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On the mobility and potential retention of iodine in the Callovovian-Oxfordian formation

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Abstract

Iodide sorption experiments were conducted on clay stone samples originating from the Callovian-Oxfordian formation under experimental conditions as close as possible to *in situ* conditions. The total natural iodine content of the formation is shown to be very constant throughout the formation, ranging from 2 to 3 ppm. This range is in agreement with a past iodine accumulation in the marine organic matter of the sediment before and during deposition, and early diagenesis. At variance with total iodine, the leached iodine concentrations are variable. If leached iodine is considered to represent porewater solute iodine, its concentration can be calculated and ranges from 0 (below detection limit) to ~60 $\mu\text{mol/L}$ and represents 0 to 25 % of the total iodine. The reason for this variability is not understood. Sorption isotherms were determined either for natural $^{127}\text{I}^-$ solutions or for $^{131}\text{I}^-$ spiked $^{127}\text{I}^-$ solutions, with concentrations ranging from 10^{-9} to 10^{-3} mol/L at solid to liquid ratios from 10 to 200 g/L. No or little sorption was encountered, K_d values being in the range 0-0.5 L/kg with statistical and analytical error bands being greater than the K_d values, with the exception of one experiment at low solid to liquid ratio (10 g/L), showing significant K_d values of ~25 L/kg. In sorption experiments with natural $^{127}\text{I}^-$ and at the lowest added iodide concentrations ($< 10^{-6}$ mol/L) an apparent negative K_d was obtained due to the iodide content in the solid porewater that was leached once the solid was suspended. The low affinity of iodide for argillite is thus confirmed. However, based only on these results and given the extent of the error bands, one cannot discard a limited iodide uptake. Literature data on iodide diffusion on similar rock materials have already shown that iodide does not behave like chloride. The retention mechanism of radio-iodide is discussed in the light of the present results and diffusion data. A model involving isotopic exchange between the natural iodine content of the geological formation and radio-iodine allows all of the results to be described.

Not all the iodine in the formation appears to participate in isotopic exchange reactions with the solution. A quantification of the isotopically labile fraction of iodine would allow the effect of isotopic exchange on radio-iodide migration throughout the Callovian-Oxfordian formation to be assessed and predicted.

Keywords: Iodine, Callovian-Oxfordian, diffusion, retention, isotopic exchange.

Introduction

Iodine 129 is an important radioactive pollutant, contributing to potential future radiation doses resulting from radioactive waste disposal in deep host-rock formations, due to its ubiquity in these wastes, its long half-life period (approximately 16 million years) and its high mobility in most rocks and sediments. This high mobility is linked to the anionic nature of dissolved iodine species and its consequent low affinity for sorption on typically negatively charged mineral surfaces.

This study aims at characterising the iodine retention capacity of the Callovian-Oxfordian clay stone in the framework of the ANDRA research program on radionuclide behaviour in its underground research laboratory (URL). Iodine retention has been studied on numerous minerals, sediments and soils over the last few decades. However, discrepancies or even apparently contradictory results between these studies preclude a reliable prediction of the retention of iodine as a function of the thermodynamic conditions and the mineral/organic content of the sample.

There is good evidence and a consensus of opinion on the absence of iodide uptake on carbonates, quartz, chlorite, montmorillonite and muscovite (e.g. MURAMATSU et al., 1990; TICKNOR and CHO, 1990; FUHRMANN et al., 1998; KAPLAN et al., 2000). However, some other mineral phases present in the Callovian-Oxfordian (e.g. GAUCHER et al., 2004) are more problematic. For instance, iodide at trace concentration has been shown to sorb efficiently onto pyrite surfaces. However, Fuhrmann et al. (FUHRMANN et al., 1998) have demonstrated by XANES spectroscopy, that the uptake mechanism is only valid for the IO_3^- solute ion, but not for the I^- ion, I^- being repelled from pyrite surfaces. Based on these results, Fuhrmann et al. have suggested that iodine tracer, introduced as I^- , could oxidise to form IO_3^- in sorption experiments, provided that no reducing agent is used. The case of illite, one of the main

mineral components of clay stone, is even more problematic than the case of pyrite. Kaplan et al. (KAPLAN et al., 2000) have shown that illite efficiently retains trace amounts of radioactive ^{125}I tracers. The derived K_d are pH dependent and range from 46 L/kg at pH 3.6 to 22 L/kg at pH 9.4, for an iodine concentration of $\sim 10^{-12}$ mol/L and a solid to liquid ratio of 1:10 g/mL. In the same publication, they reported negative K_d values for montmorillonite and interpreted them as an indication of an anion exclusion phenomenon. Given the structural similarities, the difference in the iodide sorption properties of illite and montmorillonite are not easily explained. The hypothesis of illite charged edge surface sorption is not entirely satisfactory because montmorillonite is expected to present more or less the same sites on its edge surfaces. Hence, the explanation for iodide uptake on illite needs to be confirmed. Finally, organic matter could be considered as a potential sorbing phase for iodine (YAMAGUCHI et al., 2006 and references therein). Although little data indicate significant sorption of iodide on pure minerals or organic matter, literature references showing high iodide retention on soils and sediments are very common. This retention behaviour can be linked to the effect of organic matter towards iodine. Iodine uptake on soils and sediments is affected by the pH value. Iodine uptake is furthered by acidic pH (e.g. YOSHIDA et al., 1992; FUKUI et al., 1996; KAPLAN, 2003). However, some studies stand in contradiction to this simple observation (e.g. BIRD and SCHWARTZ, 1997). The relationship pH/adsorption has often been linked to the presence of positive charges on the mineral/organic surfaces at low pH. This hypothesis has been verified for well characterised minerals like iron(III) oxihydroxides (e.g. BENES, 1979). The redox state of iodine in solution (i.e. mainly iodide, I^- , or iodate, IO_3^-) is also a key parameter. Yoshida et al. (YOSHIDA et al., 1992), Fukui et al. (FUKUI et al., 1996) and Muramatsu et al. (MURAMATSU et al., 1990) have demonstrated that iodate uptake is even more pronounced than iodide uptake, on the same soils and sediment samples. At iodine trace concentration, the conversion of iodide into iodate, and conversely, occurs during iodide, and

iodate, sorption experiments on soils (MURAMATSU et al., 1990; FUKUI et al., 1996). These redox conversions may be due to reactions on mineral surfaces, to reactions with O₂ from the atmosphere and to biologically induced reactions. Microbial activity seems to be the most important factor favouring iodine uptake on soils and sediments. Sample pretreatments by autoclaving (MURAMATSU and YOSHIDA, 1999), heating (WHITEHEAD, 1973; LIESER and STEINKOPFF, 1989; MURAMATSU et al., 1990; FUKUI et al., 1996), irradiation (MURAMATSU et al., 1990; BIRD and SCHWARTZ, 1997; DEVIVIER et al., 2004), H₂O₂ washing (WHITEHEAD, 1973; LIESER and STEINKOPFF, 1989) or antibiotic introduction (BIRD and SCHWARTZ, 1997) lead to a dramatic decrease (or disappearance) of iodide and iodate uptake, iodide being more affected than iodate. Mixing fresh soil or sediment with the treated one restores their iodine uptake capacity (MURAMATSU and YOSHIDA, 1999). Furthermore, isolating the soils or sediments from oxygen (e.g. using an N₂ atmosphere glove-box) leads to a disappearance of the iodine uptake. Placing the samples in air restores this uptake (BIRD and SCHWARTZ, 1997). Conversely, a soil accumulates iodine in the presence of oxygen and releases this iodine in anoxic and reductive conditions (MURAMATSU and YOSHIDA, 1999; YAMAGUCHI et al., 2006). In agreement with these laboratory experimental results, Price and Calvert (PRICE and CALVERT, 1973, 1977) have shown that marine iodine rich sediments are associated with oxygenated deposit areas, whereas iodine poor sediments are associated with redox reductive deposit areas.

In the light of this literature data, it appears that iodine uptake by a soil or sediment is mainly due to microbial activity. Mineral phases may also contribute to the uptake but seem to highly depend on the redox state of iodine, i.e. iodide I⁻ vs. iodate IO₃⁻. In the redox condition prevailing in a deep clayey formation waste disposal, iodine should be present as iodide (I⁻). The Callovian-Oxfordian clay stone is constituted by mineral phases that are known not to sorb iodide (e.g. carbonates, quartz, chlorite, montmorillonite, etc.) but also by mineral phases

showing contradictory results as a function of the studies (e.g. illite and pyrite) and organic matter. Organic matter is then expected to be the main sink for iodide there. However, recent studies in abiotic and reductive conditions have demonstrated that humic substances do not sorb iodine in the I^- form but only in the I_2/I_3^- form (REILLER and MOULIN, 2003). Bacterial activity is not considered to take place to a significant extent in compacted clay stone. Thus, it has been necessary to conduct iodine sorption experiments under thermodynamic and biological conditions as close as possible to the conditions prevailing in the *in situ* Callovian-Oxfordian conditions. Batch sorption experiments were conducted with stable and radioactive iodide solutions in abiotic, anoxic and reductive conditions on Callovian-Oxfordian rock samples, with iodine concentrations ranging from 10^{-9} to 10^{-3} mol/L. The results relative to these sorption experiments are compared to the distribution of natural iodine in the clay stone samples. Literature results on batch sorption but also diffusion experiments that were obtained on similar material are then discussed in the light of the present experiments. Finally, several modelling scenario attempts were performed in order to conciliate apparently contradictory results between diffusion experiments, stable iodide batch sorption experiments and radioactive batch sorption experiments.

Material and methods

Solid samples

Callovian-Oxfordian argillites

The samples mainly originated from borehole EST205 at the ANDRA's Bure site (Meuse/Haute Marne, France). Some additional materials were obtained from the PPA shaft and EST212 borehole (ANDRA URL). In addition EST312 and EST322 were also investigated as samples coming from the area surrounding the site (30 km NE and 30 SW respectively). The clay stone samples K100 and K119 originated from drilling cores EST205.

A complete description of the core sample drilling and conditioning procedures is available elsewhere (GAUCHER et al., 2004). The samples were powdered in an agate mortar by hand, ensuring a limited artificial creation of fresh surfaces. This was done in the absence of oxygen, using a N₂ filled glove-box, in order to prevent any oxidation of redox sensitive materials such as, for example, pyrite, organic matter, adsorbed Fe(II) and iodide. Thorough characterisation and identification of the minerals were carried out by optical microscopy, scanning electron microscopy, transmission electron microscopy, Fourier transformed infrared and X-ray diffraction (XRD). Minerals identified by XRD under the term “mica illite” include muscovite, biotite, illite and possibly glauconite *sensu stricto*. Given the relatively broad width of the characteristic XRD peaks, illite may be a mixed layer in illite/smectite rich in illite (>90% illite). The quantitative estimation of the different minerals (Table 1) was carried out by a calculation based on XRD, chemical analysis of the rock, cation exchange capacity and carbonate content measurements, TG-TDA analysis and FTIR results (BLANC and GAUCHER, 2003; BLANC et al., Submitted). We must observe that the accuracy of the mineral proportions is not the same according to the phase considered. Thus the proportions of minerals like pyrite, apatite/collophane and titanium oxides can be determined with a relative accuracy of about 10% on the characteristic element (S, P and Ti) by chemical analysis performed on the total rock, this means $\pm 0.05\%$ for a measured value of 0.5%. Similarly, calcimetry helps to determine the proportions of carbonates with an absolute accuracy of $\pm 1\text{--}2\%$. On the other hand, Reynolds (1989) stated that even if many characteristic parameters (chemistry and crystallography) of the clay minerals to be quantified are known, an absolute uncertainty of $\pm 5\%$ remains.

Water contents (0.057 L/kg for K100 and 0.083 L/kg for K119) were measured by heating the samples at 150°C under a vacuum, guaranteeing that a reference anhydrous state has been

reached, which is not the case at 105°C, a temperature at which clays retain a large proportion of their water of hydration (GAUCHER et al., 2004).

For one set of experiments, argilite K119 was heated to 120°C for one month in an oven. The clay stone sample was confined in a Teflon pot, whose cap threads were carefully lined with flexible Teflon tape, this pot itself being placed in a glass pot that was hermetically sealed in a N₂ atmosphere glove-box. These precautions ensured minimum O₂ contact with the solid.

Natural iodine in the Callovian-Oxfordian formation

Total natural iodine content in the Callovian-Oxfordian formation was measured by ICP-MS after digestion of the solid sample. The leachable iodine concentrations were measured with the method described in GAUCHER et al., 2004. In this method, the leachable anions were analysed by ionic chromatography in a batch experiment obtained after 24 h of interaction (20 g of powdered sample in 200 g of ultrapure water degassed with N₂).

Stable I Kd experiments

Argilite K100 and K119

All experiments with clay stone samples were conducted at room temperature (~25°C) in a N₂ atmosphere glove-box using boiled Milli-Q water degassed under N₂. Solutions (hereafter called synthetic groundwater) whose major cation and anion species were close to equilibrium with the argilite samples were prepared with salts of analytical grade (GAUCHER et al., Submitted). These solutions were split into several sub-samples and KI concentrated solutions were added to produce iodide stock solutions at concentrations ranging from 2.5×10^{-7} to 10^{-2} mol/L. 1 g of argilite was weighed in PC tubes and suspended in 5 mL of synthetic water + KI stock solutions. The tubes were shaken for 1 day with a low-speed vertical rotary shaker (~6 rpm) before being centrifuged. The supernatant was then filtrated (0.1 µm), analysed for pH, diluted and analysed for I⁻ by ICP-MS (detection limit -d.l. = 5 µg/L after dilution),

spectrophotometric method (d.l. = 2 µg/L after dilution) or ion chromatography (d.l. = 0.02 mg/L after dilution), and major cations and anions by ion chromatography (Cl^- , SO_4^{2-} , Na^+ , Ca^{2+} , K^+ , Mg^{2+} , NH_4^+). Dilution was necessary because of the relatively high concentration of accessory salts in the solution (mainly Na^+ , Cl^- and SO_4^{2-}).

Radioactive tracers / Kd experiments

Powdered clay stone samples were provided by Andra, protected from oxygen contact. The samples were stored in an inert gas box. Starting solutions with radioactive tracers were prepared with an activity of 2.377 kBq/mL ^{131}I and various stable iodine concentrations prepared from NaI. Prior to the sorption experiments, the clay stone samples were equilibrated for 2 days with the synthetic groundwater at the target solid/liquid ratio. Sorption experiments were initiated by addition of an aliquot of the radioactive tracer solution and maintaining contact with the solid for 2 days in the closed reaction vessels. Blank experiments without clay stone were run in parallel. All experiments were run in inert gas boxes (<3ppm $\text{O}_{2(\text{g})}$) to avoid oxidation of the clay stone and iodide. The ambient temperature was about 20°C. Both non-filtered and filtered (membranes with 0.22 µm pore sizes) solution samples (10 mL each) were analysed by liquid scintillation counting (spectrometer PACKARD model Tri Carb TR/AB 2500.), adding 10mL of the scintillant LLT.

Calculation of Kd values

Kd values were calculated as follows:

$$Kd = \frac{C_{added} - C_{eq}}{C_{eq}} \times \frac{1}{\rho} \quad \text{Equation 1}$$

where C_{added} is either the added stable iodide concentration or the added tracer activity, C_{eq} the iodide concentration (or activity) after equilibration and ρ the solid content of the suspension (in kg/L).

Most of the experiments described were carried out with samples in duplicate or triplicate giving an indication on the statistical dispersion of the measured Kd values (statistical error).

Moreover, the analytical error was estimated by considering the following formula:

$$\Delta Kd = \frac{\Delta C_{added}}{C_{eq}} \times \frac{1}{\rho} + \frac{C_{added} \times \Delta C_{eq}}{C_{eq}^2} \times \frac{1}{\rho} \quad \text{Equation 2}$$

Considering that the concentration at equilibrium is almost equivalent to the added concentration (see further results), the former equation reduces to:

$$\Delta Kd = x \times \left(\frac{2}{\rho} + Kd \right) \quad \text{Equation 3}$$

where $x = \frac{\Delta C}{C}$, the analytical error on the concentration measurement. Given the small extent

of iodide uptake on the clay stone, both statistical and analytical error criteria will be discussed. The uptake of iodide will be considered as significant only if statistical and analytical errors are of lesser extent than the Kd values.

Iodine diffusion data modelling

The data from Van Loon et al. (VAN LOON et al., 2003b) were modelled using the PHAST chemistry transport coupled code (PARKHURST et al., 2004, http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phast/index.html). The $^{36}\text{Cl}^-$ diffusion simulation results are shown on Figure 1 with the following diffusion parameters: porosity = 0.039 (Van Loon et al. value 0.039 ± 0.002), pore diffusion coefficient = $2.14 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, i.e. effective diffusion coefficient $D_e = 8.3 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ (Van Loon et al. value $7.9 \pm 0.4 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$). The good agreement between our fit and that of Van Loon et al. shows that the

PHAST numerical code can be used to simulate their through-diffusion results. The advantage of PHAST is that it allows different mechanisms/scenarios for iodide retention on the solid to be tested.

Results

Natural iodine in the formation

Table 2 shows the natural iodine concentrations that have been measured on Callovian-Oxfordian core samples as a function of depth. The total iodine content of the formation has a very stable value throughout the formation, both at the URL location and on the regional scale. Only a minor fraction of the total iodine content is released during leaching experiments. Considering that this iodine fraction originates from the porewater as free iodide, it is possible to calculate the iodide concentration in the porewater ($[I^-]_{\text{porewater}}$ in mmol/L) according to the formula:

$$[I^-]_{\text{porewater}} = \frac{C_{\text{leaching}}}{126.90 \times t_{\text{water}}}$$

where C_{leaching} is the measured concentration of iodide during leaching experiments (in mg/kg_{wet rock}) and t_{water} is the water content of the argilite sample (in L/kg). The derived iodide concentration values range from approximately 1 µmol/L (corresponding to samples where the iodide concentration was below the limit of quantification) to 62 µmol/L (last row in Table 2). Long term experiments on K119 samples have shown that the leached iodine concentration does not significantly change with time. After six months of equilibrium (solid to liquid ratio of 100 g/L), the calculated iodine porewater concentration was 11 ± 4 µmol/L (BLANC et al., 2004) to be compared with the 6.7 ± 2 µmol/L value given in Table 2.

The natural iodine distribution coefficient (K_d) can be calculated on the basis of the results given in Table 2. For instance, the natural iodine K_d of sample K119 is about 4 L/kg.

However, this distribution coefficient is probably not realistic for further iodine uptake by the sediment because of the disappearance of the supposed main contributors to this uptake (biological activity in the presence of oxygen).

Stable I Kd experiments on argilite

24 hour I⁻ sorption experiments at 25°C on undisturbed argilites

Figure 2 shows the results of the sorption experiments conducted at 25°C with natural iodine. Since equation 1 does not take into account the natural iodine content of the formation, Kd values must be considered as apparent Kd values. In the range of concentration $10^{-5.5}$ to 10^{-3} mol/L, iodide does not undergo any uptake process in the limits of the error bands, the Kd values being statistically distributed around the 0 value. In this concentration range, mean Kd values are 0.21 ± 0.48 L/kg for K100 and -0.02 ± 0.27 L/kg for K119. At lower concentration ($< 10^{-5.5}$ mol/L), the Kd values are negative. These negative apparent Kd values are easily explained by considering (i) that iodide does not sorb onto argilite solid products and (ii) that clay stone samples leach iodide in solution once being suspended. The solid lines in Figure 2 show the result of modelling such a phenomenon by considering a Kd value of 0 and an iodide porewater concentration of 10 μ mol/L and 20 μ mol/L for K100 and K119 samples respectively. These fitted porewater concentration values are in total agreement with the values obtained during leachate experiments (see Table 2).

I⁻ sorption kinetic experiments at 25°C on undisturbed argilites

The results of iodide sorption kinetic experiments are shown on Figure 3. They clearly indicate the absence of significant iodide uptake in a 10 day equilibration time period. Moreover, two experimental points at a total iodide concentration of 5×10^{-4} mol/L were measured after 70 days of equilibration with the K119 sample (data not shown). No

significant iodide sorption was encountered after this time period, discarding long term uptake processes under these conditions.

I⁻ sorption experiments at 25°C on argilites heated to 120°C for 1 month

Figure 4 shows the results of the sorption experiments conducted at 25°C with natural iodine on the 120°C heat treated K119 sample. The mean measured Kd is 0.03 ± 0.61 L/kg, to be compared to 0.02 ± 0.27 L/kg for the untreated sample. Hence, the heating treatment (120°C, one month) did not change the K119 behaviour towards iodide.

Radioactive tracers / Kd experiments

Figure 5 presents the results of the sorption experiments conducted at 25°C with a radioactive iodine tracer. The iodide concentration at equilibrium is calculated as follows:

$$[I^-]_{eq} = \frac{[I^-]_{added}}{[^{131}I^-]_{added}} \times [^{131}I^-]_{eq}$$

where $[I]_{eq}$ is the calculated iodide concentration at equilibrium, $[I]_{added}$ is the total added iodide concentration, $[^{131}I]_{added}$ is the total added radioactive tracer activity and $[^{131}I]_{eq}$ is the radioactive tracer activity at equilibrium.

Given the presence of natural solute iodine in the samples porewater, $[I]_{added}$ is not equivalent to the total iodine concentration and then the calculated iodide concentration at equilibrium should be considered as an apparent concentration (especially for low concentrations). However, the washing steps during clay stone samples preparation should have decrease drastically the solute iodide concentration originating from the solid porewater.

Kd values are calculated as follows:

$$Kd = \frac{[^{131}I^-]_{added} - [^{131}I^-]_{eq}}{[^{131}I^-]_{eq}} \times \frac{1}{\rho}$$

If it is considered that the natural iodine was not completely eliminated during the washing procedure, the K_d values must be considered as representative of the uptake of the radioactive tracer and not of the total solute iodine in the system.

The K_d values are distributed around the 0 value. The mean K_d values are 0.4 ± 1.0 L/kg for K100 and 0.5 ± 0.9 L/kg for K119. These data are in agreement with the results obtained with non-radioactive iodide and denote no or very weak iodide uptake by the argillite samples.

Discussion

Natural iodine in the formation

Price and Calvert (PRICE and CALVERT, 1977) have shown that the I/C_{org} molar ratio in reduced marine sediments is about 1.5×10^{-4} (2.5×10^{-3} for oxidised sediments). Considering that the total organic matter content in the Callovo-Oxfordian formation is about 0.5 % and that its I/C_{org} ratio value is 1.5×10^{-4} , the iodine content value is calculated to be about 3 ppm, in full agreement with the measured values (see Table 2). Given the redox-reduced nature of the Callovian-Oxfordian samples, one can assume that its iodine is associated with its organic matter.

Iodide leached concentrations are higher in the Callovian-Oxfordian formation porewater than in the seawater (~ 0.5 $\mu\text{mol/L}$, PRICE and CALVERT, 1977; ELDERFIELD and TRUESDALE, 1980). Iodide does not behave like other halogens (Cl^- , Br^-) that are diluted as compared to seawater (GAUCHER et al., 2004). Principal component analysis (PCA) was performed in order to link the leached iodine concentration variability with other known parameters of the formation. It was not possible to find a satisfactory correlation or anti-correlation between leached iodine and the mineralogical or organic parameters of the formation (all data were taken from GAUCHER et al., 2004, data from cores EST312, EST322, EST212 and PPA are not considered due to the data's lack of widely tested parameters). Nevertheless, one can note

that the leached iodine concentrations values lie in the concentration range commonly observed on sediments having undergone meteoric dilution and early diagenesis (e.g. see SNYDER et al., 2003).

Comparison of Kd values with literature data

The mean Kd values obtained in the present study lie between 0 and 0.5. These Kd values are low and they could be interpreted as showing the absence of a significant sorption of iodine on the solid. Devivier et al. (DEVIVIER et al., 2004) have explored the iodide uptake on a clayey rock sample (Tournemire argilite) very similar to the Callovian-Oxfordian one. They have conducted experiments under a wide range of conditions including alkaline pH and radiosterilised vs. non radiosterilised samples, all experiments being conducted in a N₂ atmosphere glove-box (O₂ concentration < 0.6 ppm). The measured Kd values ranged from 0 to 1 L/kg at solid/liquid ratio 200 g/L. The highest Kd values were attributed to a biological effect considering that they were obtained on non radiosterilised samples. The mean Kd values ranged from 0.2 to 0.5 as a function of the different experiments. A statistical error band was attributed to each Kd and was significantly lower than the Kd value itself (the error ranged from ± 0.02 for the lowest Kd values and ± 0.2 for the highest ones). However, considering equation 3, one can estimate that an analytical error of only 2 to 5 % on the concentration measurement leads to an analytical error band of the same extent as their measured Kd. This error calculation must include analytical errors on sampled volumes, on dilution and errors due to the measurement apparatus itself. Thus, we consider that the results of Devivier et al. are in full agreement with ours, giving evidence of an absence of significant iodide uptake on argilite samples in *in situ* conditions and in the absence of any microbial effect.

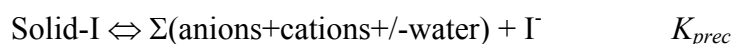
However, considering the extent of the error bands, a limited but existing iodide uptake can not be ruled out completely. Actually, diffusion experiments at trace radio-iodide

concentration clearly show that iodide is retarded compared to Cl^- in rock materials similar to the Callovian-Oxfordian one (Opalinus Clay, VAN LOON et al., 2003a; VAN LOON et al., 2003b). This could be due to different magnitudes in the effect of ion exclusion due to different ion size or it may be due to retention properties. Since diffusion experiment results are greatly influenced by any sorption process, a K_d value of $\sim 0.01\text{-}0.02$ L/kg could be extracted from these results. Equation 3 (analytical error band calculation) can be used to calculate the maximum extent of the error on iodide concentration measurement so that a given K_d value can be considered as representative, i.e. so that $\frac{\Delta K_d}{K_d} < 1$. For a K_d value of 0.02, this condition is fulfilled only with a concentration measurement precision of 0.2 %. Consequently, it is not realistic to obtain a reliable K_d value of the extent of 0.02 L/kg in our batch sorption experiments. In the following, we will consider that iodide uptake is not zero and we will discuss possible modalities with regard to the uptake as a function of the results given in the previous sections.

Modelling

Iodide uptake potential mechanisms

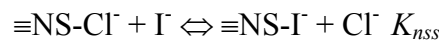
Iodide uptake in abiotic conditions encountered during the sorption and diffusion experiments could be due to solid (co)precipitation and/or surface sorption phenomena. Solid precipitation can be easily ruled out. Let us consider that an iodide solid precipitates during the experiment, with the following reaction:



where Solid-I represents one mole of the iodide containing solid, and $\Sigma(\text{anions+cations+/-water})$ is the anions, cations and water produced/consumed during the reaction. Given the experimental conditions (ion background at equilibrium with the solid), the concentration

terms relative to $\Sigma(\text{anions}+\text{cations}+\text{water})$ in the K_{prec} equation are constant. This has been further confirmed by the concentration measurements of cations and anions (data not shown). As a consequence, the I^- concentration should be kept constant, which is obviously not the case. This does rule out the precipitation control of iodine concentrations, but it does not rule out coprecipitation control, which would be compatible with various iodine concentrations. However, coprecipitation requires the active precipitation of an iodine free host phase. This has not been observed in our experiments. Hence, if it exists, iodide uptake must thereby be considered as a surface phenomenon.

Sorption processes are either specific or non-specific. The non-specific process is explored here first. Non-specific anion sorption processes are thought to take place at positively charged surfaces. Since Cl^- is the main anionic species in the porewater, one can write a non-specific sorption equation:



where $\equiv NS$ denotes a non specific site and with $K_{nss} = \frac{(\equiv NS - I^-) \times (Cl^-)}{(\equiv NS - Cl^-) \times (I^-)}$ where values in

brackets denote the activities of the species. Since the process is assumed to be non-specific, one assumes a K_{nss} value of 1. The activity of the surface species is taken as being equal to the ratio of the concentration of the given surface species compared to the sum of the concentrations of all surface species. We consider also that the surface coulombic term is here neglected owing to the fact that there is no change in ionic strength during the experiments and that this reaction does not change the surface charge. Then:

$$K_{nss} = \frac{[\equiv NS - I^-]}{([\equiv NS - I^-] + [\equiv NS - Cl^-]) \times [I^-]} \times \frac{([\equiv NS - I^-] + [\equiv NS - Cl^-]) \times [Cl^-]}{[\equiv NS - Cl^-]} = \frac{[\equiv NS - I^-] \times [Cl^-]}{[\equiv NS - Cl^-] \times [I^-]}$$

The amount of sites occupied by Cl^- is greater than that occupied by I^- , due to the high chloride concentration (0.05-0.08 mol/L) as compared to the iodine concentration and then:

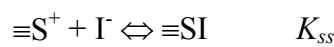
$$K_{nss} \approx \frac{[\equiv NS - I^-] \times [Cl^-]}{[\equiv NS_{tot}] \times [I^-]} = \frac{[Cl^-]}{[\equiv NS_{tot}]} \times K_d \times \rho$$

Hence:

$$[\equiv NS_{tot}] \approx \frac{[Cl^-]}{K_{nss}} \times K_d \times \rho$$

Considering a chloride concentration of 0.06 mol/L, a K_d value of 0.5 L/kg, a solid to liquid ratio of 0.2 kg/L and a K_{nss} value of 1, one obtains a total concentration of sites of 0.006 mol/L, i.e. a site amount of 0.03 mol/kg of solid. This anion exchange capacity is of the same order of magnitude as the cation exchange capacity of the solid (GAUCHER et al., 2004). Considering the nature of the solid, which is mainly composed of negatively charged clay minerals, this hypothesis may be ruled out as well. The same calculation can be performed for a K_d value of 0.02 L/kg and one obtains an anion exchange capacity of approximately 0.001 mol sites/kg. This result is more realistic but, in this case, the results presented in Figure 6 can not be modelled since the modelled K_d value remains below 0.01 L/kg. Furthermore, an anion exchange capacity of 0.001 mol sites/kg_{rock} should lead to a $^{36}Cl^-$ retardation in diffusion experiments due to an isotopic exchange between sorbed natural chloride and the radiotracer. Consequently, although it is not possible to rule out definitely non-specific interaction processes, we think it unlikely that they explain iodide vs. chloride retardation in diffusion experiments.

Specific sorption interactions are then hypothesised. Given that the experiments presented in this paper were performed in the same ionic background, iodide was the only reactant whose activity varied as a function of iodide concentration. Hence, the reaction can be written with the Langmuir notation:



where $\equiv S$ denotes a specific sorption site and with $K_{ss} = \frac{(\equiv SI)}{(\equiv S^+) \times (I^-)}$, neglecting the surface coulombic term.

Two scenarios can then be built up, (i) sites are not saturated with iodide and (ii) sites are saturated with iodide from the natural porewater. These two scenarios are discussed in the light of the present study and the Van Loon et al. iodide diffusion results (VAN LOON et al., 2003b).

Scenario I. Sorption sites are not saturated with porewater iodide

In this scenario, considering that the total amount of sites is far greater than the amount of iodide that is sorbed, the equation $K_{ss} = \frac{(\equiv SI)}{(\equiv S^+) \times (I^-)}$ resumes to $K_{ss} \times [\equiv S^+] = \frac{[\equiv SI]}{[I^-]} = C_{ste}$ and is strictly equivalent to a Kd approach if surface site concentrations are expressed in units of mol/kg. We used a porosity equal to that accessible to Cl^- (0.039) and a pore diffusion coefficient equal to $\frac{5.4 \times 10^{-13}}{0.039} = 1.38 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, since Van Loon et al. derived an effective diffusion coefficient of $5 \pm 0.4 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ for iodide with their Kd approach. One of the best fits was obtained with $K_{ss} \times [\equiv S^+] = 0.79$ (Figure 7). This value corresponds to a Kd value of approximately 0.05-0.1 L/kg, which is a little bit higher than that given by Van Loon et al. (0.01-0.02 L/kg). This is due to our use of their upper limit value for the diffusion coefficient.

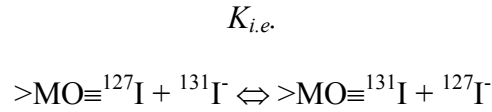
The main assumption in this modelling approach (the total amount of sites is far greater than the amount of iodide) leads to a lower limit for the total amount of accessible sites that is approximately ten times the tracer concentration, i.e. $[\equiv SI]_{\min} = 3.4 \times 10^{-10} \text{ mol/L}_{\text{porewater}}$, i.e. approximately $3 \times 10^{-11} \text{ mol/kg}_{\text{rock}}$ ($= 3.8 \times 10^{-6} \text{ ppm}$).

This model is in agreement with the diffusion results and most of the batch sorption experiments (i.e. a very low amount of sorption sites). However, the diffusion data are not very well reproduced (see Figure 7) and high K_d values at low solid to liquid content are not in agreement with this model.

Scenario II. Sorption sites are saturated with porewater iodide

If considering an iodide sorption site saturation in contact with the iodide concentration in porewater, it is then not possible to sorb more iodide by increasing its concentration in solution. The measured apparent K_d then remains negative or equal to 0, as shown by Figure 2. However, amongst literature data on iodide uptake, biotically or abiotically mediated, one notes that a major part of the uptake is reversible by adding stable $^{127}\text{I}^-$ to the suspension (MURAMATSU et al., 1990; KAPLAN et al., 2000). This desorption procedure provides evidence that part of the iodine on the solid should be isotopically exchangeable. Isotopic exchange phenomena could take place, explaining both the results shown in Figure 6 and the iodide vs. chloride retardation in diffusion experiments. The Callovian-Oxfordian argilite contains approximately 2-3 ppm of iodine that is probably bound to its organic matter (see natural iodine section). Based on $^{129}\text{I}/^{127}\text{I}$ ratio measurements in recent marine sediments, Moran et al. (MORAN et al., 1998) have suggested that marine iodine in sediment is present in two forms, a labile component that is isotopically homogeneous and a refractory component that is associated with fossil organic compounds such as kerogen. The Callovian-Oxfordian argilite has undergone a limited diagenesis and its organic matter is not exclusively kerogen (BREVET et al., 2005). Hence, it can be reasonably hypothesised (i) that part of this natural iodine is isotopically exchangeable and (ii) that the solution accessibility to this isotopically exchangeable proportion of natural iodide increases when the liquid to solid ratio increases. Then, one can model the data presented in Figure 5 and Figure 6. Calculations were performed with PHREEQC2 (PARKHURST and APPELO, 1999,

<http://www.geo.vu.nl/users/posv/phreeqc.html>). The following isotopic exchange was considered:



where $>\text{MO}\equiv\text{I}$ represents an isotopic exchange site for iodine and with $\log K_{i.e.} = 0$. The initial natural solute iodide concentration was set at 7×10^{-2} and $35 \times 10^{-2} \mu\text{mol/L}$ in the 10 and 50 g/L experiments respectively, corresponding to a pore concentration of $10 \mu\text{mol/L}$. Subsequently, the ^{131}I spiked ^{127}I solution was introduced and the isotopic system was allowed to equilibrate thanks to the isotopic calculation facilities of PHREEQC2. The results of this calculation are shown in Figure 8. The x abscissa accounts only for the added iodine and not for the total iodine and then it is labelled as an apparent concentration. For the 10 g/L experiment, the amount of isotopic exchangeable natural iodine on the solid has been set at 0.1 ppm (i.e. in $\text{mg I/kg}_{\text{solid}}$), whereas for the 50 g/L experiment, the amount of isotopic exchangeable natural iodine has been set at 0.025 ppm. If the isotopic exchange hypothesis were further confirmed, these amounts of isotopic exchangeable iodine would represent from 0.8 to 3 % of the total iodine of the samples.

This isotopic exchange model has also been tested on Van Loon et al. iodide diffusion data (VAN LOON et al., 2003b). The $^{127}\text{I}^-$ content of the solution they used in their experiments has not been reported. Although no stable iodide was added voluntarily to the solutions, one must take into consideration the presence of iodide impurities in the salts used to prepare the synthetic porewater solutions. Indeed, NaCl high purity grade salts contain a maximum amount of 0.001 % (by weight) of iodide. Given the high normality of the synthetic porewater ($[\text{Na}^+] = 0.15 \text{ mol/L}$), salt impurities dissolution would lead to a maximum stable iodide concentration of $7 \times 10^{-7} \text{ mol/L}$. Even with a thousand times less ^{127}I impurities in the

solution, the natural iodide concentration is greater than the tracer concentration (3.4×10^{-11} mol/L). As a consequence, several simulations were carried out varying this ^{127}I impurity concentration from 10^{-10} to 10^{-7} mol/L. A fit of the data, as good as that obtained with the Kd model (compare Figure 7 and Figure 9), was obtained using a porosity of 0.039 (i.e. identical to the Cl^- one), a pore diffusion coefficient of $1.35 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ and a total amount of sites given by the relationship: $[>\text{MO}\equiv\text{I}]_{\text{tot}} = 0.6 \times [\text{I}]_{\text{impurities}}$. The maximum amount of sites available for isotopic exchange in these diffusion experiments is then approximately $\sim 0.6 \times 10^{-7} \text{ mol/L}_{\text{porewater}}$, i.e. $\sim 0.6 \times 10^{-8} \text{ mol/kg}_{\text{rock}}$ or $7.6 \times 10^{-4} \text{ ppm I}$. The minimum amount of sites can be estimated to be 1000 times lower, i.e. $7.6 \times 10^{-7} \text{ ppm I}$. If compared to the values obtained in batch sorption, this range of values of available sites for isotopic exchange is in agreement with a decrease in site availability and an increase in the compaction of the system. On the one hand, sites available for isotopic exchange must be less accessible in the compacted argillite than in the suspension. On the other hand, the longer contact time between the solution and the solid during the diffusion experiment must further the isotopic exchange process. Indeed, if it exists, the isotopic exchange reaction is certainly a kinetically driven phenomenon. The iodide through-diffusion data can be fitted by considering first order kinetics for the isotopic exchange reactions:



and



Figure 10 shows the result of a diffusion simulation using the parameters: porosity = 0.039 (Van Loon et al. value 0.039 ± 0.002) and pore diffusion coefficient = $1.38 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$. The ^{127}I impurities concentration is considered to be 10^{-9} mol/L , the amount of sites $8 \times 10^{-10} \text{ mol/L}$ and the isotopic exchange kinetic rate $k_{\text{exch}} = 0.7 \times 10^{-6} \text{ mol}^{-1} \text{ s}^{-1}$.

Conclusions

It has been demonstrated in this paper that iodide uptake by Callovian-Oxfordian samples is very limited due to the mineralogy, the redox conditions and the absence of microbial activity prevailing in the clay stone formation. It is then not possible to reactivate in a short time scale the process that has led to the past accumulation of iodine in the formation up to 3 ppm.

The extent of iodide uptake is different for stable and radioactive iodide. Radioactive iodide is significantly sorbed at low concentration in batch experiments or in diffusion experiments whereas the formation is able to leach stable iodide instead of sorbing it. This behaviour is in agreement with a possible isotopic exchange between the iodide in solution and the proportion of labile iodine in the solid. The modelling of radioactive iodide diffusion experiments can be performed successfully by using such an isotopic exchange model. The quantification of the proportion of labile iodine in the formation would allow the efficiency/inefficiency of isotopic exchange on radio-iodide migration throughout the Callovian-Oxfordian formation to be assessed and predicted.

The potential retention of an I^- radioactive tracer can be calculated as a function of its pore concentration and the amount of sites available for isotopic exchange expressed as the ratio of the total iodine content of the argilite. This calculation was performed using PHREEQC2, by considering a 2.5 ppm total iodine content in the formation (Table 2), together with a 3 $\mu\text{mol/L}$ natural iodine pore concentration and with a 0.07 L/kg water content. The results are shown in Figure 11. I^- radiotracer potential retention becomes significant only for amounts of isotopic exchange sites above 0.1 % of the total iodine of the formation. This amount of sites is far greater than the amount assumed in this study, based on iodide diffusion experiments. However, it lies within the range given in iodide batch sorption experiments and it must be remembered that the isotopic exchange process is certainly kinetically driven. To date and to our knowledge, no radioactive tracer adsorption/diffusion experiments over a long time scale

(more than a year) and on natural argilite have been conducted and published. Consequently, it is difficult to estimate the real amount of sites that will participate in the isotopic exchange in the time scales considered for the simulation of a radwaste disposal. Further experiments are consequently needed to make such estimations.

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Table 1. Mineral composition of K100 and K119 argilite samples (after BLANC and GAUCHER, 2003). "tr" indicates that traces were identified with SEM or TEM analysis.

Mineral phases		Amount (% mass)	
		K100	K119
Carbonates	Calcite	22	13
	Aragonite	0	tr?
	Ankerite	6	6
	Dolomite	4	6
	Total	32	25
Silicates (excepting Phyllosilicate)	Quartz	44	21
	K-feldspar	0.5	4.0
	Plagioclase	0	2.0
	Total	44.5	27
Phyllosilicate	Biotite	tr	tr
	Phengite	tr	tr
	Illite	3	20
	Illite/Smectite IS R0	13	23
	Chlorite	0	2
	Biotite/vermiculite	tr?	tr?
	Total	16	45
Others	Pyrite	0.6	1.7
	Pyrrhotite	tr	0
	Rutile	0.4	1.4
	Celestite	5.8	0.7

Table 2. Natural iodine content in the Callovian-Oxfordian formation.

Borehole	Sample reference	Depth (m) *	Total iodine content (mg/kg _{solid})	Leached iodine content (mg/kg _{solid})	Total water content (%)	Calculated iodine in porewater (μmol/L) ‡
EST205	EST05441	422.9	2	< 0.02 **	4.8 **	< 3.2
	EST05445 - K100	424.2	< 1 - 2 **	0.11	5.7	15.3
	EST05448	426.4	2	< 0.02 **	6.1 **	< 2.6
	EST05460	429.6	2	0.1 **	1.6 **	50.7
	EST05474	432.3	2	< 0.02 **	8.7 **	< 1.8
	EST05486	435.9	2	0.04 **	6.0 **	5.2
	EST05492	438.4	2	< 0.02 **	6.1 **	< 2.6
	EST05505	442.1	2	0.04 **	9.0 **	3.5
	EST05511	444.1	2	0.04 **	8.2 **	3.8
	EST05523	447	2	0.02 **	1.5 **	10.7
	EST05533	450.7	2	0.03 **	6.6 **	3.6
	EST05554	452	2	< 0.02 **	8.6 **	< 1.8
	EST05546	453.7	2	0.02 **	7.4 **	2.1
	EST05557	456.6	2	< 0.02 **	7.5 **	< 2.2
	EST05573	459.5	2	< 0.02 **	7.1 **	< 2.2
	EST05584	463.7	2	< 0.02 **	8.7 **	< 1.8
	EST05592	465.6	2	< 0.02 **	6.8 **	< 2.4
	EST05602	467.2	2	< 0.02 **	7.4 **	< 2.2
	EST05620	471	3	< 0.02 **	7.8 **	< 2.0
	EST05632	474.9	3	< 0.02 **	8.6 **	< 1.8
	EST05641 - K119	477.2	3	0.07	8.3	6.7
	EST05646	478.2	3	< 0.02 **	7.6 **	< 2.0
	EST05653	479.8	2	< 0.02 **	7.8 **	< 2.0
	EST05666	483.3	2	< 0.02 **	8.3 **	< 1.8
	EST05681	486	2	< 0.02 **	8.1 **	< 2.0
	EST05688	489.1	2	0.04 **	8.1 **	3.9
	EST05703	493.6	2	< 0.02 **	6.5 **	< 2.4
	EST05712	495.6	3	0.02 **	7.2 **	2.2
	EST05724	498.6	3	< 0.02 **	7.3 **	< 2.2
	EST05738	501.6	2	< 0.02 **	7.4 **	< 2.2
	EST05748	504	3	< 0.02 **	7.4 **	< 2.2
EST312	EST312	463.5	1.9	0.26	6.2	33.5
	EST312	496.8	1.8	0.47	6.0	61.8
EST322	EST322	495.3	1.0	0.12	5.4	17.2
EST212	EST212	532.1	< 1	0.16	5.2	24.6
PPA	PPA	425.1	< 1	0.14	13.7	7.9

* The altitude of the core EST205 surface is 0 m. All other core sample altitudes are given relative to this reference.

‡ Calculation based on the total water content.

** Data from GAUCHER et al., 2004 (EST205).

** Depending on the sampling localisation on the core.

Figure captions

Figure 1. Result of the simulation of the $^{36}\text{Cl}^-$ diffusion experiment by VAN LOON et al., 2003b, using the PHAST coupled geochemistry transport code. $J(L, t)$ is the $^{36}\text{Cl}^-$ flux at the low concentration end of the sample (open circles). Q_{tot} is the total diffused activity (open squares). Diffusion parameters are: porosity = 0.039 (Van Loon et al. value 0.039 ± 0.002), pore diffusion coefficient = $2.14 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, i.e. effective diffusion coefficient $D_e = 8.3 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ (Van Loon et al. value $7.9 \pm 0.4 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$).

Figure 2. Iodide sorption experiment results on K100 (left) and K119 (right) samples at 25°C and after 24 hours equilibrium, using non-radioactive iodide. Solid content: 200 g/L. The solid line is the modelling result by considering a K_d value of 0, and an iodide porewater concentration of 10 $\mu\text{mol/L}$ and 20 $\mu\text{mol/L}$ for K100 and K119 samples respectively.

Figure 3. Iodide sorption kinetic experiment results on K100 (open circles) and K119 (black circles) samples at 25°C, using non-radioactive iodide. Solid content: 200 g/L. Added iodide concentration: 4.8 $\mu\text{mol/L}$.

Figure 4. Iodide sorption experiment results on 120°C heat treated K119 samples at 25°C and after 24 hours equilibrium, using non-radioactive iodide. Solid content: 200 g/L.

Figure 5. Iodide sorption experiment results on K100 (left) and K119 (right) samples at 25°C and after 48 hours equilibrium, using radioactive iodide tracers. Solid content: 50 g/L.

Figure 6. Effect of solid to liquid ratio on iodide sorption experiment results on K100 (open circles) and K119 (black circles) samples at 25°C and after 48 hours equilibrium, using radioactive iodide tracers.

Figure 7. Result of the simulation of $^{125}\text{I}^-$ diffusion experiment by VAN LOON et al., 2003b, using the PHAST coupled geochemistry transport code and a specific sorption site model. $J(L, t)$ is the $^{125}\text{I}^-$ flux at the low concentration end of the sample (open circles). Q_{tot} is the total diffused activity (open squares). Diffusion parameters are: porosity = 0.039, pore diffusion coefficient = $1.38 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ and $K_{ss} \times [\equiv \text{S}^+] = 0.79$.

Figure 8. Modelling curves of the iodide sorption experiment results on K100 (open circles) and K119 (closed circles) samples at 25°C and after 48 hours equilibrium, using radioactive iodide tracers and with solid contents of 50 g/L (dashed line) and 10 g/L (continuous line).

Figure 9. Result of the simulation of the $^{125}\text{I}^-$ diffusion experiment by VAN LOON et al., 2003b, using the PHAST coupled geochemistry transport code and an isotopic exchange model. $J(L, t)$ is the $^{125}\text{I}^-$ flux at the low concentration end of the sample (open circles). Q_{tot} is the total diffused activity (open squares). Diffusion parameters are: porosity = 0.039, pore diffusion coefficient = $1.38 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ and the relationship $[>\text{MO}\equiv\text{I}]_{\text{tot}} = 0.6 \times [\text{I}]_{\text{impurities}}$.

Figure 10. Result of the simulation of the $^{125}\text{I}^-$ diffusion experiment by VAN LOON et al., 2003b, using the PHAST coupled geochemistry transport code and a kinetic isotopic

exchange model. $J(L,t)$ is the $^{125}\text{I}^-$ flux at the low concentration end of the sample (open circles). Q_{tot} is the total diffused activity (open squares). Diffusion parameters are: porosity = 0.039, pore diffusion coefficient = $1.38 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$. The ^{127}I impurities concentration is considered to be 10^{-9} mol/L , the amount of sites $8 \times 10^{-10} \text{ mol/L}$ and the isotopic exchange kinetic rate $k_{\text{ech}} = 0.7 \times 10^{-6} \text{ mol}^{-1} \text{ s}^{-1}$.

Figure 11. Potential $^{131,125} \text{ or } ^{129}\text{I}^-$ retention as a function of the fraction of natural I available for isotopic exchange. Results are expressed in terms of tracer sorbed fraction (of total tracer concentration) as a function of concentration in solution. Calculation parameters: water content of the formation: 0.07 L/kg; natural iodine pore concentration: 3 $\mu\text{mol/L}$; total iodine content in the formation: 2.5 ppm.

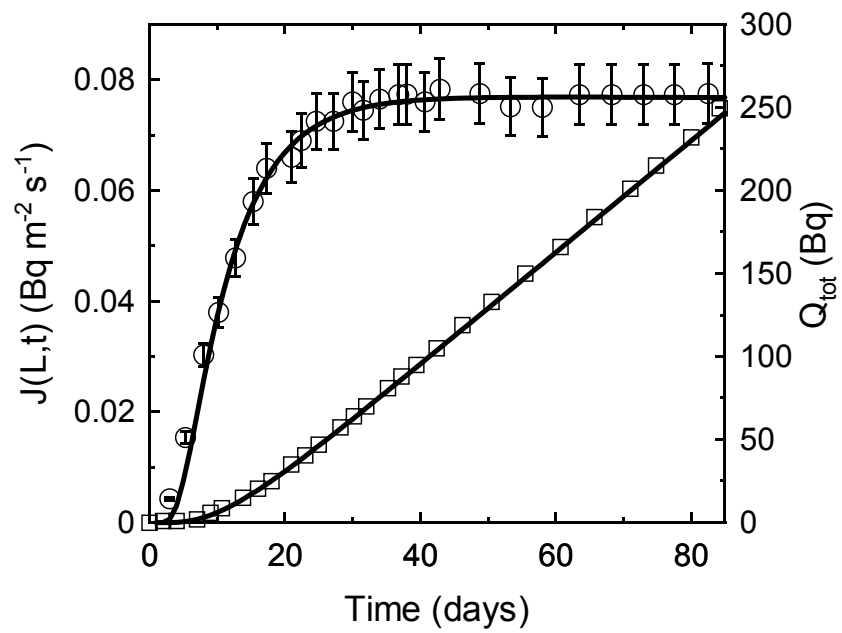


Figure 1

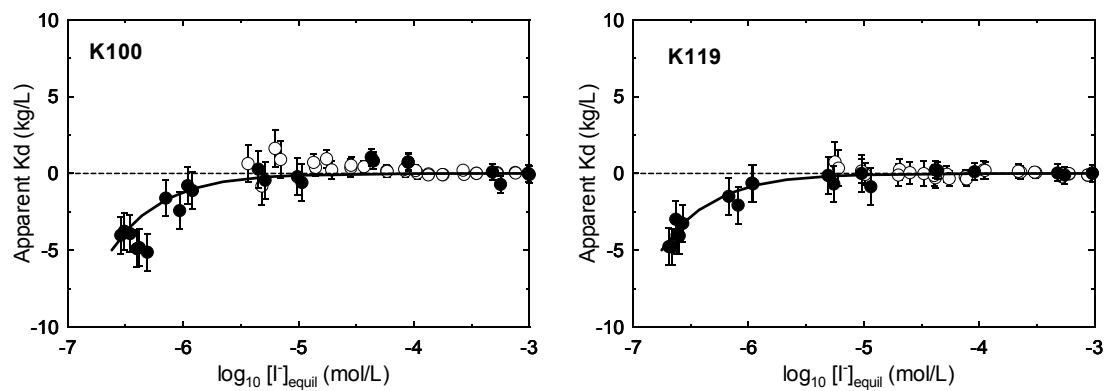


Figure 2

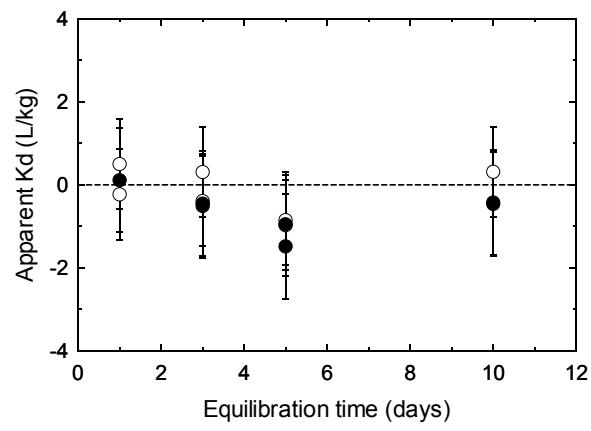


Figure 3

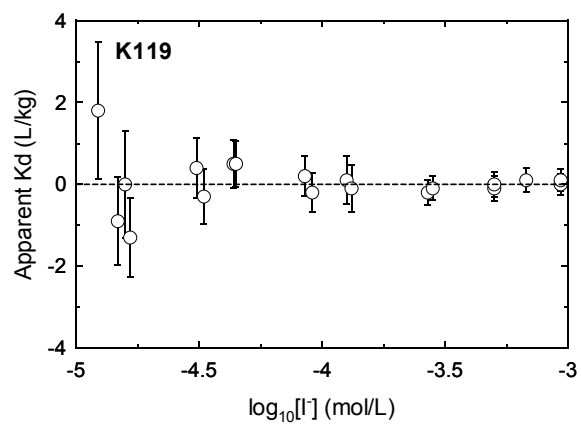


Figure 4

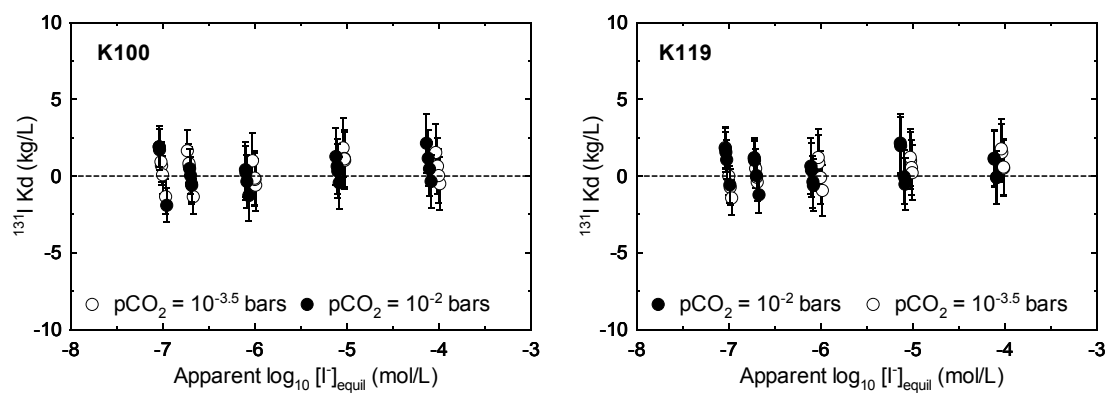


Figure 5

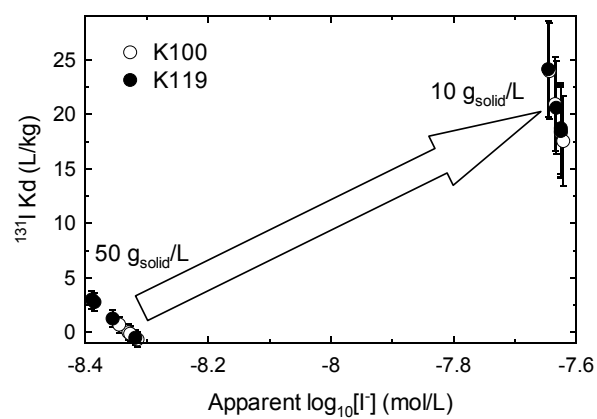


Figure 6

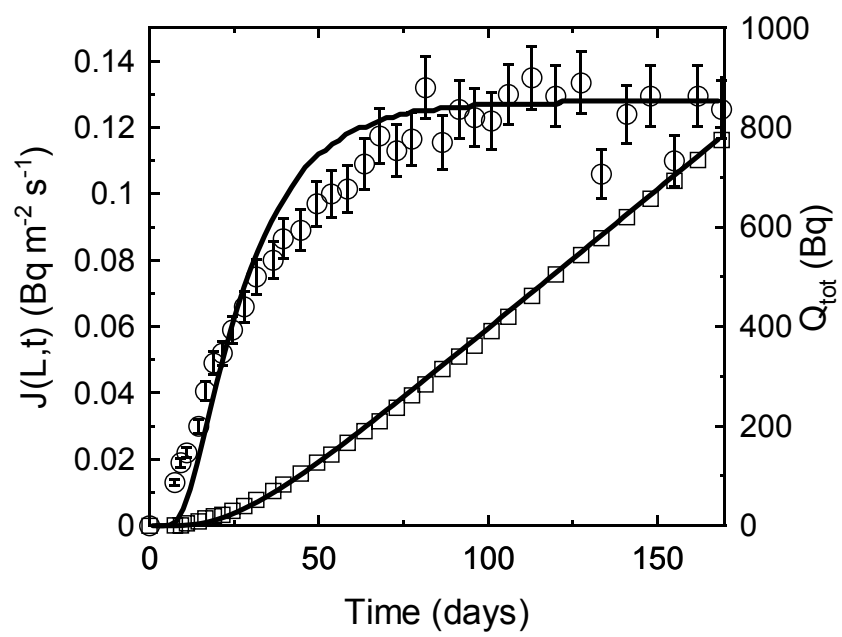


Figure 7

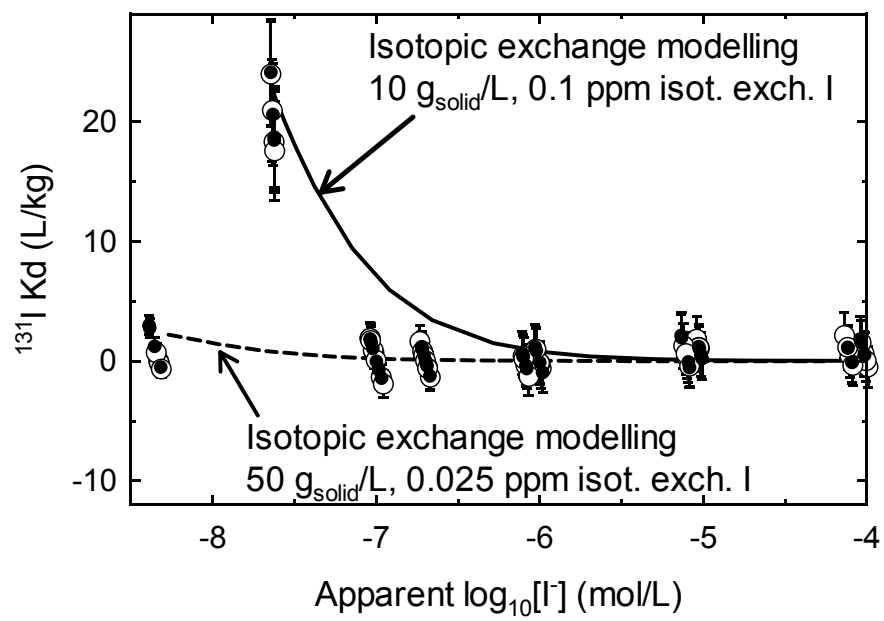


Figure 8

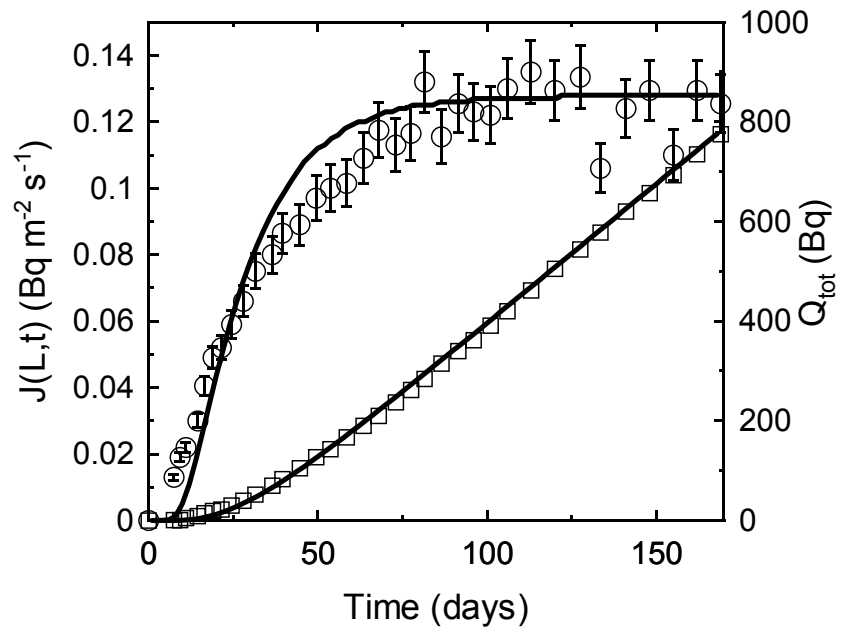


Figure 9

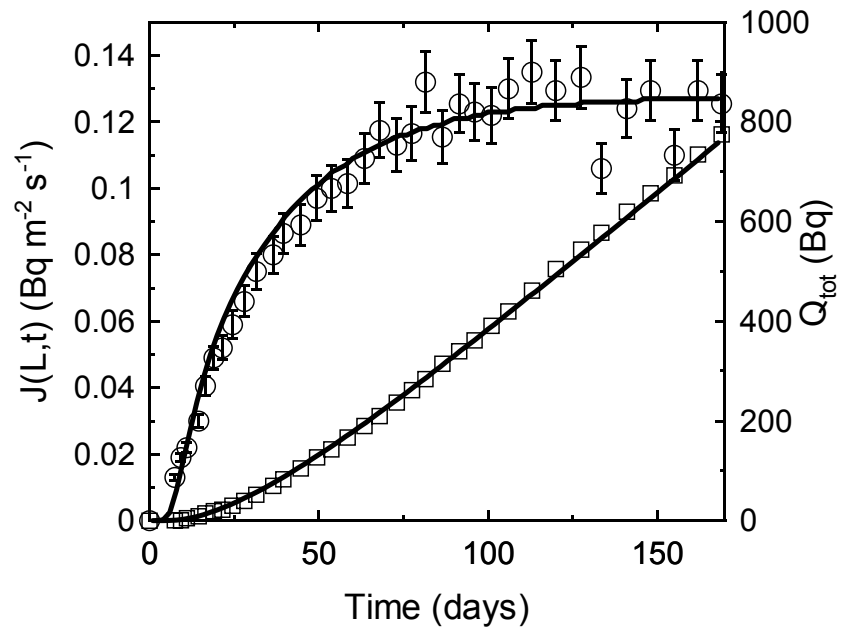


Figure 10

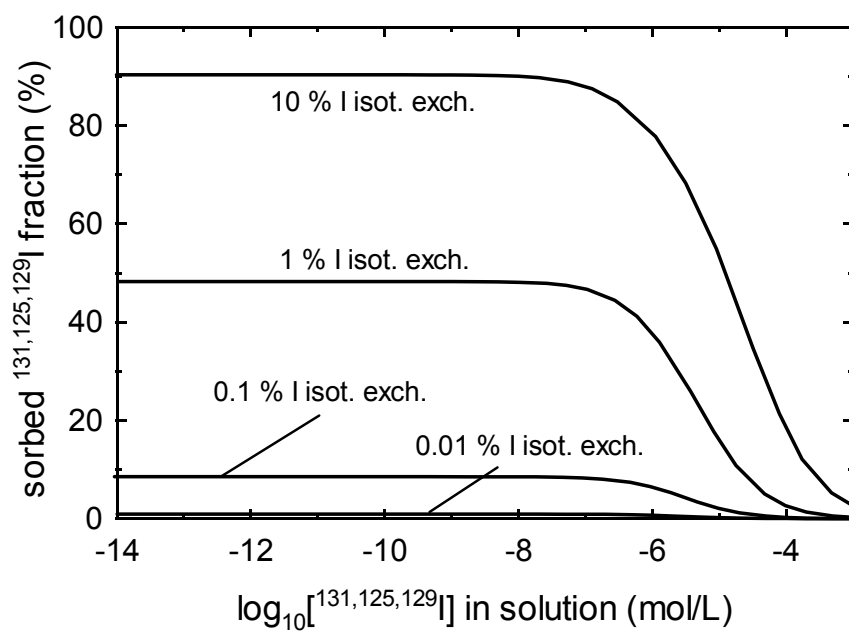


Figure 11