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1 **HTO and Selenate Diffusion Through Compacted Na-, Na-**
2 **Ca-, and Ca-Montmorillonite**

3
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10

11

12 Abstract

13 Radionuclide transport in smectite clay barrier systems used for nuclear waste disposal is controlled by
14 diffusion, with adsorption significantly retarding transport rates. While a relatively minor component of
15 spent nuclear fuel, ^{79}Se is a major driver of the safety case for spent fuel disposal due to its long half-life
16 (3.3×10^5 yr) and its low adsorption to clay ($K_D < 10$ L/kg), thus a thorough understanding of Se diffusion
17 through clay is critical for understanding the long-term safety of spent fuel disposal systems. Through-
18 diffusion experiments with tritiated water (HTO, conservative tracer) and Se(VI) were conducted with a
19 well-characterized, purified montmorillonite source clay (SWy-2) under a constant ionic strength (0.1 M)
20 and three different electrolyte compositions: Na^+ , Ca^{2+} , and a Na^+ - Ca^{2+} mixture at pH 6.5 in order to
21 probe the effects of electrolyte composition and interlayer cation composition on clay microstructure,
22 Se(VI) aqueous speciation, and ultimately diffusion. The results were modeled using a reactive transport
23 modeling approach to determine values of porosity (ϵ), D_e (effective diffusion coefficient), and K_D
24 (distribution coefficient for adsorption). HTO diffusive flux was higher in Ca-montmorillonite ($D_e = 1.68 \times$
25 $10^{-10} \text{ m}^2 \text{ s}^{-1}$) compared to Na-montmorillonite ($D_e = 7.83 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$). This increase in flux is likely due
26 to a greater degree of clay layer stacking in the presence of Ca^{2+} compared to Na^+ , which leads to larger
27 inter-particle pores. Overall, the Se(VI) flux was much lower than the HTO flux due to anion exclusion,
28 with Se(VI) flux following the order Ca ($D_e = 1.03 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$) > Na-Ca ($D_e = 2.12 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$) > Na
29 ($D_e = 1.28 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$). These differences in Se(VI) flux are due to a combination of factors, including
30 (1) larger accessible porosity in Ca-montmorillonite due to clay layer stacking and smaller electrostatic
31 effects compared to Na-montmorillonite, (2) larger accessible porosity for neutral-charge CaSeO_4 species
32 which makes up 32% of aqueous Se(VI) in the pure Ca system, and (3) possibly higher Se(VI) adsorption
33 for Ca-montmorillonite. Through a combination of experimental and modeling work, this study highlights
34 the compounding effects that electrolyte and counterion compositions can have on radionuclide transport
35 through clay. Diffusion models that neglect these effects are not transferable from laboratory
36 experimental conditions to *in situ* repository conditions.

37

38 Keywords

39 Selenium diffusion; radioactive waste; interlayer cation; engineered barriers; anion exclusion

40

41

42 1. Introduction

43 Smectite clays, 2:1 layer-type phyllosilicate minerals, are the primary clay minerals found in
44 bentonite and an important component of engineered barrier systems used for geologic storage of
45 radioactive waste. Long-term nuclear waste disposal repositories must be capable of isolating
46 radioactive waste over the time scales necessary for the decay of long-lived radioactive isotopes
47 ($> 10^6$ years). Smectite clays are good barriers for radioactive waste due to their swelling
48 capacity, ability to seal cracks, low hydraulic conductivity, and their high adsorption capacity for
49 radionuclides. Montmorillonite is a common smectite mineral which has been widely studied. It
50 has a large specific surface area ($\sim 750 \text{ m}^2/\text{g}$), cation exchange capacity ($\sim 1 \text{ mol}_c/\text{kg}$), and
51 strongly-sorbing surface complexation sites on clay edge surfaces.

52 Natural smectites contain interlayer cations, including primarily Na^+ , Ca^{2+} , and Mg^{2+} , which
53 balance the negative permanent charge arising from isomorphic substitution in the phyllosilicate
54 structure. The interlayer cation composition of smectite clays, including montmorillonite, affects
55 the hydration and swelling properties of the clays (Bleam, 1990; Honorio et al., 2017; Laird and
56 Shang, 1997; Salles et al., 2013; Subramanian and Nielsen Lammers, 2022; Teich-McGoldrick et
57 al., 2015). For example, the presence of Na^+ in the interlayer leads to a higher degree of swelling
58 compared to Ca^{2+} due to differences in the sizes and hydration energies of the cations. Natural
59 smectites can have a wide range of interlayer cation compositions; Missana et al. (2018) studied
60 bentonites currently under investigation for use in nuclear waste repositories and found Na^+
61 comprised <1 to 90% of the interlayer cation composition, with Ca^{2+} and Mg^{2+} making up
62 the bulk of the remainder. Groundwater intrusion into bentonite barriers can also alter the
63 interlayer cation composition through cation exchange.

64 In compacted clay, solute transport is controlled by diffusion, and adsorption of solutes to the
65 clay can significantly retard transport. While uranium is the primary constituent of radioactive
66 waste, selenium (^{79}Se) is a major driver of the safety case for nuclear waste disposal due to its
67 long half-life (3.3×10^5 yr) and presence as relatively mobile anionic species under a range of
68 chemical conditions (e.g., HSe^- , SeO_3^{2-} , SeO_4^{2-}). Se redox chemistry is complex, with oxidation
69 states ranging from -II to +VI over environmentally relevant conditions. While Se(-II) and Se(0)
70 are relatively immobile due to the formation of low solubility precipitates, Se(IV) and Se(VI)
71 exist as the oxyanions selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) and are highly mobile in water due

72 to their high solubility. During deep geologic disposal of nuclear waste, the near field
73 environment is characterized by a relatively short oxic period, followed by anoxic conditions.
74 However, there is significant uncertainty and range in the Eh values expected, which will depend
75 on numerous factors including the host rock type, bentonite composition, and waste canister
76 corrosion. This makes it difficult to predict the speciation of Se in engineered barriers, however
77 selenite and selenate are considered to be the dominant Se aqueous species released during
78 oxidation of spent nuclear fuel (Ma et al, 2019; Chen et al., 1999). Se adsorption to clay minerals
79 is quite low compared to other important radionuclides such as U. K_D values for selenite
80 adsorption to smectite are in the range of 1-10 L/kg (Missana et al., 2009; Montavon et al., 2009)
81 compared to values up to 10^4 for U(VI) (Tournassat et al., 2018). Selenite and selenate
82 adsorption to the clay minerals kaolinite and Ca-montmorillonite were studied by Bar-Yosef and
83 Meek (1987) over the pH range 4-8. Both selenite and selenate adsorption decreased with
84 increasing pH, with very low or negligible adsorption above pH 8. Selenate adsorption to
85 kaolinite was lower than selenite adsorption (Bar-Yosef and Meek, 1987).

86 Selenite diffusion through bentonite has been investigated in several studies (García-Gutiérrez et
87 al., 2001; Idemitsu et al., 2016; Wang et al., 2016; Wu et al., 2017). Idemitsu et al. (2016)
88 measured apparent diffusion coefficient (D_a) values of 2.5×10^{-11} to 1.9×10^{-13} m²/s over a range
89 of dry bulk densities (0.8-1.6 kg/L), ionic strengths (0.01-1.0 M NaCl), and temperatures (10-
90 55°C) for purified bentonite consisting of 99% montmorillonite. Measured D_a values for bulk
91 bentonite (*i.e.*, with lower smectite content) under similar conditions are 1-2 orders of magnitude
92 higher (Sato et al., 1995; Wu et al., 2014). Due to the lower adsorption of selenate compared to
93 selenite, selenate D_a values are expected to be even higher than observed for selenite, although
94 we could find no studies on selenate diffusion through bentonite in the literature.

95 In this paper, we present experimental and modeling results from tritiated water (HTO) and
96 Se(VI) through-diffusion experiments using a well-characterized, purified montmorillonite
97 source clay (SWy-2) with different interlayer cation compositions (Na^+ and Ca^{2+}). Previous
98 studies have observed higher diffusive flux of HTO (González Sánchez et al., 2008) and ReO_4^-
99 (Wu et al., 2018) through Ca-montmorillonite compared to Na-montmorillonite. Selenate, with a
100 charge of -2 and minimal adsorption, provides an opportunity to further probe anion diffusion
101 (*i.e.*, for divalent species) in Na and Ca-montmorillonite systems and provide direct information

102 on ^{79}Se transport through clay barriers. Experiments were conducted under a single ionic strength
103 (0.1 M) and three different electrolyte compositions representing pure Na^+ , pure Ca^{2+} , and a Na^+ -
104 Ca^{2+} mixture in order to probe the effects of electrolyte composition and interlayer cation
105 composition on clay microstructure, Se(VI) aqueous speciation, and ultimately diffusion.

106 **2. Materials and Methods**

107 **2.1 Clay Samples**

108 Selenium diffusion experiments were conducted using a well-characterized montmorillonite
109 source clay (SWy-2) obtained from the Clay Minerals Society. The montmorillonite was purified
110 in order to remove minor impurities (quartz, feldspars, and calcite). The purification procedure
111 was adapted from Tinnacher et al. (2016). The procedure included the following major steps: (1)
112 dialysis against sodium acetate at pH 5 for carbonate mineral dissolution, (2) dialysis against
113 NaCl to remove acetate and complete Na -saturation, (3) dialysis against water to remove excess
114 salts, and (4) centrifugation to remove quartz and feldspar particles greater than $2\ \mu\text{m}$.

115 Montmorillonite (50 g) was suspended in 1 L of 1 M sodium acetate solution buffered at pH 5
116 with acetic acid, placed into pre-rinsed dialysis tubing (SpectraPor7, 8 kDa), and dialyzed against
117 acetate buffer for 1 week, changing dialysis solution daily. The acetate buffer dialysis solution
118 was then replaced with 1 M NaCl (dialyzed for 3 days), then with MilliQ water (dialyzed for two
119 weeks), again changing dialysis solution daily. The clay suspensions were then transferred into
120 plastic bottles and diluted and dispersed in MilliQ water to reach a clay concentration of
121 approximately 15 g/L, and centrifuged at $1000 \times g$ for 7 minutes. This centrifugation speed and
122 time was deemed sufficient to remove all particles $> 2\ \mu\text{m}$ as calculated from Stoke's Law. The
123 replicate $< 2\ \mu\text{m}$ clay fractions were then combined into a glass beaker, dried at 60°C and ground
124 in ball mill with tungsten carbide balls.

125 In order to maintain constant aqueous porewater chemical conditions and interlayer cation
126 composition during the diffusion experiments, purified montmorillonite was pre-equilibrated
127 with the appropriate background electrolyte prior to packing in diffusion cells. 2 g of purified
128 clay was suspended in 100 mL of electrolyte solution and the clay suspension was transferred to
129 pre-rinsed dialysis tubing (SpectraPor7, 8 kDa). Clay samples were dialyzed against 1 L of
130 background electrolyte for 1.5 weeks, changing dialysis solution at least 3 times and manually

131 adjusting pH daily. Once the pH remained between 6.45-6.55 within 24 hours, the background
132 electrolyte solution was replaced with MilliQ water, and dialysis was continued for 5 days,
133 changing the MilliQ water daily. After dialysis was complete, the clay suspension was
134 transferred to 40 mL polycarbonate centrifuge tubes and centrifuged at $39\,000 \times g$ for 20
135 minutes. The supernatant was removed and the clay was dried at 60°C and ground in ball mill
136 with tungsten carbide balls and stored at room temperature prior to packing the cells. At the time
137 of packing, a subsample of each clay was dried at 150°C to determine the moisture content.

138 The cation exchange capacity (CEC) and exchangeable cation composition was measured using
139 the hexamine cobalt(III) chloride method (Hadi et al., 2013). Triplicate samples of 50 mg dry
140 clay were weighed into centrifuge tubes and 10 mL of 15 mM hexamine cobalt(III) chloride
141 solution was added. Samples were mixed on an end-over-end sample rotator for 2 hours, then
142 centrifuged at $39,000 \times g$. Solution samples were analyzed for major cations (Ca, Mg, K, and Na)
143 by ICP-MS and the cation exchange capacity was calculated from the sum of cations released
144 from the hexamine cobalt solution corrected for any soluble salts released during the water
145 extracts. CEC is expressed as mmol_c/g (mmol of charge per gram dry clay) and cation
146 composition is expressed as the charge fraction for each cation.

147 **2.2 Characterization of Filters**

148 In order to accurately model diffusion through clay, the diffusion properties of the filters used in
149 the diffusion cell must be explicitly considered. Therefore, diffusive properties of the filters were
150 measured using custom-built filter diffusion cells based on a modified design of Aldaba et al.
151 (2014). The cells consisted of two polycarbonate reservoirs with a filter connecting the two
152 reservoirs. The filter is held in place with O-rings on each side and the two reservoirs are held
153 together in a base plate. A one-hole silicone stopper was fitted in the top of each reservoir with a
154 conductivity probe inserted through the hole to monitor solute diffusion. In addition, a small
155 needle (22 G) was inserted through each stopper to allow venting and pressure equalization with
156 the atmosphere. Without this venting needle, a small pressure differential can develop between
157 the two cells due to slight differences in stopper insertion, causing water to flow between the two
158 cells. Filters were made of PEEK with a PCTFE ring (IDEX # OC-815). The filters had an
159 overall diameter of 0.95 cm, filter diameter of 0.74 cm, thickness of 0.16 cm, $5\ \mu\text{m}$ pore size, and
160 porosity of 0.26 according to the manufacturer.

161 The diffusion of sodium chloride was measured using this experimental setup in five replicate
 162 experiments. The filter was soaked in MilliQ water to remove air bubbles. 45 mL of MilliQ
 163 water was then added to each reservoir and allowed to equilibrate for at least 3 h. The low- and
 164 high-concentration reservoirs were then spiked with 5 mL MilliQ water or 1 M NaCl,
 165 respectively to start the experiment. This resulted in a concentration of 0.1 M NaCl in the high-
 166 concentration reservoir. Both reservoirs were stirred constantly throughout the experiment. The
 167 electrical conductivity of each reservoir was monitored with a conductivity probe and
 168 automatically logged every 30 min. The conductivity probes were calibrated with known
 169 concentrations of NaCl. During one experiment, 0.125 mL subsamples from each reservoir were
 170 collected and analyzed for Na by ICP-MS in order to verify that the conductivity measurements
 171 were accurately representing Na concentration. The measured Na concentrations agreed within
 172 3% for the two methods.

173 **2.3 Diffusion coefficient of filters**

174 The cumulative mass (mol) of NaCl in the low-concentration reservoir was plotted over time (s).
 175 This results in a pseudo-linear breakthrough curve for the first ~100 h during which the
 176 concentration of NaCl in the high-concentration reservoir did not change significantly. The curve
 177 was fit with a linear regression and the effective diffusion coefficient (D_e) was determined using
 178 the slope (a) from the equation given by

$$D_e = \frac{a L}{A C_0} \quad \text{Equation 1}$$

179 where L is the thickness of the filter, A is the cross-sectional area of the filter, and C_0 is the initial
 180 concentration in the high-concentration reservoir.

181 Effective diffusion coefficients measured for filters depend on the characteristics of both the
 182 filter and the solute, according to:

$$D_e = \frac{\varepsilon}{G} D_0 = \tau \varepsilon D_0 \quad \text{Equation 2}$$

183

184 where D_0 is the bulk diffusion coefficient of a solute in water, while G (or $1/\tau$) is a geometric
 185 factor that accounts for the geometry of the filter pore network. τ is often referred to as the

186 tortuosity although it lumps together the true tortuosity and the constrictivity of the material. In
 187 this filter diffusion experiment D_0 refers to the co-diffusion of Na^+ and Cl^- ($1.61 \times 10^{-9} \text{ m}^2\text{s}^{-1}$),
 188 which is calculated from the diffusion coefficients of Na^+ and Cl^- , (1.33×10^{-9} and 2.03×10^{-9} ,
 189 respectively at 25°C ; Li and Gregory (1974) according to Cussler (2009) (see details in the SI).
 190 Diffusion coefficients of aqueous species were calculated using the filter parameters and the
 191 known D_0 values for those aqueous species. D_0 values at 25°C for HTO and SeO_4^{2-} were taken at
 192 $2.30 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $9.46 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ respectively.

193 2.4 Diffusion Experiments

194 Through-diffusion experiments were conducted with purified, pre-equilibrated montmorillonite
 195 at a dry bulk density (ρ_d) of approximately 1.3 kg L^{-1} corresponding to a total porosity (ε) of
 196 approximately 0.5 according to:

$$\varepsilon = 1 - \frac{\rho_d}{\rho_g} \quad \text{Equation 3}$$

197
 198 where ρ_g is the crystal density of clay mineral layers (*i.e.*, grain density). For montmorillonite, ρ_g
 199 is approximately 2.84 kg L^{-1} (Bourg et al., 2006; Tournassat and Appelo, 2011). The dry bulk
 200 density (ρ_d) is expressed in terms of the 150°C oven dry weight of clay. There were some small
 201 differences in the calculated bulk density and porosity for the three diffusion cells because of
 202 differences in the moisture content of the clay at the time of packing (Table 2.).

203 The diffusion cells used for experiments are based on the design of (Van Loon et al., 2003), with
 204 dimensions adjusted to accommodate smaller samples (Figure S1). The clay plug inside the
 205 diffusion cells had a diameter of 9.5 mm and a length of 5 mm. Cells were machined in-house
 206 using PEEK (polyether ether ketone) plastic at Lawrence Berkeley National Laboratory.

207 Experiments were conducted under a single ionic strength (0.1 M) and three different electrolyte
 208 compositions: 0.1 M NaCl, 0.033 M CaCl_2 , and 0.085 M NaCl + 0.005 M CaCl_2 , representing
 209 pure Na^+ , pure Ca^{2+} , and a Na^+ - Ca^{2+} mixture, respectively. All experiments were performed at
 210 room temperature (23°C) at pH 6.5. The pre-equilibrated dry clay samples were weighed into
 211 PEEK diffusion cells and compacted using a custom PEEK packing rod.

212 The diffusion experiments were conducted in three phases: (1) saturation, (2) tritiated water
213 (HTO) diffusion, and (3) Se(VI) diffusion. The clay was saturated by circulating 200 mL of
214 background electrolyte at both ends of the cell at approximately 1 mL/min using a peristaltic
215 pump for 40-42 days. After the saturation period, the HTO through-diffusion phase was started
216 by replacing the background electrolyte solutions with a high HTO reservoir containing
217 background electrolyte spiked with 1110 Bq mL⁻¹ HTO (200 mL) at one end and a low HTO
218 reservoir containing only background electrolyte (20 mL) at the other end. The high-
219 concentration reservoir was sampled at the beginning and the end of the HTO diffusion
220 experiment and did not change significantly over that time period. The low HTO reservoir was
221 changed at time intervals of 3-36 h, and the HTO concentration was measured in the low
222 reservoir samples by liquid scintillation counting. An in-house-built autosampler using a 3D
223 printer (Creality Ender 3Pro) as the base was used to change the low reservoir samples at regular
224 time intervals. The HTO concentration in the low reservoir never exceeded 0.5% of the
225 concentration in the high reservoir. The HTO diffusion was continued for 16 days. After this
226 period, the high-concentration reservoir was replaced with a Se(VI)-spiked solution containing
227 1.0 mM sodium selenate in the background electrolyte with a total volume of 190 mL, marking
228 the start of the Se(VI) diffusion experiment. The low-concentration reservoirs containing only
229 background electrolyte (5-10 mL) were changed at time intervals of 12-48 h for the first 44 days,
230 then 48-170 h for the remaining 33 days, and Se concentrations were measured by ICP-MS. Se
231 concentrations in the low reservoir never exceeded 1% of the concentration in the high reservoir.
232 Subsamples of the high-concentration Se(VI) reservoir were collected at the beginning and end
233 of the experiment and did not change significantly over the experiment.

234 At the end of the Se(VI) diffusion period, the diffusion cells were disassembled and the clay plug
235 was extruded using the PEEK packing rod and sliced into thin slices. The thickness of the clay
236 slices was measured using a digital caliper with a precision of 0.1 mm. Clay slices ranged in
237 thickness from 0.3 to 0.9 mm. The clay slices were placed into 20 mL glass scintillation vials and
238 dried at 150°C for 24 hours. The dried clay was extracted with 5 mL of 0.5 M trace metal grade
239 hydrochloric acid for 3 days, then centrifuged at 39 000 × g for 20 min and filtered through a
240 0.45 µm PVDF syringe filter. Selenium concentrations were measured in the acid extracts by
241 ICP-MS. Se concentrations in the clay profiles are expressed in mmol Se per liter of total
242 porosity ($C_{\text{Se_pore}}$), calculated using the following equation:

$$C_{Se_pore} = \frac{1000 \times C_{Se_solid} \times \rho_d}{\varepsilon} \quad \text{Equation 4}$$

243

244 Where C_{Se_solid} is the concentration of Se extracted per gram of dry clay (in mmol g⁻¹).

245 **2.5 Analytical Techniques**

246 Samples were analyzed for Se by ICP-MS (Perkin-Elmer Elan DRC II) after acidification and
 247 dilution with ultrapure (ultrapure grade) 0.15 M nitric acid and internal standard addition. Selenium
 248 was measured using oxygen as the cell gas in DRC mode and using Rh as an internal standard.
 249 Spike recoveries with known concentrations of Se were run every 5 samples, and recoveries
 250 ranged from 0.80-1.25. Independent QC samples were run every 10 samples, with recoveries
 251 ranging from 0.9-1.1. HTO samples were analyzed using liquid scintillation counting (Perkin-
 252 Elmer Liquid Scintillation Analyzer Tri-Carb 2900TR) by mixing 4 mL of sample with 18 mL of
 253 Ultima Gold XR liquid scintillation cocktail and counting until the relative standard deviation
 254 was 2% or for a maximum of 90 minutes.

255 **2.6 Modeling Approach**

256 Normalized mass flux (J_N , in m day⁻¹) reaching the low-concentration reservoir is most
 257 frequently calculated in the literature using:

$$J_N = \frac{C_{low}V_{low}}{C_{high}A \cdot \Delta t} \quad \text{Equation 5}$$

258 where C_{low} is the concentration in the low-concentration reservoir, C_{high} is the concentration in
 259 the high-concentration reservoir, V_{low} is the volume of the low-concentration reservoir (from ~5
 260 to ~20 mL depending on the sampling event), A is the cross-sectional area of the diffusion cell
 261 (0.709 cm²), and Δt is the time interval since the previous sampling event. This approximation is
 262 applicable for cases in which tracer concentration in the high reservoir does not change
 263 significantly over the course of the experiment (i.e., tracer source is considered infinite) and the
 264 tracer concentration in the low reservoir remains near zero (Yaroshchuk et al., 2008). However,
 265 for modeling purposes, this representation presents some problems (discussed in detail in
 266 Tournassat et al. (2023)), which include differences in time-integrated fluxes, J_N , compared to
 267 instantaneous fluxes calculated with the analytical solution of the diffusion equations. J_N values

268 may also oscillate with time because of the irregular pattern of sampling events during the
 269 experiment. A reactive transport modeling approach makes it possible to consider all
 270 experimental features such as the above-mentioned problems, as well as varying boundary
 271 conditions, the presence of filters, the presence of an O-ring in the filters, the replacement of the
 272 low-concentration reservoir with time, *etc.* (Tournassat et al., 2023). In addition, a reactive
 273 transport modeling approach allows comparison of the modeling results directly to the raw
 274 experimental data, *i.e.* the tracer concentrations measured in each of the collected vials at all
 275 sampling times. For these reasons, all clay sample diffusion experiments were modeled using the
 276 reactive transport model CrunchClay (Steeffel and Tournassat, 2021; Tournassat and Steefel,
 277 2021; Tournassat et al., 2020). The consideration of an O-ring in the filters necessitated carrying
 278 out the calculations with a 2D-axisymmetric geometry (Tournassat et al., 2023).

279 CrunchClay was used in combination with the CrunchEase interface (Tournassat et al., 2023) to
 280 estimate clay diffusive properties within the framework of a classical $\varepsilon - D_e - K_D$ modeling
 281 approach, where ε is the diffusion porosity (-), D_e is the effective diffusion coefficient ($\text{m}^2 \text{s}^{-1}$,
 282 see Equation 2) and K_D (L kg^{-1}) is the distribution coefficient that accounts for reversible and
 283 linear adsorption processes. We assumed that HTO was present only in solution and that Se was
 284 present in solution (with c = aqueous concentration) and on surfaces (with C_{surf} in $\text{mol kg}_{\text{solid}}^{-1}$) so
 285 that C_{tot} (in $\text{mol m}_{\text{medium}}^{-3}$) can be expressed as:

$$C_{tot} = c\varepsilon + C_{surf}\rho_d \quad \text{Equation 6}$$

286 We assumed that the Se surface concentration C_{surf} was linearly related to the aqueous
 287 concentration through $C_{surf} = cK_D$ (with K_D in $\text{m}^3_{\text{water}} \text{kg}_{\text{solid}}^{-1}$) and that the adsorption process
 288 was instantaneous and reversible. Based on this assumption,

$$C_{tot} = c\varepsilon + cK_D\rho_d. \quad \text{Equation 7}$$

289 It was further assumed that the media were homogeneous. Hence D_e , ε , ρ_d and K_D are independent
 290 of x , and Fick's second law of diffusion reduces to:

$$\frac{\partial c}{\partial t} = \frac{\tau\varepsilon D_0}{\varepsilon + \rho_d K_D} \frac{\partial^2 c}{\partial x^2} = \frac{D_e}{\alpha} \frac{\partial^2 c}{\partial x^2} \quad \text{Equation 8}$$

291

292 where α is the rock capacity factor.

293 The dimensions of the diffusion cells are available in the Supporting Information (Figure S1).

294 The exact same dimensions were considered in our reactive transport simulations, which can be
295 reproduced by the readers using the CrunchEase GUI made freely available on Github

296 (<https://github.com/Tournassat/CrunchEaseForAll>).

297 In the following, the agreement of the model with the experimental data is shown on the raw data
298 (concentration measurements in vials) and the experimental time-averaged flux J_N as a function
299 of experimental conditions is only shown for comparison.

300 **3. Results and Discussion**

301 **3.1 Filter Diffusion Properties**

302 In order to characterize the baseline performance of the reaction cell, diffusion of NaCl through
303 PEEK filters was measured in five replicate experiments. An example plot of cumulative NaCl
304 mass in the low reservoir over time is shown in Figure S2. There was an initial lag period,
305 followed by a linear increase in NaCl in the low reservoir. This linear portion of the
306 breakthrough curve was used to calculate the effective diffusion coefficient of Na^+ and Cl^-
307 through the filter according to Equation 1, resulting in a measured D_e of $6.1 \times 10^{-11} \pm 0.29 \times 10^{-11}$
308 $\text{m}^2 \text{s}^{-1}$.

309 Given the known values for ε and D_0 (Table S1), we calculated G to be 6.82 ± 0.33 ($\tau = 0.147 \pm$
310 0.007). The measured D_e value was lower than for stainless steel filters with a similar pore size
311 ($1.6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$) (Aldaba et al., 2014). G and ε were slightly lower for the PEEK filters used in
312 this experiment compared to those used by Aldaba et al. (2014), which had a smaller nominal
313 pore size of $1 \mu\text{m}$.

314 **3.2 Clay Cation Composition**

315 The total cation exchange capacity of the clay after purification was $0.833 \pm 0.04 \text{ mmol}_c/\text{g}$. The
316 cation composition for the Na, Na-Ca, and Ca exchanged clays is shown in Table 1. The cation
317 composition is expressed as a % of charge ($100 \times \text{mmol}_c \text{ cation per gram/CEC in mmol}_c/\text{g}$). The

318 Na-Ca clay contained 72% (by charge) Ca. A very small amount (1%) of exchangeable Mg was
 319 present in all three clays and no K was detected.

320 **Table 1. Exchangeable cation composition of clays expressed as a charge % of the CEC.**

Clay	Na (% charge)	Ca (% charge)	Mg (% charge)
Na	98.3 ± 0.6	0.5 ± 0.6	1.2 ± 0.0
Na-Ca	26.8 ± 0.2	72.2 ± 0.2	1.0 ± 0.0
Ca	1.6 ± 0.3	97.5 ± 0.2	0.9 ± 0.1

321

322

323 3.3 Tritiated water (HTO) diffusion

324 HTO diffusion reached a steady state after approximately 100 h, with steady-state fluxes
 325 increasing in the order Na, Na-Ca, and Ca (Figure 1). A precise estimation of the τ and D_e values
 326 of HTO was achieved by modeling the data with the assumption that the total porosity was
 327 accessible to HTO (Figure 1 and Table 2). The influence of the variations in sampling time
 328 intervals and sample vial volumes during the experiment is almost perfectly captured by our
 329 modeling approach (raw data available in the SI), thus giving confidence in the modeled τ and D_e
 330 values.

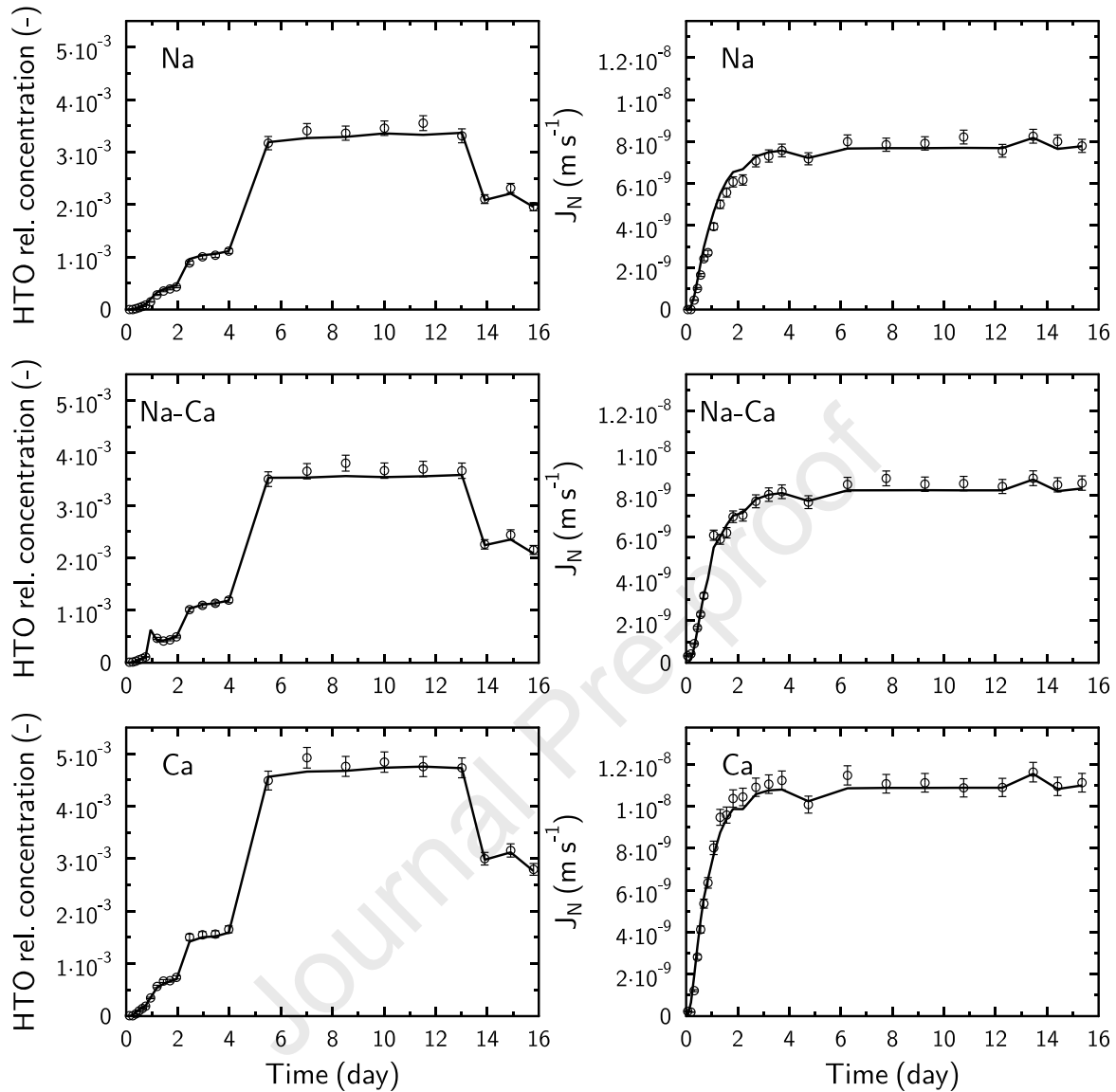
331 The small difference between the Na ($\tau_{\text{HTO}} = 0.065$) and Na-Ca ($\tau_{\text{HTO}} = 0.070$) cells might be
 332 attributed to small differences in cell packing ($\rho_d = 1.35$ vs. $\rho_d = 1.28 \text{ kg L}^{-1}$ for Na and Na-Ca
 333 cells respectively). Differences in bulk density will affect not only the total porosity, but also the
 334 sample microstructure responsible for the geometrical factor affecting diffusion processes.
 335 Archie's law relates the effective diffusion coefficient to the porosity and an empirical
 336 cementation factor, m , that captures the change of the geometrical factor as a function of porosity
 337 changes:

$$D_e = D_0 \varepsilon^m \quad \text{Equation 9}$$

338 Despite its empirical nature, Archie's law or its extended version (Van Loon and Mibus, 2015) is
 339 often able to quantitatively describe the evolution of the effective diffusion coefficient of HTO in
 340 clayey materials. The difference between the Na ($\tau_{\text{HTO}} = 0.065$) and Na-Ca ($\tau_{\text{HTO}} = 0.070$) cells

341 can be described by considering a cementation factor of $m \sim 3$, which is compatible with the
342 cementation factors commonly reported for bentonite samples (Van Loon and Mibus, 2015).
343 However, the difference between the Na-Ca ($\tau_{\text{HTO}} = 0.070$) and Ca ($\tau_{\text{HTO}} = 0.13$) cells cannot be
344 attributed to the small difference in cell packing only. A cementation factor of $m \sim 10$ would be
345 necessary, which does not fall in the range of values reported for montmorillonite. A reasonable
346 explanation of the observed difference lies in the difference of microstructure of Na- and Ca-
347 exchanged montmorillonite samples: the presence of exchangeable Ca promotes the formation of
348 thicker layer stacks (“tactoids”) compared to Na (Segad et al., 2012), which in turn promotes the
349 presence of larger interparticle pores (Holmboe et al., 2012; Ohkubo et al., 2021), hence
350 increasing the diffusivity of the material (Melkior et al., 2009; Tournassat et al., 2011;
351 Tournassat et al., 2016).

352



353

354 **Figure 1. Left: HTO normalized concentrations in the low-concentration reservoir as a**
 355 **function of time. Right: HTO normalized flux as a function of time. Na, Na-Ca, and Ca**
 356 **refers to the three different salt background and clay conditioning conditions. Circles:**
 357 **experimental data; lines: results of the $\varepsilon - D_e$ models (Table 2.). Error bars are**
 358 **representative of the analytical error on the HTO measurements (2 standard deviations).**

359

360 **Table 2. Summary of measured diffusion cell parameters, including bulk density (ρ_d), total**
 361 **porosity (ε_{tot} , calculated from Equation 3), along with reference model fitted parameters (τ ,**

362 D_e , α_{Se}), assuming $K_D = 0 \text{ L kg}^{-1}$ for both HTO and Se(VI). Note that α_{HTO} is equivalent to
 363 ϵ_{HTO} and ϵ_{tot} . Uncertainties on the D_e value were estimated from model envelop curves and
 364 experimental error bars.

Cell	ρ_d (kg L^{-1})	$\epsilon_{tot} = \epsilon_{HTO} = \alpha$ HTO (-)	τ_{HTO} (-)	$D_{e,HTO}$ ($10^{-12} \text{ m}^2 \text{ s}^{-1}$)	$\alpha_{Se} =$ $\epsilon_{Se,max}$ (-)	$\tau_{Se,min}$ (-)	$D_{e,Se}$ ($10^{-12} \text{ m}^2 \text{ s}^{-1}$)
Na	1.35	0.524	0.065	78 ± 4	0.0983	0.0138	1.3 ± 0.3
Na-Ca	1.28	0.551	0.070	89 ± 4	0.140	0.0160	2.1 ± 0.5
Ca	1.24	0.562	0.13	168 ± 8	0.450	0.0250	10.6 ± 2.3

365

366 3.4 Selenate diffusion

367 The normalized flux for Se(VI) reached steady state after approximately 300 h, with the Ca-
 368 montmorillonite showing the highest normalized flux (Figure 2). The steady-state flux of Se was
 369 much lower than that of HTO in all three cells. Total Se concentrations in clay slices also
 370 followed the trend $\text{Na} < \text{Na-Ca} < \text{Ca}$ (Figure 3). Se concentrations in the clay slice closest to the
 371 high-concentration reservoir (at $\sim 4.5\text{-}5.0 \text{ mm}$) were 0.18, 0.25, and 0.77 mM for the Na, Na-Ca,
 372 and Ca cells, respectively. The observed variations in Se concentration/flux may result from both
 373 differences in effective porosity for Se and from changes in Se adsorption in the presence of
 374 increasing Ca concentrations. The profiles in all three cells were linear with depth as expected
 375 for steady-state conditions.

376 Through-diffusion data makes it possible to extract a single set of α , D_e values for each tracer in
 377 one experiment (Crank, 1975; Van Loon et al., 2003). However, it does not provide enough
 378 constraints to extract a single set of ϵ , K_D , and τ values and additional data and/or hypotheses are
 379 necessary to derive these three quantities independently. In the first attempt, the K_D values for
 380 Se(VI) were set to zero. In this condition, the fitted porosity and tortuosity values take their
 381 maximum and minimum value respectively ($\epsilon_{max} = \alpha$ and τ_{min} ; Table 2). The corresponding fitted
 382 parameters made it possible to almost perfectly reproduce the diffusion data (Figure 2 and Figure
 383 3).

384 In Na-montmorillonite, clay layers are negatively charged and part or all of the porosity is
385 influenced by the presence of an electrical double layer (EDL) that forms at the surface, and in
386 which the solution is not electroneutral (Tournassat and Steefel, 2019). Negatively charged
387 species, including SeO_4^{2-} , are depleted in the EDL-influenced portion of the porosity because of
388 their interaction with the negative electrostatic potential field created by the surfaces of
389 montmorillonite. This process, often called anion-exclusion, is also responsible for a higher
390 geometrical factor, G (or $1/\tau$), for anions compared to neutral tracers such as HTO, because pore
391 throats, which are responsible for the pore network connectivity, may partially or totally exclude
392 anions, thus ascribing longer diffusion pathways to anions compared to neutral species.
393 Consequently, $\tau_{\text{Se}} \leq \tau_{\text{HTO}}$ and it is possible to define a minimum accessible porosity value for Se
394 corresponding to $D_{e,\text{Se}} = \tau_{\text{HTO}} \times \varepsilon_{\text{Se},\text{min}} \times D_{0,\text{Se}}$. This minimum porosity corresponds itself to a
395 maximum K_{D} value according to $\alpha_{\text{Se}} = \varepsilon_{\text{Se},\text{min}} + \rho_{\text{d}} K_{\text{D},\text{max}}$ (Table 3). We note that the very low
396 $K_{\text{D},\text{max}}$ values ($\ll 1$) in Table 3 are nearly impossible to measure in batch experiments.

397 The calculated minimum value of SeO_4^{2-} accessible porosity ($\varepsilon_{\text{Se},\text{min}} = 0.021$) was similar to the
398 values reported for Cl^- in similar compacted Na-montmorillonite materials (Tournassat and
399 Appelo, 2011). Cl^- does not adsorb on clay mineral surfaces, and thus, the difference between
400 total porosity values and Cl^- accessible porosity values reported in the literature are truly
401 representative of the excluded volume for monovalent anions. However, one would expect an
402 increased exclusion for SeO_4^{2-} compared to Cl^- because of their difference in charge. This
403 surprisingly high Se(VI) accessible porosity in the Na-montmorillonite sample may be partly
404 explained by the presence of aqueous and exchanged Mg^{2+} which originates from a limited
405 dissolution of the clay layers (Orucoglu et al., 2018). The formation of MgSeO_4 ion pairs, which
406 are neutral and, thus not excluded from the EDL, would then explain the lower value of Se(VI)
407 exclusion than expected. Mg^{2+} was a minor component (1%) of exchangeable cations at the
408 beginning of the experiment (Table 1). However, we did not measure exchangeable cations on
409 the clay at the end of the experiment or aqueous Mg^{2+} during the diffusion experiment, therefore
410 are unable to confirm the formation of MgSeO_4 ion pairs. The lowering of Se exclusion from the
411 EDL could also be related to an increased ion pairing in the EDL compared to bulk water
412 conditions (Appelo et al., 2010), which in turn would increase the apparent accessible porosity of
413 Se.

414

415 **Table 3. Summary of constraints on Se diffusion parameters in Na-, Na-Ca-, and Ca-**
 416 **montmorillonite. $K_{D,max}$ values are given in L kg⁻¹.**

Cell	$\varepsilon_{Se,min}$	$K_{D,max}$	$\varepsilon_{Se,min}$ considering CaSeO ₄ ion pair formation	$K_{D,max}$ considering CaSeO ₄ ion pair formation
Na	0.021	0.057	-	-
Na-Ca	0.032	0.084	0.036	0.081
Ca	0.086	0.29	0.18	0.22

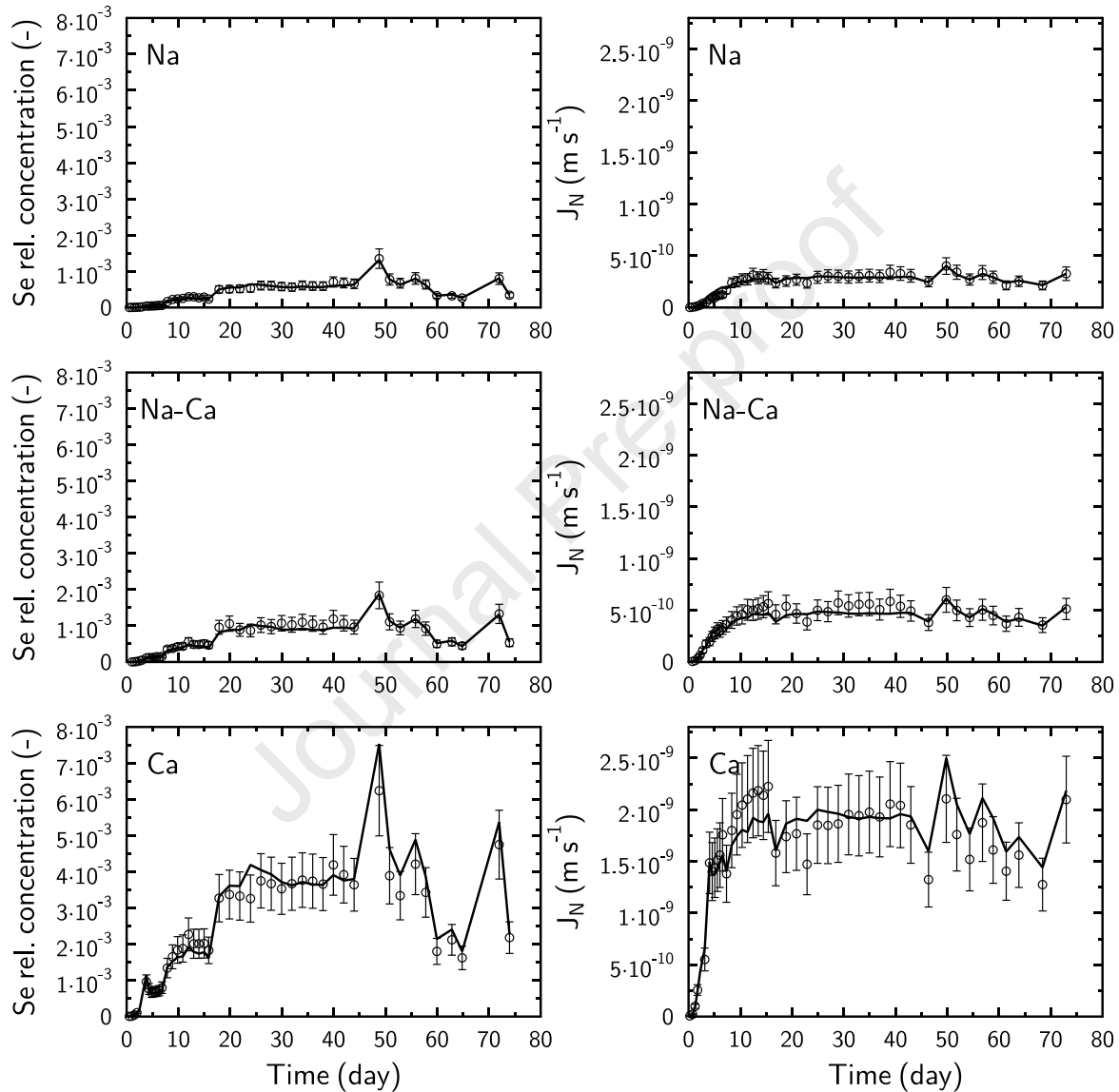
417

418 In the Ca-montmorillonite sample, the minimum accessible porosity was found to be 0.086. This
 419 higher accessible porosity for Ca-montmorillonite compared to the Na-montmorillonite sample
 420 can be explained by a combination of the following effects: the presence of wider interparticular
 421 pores, which increases the average anion accessible porosity (Tournassat et al. 2016) and a
 422 decrease of the magnitude of the negative electrostatic potential field in the presence of divalent
 423 cations (Ca²⁺). However, the presence of CaSeO₄ aqueous complexes which are neutral and thus
 424 not repelled from clay mineral surfaces will also affect the minimum accessible porosity, which
 425 is not accounted for in the above estimate ($\varepsilon_{Se,min}$ of 0.086 for Ca). Aqueous speciation
 426 calculation carried out with the Thermochemie database (Giffaut et al., 2014;
 427 <https://www.thermochemie-tdb.com/>) indicates that 32% of the total Se concentration is present
 428 in the form of CaSeO₄ in a 0.033 M CaCl₂ background solution. Equivalently, at least 32% of the
 429 total porosity is accessible to Se in this neutral form, *i.e.* a revised minimum accessible porosity
 430 of $0.32 \times 0.56 = 0.18$, giving in turn a revised $K_{D,max}$ value of 0.22 L kg⁻¹ (Table 3.). Assuming
 431 that the D_0 value for CaSeO₄ is similar to that of CaSO₄ ($D_0 = 4.71 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$ available from the
 432 PHREEQC.dat database), a $\tau_{Se,max}$ value of 0.115 can be deduced.

433 In the Na-Ca cell, with 0.005 M CaCl₂ + 0.085 M NaCl background solution, 6.6% of the total
 434 aqueous Se(VI) is in the form of CaSeO₄, leading to a minimum accessible porosity of $\varepsilon_{Se,min} =$
 435 $0.066 \times 0.55 = 0.036$. The corresponding $\tau_{Se,max}$ value is 0.123, which is very similar to the value
 436 found for the Ca-montmorillonite sample.

437 The above analysis highlights the importance of a good knowledge of the aqueous speciation to
 438 understand and predict the diffusion properties of Se and provides realistic constraints for the
 439 ranges of ε_{Se} , K_{DSe} , and τ_{Se} .

440



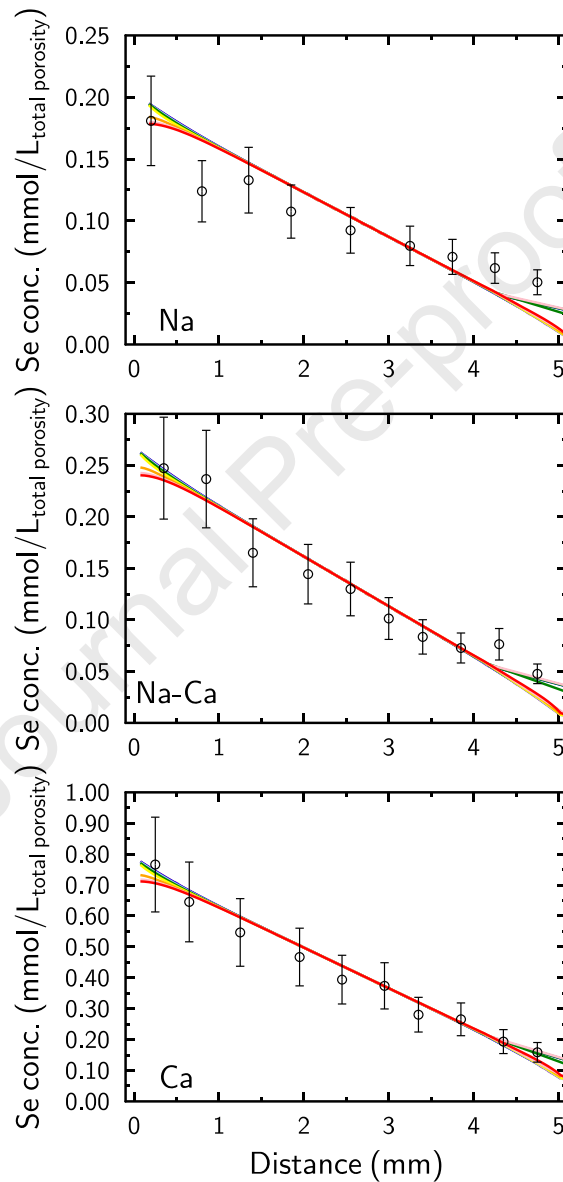
441

442 **Figure 2. Left: Se normalized concentrations in the low-concentration reservoir as a**
 443 **function of time. Right: Se normalized flux as a function of time. Na, Na-Ca, and Ca refers**
 444 **to the three different salt background and clay conditioning conditions. Circles:**
 445 **experimental data; lines: results of the $\varepsilon - D_e - K_D$ models (Table 2.) where K_D is assumed**

446 to be 0. Error bars are representative of the analytical error on the Se measurements. The
 447 y-axis scale is the same for all conditions to ease a direct comparison.

448

449



450

451 **Figure 3. Total Se profiles in clay at the end of diffusion experiments. Se concentrations are**
 452 **expressed as a concentration in the total porewater volume. Circles: experimental data;**
 453 **lines: simulated profiles using the same α_{Se} and $D_{e,Se}$ as in Figure 2. The different colors are**

454 **indicative of the different profile positions in the radial direction (the red color is for the**
455 **central grid-cells on the symmetry axis). Error bars represent the analytical error (2**
456 **standard deviations). Note that the concentrations at the downstream boundary do not**
457 **tend to zero because of the O-ring and the presence of tubings (i.e., ‘dead volumes’) in**
458 **which the tracers are accumulating between sampling events.**

459

460 **4. Conclusions**

461 An increase of Ca/Na ratio in solution and on clay surfaces is responsible for an increase in HTO
462 and selenate diffusivity in montmorillonite samples. The increase of HTO diffusivity can be
463 explained by a change of microstructure leading to an increase of the τ_{HTO} value. These changes
464 will affect the transport of all radionuclides through clay barriers, including Se. In addition, the
465 aqueous speciation of Se(VI) has a large effect on Se transport. Se(VI) diffusion is limited by
466 anion exclusion due to the formation of the negatively charged species SeO_4^{2-} . However, in the
467 presence of Ca^{2+} , the formation of CaSeO_4 neutral ion pairs, which can access a larger portion of
468 the total porosity, increases selenate diffusivity. While additional insights about the exact
469 distribution of the interlayer and interparticle porosities and the influence of the diffuse layer on
470 selenate ion pair formation would be necessary to build a comprehensive mechanistic model for
471 selenate diffusion in montmorillonite samples, we provide constraints on model parameters that
472 can be used to predict a range of Se(VI) transport in engineered barrier systems. Our analysis
473 highlights that Se(VI) diffusion parameters (*e.g.*, effective diffusion coefficients) obtained with
474 simplified laboratory systems cannot be transferred to the simulation of a repository if *in situ*
475 geochemical conditions, especially ionic strength and major element concentrations (*e.g.*, Ca),
476 are different from the laboratory conditions. Furthermore, these results have similarly important
477 implications for the diffusion of other radionuclides which are present as anions or mixed-
478 species in waste repositories, including Se(IV) (HSeO_3^- , SeO_3^{2-}), U(VI) (*e.g.*, $\text{UO}_2(\text{OH})_3^-$,
479 $\text{UO}_2(\text{OH})_4^{2-}$), Mo(VI) (MoO_4^{2-}) and others. Radionuclide aqueous speciation together with the
480 presence of an EDL must be explicitly taken into account in the model in order to accurately
481 predict their transport. The results also emphasize the need to understand the overall chemical
482 evolution of repository conditions as changes in aqueous speciation due to many factors (*e.g.*,

483 mineral dissolution/precipitation or groundwater penetration) can change the mobility of
484 important species.

485 **Supplementary Material**

486 Supplementary information, including diffusion cell schematics and additional information about
487 measuring diffusive properties of the filters is provided in a separate file and is available free of
488 charge online.

489 **Data Availability**

490 Raw experimental data used in this manuscript is available on Mendeley Data (Fox et al., 2024).

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495 **References**

496 Aldaba, D., Glaus, M., Leupin, O., Loon, L.V., Vidal, M., Rigol, A., 2014. Suitability of various
497 materials for porous filters in diffusion experiments. *Radiochimica Acta* 102, 723-730.

498 Appelo, C., Van Loon, L., Wersin, P., 2010. Multicomponent diffusion of a suite of tracers (HTO,
499 Cl, Br, I, Na, Sr, Cs) in a single sample of Opalinus Clay. *Geochimica et Cosmochimica Acta* 74,
500 1201-1219.

501 Bar-Yosef, B., Meek, D., 1987. Selenium Sorption by Kaolinite and Montmorillonite. *Soil Science*
502 144, 11-19.

503 Blear, W.F., 1990. The Nature of Cation-Substitution Sites in Phyllosilicates. *Clays and Clay*
504 *Minerals* 38, 527-536.

505 Bourg, I.C., Sposito, G., Bourg, A.C.M., 2006. Tracer diffusion in compacted, water-saturated
506 bentonite. *Clays and Clay Minerals* 54, 363-374.

- 507 Chen, F., Burns, P.C., Ewing, R.C., 1999. 79Se: geochemical and crystallo-chemical retardation
508 mechanisms. Journal of Nuclear Materials 275, 81-94.
- 509 Crank, J., 1975. The mathematics of diffusion. Oxford University Press.
- 510 Cussler, E. L., 2009. Diffusion: mass transfer in fluid systems, Cambridge university press. García-
511 Gutiérrez, M., Missana, T., Mingarro, M., Samper, J., Dai, Z., Molinero, J., 2001. Solute transport
512 properties of compacted Ca-bentonite used in FEBEX project. Journal of Contaminant Hydrology
513 47, 127-137.
- 514 Giffaut, E., Grivé, M., Blanc, P., Vieillard, P., Colàs, E., Gailhanou, H., Gaboreau, S., Marty, N.,
515 Madé, B., Duro, L., 2014. Andra thermodynamic database for performance assessment:
516 ThermoChimie. Applied Geochemistry 49, 225-236.
- 517 Fox, P. M., Tournassat, C., Steefel, C., Nico, P.S., 2024. Data for: HTO and Selenate Diffusion
518 Through Compacted Na-, Na-Ca-, and Ca-Montmorillonite. Mendeley Data. DOI:
519 10.17632/9wy2v6tpxk.1
- 520 González Sánchez, F., Van Loon, L.R., Gimmi, T., Jakob, A., Glaus, M.A., Diamond, L.W., 2008.
521 Self-diffusion of water and its dependence on temperature and ionic strength in highly compacted
522 montmorillonite, illite and kaolinite. Applied Geochemistry 23, 3840-3851.
- 523 Hadi, J., Tournassat, C., Ignatiadis, I., Greneche, J.M., Charlet, L., 2013. Modelling CEC
524 variations versus structural iron reduction levels in dioctahedral smectites. Existing approaches,
525 new data and model refinements. J.Colloid Interface Sci. 407, 397-409. DOI:
526 10.1016/j.jcis.2013.05.014
- 527 Holmboe, M., Wold, S., Jonsson, M., 2012. Porosity investigation of compacted bentonite using
528 XRD profile modeling. Journal of Contaminant Hydrology 128, 19-32.
- 529 Honorio, T., Brochard, L., Vandamme, M., 2017. Hydration Phase Diagram of Clay Particles from
530 Molecular Simulations. Langmuir 33, 12766-12776.
- 531 Idemitsu, K., Kozaki, H., Yuhara, M., Arima, T., Inagaki, Y., 2016. Diffusion behavior of selenite
532 in purified bentonite. Progress in Nuclear Energy 92, 279-285.

- 533 Laird, D.A., Shang, C., 1997. Relationship Between Cation Exchange Selectivity and Crystalline
534 Swelling in Expanding 2:1 Phyllosilicates. *Clays and Clay Minerals* 45, 681-689.
- 535 Li, Y.-H., Gregory, S., 1974. Diffusion of ions in sea water and in deep-sea sediments. *Geochimica
536 et Cosmochimica Acta* 38, 703-714.
- 537 Ma, B., Charlet, L., Fernandez-Martinez, A., Kang, M., Madé, B., 2019. A review of the retention
538 mechanisms of redox-sensitive radionuclides in multi-barrier systems. *Applied Geochemistry* 100,
539 414-431.
- 540 Melkior, T., Gaucher, E.C., Brouard, C., Yahiaoui, S., Thoby, D., Clinard, C., Ferrage, E.,
541 Guyonnet, D., Tournassat, C., Coelho, D., 2009. Na⁺ and HTO diffusion in compacted bentonite:
542 Effect of surface chemistry and related texture. *Journal of Hydrology* 370, 9-20.
- 543 Missana, T., Alonso, U., Fernández, A.M., García-Gutiérrez, M., 2018. Colloidal properties of
544 different smectite clays: Significance for the bentonite barrier erosion and radionuclide transport
545 in radioactive waste repositories. *Applied Geochemistry* 97, 157-166.
- 546 Missana, T., Alonso, U., García-Gutiérrez, M., 2009. Experimental study and modelling of selenite
547 sorption onto illite and smectite clays. *Journal of Colloid and Interface Science* 334, 132-138.
- 548 Montavon, G., Guo, Z., Lützenkirchen, J., Alhajji, E., Kedziorek, M.A.M., Bourg, A.C.M.,
549 Grambow, B., 2009. Interaction of selenite with MX-80 bentonite: Effect of minor phases, pH,
550 selenite loading, solution composition and compaction. *Colloids and Surfaces A: Physicochemical
551 and Engineering Aspects* 332, 71-77.
- 552 Ohkubo, T., Yamazaki, A., Fukatsu, Y., Taichi, Y., 2021. Pore distribution of compacted Ca-
553 montmorillonite using NMR relaxometry and cryoporometry: Comparison with Na-
554 montmorillonite. *Microporous and Mesoporous Materials* 313, 110841.
- 555 Orucoglu, E., Tournassat, C., Robinet, J.-C., Made, B., Lundy, M., 2018. From experimental
556 variability to the sorption related retention parameters necessary for performance assessment
557 models for nuclear waste disposal systems: The example of Pb adsorption on clay minerals.
558 *Applied Clay Science* 163, 20-32.

- 559 Salles, F., Douillard, J.-M., Bildstein, O., Gaudin, C., Prelot, B., Zajac, J., Van Damme, H., 2013.
560 Driving force for the hydration of the swelling clays: Case of montmorillonites saturated with
561 alkaline-earth cations. *Journal of Colloid and Interface Science* 395, 269-276.
- 562 Segad, M., Hanski, S., Olsson, U., Ruokolainen, J., Åkesson, T., Jönsson, B., 2012.
563 Microstructural and Swelling Properties of Ca and Na Montmorillonite: (In Situ) Observations
564 with Cryo-TEM and SAXS. *The Journal of Physical Chemistry C* 116, 7596-7601.
- 565 Steefel, C.I., Tournassat, C., 2021. A model for discrete fracture-clay rock interaction
566 incorporating electrostatic effects on transport. *Computational Geosciences* 25, 395-410.
- 567 Subramanian, N., Nielsen Lammers, L., 2022. Thermodynamics of ion exchange coupled with
568 swelling reactions in hydrated clay minerals. *Journal of Colloid and Interface Science* 608, 692-
569 701.
- 570 Teich-McGoldrick, S.L., Greathouse, J.A., Jové-Colón, C.F., Cygan, R.T., 2015. Swelling
571 Properties of Montmorillonite and Beidellite Clay Minerals from Molecular Simulation:
572 Comparison of Temperature, Interlayer Cation, and Charge Location Effects. *The Journal of*
573 *Physical Chemistry C* 119, 20880-20891.
- 574 Tinnacher, R.M., Holmboe, M., Tournassat, C., Bourg, I.C., Davis, J.A., 2016. Ion adsorption and
575 diffusion in smectite: Molecular, pore, and continuum scale views. *Geochimica et Cosmochimica*
576 *Acta* 177, 130-149.
- 577 Tournassat, C., Appelo, C.A.J., 2011. Modelling approaches for anion-exclusion in compacted Na-
578 bentonite. *Geochimica et Cosmochimica Acta* 75, 3698-3710.
- 579 Tournassat, C., Bizi, M., Braibant, G., Crouzet, C., 2011. Influence of montmorillonite tactoid size
580 on Na–Ca cation exchange reactions. *Journal of Colloid and Interface Science* 364, 443-454.
- 581 Tournassat, C., Gaboreau, S., Robinet, J.-C., Bourg, I.C., Steefel, C.I., 2016. Impact of
582 microstructure on anion exclusion in compacted clay media.
- 583 Tournassat, C., Steefel, C.I., 2021. Modeling diffusion processes in the presence of a diffuse layer
584 at charged mineral surfaces: a benchmark exercise. *Computational Geosciences* 25, 1319-1336.

- 585 Tournassat, C., Steefel, C.I., Fox, P.M., Tinnacher, R.M., 2023. Resolving experimental biases in
586 the interpretation of diffusion experiments with a user-friendly numerical reactive transport
587 approach. *Scientific Reports* 13, 15029.
- 588 Tournassat, C., Steefel, C.I., Gimmi, T., 2020. Solving the Nernst-Planck equation in
589 heterogeneous porous media with finite volume methods: Averaging approaches at interfaces.
590 *Water resources research* 56, e2019WR026832.
- 591 Tournassat, C., Tinnacher, R.M., Grangeon, S., Davis, J.A., 2018. Modeling uranium(VI)
592 adsorption onto montmorillonite under varying carbonate concentrations: A surface complexation
593 model accounting for the spillover effect on surface potential. *Geochimica et Cosmochimica Acta*
594 220, 291-308.
- 595 Van Loon, L.R., Mibus, J., 2015. A modified version of Archie's law to estimate effective
596 diffusion coefficients of radionuclides in argillaceous rocks and its application in safety analysis
597 studies. *Applied Geochemistry* 59, 85-94.
- 598 Van Loon, L.R., Soler, J.M., Bradbury, M.H., 2003. Diffusion of HTO, $^{36}\text{Cl}^-$ and $^{125}\text{I}^-$ in
599 Opalinus Clay samples from Mont Terri: Effect of confining pressure. *Journal of Contaminant*
600 *Hydrology* 61, 73-83.
- 601 Wang, Z., Wang, H., Li, Q., Xu, M., Guo, Y., Li, J., Wu, T., 2016. pH effect on Re(VII) and Se(IV)
602 diffusion in compacted GMZ bentonite. *Applied Geochemistry* 73, 1-7.
- 603 Wu, T., Wang, Z., Wang, H., Zhang, Z., Van Loon, L.R., 2017. Salt effects on Re(VII) and Se(IV)
604 diffusion in bentonite. *Applied Clay Science* 141, 104-110.
- 605 Wu, T., Wang, Z., Tong, Y., Wang, Y., Van Loon, L.R., 2018. Investigation of Re(VII) diffusion
606 in bentonite by through-diffusion and modeling techniques. *Applied Clay Science* 166, 223-229.
- 607 Yaroshchuk, A. E., Glaus, M., Van Loon, L.R., 2008. Diffusion through confined media at variable
608 concentrations in reservoirs. *Journal of Membrane Science* 319(1): 133-140.
- 609

Highlights

- Selenate diffusion through clay is limited by anion exclusion
- Clay layer stacking in Ca-montmorillonite promotes higher HTO and Se diffusion
- Formation of neutral aqueous CaSeO_4 species increases Se(VI) flux
- Models must consider aqueous speciation to be applied repository conditions

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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