Chlorine and bromine isotope evolution within a fully developed Upper Permian natural salt sequence

H.G.M. Eggenkamp [a,*], P. Louvat [b], J. Griffioen [c,d], P. Agrinier [a]

[a] *Équipe de Géochimie des Isotopes Stables, Institut de Physique du Globe de Paris, Sorbonne Paris Cité, UMR 7154, CNRS, 1 rue Jussieu, 75238 Paris Cedex 05, France*
[b] *Équipe de Géochimie des Enveloppes Externes, Institut de Physique du Globe de Paris, Sorbonne Paris Cité, UMR 7154, CNRS, 1 rue Jussieu, 75238 Paris Cedex 05, France*
[c] *TNO Geological Survey of the Netherlands, P.O. Box 80015, Utrecht, the Netherlands*
[d] *Copernicus Institute of Sustainable Development, Utrecht University, P.O. Box 80115, Utrecht, the Netherlands*

Abstract

The behaviour of chlorine and bromine isotopes in evaporite deposits differs significantly. We studied the isotope variations of both elements in a fully developed natural salt sequence from Zechstein evaporite deposits (Wuchiapingian, Upper Permian) in the Northern Netherlands. We observed that the Cl isotope variations follow previously predicted characteristics, showing slightly positive $\delta^{37}Cl$ (relative to seawater) in halite ($NaCl$) dominated layers (up to +0.05‰), decreasing to moderately negative values in carnallite ($KMgCl_3 \cdot 6H_2O$) and bischofite ($MgCl_2 \cdot 6H_2O$) dominated layers (down to −0.55‰). Bromine isotope variations, the first ever measured in marine evaporite samples, show a different characteristic. $\delta^{81}Br$ values decrease quickly in layers dominated by halite (from +0.2 to −0.5‰) and increase again in layers dominated by carnallite and bischofite (up to −0.1 ± 0.2‰). These observations suggest that the Br isotope fractionation ($10^3\ln\alpha$) during precipitation of halite can be as high as +1.3, 3.8 times as large as Cl isotope fractionation. The increasing $\delta^{81}Br$ values during precipitation of magnesium salts may suggest a negative fractionation ($10^3\ln\alpha$) of −0.9, meaning that the Br isotope ratio in the precipitated salt is lower than in the brine. We suggest that the difference in behaviour between Cl and Br can be explained by the fact that Br, as a minor component in the brine, has to compete with Cl to fit into the crystal lattice of Cl salts, where it does not fit perfectly due to its slightly larger ionic radius than Cl, resulting in relatively large isotope fractionation. Further research is however needed to confirm or reject this suggestion.

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1. INTRODUCTION

Evaporites and their fluid inclusions are used to reconstruct the evolution of the chemical composition of seawater over geologic times (Horita et al., 2002; Lowenstein et al., 2003, 2005), which is very important to understand the evolution of our planet and of its climate, a major concern today for the future. Because chloride and bromide are supposedly conservative in seawater, measuring chlorine and bromine isotope ratios in evaporite deposits could bring additional valuable information regarding the conditions in which the huge salt deposits formed, and thus to ancient environmental settings of the oceans. But before addressing the long-term evolution of Cl and Br isotopes in the ocean, it is important to understand what their

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signatures in evaporite deposits represent, whether the seawater signal can be preserved or at least deduced from the evaporite compositions, or if these signatures have a different meaning (e.g. can trace certain conditions under which seawater evaporation and salt precipitation took place).

The evolution of chlorine stable isotopes within single salt sequences has been discussed regularly since our first contribution on this subject (Eggenkamp et al., 1995, 2016; Eastoe et al., 1999; Xiao et al., 1997, 2000; Sun et al., 1998; Tan et al., 2009; Luo et al., 2012, 2014, 2015; Eggenkamp, 2015a; Eastoe et al., 2007, Eastoe, 2016). In these studies, the evolution of salt that precipitates during the evaporation of saturated brines is discussed based on the stable chlorine isotope fractionation of the individual salt components NaCl, KCl and MgCl$_2$, the experimental evaporation of a seawater sample, or the salt composition of evaporites in non-marine inland basins. The general trend is that the chlorine isotope ratio (^{37}Cl/^{35}Cl expressed as δ^{37}Cl relative to SMOC, modern seawater, in ‰ unit) decreases during precipitation of salt from the evaporite brine. The δ^{37}Cl value of the initial precipitate is about +0.35‰, decreasing to a minimum value of about −0.69‰ when bischofite (MgCl$_2$·6H$_2$O) starts to precipitate. This change reflects the equilibrium isotope fractionation between chloride in brine and chloride in precipitated halite (Eggenkamp et al., 2016). The fractionation is less well understood for potassium and magnesium chloride precipitation: Eastoe et al. (1999) observed that the chlorine isotope ratio increases, whereas Luo et al. (2012, 2014) observed on the contrary that it continues to decrease. The chlorine isotope fractionation factor (10^3lnα, where α is the ratio of ^{37}Cl/^{35}Cl in the salt to ^{37}Cl/^{35}Cl in the brine) for this last evaporation stage can thus be either lower or higher than 1. It is expected that the chlorine isotope variation in this last evaporation stage is very limited, as bischofite precipitates with 6 molecules of water, while by the time the brine is saturated in bischofite the total amount of water present in the brine is only 9.5 molecules per mole MgCl$_2$ (Clynne and Potter, 1979; Atbir et al., 2000; Table 4 in Eggenkamp et al, 2016). Hence, only a small amount of water will need to evaporate before the brine completely solidifies.

On the contrary, the evolution of bromine stable isotopes in salt sequences has not been studied in much detail yet. One study we know of investigated the bromine isotope fractionation of individual bromide salts such as NaBr, KBr, MgBr$_2$ and CaBr$_2$ during precipitation from their saturated solutions (Eggenkamp et al., 2016). From this study, one can hypothesize that only little bromine isotope variation (less than 0.2‰) will be observed in salt sequences. It has to be realised however that bromide, due to its low concentration and similar ionic radius as chloride, does not form evaporite minerals of its own, so that the precipitation processes it observes can be significantly differing from those of chloride.

A second study (Hanlon et al., 2017) investigated for the very first time the bromine and chlorine isotope variation in salts, associated waters and volatiles from a series of salt lakes in Nebraska and Kansas (USA). They observed

clearly different behaviour of bromine and chlorine isotopes in these lake systems. ^{37}Cl was consistently more enriched in the salt than in the fluid, while ^{81}Br was consistently more enriched in the fluid compared to the precipitated salt.

In the present study, we first aim to characterise the evolution of the chlorine and bromine stable isotope ratios within one single natural salt sequence, the Zechstein salt sequence from the Northeastern Netherlands. The chlorine isotope variations in a salt deposit that consists of the full salt development sequence from halite to bischofite (Braitsch, 1962) should confirm (or contradict) the results from earlier chlorine isotope studies in evaporites. Second, we aim to determine whether the same principles hold for the bromine isotope variation as for the Cl isotope variation, or if the bromine isotope variation is determined by other principles and, if so, which ones.

Northeastern Netherlands is particularly suitable for a study on chlorine and bromine isotopes in a fully developed salt sequence due to the large amount of magnesium salt deposits present (Coeleweij et al., 1978). Our samples are taken from the same drill core that was studied by Eggenkamp et al. (1995) and that was described in detail earlier by Buyze and Lorenzen (1986). The core was resampled for the current research. The samples were selected based on their mineral composition and were sampled from layers that were dominated by halite (NaCl dominated samples), carnallite (KMgCl$_3$·6H$_2$O dominated samples) or bischofite (MgCl$_2$·6H$_2$O dominated samples).

Eggenkamp et al. (1995) observed significant variation of ^{37}Cl/^{35}Cl in the natural, fully developed salt sequence of Zechstein deposits (Wuchiapingian, Upper Permian) in the Netherlands. However, the trend was merely described qualitatively as no direct chemical analyses were made on the salt samples measured for Cl isotopes. In the present study, we took samples from the same boring as the earlier study and the chemical composition was characterised in detail as well. Thus, the compositional evolution of the sequence can be considered in parallel with the evolution of the chlorine and bromine isotope ratios.

2. MATERIAL

Samples were taken from core TCI-2 (Tripscompagnie-2, original name TR-2) that was drilled in 1982 through the Veendam structure near Groningen, Northern Netherlands to explore the Zechstein (Wuchiapingian, Upper Permian) salt deposits for magnesium mining (Coeleweij et al., 1978; Buyze and Lorenzen, 1986, Fig. 1). This core contains carnallite and bischofite in addition to kainite (KMgClSO$_4$·3H$_2$O) and halite. The core, therefore, allows the study of the final stages of the evaporation process.

The Zechstein (Wuchiapingian, Upper Permian) is a European sedimentary rock unit that contains massive marine salt deposits (Warren, 2010). Core TCI-2 is from the upper part of the Zechstein III Formation (Nederlandse Aardolie Maatschappij and Rijks Geologische Dienst, 1980). It samples subformations Zechstein-III-1, -2, and -3. All three subformations are again divided in a lower part a, which contains mainly halite, and a carnallite- and
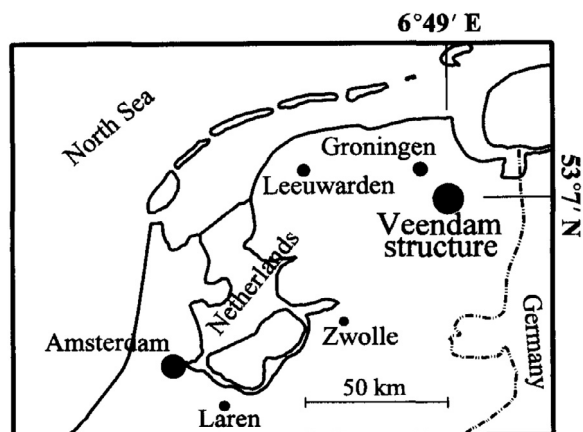
Fig. 1. Location of the Veendam Salt Structure in the Netherlands (after Coeleweij et al., 1978).

bischofite-rich upper part b. These formations were described in detail by Coeleweij et al. (1978) using the different, but geologically similar core VDM-4 (Veendam-4).

The salt composition of core TCI-2 is summarised in Fig. 2. Below 1770 m (Zechstein-III-la), the core contains massive halite with some sylvite (KCl) and langbeinite ($K_2Mg_2(SO_4)_3$) layers. These are not primary minerals, indicating secondary processes due to conversion at temperatures above 83 °C (Braitsch, 1962). From 1770 to 1693 m, a layered sequence (Zechstein-III-1b) of carnallite, bischofite, halite, and some kieserite ($MgSO_4·H_2O$) is found. From 1693 to 1654 m, formation Zechstein-III-2a with halite and some carnallite is found. Between 1654 and 1640 m, carnallite, halite, and kieserite are present. Here the core is red, indicating the presence of iron oxides, with some banding (Zechstein-III-2b). From 1640 to 1631 m, it contains halite with some carnallite (Zechstein-III-3a). Above this, the core contains halite, carnallite, and kieserite (Zechstein-III-3b, Haug, 1982). The two potassium-magnesium cycles, Zechstein-III-1b and -2b are very different (Coeleweij et al., 1978). Zechstein-III-2b shows no distinct subcycles, whereas in Zechstein-III-1b nine subcycles are present, each containing several mini-cycles (Eggenkamp et al., 1995). For the current study samples were selected from subformation Zechstein-III-2a which is predominantly halite at coring depths from 1678 to 1689 m, and subformation Zechstein III-1b for predominantly carnallite samples at depths between 1700 and 1704 m and for predominantly bischofite rich samples at depths between 1715 and 1719 m (see Fig. 2).

Detailed information on the boreholes can be obtained from the Dutch government website on oil, gas and geothermal energy exploration and production in the Netherlands http://www.nlog.nl/en/. The core is stored at TNO Geological Survey (Zeist, The Netherlands).

Samples were taken from three depth intervals that are each dominated by one of the salt minerals halite, carnallite or bischofite. The first set of six samples, dominated by sodium salts, was taken at coring depths between 1678 and 1689 m (that is, due to the deviation of the boring, between 1672 and 1689 m below Dutch reference level,
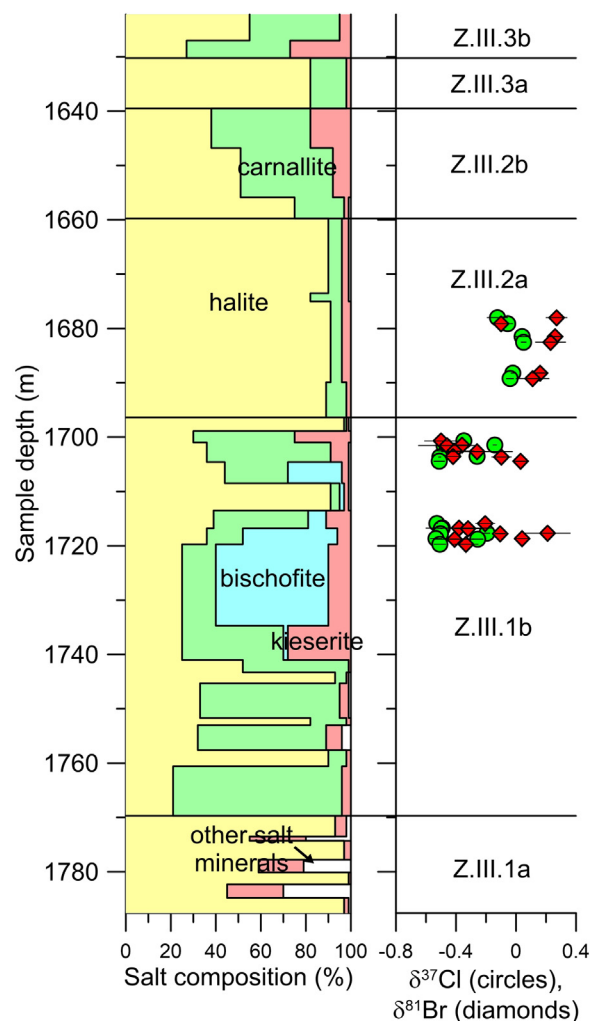

Fig. 2. Left, stratigraphic column of drillhole TCI-2 indicating the average mineral composition of the salt minerals per interval. Other salt minerals indicate mainly sylvite and langbeinite. Right, measured $\delta^{37}Cl$ (circles) and $\delta^{81}Br$ (diamonds) values of the samples taken from the indicated depths. Both isotope systems are plotted in the same column so that it is easily visible that the isotope behaviour of Cl and Br depends on the mineralogical composition of the salt. Compared to samples analysed in the research by Eggenkamp et al. (1995) samples are not taken evenly over the length of the core but from sections dominated by halite, carnallite and bischofite in order to obtain characteristic isotope data for samples dominated by these minerals.

NAP) and consists on average of 91% halite, 4% kieserite and 5% carnallite by weight, based on the original analysis of the core. The second set of eight samples, dominated by potassium salts, was taken at coring depths between 1701 and 1704 m (between 1695 and 1699 m below NAP) and has an average composition of 36% halite, 8% kieserite, and 55% carnallite by weight. The third set of eight salts, dominated by magnesium salts, was sampled at coring depths of 1716 and 1719 m (1710–1713 m below NAP) and consists on average of 36% halite, 6% kieserite, 16% carnallite and 42% bischofite by weight.

3. METHODS

Samples were prepared for chemical and isotopic analyses by diluting the whole sample (without separating into individual minerals) in two steps. The first step included dissolving about 1 g of sample in 9 g of MilliQ water for isotopic analyses. For elemental analyses, the above samples were diluted an extra 1000 times (30 mg of the first solution in 30 g of MilliQ water), leading to samples containing about 100 mg/L dissolved solids that could be analysed by ICP.

All samples were analysed for major element (Cl^-, Br^-, SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+}) and for Cl and Br isotopic compositions ($\delta^{37}Cl$ and $\delta^{81}Br$) at the Institut de Physique du Globe de Paris. Chloride and bromide were determined by ICP-MS on an Agilent 7900 ICP-MS. The cations and sulphate (measured as S) were analysed by ICP-OES on a Thermo Scientific iCAP 6000 Series. These concentrations allowed us to back calculate the chemical compositions of the salts, which are reported in Table 1 in g per kg of salt.

Chlorine isotope compositions were measured according to the method developed by Kaufmann (1984) and described in detail in Eggenkamp (1994) and Godon et al. (2004). In short, Cl^- in the samples was precipitated as AgCl by adding $AgNO_3$, which was reacted with CH_3I to form CH_3Cl. $^{37}Cl/^{35}Cl$ ratios were subsequently determined with dual-inlet mass spectrometry on a ThermoFisher Delta PlusXP mass spectrometer. The results are reported in δ notation ($\delta^{37}Cl$) defined as:

$$\delta^{37}Cl = \left[\left(^{37}Cl/^{35}Cl \right)_{sample} / \left(^{37}Cl/^{35}Cl \right)_{SMOC} - 1 \right] \times 1000$$

with ‰ relative to SMOC (Standard Mean Ocean Chloride, Kaufmann et al., 1984) and an average standard deviation (1σ) of 0.05‰.

The bromine isotope compositions were determined on a Thermo Scientific Neptune multicollector ICP-MS. Samples were prepared in one of two possible methods. From samples with a high Br/Cl ratio, bromine is extracted by ion exchange chromatography on anion exchange resin AG 1X4 using 0.2 M NH_4NO_3 as eluting solution (Louvat et al., 2016). For precise measurements 10–20 μg of bromine (in 2 mL solution) are necessary, so that samples with low Br/Cl-ratios could not be treated this way. As the exchange columns are filled with 1 mL of anion exchange resin with a maximum capacity of 1 meq/mL, the Br^- content in solutions with low Br/Cl is less than that required for isotope analysis. Modification of the extraction protocol by using larger volumes of resin would also have increased the final elution volume, thus diluting the Br concentration for MC-ICP-MS measurements even more, and was therefore not explored. For these reasons, bromine from samples with low Br/Cl ratios was extracted by oxidative distillation following Eggenkamp and Louvat (2018, after Murphy et al., 1954) In these samples, bromide is oxidised to bromine gas by a 14% boiling nitric acid solution and distilled into a 0.5 N ammonia solution. In this alkaline solution, Br_2 is trapped and most probably reduced back to bromide. This solution can be measured the same way as the bromide solution obtained by the ion exchange method. The samples were introduced to the MC-ICP-MS through a small (20 mL) quartz spray chamber with a self-aspiring PFA nebulizer at 50 μL/min uptake rate. The measurements were done in low-resolution mode after careful tuning of the instrument, in order to minimize Ar_2H^+

Table 1

Results of the chemical and isotopic analyses of the samples from core TCI-2. $\delta^{37}Cl$ errors are defined as the 1 standard deviation of multiple measurements (mostly 2, sometimes 3). $\delta^{81}Br$ errors are defined as the 2 standard deviation of 5 $\delta^{81}Br$ measurements based on measurements of the sample and of a bracketing solution (Std-Smpl-Std-Smpl-Std-Smpl-Std). The bracketing standard solutions are prepared to the same Br and Cl concentrations as the analysed samples, in order to avoid linearity bias and matrix effects.

Sample	Depth (m below surface)	Na+ g/kg salt	K+	Mg2+	Ca2+	Cl-	Br-	SO_4^{2-}	$\delta^{37}Cl$ ‰ vs. SMOC	$\delta^{81}Br$ ‰ vs. SMOB	Br/Cl Weight units
NL09	1678.0	391.00	1.36	2.47	0.80	601.44	0.21	10.50	-0.12 ± 0.07	$+0.27 \pm 0.07$	0.00035
NL10	1679.1	393.47	1.17	0.73	0.05	603.19	0.32	0.42	-0.06 ± 0.03	-0.10 ± 0.05	0.00054
NL11	1681.5	394.04	2.52	4.12	1.52	608.77	0.22	12.53	$+0.04 \pm 0.04$	$+0.26 \pm 0.05$	0.00036
NL12	1682.5	397.63	5.14	4.83	0.40	617.82	0.24	8.28	$+0.05 \pm 0.02$	$+0.20 \pm 0.08$	0.00038
NL13	1688.2	360.97	0.22	14.34	0.45	561.36	0.14	54.13	-0.02 ± 0.01	$+0.16 \pm 0.05$	0.00025
NL14	1689.2	324.47	0.22	28.85	1.21	517.30	0.20	106.64	-0.04 ± 0.02	$+0.11 \pm 0.11$	0.00039
NL15	1700.7	158.93	83.94	55.03	3.10	479.03	2.88	7.38	-0.35 ± 0.10	-0.50 ± 0.11	0.00602
NL16	1701.5	354.40	4.01	5.12	16.60	561.01	0.47	44.22	-0.14 ± 0.01	-0.36 ± 0.05	0.00084
NL17	1701.6	96.57	98.13	74.23	4.65	433.12	3.47	40.20	-0.48 ± 0.07	-0.46 ± 0.19	0.00800
NL18	1702.6	56.48	118.27	82.49	2.85	428.51	4.20	11.50	-0.42 ± 0.01	-0.41 ± 0.13	0.00980
NL19	1702.7	11.71	68.64	122.41	3.30	228.38	2.63	291.19	-0.46 ± 0.03	-0.26 ± 0.24	0.01151
NL20	1703.6	333.88	13.24	12.24	2.24	551.32	0.66	17.95	-0.26 ± 0.01	-0.42 ± 0.05	0.00119
NL21	1703.7	54.51	116.43	82.68	2.07	426.92	4.17	5.67	-0.51 ± 0.01	-0.09 ± 0.07	0.00977
NL22	1704.5	6.53	7.94	113.65	0.39	346.22	4.82	1.49	-0.51 ± 0.04	$+0.03 \pm 0.05$	0.01391
NL23	1715.9	1.61	136.28	96.91	0.00	402.50	5.67	2.44	-0.53 ± 0.01	-0.20 ± 0.06	0.01409
NL24	1716.8	23.37	99.76	94.94	0.09	332.03	4.09	101.70	-0.49 ± 0.03	-0.23 ± 0.21	0.01232
NL25	1716.9	27.32	128.52	92.64	0.01	421.41	5.47	3.18	-0.50 ± 0.01	-0.32 ± 0.09	0.01298
NL26	1717.7	334.23	23.21	18.20	1.67	581.81	1.27	4.58	-0.19 ± 0.02	$+0.20 \pm 0.15$	0.00218
NL27	1718.6	9.16	0.66	125.26	0.00	359.55	6.22	25.36	-0.50 ± 0.01	-0.13 ± 0.17	0.01730
NL28	1718.7	7.73	2.09	122.18	0.00	361.12	6.24	7.53	-0.53 ± 0.04	$+0.04 \pm 0.04$	0.01728
NL29	1718.8	313.74	29.21	21.29	0.24	567.08	1.56	2.99	-0.26 ± 0.04	-0.04 ± 0.32	0.00275
NL30	1719.7	1.18	0.00	129.19	0.00	349.83	6.33	36.93	-0.51 ± 0.04	-0.33 ± 0.08	0.01810

interference and to maximize ^{79}Br and ^{81}Br signals (Louvat et al., 2016). The Ar_2H^+ interference was corrected by blank subtraction. Bromine isotope ratios were measured by sample-standard bracketing with the NIST SRM 977 reference material solution at the same concentration as that of the sample solution. Blank was measured before each sample or standard, and each sample was measured three times. Seawater (MOMARSAT, Indian Ocean, sampled in January 2010 on the MD 175 cruise, latitude

$-32.45°$S, longitude $+84.01°$E) was passed through the same Br extraction procedures as the samples to check both extraction yield and accuracy of the isotope ratio measurements. The results are finally reported in δ notation (δ^{81}Br) defined as:

$$\delta^{81}\text{Br} = \left[\left({}^{81}\text{Br}/ {}^{79}\text{Br} \right)_{\text{sample}} / \left({}^{81}\text{Br}/ {}^{81}\text{Br} \right)_{\text{SMOB}} - 1 \right] \times 1000$$
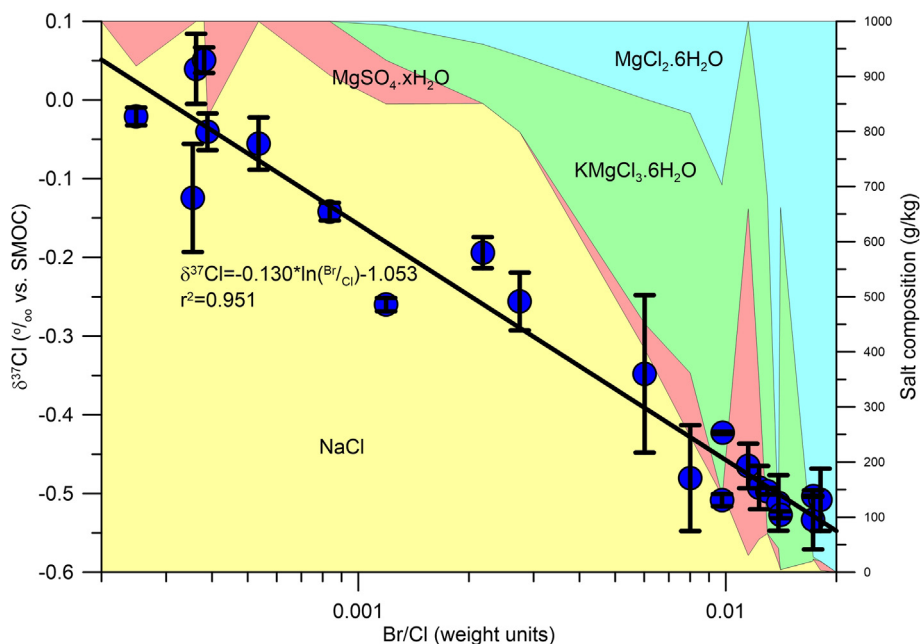

Fig. 3. Relationships between δ^{37}Cl, Br/Cl ratio and the mineralogical composition of the samples.

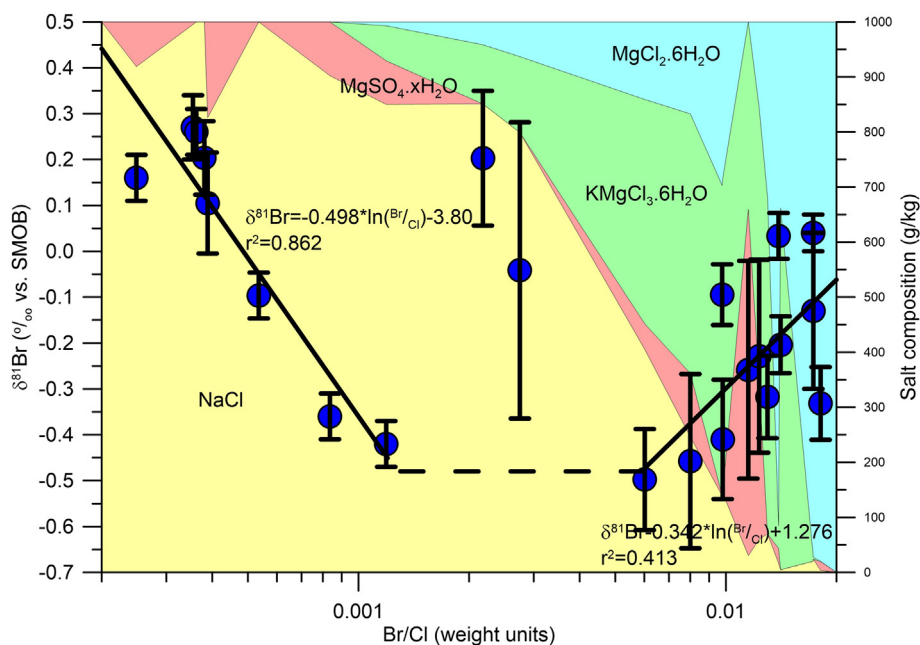Fig. 4. Relationships between δ^{81}Cl, Br/Cl ratio and the mineralogical composition of the samples.

with ‰ relative to SMOB (Standard Mean Ocean Bromide; Eggenkamp and Coleman, 2000) and an average standard deviation (1σ) that is generally better than 0.1‰. Unfortunately the precision of some samples is worse than this. Some samples had too little bromide to be analysed using the ion exchange chromatography method, and needed to be analysed using the oxidation method that was still under development in the course of this project.

4. RESULTS

The chemical composition, and $\delta^{37}Cl$ and $\delta^{81}Br$ values of the salt samples are reported in Table 1. Because the Br/Cl ratio is used as a measure for the salt evolution it is also given. The three sets of samples can be well recognised in this table. Group 1, the halite dominated samples, (NL09 to NL14) is clearly dominated by NaCl. The samples in Group 2 (NL15 to NL22) were supposedly dominated by carnallite, but the compositions vary considerably (Table 1): K^+ is frequently high but Na^+ and also SO_4^{2-} can be high as well. In these presumably carnallite-dominated samples, it is, however, expected that both Mg^{2+} and Na^+ are also regularly a common cation. In Group 3, the samples dominated by bischofite (NL23 to NL30), the magnesium concentration is indeed mostly high. There are, however, two samples in this group (NL26 and NL29) that contain low magnesium concentrations and are dominated by NaCl. These samples are indicative of the large compositional variability in the sampled core, and especially in the Zechstein-III-1b unit. The sample variability shows that NaCl dominated layers are well defined. In potassium and magnesium dominated layers however, alternation between Mg-rich layers and K-rich layers is quite common, most probably because of intermittent inflow of less evolved brines in the basin at irregular time intervals (Coeleweij et al., 1978).

It is well known that the Br/Cl ratio is related to brine and salt evolution: the more evolved a brine, the higher the Br/Cl ratio in the precipitate (Braitsch, 1962). As proposed by Valyashko (1956), the bromide content in evaporites can be used as a genetic and prospecting tool. Indeed, the Br/Cl ratio is low in first stage halite samples (down to 0.00025 in this dataset), and much lower than the Br/Cl in seawater (0.0034) as Br incorporates much less in the salt crystals than Cl. The ratio increases significantly with increasing Mg concentrations and reaches its highest values (up to 0.018) in samples with the highest Mg concentrations. Consistent with this, $\delta^{37}Cl$ decreases from about +0.05‰ in pure halite samples with the lowest Br/Cl ratios, to about −0.55‰ in pure bischofite samples with the highest Br/Cl ratios. A clear relationship is observed between the Cl isotope composition of the salts and the log-value of their Br/Cl ratios (Fig. 3).

The relationship between the log value of Br/Cl ratio and $\delta^{81}Br$ is not as straightforward as for $\delta^{37}Cl$. The samples with the lowest Br/Cl ratios have positive $\delta^{81}Br$ values (+0.2‰) that decrease to negative values (down to −0.5‰) with increasing Br/Cl ratio as long as halite is the most common salt in the deposit. When carnallite and bischofite become the most common salts in the deposit, $\delta^{81}Br$ values

appear to increase again with increasing Br/Cl ratios up to a value of about 0‰, albeit with considerable scatter, and a rather low r^2 of only 0.41. The two NaCl rich samples (NL26 and NL29) deviate from this general trend. They have high $\delta^{81}Br$ values (+0.20 and −0.04‰) while their Br/Cl ratios are intermediate between the Br/Cl ratios of the sodium dominated and of the potassium and magnesium dominated samples. However, these two samples do not belong to group 1 (i.e., the halite rich samples) but they are the two above-mentioned NaCl rich samples that lie interbedded between the $MgCl_2$ dominated samples of Group 3 (Fig. 4).

Figs. 3 and 4 reflect the variability in the $\delta^{37}Cl$ and the $\delta^{81}Br$ data as function of the Br/Cl ratio of the samples. The background colours in the figures show the mineral composition of the samples so that the variability in the isotope ratios can visually be related to the sample composition. Globally the range in $\delta^{81}Br$ values is larger than that for $\delta^{37}Cl$ (0.8‰ vs. 0.6‰), and unlike Cl isotopes, it is not possible to draw a single simple trend function through the bromine isotope data. Fig. 5 shows how the chlorine and bromine isotope variations are related to each other. In this figure the salt precipitation evolution runs from right (high $\delta^{37}Cl$ values) to left (low $\delta^{37}Cl$ values). The trends that are visible are comparable to the trends visible in Fig. 4, showing (from right to left) a decreasing $\delta^{81}Br$ at high $\delta^{37}Cl$ values, and an increasing $\delta^{81}Br$ at low $\delta^{37}Cl$ values. Just like in Fig. 4 samples NL26 and NL29 also fall outside the trend. The same background colours as in Figs. 3 and 4 are used to show the mineral composition
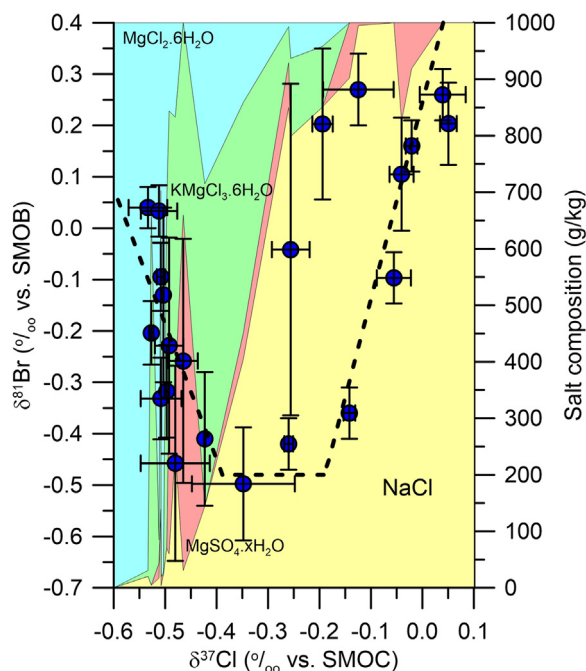

Fig. 5. Relationships between $\delta^{37}Cl$, $\delta^{81}Cl$ and the mineralogical composition of the samples. Please not that the first precipitated salt is the salt with the highest $\delta^{37}Cl$ value that is located on the right of the figure. Salt evolution evolved to the left in this figure.

of the samples so that the variability of the isotope ratios can again be visually related to the sample composition.

5. DISCUSSION

5.1. Br/Cl ratios

The bromide content of salts that precipitate from modern seawater has long been of interest (Boeke, 1908; Kühn, 1955; Valyashko, 1956, Braitsch and Hermann, 1963, 1964; Hermann, 1972, 1980; Hermann et al., 1973; McCaffrey et al., 1987). It is related to the bromide (and chloride) content of the brine and to the crystal structure of each salt mineral, each of which incorporates a different amount of bromide relative to chloride (Braitsch and Hermann, 1963). Eggenkamp et al. (1995) used the mineral composition during the different stages of salt precipitation in combination with the Cl isotope fractionation of the individual salt minerals to calculate the Cl isotope fractionation factors in four stages of evaporite precipitation, respectively dominated by halite, kainite (the first precipitating KCl salt: $KMgClSO_4 \cdot 3H_2O$), carnallite and bischofite precipitation. The same set of data can be used to estimate the bromide concentration of the salts during the precipitation sequence, assuming that: 1/ the bromide distribution factor, defined as $b = Br_{wt\% \text{ in salt}} / Br_{wt\% \text{ in solution}}$ (Braitsch and Hermann, 1963) decreases from 0.14 to 0.073 during the first stage, when only halite precipitates; 2/ the distribution factor is 0.22 for kainite and 0.073 for halite when kainite is the most prominent precipitating salt; 3/ it is 0.52 for carnallite and 0.073 for halite when carnallite is the prominent precipitating salt and finally 4/ it is 0.66 when bischofite is the prominent precipitating salt (Braitsch and Hermann, 1963). These distribution factors are experimentally determined for slowly precipitating salt in equilibrium with brine. It is then possible to compare the salt compositions calculated by Braitsch (1962) with those measured in the present study.

The chemical composition of ocean water in the Late Permian Epoch, from which the Zechstein deposits originate, was comparable to that of modern ocean (Horita et al., 2002; Lowenstein et al., 2003, 2005), except that the sulphate concentration was about 25% lower than today. For simplicity, the comparison is made with the salt compositions as calculated by Braitsch (1962), starting from today's chemical composition of seawater. The bromide distribution factors lead to predicted Br/Cl ratios systematically increasing during the halite phase from 0.00008 to 0.00021, during the kainite phase from 0.00064 to 0.00096, during the carnallite phase from 0.0021 to 0.0026 and during precipitation of bischofite from 0.0048 to higher.

This large range in Br/Cl ratios is not observed in our samples. The lowest Br/Cl ratio measured in nearly pure halite samples is higher than predicted, 0.00025 instead of 0.00008. On the other end of the spectrum, predicted Br/Cl ratios of bischofite agree much better with the expected ratios. The trend is clear, the Br/Cl ratio increases with increasing salt evolution (Figs. 3 and 4). The observation that the measured Br/Cl ratios are larger than the predicted

values can be explained in three different ways. 1/ If the precipitation of the salt was out of equilibrium due to fast precipitation of salt, the factor b is larger as more Br is incorporated in the salt phase (Herrmann, 1980). 2/ Fluid inclusions that are present in the salt, containing the original brine with high Br/Cl ratios, may increase the Br/Cl ratio of the analysed salt. 3/ High Br/Cl could also reflect either residual brines that were trapped between the salt deposits and evaporated at a later stage, or possibly a mixing of residual brine from the Zechstein Sea with more dilute seawater (originating from the Paleotethys Ocean?), which caused an extension of the halite precipitation stage but with increased Br/Cl ratio. As the Br/Cl ratio of seawater is 0.0034 and that of the residual brines it is even higher, only small amounts are necessary to significantly increase the Br/Cl ratios of the precipitated salts, especially during precipitation of Br-poor halite. Even when these discrepancies between predicted and measured Br/Cl ratios are taken into account, the Br/Cl ratio still appears as a good tracer of salt evolution stage because the Cl isotope composition and also the salt composition of the samples are well correlated with the measured Br/Cl ratio.

5.2. Cl isotope evolution

As expected from previous studies, the Cl isotope ratio of the samples decreases with increasing salt evolution (Fig. 3) and reaches a minimum $\delta^{37}Cl$ of about $-0.55‰$ in the samples with the highest Br/Cl ratios, which consist of almost 100% bischofite. The $\delta^{37}Cl$ values of the samples show a good logarithmic relationship with the Br/Cl ratios ($r^2 = 0.951$; Fig. 3). According to calculations based on the various experimental determinations of Cl isotope fractionation during precipitation of salt samples (Eggenkamp et al., 1995, 2016; Luo et al., 2012, 2014, 2015; Eggenkamp, 2015a), either the lowest $\delta^{37}Cl$ values should be reached right at the beginning of bischofite precipitation (Eggenkamp et al., 2016), or $\delta^{37}Cl$ should continue to decrease even when Mg chlorides precipitate (Luo et al., 2014). Thus the predicted $\delta^{37}Cl$ at the onset of bischofite precipitation is either about $-0.5‰$ considering the isotopic fractionation factors determined by Eggenkamp et al. (2016), or about $-1.0‰$ considering those of Luo et al. (2014). In the present study, $\delta^{37}Cl$ is about $-0.5‰$ in samples from the last evaporation stages, which confirms that the Cl isotope fractionation factor for halite is close to 1.00035, as determined by Eggenkamp et al. (2016), and not 1.00051, as determined by Luo et al. (2014).

The Cl isotope fractionation factor of bischofite cannot be deduced from the present dataset, as hardly any significant Cl isotope variation is found for the bischofite dominated samples. This is, however, an indication that the Cl isotope fractionation factor for bischofite is most probably very close to 1 as determined by Eggenkamp et al. (2016). With a value of 0.99998 ± 0.00002, they concluded that the bischofite Cl isotope fractionation factor is not significantly different from 1. Here, it may be realised that the mole ratio $MgCl_2:H_2O$ is 1:9.5 when a brine is saturated in bischofite (Clynne and Potter, 1979; Atbir et al., 2000) and 6 of these water molecules will precipitate with $MgCl_2$

in bischofite. So the loss of only little water from such brine will result in the total solidification of the remaining brine into bischofite without any possibility for further Cl isotope fractionation and thus any further change in the Cl isotope composition.

5.3. Br isotope evolution

The bromine isotope composition follows a different path than the Cl isotope composition during its evolution from halite to bischofite. Unlike Cl, there seems to be no relationship with the predicted isotope fractionation based on the experimentally determined isotope fractionation during Br salt precipitation (Eggenkamp et al., 2016). The relationship between the Br isotope composition and the brine/evaporite evolution as represented by the Br/Cl ratio is shown in Fig. 4. As in Fig. 3, the proportions of the major salt phases for each sample are shown in the figure so that the isotope composition can be compared easily with the salt evolution in the samples.

It appears that the first bromide salts precipitated from the Zechstein Sea have positive ($\approx$+0.2‰) δ^{81}Br values. Then δ^{81}Br decreases quickly in halite-dominated samples to $\approx$−0.5‰. As with δ^{37}Cl, there appears to be a fairly good relationship between δ^{81}Br and the log-value of the Br/Cl ratio in the most halite-dominated samples (Br/Cl $\leq$ 0.0012), with $r^2 = 0.86$. The slope of the regression line is significantly steeper than for δ^{37}Cl, suggesting a much larger isotopic fractionation for Br than for Cl during halite precipitation. As a first approximation, it is presumed here that the slope on the log(Br/Cl-ratio) vs. δ^{37}Cl or δ^{81}Br has a linear relationship with the isotope fractionation 1000lnα. On the Cl plot (Fig. 3), the slope is −0.130, equivalent to a fractionation factor (1000lnα) of 0.35 as determined by Eggenkamp et al. (2016). For Br, the slope at low Br/Cl values is −0.498 (Fig. 4). This value is 3.8 times greater in magnitude than for Cl, and suggests an isotopic fractionation factor (1000lnα) of 1.3 ($\alpha = 1.0013$) for Br during halite precipitation, following the formula (−0.498/−0.130) * 0.35 = 1.3, where −0.498 is the slope of the Br isotope values, −0.130 the slope of the Cl isotope values and 0.35 1000lnα for Cl. It has to be realised that this is only a first approximation based on a single set of observations on natural samples, which needs to be confirmed by more observations, including experimental. However, the suggestion of such a large isotope fractionation might explain the large variation of Br isotope values in certain environments.

On the contrary, in the carnallite and bischofite dominated part of the sequence (Br/Cl ratio >0.005), the δ^{81}Br values appear to increase again, although with considerable scatter, from about −0.5‰ to about −0.1 ± 0.2‰ for the most evolved samples. The r^2 of 0.41 suggests only a weak relationship between δ^{81}Br and the log-value of the Br/Cl ratio (see Fig. 4). The positive slope of this regression (+0.342) suggests an isotope fractionation of −0.9 ($\alpha = 0.9991$). This value is determined by dividing the log (Br/Cl) vs δ^{81}Br slope of the high Br/Cl Br isotope trend by the general slope log(Br/Cl) vs δ^{37}Cl, and multiplying with the Cl isotope fractionation factor. This gives a value of 1000lnα(+0.342/−0.130)*0.35 = −0.9 where +0.342 is the slope of the Br isotope values, −0.130 the slope of the Cl isotope values and 0.35 is 1000lnα for Cl (during halite precipitation). This value suggests that the bromide that precipitates in carnallite and bischofite is isotopically lighter than bromide in the brine. It also is possible that, in the very evolved brines from which these salts precipitate volatile halide gases have escaped in a similar fashion as suggested by Hanlon et al. (2017). Hanlon et al. (2017) find that halide volatiles that escape from terrestrial lakes during evaporation are enriched in ^{79}Br, indicating that the remaining brine will increase in ^{81}Br, a trend that is also suggested in our samples. Given the only weak indications for the proper fractionation process the suggested Br isotope fractionation during carnallite and bischofite precipitation clearly needs further confirmation in future studies.

Two samples (NL26 and NL29) with intermediate Br/Cl ratios have δ^{81}Br values that strongly deviate from the observed trends (+0.2 and −0.04‰, for Br/Cl of 0.0022 and 0.0028, respectively). Their δ^{81}Br values indicate that these samples are among the first salts precipitating from a saturated solution, while their intermediate Br/Cl ratios rather suggest a brine that is more evolved than the rest of the halite samples. Unlike the other halite rich samples, these two samples are from the bischofite dominated group of samples and their halite content that is over 80%, is much higher than their neighbouring samples. This suggests, as previously discussed, that less evolved or seawater-admixed brines may have been present within the bischofite dominated salt layers at certain periods, and that some of the salts (of a less evolved type) precipitated from them.

Considering the very small Br isotope fractionation measured during precipitation of bromide salts from saturated bromide solutions ($\alpha_{salt-brine} = 0.99993 \pm 0.00005$ for NaBr, 1.00000 ± 0.00001 for KBr and 1.00006 ± 0.00006 for MgBr$_2$; Eggenkamp et al., 2016), no variations beyond ± 0.1‰ from the bromine isotope composition of the oceans are expected for any salt sequence if the same process as for chlorine isotopes applies. The total variation of about 0.8‰ for the δ^{81}Br of the presently studied natural Zechstein salt sequence thus indicates that a different explanation needs to be sought.

Realising this, the process of uptake of bromide in chloride salt minerals can indeed not be compared to the uptake of chloride in these minerals. While the brine is saturated in chloride when chloride salts precipitate, the brine is not saturated with bromide and the minerals formed are not bromide but chloride salts. The incorporation of bromide as impurity in Cl salt minerals is a different process that is probably considerably more complex due to interactions between chloride and bromide ions (and possibly other ions) both in the solution and at the crystal lattice. Although these interactions also play a role for chloride, they are negligible, while they play a major role for bromide due to the low concentration of bromide ions as compared to chloride ions in the brine and even more so in the chloride salt. In brines that predominately precipitate halite, where the amount of bromide relative to chloride incorporated in the crystals is about one tenth of that present in the brine (Braitsch and Hermann, 1963), the uptake of bromide in Cl salt minerals appears to result in a considerable

positive bromine isotope fractionation (1000lnα) of 1.3‰. For potassium and magnesium rich brines, that precipitate carnallite and bischofite, the bromide content relative to chloride in the crystals is over half that present in the brine (Braitsch, 1962). The uptake of bromide in carnallite and bischofite now appears to result in an also considerable, but negative bromine isotope fractionation (1000lnα) of −0.9‰.

Although these crystallisation effects might be reasonable explanations for the isotopic fractionation effects during the incorporation of bromide in chloride salts, additional laboratory experiments and computer simulations are needed for confirmation and to understand the exact processes. Isotope analysis of other fully developed salt sequences would also provide insights of whether the effects observed here for the Dutch Zechstein salt deposits are universally present.

The possibility of large isotope fractionation due to uptake of bromide in salts during precipitation is still speculative, but after Hanlon et al. (2017), this is the second study that provides evidence that precipitation of salt from brine results in large bromine isotope fractionation. It is well possible that different processes than those proposed above have taken place. Eggenkamp (2015b) discussed several of these potential effects that could cause unexpectedly large bromine isotope variation, as observed in most bromine isotope studies. Most fractionation processes that are fairly well understood and that do not involve redox reactions, show much smaller fractionation factors for Br than for Cl. For example, fractionation factors for kinetic process are about two times smaller for Br than for Cl (e.g. Eggenkamp and Coleman, 2009), as Br is about twice as heavy as Cl. Fractionation factors during salt precipitation are more erratic, but can be up to 5 times smaller for Br than for Cl (Eggenkamp et al., 2016). In the case of redox reactions, the fractionation factors for Br are also much smaller than for Cl, as was already theoretically determined in detail at a very early date by Urey and Greiff (1935) and Urey (1947) who found that the reaction between HX and X_2 ($X = Cl$ or Br) would lead to a fractionation between the two phases of 3‰ for Cl, but only 0.4‰ for Br. Further oxidation of X_2 to XO_3^- would result in considerable fractionation of up to 46‰ for Cl and (only!) 8‰ for Br. Although isotope fractionation factors are much smaller for Br than for Cl, Eggenkamp (2015b) argued that, because Br is much easier to oxidise than Cl, it still can lead to a considerably larger total isotope variation.

Can the Br isotope variation in the Dutch Zechstein samples be explained by isotope fractionation due to redox reactions? Bromide is relatively easy to oxidise to Br_2 under ultraviolet light (e.g. Halman and Porat, 1988), but only under acid conditions. Most probably, such conditions do not exist during evaporative precipitation of salts from seawater. Bromide may also be oxidised by biological reactions where bromide is converted to bromomethane (as described e.g. by Blei et al., 2012) and such reactions do not need to take place in acid solutions. In both processes gaseous products are formed that would escape from the aqueous environment. Hanlon et al. (2017) suggested that this type of processes might happen in terrestrial evaporating salt

lake environments which have very high amounts of organic matter. They observed very negative $\delta^{81}Br$ values in gases that escaped from the brine with values down to −1‰ vs. SMOB. The composition of the gas samples was not determined, but it was suggested it consisted of oxidised Br species. As the gaseous products are of a higher oxidation state than the original bromide they are expected to be isotopically heavier, as was calculated by Urey and Greiff (1935), and the $\delta^{81}Br$ of the residual bromide would be lower. Considering the very low $\delta^{81}Br$ values in the gases measured by Hanlon et al. (2017) it may be possible that the process is different from a strict redox reaction and fractionation might be complicated by complex biological reactions. It is not strictly impossible that this effect might also have taken place in our salt sequence, either in the brine, before the precipitation of salt, or in the precipitated salt due to the activity of for example halobacteria (e.g. Schubert et al., 2009). We believe however that in our salt sequence the proposed process is highly unlikely to have taken place. Indeed, to obtain the significantly large isotope variation as observed in our salt sequence, a very large percentage of the bromide should have been oxidised and released to the atmosphere. As a result, the bromide content in the salt should be considerably reduced as a result. On the contrary, the bromide content in our samples appears to be even higher than expected from plain evaporation of seawater (as given by e.g. Braitsch, 1962).

Diffusion can also lead to significant bromine isotope variations (Eggenkamp and Coleman, 2009). Large isotope variations are, however, only expected when large concentration differences between end-members are encountered, which is not the case here. Moreover, very negative $\delta^{81}Br$ values are only reached in the samples with low concentrations during diffusion, while positive $\delta^{81}Br$ values are difficult to obtain by diffusion only (Eggenkamp and Coleman, 2009). For the present dataset, it is unlikely that diffusion could have played a role.

Despite our lack for explanation, the present study of Cl and Br isotopes in a fully developed salt sequence shows large bromine isotopes variations in salt deposits. They are still enigmatic in the sense of present day knowledge of bromine stable isotope behaviour, which is still in its infancy. Bromine deserves more research on both experimental and natural samples to explore the source of its isotope variations and promote its use as a geochemical tracer. Of the processes discussed above, the physico-chemical process that is responsible for the uptake of bromide in the chloride salts might be the most relevant.

6. CONCLUSIONS

We measured the chlorine and bromine isotope variations in a single salt sequence from Dutch Zechstein deposits. The evaluated salt deposit contains the full salt sequence from early stage pure halite deposits to last stage pure bischofite deposits. The results show that chlorine and bromine isotopes undergo very different processes while they precipitate from a saturated brine and get transformed into salt deposits. The salt evolution can be tracked using the Br/Cl ratio, which increases regularly in the evolving salt

deposits from low values in pure halite to high values in pure bischofite deposits. The isotope analyses indicate that $\delta^{37}Cl$ decreases with increasing Br/Cl ratio, from about $+0.05‰$ in halite samples, to about $-0.55‰$ in bischofite samples. This is in line with previous research and confirms the earlier established Cl isotope fractionation factor $\alpha_{salt-brine}$ of 1.00035. Bromine isotopes show a different behaviour, with decreasing $\delta^{81}Br$ values (from $+0.3$ to $-0.5‰$) during the precipitation of halite and increasing $\delta^{81}Br$ values (from -0.5 to $0.0‰$) during carnallite/bischofite precipitation. These values, based on the relationship between the isotope composition and the log(Br/Cl ratio), suggest a Br isotope fractionation factor $\alpha_{salt-brine}$ of 1.0013 during halite precipitation and a isotope fractionation factor $\alpha_{salt-brine}$ of 0.9991 during carnallite/bischofite precipitation. We suggest that the processes that are responsible for the distribution of bromide between a chloride saturated seawater-derived brine and chloride salts are responsible for two different effects. 1/ They may cause the larger than expected Br isotopic fractionation factors compared to the values expected for the precipitation of pure bromide salts from pure bromide brines. 2/ They may also cause the large differences in Br isotope fractionation factors during bromide incorporation in different Cl salts. We argue that other processes such as photo- or bio-oxidation and diffusion that may in theory fractionate bromine isotopes in salt deposits cannot account for the large $\delta^{81}Br$ variations observed here. Further experimental and theoretical studies on the bromine isotope fractionation accompanying incorporation of bromide in chloride salts are necessary to fundamentally understand Br isotope ratios in natural salt sequences.

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