



**HAL**  
open science

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

C. Le Gal La Salle, J.M Matray, F. Bensenouci, J.L. Michelot, A. Dauzères, Ch. Wittebroodt, S.K. Frape, R. Rebeix

### **► To cite this version:**

C. Le Gal La Salle, J.M Matray, F. Bensenouci, J.L. Michelot, A. Dauzères, et al.. Modeling Cl- concentration and  $\delta^{37}\text{Cl}$  profiles in porewater across a 250m-thick induced argillite at the Tournemire URL (France). 14th International Symposium on Water-Rock Interaction, WRI 14, Jun 2013, Avignon, France. pp.471-474, <10.1016/j.proeps.2013.03.158>. <hal-00817819>

**HAL Id: hal-00817819**

**<https://hal.science/hal-00817819v1>**

Submitted on 29 Nov 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons CC BY-NC-ND 4.0 - Attribution - Non-commercial use - No Derivative Works - International License

Water Rock Interaction [WRI 14]

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

Le Gal La Salle Corinne<sup>a,b,\*</sup>, Matray Jean-Michel<sup>c</sup>, Bensenouci Fethi<sup>c,d</sup>, Michelot  
Jean-Luc<sup>d</sup>, Dazères Alexandre<sup>c</sup>, Wittebroodt Charles<sup>c</sup>, Frape Shaun<sup>e</sup>, Shouakar-  
Stashe Orphan<sup>e</sup>, Rebeix Romain<sup>a,b</sup>, Lancelot Joël<sup>a,b</sup>

<sup>a</sup>Université de Nîmes / Site GIS - 30035 Nîmes cedex 01, France

<sup>b</sup>Aix-Marseille Université, CEREGE UMR7330, 13545 Aix en Provence, France

<sup>c</sup>IRSN, BP17 – 92262 Fontenay-aux-Roses Cedex, France

<sup>d</sup>IDES, UMR CNRS 8148 Université Paris-Sud - 91405 Orsay Cedex, France

<sup>e</sup>University of Waterloo, 200 University Avenue. West Waterloo, Ontario Canada N2L 3G

---

**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  $0.6 \pm 0.1$  g/L, compared to 19 g/L for the original connate seawater. Dissolved chloride shows high  $\delta^{37}\text{Cl}$  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  $85 \pm 10$  Ma for Cl, which correlates with a major erosional period. Simulated  $\delta^{37}\text{Cl}$  values between 1.002 and 1.003 agree with observed porewater  $\delta^{37}\text{Cl}$ . 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.

© 2013 The Authors. Published by Elsevier B.V. Open access under [CC BY-NC-ND license](https://creativecommons.org/licenses/by-nc-nd/4.0/).

Selection and/or peer-review under responsibility of the Organizing and Scientific Committee of WRI 14 – 2013

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

---

\* Corresponding author. Tel.: +33 -(0) 46-670 9971 ; fax: +33-(0)46-670 9988.

E-mail address: [Corinne.legallasalle@unimes.fr](mailto:Corinne.legallasalle@unimes.fr).

## 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  $^{36}\text{Cl}$ , 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  $\text{Cl}^-$  and  $\text{Br}^-$ . 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.

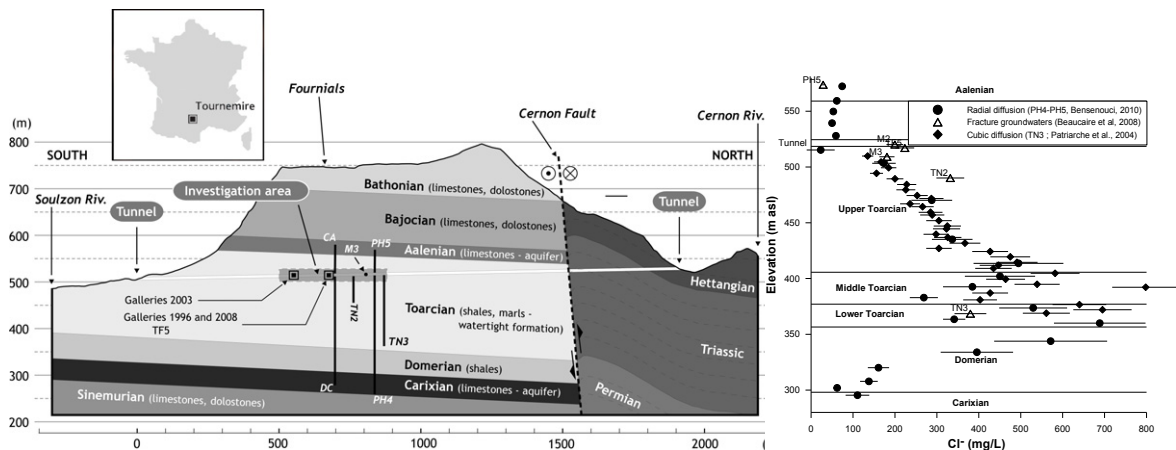


Fig. 1 Cross section of the Tournemire URL with the location of the boreholes dedicated to Cl concentration measurements.

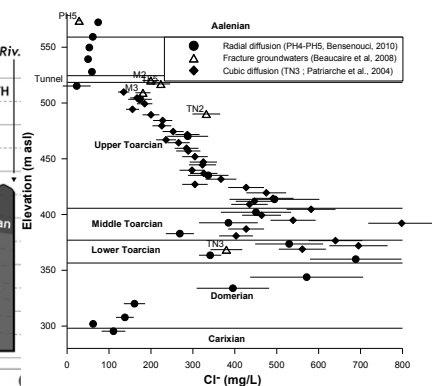


Fig.2 Profile of Cl concentration in porewater at the Tournemire URL.

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 ( $^{37}\text{Cl}$  and  $^{35}\text{Cl}$ ) 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  $\delta^{37}\text{Cl}$  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 $\delta^{37}\text{Cl}$ profiles across the Toarcian/Domerian argillite

Seawater composition was set as the initial condition for the argillite porewater (Cl = 557 mmol/L,  $\delta^{37}\text{Cl} = 0\text{‰}$  vs. SMOC) assuming no change in the marine  $^{37}\text{Cl}$  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  $\delta^{37}\text{Cl}$  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,  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ ,  $\theta$  the porosity accessible to Cl,  $D_p$  the Cl pore diffusion coefficient ( $\text{m}^2 \cdot \text{s}^{-1}$ ) 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)	$D_p \text{Cl} \perp \times 10^{-11} [\text{m}^2 \cdot \text{s}^{-1}]$	$\theta$ (% 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  $85 \pm 10$  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  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  isotopes at different modelling times (between 5 and 100Ma) and various diffusion coefficient ratios ( $\alpha = D^{35}\text{Cl}/D^{37}\text{Cl}$ ) 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  $\delta^{37}\text{Cl}$  values.

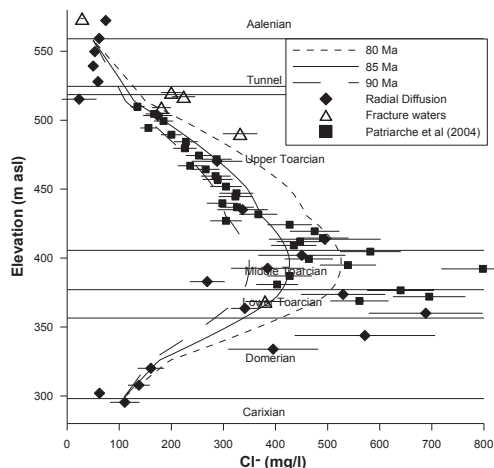


Fig. 3 Experimental chloride profile compared to modelled curves of a diffusive exchange between seawater and freshwater since aquifer activation.

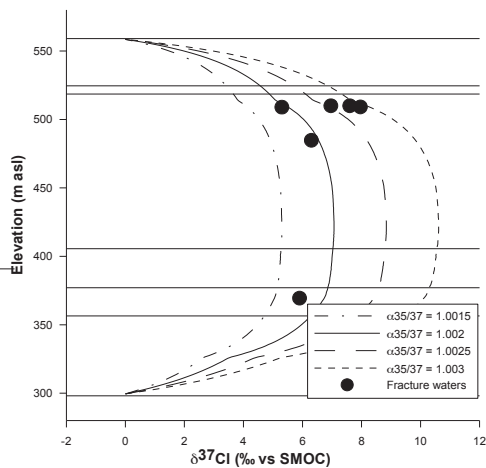


Fig. 4 Comparison of  $\delta^{37}\text{Cl}$  values in fracture water with model curves obtained for a diffusive exchange of 85 Ma with different  $\alpha$  values.

### 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  $^{37}\text{Cl}$ , 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  $\delta^{37}\text{Cl}$  determined for porewater converge towards a diffusion time of about  $85 \pm 10$  Ma. This period is older than the 53 Ma initially proposed [1].

### 4. References

- [1] Patriarche D, Ledoux E, Michelot JL, Simon-Coinçon R, Savoye S. Diffusion as the main process for mass transport in very low water content argillites. Fluid flow and mass transport modeling. *Water Resour Res* 2004; **40**; W01517.
- [2] Bensenouci F. Apport des traceurs naturels à la compréhension des transferts au sein des formations argileuses compactées. *PhD thesis, Univ. Paris-Sud, Orsay* 2010; 160 p.
- [3] Wittebroodt C, Savoye S, Jacquier P, Beaucaire C, Bensenouci F, Pitsch H, Gouze P, Michelot JL. Comparison between radial diffusion and leaching for determining chloride and sulfate in Tournemire argillite porewater. *International Meeting on Clays in Natural and Engineered Barriers for radioactive waste confinement, Lille* 2007; 485-486.
- [4] Matray JM, Savoye S, Cabrera J. Desaturation and structures relationships around drifts excavated in the well-compacted Tournemire's argillite and their impact on the hydraulic head profiles. *Eng Geol* 2007; **90**: 1-16.
- [5] Kaufmann RS, Long A, Bentley H, Davis S. Natural chlorine isotope variations. *Nature* 1984; **309**: 338-340.
- [6] Lavastre V, Jendrzewski N, Agrinier P, Javoy M, Evrard M. Chlorine transfer out of a very low permeability clay sequence (Paris Basin, France):  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  evidence. *Geochim Cosmochim Acta* 2005; **69**-21: 4949-4961.
- [7] Matray JM, Dauzères A. Origin of high Cl and  $\delta^{37}\text{Cl}$  values in radiocarbon dated-fracture groundwaters at the Tournemire clayrock URL (France) *Procedia Earth and Planetary Science* (this issue).
- [8] Van der Lee Y, de Windt L, Lagneau V, Goblet P. Presentation and application of the reactive transport code HYTEC. *Comput Meth Wat Res* 2002; **1**: 599-606.
- [9] Richter FM, Mendybaev RA, Christensen JN, Hutcheon ID, Williams RW, Sturchio NC, Abelardo Beloso D Jr. Kinetic isotopic fractionation during diffusion of ionic species in water. *Geochim Cosmochim Acta* 2006; **70**: 277-289.
- [10] Eggenkamp HGM, Coleman ML. The effect of aqueous diffusion on the fractionation of chlorine and bromine stable isotopes / *Geochim Cosmochim Acta* 2009; **73**: 3539-3548.
- [11] Beekman HE, Eggenkamp HGM, Appelo CAJ. An integrated modelling approach to reconstruct complex solute transport mechanisms - Cl and  $\delta^{37}\text{Cl}$  in pore water of sediments from a former brackish lagoon in The Netherlands. *Appl Geochem* 2011; **26**: 257-268.
- [12] Gimmi T, Waber HN. Modelling of tracer profiles in pore water of argillaceous rocks in the BenKen Borehole: Stable water isotopes, chloride and chlorine isotopes. *NAGRA Tech Rep* 2004; **04**-05: 90.