

# Cl/Br and $\delta^{37}\text{Cl}$ evolution in seawater expelled during the compaction of MX-80 smectite

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**Abstract.** During a high pressure (up to 150 MPa) high temperature (up to 150°C) compaction experiment of MX-80 smectite equilibrated with ocean water, it was found that the Cl and Br concentrations in the expelled solution are progressively being decreased while simultaneously being increased in the compacted clay. This significant retention of Cl and Br in the pore water of the compacted clay is indicative of ultrafiltration by the clay. Despite the size difference between the two anions no significant chemical partitioning between Cl and Br is observed in the expelled water. The  $\delta^{37}\text{Cl}$  value of the expelled water shows a sharp decrease (from -0.1 ‰ down to -0.5‰) during the first steps of compactions (between 45MPa – 21°C and 65MPa – 30°C) and then remains stable until 125MPa – 120°C. The largest impact on anion and stable isotope composition is seen during the earlier phases of the compaction. It is supposed that the surface chemistry of the clay in combination with decreasing porosity result in re-equilibration of compressed and overlapping diffuse double layers which in part, drive the anion and  $\delta^{37}\text{Cl}$  evolution.

## 1 Introduction

The provenance and transport mechanisms of water in clay rich rocks span across many fields of interest, including the origin of the fresh formation waters [1]. However, the sampling of pore water and understanding of its composition remains a challenge due to the small volumes that are extractable as well as the complexity of the interactions between water and clays. The monovalent anions of chloride and bromide are good natural tracers of the origin and evolution of surface- and ground water. The small size of these ions, ~0.3-0.35 nm [2, 3], and its hydrophilic nature allow them to dissolve easily and behave conservatively (mostly unreactive) once dissolved [4, 5]. These anions, therefore, display a considerably steady concentration in its respective reservoirs since the early Proterozoic [6]. The two stable isotopes that exist for both chlorine ( $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ ) and bromine ( $^{79}\text{Br}$  and  $^{81}\text{Br}$ ) are fractionated by natural and anthropogenic processes during their cycling

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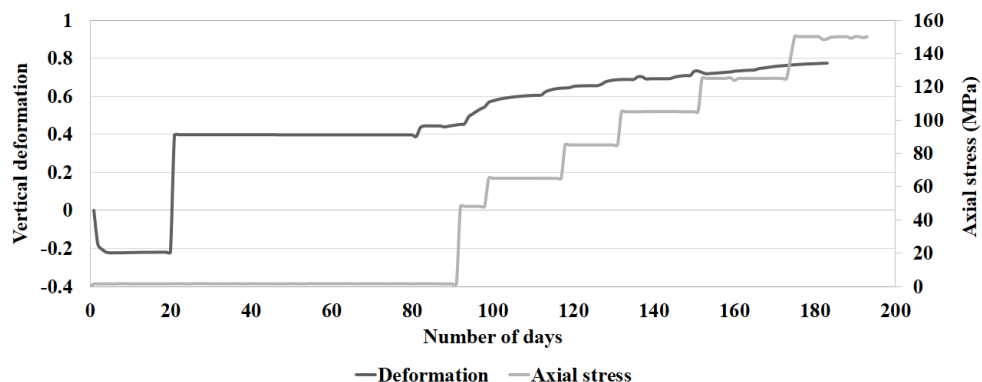
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between reservoirs. The Cl/Br ratio has been widely used to categorise surface- and ground waters while the Cl and Br isotopic compositions are useful to follow subsurface processes that are understood to impact the waters composition. Of particular interest is the observed decrease in concentrations of Cl and Br when groundwater flows through fine grained clay rich layers [7]. This slowing of solutes compared to fluid flow is known as ultrafiltration. Dissolved constituents in pore water of clay rich layers balance the negatively charged surfaces of clay minerals either in interlayer water, bound water constituting the diffuse double layer (DDL), or free (mobile) water. Smaller cations are prominent in interlayer and bound water while larger anions dominate the free water fraction. However, chlorine and bromine form sufficiently strong associations with cations to occur as neutral or positively charged ion pairs or clusters in the DDL [7] as have been quantified by molecular dynamics simulations [8-10]. The thickness of the diffuse double layer is a response to both the surface charge distribution and the ionic strength of the solution as defined in the Debye length [11, 12]. Compacting low porosity clay rich rocks could cause overlapping of DDL's which results in size specific anion exclusion. According to [13], chlorine preferentially concentrates in the bound water while bromine preferentially concentrates in the free water fraction as Cl associates with cations preferentially compared to Br [14]. In order to follow the effect of compaction on the fluid chemistry of water expelled from clay rich rocks, a high pressure squeezing experiment has been developed to extract pore water volumes large enough to study chlorine stable isotope fractionation in parallel with the Cl and Br evolution of the pore water during stepwise pressure and temperature increases.

## 2 Material and methods

A high pressure/high temperature oedometric type cell, 10 cm diameter and 10 cm height, was developed for this study. 400 g of MX-80 smectite [15] was compacted for 200 days following a series of pressure and temperature steps allowing time between each step to re-equilibrate to the new conditions. The cell is connected to two syringe pumps employed for generating pore fluid pressure, and a third for inducing the vertical stress. The use of two pumps simulates an 'open flow' system allowing for continuous collection of expelled fluid in one of the pumps. The expelled fluid was sampled as soon as the minimum volume required for analysis, has accumulated. For the duration of the experiment the pore pressure was maintained at 45 MPa while the vertical stress was increased from 45 MPa to 150 MPa (maximal effective stress: 105 MPa) by increments of  $\sim 25$  MPa and temperature increments of 30°C (Fig. 1). MX-80 smectite clay, was selected for its high negative charge and because it is widely studied and well characterized [15]. The experiment initiated by hydrating the MX-80 with filtered Atlantic Ocean water, in the cell. When the clay was fully hydrated, i.e. no more swelling occurred, ocean water was continuously flowed through the clay column for 60 days to establish chemical equilibrium. Despite the small number of samples that could be collected, the volumes collected were sufficient for ICP-MS analysis as well as a number of stable isotope measurements. Only Cl and Br contents and Cl isotope compositions are considered here.

For the extraction and measurement of chlorine, the protocol thoroughly described by [16] was closely followed to extract and capture Cl as  $\text{CH}_3\text{Cl}$ . The measurements were made on a dual inlet mass spectrometer (ThermoFisher DeltaPlus XP), configured specifically to allow precise measurements of  $\text{CH}_3\text{Cl}$ .

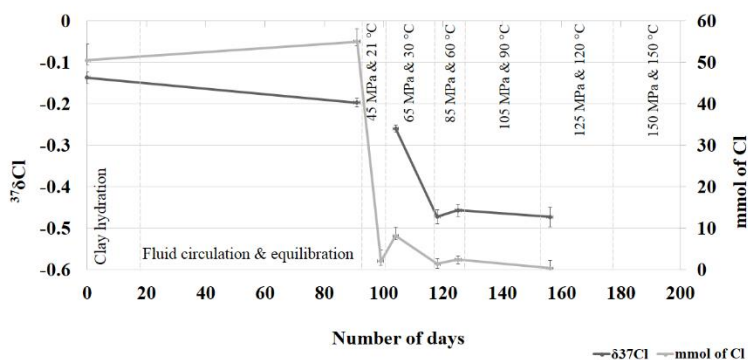


**Fig. 1:** Vertical deformation and axial stress as a function of time.

### 3 Results and discussion

The initial concentrations of Cl and Br in the ocean water used for the compaction experiment are 524 mmol/l and 0.88 mmol/l respectively, giving a molar Cl/Br value of 597, typical for pore water of coastal sediments [17]. The  $\delta^{37}\text{Cl}$  of the ocean water is -0.14 (very close to the Standard Mean Ocean Chlorine that has a  $\delta^{37}\text{Cl}$  of 0.00‰). When the ocean water is first cycled through the clay column under a minimum load of 1.5 MPa, to obtain equilibrium between the clay and ocean water, the Cl and Br concentrations of the fluid increases to 570 mmol/l and 0.97 mmol/l respectively. Increasing the compaction leads to a drastic changes of the expelled water composition (Table 1 and Fig. 2). However, to be relevant, the concentrations have to be treated in terms of mass balance. Table 1 gives, for Br and Cl, the concentrations of the expelled water and the calculated concentration of the water still trapped in the clay porosity. Two important results have to be highlighted. The first is the continuous increase of Cl and Br concentrations (up to 602 mmol/l for Cl and 1.03 mmol/l for Br) in the trapped water when the compaction increases. The second is the good correlation between Cl and Br concentrations in the water (Fig. 3) implying that, within the accuracy of the analysis, no significant chemical partitioning exists between Cl and Br.

Concerning Cl isotopes, after the equilibrium step the  $\delta^{37}\text{Cl}$  of the equilibrated ocean water has changed to -0.2 ‰ indicating that significant Cl isotope fractionation can occur without compaction. When compaction increases, the  $\delta^{37}\text{Cl}$  values become even more negative between day 104 and day 118, decreasing from -0.26 ‰ to -0.47 ‰ (Fig. 2). The sample collected on day 118 was sampled immediately after the load increase to 85 MPa/60 °C has been completed. This result shows that the response to the decrease in porosity is instantaneous to re-equilibrating the pore water to the new set of pressure and temperature conditions. Fig. 2 shows that the lower the concentration of Cl is in the water expelled from the cell, the lower the  $\delta^{37}\text{Cl}$  value. The mechanism of fractionation by diffusion in fluids (or in this case free water) is well explained by [16]. Due to, amongst other, their difference in size the lighter isotope  $^{35}\text{Cl}$  diffuses/moves more easily in and therefore will be preferentially expelled as compaction progresses, while the heavier isotope  $^{37}\text{Cl}$  is preferentially retained in the clay [18]. However the influence of temperature on diffusion not addressed here is also a key parameter that will be investigated in following experiments.

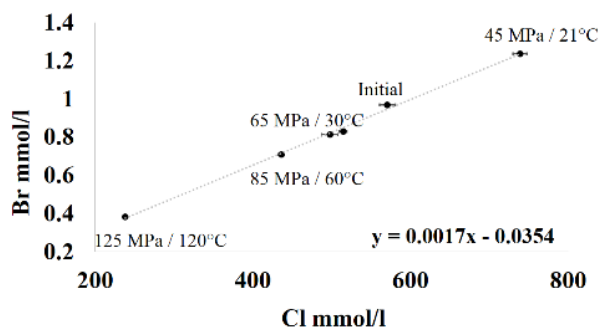


**Fig. 2.** Cl concentration and isotope composition measured in the expelled water for the compaction experiment. The steps and various conditions for temperature and axial stress for each are indicated. The pore pressure was kept constant at 45 MPa for all the compaction phases. For day 99, a reliable  $\delta^{37}\text{Cl}$  value could not be determined due to insufficient amount of recovered expelled water.

**Table 1:** Concentration mass balance for Cl and Br in expelled water and clay system.

Cl						
Day	Volume of sample / expelled water (ml)	Conc. in expelled water (mmol/l)	Amount in expelled water (mmol)	Volume remaining in clay (l)	Amount remaining in clay (mmol)	Conc. remaining in clay (mmol/l)
Initial pore fluid*	96.31	570.70	54.96			570.70
99	2.79	738.64	2.06	0.0935	52.90	565.68
104	16.44	497.79	8.18	0.0771	44.72	580.17
118	2.69	514.61	1.38	0.0744	43.33	582.54
125	5.52	436.26	2.41	0.0689	40.92	594.27
156	1.5	238.17	0.36	0.0674	40.57	602.20
Br						
Initial pore fluid*	96.31	0.97	0.0932			0.97
99	2.79	1.24	0.0034	0.09352	0.0898	0.96
104	16.44	0.81	0.0134	0.07707	0.0764	0.99
118	2.69	0.83	0.0022	0.07439	0.0742	1.00
125	5.52	0.71	0.0039	0.06886	0.0703	1.02
156	1.5	0.38	0.0006	0.06736	0.0697	1.03

\*Equilibrated with the clay.



**Fig. 3.** Br vs Cl concentration in the expelled pore water.

As mechanical compression starts, the porosity is drastically reduced and a large portion of free water is expelled. Compacting the clay particles results in decreasing the interlayer space and increasing the grain to grain contacts. This in turn reduces the clays external surface area and redistributes the surface charge. Consequently, the thickness of the DDL decreases. Overlapping of diffuse double layers can occur at pore constrictions as illustrated by [19]. The cation composition of the DDL's, as well as the associated counterbalancing anion composition, adjusts accordingly. It is explained by [14] that the result is that anions occurring in the DDL would be expelled from the DDL, adding to the increasing concentration of Cl and Br anions in the free pore water fraction remaining in the clay. Additionally, overlapping of the DDL's also results in increased tortuosity for anions therefore limiting or blocking their mobility. Mercury intrusion porosimetry on the post compaction clay disk found that it has a total porosity of 16.87 % of which 9.14 % is trapped porosity where anions could be blocked.

## 4 Conclusion

To conclude, after some initial equilibration, we see a general decrease of the Cl and Br concentrations in the water expelled from the compacted clay with no significant Cl/Br fractionation. The  $\delta^{37}\text{Cl}$  value becomes more and more negative as the Cl concentration decreases in the expelled water. The most significant fractionation of Cl isotopes occurs with the early stages of compaction. Cl isotopes fractionate as a result of the modification of both the clay mineral surface chemistry and the decreasing porosity, the heavier  $^{37}\text{Cl}$  isotope being preferentially retained in compacted clay column, either as bound water of the DDL or trapped as remaining pore water. Therefore, the origin of low-salinity waters associated with ultrafiltration in sedimentary basins may partly be explained by clay compaction.

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