



The bromine and chlorine isotope composition of primary halite deposits and their significance for the secular isotope composition of seawater

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Abstract

We determined the chlorine and bromine isotope compositions of 83 halite samples from nine different geological periods between the Orosirian and the present in order to study the secular Cl and Br isotope variations in the ocean during the last 2 billion years. Relatively large Cl (−0.24 to +0.51‰ vs. SMOC) and Br (−0.24 to +1.08‰ vs. SMOB) isotope variations are found in these halite samples. Two different methods, one in which the isotope fractionation between the brine and the salt is used, and a second in which the relationship between the isotope compositions and the Br/Cl ratios in the halite samples is used were applied to establish the original Cl and Br isotope compositions of the ocean. Both approaches showed that the Cl and Br isotope compositions of the ocean have always been close to the modern value (which is by definition 0‰ for both isotope systems) and that at most very small variations in Br and Cl isotope composition of seawater have occurred during the last 2 billion years. This indicates that, unlike in other isotope systems that often show significant isotope variations over geologic time, Cl and Br isotope compositions can be used directly to determine processes that occurred in the deposits of interest without need for correction for secular variations.

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1. INTRODUCTION

Of the geochemically significant halogen elements (fluorine, chlorine, bromine and iodine) only chlorine (Cl) and bromine (Br) have two stable isotopes. It is only of these two that the stable isotope geochemistry can be studied. Chlorine consists of the isotopes ³⁵Cl and ³⁷Cl which exist

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in a ratio of approximately 3:1. Bromine consists of the isotopes ^{79}Br and ^{81}Br which exists at about equal abundances. For both elements the internationally accepted standard is the isotope ratio of seawater (Standard Mean Ocean Chloride, SMOC (Kaufmann, 1984) for chlorine and Standard Mean Ocean Bromide (Eggenkamp and Coleman, 2000) for bromine. Their isotope variations are reported as $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ values that indicate the per mil (‰) difference of the ratio of the isotope of interest, relative to that ratio in the international standard. $\delta^{37}\text{Cl}$ is defined as:

$$\delta^{37}\text{Cl} = \left(\frac{^{37}\text{Cl}/^{35}\text{Cl}}{^{37}\text{Cl}/^{35}\text{Cl}} \right)_{\text{sample}} / \left(\frac{^{37}\text{Cl}/^{35}\text{Cl}}{^{37}\text{Cl}/^{35}\text{Cl}} \right)_{\text{standard}} - 1$$

where $(^{37}\text{Cl}/^{35}\text{Cl})_{\text{sample}}$ is the Cl isotope ratio in the sample and $(^{37}\text{Cl}/^{35}\text{Cl})_{\text{standard}}$ in the standard. $\delta^{81}\text{Br}$ is defined as:

$$\delta^{81}\text{Br} = \left(\frac{^{81}\text{Br}/^{79}\text{Br}}{^{81}\text{Br}/^{79}\text{Br}} \right)_{\text{sample}} / \left(\frac{^{81}\text{Br}/^{79}\text{Br}}{^{81}\text{Br}/^{79}\text{Br}} \right)_{\text{standard}} - 1$$

where $(^{81}\text{Br}/^{79}\text{Br})_{\text{sample}}$ is the Br isotope ratio in the sample and $(^{81}\text{Br}/^{79}\text{Br})_{\text{standard}}$ in the standard.

The chlorine isotope geochemistry of evaporite deposits has been studied extensively. The chlorine isotope fractionation has been studied experimentally in individual evaporite minerals and brines (Eggenkamp et al., 1995, 2016; Luo et al., 2012, 2014) and isotope variations have been studied in detail both in marine evaporites (Eastoe and Peryt, 1999; Eastoe et al., 1999, 2001, 2007; Eggenkamp et al., 2019) and terrestrial evaporites (Xiao et al., 1994, 1997, 2000; Liu et al., 1997; Tan et al., 2005, 2006, 2009; Luo et al., 2012; Eastoe, 2016). As a result, the chlorine isotope behaviour of an evaporating seawater body is now quite well understood. During evaporation of modern seawater, the chlorine isotope ratio of the precipitated halite decreases from slightly positive values in the first precipitated halite to fairly negative values when K, Mg and (potentially) Ca salts start to precipitate. This effect is due to a Rayleigh-type fractionation because the precipitated halite has a higher chlorine isotope ratio than the brine. As the heavier chlorine isotope is removed preferentially from the brine the remaining brine becomes lighter, and halite that precipitates later thus has lighter isotope compositions. This effect has recently been confirmed to exist in natural salt sequences by Eggenkamp et al. (2019) in a study on Cl and Br isotope variations in a fully developed Zechstein (Upper Permian) salt sequence from the Netherlands. The Cl isotope data observed in both natural salt deposits (Eggenkamp et al., 1995, 2019) and experimental evaporation of seawater (Eastoe et al., 1999) indicate that salt precipitates from brine in an open system. If salt were to precipitate in a closed system this would indicate that its isotope ratio could not be lower than the original isotope ratio of the brine, and these studies already showed that lower ratios are possible in significantly evolved salt deposits.

The chlorine isotope composition of an extensive set of Late Proterozoic to Miocene salts has been previously measured by Eastoe et al. (2007) who concluded that the chlorine isotope composition of the ocean could not have varied significantly from its modern composition. They observed that all $\delta^{37}\text{Cl}$ values of marine evaporites were in the range of $0.0 \pm 0.9\text{‰}$ relative to SMOC (Standard Mean Ocean Chloride, equivalent to the Cl isotope composition of the

modern ocean) with most of the data in the range of $0.0 \pm 0.5\text{‰}$, but with larger ranges observed in smaller basins. On average, lower Cl isotope values were found in potash-rich basins. These data suggest that no detectable change in Cl isotope ratio of seawater has taken place during the Phanerozoic. Cl isotope values measured in Precambrian cherts, barite, dolomite and halite confirmed that values must have been relatively constant during the Precambrian too, although the data suggest a possibly wider range than for the Phanerozoic (Sharp et al., 2007, 2013).

The isotope fractionation of chlorine during precipitation of chloride salts from saturated solutions has been studied extensively (Eggenkamp et al., 1995, 2016; Luo et al., 2012, 2014). Based on the isotope fractionation factors for halite (NaCl), it is possible to estimate, within an approximate range of 0.5‰ , what was the original Cl isotope composition of seawater if the Cl isotope composition of halite salts of a marine evaporite deposit is measured. This approach makes it possible to impose a better constraint on and explore some limited variations in the original Cl isotope composition of the ocean during the Phanerozoic and to resolve whether limited Cl isotope variations in the seawater compositions occurred.

In their recent paper Eggenkamp et al. (2019) showed that the chlorine isotope composition within a single salt sequence correlates very well with its Br/Cl ratio. As a consequence, the combination of the Cl isotope ratio with the Br/Cl ratio for a sample makes it possible to estimate the original Cl isotope composition of the brine from which a salt precipitated as the Br/Cl ratio of the first precipitating halite is known for the Phanerozoic (Siemann, 2003). Consequently, combining Cl isotope values and Br/Cl ratios, it might be possible to determine the original Cl isotope ratio of a brine more precisely than with other techniques.

Compared to Cl, our knowledge of the Br isotope composition of evaporites and ancient seawater is very limited. This knowledge was only based on a small number of Br isotope determinations of formation waters with very low Br/Cl ratios (Eggenkamp, 2014), which, as a consequence, should have most of their Cl and Br content from the dissolution of Br-poor (and halite-rich) evaporite deposits. Only eight such samples were recognised and published prior to 2016 (Shouakar-Stash et al., 2007; Boschetti et al., 2011; Bagheri et al., 2014) and they suggest an average $\delta^{81}\text{Br}$ value of $+0.60 \pm 0.29\text{‰}$ for evaporites. This value is at first sight not consistent with Br precipitation from modern seawater with a value of 0‰ vs. SMOB, as an almost negligible Br isotope fractionation between brine and precipitating salt was expected (Eggenkamp, 1995; Eggenkamp et al., 2016), indicating either a significantly more positive Br isotope ratio in ancient seawater or a significant isotope fractionation accompanying incorporation of bromide into chloride minerals during precipitation of salt from brine. The Br isotopes in a salt sequence from the Dutch Zechstein deposit seems even more complex (Eggenkamp et al., 2019). From slightly positive $\delta^{81}\text{Br}$ values ($+0.2\text{‰}$) in the samples with the lowest Br/Cl ratios, $\delta^{81}\text{Br}$ values decreased sharply (to -0.5‰) in samples with slightly higher Br/Cl values, and increases again (to $0.1 \pm 0.3\text{‰}$) in samples with very high Br/Cl ratios

(carnallite- and bischofite-dominated samples). This effect was explained as a competition effect between Br^- and Cl^- ions in solution for incorporation into a chloride salt. Due to its slightly larger size, Br^- ions are more difficult to be incorporated into the salt and will thus concentrate in the brine. This effect has been explained to produce a considerably larger isotope fractionation factor than the equilibrium between Br^- in solution and Br^- in a pure bromide salt (Eggenkamp et al., 2016, 2019). This effect must be related to the fact that there is only 1 Br^- ion for 600 Cl^- ions in seawater as compared to Br^- ions only in pure bromide brine.

For the present study, we collected a total of 83 presumably primary (unaltered) salt samples dominated by halite so that it could be expected that they were precipitated during early stages in salt precipitation. The geologic ages of the samples range from the Paleoproterozoic to recent salt pans, covering approximately 2 billion years. For all samples, chemical compositions and Cl and if possible Br isotopic compositions were determined in order: 1/ to assess if it were possible to constrain the Cl isotope variations to a narrower band than had been done before by Eastoe et al. (2007); 2/ to assess if the Br isotope composition of the ocean was as stable as the Cl isotope composition; and 3/ to refine the understanding on the Br isotope variations observed in halite-dominated salt samples.

2. MATERIAL

We collected 73 salt samples from various evaporite deposits from Pliocene to Orosirian ages, as well as 10 recent salt pan samples for comparison with the ancient samples. The ancient samples are from 16 different geological stages and were sampled from different locations in North America, Europe, Asia, and Australia. Some samples were individual samples, while others were related samples taken from a single drill-core or from within a restricted area. A brief description of the samples used in this study follows, sorted by age from the most recent to the most ancient. The analytical results are presented in Table 1. In the discussion, the samples from each geological period are combined in order to have a large enough set of samples per time period to properly estimate Cl and Br isotope trends. The samples often originate from several sub-periods as discussed below.

2.1. Recent samples

10 samples of modern sea salts were mostly bought from supermarkets in France and the Netherlands. The salts are from different locations, most of them in Europe with a focus on France. Of these MO1 is JOZO salt (AKZONobel) of unknown origin, MO2 is from the Mediterranean coast of France (La Baleine), MO3 is Maldon salt from the United Kingdom, MO4 is from the South Coast of Portugal (Atlantis salt), MO5 and EVA27 are Fleur de Sel from Guérande, MO6 is from Le Saunier, and MO7 is from Noirmoutier. The last three are from France, MO6 from the Mediterranean coast (Camargue), while MO5 and MO7 are from the Atlantic coast. EVA 6 and EVA10 are

from Sicily (Mediterranean Sea). All samples except MO3 are produced from salt pans, where seawater is introduced into individual pans and left to evaporate by the sun. Evaporation is enhanced by regularly turning the salt. MO3 is produced by seething, a process by which seawater is filtered and boiled in salt pans until it crystallises (see <http://www.maldonsalt.co.uk/The-Story-How-Maldon-Salt-is-made.html>).

2.2. Neogene

2.2.1. Plio-Pleistocene (about 2.6 Ma)

One sample (H1) was taken from the Sedom salt deposit in Israel (Zak, 1967; Weinberger et al., 1997; Stein et al., 2000).

2.2.2. Messinian (about 6.3 Ma)

Nine samples from Messinian salt deposits were analysed. EVA2, EVA9, EVA12, and EVA24 are from Sicily in Italy: EVA 2 (Pe38 3D) and EVA12 (Pe38 6D) from borehole Porto Empedocle 38, (Caltanissetta basin), EVA9 (Mess1) from Realmonte Mine and EVA24 (Cat5) from Cattolica Eraclea borehole. EVA15 (L4 212) and EVA23 (L4 228) are from Lorca in Spain (Paris et al., 2010). IR1, IR2 and IR3 are from the Garmsar Salt Dome in North Iran (Alijani, 2000), deposited in a lagoon during the Ghom sea regression. Upon analysis, sample IR1 happened to be a KCl salt and was not used as a primary source in the following study to determine the original Cl isotope composition of the Messinian Ocean.

2.2.3. Serrevalian (about 12.7 Ma)

Two samples (EVA5 and EVA7) from Serravallian salt deposits in Poland, taken from the section Woszczyce IG-1, were analysed (Paris et al., 2010).

2.3. Paleogene

2.3.1. Eocene-Oligocene transition (about 33.9 Ma)

The three samples EVA8 (EZ8 1229), EVA14 (EZ8 1230.7) and EVA18 (EZ8 1400) were from the Eocene-Oligocene salt deposits from Bresse in Eastern France (Paris et al., 2010).

2.3.2. Priabonian (about 35.9 Ma)

The three samples EVA16 (BI 436/1), EVA20 (BI 436/2) and EVA21 (BI 427) were from Priabonian salt deposits from the Lower Evaporite Unit of the Biurrun borehole in Navarra, Spain (Paris et al., 2010).

2.4. Triassic

2.4.1. Carnian/Norian (about 227 Ma)

One French Keuper sample from the Paris Basin was analysed (H2).

2.4.2. Anisian (about 245 Ma)

Seven samples (NL02 to NL08) were taken from the drill-core TWR-515 from depths between 418.3 and 424.2 m. These samples are from Röt (Triassic) deposits

Table 1

Chemical and isotopic composition of the salt samples studied in this research. n.d. means not determined (sample too small). The error in the isotope measurements is the 1 σ standard deviation of two measurements for Cl or the 2 σ standard deviation of five standard bracketing determinations for Br. When no error value is noted only a single measurement was possible.

Sample	Stage	Age (Ma)	$\delta^{37}\text{Cl}$ (‰)	$\delta^{81}\text{Br}$ (‰)	Na^+ (g/kg)	K^+ (g/kg)	Mg^{2+} (g/kg)	Ca^{2+} (g/kg)	Cl^- (g/kg)	Br^- (g/kg)	SO_4^{2-} (g/kg)	Br/Cl (g/g)
EVA06	Recent	0	+0.37 ± 0.01	−0.24 ± 0.12	401	3.0	8.5	0.9	520	0.47	13.9	0.00091
EVA10	Recent	0	+0.33 ± 0.04	+0.05 ± 0.13	392	1.5	3.9	1.2	605	0.33	7.8	0.00054
EVA27	Recent	0	+0.31 ± 0.02	+0.21 ± 0.03	375	1.7	7.1	1.7	623	0.44	16.0	0.00071
M1	Recent	0	+0.21 ± 0.01	+0.16 ± 0.05	414	0.2	0.1	0.5	636	0.12	1.6	0.00019
M2	Recent	0	+0.26 ± 0.01	+0.18 ± 0.09	429	0.1	0.0	0.4	657	0.12	1.2	0.00018
M3	Recent	0	−0.07 ± 0.01	−0.02 ± 0.09	390	0.2	0.6	1.5	601	0.09	5.3	0.00016
M4	Recent	0	+0.18 ± 0.03	+0.71 ± 0.08	404	0.7	1.8	1.2	625	0.22	6.1	0.00035
M5	Recent	0	+0.51 ± 0.02	+0.51 ± 0.11	326	0.9	3.4	2.3	508	0.25	11.4	0.00050
M6	Recent	0	+0.25 ± 0.01	−0.02 ± 0.07	379	0.1	0.9	0.5	586	0.20	1.8	0.00034
M7	Recent	0	+0.42 ± 0.01	+0.19 ± 0.08	376	1.6	6.8	4.2	593	0.42	20.7	0.00071
H1	Pliocene/Pleistocene	2.6	−0.07 ± 0.01	+0.19 ± 0.06	388	0.7	0.5	1.5	598	0.23	5.2	0.00038
EVA02	Messinian	6.3	+0.07 ± 0.04	+0.05 ± 0.02	397	0.1	0.2	0.1	625	0.07	0.7	0.00012
EVA09	Messinian	6.3	+0.07 ± 0.02	+0.24 ± 0.16	400	0.2	0.2	0.2	618	0.07	0.6	0.00011
EVA12	Messinian	6.3	+0.06 ± 0.04	n.d.	402	0.1	0.1	0.3	608	0.07	1.2	0.00011
EVA15	Messinian	6.3	−0.05 ± 0.05	+0.17 ± 0.11	388	0.7	1.7	4.4	610	0.18	12.5	0.00029
EVA23	Messinian	6.3	+0.03 ± 0.01	+0.21 ± 0.04	402	0.2	0.6	1.7	595	0.13	4.9	0.00022
EVA24	Messinian	6.3	−0.24 ± 0.06	0.00 ± 0.07	399	0.2	0.0	0.2	621	0.20	0.8	0.00032
IR1	Messinian	6.3	−0.53 ± 0.01	−0.11 ± 0.14	200	261	0.0	0.7	538	0.84	2.2	0.00156
IR2	Messinian	6.3	+0.22 ± 0.04	+0.24 ± 0.09	400	0.1	0.0	2.4	607	0.04	6.2	0.00007
IR3	Messinian	6.3	+0.25 ± 0.01	+0.32 ± 0.09	401	0.1	0.0	1.3	610	0.03	3.5	0.00006
EVA05	Badenian/Serrevalian	12.7	+0.33 ± 0.02	+0.32 ± 0.08	366	0.3	0.1	0.3	615	0.04	2.0	0.00006
EVA07	Badenian/Serrevalian	12.7	+0.28 ± 0.09	+1.08 ± 0.13	395	0.1	0.1	0.2	630	0.03	0.8	0.00005
EVA08	Eocene/Oligocene	12.7	−0.20 ± 0.10	+1.00 ± 0.08	415	0.3	0.2	1.2	542	0.15	2.8	0.00028
EVA14	Eocene/Oligocene	33.9	−0.20 ± 0.01	+0.91 ± 0.18	392	0.4	0.4	1.4	628	0.26	3.1	0.00041
EVA18	Eocene/Oligocene	33.9	−0.15 ± 0.01	+0.83 ± 0.13	389	1.2	0.1	0.2	640	0.18	0.2	0.00028
EVA16	Priabonian	35.9	−0.03 ± 0.03	+0.51 ± 0.20	320	23.6	8.3	23.6	478	0.11	116	0.00024
EVA20	Priabonian	35.9	−0.05 ± 0.04	+0.27 ± 0.14	388	2.1	0.6	1.9	620	0.13	9.7	0.00021
EVA21	Priabonian	35.9	−0.12	+0.25 ± 0.10	377	3.2	1.1	2.9	625	0.20	14.7	0.00031
H2	Carnian/Norian	227	+0.06 ± 0.01	−0.16 ± 0.15	394	0.0	0.1	2.4	607	0.10	6.3	0.00017
NL02	Anisian	245	+0.30 ± 0.02	+0.28 ± 0.11	403	0.0	0.0	0.3	618	0.04	1.0	0.00007
NL03	Anisian	245	+0.02 ± 0.02	+0.11 ± 0.05	408	0.1	0.1	0.0	624	0.18	0.1	0.00029
NL04	Anisian	245	+0.07 ± 0.01	+0.31 ± 0.05	392	0.0	0.0	0.0	603	0.19	0.0	0.00031
NL05	Anisian	245	+0.05 ± 0.02	+0.07 ± 0.04	399	1.2	1.4	1.0	611	0.21	9.5	0.00034
NL06	Anisian	245	+0.03 ± 0.01	+0.38 ± 0.04	408	0.3	0.1	0.1	622	0.32	0.7	0.00051
NL07	Anisian	245	+0.19	+0.06 ± 0.03	407	0.3	0.1	4.5	621	0.07	11.9	0.00011
NL08	Anisian	245	+0.24 ± 0.08	+0.51 ± 0.11	412	0.0	0.0	0.4	628	0.03	1.0	0.00005
H3	Changhsingian	253	+0.25	+0.42 ± 0.06	392	0.1	0.1	2.7	603	0.05	7.0	0.00008
EVA03	Wuchiapingian	257	−0.06 ± 0.01	+0.02 ± 0.05	393	1.9	1.2	2.2	605	0.29	10.3	0.00049
NL09	Wuchiapingian	257	−0.12 ± 0.07	+0.27 ± 0.07	391	1.4	2.5	0.8	601	0.21	10.5	0.00035
NL10	Wuchiapingian	257	−0.06 ± 0.03	−0.10 ± 0.05	393	1.2	0.7	0.1	603	0.32	0.4	0.00054
NL11	Wuchiapingian	257	+0.04 ± 0.04	+0.26 ± 0.05	394	2.5	4.1	1.5	609	0.22	12.5	0.00036
NL12	Wuchiapingian	257	+0.05 ± 0.02	+0.23 ± 0.10	397	5.1	4.8	0.4	618	0.24	8.3	0.00038

NL13	Wuchiapingian	257	-0.02 ± 0.01	+0.16 ± 0.05	361	0.2	14.3	0.4	561	0.14	54.1	0.00025
NL14	Wuchiapingian	257	-0.04 ± 0.02	+0.11 ± 0.11	324	0.2	18.8	1.2	517	0.20	107	0.00039
H4	Givetian	385	+0.23 ± 0.01	+0.20 ± 0.16	400	0.1	0.1	0.1	617	0.05	0.5	0.00008
EVA01	Givetian	385	+0.13 ± 0.05	+0.97 ± 0.16	411	0.2	0.1	3.0	543	0.05	7.3	0.00009
EVA04	Givetian	385	+0.14 ± 0.01	+0.41 ± 0.12	394	0.1	0.1	2.4	619	0.07	5.8	0.00011
H5a	Ordovician/Silurian	444	-0.06 ± 0.02	-0.05 ± 0.12	401	0.2	0.0	0.3	618	0.18	0.8	0.00028
H5b	Ordovician/Silurian	444	-0.04 ± 0.04	-0.04 ± 0.09	402	0.2	0.1	4.2	620	0.20	10.1	0.00032
H6	Terreneuvian	531	+0.03 ± 0.03	-0.17 ± 0.10	390	0.2	0.0	2.0	600	0.21	5.2	0.00034
H7	Ediacaran	545	-0.17 ± 0.05	+0.06 ± 0.08	389	2.4	0.9	1.8	600	0.14	10.1	0.00024
IR4	Ediacaran	545	+0.03 ± 0.01	+0.52 ± 0.10	400	0.2	0.0	2.0	608	0.08	5.2	0.00013
IR5	Ediacaran	545	+0.10 ± 0.03	+0.24 ± 0.15	402	0.3	0.0	0.9	611	0.07	2.4	0.00012
IR6	Ediacaran	545	+0.19 ± 0.02	+0.17 ± 0.08	401	0.2	0.0	1.2	610	0.07	3.1	0.00011
AU1	Tonian	820	-0.09 ± 0.01	-0.03 ± 0.05	363	0.3	0.2	3.6	558	0.18	9.0	0.00032
AU2	Tonian	820	-0.02 ± 0.01	-0.02 ± 0.13	385	0.3	0.1	1.6	594	0.17	4.0	0.00028
AU3	Tonian	820	-0.02 ± 0.01	0.00 ± 0.10	398	0.2	0.0	3.2	611	0.14	8.0	0.00023
AU4	Tonian	820	+0.01	-0.18 ± 0.09	370	0.2	0.2	5.6	571	0.11	13.4	0.00019
AU5	Tonian	820	+0.01 ± 0.01	0.00 ± 0.01	377	0.2	0.2	3.4	581	0.12	8.4	0.00021
AU6	Tonian	820	+0.05 ± 0.01	+0.69 ± 0.04	336	0.1	0.2	37.2	517	0.10	92.5	0.00020
A02	Orosirian	2000	-0.10 ± 0.03	n.d.	296	0.3	33.6	5.7	459	0.01	148	0.00003
A03	Orosirian	2000	-0.12 ± 0.03	n.d.	375	1.1	6.8	0.6	579	0.02	30.6	0.00004
A04	Orosirian	2000	-0.15 ± 0.05	n.d.	343	0.5	4.3	30.9	530	<0.01	91.2	<0.00001
A05	Orosirian	2000	-0.13 ± 0.01	n.d.	296	2.2	35.2	20.8	460	0.02	186	0.00004
A06	Orosirian	2000	-0.10 ± 0.02	n.d.	379	0.1	3.6	4.6	577	<0.01	35.4	<0.00001
A07	Orosirian	2000	-0.13 ± 0.01	n.d.	380	0.3	2.7	6.8	592	0.01	19.0	0.00001
A08	Orosirian	2000	-0.10 ± 0.03	n.d.	386	0.2	2.6	0.9	590	0.01	20.5	0.00001
A09	Orosirian	2000	-0.09 ± 0.04	n.d.	294	2.2	4.1	52.8	322	<0.01	324	<0.00001
A09a	Orosirian	2000	-0.13 ± 0.01	n.d.	378	3.0	0.0	9.0	582	<0.01	27.4	<0.00001
A10	Orosirian	2000	-0.07 ± 0.03	n.d.	300	1.2	3.7	63.0	452	0.02	178	0.00003
A10a	Orosirian	2000	-0.11 ± 0.01	n.d.	357	0.3	2.6	17.1	495	<0.01	128	<0.00001
A11	Orosirian	2000	-0.08 ± 0.03	n.d.	353	0.2	9.8	13.6	523	<0.01	101	<0.00001
A12	Orosirian	2000	-0.08 ± 0.01	n.d.	363	0.8	7.1	14.7	587	<0.01	27.9	<0.00001
A13	Orosirian	2000	-0.09 ± 0.01	+0.69 ± 0.06	353	8.1	6.6	2.6	545	0.02	42.5	0.00003
A14	Orosirian	2000	-0.07 ± 0.07	n.d.	391	0.3	1.1	0.1	603	0.01	4.2	0.00002
A15	Orosirian	2000	-0.07 ± 0.06	n.d.	240	54.4	30.0	33.3	348	<0.01	295	<0.00001
A15a	Orosirian	2000	-0.11 ± 0.01	n.d.	325	25.7	8.0	21.5	490	<0.01	130	<0.00001
A16	Orosirian	2000	-0.09 ± 0.02	+0.46 ± 0.12	308	0.5	8.1	33.8	462	0.02	132	0.00004
A17	Orosirian	2000	-0.04 ± 0.01	n.d.	302	1.2	1.5	72.4	537	<0.01	85.8	<0.00001
A17a	Orosirian	2000	-0.11 ± 0.02	n.d.	333	0.2	2.8	46.8	568	<0.01	49.6	<0.00001
A18	Orosirian	2000	-0.07 ± 0.02	n.d.	392	0.1	0.4	0.1	605	<0.01	2.0	<0.00001
A20	Orosirian	2000	-0.12 ± 0.01	n.d.	381	0.1	0.3	8.2	583	<0.01	26.9	<0.00001
A21	Orosirian	2000	-0.09 ± 0.03	n.d.	295	10.2	19.0	36.7	429	<0.01	210	<0.00001

of Anisian age. The core was drilled in 2000 by AKZO in order to explore for table salt. The description of the core can be found at the Dutch Oil and Gas Portal (<http://www.nlog.nl/en>): click on "boreholes" and "listing boreholes" then search for TWR-515. The purest halite samples were selected from this core based on their translucency.

2.5. Permian

2.5.1. Changhsingian (about 253 Ma)

One sample (H3) is taken from the Changhsingian Salado salt deposit in New Mexico (Maley and Huffington, 1953; Pierce and Rich, 1962).

2.5.2. Wuchiapingian (about 257 Ma)

Six of the samples described in Eggenkamp et al. (2019), which are halite salt samples are incorporated in this study. These samples were recently taken from drill core TCI-2, which was described and studied earlier by Eggenkamp et al. (1995). A general description of this core is given in Coeleweij et al. (1978) and Buyze and Lorenzen (1986).

2.6. Late Ordovician to Middle Devonian

2.6.1. Givetian (about 385 Ma)

The three samples EVA1 (15.34.93.24 W4), EVA4 (6.80.36.13 W4) and H4 were taken from the Givetian (Mid-Devonian) Canadian Prairie Formation (Grobe, 2000). EVA1 and EVA4 were made available from the collection of the Muséum Nationale de Histoire Naturelle in Paris.

2.6.2. Late Ordovician/Early Silurian (about 444 Ma)

One sample (H5) was taken from the Western Australian Caribuddy Formation of the Late Ordovician to Early Silurian age (Haines, 2009). As this sample was visibly heterogeneous, containing white and red parts, it was split into two, H5a containing the white salt and H5b containing the red salt.

2.7. Ediacaran to Early Cambrian

2.7.1. Terreneuvian (about 531 Ma)

One sample (H6) was taken from the East Siberian Angarskaya Formation (Petrychenko et al., 2005).

2.7.2. Ediacaran (about 545 Ma)

One sample (H7) is taken from the Ara Formation in Oman (Mattes and Conway Morris, 1990; Schröder et al., 2005) and three (IR4, IR5 and IR6) from the Iranian Hormuz Formation (Kent, 1979; Alavi, 2004). These samples are of comparable age and are lateral equivalent to each other.

2.8. Tonian (about 820 Ma)

Six samples (AU1 to AU6) were collected from the Gillen Formation of the Bitter Springs Group, Amadeus Basin in central Australia. The Gillen Formation was, until recently, the oldest known massive salt deposit (Naughton

et al., 1968; Stewart, 1979). Samples AU1 AU3 were collected from drill core Mt Charlotte-1 at depths of 1875.34 to 1875.44, 1877.85 to 1877.92 and 2060.14 m respectively. Samples AU4 to AU6 were collected at depths of 556', 306' and 600' from diamond drill core Mt Liebig-1 and represent massive, orange-coloured halite.

2.9. Orosirian (about 2000 Ma)

This deposit represents a recently discovered massive and thick evaporite (halite and anhydrite) deposit that is only recognised in the Onega parametric well in Russia (Morozov et al., 2010; Krupenik and Sveshnikova, 2011; Gorbachev et al., 2011; Glushanin et al., 2011). These are the oldest currently known massive halite deposits on Earth. They are described as marine evaporites (Blättler et al., 2018). It is not known yet if their thickness in the drill core represents stratigraphic thickness or the thickness of the evaporite interval in a salt diapir. 23 samples from this core were available for this study. Magnesium and calcium isotopes of this evaporite deposit have recently been studied and interpreted to record the Great Oxidation Event that can explain the high sulphate contents in these deposits (Blättler et al., 2018). Several of the samples analysed in this study from this deposit were previously measured for their Cl isotope composition by Sharp et al. (2013).

3. METHODS

All samples, except those labelled "EVA" were available as solid salt samples. The "EVA" samples were available as solutions prepared previously with approximately seawater chloride concentrations (see Paris et al., 2010). Solid salt samples were dissolved in water in a ratio of 1:9 (1 gram of salt and 9 grams of distilled water) for Cl and Br isotope measurements. This 1:9 solution was diluted by an extra 1000 times to obtain solutions diluted enough for ICP-OES and ICP-MS measurement of the chemical composition. All dissolved samples were analysed for the determination of chemical (Cl^- , Br^- , SO_4^{2-} , Na^+ , K^+ , Mg^{2+} and Ca^{2+}) and isotopic ($\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$) compositions at the Institut de Physique du Globe de Paris, France.

Cl^- and Br^- concentrations were measured by ICP-MS on an Agilent Technologies 7900 ICP-MS. The cations and sulphate (measured as S) were analysed by ICP-OES on a Thermo Scientific iCAP 6000 Series ICP Spectrometer. The results were calculated back to the chemical composition of the salts and are reported in Table 1 in the unit of g per kg salt.

The chlorine isotope composition was measured according to the method described by Kaufmann (1984), Eggenkamp (1994) and Godon et al. (2004). In short, Cl^- is precipitated as AgCl by adding AgNO_3 , which was reacted with CH_3I to form CH_3Cl . CH_3Cl is separated from CH_3I by two gas chromatograph runs using a Périchrom IGC-11 gas chromatograph (with dry pure He at 130 °C, 2.1 bar and 15 ml/min) in two identical packed columns (Porapak-Q 80–100 mesh, 2 m length and 3.175 mm outer diameter). A thermal conductivity detector is used to check the progress of this purification and to detect any leaks.

$^{37}\text{Cl}/^{35}\text{Cl}$ ratios were subsequently determined on the $\text{CH}_3\text{-Cl}$ with dual-inlet mass spectrometry on a ThermoFisher Delta PlusXP mass spectrometer (IRMS). The results are reported in the δ notation (as $\delta^{37}\text{Cl}$) in ‰ relative to SMOC (Standard Mean Ocean Chloride, Kaufmann et al., 1984), with a standard deviation (1σ) of 0.05‰.

The bromine isotope composition was measured on a Neptune (ThermoFisher) multicollector ICP mass spectrometer (MC-ICP-MS). Due to the low Br/Cl ratios of the halite samples, it was not possible to extract the bromide using the classic ion-exchange method (Louvart et al., 2016); bromine was extracted through oxidative distillation following Murphy et al. (1954) as described by Eggenkamp and Louvart (2018). Bromide is oxidised to bromine gas by a 14% boiling nitric acid solution and distilled into a 0.5 N ammonia solution, where bromine is trapped and disproportionated into bromide and bromate. Due to the reducing nature of the ammonia solution, bromate is reduced to bromide. The extraction efficiency of this distillation is about 50%. As shown by Eggenkamp and Louvart (2018) no isotope fractionation was observed during the distillation process. This solution can be measured directly by MC-ICP-MS as a wet plasma as described by Louvart et al. (2016). Results are reported in the δ notation (as $\delta^{81}\text{Br}$) in ‰ relative to SMOB (Standard Mean Ocean Bromide, Eggenkamp and Coleman, 2000) with an average standard deviation (1σ) of about 0.1‰.

For both Cl and Br isotope measurements ocean water sampled in the Indian Ocean (sampled in January 2010 during the MD 175 cruise, latitude 32.45°S, longitude 84.01°E) was prepared and measured 13 times for its $\delta^{37}\text{Cl}$ composition (with better than 0.05‰ 1σ standard deviation, which is comparable to the typical long-term external reproducibility of $\delta^{37}\text{Cl}$ measurements obtained at IPGP on both seawater and unknown samples; e.g., Godon et al., 2004 and Bonifacie et al., 2007) and prepared and measured 5 times for its $\delta^{81}\text{Br}$ composition (with better than 0.10‰ 1σ standard deviation).

Results of the $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ measurements are also reported in Table 1. The accuracy of the measurements is indicated in the Table showing the 1σ standard deviation of multiple (mostly two) preparations and measurements of the same sample.

4. RESULTS

Data reported in Table 1 show that all samples except one (IR1) are predominately composed of halite. Varying amounts of K, Mg and Ca are present, indicating that the evaporates formed during various stages of halite-dominated precipitation. As the Br/Cl ratio can be used as a proxy for the evaporation stage (Valyashko, 1956; Braitsch, 1962; Herrmann et al., 1973; McCaffrey et al., 1987; Eggenkamp et al., 2019), it was calculated for all samples and included in Table 1. The samples show a considerable range in Br/Cl ratios, from <0.00001 to 0.00091. All samples with very low Br/Cl ratios (<0.00005) are taken from the Onega parametric well in Russia (A02 to A21), and due to their low Br content and insufficient amount of sample available it was only possible to analyse two of

these samples for Br isotopes. The total range of Cl isotope ratios in the sample set ranges from -0.24 to $+0.51$ ‰, while the range of Br isotope ratios is from -0.24 to $+1.08$ ‰. The total range of Br isotope ratios is thus considerably larger than that for Cl isotope ratios.

5. DISCUSSION

Based on a set of 132 salt samples with ages ranging from the Late Neoproterozoic (ca. 550 Ma) to the Messinian (ca. 6.3 Ma), Eastoe et al. (2007) concluded that significant variations in the Cl isotope composition of the ocean were unlikely during this period. They reported no range within which the Cl isotope composition could have varied (however small it may have been), which was based on the observation that the overwhelming majority of salt samples had $\delta^{37}\text{Cl}$ values between -0.50 and $+0.50$ ‰ relative to SMOC. We expect that it should be possible to constrain the $\delta^{37}\text{Cl}$ secular trend of the ocean within a narrower limit using our recent constraints for the isotope fractionation of chloride during chloride salt precipitation from saturated brine. There are several studies that determined the isotope fractionation of chlorine during precipitation from saturated brine (Eggenkamp et al., 1995, 2016; Luo et al., 2012, 2014). The fractionation factors obtained in these studies varied considerably. Eggenkamp et al. (1995) reported a value of $\alpha = 1.00026$, Eggenkamp et al. (2016) reported 1.00035 and the average of the values reported by Luo et al. (2012, 2014) is 1.00049. This relatively large variability has to be taken into account, if the original $\delta^{37}\text{Cl}$ of seawater is to be determined. If the fractionation factor is larger, the $\delta^{37}\text{Cl}$ values of the precipitated halite diverge progressively with precipitation (see e.g. the discussion by Eggenkamp (2015a) and Luo et al. (2015)). Thus, the estimate of secular seawater $\delta^{37}\text{Cl}$ values requires relatively large corrections, if the larger fractionation factors are assumed. The Br isotope data in the present paper are the first of a notable number of halite samples, and the seawater record of the Br isotopes will be discussed despite our limited knowledge of Br isotope fractionation during sea-salt precipitation.

5.1. Estimate of the secular $\delta^{37}\text{Cl}$ values of seawater

Here we apply two methods to estimate the original $\delta^{37}\text{Cl}$ of the ocean based on the $\delta^{37}\text{Cl}$ values of the analysed halite samples. At first, an approach solely based on $\delta^{37}\text{Cl}$ values is applied, while the second approach is based on the Br/Cl ratio used as a parameter in combination with the $\delta^{37}\text{Cl}$ of the samples to infer the original $\delta^{37}\text{Cl}$ of the ocean from which the halite was precipitated.

5.1.1. Estimate based on $\delta^{37}\text{Cl}$ of halite salt only

When salt precipitates from a saturated solution it removes heavy chlorine isotope from the brine that, as a result, becomes enriched in the lighter isotope. This effect is a classic Rayleigh effect that has been described before (Eggenkamp et al., 1995; Luo et al., 2014; Eggenkamp, 2015a). As long as halite is the only chloride-precipitating mineral, this process is gradual. The previous studies have

demonstrated that the first halite that precipitates is heavier in Cl isotopes than that of seawater, and that it becomes progressively lighter until 82.5% of all chloride is precipitated and the first potassium chloride (kainite [$\text{K}_4\text{Mg}_4\text{Cl}_4(\text{SO}_4)_4 \cdot 11\text{H}_2\text{O}$]) starts to precipitate (Braitsch, 1962). From this stage, precipitating salt is no longer a pure halite so that isotope fractionation, as well as Br distribution, will be different from there on. Thus, if we use the $\delta^{37}\text{Cl}$ of a primary halite to infer the seawater composition it must have precipitated before 82.5% of the chloride present in the brine has been precipitated. The $\delta^{37}\text{Cl}$ of salt that precipitated from modern seawater with a $\delta^{37}\text{Cl}$ value of 0‰ decreases depending on the fractionation factor that is used. For example, if we assume a fractionation factor of 1.00026, the halite precipitated initially will have a $\delta^{37}\text{Cl}$ of +0.26‰ and the last batch (when potassium-bearing chloride starts to precipitate) will have a $\delta^{37}\text{Cl}$ of -0.19‰. If we use a fractionation factor of 1.00035, $\delta^{37}\text{Cl}$ of the precipitated halite decreases from +0.35‰ to -0.26‰ due to the Rayleigh effect. Similarly, if we use a fractionation factor of 1.00049, the $\delta^{37}\text{Cl}$ of the halite decreases from +0.49‰ to -0.36‰. To know the $\delta^{37}\text{Cl}$ composition of the original seawater, these $\delta^{37}\text{Cl}_{\text{halite}}$ values need to be inverted. That means that in the case of a fractionation factor of 1.00026 the original $\delta^{37}\text{Cl}$ value of the ocean was somewhere between 0.26‰ lower and 0.19‰ higher than the $\delta^{37}\text{Cl}$ of the halite sample, depending on where the sample was precipitated on the Rayleigh curve. For higher fractionation factors, these numbers are between 0.35‰ lower and 0.26‰ higher for $\alpha = 1.00035$ and between 0.49‰ lower and 0.36‰ higher for $\alpha = 1.00049$. This result in fairly large potential ranges for the original $\delta^{37}\text{Cl}$ of the oceans, as it is unknown at what point on the Rayleigh curve the samples precipitated. Fig. 1 shows how this process is applied to seawater with a $\delta^{37}\text{Cl}$ of 0‰ and halite with a fractionation factor of 1.00035. However, since we have measured multiple halite samples for each geological period, it is possible to decrease the calculated range of $\delta^{37}\text{Cl}$ in seawater.

Indeed, assuming primary, unaltered $\delta^{37}\text{Cl}$ values of the salt samples, the possible range of $\delta^{37}\text{Cl}$ in the ocean must be the overlapping part of all the $\delta^{37}\text{Cl}$ ranges from the individual samples corresponding to the concerned geological period. Fig. 2 illustrates how this works for one of the geological periods, the Permian, a period from which we analysed eight samples. For each of the eight samples we calculate the maximum range of possible original $\delta^{37}\text{Cl}$ of the seawater for $\alpha = 1.00035$. This figure shows that the range, within which the original $\delta^{37}\text{Cl}$ must have fallen, decreases significantly when more samples from a period were measured. In the case where a smaller or larger value for α is used, the original $\delta^{37}\text{Cl}$ range will be smaller or larger. It is clear from this figure that the effective range of $\delta^{37}\text{Cl}$ of the seawater is where all eight $\delta^{37}\text{Cl}$ of the seawater ranges of the samples overlap. In the case of the Permian the figure shows that assuming a fractionation factor α of 1.00035 the original $\delta^{37}\text{Cl}$ of the oceans must have been between -0.10‰ and +0.14‰. This range would be smaller (between -0.01‰ and +0.07‰) assuming $\alpha = 1.00026$, or larger (between -0.24‰ and +0.24‰) assuming $\alpha = 1.00049$.

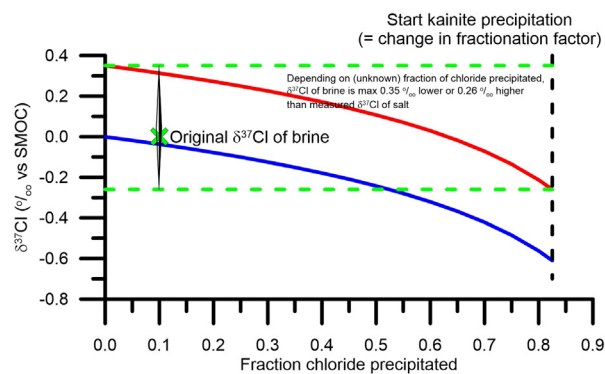


Fig. 1. Estimate for the range of possible seawater $\delta^{37}\text{Cl}$ values based on the $\delta^{37}\text{Cl}$ value for halite samples. The blue (lower solid) line indicates the evolution of the brine, the red (upper solid) line that of the precipitate (which is always 0.35‰ higher). Figure shows how the $\delta^{37}\text{Cl}$ of a salt is related to the original $\delta^{37}\text{Cl}$ of the brine. In this case, the original $\delta^{37}\text{Cl}$ of the brine is 0‰, and the salt that precipitates from it is between the upper and the lower green lines, or between +0.35‰ and -0.38‰. An indication for the original brine $\delta^{37}\text{Cl}$ of 0‰ is plotted slightly to the right for visibility. As soon as salt starts to precipitate the $\delta^{37}\text{Cl}$ of the remaining brine starts to decrease. Inverted, it means that if the $\delta^{37}\text{Cl}$ of the salt is known the $\delta^{37}\text{Cl}$ of the original brine must be between 0.38‰ higher and 0.35‰ lower, which is indicated by the green dashed lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

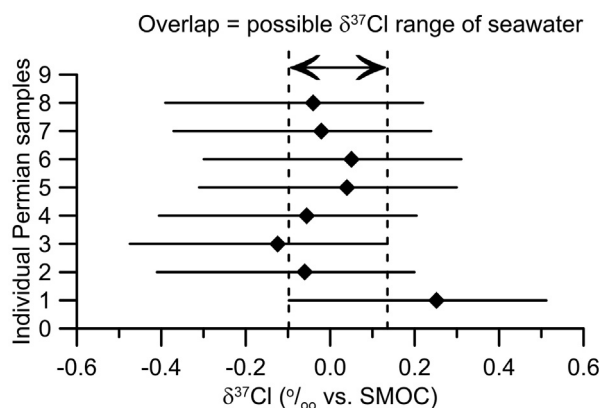


Fig. 2. Possible $\delta^{37}\text{Cl}$ range for Permian seawater based on the maximum and minimum possible $\delta^{37}\text{Cl}$ values for the individual samples. The dashed lines indicate the possible $\delta^{37}\text{Cl}$ range the Permian seawater could have based on the measured $\delta^{37}\text{Cl}$ of the 8 Permian samples (diamonds) and the possible $\delta^{37}\text{Cl}$ range based on each of these 8 samples (horizontal lines). The possible $\delta^{37}\text{Cl}$ range of Permian seawater cannot be larger than the overlap of these horizontal lines.

These calculations were made for all the geologic periods considered here and the results are summarised in Table 2. This table highlights also weaknesses of this approach. For two periods, the Recent and the Neogene, the range in $\delta^{37}\text{Cl}$ of the seawater was larger than the possible isotope variation if we assume $\alpha = 1.00026$. As a consequence, the minimum value in this approach is higher than the maximum

Table 2

Minimum, maximum and midpoint values for the possible $\delta^{37}\text{Cl}$ values of the oceans in the past, without taking into account the Br/Cl ratios of the salt that precipitates from it. The possible values are determined for the three different fractionation factors discussed in the text. The table clearly shows that for the Recent and the Neogene it is not possible to reconstruct a possible $\delta^{37}\text{Cl}$ value for an α -value of 1.00026 as the minimum possible value is larger than the maximum possible value. In the table this is indicated by italicising the calculated values.

Period	Age (Ma)	$\alpha = 1.00026$		$\alpha = 1.00035$		$\alpha = 1.00049$		Midpoint
		min	max	min	max	min	max	
Recent	0	<i>0.25</i>	<i>0.12</i>	0.16	0.19	0.02	0.29	0.19
Neogene	7	<i>0.07</i>	<i>-0.05</i>	-0.02	0.02	-0.16	0.12	0.07
Paleogene	35	-0.29	-0.01	-0.38	0.06	-0.52	0.16	-0.15
Triassic	243	0.04	0.21	-0.05	0.28	-0.19	0.38	0.13
Permian	256	-0.01	0.07	-0.10	0.14	-0.24	0.24	0.03
Ordov./Dev.	409	-0.03	0.13	-0.12	0.20	-0.26	0.30	0.05
Edia./Cambr.	542	-0.07	0.02	-0.16	0.09	-0.30	0.19	-0.03
Tonian	850	-0.21	0.10	-0.30	0.17	-0.44	0.27	-0.05
Orosirian	2000	-0.30	0.04	-0.39	0.11	-0.53	0.21	-0.13

value, and that means that the seawater $\delta^{37}\text{Cl}$ cannot be explained with a fractionation factor of 1.00026. The range can be explained however with higher fractionation factors, and the most straightforward conclusion is that the chlorine isotope fractionation factor for the precipitation of halite from ocean water must be larger than 1.00026. The second problem is the reconstructed $\delta^{37}\text{Cl}$ of seawater based on modern salt samples. The mean value of the reconstructed $\delta^{37}\text{Cl}$ (based on fractionation factors 1.00035 and 1.00049) is +0.18‰, while the $\delta^{37}\text{Cl}$ of today's oceans is by definition 0‰. While the values obtained for ancient seawater seem to reflect the original $\delta^{37}\text{Cl}$ of those periods the recent samples seem not to, which might reflect differences in the precipitation process. All historic samples are precipitated from evaporating seawater in a static way, where a batch of seawater evaporated until it became saturated with halite and halite will precipitate to the bottom of the evaporite basin. The modern samples on the other hand (except MO3) were precipitated in an active way, where the precipitation of salt from seawater was as quickly as possible to improve the precipitation rate, especially by keeping the ponds as shallow as possible and to remove the salt immediately upon precipitation so that it can be dried in the sun. These effects considerably increase the kinetics of salt precipitation and this might result in possible non-equilibrium precipitation of halite from these seawaters as well as the significant isotope variation among these samples, including some that are from the same location. It has to be realised that all calculations above were made as if the chemical composition of ocean water had not changed during geologic history, while this composition obviously has changed (Babel and Schreiber, 2014). We have decided to work in this preliminary study using the modern composition of ocean water in order to simplify the calculations, although, as sulphate concentrations in the past were generally lower than they are today, the halite only phase may have been more extended and might have been up to 86.9% when carnallite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$) starts to precipitate (Eggenkamp et al., 1995) for sulphate free brines.

5.1.2. Estimate based on $\delta^{37}\text{Cl}$ and Br/Cl ratios of halite

It is well established that during precipitation of salt from seawater brine not only the $\delta^{37}\text{Cl}$ value of the brine decreases due to a Rayleigh type isotope fractionation, but also that the Br/Cl ratio increases. Because the Br/Cl ratio of precipitated halite is significantly lower than the Br/Cl ratio in seawater, controlled by the distribution coefficient, the Br/Cl ratios of the precipitated salt and the remaining brine evolve in a fashion very similar to that of the $\delta^{37}\text{Cl}$, following a Rayleigh fractionation process. This effect has been studied extensively in the past (e.g. Boeke, 1908; Kühn, 1955; Valyashko, 1956; Braitsch, 1962; Herrmann, 1972; Herrmann et al., 1973). Eggenkamp et al. (2019) have shown that a clear relationship between $\delta^{37}\text{Cl}$ and Br/Cl ratios is observed in a well-developed salt sequence. Fig. 3 shows the relationship between the $\delta^{37}\text{Cl}$ and the Br/Cl ratios of the salt samples that were measured for the present study. The sample set can be separated into three populations. To the left a series of samples with a large variation in low Br/Cl ratios and very constant $\delta^{37}\text{Cl}$ values around -0.1‰, to the right a group of samples with high Br/Cl values and relatively high $\delta^{37}\text{Cl}$ values, and in the centre, which is the largest set of samples, a group of samples showing an inverse correlation between $\delta^{37}\text{Cl}$ values and Br/Cl ratios.

In more detail, the first group of samples (with a large variation in very low Br/Cl ratios and nearly constant and low $\delta^{37}\text{Cl}$ values) are all Orosirian samples from the Onega parametric well in Russia. These two billion years old evaporites show extremely low Br contents, but also very similar $\delta^{37}\text{Cl}$ values. We can explain this by repeated dissolution and reprecipitation cycles in which the Br content decreased in each cycle (due to Br^- enrichment in the brine that for a large part disappeared from the deposit), while the $\delta^{37}\text{Cl}$ values became homogenised during this process. This interpretation is consistent with the Sr and S isotope data (Krupenik and Sheshnikova, 2011; Blättler et al., 2018), indicating a depositional system largely disconnected from the open ocean and potential dissolution-reprecipitation and mixing related to diapir growth.

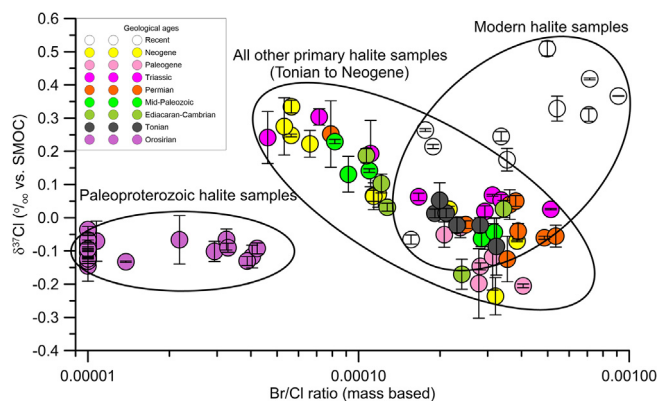


Fig. 3. Plot showing the $\delta^{37}\text{Cl}$ versus the Br/Cl ratio of the individual halite samples. The vertical error bars are the errors as defined in Table 1. Colours indicate samples from different geologic ages. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The second group of samples (with high Br/Cl ratios and high $\delta^{37}\text{Cl}$ values), are all modern “table” salts that were produced with modern industrial production techniques as described above. The high Br/Cl ratios in these salts might reflect kinetic rather than equilibrium fractionation, as still wet salt is removed from the salt pans and put aside to dry in the sun. Consequently, wet salt contains significant amounts of brine with very high Br/Cl ratios, increasing the Br content of the final salt. The high $\delta^{37}\text{Cl}$ ratios of industrial salt samples indicate much larger kinetic fractionation as compared to equilibrium fractionation as precipitates were removed from the brine well before the thermodynamic equilibrium could have been reached. Similarly, this large difference between kinetic and equilibrium fractionation factors might explain the large range of frac-

tionation factors involved in halite precipitation from brine discussed above. The fact that the modern, industrially produced, salt differs from ancient primary salt deposits confirms that the reconstructed $\delta^{37}\text{Cl}$ of the modern ocean does not agree with the actual $\delta^{37}\text{Cl}$ of the seawater from which it precipitates.

The third and largest group of samples, which contains all the samples from ancient primary salt deposits, shows promising relationships. These samples fall on a trend showing a negative correlation between $\delta^{37}\text{Cl}$ values and the Br/Cl ratios. Using this relationship, it might be possible to retrieve the original $\delta^{37}\text{Cl}$ values of the seawater for each geological period. This was tested for each period by applying the relationships between Br/Cl ratio and $\delta^{37}\text{Cl}$. Seven plots are produced (Fig. 4) that show the expected

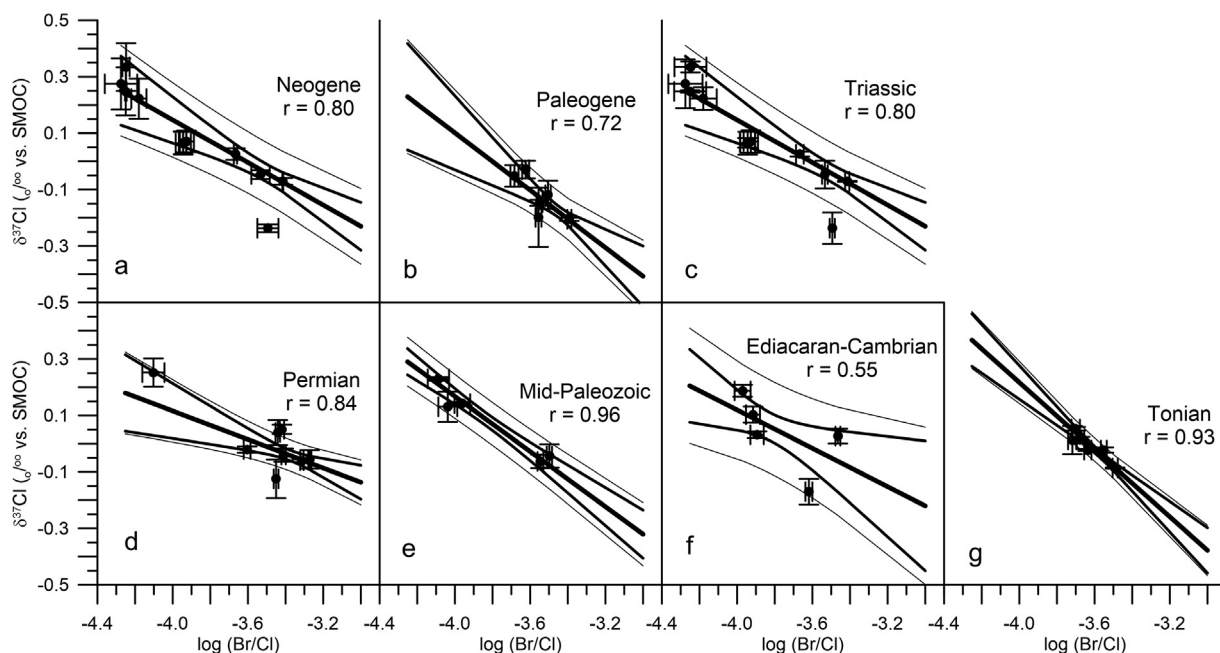


Fig. 4. Correlations between $\delta^{37}\text{Cl}$ and $\log(\text{Br}/\text{Cl})$ for each geological period (except the Recent and the Orosirian samples). All figures are extrapolated to a lowest Br/Cl value of 0.00005 ($= -4.3$ in log units). The figures indicate that the $\delta^{37}\text{Cl}$ of the first precipitated salt is close to $+0.35\text{‰}$ indicating (within errors) only little possible $\delta^{37}\text{Cl}$ variation during Earth’s history.

negative relationship between $\delta^{37}\text{Cl}$ values and the logarithm of the Br/Cl ratio with varying degrees of uncertainties that are reflected by hyperbolas. Extrapolation to the logarithm of the Br/Cl ratio of the first precipitating halite yields an estimate of $\delta^{37}\text{Cl}$ of the first precipitated halite and from that the $\delta^{37}\text{Cl}$ of the seawater can be (in theory) recovered/retrieved.

The Br content of the first precipitated halite can be obtained theoretically from the bromide content in the brine at the stage of the first halite precipitation and from the Br distribution coefficient between halite and the brine. This distribution coefficient (defined as $b = \text{mass}\% \text{ Br in salt}/\text{mass}\% \text{ Br in brine}$) is 0.14 (Braitsch, 1962). Since the Br content in the brine at the moment of first halite precipitation is about 0.053%, the Br content in the first precipitated halite is 0.0074%, and the Br/Cl ratio in this halite is 0.00012. However, this is only correct if we assume that seawater had the same chemical composition as the modern ocean. Yet, the chemical composition of seawater has changed considerable over geological history (see e.g. Horita et al., 2002; Lowenstein et al., 2014). These changes in seawater composition also had a significant influence on the amount of Br that is incorporated in the first precipitated halite (cf. Siemann and Schramm, 2000; Siemann, 2003). These studies have shown that in most of the Phanerozoic the bromide content in the first halite that precipitated was lower than at present. According to their results, in the geological periods of interest, the first precipitated halite should show Br/Cl ratios of 0.00017 (Neogene), 0.00010 (Paleogene), 0.00015 (Triassic), 0.00014 (Permian), 0.00008 (Ordovician-Devonian) and 0.00017 (Ediacaran-Cambrian). The ratio is not known for the Tonian. These values were recalculated from $\mu\text{g Br/g NaCl}$ ratios as presented by Siemann (2003) to Br/Cl mass ratios. It is, however, important to consider these Br/Cl ratio calculations with caution (Lowenstein et al., 2014), because Br concentrations reported from the first precipitated halite in modern marine settings vary substantially from study to study. For comparison, 38 ppm in halite grown experimentally from Mediterranean seawater (Bloch and Schlerb, 1953) to 50 ppm in modern halite from Baja California, Mexico (Holser, 1966), to 100 ppm from evaporated North Sea seawater (Siemann, 2003). Br concentrations in the

recent commercial salt samples measured in this study are even higher than these observations, but as discussed above this is probably due to non-equilibrium processes by which these salts were produced.

The same uncertainties are also notable in our set of samples. The global relationship between Br/Cl ratios and $\delta^{37}\text{Cl}$ values on Fig. 3 shows that in our dataset the lowermost Br/Cl limit of primary samples (thus excluding the Paleoproterozoic samples) can be as low as 0.00005 for a Triassic sample, comparable to the ratio expected for the periods with the lowest suggested Br/Cl ratio by Siemann (2003), but unfortunately not the Triassic, which should have a two to three times higher Br/Cl ratio for first precipitated halite. These results indicate that model Br/Cl data for the first precipitated halite as determined by Siemann (2003) must be used with caution and for the purpose of the present study we will use the lowest Br/Cl ratio measured in our dataset (0.00005) to estimate the original $\delta^{37}\text{Cl}$ of the ocean for the different geologic periods.

On Fig. 4 the regression lines as well as the uncertainty hyperbolas are extrapolated to a Br/Cl ratio of 0.00005 ($= -4.3$ in log units) for samples from all geological period samples that were available in this study. The resulting $\delta^{37}\text{Cl}$ values (and uncertainties) are summarised in Table 3.

At first approximation these values can be considered as the $\delta^{37}\text{Cl}$ of the first precipitated halite for each geologic period. The original seawater $\delta^{37}\text{Cl}$ can then be determined by subtracting $10^3 \ln \alpha$ ($\alpha =$ fractionation factor) from these extrapolated $\delta^{37}\text{Cl}$ values, using α values of 1.00026, 1.00035 and 1.00049 (Eggenkamp et al., 1995, 2016; Luo et al., 2012). This results in lower reconstructed $\delta^{37}\text{Cl}$ values for larger fractionation factors. Importantly, no large variations are observed between the different secular $\delta^{37}\text{Cl}$ values of the ocean, and the average secular values are about 0.01‰ assuming a fractionation factor of 1.00026, -0.08‰ assuming a fractionation factor of 1.00035 and -0.22‰ assuming a fractionation factor of 1.00049. These data thus suggest an only slightly negative $\delta^{37}\text{Cl}$ value for the seawater during the last billion years with little temporal variation. The low inferred (average) $\delta^{37}\text{Cl}$ value for a fractionation factor of 1.00049 with respect to the modern seawater composition again indicates that this fractionation factor is non-realistically high as it would imply a drastic

Table 3

Average and possible range of $\delta^{37}\text{Cl}$ values of the first precipitating halite in the past when Br/Cl ratios are taken into account assuming that during the whole geological history the first precipitating halite has a Br/Cl ratio of 0.00005.

Period	Age (Ma)	Average @ Br/Cl = 0.00005	Range		Range	
			Student's t-test		95% probability	
			min	max	min	max
Neogene	7	0.26	0.13	0.39	0.10	0.42
Paleogene	35	0.25	0.05	0.45	0.04	0.47
Triassic	243	0.26	0.13	0.39	0.10	0.42
Permian	256	0.19	0.05	0.34	0.04	0.34
Ordov./Dev.	409	0.31	0.26	0.37	0.23	0.40
Edia./Cambr.	542	0.22	0.08	0.36	0.01	0.43
Tonian	850	0.40	0.30	0.50	0.29	0.50

change in $\delta^{37}\text{Cl}$ of the ocean between the Miocene and the present, which is not sensible. Note that the calculations are made using the lowermost first halite Br/Cl ratio. As there is a negative relationship between the $\delta^{37}\text{Cl}$ and the Br/Cl ratio, the calculated $\delta^{37}\text{Cl}$ values for the ocean become even lower if higher first halite precipitated Br/Cl ratios, such as those suggested by [Siemann \(2003\)](#), are used in the calculations. This may indicate that the initial Br/Cl ratios of the first precipitated halite have always been lower than those suggested by [Siemann \(2003\)](#).

5.1.3. Comparison of the two approaches to establish the $\delta^{37}\text{Cl}$ of seawater from precipitated halite and the most probable seawater $\delta^{37}\text{Cl}$ values over geological history

The two approaches to estimate the $\delta^{37}\text{Cl}$ values of the ocean during the geological past yield different results, but combined together they are able to constrain the approximate value of $\delta^{37}\text{Cl}$ of the ocean during the geological past. The combined results of the two approaches are summarised in [Fig. 5](#). The results obtained for the recent salt-pan samples are omitted as they do not reflect the $\delta^{37}\text{Cl}$ composition of current seawater. The $\delta^{37}\text{Cl}$ value of the ocean during the Paleoproterozoic could not be determined via the second approach (with Br/Cl ratio) due to their extremely low Br contents, but the results of the first approach (range of possible $\delta^{37}\text{Cl}$ in seawater) are shown. The first “Cl only” approach is shown as coloured bands in the background of the figure as it is not possible to give an average value but only a range of overlapping possible $\delta^{37}\text{Cl}$ ranges for all samples within a specific geologic period. This range gets larger if higher fractionation factors are assumed. Estimated $\delta^{37}\text{Cl}$ values of the ocean from the second “Br/Cl ratio” approach are shown as three lines with increasing fractionation factors with uncertainties

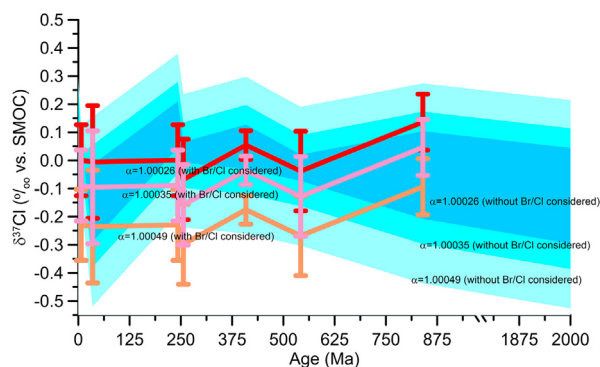


Fig. 5. Possible $\delta^{37}\text{Cl}$ variations in the Earth's history for the different scenarios described in this paper. Blue areas define (from lighter to darker) the possible $\delta^{37}\text{Cl}$ ranges for higher to lower fractionation factors; the lines indicate the calculated $\delta^{37}\text{Cl}$ of the ocean depending on the isotope fractionation and the Br/Cl ratio of the samples. Although differences between the various scenarios are visible, it is obvious that the most logical scenario is defined by a Cl isotope fractionation factor of 1.00035, as the overlap between the scenarios with and without the Br/Cl ratio taking into account is best at this fractionation factor (overlap middle blue field with pink line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

shown as 2σ error bars. There is considerable overlap between the two approaches. It is clear however that assuming a fractionation factor of 1.00049 the $\delta^{37}\text{Cl}$ range determination with the second approach falls really at the lower end of the first approach. This seems to indicate again that our data do not support a Cl isotopic fractionation factor as large as 1.00049 between brine and precipitating halite.

The overlap between the two approaches is much better for fractionation factors of 1.00026 and 1.00035. However, as a fractionation factor of 1.00026 leads to the impossibility to determine the ocean's $\delta^{37}\text{Cl}$ for the Neogene it is not likely that the fractionation factor is so small and it is most likely close to the recently published value of 1.00035 ([Eggenkamp et al., 2016](#)).

The data suggest small variations in the $\delta^{37}\text{Cl}$ of the ocean during the geological past that are smaller than the uncertainties in the data. Variations are largest in the reconstructions of the first approach that might originate in the speculation that in these periods samples are more biased towards early or late stage halite. The second approach corrects for this bias as it extrapolates to the $\delta^{37}\text{Cl}$ values of the first precipitated halite.

In summary we conclude that $\delta^{37}\text{Cl}$ variations of the ocean during the geologic past were small, as has been suggested by [Eastoe et al. \(2007\)](#). The first approach suggests $\delta^{37}\text{Cl}$ values between about +0.2 and -0.4‰ , and these are confirmed by the second approach. Overall $\delta^{37}\text{Cl}$ values of the ocean can be estimated to have fallen into the range $-0.10 \pm 0.25\text{‰}$ for the past two billion years (see [Fig. 5](#)).

5.1.4. Comparison with $\delta^{37}\text{Cl}$ estimates reconstructed by [Eggenkamp et al. \(2016\)](#)

[Eggenkamp et al. \(2016\)](#) reconstructed the $\delta^{37}\text{Cl}$ history of the past billion years based on theoretical constraints of the isotope fractionation between brine and salt of NaCl (halite) in combination with deposition and subsrosion of salt deposits as reconstructed by [Hay et al. \(2006\)](#). [Eggenkamp et al. \(2016\)](#) concluded that the $\delta^{37}\text{Cl}$ of the ocean should have decreased by about 0.25‰ during the last billion years since during that time period more halite has been removed from the ocean than has been returned to it via subsrosion. Net removal of halite should result in a decrease in the $\delta^{37}\text{Cl}$ of the ocean as the heavier chlorine isotope preferentially precipitates out of the brine. The results of this study however suggest that this decrease in $\delta^{37}\text{Cl}$ is not empirically supported, and it seems even more likely that the $\delta^{37}\text{Cl}$ of the ocean was slightly lower than today. The prediction of [Eggenkamp et al. \(2016\)](#) was based on the assumption that precipitation of halite and subsrosion of salt deposits are the only processes that determine the $\delta^{37}\text{Cl}$ of the ocean over geological periods of time, but several other processes could also impact it such as removal of chlorine at subduction zones and addition of chlorine during volcanic activity. To evaluate the isotopic mass balance of the chlorine cycle on the geologic time scale, it is necessary to carry a comprehensive isotopic study of the chlorine cycle and ensure that the isotope composition and isotope fractionation of the various chlorine fluxes is taken into account. Although the chlorine cycle is fairly well understood (see e.g. [Jarrard, 2003](#)) addition of the

isotope compositions and fractionations to the fluxes will surely improve our understanding.

5.2. Estimate of the secular $\delta^{81}\text{Br}$ values of seawater

Unlike chlorine isotopes, behaviour of bromine isotopes during the precipitation of salt is not yet well understood. Eggenkamp et al. (2016) suggested very little fractionation based on experimental precipitation of pure bromide salts. However, this interpretation could not explain the highly positive Br isotope values of formation waters that had likely acquired their Br from dissolving evaporites (Eggenkamp, 2015b). Subsequently, it was found that Br isotope compositions of a fully developed salt sequence (halite to bischofite) do have large and systematic Br isotope variations and it was concluded that isotope fractionation of Br when it precipitates with halite must be much larger than previously expected, and that its fractionation might be as large as 1.0013 (Eggenkamp et al., 2019). This

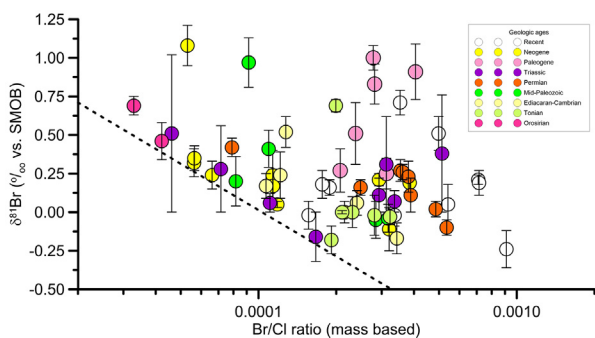


Fig. 6. Plot showing the $\delta^{81}\text{Br}$ versus the Br/Cl ratio of the individual halite samples. The vertical error bars are the errors as defined in Table 1. It is visible that the relationship between $\delta^{81}\text{Br}$ and Br/Cl is not as clear as between $\delta^{37}\text{Cl}$ and Br/Cl. Striking is the line showing that the lowest possible $\delta^{81}\text{Br}$ value for each given Br/Cl ratio increases with decreasing Br/Cl ratio.

large fractionation factor makes it difficult to infer the original $\delta^{81}\text{Br}$ of the ocean based on the Br isotope composition alone. With a Br isotope fractionation factor of 1.0013, the first halite to precipitate from seawater would have a $\delta^{81}\text{Br}$ of 1.3‰, which would progressively decrease to $-1.0‰$ when the last halite to precipitate. The original $\delta^{81}\text{Br}$ of seawater would then fall between 1.3‰ lower to 1.0‰ higher than the measured $\delta^{81}\text{Br}$ of a halite sample, which is a considerable range. Based on the $\delta^{81}\text{Br}$ values of samples measured in this study, the $\delta^{81}\text{Br}$ value of the ocean might have ranged between approximately -0.6 and $+1.0‰$ during the last 2 billion years. Such a large plausible range is unfortunately not very useful to constrain the secular seawater $\delta^{81}\text{Br}$ evolution.

The second (Br/Cl ratio) approach that we applied to constrain seawater Br isotope variations during the past shows ambiguous results. Fig. 6 shows that the relationship between the $\delta^{81}\text{Br}$ and the Br/Cl ratios of the whole set of halite samples is much more diffuse than that between the $\delta^{37}\text{Cl}$ and the Br/Cl ratios (Fig. 2).

However, it is clear from Fig. 6 that some relationship between $\delta^{81}\text{Br}$ and Br/Cl ratio exists. The lowest possible $\delta^{81}\text{Br}$ value is a function of the Br/Cl ratio. Fig. 6 shows that the lower $\delta^{81}\text{Br}$ limit decreases with increasing Br/Cl ratio, pointing a minimum $\delta^{81}\text{Br}$ value of $+0.33‰$ vs SMOB at a Br/Cl ratio of 0.00005. This suggests a minimum possible isotope fractionation between Br^- in solution and Br^- in solid NaCl of about 1.0003. Note that the two samples with the lowest Br/Cl ratios in this Figure are from the Russian sample set and, as their Br content has been decreased considerably after salt deposition they should not be taken into account when the lowest possible $\delta^{81}\text{Br}$ is determined. Nonetheless, in three of the nine sample groups (Permian, Ordovician-Silurian and Ediacaran-Cambrian) a reasonably high correlation coefficient is observed with a negative Br/Cl vs. $\delta^{81}\text{Br}$ trend, and these three sample groups point to $\delta^{81}\text{Br}$ values of halite (at a Br/Cl ratio of 0.00005, $= -4.3$ in log units) between 0.6 and 0.8‰ (Fig. 7).

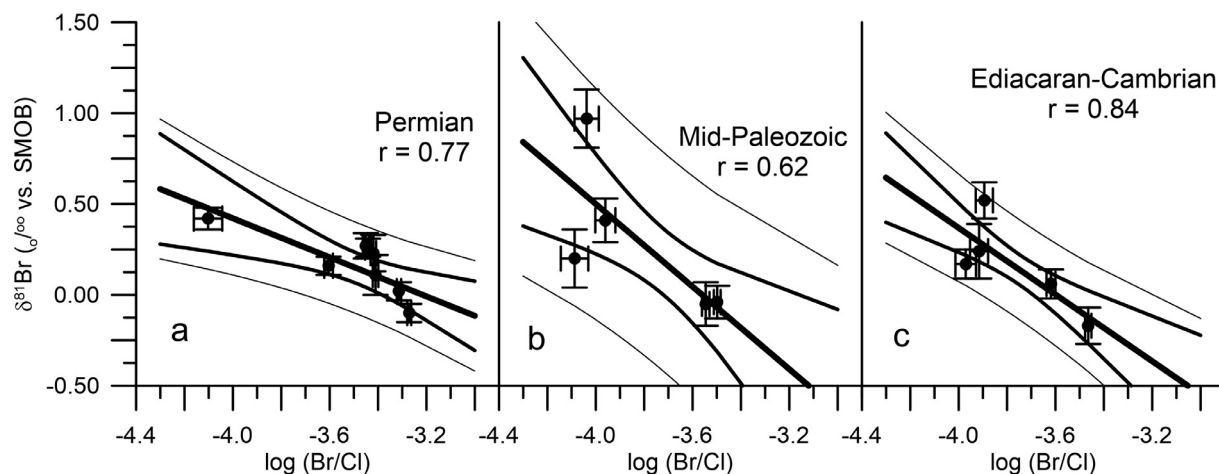


Fig. 7. Correlations between $\delta^{81}\text{Br}$ and Br/Cl ratios for the geological periods with high correlation coefficients between $\delta^{81}\text{Br}$ and Br/Cl ratio (Permian, Mid-Paleozoic and Ediacaran-Cambrian). These relationships point to a negative ($\delta^{81}\text{Br}$ -Br/Cl) relationship with a $\delta^{81}\text{Br}$ value of approximately $+0.7‰$ at the lowest Br/Cl value of 0.00005 ($= -4.3$ in log units).

Fig. 7 shows the reconstructed relationships with uncertainty hyperbolas for these three sample groups with high correlation coefficients. These three subsets point to $\delta^{81}\text{Br}$ values in the first precipitated salt between 0.6 and 0.8‰ and the line showing the lowermost $\delta^{81}\text{Br}$ value suggests a value higher than 0.3‰. As a result, these data suggest a lower bromine isotope fractionation factor than suggested by Eggenkamp et al. (2019). Fig. 8 shows a visual interpretation of these data in a manner similar to that utilised for Cl in Fig. 5. It shows the possible range in $\delta^{81}\text{Br}$ values following the first, isotope only approach, for fractionation factors of 1.003, 1.007 and 1.013, combined with the data for three periods following the second approach that takes the Br/Cl ratio in account, for the same isotope fractionation factors.

Considering the fractionation factor of 1.0013 as suggested by Eggenkamp et al. (2019) this translates to an original $\delta^{81}\text{Br}$ value of seawater between -0.7 and -0.5 ‰. Although this range is close to the lowest possible $\delta^{81}\text{Br}$ values of seawater following the total possible range as indicated in Fig. 8 they seem not realistic as values more within the central part of the total range would have been expected. From Fig. 8 it is also deducible that a fractionation factor of 1.003 is not realistic. With such a low isotope fractionation factor it is mostly not possible to reconstruct the $\delta^{81}\text{Br}$ values of seawater using the $\delta^{81}\text{Br}$ only approach for all but the oldest Russian samples. For all younger geologic periods the minimum possible value is higher than the maximum possible value. The reconstruction based on an isotope fractionation factor of 1.007 seems however feasible. Following the $\delta^{81}\text{Br}$ only approach $\delta^{81}\text{Br}$ of the ocean then has always been in the range between approximately 0 and $+0.5$ ‰ vs. SMOB. Adding the three possible computa-

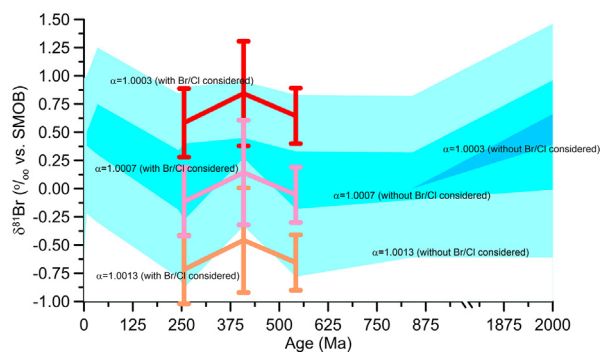


Fig. 8. Possible $\delta^{81}\text{Br}$ variations in the Earth's history for the different scenarios described in this paper. Blue areas define (from darker to lighter) the possible $\delta^{81}\text{Br}$ ranges for lower to higher fractionation factors, the lines indicate the calculated $\delta^{81}\text{Br}$ values of seawater depending on the isotope fractionation and the Br/Cl ratio of the samples. Although differences between the various scenarios are visible, it is clear that the most reasonable scenario is defined by a Br isotope fractionation factor of 1.0007, as the overlap between the scenarios with and without the Br/Cl ratio taking into account is best at this fractionation factor (overlap middle blue field with pink line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

tions of the combined $\delta^{81}\text{Br}$ and Br/Cl ratio approach, which point to a $\delta^{81}\text{Br}$ value of seawater (at least during most of the Palaeozoic) that was close to 0‰ (Fig. 8), suggest that the $\delta^{81}\text{Br}$ of the ocean has been at its present value. The combination of the two approaches thus suggest that the Br isotope fractionation between bromide in brine and halite is about 1.007 and that the Br isotope composition of the oceans has always been close to (or very slightly larger than) its current value. Considering the small number of data, combined with a considerable scatter in $\delta^{81}\text{Br}$ data of evaporites, these values certainly need further refinement along with future research on the Br isotope fractionation during seawater evaporation.

It is clear that, to better understand secular seawater variations in $\delta^{81}\text{Br}$ further research is needed on this isotope system. This includes not only more measurements of Br isotope ratios in salt samples, but also considerable experimental research to precisely determine the isotope fractionation factor for Br precipitation with NaCl under various conditions such as different Br/Cl ratios, different initial seawater compositions and during precipitation of salt from complex brines, as the composition of these brines changes during salt precipitation. Finally theoretical (ab-initio) calculations are also needed to understand the thermodynamics and other properties of the processes studied, such as the competition between Br^- and other major and trace ions for incorporation into halites.

6. CONCLUSIONS

We have measured the Cl and Br isotope values for a large set of halite samples in order to better constrain Cl isotope compositions and variations in the oceans during the Earth's history, as well as the first constraints on the secular seawater Br isotope variations. Based on two different approaches, the Cl isotope variations were small to negligible, with average values in the range -0.10 ± 0.25 ‰ vs. SMOB during the last 2 Ga. Although with a larger degree of uncertainty, it was also possible to obtain an indication of the seawater Br isotope variations during this period. The data obtained in this study suggest a Br isotope fractionation between bromide in brine and bromide in halite of about 1.0007. Combined with the possible Br isotope range of the ocean obtained through the $\delta^{81}\text{Br}$ only approach, the range of Br isotope compositions in the ocean may have been between 0.00 and $+0.25$ ‰ vs. SMOB (Fig. 8) for at least the last billion years with very little variation.

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APPENDIX A. SUPPLEMENTARY MATERIAL

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.gca.2019.08.005>.

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