



Bromine stable isotope fractionation in evaporites

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Bromine isotope measurements of formation waters with low bromide concentrations, that originate from the dissolution of evaporites, show relatively high values with an average $\delta^{81}\text{Br}$ of $+0.6\text{‰}$ relative to SMOB (Standard Mean Ocean Bromide). These values are difficult to explain as the isotope fractionation between saturated bromide brine and pure bromide salts is nearly negligible.

We collected a large set of salt samples and studied their bromine isotope compositions to understand the systematics involved. The samples concerned were mostly halite samples but also a few more evolved carnallite and bischofite samples.

As the Br/Cl ratio of natural halite samples is about 10 times lower than in seawater the measurement of its isotope composition is challenging. It is not possible to extract enough bromide from 1 mL of solution with ion-exchange resins. We, therefore, choose a distillation method to extract bromide from chloride rich solutions. In order to extract bromide from solution and concentrate it in a small volume, the sample is mixed with nitric acid as oxidiser that upon heating oxidises the bromide to bromine. This is distilled into a reducing ammonia solution where the bromine is reduced to bromide that can be analysed directly by MC-ICP-MS.

Using this technique we were able to analyse $\delta^{81}\text{Br}$ of a set of salt samples from a Zechstein salt sequence from the Northern Netherlands. Results showed a steep decrease of $\delta^{81}\text{Br}$ in halite dominated samples related to the Br/Cl ratio as a measure of the salt evolution. $\delta^{37}\text{Cl}$ measured in the same set of samples showed a less steep slope. The slope of this relationship is, at a first approximation, related to the isotope fractionation between bromide or chloride in solution and in salt. As the bromine slope is 3.9 times steeper than the chlorine slope, the bromine isotope fractionation between brine and salt may also be 3.9 times larger than the chlorine isotope fractionation. As the chlorine isotope fractionation is known as $+0.35\text{‰}$ this suggests a bromine isotope fractionation of $+1.3\text{‰}$. Interestingly, it seems that $\delta^{81}\text{Br}$ increases again if magnesium chloride becomes precipitated. Following the same procedure this suggests a bromine isotope fractionation of -0.9‰ .

In order to test these findings, $\delta^{81}\text{Br}$ was measured on halite samples from different geological ages between the Tonian and the Messinian. Within most individual periods the relationships are not as significant as in the Upper Permian Zechstein, which was chosen to analyse samples from a single sequence. In spite of that the results still indicate higher $\delta^{81}\text{Br}$ in early deposited salt and lower $\delta^{81}\text{Br}$ in later halite. The isotope fractionation concerned might be a little less.

These results show a good example how a case study can be used to estimate the previously unknown bromine isotope fractionation for incorporation of Br in Cl salts. However, the results are not conclusive yet and experiments are currently performed to better understand and constrain the isotope fractionation and the processes involved that explain the interesting bromine isotope fractionation observed in evaporite deposits.