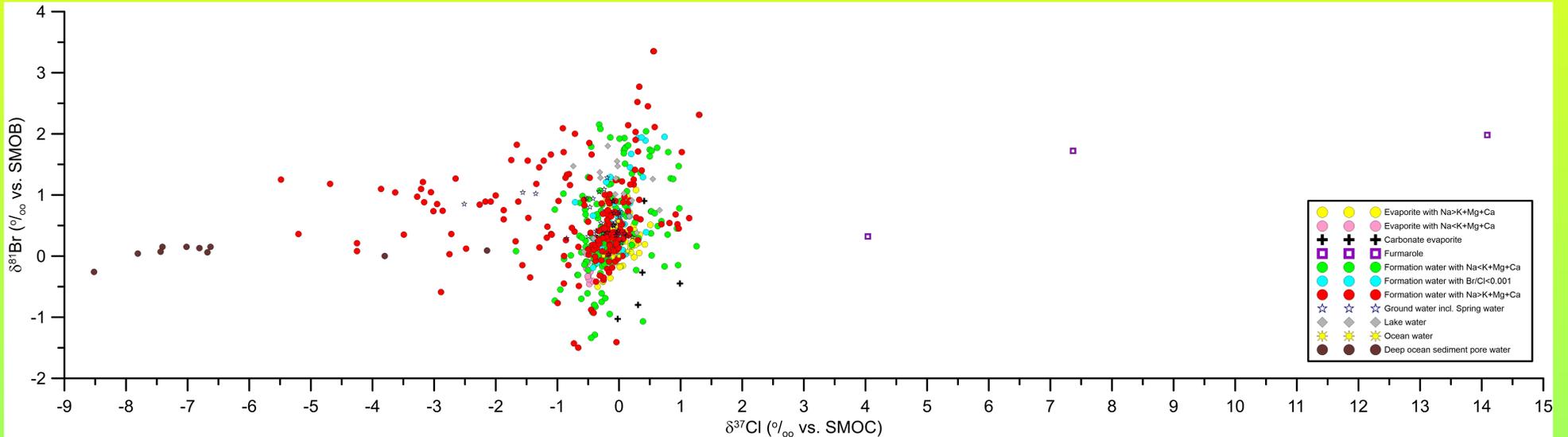


Relationships between $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ in natural water and salt samples



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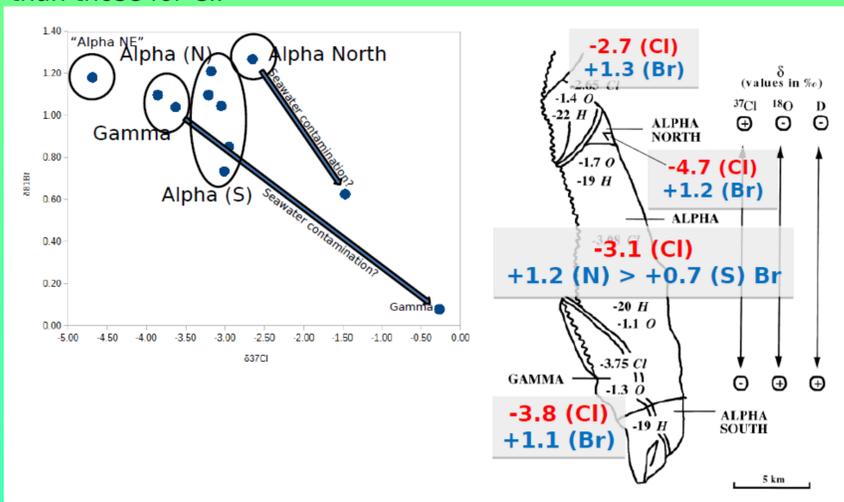


INTRODUCTION

The halogen elements chlorine (Cl) and bromine (Br) are chemically similar elements. On Earth their dominant redox state is -1, in the form of the halide ion, which is mostly concentrated in the oceans. As these ions do not fit easily in most mineral lattices they are mostly found in evaporites that precipitate from ocean water. In (silicate) rocks Cl and Br are merely trace elements and are concentrated in only a few minerals such as sodalite.

Cl and Br have both two stable isotopes, so that their isotope ratios can be studied. The first comprehensive studies appeared in 1984 for Cl and in 2000 for Br. Due to their chemical similarities it was originally assumed that Cl and Br would show similar isotope characteristics, where Br isotope variation would be about half that of Cl. The figure at the top of this poster presents the Br and Cl isotope data of all 430 samples published until mid 2017 and includes 130 additional samples measured by me in the last year.

It is clear from this figure that the relationships between Cl and Br isotopes are rather complex, and when outliers are not taken into consideration it appears that Br isotope variations may even be larger than those for Cl.

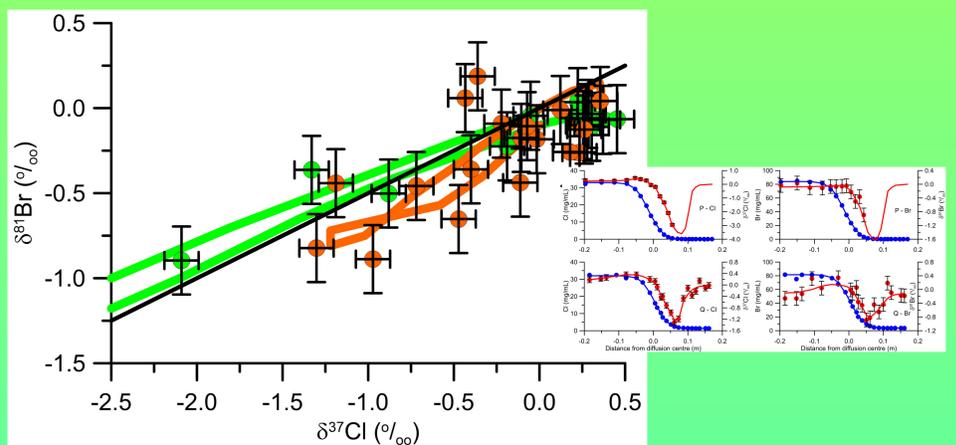


EXAMPLE: OSEBERG FORMATION WATER

In the first Br isotope paper, presenting the original IRMS method, formation water samples from the Norwegian Oseberg Field were analysed (Eggenkamp & Coleman, 2000). Cl isotopes of the same samples were known at the time, but were only published later (Ziegler et al., 2001) and these Cl and Br isotope data were never discussed in tandem. When Cl and Br isotope data of the various sub-fields are plotted it is clear that Cl and Br isotopes show very different characteristics. While each sub-field is characterised by a different Cl isotope value, Br isotope values in all sub-fields are comparable at +1.2‰ to +1.3‰, and in sub-field Alpha $\delta^{81}\text{Br}$ decreases from +1.2‰ in the north to +0.7‰ in the south. Is this characteristic for formation waters? We don't know yet, but it is advisable to focus future studies on formation waters as they are economically important, and are regularly characterised by negative Cl data and positive Br data (see figure at top of poster).

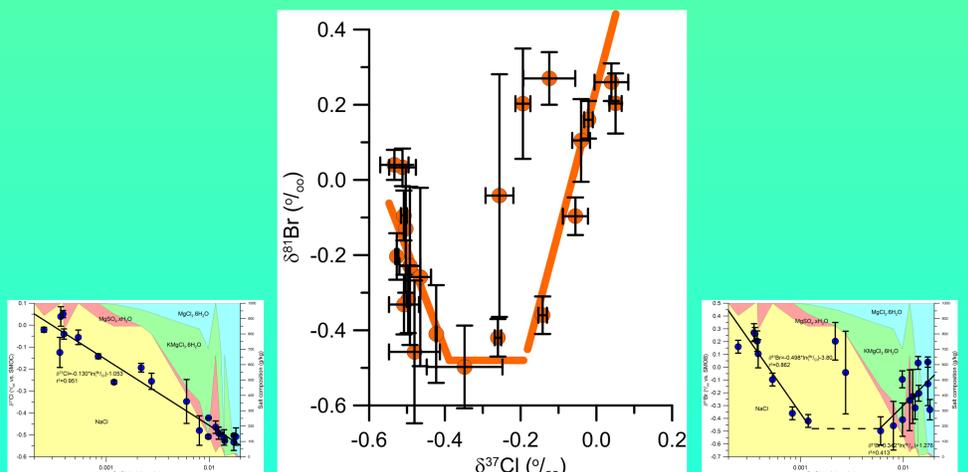
STUDIES WITH SYSTEMATIC CL AND BR VARIATIONS

There are only few studies in which Cl and Br isotopes are both measured and were they can be related to a known process. Two will be discussed here, first an experimental study in which both Br and Cl isotope variations were followed in the diffusion process and second where they are followed in a well defined salt sequence showing the full development of salts from a seawater type solution.



DIFFUSION OF BOTH CL AND BR IN ONE SYSTEM

Two experiments were done like those presented by Eggenkamp & Coleman (2009) that contained both Cl and Br (Eggenkamp & Coleman, 1998, never published). It is clear that in this system Cl and Br behave comparable, and very much the same as in experiments with only Cl or Br. Although not very clear due to the large errors in these very old measurement the Cl and Br isotope values are related by approximately a linear relationship with slope 1/2.



ISOTOPE EFFECTS DURING PRECIPITATION OF SALT

During the precipitation of salt it is clear that Cl and Br behave differently. Cl shows relatively modest fractionation, while Br appears to show large fractionation factors that are opposite each other for Na and K/Mg dominated salts. This effect is probably due to the fact that Cl precipitates from a Cl saturated solution while Br does not, and has to compete with Cl while it fits less easily in the crystal due to its larger ionic radius. Thus a different process than Cl so that its fractionation is different from the expected for a saturated solution. We are currently running experiments to study these effects in detail.



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