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WHY ARE VARIATIONS IN BROMINE ISOTOPE COMPOSITIONS IN THE EARTH'S HISTORY LARGER THAN CHLORINE ISOTOPE COMPOSITIONS?

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ABSTRACT

In this paper we discuss the marked discrepancy in global chlorine and bromine isotope variations. While, based on experimentally and theoretically determined fractionation factors, it is expected that bromine isotope variations should be, depending on the process, 2 to 7 times less than chlorine isotope variations it is observed that in formation brines the isotope variations of bromine are at least of the same size as chlorine isotope variations, and regularly even larger. In this paper we argue that this is caused by the fact that oxidation-reduction processes play a more important role in bromine isotope geochemistry than in chlorine isotope geochemistry. Due to the fact that the bromide ion is more easily to oxidise than the chloride ion Rayleigh effects can cause the observed larger variations in bromine isotope geochemistry. In this paper we propose that biochemical reactions (oxidation of bromide ions to methyl bromide) may be the major cause for this effect. Although we do not yet understand the full processes that take place we show that oxidation-reduction processes must be the main effect to explain the differences between the two isotope systems and propose that more research is developed to understand how the processes cause the observed variations.

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1. INTRODUCTION

Before bromine isotopes could be analysed routinely it was expected that the bromine isotope compositions of natural samples would correlate with the chlorine isotope compositions of the same samples but with smaller variations due to the smaller relative mass difference between the two stable bromine isotopes (^{79}Br and ^{81}Br) as compared to the stable chlorine isotopes (^{35}Cl and ^{37}Cl) as for example was suggested during the earliest studies [13] and was later also confirmed in simple diffusion experiments [15]. It was however already observed in the first study on natural bromine isotope variations [14] that the chlorine and bromine isotope compositions of these samples did not correlate very well. In this first study they even correlated (although not very well) negatively. These observations were confirmed in all later studies of bromine isotopes in formation waters [3, 5, 34, 36]. These studies concerned only formation waters as formation waters are the only type of natural samples that contain bromide concentrations that are high enough to be analysed with currently available techniques.

Although these studies, summarised by Eggenkamp [12], indicated that in some environments diffusion might have played a role, which was shown by a rough correlation between δ^{37}Cl and δ^{81}Br with a slope of about ½, in most studies this correlation was not so obvious, and that it was concluded that fractionation processes for chlorine and bromine isotopes were not 1 to 1 related. Some striking observations were made when chlorine and bromine isotope compositions were compared. While chlorine isotope compositions were mostly centred at values that are negative compared to the international standard, defined as the average chlorine isotope composition of modern ocean water, with the large majority of values between -1.21‰ and +0.40‰, bromine isotope compositions were in general more positive than the bromine isotope standard, defined as the average bromine isotope composition of modern ocean water, with the large majority of samples between –0.06‰ and +1.45‰ [12]. Of particular interest were a few samples that contain bromide that originated from (dissolved) evaporite deposits. The bromine isotope compositions of these samples are consistently positive with values between +0.12‰ and +0.87‰ (average +0.60‰, standard deviation 0.29‰, n=8). As isotope fractionation of bromine during precipitation of NaBr from a saturated solution is only small, and as the bromine isotope composition of NaBr that precipitates from a saturated NaBr solution is even negative at -0.16‰ [11] these values cannot have their origin from direct precipitation of bromide from ocean water with an isotope composition that is equal to modern ocean water.

Another very interesting observation was made on formation waters from the Williston Basin in North Dakota [33]. These formation waters, with ages between 330 and 500 Ma, showed chlorine isotope variations that were mostly within 0.5‰ from SMOC, where the measured data showed that significant isotope variations between the different formations are in existence, in spite of the relatively small variations. The bromine isotope compositions however showed very clearly that large and significant variations between the various geological formations in this

basin are found. The trend followed those of chlorine isotopes, but the variations were much larger varied between about +2.0‰ and -0.7‰ depending on the formation from which the waters were sampled from.

As a general conclusion it can be stated that although most research up to the present indicates that while the chlorine isotope composition of the oceans varied only relatively little during the cause of the Phanerozoic [10] the variations in bromine isotope compositions are considerably larger and current indications are that the bromine isotope compositions varied at least between -1‰ and +2‰ during the Phanerozoic.

In the current paper we will discuss a possible origin for these variations and hope to point to possible future research to solve the enigmatic different behaviour of chlorine and bromine isotope compositions during the geological history. In order to study these effects we will compare knowledge on the distribution of chloride and bromide in the oceans during the Phanerozoic, and the effects that fractionation processes have on the isotope composition of chlorine and bromine in the oceans, evaporites and formation waters. As the research done on this subject is still rather limited we have to realise that the conclusions of this paper will not be much more than an invitation to test the proposed processes with more research on both experimental and natural isotope variations and isotope fractionation of chlorine and bromine.

2. THE EVOLUTION OF CHLORIDE AND BROMIDE IN THE OCEANS DURING THE PHANEROZOIC

During the last decades it has been realised that the chloride that is currently present in the oceans has been outgassed from the Earth's interior relatively quickly after the formation of the Earth [21]. It is now thought that the salinity in the early ocean, during Archean times, was about 1.5 to 2 times as high as it is in the current ocean, and only decreased significantly after massive evaporite deposits could be deposited. These deposits could only form when continents large enough to facilitate large basins in which the enormous amounts of evaporite could deposit were formed, which was about 2.5 Ga ago [37]. This agrees fairly well with the age of the oldest known massive halite deposits which are found in Early Proterozoic formations in Russia [29]. As most evaporite deposits have been formed in a few large stages during the last Ga it should have been only during that period that the salinity of the oceans has gradually decreased [24]. This salinity decrease has been studied in detail from the deposition and erosion history of the evaporites by Hay et al [20]. Their research showed that during periods of large evaporite deposition the salinity of the oceans decreased, while in periods with little deposition, when evaporites showed a net erosion the salinity increased again. Overall however the salinity of the oceans has decreased from about 50 g/L (depending on the model applied) at the start of the Phanerozoic to about 35 g/L in the current oceans.

Considering the fact that in Proterozoic times also possibly (but as yet unknown) large amounts of salt may have been deposited [25] the chloride concentration might indeed have been (more than) two times as much as the current salinity at the start of the Proterozoic.

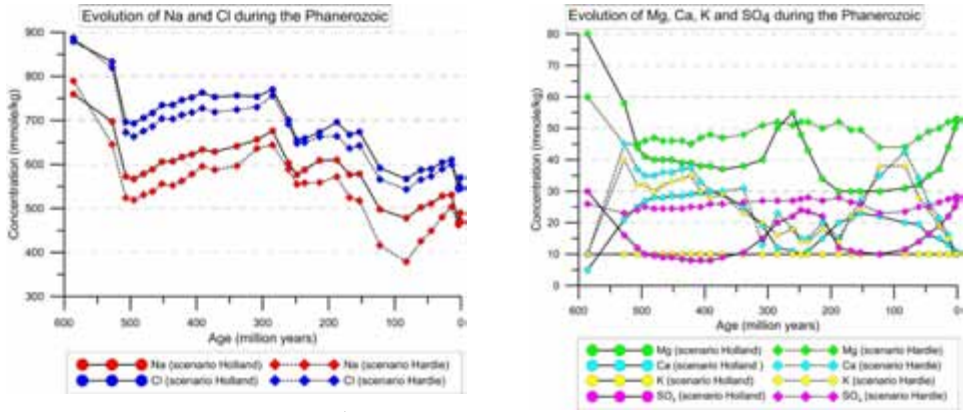

Figure 1: A) Evolution of Na^+ and Cl^- in ocean water during the Phanerozoic. "Scenario Holland" is according to ref. [19], "scenario Hardie" according to ref. [19]; **B)** Evolution of Mg^{2+}, Ca^{2+}, K^+ and SO_4^{2-} in ocean water during the Phanerozoic. "Scenario Holland" is according to ref. [22], "scenario Hardie" according to ref. [19].

Not only did the total salinity of the oceans vary considerably during the Proterozoic, also the concentrations and ratios between the concentrations of the most important ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}) did vary considerably during the Phanerozoic [18,19]. These latter two studies present mostly historical variations of K^+, Mg^{2+}, Ca^{2+}, and SO_4^{2-} ion concentrations during the Phanerozoic, from which Na^+ and Cl^- ion concentrations can be deducted, using the salinity of the oceans. The two studies use different approaches to reconstruct the historic concentrations of K^+, Mg^{2+}, Ca^{2+} and SO_4^{2-} in the Earth's oceans. Hardie [19] approached the composition by using the secular variation in the production rate of oceanic crust, while Holland [22] used the composition of fluid inclusions in halite deposits. The differences between the two scenarios are considerable (see Figures 1a and 1b). The two models however agree with each other in the definition of five evaporite stages during the Phanerozoic, depending on whether the Ca^{2+} concentration is larger than SO_4^{2-} (so that $CaCl_2$ can precipitate as evaporite mineral) or the Ca^{2+} is smaller than SO_4^{2-} (so that all Ca^{2+} is removed from the brine as gypsum precipitate so that $CaCl_2$ can not precipitate as evaporite mineral). The former are defined as $CaCl_2$ seas, the latter as $MgSO_4$ seas [26]. Table 1 shows the periods of the $CaCl_2$ and $MgSO_4$ seas for the two scenarios [19, 22] described above during the Phanerozoic.

TABLE 1: Periods that the oceans were dominant in Ca^{2+} ($CaCl_2$ ocean) or SO_4^{2-} ($MgSO_4$ ocean) during the Phanerozoic according to the scenarios from Hardie [19] or Holland [22] as described in the text.

	Hardie [18]	Holland [19]
$MgSO_4$	0-40 Ma	0-45 Ma
$CaCl_2$	40-140 Ma	45-200 Ma
$MgSO_4$	140-340 Ma	200-300 Ma
$CaCl_2$	340-550 Ma	300-550 Ma
$MgSO_4$	550-? Ma	550-? Ma

There is in general a fairly good agreement of the different periods between the two models. Periods that do not show overlap for the two models are in general periods with no or very limited deposition of evaporites so that no or only limited information from fluid inclusions could be obtained.

Also the bromide concentration in the oceans varied considerably during the Phanerozoic. The historic variations in the bromide contents were determined by Siemann [35] and were based on the bromide concentration of basal halite, which is the first halite that is precipitated from a saturated seawater brine. The bromide concentration seems to have a relationship with the Mg^{2+}, Ca^{2+} and SO_4^{2-} concentrations during the Phanerozoic, suggesting that it might also be related to the production rate of the oceanic crust. There is however no relation with the historical chloride concentration during the Phanerozoic as is clearly visible from Figure 2. The origin for this lack in correlation is not clear yet. As bromide prefers to concentrate in solution during evaporite precipitation it is expected that the bromide concentration in the oceans would increase during periods of net accumulation of evaporites, and decrease when evaporites are eroded. Although the bromide concentration in the oceans appears to decrease in more or less the same periods that more evaporite is formed than eroded, the correlation is not perfect. This means that the formation and erosion of evaporites is not the only effect that regulates the bromide concentration in the oceans.

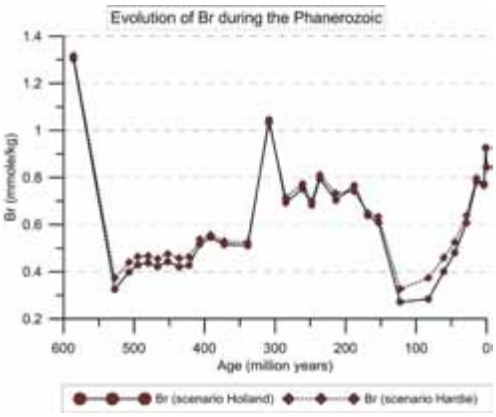

Figure 2: Evolution of Br^- in ocean water during the Phanerozoic. "Scenario Holland" is according to ref. [22], "scenario Hardie" according to ref. [19].

3. (BIO)GEOCHEMICAL EFFECTS OF CHLORINE AND BROMINE REDOX STATES

Although chlorine and bromine, being halogens, are often considered to have a very similar geochemistry (they tend to concentrate in the fluid phase and are mostly found in the -I oxidation state) there are very different effects when biogeochemical reactions are taken into consideration. The effects that take place in biogeochemical reactions are to be considered as oxidation-reduction reactions. That means that the effects that are observed have to be examined considering the difference in redox behaviour of the two elements, chlorine and bromine. It is already known at least since the early 19th century that the redox behaviour of chlorine and bromine is different. In fact it was the difference in redox behaviour that made the discovery of bromine possible [2, 27], and it was also the difference in redox behaviour that makes it possible to separate bromine from chlorine in natural samples for bromide concentration measurements [9, 16] and isotope measurements [14].

This means that it takes less strong oxidising agents and less energy to oxidise bromides ion than to oxidise chloride ions. As a result of this effect it is easier for various organisms (such as bacteria, algae and fungi) to use bromides in their metabolic system. By now, it is well known that there are many processes in organisms that produce organohalogen compounds [17] and of the almost 3200 known that are naturally occurring more than 1600 these compounds, more than 50% of the known compounds, contain bromine [18]. The fact that it is so much more easy to oxidise bromide is the reason that this very large array of organobromine metabolites is found in organisms. It is also the reason that in environments where methyl-halides are formed by organic activity it is observed that the formation of CH_3Br is much more efficient than CH_3Cl. For example, in Scottish salt marshes it has been observed that the production rate of CH_3Cl is only on average 2.2 times as large as the production rate of CH_3Br from vegetation that contains about 100 and 250 times more (mass/mass) chloride than bromide [4]. A very interesting application of the process that bromides are more easily to oxidise than chlorides is observed in higher animals where certain white blood cells prefer to oxidise bromide dissolved in the blood to hypobromite above the oxidation of chloride as remedy against certain parasites [28].

For the current study it is mostly interesting how the isotope fractionation of chlorine and bromine is different in these environments, and if the cumulative fractionation effects over time may explain the larger variation of bromine isotope compositions as compared to the chlorine isotope compositions. The chlorine isotope fractionation during formation of organic compounds from chloride has been researched in a few studies. Very important was a study [1] where the chlorine isotope fractionation during two important pathways for enzymatic natural halogenation was studied: chlorination by chloroperoxidase and chlorination by flavin-dependent halogenase. Of these processes chloroperoxidase chlorination showed a very large fractionation of -12.6±0.9‰ which is comparable to results

obtained in earlier studies [30]. On the other hand, flavin-dependent halogenase showed no significant fractionation with a value of -0.3 ± 0.6‰. This large difference in the fractionation factors of the two processes is attributed to the largely different reaction mechanisms employed by the enzymes. It was shown [1] that the $\delta^{37}Cl$ in bulk organochlorine compound mixtures that was extracted from boreal forest soils were only slightly depleted in ^{37}Cl relative to inorganic chlorine. This showed to be in contrast to earlier suggestions [30] that chloroperoxidase chlorination plays a key role in production of soil chlorinated organic compounds. As a result it was concluded [1] that this observation points to the additional involvement of either different chlorination pathways, or that dechlorination of naturally produced chlorinated organic compounds can neutralize $\delta^{37}Cl$ shifts caused by chloroperoxidase chlorination.

Fractionation during the formation of CH_3Br has only been estimated in one study [23] and this study showed that CH_3Br might be a few (up to 2) ‰ lighter than the bromide from which it is formed, and during formation of brominated phenols it was shown that the bromine isotope composition increases in value [39]. At first sight the results seem to be contradictory so that more research to study the isotope fractionation of organobromine compound production due to biogeochemical processes is duly needed.

These studies indicate that it is still very difficult to conclude anything sensible about the "real" isotope fractionation of chlorine and bromine during formation of CH_3Cl and CH_3Br in natural environments. It appears however that the methyl-halides that are formed have more negative isotope values than the halide ion from which they are formed. This is in contradiction with the expected, theoretical fractionation. Theoretical calculations [31] indicate that at equilibrium the reaction between HCl (gas) and CH_3Cl (gas) would lead to isotope values where the latter is 4.95‰ heavier at 0 ^{o}C and 4.09‰ heavier at 25 ^{o}C. This would be more in line with other equilibrium calculations between chlorine species of different redox values. The more oxidised species has a higher isotope ratio. No calculations are known for the equilibrium reaction between HBr and CH_3Br, but from theoretical calculations [8, 38] it can be deducted that isotope fractionation of chlorine isotopes (for the equilibrium between HCl and Cl_2) is about 7 times larger than bromine isotope fractionation between HBr and Br_2. If this would also follow for the equilibrium between HBr (gas) and CH_3Br (gas) the fractionation for this reaction would be 0.7‰ at 0 ^{o}C and 0.6‰ at 25 ^{o}C.

4. CAN REDOX EFFECTS SIGNIFICANTLY ALTER CHLORINE AND BROMINE ISOTOPE COMPOSITIONS ON GEOLOGICAL TIME SCALES?

Although it is still difficult to assess the actual isotope fractionation between inorganic halide ions and methyl-halides as they may be produced through different

pathways that can generate different isotope fractionation factors it may be possible to assess if the possible fractionation is large enough to cause isotope variations over geological time scales. The effect will be approached through an extremely simplified calculation, using CH_3Cl and CH_3Br sources and sinks that are determined to understand its effects on stratospheric ozone depletion [7]. Unfortunately a potentially large source for CH_3Br is not quantified in this study (tropical leaf litter) and this is estimated to be about 10 times less for CH_3Br as compared to CH_3Cl, in line with the average of other terrestrial sources that produce on average ten times less CH_3Br than CH_3Cl. Overall this adds to a total production of 3658 Gg/yr CH_3Cl and 284 Gg/yr CH_3Br, for the large majority due to natural processes. It is assumed that during the formation of methyl-halides fractionation as estimated above, based on theoretical estimates, takes place, and that during decomposition in the sinks no fractionation takes place. The total amount of chloride and bromide in the oceans is $2.71*10^{13}$ Gg and $9.38*10^{10}$ Gg respectively [32]. When these amounts are divided by the annual production this gives an impression how long it would take for all chloride or bromide in the oceans to transfer into the methyl-halides if none of it would be reduced back to the halide ions. In the case of CH_3Cl the result of this calculation is $1.05*10^{10}$ years, more than double the age of the Earth, in the case of CH_3Br it is only $3.9*10^{8}$ years or less than a tenth of the age of the Earth. This calculation indicates that, while it is not possible for all chloride to have been oxidised through biological reactions, for bromide it may be possible. These data have been used to calculate the possible maximum isotope effect for chlorine and bromine due to the reaction of halide ion to methyl-halides. For these calculations extreme conditions have been assumed, for example that the methyl-halides that are formed do not react back to the halide ions. In this case it is relatively easy to calculate the (theoretical) isotope effects for chlorine and bromine during the geological history. In Figure 3 the isotope trend for chlorine and bromine concerning the reaction from halide to methyl-halide is calculated assuming no back reaction has taken place, starting from a chlorine and bromine pool that has values of 0‰ relative to SMOC and SMOB at the beginning of the Cambrian, 541 million years ago. In spite of the fact that the isotope fractionation for chlorine is about 7 times larger than for bromine the calculations indicate that while the chlorine isotope composition would decrease by 0.22‰ the bromine isotope composition would decrease by 0.83‰. The reason for this effect is that, although the chlorine isotope fractionation is so much larger than the bromine isotope fractionation bromide is so much more, about 25 times, as reactive. The simple fact that bromide is so much more reactive than chloride might explain that bromine isotope compositions are more pronounced during the history of the Earth than chlorine.

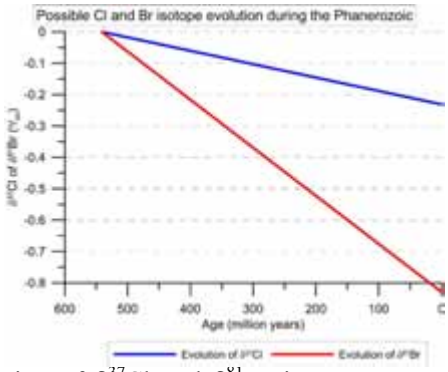

Figure 3: Possible evolution of $\delta^{37}Cl$ and $\delta^{81}Br$ in ocean water during the Phanerozoic assuming isotope fraction factors for the reaction between the halide ion and methyl-halide of 4.5‰ for chlorine and 0.6‰ for bromine and a bromide reaction rate that is 26.9 times larger than for chlorine.

It is however very important to realise that although theses calculations give a good impression of the possible differences between the chlorine and bromine isotope evolution during the geological history it must be realised that it has certain drawbacks. For example, the actual lifetime of methyl-halides in the atmosphere is only relatively short, at most several decades [6], so that back reactions should in fact be taken into account. Most of the chlorine and bromine will not escape into space but will return to the surface pool (most likely the ocean) and the isotope values will be averaged again. Following this it would be much more likely that the average isotope composition of the ocean, due to the described processes would stay more or less the same. But, it also has to be realised that the observed isotope differences between chlorine and bromine are real, and without oxidation-reduction reactions, in combination with differences in reaction rates they can not be understood or explained.

The theoretical calculation presented in Figure 3 shows, however, one very important effect. While the isotope fractionation factor of bromine in oxidation-reduction processes is about seven times smaller than the isotope fractionation of chlorine in oxidation-reduction processes the reaction rate of bromine is so much larger than the reaction rate of chlorine that the total bromine isotope variation indeed can grow to significantly larger numbers than the chlorine isotope variation. However, to be able to explain the larger than expected variation of bromine isotopes compared to chlorine it is necessary to not only find the processes that in theory can cause these effect, but also to understand where they have taken place during the geological history of the Earth, and understand that the various sinks with different isotope compositions are located. It is not only absolutely necessary to find and measure them, but it is essential that we understand where they are and what their isotope composition should be.

5. CONCLUSIONS

When the isotope geochemistry of chlorine and bromine in natural environments is studied in most cases only the geochemistry of the halide (chloride or bromide) ion is taken into consideration. However, it is now clear from the stable isotope geochemistry of these two elements that this can not explain the full picture. When only halide ions are considered it is known that the isotope variations for chlorine should be larger than for bromine. As in most studies in which both chlorine and bromine isotopes are examined it is observed that the bromine isotope variation is at least comparable, and sometimes even larger, to the chlorine isotope variation this is a clear indication that processes in which only halide ions play a role (such as diffusion or evaporite precipitation) can not be the sole processes that took place.

Other processes that took place can only be oxidation-reduction processes, especially concerning the bromine isotope variations. Oxidation-reduction processes normally cause larger isotope fractionation than processes that only involve one oxidation state. As the bromide ion is easier to oxidise than the chloride ion this can explain the larger isotope variation for bromine isotopes than chlorine isotopes. Even when it is considered that the equilibrium isotope fractionation of bromine between species with different oxidation state is approximately 7 times smaller than chlorine isotope fractionation, due to the fact that bromide is easier to oxidise the reaction rate for reactions between bromine species can be 10 to 100 times larger than the reaction rate for reactions between chlorine species. The final effect then is indeed that bromine shows larger isotope variations than chlorine.

In this paper we have shown that, although for an extremely simplified process, the biological oxidation of halide ions to methyl halide gases would be able to obtain, over a very long time scale, an about four times larger isotope variation for bromine than for chlorine. The process used for this calculation might not be the process that is responsible in nature for the large bromine isotope variation as methyl-halides are relatively unstable in the atmosphere. However, the calculations did show that in oxidation-reduction processes, in spite of the smaller bromine isotope fractionation factors, a larger isotope ratio variation can be found as the oxidation-reduction reactions for bromine species are so much more efficient than for chlorine species, and they are much more likely to occur in processes that take place on the Earth. These effects should be prime targets for future research on chlorine and bromine stable isotope geochemistry.

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