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Water Rock Interaction [WRI 14]**Origin of Cl⁻ and high $\delta^{37}\text{Cl}$ values in radiocarbon dated-fracture groundwaters at the Tournemire URL (France)**Matray Jean-Michel^{a,*}, Dauzères Alexandre^a^a*IRSN, BP17 – 92262 Fontenay-aux-Roses Cedex, France*

Abstract

Fracture groundwaters collected from the indurated Toarcian/Domerian clayrock in the IRSN Underground Research Laboratory (URL) at Tournemire (south of France) are rare and limited in volume. The present study aims at resolving an apparent contradiction observed for these groundwaters: how can these groundwaters in transmissive fractures contain indicators of both geologically young and old residence times? Young residence times on the order of a few thousand years are indicated by the presence of ¹⁴C, and old residence times appear to be indicated by the extraordinarily positive $\delta^{37}\text{Cl}$ values, between 5 and 8‰ vs SMOC. These highly enriched $\delta^{37}\text{Cl}$ values might be attributed to a long diffusive transport (on the order of tens of million years) between the semi-permeable clayrock sequence and its surrounding aquifers, as estimated by modeling in a companion paper [1].

Knowledge of the geometry of the fractures and the diffusion parameters in the intact clayrock allowed us to propose a 2D modeling for the transport of chloride and its stable isotopes using the Hytec code. Simulations applied to borehole M3 data show that the measured Cl values in the fracture groundwater are consistent with a diffusive exchange between the unaltered argillite porewater and meteoric waters that infiltrated in the fracture about 26 ka ago and have become isolated since then. This result is in good agreement with previously estimated maximum ¹⁴C residence times for these fracture groundwaters. The modeled $\delta^{37}\text{Cl}$ value at 26 ka would be enriched by only 0.02‰ with respect to the initial imposed value for the argillite, which remains in the analytical uncertainty of $\pm 0.2\%$. These simulations provide evidence that the aqueous chloride and high $\delta^{37}\text{Cl}$ values may reflect values of the unaltered argillite porewater.

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Keywords: argillite, fracture groundwaters, chlorides, chlorine isotopes, diffusion, transport modelling.

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1. Background

The Tournemire URL owned by IRSN is located in an overconsolidated clay rock, namely argillite, which is mainly composed of clay minerals (50%) dominated by illite (40%) and smectite in I/S, carbonates (10-30%), quartz (15%), accessory minerals and organic matter [2]. This argillaceous rock is cross-cut by subvertical fractures some of which produce water. These fractures are the only opportunity to directly obtain free waters from the aquitard while the undamaged and undisturbed argillaceous rock is very impervious. Hydraulic tests revealed a hydraulic conductivity between 10^{-14} and 10^{-15} m/s for the intact rock and in the order of 10^{-10} m/s for the transmissive fractures [3]. The geometry of these fractures is well known [2]. These vertical structures, such as shown in Fig 1, are known to have been connected in the past or at present time with the surrounding carbonated aquifers. Only simple metric to decametric fractures are known to show the occurrence of free water in geodes located at their relay zones. Through the fractured clayrock, water flows downward between the free upper aquifer and the captive lower aquifer, with a hydraulic gradient of about 0.5 m/m [2]. The fracture groundwaters collected in the URL since the 1990s are rare. Boreholes intersecting these fractures at the tunnel level never produced more than 30 liters. They show a Na-SO₄-Cl type, a low salinity (2.7 to 5.1 g/L) and their chloride content (from 4.3 to 5.11 mmol/L) is much lower than that of seawater trapped during sedimentation (connate seawater with 557.9 mmol/L). Chlorinity of the fracture groundwaters is 20 to 40 times larger than aquifers one (from 0.14 to 0.28 mmol/L). Residence time of these waters was estimated by radiocarbon dating between 17 and 29 ka [4]. For the intact or undamaged/undisturbed rock, molecular diffusion or ion filtration is the only possible mechanism to enrich the chlorine stable isotopes in ³⁷Cl and in a sedimentary context [5]. Recent works ([6],[7]) show that diffusion alone remains the dominant transport phenomenon for chloride both in the intact clayrock. Methods implemented at Tournemire for the acquisition of chloride concentrations and diffusive transport parameters, such as the cubic and radial diffusion, or through diffusion, have provided profiles of chlorides and diffusive transport parameters (diffusion coefficients and accessible porosities) over the entire sedimentary column [9]. This study aims in particular to verify by modelling that the chloride concentrations and their isotope ratios in the sampled fracture groundwaters can result from a diffusive exchange between the intact matrix porewater and a fresh, low-Cl water that infiltrated in the fracture about 17-29 ka ago and has become isolated since then.

2. Methods

Fracture groundwaters were collected during two sampling campaigns at the fracture level to avoid any evaporation. Anion concentrations were determined at the IRSN laboratory using ion chromatography with an accuracy of about 2%. The chlorine stable isotopes were analysed either in 2007 at the University of Waterloo (UW) or in 2012 at the University of Illinois in Chicago (UIC) (Table 1).

Table 1. Measurements performed on fracture groundwaters.

Borehole	TN2	TN3	TF5	GSM135	GSM225	M3
Cl mmol/L	9,2	10,2	6,18	4,3	5,9	5,1
SO ₄ mmol/L	6,8	18,9	0,04	30,8	22,2	10,4
δ ³⁷ Cl ‰ vs SMOC Laboratory	6.30 ± 0.1 UW	5.90 ± 0.1 UW	5.30 ± 0.1 UW	6.96 ± 0.2 UIC	7.60 ± 0.2 UIC	7.96 ± 0.2 UIC

For both labs the chlorides were precipitated as AgCl and converted to CH₃Cl. At the UW lab, analyses used a CF-IRMS coupled with GC on <0.1 mg of total chloride. For the UIC lab, analyses were done in dual-inlet mode on a ThermoFinnigan Delta Plus XL IRMS on 3mg of total chloride. Results show very positive $\delta^{37}\text{Cl}$ values ranging between +5.3 and +7.96‰ with respect to the Standard Mean Ocean Chlorine (SMOC). The reproducibility, based on replicates of seawater run with the samples, is of $\pm 0.2\%$ (1σ) or better. The data accuracy was questioned as both labs have used the same preparation method known in the past to be sensitive to SO₄ during the precipitation of AgCl with a potential ^{37}Cl enrichment in the precipitate [8]. However, labs have greatly improved their purification technique since then. Moreover, the poor determination coefficient ($r^2=0.20$) existing in the linear SO₄ vs $\delta^{37}\text{Cl}$ relationship and the high $\delta^{37}\text{Cl}$ value measured in the TF5 sulphate-free sample (+5.3‰) clearly indicate that the enrichment is not an artifact. At last, studies having used the same preparation technique as for UW and UIC with rather similar argillite porewater types have never reported such positive values [9,10].

3. Modeling transport of chlorine concentration and isotopes

The simulations aimed at estimating the time required for porewater chlorides to equilibrate by diffusive exchange with a freshwater infiltrated into a fracture. The initial conditions for the groundwater fracture are those of the upper aquifer, $\text{Cl} = 0.14 \text{ mmol/L}$ and $\delta^{37}\text{Cl} = 0\%$ typical of a surface water [9], with $\text{DpCl} = 2.0 \cdot 10^{-9} \text{ m}^2/\text{s}$ and $\omega_{\text{accessCl}} = 100\%$. For the argillite porewater, the composition of the fracture groundwater M3 was considered ($\text{Cl} = 5.07 \text{ mmol/L}$, $\delta^{37}\text{Cl} = +7.96\%$ vs. SMOC). Diffusive transport parameters in the clayrock were determined at the tunnel level, close to M3 borehole ($\text{DpCl} = 1.7 \cdot 10^{-11} \text{ m}^2/\text{s}$ and $\omega_{\text{accessCl}} = 8\%$ [7]). Isotopic contents were calculated individually for ^{35}Cl and ^{37}Cl considering a diffusion coefficient ratio ($\alpha = \text{Dp}^{35}\text{Cl}/\text{Dp}^{37}\text{Cl}$) of 1.0025, the best fitted α value for the Tournemire site [1] and not far from the averaged value (1.002 ± 0.007) proposed for the similarly very impervious siltite at Marcoule [10]. The numerical approach was performed with the transport code Hytec [11] based on finite volumes. The mesh was divided in 3 domains: i) Argillite - 10m(length, l) \times 10m(width, w) \times 1m (thickness, t); ii) Argillite - 4m(l) \times 10m(w) \times 1m(t) generated to facilitate the representation of the fracture; iii) Fracture - 3m (l) \times 0.01m(w) \times 1m(t) to reach a maximum volume of 30 L.

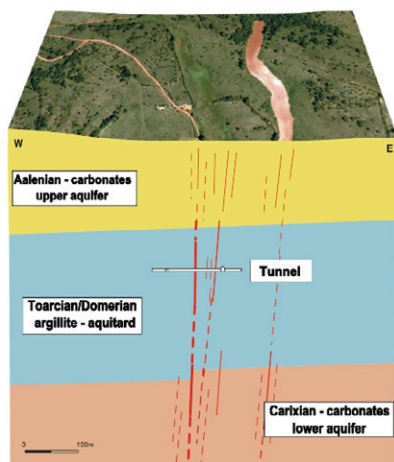


Fig. 1. Schematic view of the fracture network observed at the Tournemire URL

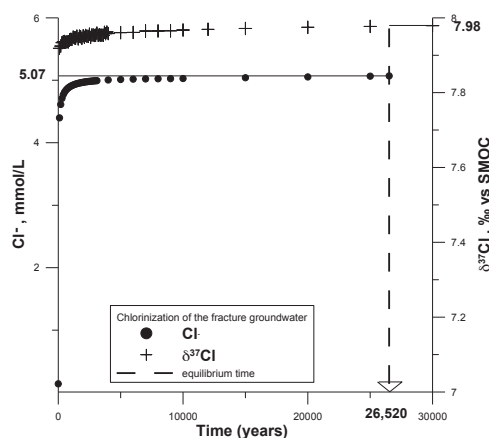


Fig. 2. Simulation results for Cl concentrations and $\delta^{37}\text{Cl}$ values in the M3 fracture groundwater

4. Discussion and conclusions

Simulation results (Fig 2) show that the time required for the fracture groundwater to reach the chlorinity of the argillite porewater (5.07 mmol/L) would be of 26.5 ka. This result fits well with the range of maximum residence times estimated by radiocarbon dating on these fracture groundwaters (17–29 ka after [4]). At this corresponding residence time, the modeled $\delta^{37}\text{Cl}$ value would be enriched of about 0.02‰ with respect to the initial imposed value for the argillite. As this enrichment is 10 times lower than the analytical precision, this result indicates that the $\delta^{37}\text{Cl}$ value measured in the M3 fracture groundwater also reflects well that of the argillite porewater sampled at the same level. However, such positive values are rarely encountered in the literature. In the absence of any possibility of ion-filtration [6] the only explanation is ^{37}Cl enrichment by preferential diffusion of ^{35}Cl within the semipermeable.

The next step, reported in the companion paper [1] has consisted in simulating the transport of chlorine and its isotopes across the semi-permeable aquifer and its surrounding aquifers to verify that the time required for the ^{37}Cl enrichment in the semipermeable, controlled by ^{35}Cl preferential diffusion within the pore water, is compatible with the dilution start of the connate seawater by meteoric water, i.e. since the sea regression at the Cretaceous/Tertiary limit. More generally, those modeling results indicate that the chlorides are essentially sourced from the intact argillite porewater. What is true for chlorides is also for other mobile anions such as sulphates that are not constrained by equilibrium with a mineral phase [12]. The chemical composition of the fracture groundwaters undisturbed by degassing, oxidation or bacterial reduction would therefore witness the argillite porewater composition.

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