

**A COMPARISON OF CL AND BR ISOTOPE FRACTIONATION IN DIFFUSION; GEOCHEMICAL CONSEQUENCES.** H.G.M. Eggenkamp and M.L. Coleman, Postgraduate Research Institute for Sedimentology, The University of Reading, P.O.Box 227, Whiteknights, Reading RG6 6AB, United Kingdom. H.G.M.Eggenkamp@reading.ac.uk; M.L.Coleman@reading.ac.uk.

Experimental aqueous diffusion of NaCl and NaBr has been conducted in polyacrylamide gel (85% porosity) to be able to compare diffusion coefficients and isotope fractionation of Cl and Br. Both of these halogens have two stable isotopes, of which, as expected, the lighter isotopes ( $^{35}\text{Cl}$ ,  $^{79}\text{Br}$ ) is moving faster than the heavier ( $^{37}\text{Cl}$ ,  $^{81}\text{Br}$ ) during diffusional transport. Isotope fractionation is related to the relative mass differences of the isotopes, so that a smaller fractionation is expected for Br than for Cl.

The experiments were conducted in glass tubing with 16mm ID after a method developed by Schreiner *et al.* (1982). A polyacrylamide gel was prepared according to Davison *et al.* (1994) and poured into the tubing, filling a ~20cm length. After setting, another gel was prepared but containing NaCl or NaBr solution, which was poured on top of the set gel. From that moment the Cl or Br could diffuse into the first gel. After an appropriate time the glass was broken, and the gel sliced. The gel slices were equilibrated with water, the Cl or Br concentration determined by colorimetry, and  $^{37}\text{Cl}$  and  $^{81}\text{Br}$  were determined using conventional mass spectrometry of  $\text{CH}_3\text{Cl}$  or  $\text{CH}_3\text{Br}$  (Willey & Taylor, 1978). The diffusion coefficient and isotope fractionation were calculated from the Cl or Br concentrations and isotopic compositions of the samples.

The diffusion coefficients of aqueous Cl and Br are similar at specific temperatures, but highly temperature-dependent, giving  $D_{\text{Cl}}$  of  $12 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$  at  $22^\circ\text{C}$ , and  $6.5 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$  at  $2^\circ\text{C}$ . The isotope fractionation is less temperature-dependent. However, for Br it is approximately half that of Cl, giving an  $\alpha$  of 1.0008 for Br, and 1.0015 for Cl, both at  $22^\circ\text{C}$ .

Our results so far agree perfectly with expected isotope fractionation in the halogens. An isotope fractionation of Br which is about half that of Cl agrees with data obtained 30 years ago on liquid  $\text{PbCl}_2$  and  $\text{PbBr}_2$  (Klemm & Lundén, 1955; Cameron *et al.*, 1956). Also Cl fractionation data agree with those as measured in nature (Beekman *et al.*, 1992). No other natural Br diffusion data have been reported yet.

These results indicate that measuring both the Cl and Br isotope composition of a suite of samples could be very important to determine the type of fractionation process that has occurred. If diffusion is the main cause of fractionation, Cl and Br isotope data should have a positive correlation and when plotted the slope should be approximately 0.5.

To date there have been no substantiated reports of Br isotope fractionation in natural samples and it was always expected that fractionation of Cl and Br

isotopes would be similar, as the elements have a very similar chemistry. However, as we have shown (Eggenkamp & Coleman, 1997), while experimental precipitation of NaCl from a brine fractionates the heavier isotope into the solid phase, NaBr shows a depletion of the heavy isotope relative to the solution. This was the first valid indication that the isotopic fractionations of Cl and Br are not completely similar.

We have recently measured Br isotope data from a set of waters from an oil-field and shown that this is also the case in nature. These samples, which have (very) negative  $^{37}\text{Cl}$  values, show a range of positive  $^{81}\text{Br}$  values up to +1.4% vs. SMOB.

SMOB (Standard Mean Ocean Bromide) is proposed as the standard for Br isotope measurements, as SMOC is for Cl and until we have contrary evidence we will assume isotope composition of Br is constant all over the oceans, as is Cl, since the residence time for Br in the oceans is even longer than that of Cl.

The fact that the Cl and Br isotope data of the oil-field samples do not correlate positively indicates that in the system concerned diffusion is not the pertinent process. We have defined a halide source for brines with distinctive Cl and Br isotopic compositions, but much research will be necessary to determine the processes that are responsible for the different isotope fractionations found for Cl and Br.

#### References:

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