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Modeling Cl^- concentration and $\delta^{37}Cl$ profiles in porewater across a 250m-thick indurated argillite at the Tournemire URL (France)

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Abstract

Dissolved chloride in argillite porewater has been studied as a natural analogue for radionuclides potentially released from radioactive waste disposal. The Tournemire URL intersects impervious and compacted argillite. A previously obtained chloride concentration profile of intact rock is symmetric with a maximum concentration of 0.6±0.1 g/L, compared to 19 g/L for the original connate seawater. Dissolved chloride shows high $\delta^{37}Cl$ values, ranging between +6 and +8‰ vs. SMOC. The modeled profile considers diffusive exchange between connate seawater and meteoric freshwater. Transport parameters were obtained by radial diffusion experiments. Numerical modeling was performed with the coupled reactive-transport code Hytec. Simulations suggest a diffusive-exchange time of 85±10 Ma for Cl, which correlates with a major erosional period. Simulated $\delta^{37}Cl$ values between 1.002 and 1.003 agree with observed porewater $\delta^{37}Cl$. This study strongly suggests that the dissolved chloride profile in the argillites results from diffusive exchange and indicates that unfractured argillites can provide good confinement.

Keywords: argillite; fracture groundwater; porewater; chloride; chlorine isotopes; diffusion; transport modelling; Tournemire URL.

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1. Introduction

Safety studies on High Level and Intermediate Level Long Lived radioactive wastes in deep geological formations include assessing the potential transfer of the most mobile radionuclides, such as ^{36}Cl, from the host rock to the biosphere. This requires developing conceptual models for calculating the flows of water and solute through geological formations. These models are mainly based on the study of natural tracers that indicate past and present transfers across a sedimentary pile. The tracers used are generally the most mobile, such as the halides Cl^- and Br^-. Since the 1990s, the Tournemire Underground Research Laboratory (URL) owned by the French Institute for Radiological Protection and Nuclear Safety (IRSN) has developed methods for the characterization of chloride in a compacted argillite ([1], [2] and [3]). The URL, located in the south of France (Fig. 1), crosses an over-consolidated argillite mainly composed of clay minerals (50%) dominated by illite (40%), with carbonates (10-40%) and silts (15%) [4]. The hydraulic conductivity of the intact rock was estimated to be between 10^{-14} and 10^{-15} m/s [4], which definitely classifies the formation as an aquitard. This argillaceous rock is cross-cut by subvertical water-saturated fractures with equivalent hydraulic conductivities on the order of 10^{-10} m/s. The study of dissolved chloride in the Toarcian/Domerian argillite porewater and its diffusive transport parameters were mainly discussed in two complementary PhD theses ([1] and [2]) performed on samples taken from the unfractured rock. The aqueous chloride concentrations (Fig. 2) were determined from either diffusion experiments on small cubic pieces of argillite (boreholes TN2 and TN3 [1]) or radial diffusion experiments on core samples (boreholes PH4 and PH5 [2]). The two sets of data were in good agreement.

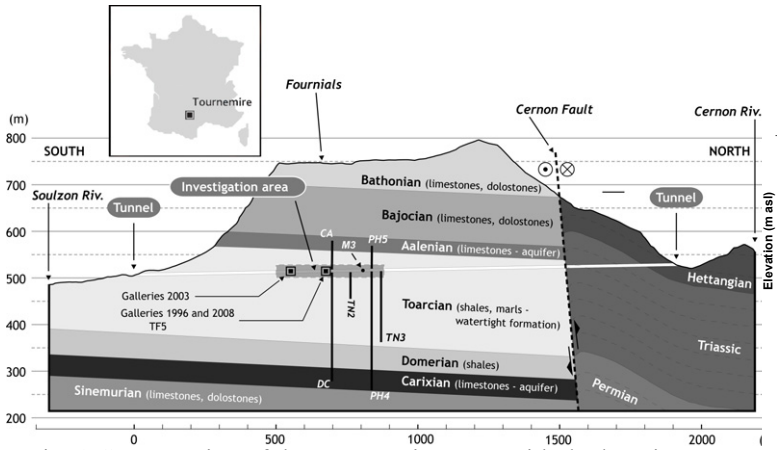

Fig. 1 Cross section of the Tournemire URL with the location of the boreholes dedicated to Cl concentration measurements.

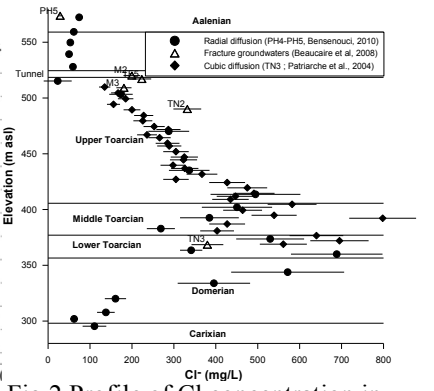

Fig.2 Profile of Cl concentration in porewater at the Tournemire URL.

The bell-shaped Cl profile (Fig 2) suggested binary mixing between saline water preserved in the argillite and freshwater contained in the surrounding aquifers. Their conceptual models proposed seawater as the unique source of chloride as no indication of brine occurrence has been found at Tournemire, so far. They also assumed that the salinity of argillite porewater started to decrease by diffusive mixing with meteoric water after it reached the argillite borders. It was initially proposed that this contact was initiated with the Pyrenean orogeny, some 53 Ma ago [1]. Next, it was suggested that the diffusive transport could have started much earlier - in the upper Cretaceous [2]. This period coincides with a major regression phase leading to the erosion of nearly 1000 m of sediment in the Cevennes area before a last and fast sea incursion, some 60 Ma ago [2]. If diffusion is responsible for the Cl transport, then it must also have induced a fractionation of its stable isotopes (^{37}Cl and ^{35}Cl) in agreement with the Cl transport time

deduced from modelling. Indeed, only diffusion and saline filtration are known to fractionate chlorine stable isotopes during transport [5, 6]. The goal of this study is to verify the consistency of diffusive exchange between seawater and freshwater by modelling the diffusive transport of Cl and of its stable isotopes through the Tournemire argillite. The modelled chlorine stable isotope contents also have to agree with the high and positive δ^{37}Cl values (between 6 and 8 ‰ vs. SMOC) measured in fracture water samples and assumed to be representative of argillite porewater located at their contact [7].

2. Modelling the Cl and δ^{37}Cl profiles across the Toarcian/Domerian argillite

Seawater composition was set as the initial condition for the argillite porewater (Cl = 557 mmol/L, δ^{37}Cl = 0‰ vs. SMOC) assuming no change in the marine ^{37}Cl composition over geological time. Boundary conditions were those presently measured in the Carixian and Aalenian aquifers, respectively 1.41 and 3.10 mmol/L for Cl, and 0‰ vs. SMOC for δ^{37}Cl values. Simulations of diffusion in the vertical direction were performed assuming that, throughout the simulation time, dispersion was dominated by diffusion. Therefore, the 1D dispersion equation is: $\partial/\partial z\ (D_p\ \partial C/\partial z\ ) = \theta\ \partial C/\partial t$ where C is the concentration for total Cl, ^{35}Cl and ^{37}Cl, θ the porosity accessible to Cl, D_p the Cl pore diffusion coefficient ($m^2 \cdot s^{-1}$) and z the elevation in metres above sea level (masl). All parameters were estimated at different depths by the radial diffusion method [2], and are summarized in Table 1. The numerical modelling was performed with the coupled reactive-transport code Hytec [8]. The argillite formation was divided into eight units to account for variations of transport properties. Each unit was divided into 1m x 1m quadrilaterals, leading to a number of computational elements equal to the column height. As the D_p values were determined parallel to the bedding, they were divided by 3 to account for the known anisotropy of the argillite in the normal direction.

Table 1: Summary of the chloride pore diffusion coefficients and accessible porosity utilized as inputs in the simulations.

Formation	Interval (m asl)	$D_p Cl^- \perp$ x10^{-11} [$m^2.s^{-1}$]	θ (% vol/vol)
Upper Toarcian 1	558-513	1.7	8.0
Upper Toarcian 2	503-450	1.1	6.0
Upper Toarcian 3	450-430	1.2	6.4
Upper/Middle Toarcian	430-400	0.72	3.5
Middle Toarcian	400-380	0.8	7.2
Middle/Lower Toarcian	380-370	0.7	6.0
Lower Toarcian/Domerian	370-325	0.8	3.0
Domerian	325-298	1.4	4.0

The modelled curves for chloride are reported in Figure 3 and compared to experimental data [2]. Simulations are shown for a large but realistic time span since marine regression started at the end of the Tithonian, some 145 Ma ago [2]. This figure shows that most of the experimental data plot on the 85 ± 10 Ma curve, a reasonable estimate as the very last brief marine intrusion is known to have taken place in the early Palaeocene - some 60 Ma ago. The dispersion equation was also applied separately to ^{35}Cl and ^{37}Cl isotopes at different modelling times (between 5 and 100Ma) and various diffusion coefficient ratios ($\alpha = D^{35}Cl/^{37}Cl$) ranging between 1.0015 and 1.003. The best agreement was obtained for an evolution time of 85 Ma and for values of $\alpha_{35/37}$ ranging between 1.002 and 1.003 (Fig. 4). These values compare well with the previous estimates of $\alpha_{35/37}$ while remaining in the upper range. Indeed in previous studies $\alpha_{35/37}$ range from 0,9981 in water [9], to 1.00128 at 2 °C to 1.00192 in polyacrilamide gel [10], and 1.0017 in lagoon sediments [11]. Gimmi and Waber considered $\alpha_{35/37}$ values up to 1.003 in argillaceous rocks [12]. The lower values obtained here may be due to the extremely impermeable nature of the argillite. This result clearly indicates that the pure diffusive model is realistic as it explains both the Cl and δ^{37}Cl values.

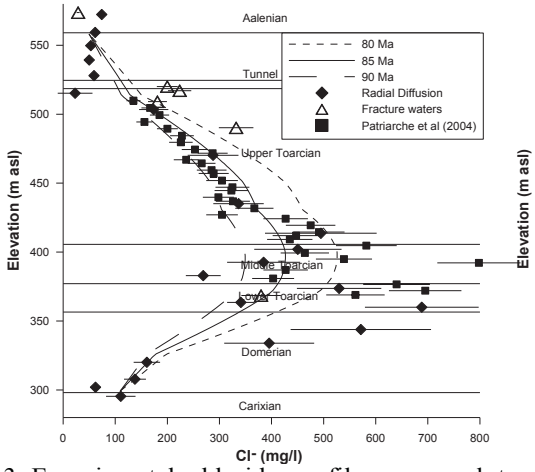

Fig. 3 Experimental chloride profile compared to modelled curves of a diffusive exchange between seawater and freshwater since aquifer activation.

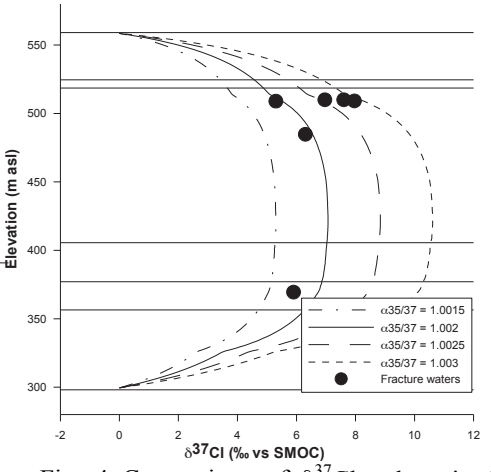

Fig. 4 Comparison of $\delta^{37}Cl$ values in fracture water with model curves obtained for a diffusive exchange of 85 Ma with different α values.

3. Conclusions

The scenario of diffusive transport in the Toarcian/Domerian argillite between marine water and meteoric water reservoirs, and initiated during Cretaceous times, is supported both by the geological history of the basin and the common behaviour of the Cl and stable isotopes. Indeed modelling of diffusion, for both Cl and ^{37}Cl, considering diffusion coefficient ratios $\alpha_{35/37}$ between 1.002 and 1.003, agrees well with the data. The simulated time span required to reach the present-day chloride profile and to reach the high values of $\delta^{37}Cl$ determined for porewater converge towards a diffusion time of about 85±10 Ma. This period is older than the 53 Ma initially proposed [1].

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