014) is metastable, so the crystallization of chloride is not at a constant rate; this precipitated process simulates natural salt precipitation. For example, in the natural brine system, when the concentrations of the K^+ and Mg^{2+} in the solution reach saturation and the system nears eutectic crystallization in the metastable state, new phase carnallite or bischofite will swiftly crystallize (Luo et al., 2012). We consider this is also the reason that it appears the δ^{37}Cl values in the bischofite facies does not decrease significantly with increasing degree of evaporation (Luo et al., 2012) which Eggenkamp noted.

Eggenkamp argues that it is difficult to make any justified statement on the development of δ^{37}Cl evolution of the evaporation of modern seawater from the Fig. 7 in his comment. We consider the reason is not by the errors, but by the curves is not determined in experiments. As experimental curves, there are several solid–liquid samples collected during experiments of progressive evaporation respectively, therefore a conclusion seems justified that the δ^{37}Cl values in the brine show decreasing trend (Luo et al., 2012, 2014).

3. Conclusion

We thank Eggenkamp for his comment on the paper "Stable isotope fractionation of chlorine during the precipitation of single chloride minerals". We reject his comments and confirm our viewpoint: with progressive evaporation, the δ^{37}Cl values for the NaCl, KCl, and $MgCl_2$ solutions significantly decreased. We also confirm the exchange program that samples can be exchanged and measured in these different laboratories with different techniques, but the experiments should be conducted in way of progressive evaporation.

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