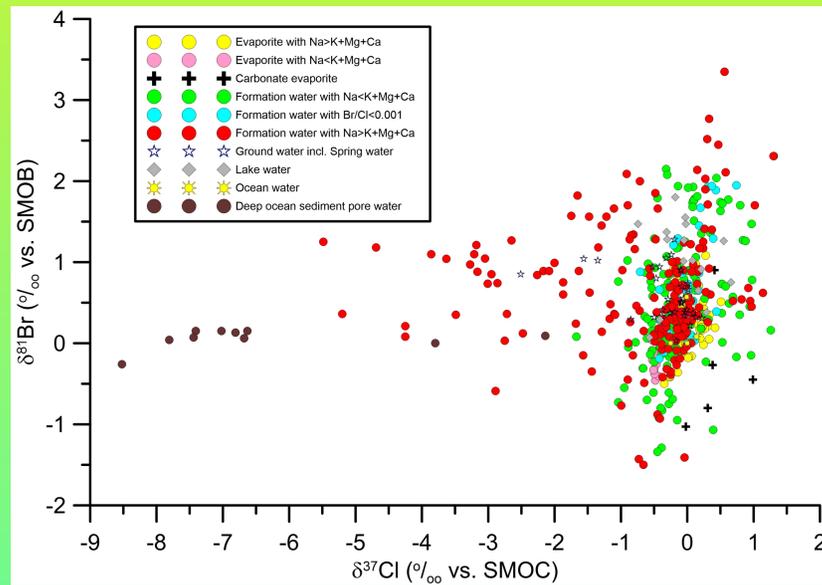




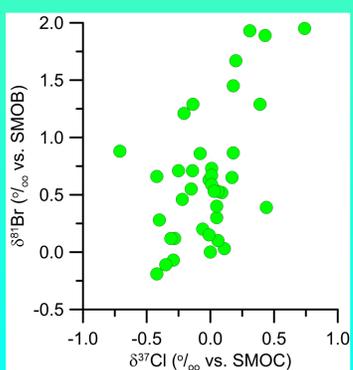
Bromine stable isotope fractionation in evaporites

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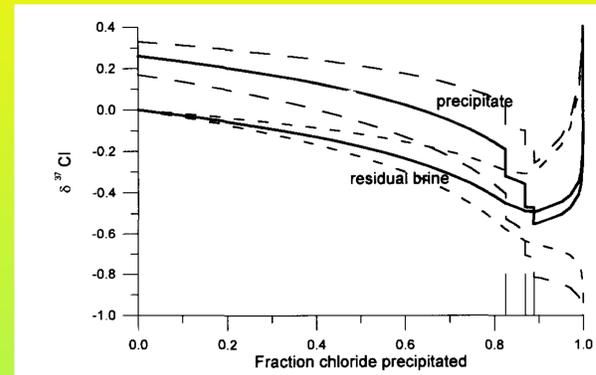
INTRODUCTION

The halogen elements chlorine and bromine have a similar chemistry, but their stable isotope compositions are in general not well correlated. Cl isotopes are mostly between -0.5 and 0‰ relative to the ocean composition, but with some very large negative excursions in rare formation and deep-sea pore waters, while Br isotopes are mostly between -0.5 and +1‰ relative to the ocean composition, and does not show very extreme numbers.



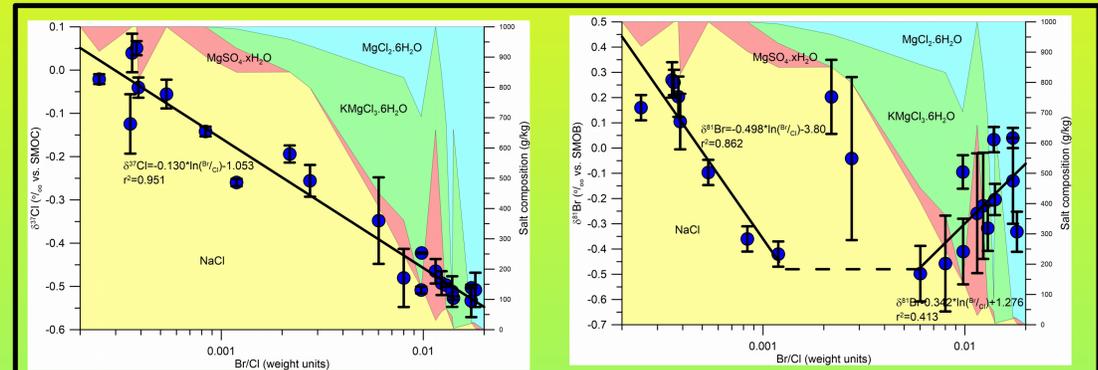
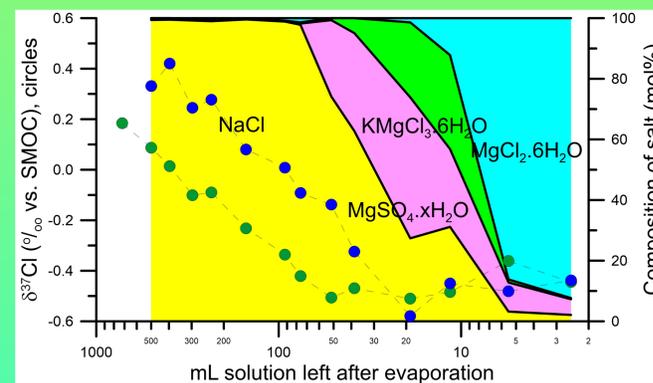
Br ISOTOPES IN EVAPORITE DERIVED FORMATION WATERS

Until recently Br isotopes could not be measured in evaporite samples. The Br isotope composition could however be determined through the measurement of Br isotopes in formation waters with very low Br/Cl ratios (<0.001) that represent dissolved halite. The ranges of the Cl and Br isotopes in this type of formation waters are shown to the left.



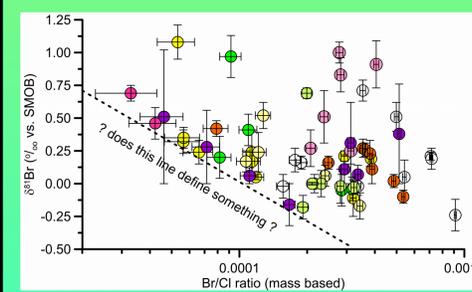
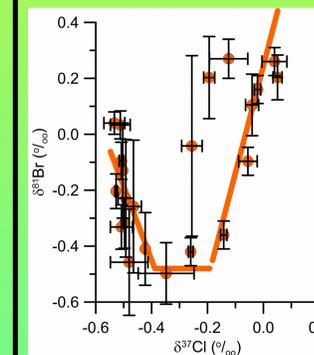
Cl ISOTOPES IN EVAPORITES

Cl isotope behaviour in evaporites is well studied. Isotope fractionation between brine and precipitate of NaCl, KCl, MgCl₂ and CaCl₂ differs for each. While NaCl is much more positive (+0.35‰) than brine, KCl is negative (-0.12‰). MgCl₂ and CaCl₂ fractionation negligible. The figures show that predicted Cl isotope evolution (above) agrees with experimental data (below). In both figures: x-axis decreasing volume left, y-axis Cl isotope composition of brine and salt.



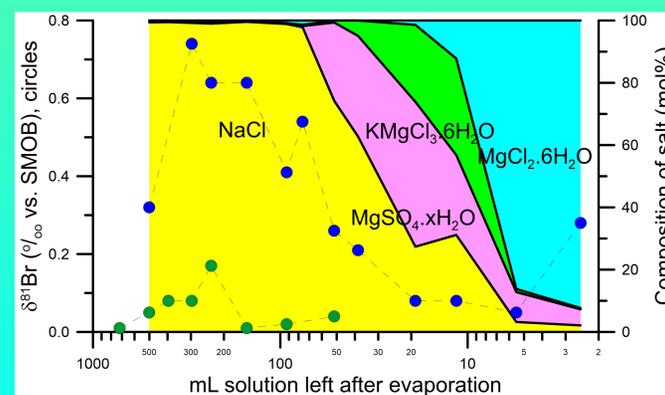
Br AND Cl ISOTOPES IN A FULL SALT SEQUENCE

In a full Zechstein salt sequence from the Netherlands Cl isotopes continuously decrease with increasing salt evolution (represented by the Br/Cl ratio). Br isotopes are different, at first they decrease with a steeper slope, suggesting a much larger isotope fractionation than Cl (about 1.3‰ for halite), and increase during the last phase, suggesting a reversal of the isotope fractionation to about -0.9‰ for last stage salt.



Br ISOTOPES IN HALITE OF DIFFERENT AGES

The Br isotope compositions of a large set of primary halite from ages down to late Proterozoic also indicate significant fractionation between brine and salt, but is difficult to quantify. Data suggest that no to little historical variation has occurred in the Br isotope compositions of the oceans.



EXPERIMENTAL DETERMINATION OF Br ISOTOPE FRACTION IN SALT MIXTURES

The Br isotope fractionation of pure salts is negligible. As this deviates so much from observations in natural salts we determined the Br isotope fractionation during precipitation of salt from a brine mixture that represents modern seawater during evaporation to dryness. What we observe is that the δ⁸¹Br in brine stays constant while δ⁸¹Br of the precipitated salt is high in early precipitated salt and seems to decrease later. The observed fractionation is about +0.7‰ and decreasing, indicating a significant Br isotope fractionation during salt precipitation, that is variable with the brine composition. This observation shows nicely the importance of combining experimental with case studies.

