

# The effect of aqueous diffusion on the fractionation of chlorine and bromine stable isotopes

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## Abstract

Diffusive isotopic fractionation factors are important in order to understand natural processes and have practical application in radioactive waste storage and carbon dioxide sequestration. We determined the isotope fractionation factors and the effective diffusion coefficients of chloride and bromide ions during aqueous diffusion in polyacrylamide gel. Diffusion was determined as functions of temperature, time and concentration. The effect of temperature is relatively large on the diffusion coefficient ( $D$ ) but only small on isotope fractionation. For chlorine, the ratio,  $D_{^{35}\text{Cl}}/D_{^{37}\text{Cl}}$  varied from  $1.00128 \pm 0.00017$  ( $1\sigma$ ) at 2 °C to  $1.00192 \pm 0.00015$  at 80 °C. For bromine,  $D_{^{79}\text{Br}}/D_{^{81}\text{Br}}$  varied from  $1.00098 \pm 0.00009$  at 2 °C to  $1.0064 \pm 0.00013$  at 21 °C and  $1.00078 \pm 0.00018$  ( $1\sigma$ ) at 80 °C. There were no significant effects on the isotope fractionation due to concentration. The lack of sensitivity of the diffusive isotope fractionation to anything at the most common temperatures (0 to 30 °C) makes it particularly valuable for application to understanding processes in geological environments and an important natural tracer in order to understand fluid transport processes.

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## 1. INTRODUCTION

The halogen elements, chlorine and bromine, are significant constituents of ocean waters and interstitial brines derived from them. Chloride and bromide are the least reactive components of such brines, and it is this property which allows them to display the isotopic effects of physical processes without the added complexity of fractionation from chemical reactions. For example, mixing of aqueous fluids may be advective or diffusive and while the former produces no isotopic fractionation, the latter does. With

knowledge of the isotopic diffusion coefficients it is possible to apply quantitative interpretation to the results. For example, Eggenkamp et al. (1994) showed that the chloride concentration profile in sediment porewaters was the result of a diffusive process related to a change from freshwater to marine conditions. Coleman et al. (2001) and Lavastre et al. (2005) measured the chlorine isotope compositional profiles at potential sites for construction of a subsurface radioactive waste storage test facility. The aim was to identify the extent to which each was hydrodynamically stable and thus less liable to affect stable, long-term storage. One of these sites showed active advective mixing while another indicated a 15 million year history of steady diffusive mixing of marine brine pore fluids with those of freshwater origin. An as yet unexploited use for this approach would be to test the diffusive permeability of the seals of geological formations potentially of value for sequestration of carbon dioxide to ameliorate the effects of global climate change. Thus,

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accurate and precise determination of the fractionation factors is of great value.

Chlorine and bromine each have two stable isotopes ( $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  and  $^{79}\text{Br}$  and  $^{81}\text{Br}$ , respectively). By 1921, there was the theoretical proposition that the different stable isotopes of an element, because of their different masses, would fractionate by the process of diffusion (Lindemann, 1921). As early as 1943, it was shown that isotopes actually do fractionate as a result of diffusion, when experiments were performed showing that  $^{63}\text{Cu}$  was enriched (relative to  $^{65}\text{Cu}$ ) if Cu was diffused into  $\text{Ag}_2\text{S}$  (Klemm, 1943). In 1955, Senftle and Bracken described the theoretical effect of diffusion on isotopic fractionation in rocks and their associated fluids.

Isotope fractionation effects in chlorine were studied a long time ago. Madorsky and Strauss (1948) enriched a NaCl solution in  $^{35}\text{Cl}$  by a counter-current method. They found, using a solution containing 33 gram NaCl per liter that the diffusion coefficient (separation factor) of  $^{35}\text{Cl}$  is 1.001–1.002 times that of  $^{37}\text{Cl}$ . Konstantinov and Bakulin (1965) did experiments comparing Cl fractionation of NaCl, LiCl and HCl solutions at various concentrations and found that the Cl isotope fractionation for HCl is much smaller than for LiCl and NaCl, and that fractionation increases with concentration. For molten TiCl (Herzog and Klemm, 1958) it was shown that at a higher ( $\sim 710^\circ\text{C}$ ) temperature the isotope fractionation, defined as the ratio of the diffusion coefficients between  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ , was smaller (1.0031) than at lower temperature ( $\sim 565^\circ\text{C}$ ; 1.0043). In these older experiments diffusion was accelerated by electric currents, as during the early years of Cl isotope chemistry precision of mass spectrographs and mass spectrometers was not sufficient to measure the relatively small natural variation of only a few per mil (Long et al., 1993). After the development of techniques precise enough to measure small variations (Kaufmann, 1984) it was possible to trace evidence for diffusion of Cl in nature. Eggenkamp (1994) calculated, using equations described by Duursma and Hoede (1967) that chloride could fractionate considerably in diffusion processes. Several studies are known (Desaulniers et al., 1986; Beekman et al., 1992; Eggenkamp et al., 1994; Groen et al., 2000; Hesse et al., 2000) that show that certain natural Cl isotope distributions can be fitted to hydrogeologic models that include a mass dependence of the chloride diffusion coefficient. These studies show that the combination of Cl concentration and Cl isotope variations is very powerful in solving complex historical fluid transport mechanisms. Richter et al. (2006) measured diffusion of Cl in relation to diffusion of  $\text{Mg}^{2+}$  and  $\text{Li}^+$ . Their data seem to have substantial scatter, which is not yet understood, but their  $D_{^{35}\text{Cl}}/D_{^{37}\text{Cl}}$  of  $1.00143 \pm 0.00040$  ( $1\sigma$ ) is clearly in line with values from other experimental determinations of diffusion fractionation.

On the contrary, very few studies are known describing isotope effects of bromine. There are two studies in which the fractionation of Br isotopes was determined, in liquid  $\text{PbBr}_2$  (Cameron et al., 1956), and  $\text{ZnBr}_2$  (Lundén and Lodding, 1960). It was found that the fractionation of Br in liquid  $\text{PbBr}_2$  is approximately  $1/3$  that of Cl in liquid  $\text{PbCl}_2$ . No measurable natural variation was found in studies from

this era (e.g. Cameron and Lippert, 1955). Recently several studies have been published describing analytical techniques to measure Br isotopes (Eggenkamp and Coleman, 1997, 2000; Shouakar-Stash et al., 2005; Sylva et al., 2007). These studies also present Br isotope variations in natural samples which are not only much larger than the analytical error, but also show characteristics which are very different from those of chlorine, indicating the importance of looking into the isotope geochemistry of bromine.

In this paper, we describe the first attempt to measure isotope fractionation of both Cl and Br in a laboratory environment that is comparable to the situation in nature. So, pure concentration derived diffusion has been applied to a chloride or bromide solution, captured in a gel, from which after a period of diffusion the Cl or Br isotope composition is determined. The diffusion experiments are similar in concept to those developed to measure the diffusion of actinides in clay (Schreiner et al., 1982), but in our case we measured diffusion of Cl and Br in a polyacrylamide gel. In total, 10 experiments were performed, seven with  $\text{Cl}^-$  as the diffusing anion, and three with  $\text{Br}^-$ . Experiments were undertaken at different temperatures and concentrations to be able to assess their effects on diffusion and fractionation of Cl and Br.

## 2. EXPERIMENTAL

### 2.1. Diffusion experiments

The diffusion experiments are carried out in a polyacrylamide gel (Laemmli, 1970; Davison et al., 1994). The gel is prepared by mixing 14 ml distilled water, 6 ml Acrylaide<sup>®</sup> cross-linker (FMC Bioproducts, 2% aqueous solution) and 20 ml 30% acrylamide solution (Boehringer Mannheim). 400  $\mu\text{L}$  of a 3%  $\text{K}_2\text{S}_2\text{O}_8$  solution (BDH, AnalaR grade) and 40  $\mu\text{L}$  TEMED (N,N,N',N'-tetramethylethylenediamine, Sigma Chemical Co.) were added to initiate the polymerization. A borosilicate glass tube (inner diameter 16 mm) was filled with 40  $\text{cm}^3$  liquid gel (15% acrylamide). A small amount of Cl or Br was added to some of these gels to facilitate a measurable, low quantity of Cl or Br to be able to measure  $\delta^{37}\text{Cl}$  and  $\delta^{81}\text{Br}$  even in the samples with the lowest concentrations. After setting, generally in two to 3 h, 40  $\text{cm}^3$  of the same type of gel, into which NaCl or NaBr was dissolved, was added to the tube. It was not known beforehand what effect the addition of  $\text{Cl}^-$  or  $\text{Br}^-$  would have on the setting of the gel, but we observed that it sets even faster in this case. The tube was placed in a horizontal position and diffusion of  $\text{Cl}^-$  or  $\text{Br}^-$  then was allowed for a time estimated to produce a clear diffusion profile. A total of seven experiments with  $\text{Cl}^-$ , and three with  $\text{Br}^-$ , were performed, with different initial concentrations and at different temperatures. At the end of each experiment the glass was broken and removed from the gel. The gel was sliced into 1–2 cm slices with a scalpel, and put in 30 mL HDPE bottles to which 18–20 mL distilled de-ionized water was added. The gel was equilibrated with the water, so that the Cl or Br concentration became equal in both gel and water (Krom et al., 1994). We waited always at least one week to be sure that equilibrium between water and gel was reached, in fact more than twice the time suggested by Krom et al. (1994). The Cl or Br

concentration of the solution was determined by colorimetry and data were recalculated to the original concentration in the gel. Prior to isotope analyses  $\text{Cl}^-$  or  $\text{Br}^-$  in solution was converted to  $\text{AgCl}$  or  $\text{AgBr}$  (Taylor and Grimsrud, 1969; Willey and Taylor, 1979), and subsequently converted to  $\text{CH}_3\text{Cl}$  or  $\text{CH}_3\text{Br}$  on which Cl or Br isotope data were measured (Long et al., 1993; Eggenkamp, 1994; Eggenkamp and Coleman, 2000). The analytical precision for  $\delta^{37}\text{Cl}$  and  $\delta^{81}\text{Br}$  measurements for this procedure is normally 0.1‰ or better (see e.g. Long et al., 1993; Eggenkamp, 1994).

## 2.2. Diffusion model

The model used to describe the results of the experiments is a simple one dimensional diffusion model that allows us to calculate concentration and isotope composition of the samples. Diffusion, according to Fick's second law (Fick, 1855) is defined as:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (1)$$

The solution, for  $c$  (concentration) as a function of  $x$  (distance) and  $t$  (time) for a two dimensional system of infinite length (Crank, 1975) is:

$$c(x, t) = \frac{c_0}{2} \operatorname{erfc} \frac{x}{2\sqrt{Dt}} \quad (2)$$

$D$  is the diffusion coefficient,  $c_0$  is the initial concentration at the high-concentration side,  $x$  is the distance from the gel-gel interface,  $t$  is the time since the beginning of the experiment and  $\operatorname{erfc}(z)$  is the complementary error function, which is defined as (Duursma and Hoede, 1967):

$$\operatorname{erfc}(z) = \frac{2}{\sqrt{\pi}} \int_z^\infty e^{-y^2} dy \quad (3)$$

## 2.3. Notation of isotope data

Isotope variations are reported as  $\delta^{37}\text{Cl}$  and  $\delta^{81}\text{Br}$  values, indicating the per mil (‰) variation of the ratio of the isotope of interest, relative to that ratio in an international standard material, e.g.

$$\delta^{37}\text{Cl} = \left( \frac{(^{37}\text{Cl}/^{35}\text{Cl})_{\text{sample}}}{(^{37}\text{Cl}/^{35}\text{Cl})_{\text{standard}}} - 1 \right) * 1000 \quad (4)$$

A comparable definition for Br can be produced, defining  $\delta^{81}\text{Br}$  from the  $^{81}\text{Br}/^{79}\text{Br}$  ratio. The internationally accepted standard for both Cl and Br is seawater (Standard Mean Ocean Chloride, SMOC (Kaufmann, 1984; Long et al., 1993; Godon et al., 2004), and Standard Mean Ocean Bromide, SMOB (Eggenkamp and Coleman, 2000; Shoukar-Stash et al., 2005, 2007).

$\delta^{37}\text{Cl}$  and  $\delta^{81}\text{Br}$  values in the diffusion models are calculated by computing the concentration for both the light and the heavy isotope and then calculating  $\delta^{37}\text{Cl}$  or  $\delta^{81}\text{Br}$  according to Eq. (4).

## 3. RESULTS

All experiments showed similar characteristics. These are shown in Fig. 1. The measured concentrations (individ-

ual symbols in the figures to the left) as a function of the length of the glass tubing in which the experiment was done, follow the modeled concentrations (lines in the figures on the left) generally very well. It is also shown that the measured isotopic data (individual symbols in the figures to the right) agree well with the modeled isotopic characteristics for the same experiment (lines in the figures on the right). The  $\text{Cl}^-$  or  $\text{Br}^-$  concentrations in the experiments were determined for each slice of gel, but the isotopic composition could only be determined if sufficient  $\text{Cl}^-$  or  $\text{Br}^-$  was present. Due to the fact that a minimum amount of 20  $\mu\text{mol}$  of  $\text{Cl}^-$  or  $\text{Br}^-$  is necessary to measure the isotopic composition, it was only possible to measure those samples which had at least a  $\text{Cl}^-$  or  $\text{Br}^-$  concentration of approximately 1000 ppm. It is clear from Fig. 1 that a much larger isotope variation appears in the side to which the diffusing substance is moving. The reason for this effect is that the relative influence of the faster moving light isotope is much larger if the concentration is low, compared with when the concentration is high (see e.g. Eggenkamp, 1994; Richter et al., 1999). In experiments with a measurable amount of Cl or Br in the low concentration end it is observed that  $\delta^{37}\text{Cl}$  or  $\delta^{81}\text{Br}$  returns to the original value towards the end of the diffusion tube. This happens because the diffusion front, containing higher  $^{35}\text{Cl}$  contents as this isotope is lighter and faster than  $^{37}\text{Cl}$ , has not yet reached that part of the experiment, so that the value is still approaching the original value.

The modeled diffusion profiles were calculated using the equations described above, and are fitted to the measured data (by minimizing the sum of the least square differences) using the Solver™ add-in of the Microsoft® Excel® spreadsheet programme. The following variables were used to match them as closely as possible: low-end concentration, high-end concentration, diffusion coefficient, ratio between diffusion coefficients of the light and the heavy isotope, the offset from the center and the initial  $\delta^{37}\text{Cl}$  or  $\delta^{81}\text{Br}$  value. The diffusion time and the length of the two parts of the column were set fixed, as these were exactly known. The concentration values were constrained to be within the range of the measured value and its uncertainty bounds. The values calculated for all variables are in Table 1. Data in Table 1 also incorporate calculated tortuosities as will be discussed later.

## 4. DISCUSSION

### 4.1. Diffusion coefficient

The diffusion coefficient of electrolytes in a solid, porous medium is dependent on several parameters such as the concentration, the temperature and the structure of the medium. The set up of our experiments, adding NaCl or NaBr to a gel, imposes diffusion of the chloride or bromide ion to be coupled with that of the sodium ion. The diffusion of the chloride ion at infinite dilution can then be calculated as:

$$D_{12}^0 = \frac{(|Z_1| + |Z_2|)D_1^0 D_2^0}{|Z_1|D_1^0 + |Z_2|D_2^0} \quad (5)$$

In this equation  $D_{12}^0$  is the salt diffusion coefficient of  $\text{Na}^+$  and  $\text{Cl}^-$  or  $\text{Br}^-$ ,  $Z_1$  and  $Z_2$  the charge of  $\text{Na}^+$  and

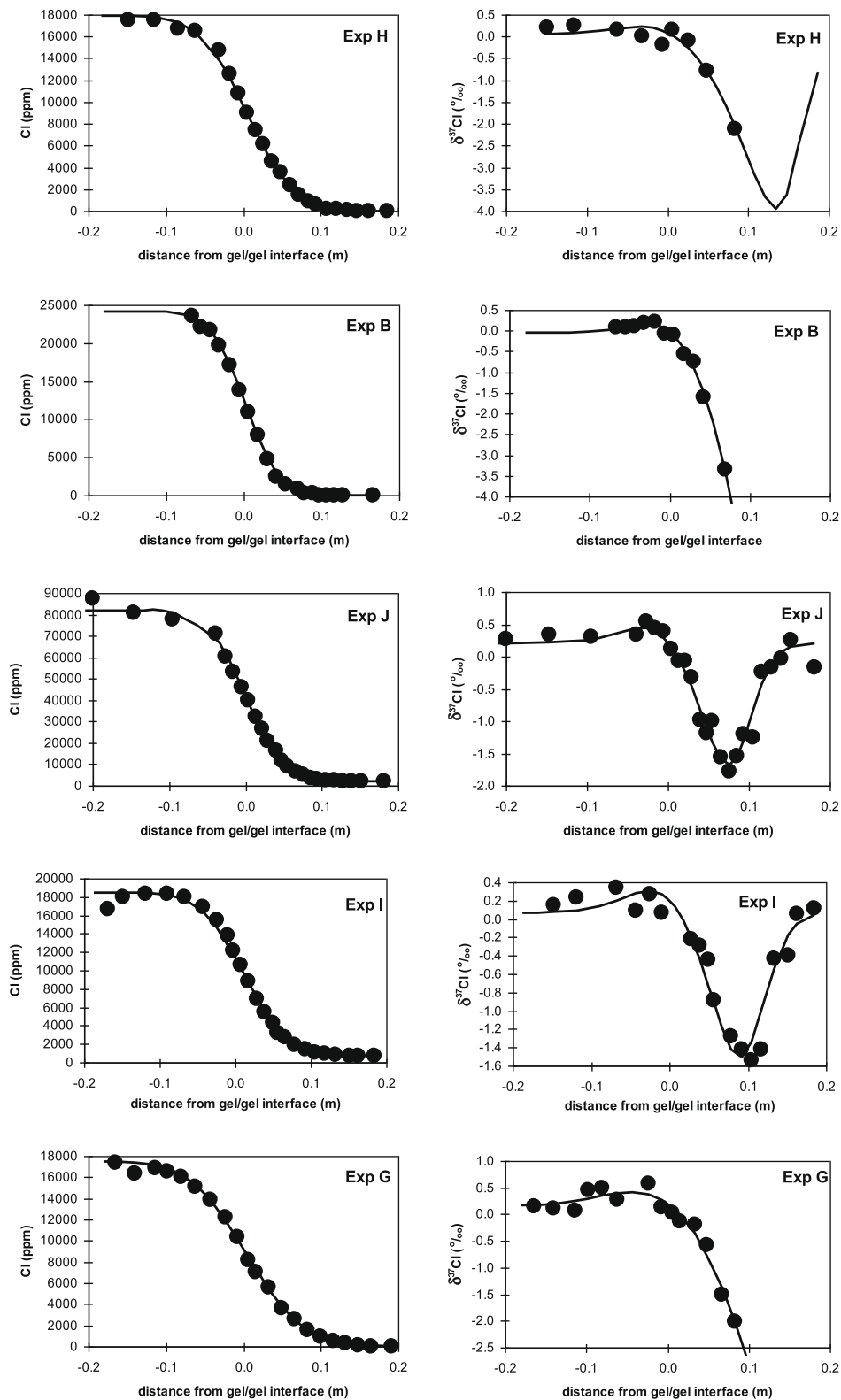


Fig. 1. Concentration and isotope data for all diffusion experiments. Experiments are sorted in the same order as in Table 1. Refer to this Table for information on experimental conditions and end-member concentrations. Measured values are shown as solid circles and the models as continuous lines. To the left are the measured and modelled Cl and Br concentrations, to the right the measured and modelled  $\delta^{37}\text{Cl}$  and  $\delta^{81}\text{Br}$  data. Samples that could not be measured are not represented in these figures.

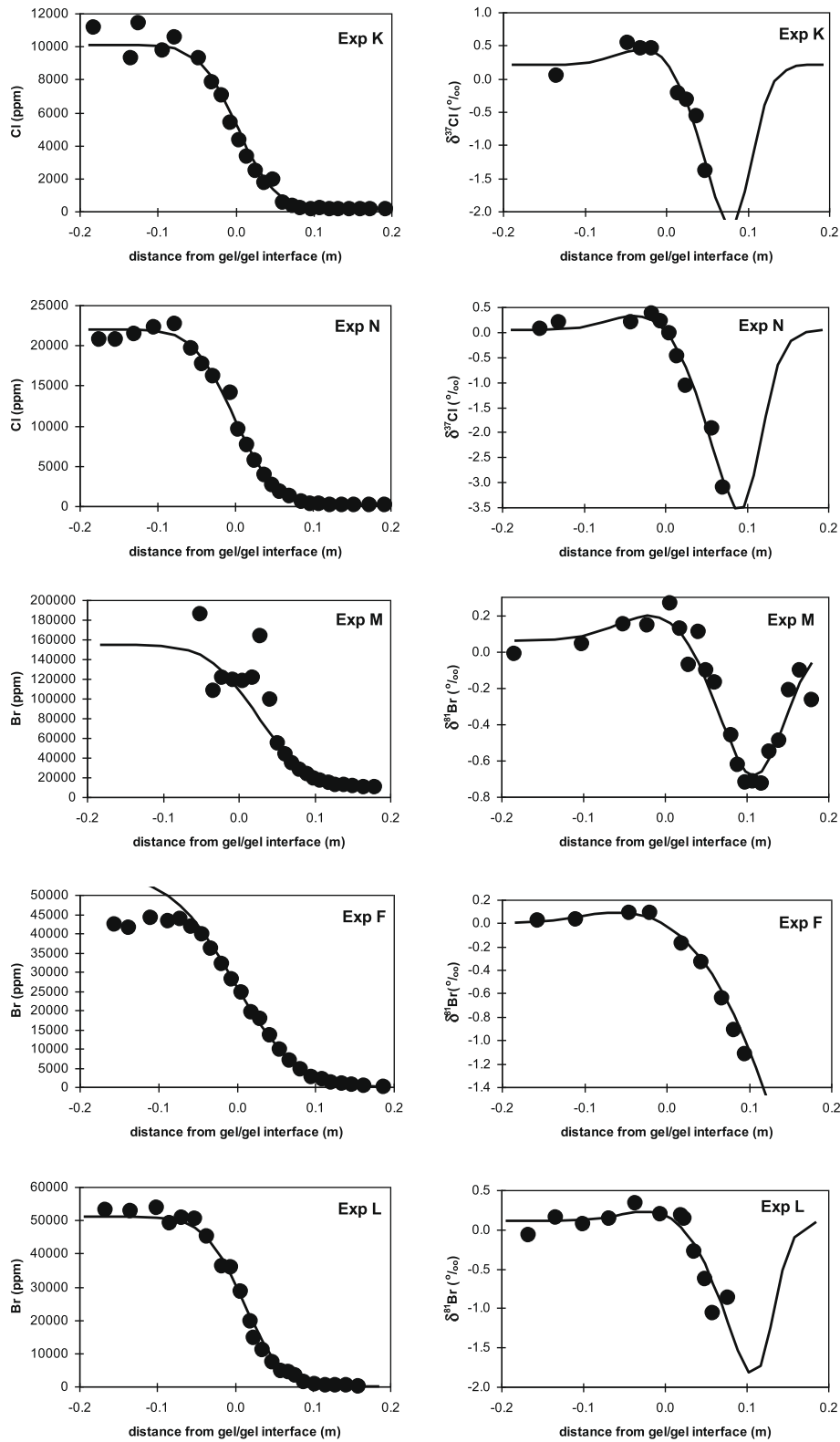


Fig 1. (continued)

$\text{Cl}^-$  or  $\text{Br}^-$  and  $D_1^0$  and  $D_2^0$  are the self-diffusion coefficients of  $\text{Na}^+$  and  $\text{Cl}^-$  or  $\text{Br}^-$  (see Li and Gregory, 1974).

The self-diffusion of ions in water at different temperatures can be calculated using the Stokes–Einstein relation, as shown by Simpson and Carr (1958):

Table 1

Parameters from the diffusion experiments. Ion, time and temperatures were known, the other parameters were calculated using the Solver™ plug-in from the Microsoft® Excel® spreadsheet. \* $D_L/D_H$  means  $D_{35Cl}/D_{37Cl}$  for chlorine,  $D_{79Br}/D_{81Br}$  for bromine. The analytical uncertainty in the concentration measurements is 8.5%. The tortuosity is calculated from the experimentally determined diffusion coefficient and the salt diffusion coefficient as defined in Li and Gregory (1974).

Experiment	Ion	Time (days)	Temperature (°C)	Concentration low half (ppm)	Concentration high half (ppm)	Diffusion coefficient ( $m^2 s^{-1}$ )	Fractionation ( $D_L/D_H$ )*	Tortuosity
H	Cl <sup>-</sup>	18.15	2	18	18,000	$0.74 \pm 0.06 * 10^{-9}$	$1.00128 \pm 0.00017$	$1.07 \pm 0.04$
B	Cl <sup>-</sup>	6.74	21	0	24,000	$1.05 \pm 0.10 * 10^{-9}$	$1.00155 \pm 0.00009$	$1.18 \pm 0.06$
J	Cl <sup>-</sup>	8.96	21	2100	82,000	$1.09 \pm 0.03 * 10^{-9}$	$1.00167 \pm 0.00016$	$1.16 \pm 0.02$
I	Cl <sup>-</sup>	10.82	21	700	18,000	$1.13 \pm 0.05 * 10^{-9}$	$1.00166 \pm 0.00018$	$1.14 \pm 0.03$
G	Cl <sup>-</sup>	15.04	21	17	18,000	$1.29 \pm 0.06 * 10^{-9}$	$1.00177 \pm 0.00014$	$1.07 \pm 0.02$
K	Cl <sup>-</sup>	3.23	54	140	10,000	$2.67 \pm 0.41 * 10^{-9}$	$1.00165 \pm 0.00014$	$0.98 \pm 0.08$
N	Cl <sup>-</sup>	2.73	80	150	22,000	$3.51 \pm 0.60 * 10^{-9}$	$1.00192 \pm 0.00015$	$0.99 \pm 0.09$
M	Br <sup>-</sup>	17.10	2	9000	160,000	$0.94 \pm 0.30 * 10^{-9}$	$1.00098 \pm 0.00009$	$0.96 \pm 0.16$
F	Br <sup>-</sup>	15.14	21	18	50,000	$1.53 \pm 0.17 * 10^{-9}$	$1.00064 \pm 0.00013$	$0.98 \pm 0.06$
L	Br <sup>-</sup>	2.70	80	130	51,000	$3.40 \pm 0.43 * 10^{-9}$	$1.00078 \pm 0.00018$	$1.00 \pm 0.06$

$$\left(\frac{D_j^0 * \eta^0}{T}\right)_{T_1} = \left(\frac{D_j^0 * \eta^0}{T}\right)_{T_2} \quad (6)$$

where  $\eta$  is the viscosity of water. The temperature dependence of the viscosity of water is well known (Dorsey, 1940). We assume that this relationship also counts for salt diffusion and taking self-diffusion coefficients at 25 °C from Li and Gregory (1974), and using (6) we could calculate the salt-diffusion coefficients of sodium chloride and sodium bromide at the temperatures of the experiments (Table 2).

Diffusion in porous media is normally slower than as calculated above. This is due to the effect of tortuosity ( $\tau$ ) which indicates the longer path length an ion travels in these media relative to the total length of the medium. Tortuosity and diffusion are related according to the equation (Ullman and Aller, 1982):

$$D_i^a = D_i^0 / \tau^2 \quad (7)$$

In this equation,  $D^a$  is the apparent diffusion coefficient in the gel. The tortuosities as calculated from the measured, effective diffusion coefficients and the calculated self-diffusion coefficients are incorporated in Table 1.

The diffusion coefficient is highly dependent on the temperature. We find in our experiments that the apparent diffusion coefficient of chloride increases from  $0.74 * 10^{-9} m^2 s^{-1}$  at 2 °C to  $3.51 * 10^{-9} m^2 s^{-1}$  at 80 °C. The diffusion coefficient of bromide increased from  $0.94 * 10^{-9} m^2 s^{-1}$  at 2 °C to  $3.40 * 10^{-9} m^2 s^{-1}$  at 80 °C

Table 2

Calculated salt diffusion coefficients for Na<sup>+</sup>Cl<sup>-</sup> and Na<sup>+</sup>Br<sup>-</sup> in water. Calculated from self-diffusion coefficients in Li and Gregory (1974).

Temperature (°C)	Cl <sup>-</sup>	Br <sup>-</sup>
	$D_0$ in $m^2 s^{-1}$	$D_0$ in $m^2 s^{-1}$
2	$0.84 * 10^{-9}$	$0.86 * 10^{-9}$
21	$1.47 * 10^{-9}$	$1.48 * 10^{-9}$
54	$2.57 * 10^{-9}$	$2.56 * 10^{-9}$
80	$3.43 * 10^{-9}$	$3.41 * 10^{-9}$

not showing any significant difference from chloride (Fig. 2).

When looking at the tortuosities it is striking that all values for Br<sup>-</sup> and perhaps also for Cl<sup>-</sup> (with the exception of experiments at 21 °C) have a tortuosity which is not significantly different from 1.0. Each of the four experiments with Cl<sup>-</sup> at 21 °C has a tortuosity which is significantly higher than 1.0, but which decreases with increasing diffusion time, and also tends to a value of 1.0 at the longest diffusion time. This could indicate that the cross-links in the polyacrylamide gel do not have a large influence on the tortuosity, and that the structure of the gel approaches that of water very closely.

Based upon the combination of data obtained from natural diffusion profiles (Desaulniers et al., 1986; Beekman et al., 1992; Eggenkamp et al., 1994) we expected to find a relationship between diffusion coefficient and concentration. However, in this dataset we did not find, or at least did not recognize, such relationship.

## 4.2. Isotope fractionation

Isotope fractionation due to diffusion is a kinetic process, caused by the difference in mass between the diffusing

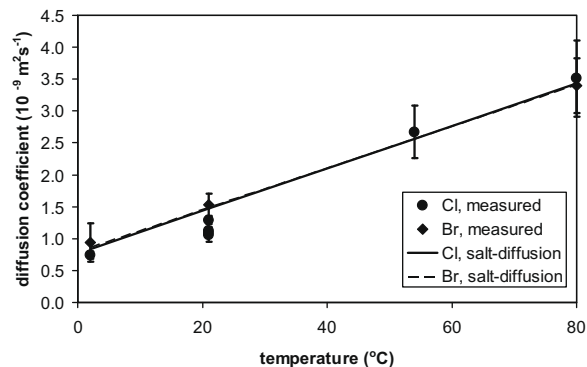


Fig. 2. Relationship between measured diffusion coefficient and temperature (symbols, error bars represent 1 $\sigma$  errors) and the salt-diffusion determined from data in Li and Gregory (1974, lines).

species, and as such of the speed of the isotopes of interest. In the case of Cl the moving species are  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ , or, more correctly, these isotopes plus their respective hydration spheres. Theoretical and molecular dynamics simulation studies in Lennard–Jones fluids (Bhattacharyya and Bagchi, 2000; Ali et al., 2002; Willeke, 2003), molten MgO (Tsuchiyama et al., 1994) and liquid water (Bourg and Sposito, 2007, 2008) can be modeled with an inverse power-law relation:

$$\alpha = (M_{\text{H}}/M_{\text{L}})^{\beta} \quad (8)$$

with  $0 \leq \beta < 0.5$ . In Eq. (8),  $\alpha$  is the fractionation factor defined as the ratio of the diffusion coefficients of the light and heavy isotope ( $D_{\text{L}}/D_{\text{H}}$ ) and  $M_{\text{H}}$  and  $M_{\text{L}}$  are the masses of the heavy and light isotope, respectively. In the case of elastic collisions, such as in ideal gases the factor  $\beta$  is 0.5 (Graham's Law). As collisions in solution are non-elastic the factor  $\beta$  will be lower and the diffusion fractionation in solutions will be lower than would be predicted by Graham's Law. Deviations from Graham's law were generally explained by assuming a larger moving species. As it is assumed the ion is moving with its hydration shell, there is need to know the hydration number of ions in water. This however is not very well known, and opinions in the literature differ. Our measured variations in the isotope fractionation due to diffusion are not very large. Measured ratios are between 1.00128 and 1.00192 ( $D_{^{35}\text{Cl}}/D_{^{37}\text{Cl}}$ ), with errors that can be as large as 0.00018. The reason for these small differences is probably due not only to non-elastic collisions and the number of water molecules in the hydration shell, but also to the structure of that shell. Mancinelli et al. (2007) used neutron diffraction to demonstrate that the hydration shell hardly varied significantly with increase in concentration, from  $6.1 \pm 1.1$  water molecules in a 1:83 NaCl solution down to  $5.6 \pm 1.6$  in a 1:19 NaCl solution. However, and more significantly, they showed that the chloride ion and its hydration shell were effectively incorporated into the water structure, which would act as a considerable impedance to its mobility and produce the observed reduction in the effect of the mass differences of the ions. This may be the reason that the observed diffusion fractionation is much lower than would be predicted based upon Graham's Law with a hydration number of approximately 6. Recent research, however, based upon calculations published by Impey et al. (1983), showed that deviations in the factor  $\beta$  are dependent on the strength of solute–solvent interaction, defined as the average residence time of water molecules in the first solvation shell of ions (Bourg and Sposito, 2007).

It would normally be expected that the change in temperature would have an influence on the fractionation due to diffusion. The reason for this is that at higher temperatures either the hydration shell around the diffusing ions contains fewer water molecules, so that at higher temperatures the low/high mass ion ratio is smaller, or that the average residence time of water molecules in the first solvation shell is shorter, and thus the difference in the diffusion coefficient would be larger. This effect is not clearly seen in our experiments. For bromide we find a higher fractionation in the experiment at 2 °C, while for chloride we seem

to be able to show this effect, but only in the coldest experiment, with a lower fractionation, and the warmest with a higher fractionation. The experiments at 21 and 54 °C do not show variations outside the analytical error. If this minor dependence on temperature were to be proven, then it is more likely to reflect changes in the structure of the water and hydrated ion system, rather than just in the hydration shell. This may be due to a comparable effect as described above.

The fact that the isotopic fractionation factors do not depend on the normally expected factors is a great advantage in using this approach. When applying the isotopic data just as we have them, even the influence of temperature seems to be only minor, while this is the only parameter that shows a slight positive effect over the whole measured range.

It is important to note that the experimental data agree very well with the theoretical data calculated by Eggenkamp (1994) based upon formulas presented by Duursma and Hoede (1967). The experimental results could be described near perfectly using the same equations used to produce the theoretical diffusion and isotopic profiles. Thus in relatively simple systems diffusion of conservative ions behaves exactly as expected.

#### 4.3. Comparison to natural data and other experimental data

The diffusion coefficient in combination with the fractionation due to diffusion has only been determined rarely in natural systems. Table 3 shows reported data from four publications from the period 1986 to 2000. All situations where they have been determined consist of systems where more saline pore water diffuses into less saline pore water, in environments where salinity of pore water has varied over the past several 100s to 1000s of years. In these systems, where the past salinity history is fairly well known it was possible to determine both the diffusion coefficient and fractionation. A minor problem is that in most natural observations the temperature is not known with much precision, although a general approximation can normally be made. On the other hand, in each of the observations, considering the duration of the processes, it is just possible that the temperature may have varied substantially, and the observed data will reflect this as an average effect. However, since the influence of temperature on the isotope fractionation is quite limited, in natural systems this influence will normally fall within the modeling errors.

The diffusion effects in these observations were not always determined directly, but based upon earlier measurements (Desaulniers et al., 1986) or theoretical constraints (Eggenkamp et al., 1994). In all cases, they were based ultimately upon data from Li and Gregory (1974), applied to the local environment. Because of the complex geology, it often was not possible to measure the diffusion constant directly (e.g. because of advective groundwater movement). Based upon the higher temperature in the environment they studied Eggenkamp et al. (1994) determined a much higher diffusion coefficient than Desaulniers et al. (1986) or Beekman et al. (1992). Groen et al. (2000) also had samples from a tropical environment, but determined

Table 3

Diffusion coefficient and isotope fractionation of earlier observations.  $D_{35\text{Cl}}/D_{37\text{Cl}}$  is the ratio of the diffusion coefficients of  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ . Temperatures of diffusion were estimated from sample locations. Statistical errors are not mentioned in these papers.

Reference and country	Estimated (average) temperature (°C)	Diffusion coefficient ( $10^{-9} \text{ m}^2 \text{ s}^{-1}$ )	Isotope fractionation ( $D_{35\text{Cl}}/D_{37\text{Cl}}$ )
Desaulniers et al. (1986), Canada	5	0.60	1.0012
Beekman et al. (1992), Netherlands	10	0.84	1.0023
Eggenkamp et al. (1994), Indonesia	25	1.31	1.0023
Groen et al. (2000), Suriname	25	0.70	1.0027

the diffusion coefficient directly and as a fairly low value. In spite of this, the diffusion coefficients as determined in our experiments agree well (within a factor of 2) with the naturally obtained data, which indicates that natural and theoretical diffusion of chloride are in good agreement and that the theoretical calculations describe natural diffusion very well.

We find that most natural observations (with the exception of Desaulniers et al., 1986) show isotopic fractionations larger than those we measured, and also larger than others determined experimentally (Madorsky and Strauss, 1948; Konstantinov and Bakulin, 1965; Richter et al., 2006). Most experimental determinations give fractionation factors of, on average, 1.0015, with values from 1.0009 to 1.0019 (only the most extreme measurement in Madorsky and Strauss (1948) gave a higher value of 1.0021). Since most experimental data agree with each other, the anomalously higher measurements in natural systems need to be explained. The reason may be that the scatter of measurements is so large that the error is very large. Beekman et al. (1992) show that both Cl concentration and isotope composition can be modeled very well in a complex system. Groen et al. (2000) on the other hand, show data for which the isotope profile generally does not follow the modeled isotope data. Systems described by Beekman et al. (1992) and Groen et al. (2000) both show a very complex history, with (potentially) changes in chloride concentrations in the water. In these systems, often the chloride concentration was modeled first, and the isotopic modeling was done afterwards. This may have resulted in the larger than expected isotope fractionation uncertainties relative to experimental data, which do not show such complex behavior. It is therefore always recommended to model the Cl (or Br) concentration in the same run that models the isotope composition as done by Beekman et al. (1992).

It is also possible to explain fractionation factors which are too high if the lower concentration end-member has been given an estimated  $\delta^{37}\text{Cl}$  (or  $\delta^{81}\text{Br}$ ) value which is too high. In this case the isotope fractionation is assigned a value which is too high to explain the large isotope variation in a series of observations. The estimate for a too high lower end-member concentration can occur when, for example, some chloride has mixed with it after diffusion has started, obscuring the original low chloride concentration. This certainly is something to take into account when observing the low concentration end-member in a

system where the chloride isotope fractionation is to be determined.

## 5. CONCLUSIONS

We have determined the isotope fractionation for chloride and bromide during diffusion in a system that approaches natural diffusion closely. We attempted to determine different controls on diffusion, of which concentration and time were the most important. It was found that the isotope fractionation lacks sensitivity to almost all variables, except (perhaps) temperature. This makes it relatively easy to apply to geological systems where temperature and its history of variation can be determined. Isotopic fractionation for chlorine (defined as  $D_{35\text{Cl}}/D_{37\text{Cl}}$ ) is between 1.00128 and 1.00192. Using the same assumptions as for Cl, the isotopic fractionation of Br due to diffusion (defined as  $D_{79\text{Br}}/D_{81\text{Br}}$ ) is between 1.00064 and 1.00098. Our measurements of chloride isotope fraction are in good agreement with virtually all earlier experimental determinations; however, they do not conform with most natural observations interpreted as fractionation due to diffusion. Except for Desaulniers et al. (1986),  $D_{35\text{Cl}}/D_{37\text{Cl}}$  inferred from natural observations, ranged from 1.0023 to 1.0027. Fractionation factors determined in these environments are probably too high because the isotope composition could not be modeled properly, or because the estimated chloride composition of the lower concentration end-member was too high, resulting in a high fractionation factor needed to explain the large variation in Cl isotope composition.

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