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1 **From experimental variability to the sorption related retention parameters**
2 **necessary for performance assessment models for nuclear waste disposal**
3 **systems: the example of Pb adsorption on clay minerals.**

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18

19

20 **Abstract**

21 Surface complexation models (SCMs) have been developed in the last decades to describe
22 metal ion sorption to clay minerals and especially to montmorillonite. In principle, these
23 models can provide relevant information about sorption of radionuclides to be used in
24 performance assessment (PA) of radioactive waste disposal systems. However, these SCMs
25 have been developed in parallel with the acquisition of distinct adsorption datasets, which are
26 not always consistent with each other. The objective of this study was to compare new
27 experimental adsorption results with literature data to understand these discrepancies and to
28 propose a SCM approach that could be amenable to determine sorption related retention
29 parameters necessary for PA calculations. This study focused on lead (Pb) adsorption on
30 montmorillonite, illite and in a natural clay (Callovo Oxfordian) as case studies of a strongly
31 sorbing radionuclide that undergoes a range of retention processes depending on the chemical
32 conditions. The experiments showed that many experimental artifacts lead to
33 misinterpretations of the processes underlying the measured retention values. These include
34 Pb precipitation in the presence of carbonate in solution. The determination of SCM
35 parameters to provide sorption related information for PA of clay minerals should rely on
36 preliminary building of an adequate adsorption database, where adequate means that all
37 experimental conditions are met to quantify surface complexation only.

38 1. Introduction

39 In recent years, the scientific community has seen a remarkable surge of interest in the
40 properties and behavior of clays as they apply to a variety of natural and engineered settings.
41 Clay materials are known as an important part of the multi-barrier system for nuclear waste
42 storage around the world, and their performance must be demonstrated on the time scale of
43 hundreds to millions of years (Altmann 2008, Busch et al. 2008, Chapman and Hooper 2012,
44 Armitage et al. 2013, Neuzil 2013). In these applications, the low hydraulic conductivity of
45 the clay mineral-rich geological formations or of the engineered clay barriers provides at least
46 part of the basis for isolating radionuclide contaminants (RN). Clay minerals have high
47 adsorption capacity for a large range of radionuclides (Bradbury and Baeyens 2005a). The
48 strong adsorption and resulting retardation of many contaminants by clay minerals make them
49 ideal for use in natural or engineered barrier systems, particularly where there is a desire to
50 improve confidence in the safety case beyond the reliance on slower transport rates alone
51 (Altmann et al. 2012, Gaboreau et al. 2012, Borisover and Davis 2015, Grangeon et al. 2015).
52 Because contaminant mobility in clay materials is mainly driven by diffusion and adsorption
53 processes, a typical (simplified) scheme for estimating radionuclide release relies on knowing
54 three parameters. The first is the effective diffusion coefficient (D_e), which quantifies the
55 transport of each radionuclide across the barriers. The second is the distribution ratio of the
56 radionuclide between the solution and the solid phases/surface (R_D or K_D if the retention is
57 reversible), which quantifies the accumulation on the solid and the retardation of the
58 radionuclide as it migrates from the repository across the barriers. The third is the solubility,
59 which controls the maximum concentration in solution of the radionuclide of interest
60 according to the geochemical conditions. These parameters are site specific, so to determine
61 them specific data acquisition programs are needed. However, there is a fundamental
62 difference between solubility and K_D values. Solubility values are usually obtained from the
63 interpretation of experimental data with thermodynamic laws, which can be considered to be
64 always valid, so solubility values can be applied to site-specific conditions, if environmental
65 conditions such as temperature, pressure, and pore water composition are known, and with the
66 assumption of precipitation/dissolution at thermodynamic equilibrium. Conversely, K_D values
67 are directly measured in the presence of experimental conditions that are supposed to be
68 representative of the *in situ* environmental conditions. As a direct consequence, knowledge
69 about K_D values cannot be easily transferred from one site condition to another. For decades,
70 quasi-thermodynamic models have been developed to predict the adsorption properties of
71 many natural materials including clay minerals, oxides and organic matter. These models,
72 grouped here under the term surface complexation models (SCM), aim to predict adsorption
73 processes in a wide range of environmental conditions (Sposito 1984, Davis and Kent 1990,
74 Dzombak and Morel 1990, Hiemstra and Van Riemsdijk 1996, Davis et al. 1998). If complete
75 enough, they can be transferred from one site condition to another, providing that the
76 dominant mechanisms have been identified and adequately quantified. In principle, these
77 models could be used in performance assessment (PA) with calculations carried out with
78 reactive transport codes. In practice, this is seldom the case, but recently, a hybrid approach,
79 named “Smart K_D ”, which takes advantage of SCM flexibility with regards to changes in
80 environmental conditions together with simplified models more amenable to PA calculations,

81 has been advanced to include more flexibility, predictability and transferability in these PA
82 calculations (Richter et al. 2009, Stockmann et al. 2012, Druteikien et al. 2017). Near-field
83 conditions will change over time following local perturbations induced by the presence of the
84 waste repository. As an example, heat release from a radioactive waste package will
85 temporarily increase the temperature that will itself influence the adsorption properties of clay
86 minerals because of at least two processes. First, the affinity of the clay surfaces for a given
87 RN is dependent on temperature (Tertre et al., 2005). Second, a temperature change
88 influences the geochemical characteristics of the porewater, especially the pH, changing the
89 distribution of species (speciation) in solution for the elements of interest (Gailhanou et al.
90 2017). So estimating SCM parameters and their associated uncertainties in as wide a range of
91 conditions as possible is a key aspect in developing these PA approaches.

92 SCM parameters must be calibrated with experimental data in well-defined and well-
93 controlled conditions. This is necessary in order to extrapolate the results in a wide range of
94 conditions and to apply them to natural materials using a component additivity (CA) approach
95 (Davis et al. 2004, Chen et al. 2014a, 2014b). The choice of the SCM is also important. A
96 range of SCM that is applied to clay minerals and especially to montmorillonite have been
97 developed and described in the literature (Zachara and Smith 1994, Bradbury and Baeyens
98 1997, Ikhsan et al. 2005, Gu and Evans 2007, Marcussen et al. 2009, Tertre et al. 2009, Gu et
99 al. 2010, Akafia et al. 2011). These SCMs were developed in parallel with the acquisition of
100 distinct adsorption datasets, which are not always consistent with each other (Tournassat et al.
101 2013). Several sources of discrepancies explain these inconsistencies, including differences in
102 the properties of the clay materials (for example, natural variability in chemistry and size
103 distribution, and preparation prior to experiments including sedimentation techniques and
104 chemical treatments to remove mineral and organic impurities), differences in experimental
105 procedures (order of reagent addition), and experimental artifacts. So the objective of this
106 study was to compare new experimental adsorption results with literature data in order to
107 understand these discrepancies and to propose a SCM approach that could be amenable to the
108 determine sorption related retention parameters necessary for PA calculations. This study was
109 focused on Pb adsorption as a case study of a strongly sorbing radionuclide on
110 montmorillonite, illite and a natural clay mineral (Callovian-Oxfordian) (COx) that undergoes
111 a range of retention processes as a function of chemical conditions.

112 **2. Material and Methods**

113 **2.1. Overview of Experiments**

114 Batch adsorption experiments were conducted with three different reference clay minerals,
115 namely two montmorillonites (MX-80 and Kunipia-P) and one illite, and with a natural clay
116 mineral assemblage present in COx claystone, in order to quantify the main adsorption
117 mechanisms of Pb on clays. To clarify the effect of each of these mechanisms, various
118 adsorption experiments were designed spanning a range of different solid/liquid ratio (R_{SL} in
119 $\text{g}\cdot\text{L}^{-1}$), ionic strength (NaCl as a background electrolyte), pH, temperature, and initial Pb
120 concentrations (Table 1).

121 Table 1. Summary of experimental conditions used with three different reference clays
 122 (purified MX-80, Kunipia and illite and one clay fraction of COx claystone).

Initial Pb concentration (μM)	R_{SL} ($\text{g}\cdot\text{L}^{-1}$)	NaCl concentration (M)	pH range	T ($^{\circ}\text{C}$)
1	1	0.1	3-9	20*
10	1	0.1	3-9	20*
50	1	0.1	3-9	20*
1	0.5	0.025	3-9	20*
1	1	0.1	3-7	67

123 * Room temperature

124

125 2.2. Chemicals

126 All chemicals used in the experiments were analytical grade: $\text{Pb}(\text{NO}_3)_2$ (Prolab R.P.
 127 Normapur, > 99.5%), NaCl (Merck, 99.6%), 30% HCl (Merck, Suprapur), NaOH pellets
 128 (Merck, > 99%), 65% HNO_3 (VWR Prolabo, 69.4% for cleaning, and Merck, Suprapur for
 129 AAS measurements), acetic acid ($\text{C}_2\text{H}_4\text{O}_2$, VWR Prolab, 96%), citric acid ($\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}$,
 130 Carlo Erbar, >99.8%), sodium bicarbonate (NaHCO_3 , ACS Amresco), 30% H_2O_2 (Merck),
 131 sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$), MES ($\text{C}_6\text{H}_{13}\text{NO}_4\text{S}$, Sigma Aldrich, >99%), MOPS ($\text{C}_7\text{H}_{15}\text{NO}_4\text{S}$,
 132 Sigma Aldrich, >99.5%), tri sodium citrate dehydrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7\cdot 2\text{H}_2\text{O}$, Fluka, 99.99%).
 133 Milli-Q 18 M Ω water was used in all solution preparation, clay suspension and clay
 134 purification processes.

135 2.3. Solution Preparation

136 NaCl stock solutions (0.1 M and 0.025 M) were prepared from crystalline NaCl. HCl stock
 137 solution (1 mM) and NaOH stock solution (1 mM) were prepared from 30% HCl acid solution
 138 and NaOH pellets, respectively. Two 1 mM Pb stock solutions at two different ionic strength
 139 were prepared by dissolving crystalline $\text{Pb}(\text{NO}_3)_2$ in a 1 mM HCl / 0.1 M NaCl solution and in
 140 a 1 mM HCl solution. For experiments conducted with low Pb concentrations, 10 and 100 μM
 141 stock solutions were prepared by diluting these solutions in a 1 mM HCl / 0.1 M NaCl
 142 solution and in a 1 mM HCl solution. All solutions were prepared in an air atmosphere.

143 2.4. Clay Material

144 Clay stock dispersions with a solid / liquid ratio of $2 \text{ g}\cdot\text{L}^{-1}$ were prepared in a 0.1 M NaCl
 145 solution background for two montmorillonites (MX-80, and Kunipia-P), one purified illite
 146 (Illite du Puy, IdP), and the clay fraction of COx claystone. MX-80 montmorillonite was
 147 extracted from a stock of MX-80 bentonite and the clay fraction of COx claystone was
 148 obtained from the core EST 51779 (borehole OHZ6126 – depth: -476.5 m), which was drilled
 149 from the main gallery of Andra's Underground Research Laboratory sited at Bure in the
 150 Meuse district (LSMHM, France). The borehole was extracted from a formation level that is
 151 representative of the clayey unit of the COx formation; COx argillite mineralogical
 152 composition is made of clay minerals (mainly illite, mixed layer illite/smectite, kaolinite, mica
 153 and chlorite), tectosilicates (mainly quartz and feldspars) as well as carbonates (mainly calcite
 154 and dolomite) (Gaucher et al. 2004).

155 The clay fraction of this CO_x claystone is named hereafter CO_x clay. MX-80 and CO_x clay
156 were separated and purified in four stages with a procedure which was already published
157 (Jackson 1975, Tournassat et al. 2007, 2011). A fine clay particle fraction (<2 μm) was
158 separated by sedimentation and/or centrifugation according to Stoke's law. Carbonates were
159 removed by adding 0.1 M acetic acid in 0.5 M NaCl (pH ~5) and the clays were then washed
160 with three cycles of centrifugation and re-dispersion in 0.5 M NaCl solution. The above
161 treatment was repeated twice. Next Fe and Mn oxides were removed with DCB (dithionite–
162 citrate–bicarbonate) treatment using dithionite diluted in 0.2 M citrate (C₆H₈O₇·H₂O), 0.5 M
163 NaCl, 0.1 M NaHCO₃. The clays were then washed with three cycles of centrifugation and re-
164 dispersion in 0.5 M NaCl solution. The above treatment was repeated twice. Finally, organic
165 matter was removed with 3% H₂O₂, 0.5 M NaCl solution at 60°C. After cooling, the clays
166 were washed with three cycles of centrifugation and re-dispersion in 0.5 M NaCl solution.
167 Centrifugation steps were carried out in Sigma 6K 10 Bioblock Scientific centrifuge at 13000
168 g for 30 min at 20°C. The extracted clay fraction of MX-80 usually contains minor amounts (<
169 20%) of quartz, cristobalite and amorphous silica impurities (Gailhanou et al. 2007,
170 Tournassat et al. 2009). The CO_x clay composition was not determined in this study and was
171 considered to be representative of the clay fraction of the claystone, i.e. approximately 50%
172 illite and 50% illite smectite mixed layer minerals (IS). Purified Illite du Puy (IdP) was
173 obtained from a previous project. Its preparation procedure and characterization is described
174 elsewhere (Gaboreau et al. 2016). The purified material was composed of illite layers (90–
175 94%) and negligible smectite layer (4–6%) and K-feldspar (less than 5%). Kunipia-P is a
176 highly purified Na-montmorillonite that contains nearly 100% montmorillonite, and that is
177 produced by Kunimine Industries Co. Ltd. (Tachi and Yotsuji 2014).

178 **2.5. Adsorption Experiments**

179 The following procedure was used for all experimental conditions summarized in Table 1.
180 First, Thermo Scientific™ Nalgene™ Oak Ridge High-Speed Polypropylene centrifuge tubes
181 were acid treated (HNO₃) and washed three times with Milli-Q water before use. Then, 5 or
182 10 mL of the clay stock dispersion was equilibrated at the target ionic strength and pH by
183 adding the correct amount of Milli-Q water, 0.1 M or 0.025 M NaCl, 0.01 M or 0.1 M HCl
184 and 0.01 M or 0.1 M NaOH stock solutions to reach a total volume of 18 or 19 mL. In order
185 to minimize the uncertainty on R_{SL}, the stock solution was stirred with a magnetic stirrer
186 during its sampling. Then, 1 or 2 mL of acidified Pb stock solution (10 μM, 100 μM or 1
187 mM) was added to reach the target total Pb concentration (1 μM, 10 μM or 50 μM). The final
188 pH value was always lower than the initial pH after clay dispersion pre-equilibration because
189 the Pb stock solutions were acid. This acid addition corresponded to approximately 20 μL 0.1
190 M HCl per tube. At near neutral pH value, the pH value dropped by 1 to 1.5 pH units. A
191 preliminary kinetic experiment showed that steady-state Pb concentration was reached after a
192 few hours in the conditions tested. As a result, a contact time of four days was chosen in order
193 (i) to ensure steady state in the system, and (ii) to be in agreement with contact times of one
194 to seven days considered in other similar studies reported in the literature (Gu and Evans
195 2007, Gu et al. 2010, Marques Fernandes et al. 2015). Samples at room temperature were put
196 on a horizontal shaker (Heidolph Rotamax 120) during the equilibration time.

197 One of the objectives of this study was to understand the variation of clay mineral affinity for
198 lead in response to a moderate increase of temperature expected in the environment of
199 radioactive waste disposal. For this reason, experiments were conducted at 67°C. For these
200 experiments, the pH was initially adjusted at room temperature with addition of NaOH and
201 HCl solutions. Clay dispersions were then heated and equilibrated for seven days at 67°C. Pb
202 was then added at 67°C and the clay dispersions were equilibrated for four days at 67°C in a
203 DigiPREP dry bath heater and were frequently agitated manually to re-suspend the settled
204 clay particles. Additionally control samples were prepared for each of the experiment
205 conditions. They were prepared with the same procedure except that the clay stock dispersion
206 was replaced by NaCl stock solutions. C_{init} was determined from their average Pb
207 concentrations at pH values below 6.5.

208 All preparations were done in an air atmosphere except a few experiments that were carried
209 out in a N₂ atmosphere glove-box (MBraun Unilab) with stock solutions that were prepared
210 inside the glove-box with Milli-Q that was degassed with N₂-bubbling in order to purge their
211 CO₂/bicarbonate/carbonate content. In the glove-box, seven sorption experiments were
212 conducted with 50 µM Pb, MX-80 clay at 5.7-9.4 pH range. For these samples, an aliquot of
213 the clay stock dispersion was degassed by letting it equilibrate with the glove-box atmosphere
214 for ten days. In addition, three control experiments were prepared without clay at pH 6.3 and
215 9.6. They were prepared with the same procedure as described above except that the clay
216 stock dispersion was replaced by 0.1 M NaCl solutions.

217 After equilibration, samples were centrifuged at ~12700 g for 15 minutes in Sigma 6K 10
218 Bioblock Scientific centrifuge. For the samples equilibrated at 67°C the centrifuge temperature
219 was set at 40 °C (the maximum value), and the samples were then put back into the dry bath
220 heater at 67°C for a few hours. pH was measured at 67°C after calibration of the electrode
221 response at 67°C. Then a 5 mL aliquot of supernatant was acidified with ~20 µL of 65% M
222 HNO₃ in polystyrene tubes for Pb measurements. Another 5 mL aliquot was preserved
223 without acidification for measurements (especially alkalinity). The volume of HNO₃ solution
224 added was taken into account for correcting the measurement of final Pb concentration.
225 Additional control experiments without addition of Pb solution made it possible to measure
226 the release of Pb into solution naturally present in the clay minerals.

227 In addition to the samples investigated with the above procedure, some tests were also run to
228 study the effect of the order of reagent addition (pH set before or after Pb addition), as well as
229 the presence of pH buffers (sodium acetate/acetic acid at pH 3.6-4.6, MES at pH 5.5-6, and
230 MOPS at pH 6.5-7), i.e. buffers whose use has been frequently reported in adsorption
231 experiments described in the literature (Baeyens and Bradbury 1997, Marques Fernandes et
232 al. 2016)) and filtering (0.1 µM Millex Syringe filters) the supernatant before Pb
233 measurement. All of these tests were carried out with Kunipia-P montmorillonite.

234 **2.6. Concentration and pH Measurements**

235 An InLab micro electrode (Mettler Toledo) was used to measure the final pH in the
236 supernatant of centrifuged dispersions. Before use, the tubes dedicated to Pb measurements
237 were washed with 5% HNO₃ acid and then rinsed repeatedly with Milli-Q water. Pb
238 concentrations were measured by furnace atomic absorption spectroscopy (AAS 220 Z,
239 Spectra AA) or by inductively coupled-plasma mass spectrometry for the lowest

240 concentrations (ICP-MS-NEXION 350 X, Perkin Elmer). The comparison of AAS and ICP-
 241 MS independent measurement results also made it possible to control the accuracy of the
 242 measurements. Alkalinity was measured with an automatic titrator (736 GP Titrimo Metrohm),
 243 using the Gran method. Dissolved inorganic carbon (DIC) concentrations were calculated
 244 from alkalinity and pH values.

245 2.7. Quantification of Adsorption

246 Surface coverage (C_{ads} in $\text{mol}\cdot\text{kg}^{-1}$) and distribution coefficient (R_D in $\text{L}\cdot\text{kg}^{-1}$) were calculated
 247 from the initial Pb concentration (C_{init} in $\text{mol}\cdot\text{L}^{-1}$), the equilibrium Pb concentration in
 248 solution (C_{eq} in $\text{mol}\cdot\text{L}^{-1}$) and the solid/liquid ratio (R_{SL} in $\text{kg}\cdot\text{L}^{-1}$).

$$C_{ads} = \frac{C_{init} - C_{eq}}{R_{SL}} \quad (1)$$

$$R_D = \frac{C_{init} - C_{eq}}{C_{eq} \times R_{SL}} \quad (2)$$

249 The error bands were calculated as follows (Tournassat et al. 2013):

$$uC_{ads} = \frac{\sqrt{uC_{init}^2 + uC_{eq}^2}}{R_{SL}}; \Delta C_{ads} = k \times uC_{ads} \quad (3)$$

$$uR_D = \sqrt{\left(\frac{uC_{init}}{R_{SL} \cdot C_{eq}}\right)^2 + \left(\frac{C_{init} \cdot uC_{eq}}{R_{SL} \cdot C_{eq}^2}\right)^2}; \Delta R_D = k \times R_D \quad (4)$$

250 Where Δ values are the considered error bands, k is the coverage factor ($k=2$, corresponding
 251 to a 95% confidence interval), uC_{init} and uC_{eq} are the uncertainties associated with the total
 252 concentration and the equilibrium concentration respectively, considered at 2% of the values.
 253 Uncertainty of the R_{SL} was neglected.

254 2.8. Modeling

255 The modeling of the data combined ion exchange on basal sites, surface complexation on
 256 edge sites and precipitation reactions. Geochemical modeling was carried out with PHREEQC
 257 v3 (Parkhurst and Appelo 2013). The ThermoChimie v9b database (Giffaut et al. 2014) was
 258 used to calculate aqueous and precipitation/dissolution reactions. The influence of the
 259 complexation reactions in solution (e.g. Pb^{2+} with Cl^- and HCO_3^-) was thus explicitly taken
 260 into account. The Debye-Huckel equation was used for ionic strength correction. In
 261 ThermoChimie, the temperature dependence of the equilibrium constants is estimated with the
 262 Van't Hoff equation. A standard temperature of 25°C was considered to model the data
 263 obtained at 20°C . The software PHREEPLOT was used to plot predominance diagrams and
 264 contour plots (Kinniburgh and Cooper 2011).

265 Sorption model parameters for ion exchange and surface complexation reactions were
 266 determined by a fitting procedure applied to the whole dataset, starting from the determination
 267 of selectivity coefficients for cation exchange reactions using experimental data sets at two
 268 different ionic strength and at low pH values. Then the surface complexation constants and
 269 the surface site densities were determined with the data measured in the pH range from 4 to
 270 6.5.

271 **3. Results**

272 **3.1. Influence of Experimental Procedures on Pb Retention**

273 *3.1.1. pH Buffers and Filtration*

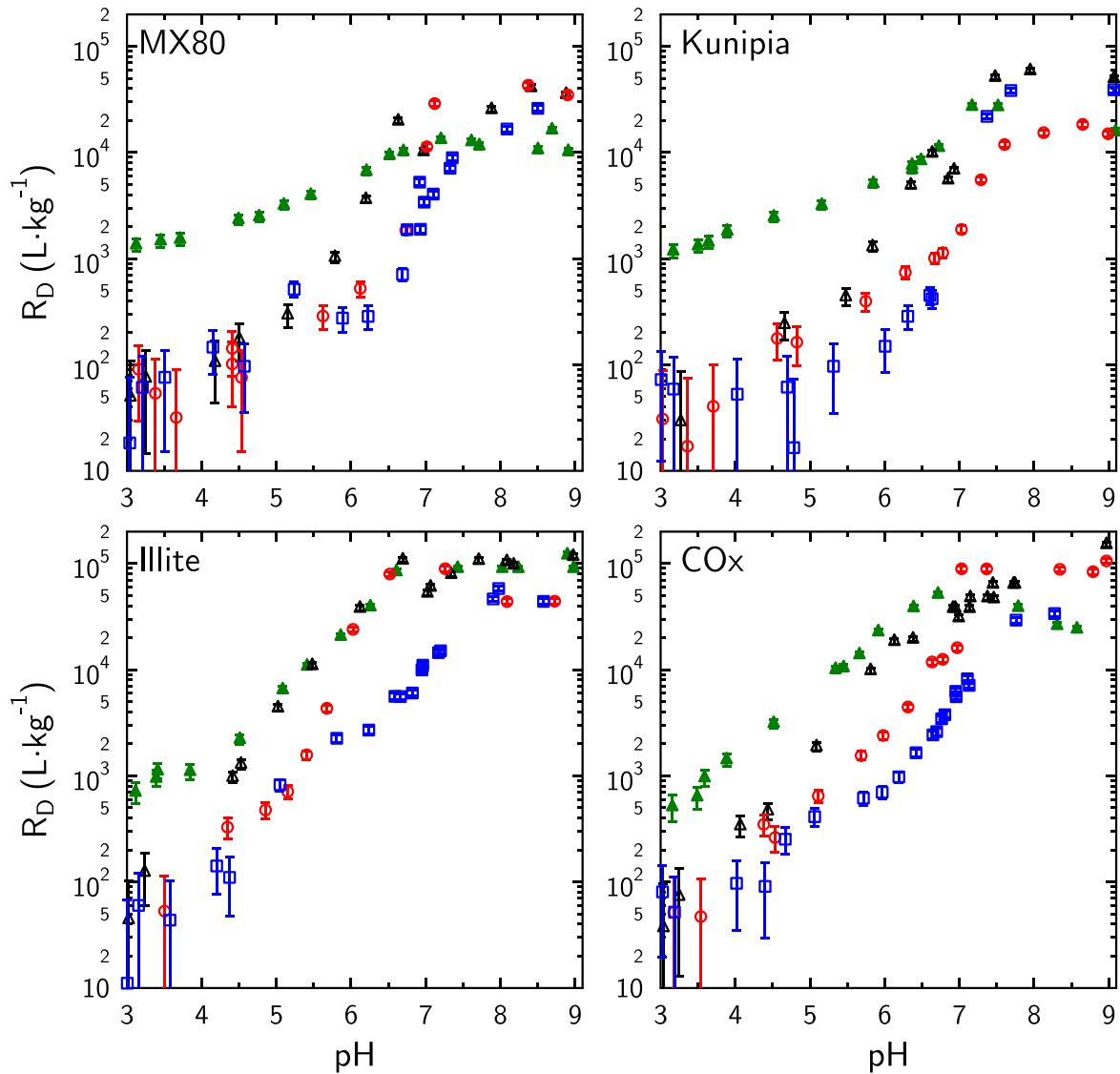
274 Adding buffers to stabilize the pH had a marked impact on the measured R_D and surface
275 coverage (C_{ads}) values (Figure S-1, Supporting information), contrasting with the results of
276 previous studies, which showed that the presence of pH-buffers had little or no effect on the
277 adsorption of divalent metals on montmorillonite (Baeyens and Bradbury 1997). Because it
278 was very difficult to fix the pH at a desired value without using a buffer, this experimental
279 artefact prevented the acquisition of a Pb adsorption edge as a function of concentration and at
280 constant pH. Instead, the Pb adsorption edge was established at constant Pb concentration
281 and as a function of pH, with various total Pb concentrations from 1 μM to 50 μM . Using
282 filters had little impact on the Pb concentration measurements at equilibrium. Consequently,
283 Pb concentration was measured without filtering of the supernatant in agreement with
284 procedures frequently reported in clay adsorption studies (Baeyens and Bradbury 1995, Yang
285 et al. 2010, Marques Fernandes et al. 2015).

286 *3.1.2. Order of Addition of Reagents*

287 The order of addition of reagents had a big impact on the measured R_D values especially for
288 pH values above 6, i.e. for pH values that necessitated the addition of NaOH to reach the
289 target value: the addition of Pb prior to pH adjustment increased the measured retention of Pb
290 compared to the case where Pb was added after pH adjustment. (Figure S-2). Consequently,
291 the pH adjustments were done before spiking the solution with Pb in all experiments reported
292 in the following.

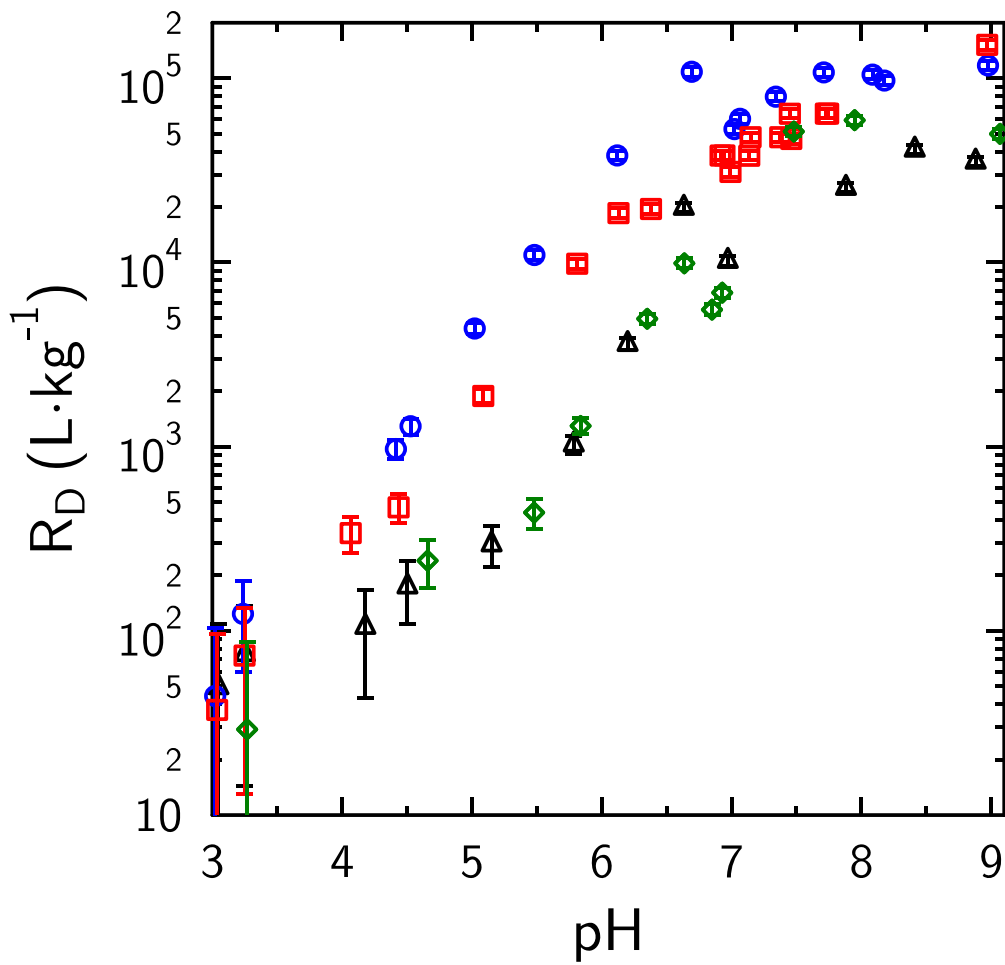
293 **3.2. Pb Retention Behavior under Varying Chemical Conditions**

294 Similar trends were observed for pH-dependent retention isotherms with all clay minerals at
295 different ionic strengths (Figure 1) and at different total Pb concentrations. At room
296 temperature, Pb retention increased with decreasing ionic strength at constant Pb
297 concentration and constant pH, and it increased with increasing pH at constant ionic strength
298 and total Pb concentration. Although similar in shape for all clay samples, Pb retention curves
299 exhibited contrasted retention maxima depending on the clay samples' nature (Figure 2).
300 Kunipia and MX-80 had very similar affinity for Pb and were the materials tested that had
301 lowest Pb affinity. IdP had the greatest affinity, and COx clay sample exhibited retention
302 behavior intermediate between montmorillonite and IdP, in qualitative agreement with its
303 mineralogical composition containing illite and illite smectite mixed layers. The effect of
304 ionic strength on retention was maximum at pH value below 5 for montmorillonite (MX-80
305 and Kunipia), and was otherwise limited. Changes in ionic strength had little effect on overall
306 Pb retention for IdP and COx clay samples. A temperature increase had also no significant
307 effect on Pb adsorption for all clay types in the investigated conditions ($C_{tot}=1 \mu\text{M}$, 0.1 M
308 NaCl, and 67°C) (Figure 3).



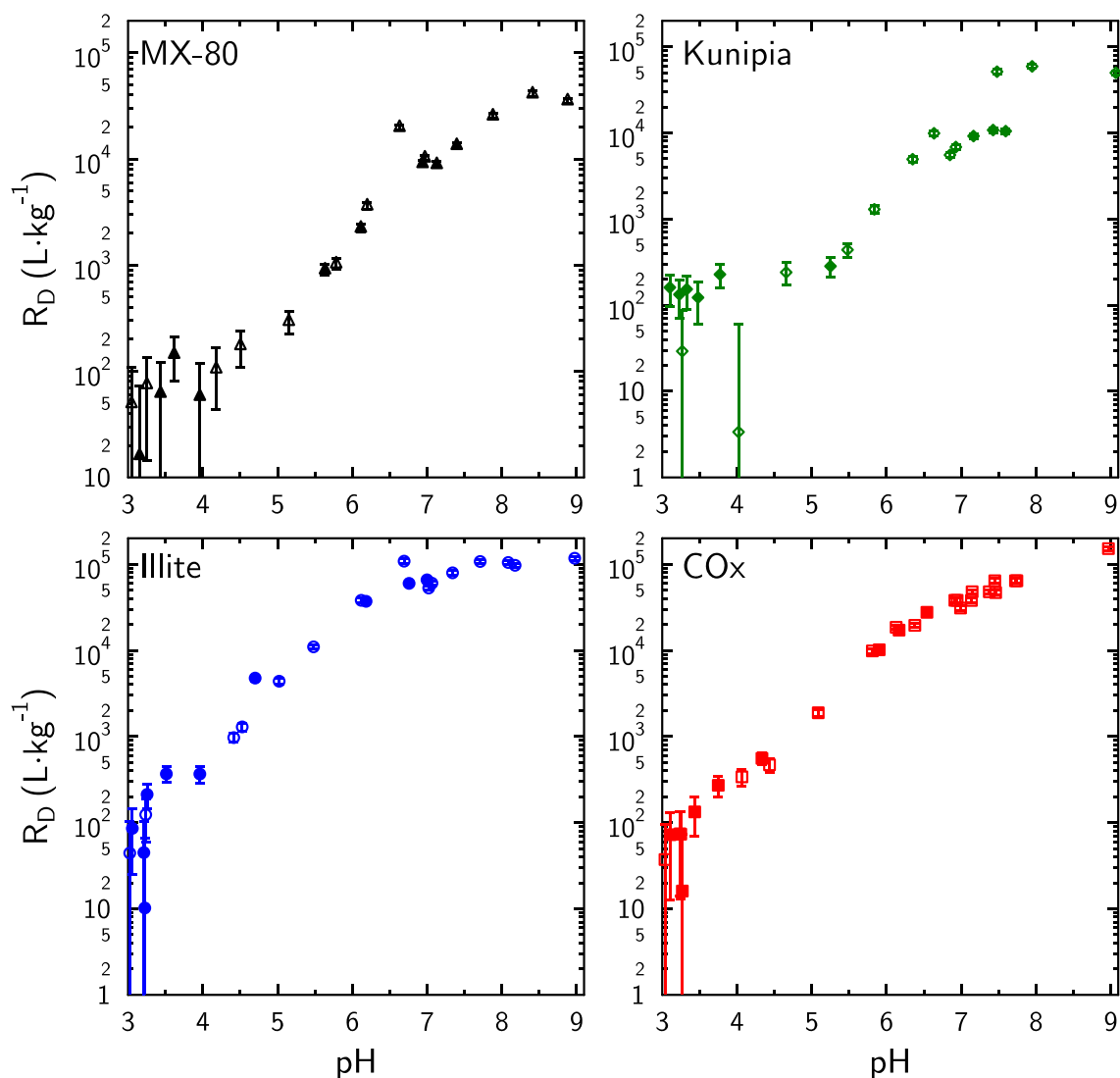
309

310 Figure 1. Comparisons of experimental datasets for Pb retention at room temperature on MX-
 311 80, Kunipia-P, IdP and COx clay as a function of pH, ionic strength (0.025 M NaCl = closed
 312 symbols; 0.1 M NaCl = open symbols), and total Pb initial concentrations (triangle symbols: 1
 313 μM ; circle symbols: 10 μM ; square symbols: 50 μM) (Details of the datasets are given in
 314 supporting information file).



315

316 Figure 2. Comparison of Pb retention on MX-80 (triangles), Kunipia (diamonds), IdP (circles)
 317 and COx clay (squares) at room temperature as a function of pH, in the presence of 0.1 M
 318 NaCl background electrolyte and a total Pb concentration of 1 μ M.



319

320 Figure 3. Pb retention on MX-80 (triangles), Kunipia (diamonds), IdP (circles) and COx clay
 321 (squares) at room temperature (open symbols) and 67°C (closed symbols) as a function of pH,
 322 in the presence of 0.1 M NaCl background electrolyte and a total Pb concentration of 1 μM
 323 (Details of the datasets are given in supporting information file).

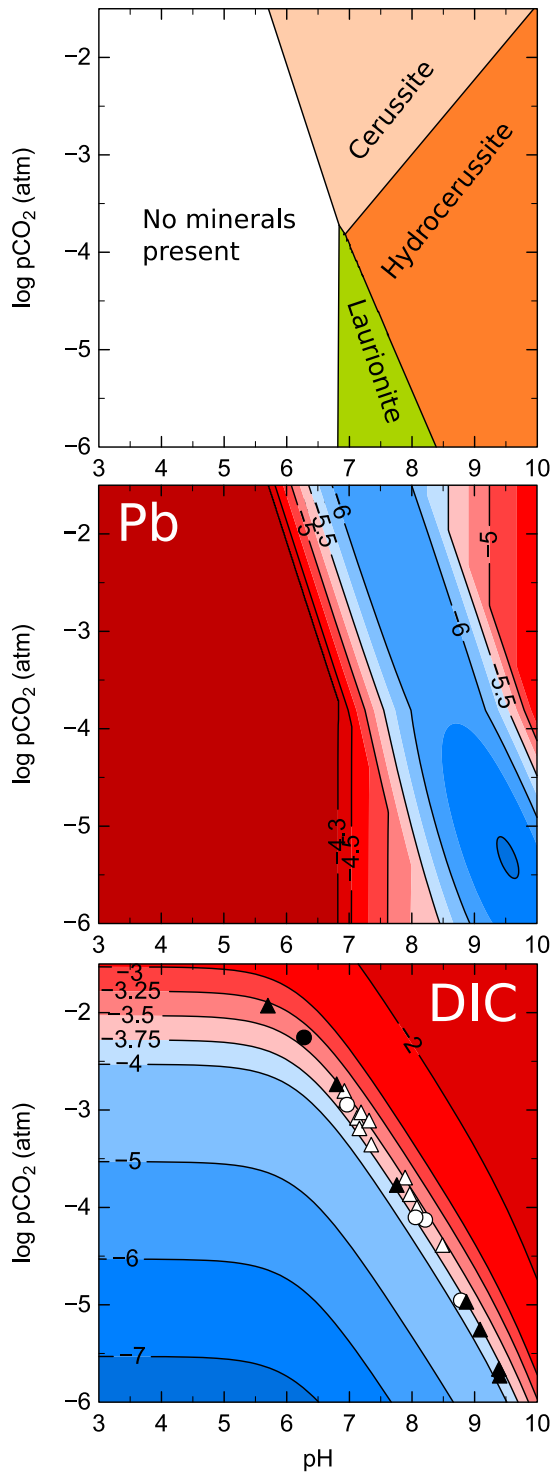
324 3.3. Alkalinity and DIC concentrations

325 Samples tested at room temperature had alkalinity values within the range 0.17-0.31 $\text{meq}\cdot\text{L}^{-1}$
 326 in the presence or absence of clay and for pH ranging from ~5.5 to 9. These alkalinity values
 327 corresponded to calculated DIC concentrations that were consistent with a near equilibrium of
 328 stock solutions and dispersion with atmospheric CO_2 ($\log p\text{CO}_2 = -3.5$) before the adsorption
 329 experiment (Figure 4, bottom) at pH 7-8. For this reason, a constant DIC concentration of ~
 330 $0.25 \text{ mmol}\cdot\text{L}^{-1}$ (-3.6 in \log_{10} scale) was considered to be present in all samples. Despite the
 331 care to exclude CO_2 from the experiment conducted in the glove-box, alkalinity/DIC
 332 concentration values were similar to values obtained in experiments conducted outside the
 333 glove-box (Figure 4, bottom). This observation echoes the results of Tournassat et al. (2018)
 334 on U(VI) adsorption experiments on montmorillonite, where the DIC concentrations
 335 measured in “ CO_2 -free” experiment ranged from $8.2 \cdot 10^{-3}$ to $6.2 \cdot 10^{-2} \text{ mmol}\cdot\text{L}^{-1}$ in the pH
 336 range 3.9-9.9.

337 **4. Modelling and Discussion**

338 **4.1. Adsorption versus (Co-)Precipitation**

339 It is well known that divalent heavy metals such as Pb can precipitate at near natural or
340 alkaline conditions depending on their concentration in the aqueous solution and on the water
341 composition (Marani et al. 1995, Echeverría et al. 2005, Sipos et al. 2008, Tournassat et al.
342 2013). Thermodynamic calculations evinced that for a total Pb concentration of 50 μM , Pb
343 precipitation was expected to occur at pH ~ 6.7 in the presence of atmospheric CO_2 partial
344 pressure ($\log p\text{CO}_2 = -3.5$) (Figure 4, top). Therefore Pb precipitation could have occurred in
345 the form of cerussite (PbCO_3), hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$) or laurionite (PbClOH)
346 above pH 6.7 for the highest investigated total Pb concentration (50 μM). Based on
347 experiments with direct precipitation in solution, Marani et al. (1995) showed that cerussite
348 and hydrocerussite can indeed form easily in conditions similar to the experimental conditions
349 in this work. Pb (co-)precipitation may explain the discrepancy observed between
350 experiments with Pb addition made before or after pH adjustment (Figure S-2): increasing the
351 pH after Pb addition could have been responsible for (surface) precipitation when the
352 concentrated NaOH solution entered into contact with the clay-Pb dispersion. Such (surface)
353 precipitation and/or surface polymerization in the presence of clay minerals was evidenced in
354 previous studies using EXAFS (Strawn and Sparks 1999) and by direct SEM observations
355 (Echeverría et al. 2005), but with total Pb concentrations higher than those used in this study.
356 In practice, data interpretation with an adsorption model needs to be restricted to the pH
357 domain where precipitation does not occur (Tournassat et al. 2013). Consequently, the
358 complexation of free Pb^{2+} by bicarbonate and carbonate in solution as well as the possible
359 precipitation of Pb carbonate minerals must be taken into account for the quantitative
360 interpretation of the results with SCM.



361

362 Figure 4. Top figure: Pb solid phase predominance as a function of pH and pCO₂ in the
 363 absence of adsorption processes. Minerals allowed to precipitate: cerussite (PbCO₃),
 364 hydrocerussite (Pb₃(CO₃)₂(OH)₂), cotunnite (PbCl₂), laurionite (PbClOH), paralaurionite
 365 (PbClOH) and Pb(OH)₂(s): Total Pb concentration: 50 μM (log [Pb]_{tot} = -4.3). Middle figure:
 366 Contour plot of calculated Pb concentration in solution (log₁₀ scale) as a function of pH and
 367 pCO₂. The color change between two contour lines indicates a change of 0.25 log₁₀ scale
 368 units. Bottom figure: Contour plot of calculated DIC concentration as a function of pH and
 369 pCO₂ (log₁₀ scale). Symbols correspond to experimental measurements in the presence
 370 (triangles) or absence (circles) of clay and with sample preparation in contact with atmosphere

371 (white symbols) or in the glove-box (black symbols). The background electrolyte
372 concentration is 0.1 M NaCl for all figures.
373 The data, obtained with correct reagent addition order, and in conditions where Pb
374 precipitation was not expected from a thermodynamic point of view, were in qualitative
375 agreement with the adsorption mechanisms of divalent metals on clay mineral surfaces that
376 have been identified for many years, using a combination of wet chemistry experiments with
377 diffractometric and spectrometric characterization (Tournassat et al. 2013, Borisover and
378 Davis 2015). According to these mechanisms, cation exchange on basal and interlayer
379 surfaces was responsible for Pb adsorption at low pH (below 3 to 5 depending on the clay
380 material) where nearly constant R_D values were measured. As expected, changes in ionic
381 strength impacted R_D values more for montmorillonite than for illite (Figure 2) because the
382 cation exchange capacity of montmorillonite is higher than that of illite. R_D values with COx
383 clay, which has intermediate cation exchange capacity between montmorillonite and illite,
384 accordingly exhibited intermediate behavior. Surface complexation on the edge surfaces was
385 responsible for Pb adsorption at higher pH, and a strong influence of pH on R_D values was
386 recorded for all four types of samples. Note also that little effect of ionic strength was
387 recorded.

388 **4.2. Modeling Pb adsorption on clay mineral surfaces**

389 *4.2.1. Choice of model*

390 SCMs quantify adsorption processes based on a set of protonation/deprotonation and
391 adsorption reactions, which links the surface charge to the surface potential and the specific
392 surface area where the reactions taken place. SCMs were initially developed to model the
393 reactivity of oxide surfaces and gave rise to numerous variants, of which the most extensively
394 used are the Constant Capacitance Model – CCM – (Goldberg 2013), Diffuse-Double Layer
395 model – DDL – (Dzombak and Morel 1990), the Triple Layer Model – TLM – (Davis and
396 Kent 1990), and the Charge Distribution model – CD(-MUSIC) – (Hiemstra and Van
397 Riemsdijk 1996). Numerous SCM using these classical approaches have been published in the
398 literature to describe adsorption on clay mineral surfaces (Zachara and Smith 1994, Turner et
399 al. 1998, Barbier et al. 2000, Ikhsan et al. 2005, Gu and Evans 2007, Gu et al. 2010, Akafia et
400 al. 2011) These models, however, have not taken into account the unique characteristics of
401 electrostatic surface potentials that occur at clay edge sites, where the electrostatic surface
402 potential of basal plane cation exchange sites influences the surface potential of neighboring
403 edge sites, i.e. the ‘spillover’ effect (Secor and Radke 1985, Chang and Sposito 1996). Indeed,
404 the spillover effect invalidates the use of classical SCMs such as DDL, CCM and TLM to
405 quantify the effect of clay edge surface charge potential on adsorption (Bourg et al. 2007,
406 Tournassat et al. 2013, 2016). The inadequacy of the classical DLM model to reproduce
407 divalent metal adsorption on montmorillonite surface in a wide range of pH and ionic strength
408 conditions has been put forward repeatedly for more than twenty years (Baeyens and
409 Bradbury 1997, Akafia et al. 2011). Only recently, a SCM that included the spillover effect in
410 the evaluation of the surface potential was successfully applied to quantify U(VI) adsorption
411 on montmorillonite in a wide range of pH, ionic strength and DIC concentration conditions
412 (Tournassat et al. 2018). In this study, quantifying Pb adsorption were investigated on
413 montmorillonite samples, but also on illite samples and on a natural assemblage of illite,

414 illite/smectite mixed layer mineral (IS) and smectite. A second objective was the prediction of
415 adsorption properties of natural Callovian-Oxfordian claystone in the presence of *in situ*
416 conditions (pH~7.2 and pCO₂~10⁻² bar at 25°C). Unfortunately, the above mentioned
417 ‘spillover’ model has been developed only for montmorillonite, not for illite. Alternatively,
418 instead of a comprehensive model that includes as many physically grounded mechanisms as
419 possible, simpler, yet successful, models can be developed. A good example of this kind of
420 model is the 2SPNE SC/CE Model (2 site protolysis non-electrostatic surface complexation
421 and cation exchange model) developed by Bradbury and Baeyens (1997). The authors noted
422 that their data were better fitted if the electrostatic term was canceled. In this model, surface
423 complexation of divalent metals on the clay mineral edge surfaces was ascribed to two types
424 of sites: high-energy (strong) sites that are present in low amounts (typically ~2 mmol·kg⁻¹)
425 and have high affinity for the adsorbate, and low energy (weak) sites that, conversely, are
426 present in large amounts (typically ~50 mmol·kg⁻¹) and have low affinity for the adsorbate.
427 Because this type of model aims for efficiency and simplicity and because it does not include
428 physical features that play a significant role in the adsorption mechanism, it must fulfil the
429 parsimony rule, i.e. that the least number of parameters must be considered to fit the data
430 (Tournassat et al. 2013). In this modeling effort, this approach was applied together with a
431 non-electrostatic model in order to fit the adsorption data on IdP and MX-80 samples, and
432 then it was used to predict the adsorption on Kunipia and COx clay. The component additivity
433 (CA) approach was used to model the adsorption on the COx clay with the assumption that
434 the reactivity of edge site of illite/smectite mixed layers was similar to this combination of
435 montmorillonite and illite layer edges (Davis et al. 2004, Chen et al. 2014a, 2014b).

436 4.2.2. Modeling the data at room temperature

437 A very simple model with only one cation exchange site and one edge surface complexation
438 site (Table 2) was sufficient to fit all the data at room temperature (Figure 5 and Figure 6).
439 The cation exchange selectivity coefficients for Pb on MX-80 and IdP (log K = 0.6 and 0.7
440 respectively) had values similar to values reported for other divalent metals (e.g. Ni, Cu, Co,
441 Zn, Fe) (Fletcher and Sposito 1989, Bradbury and Baeyens 2005a, Charlet and Tournassat
442 2005, Tournassat et al. 2009). The surface complexation site density values (0.01 and 0.035
443 mol·kg⁻¹ for MX-80 and IdP respectively) were in the range of low energy site densities
444 described in the literature for montmorillonite and illite, indicating that high energy sites may
445 not be present on these samples or may be present at very low site density (Baeyens and
446 Bradbury 1997, Bradbury and Baeyens 2005b). The presence of an additional high energy
447 adsorption site in this model did not improve markedly the overall fitting of the data, so it was
448 decided not to include it. The protonation of the surface was not needed in this model to fit the
449 data (Tournassat et al. 2013). In the presence of high total Pb concentration and near neutral to
450 alkaline pH values, (hydro)cerussite precipitation was in quantitative agreement with the
451 observed sharp R_D increase. Retention data on Kunipia were adequately predicted with the
452 same model as for MX-80. Retention data on COx clay were well predicted with a model
453 mixing 50% of illite and 50% of montmorillonite. These proportions correspond roughly to
454 the proportion of, respectively, illite and illite smectite mixed layers minerals in the clay
455 fraction of the COx clay (Gaucher et al. 2004, Chen et al. 2014a) and indicate that the

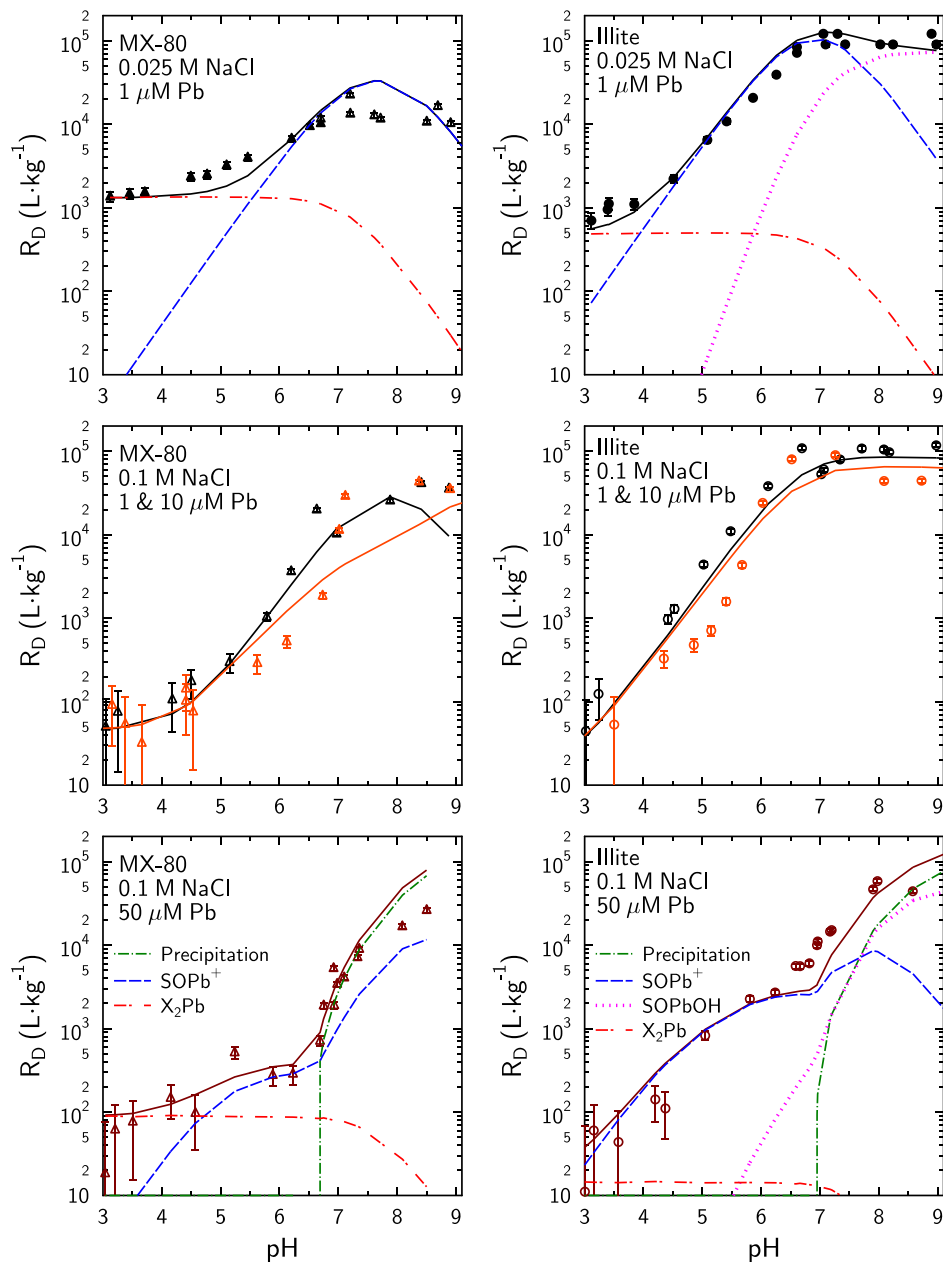
456 reactivity of illite smectite mixed layers minerals can be modeled with edge surface
 457 adsorption properties similar to those of montmorillonite.

458 Table 2. Parameters used in the non-electrostatic SCM at 25°C (values in parenthesis are for
 459 67°C).

	Montmorillonite	Illite
Cation exchange		
CEC (X^- site density) in mol·kg ⁻¹	0.78 ⁽¹⁾	0.2 ⁽²⁾
Edge surface complexation		
Site density (>S) in mol·kg ⁻¹	0.01	0.035
Reactions	log K	
$2 XNa + Pb^{2+} = X_2Pb + 2 Na^+$	0.6 (0.9)	0.7 (0.9)
$2 XNa + Mg^{2+} = X_2Mg + 2 Na^+$	0.6	0.7
$2 XNa + Ca^{2+} = X_2Ca + 2 Na^+$	0.5	0.5
Reactions	log K	
$>SOH = >SO^- + H^+$	-8.1	-6.6
$>SOH + Pb^{2+} = >SOPb^+ + H^+$	0 (0.2)	0.6 (0.9)
$>SOH + Pb^{2+} + H_2O = >SOPb(OH) + 2H^+$	Not necessary	-7.2 (-6.7)

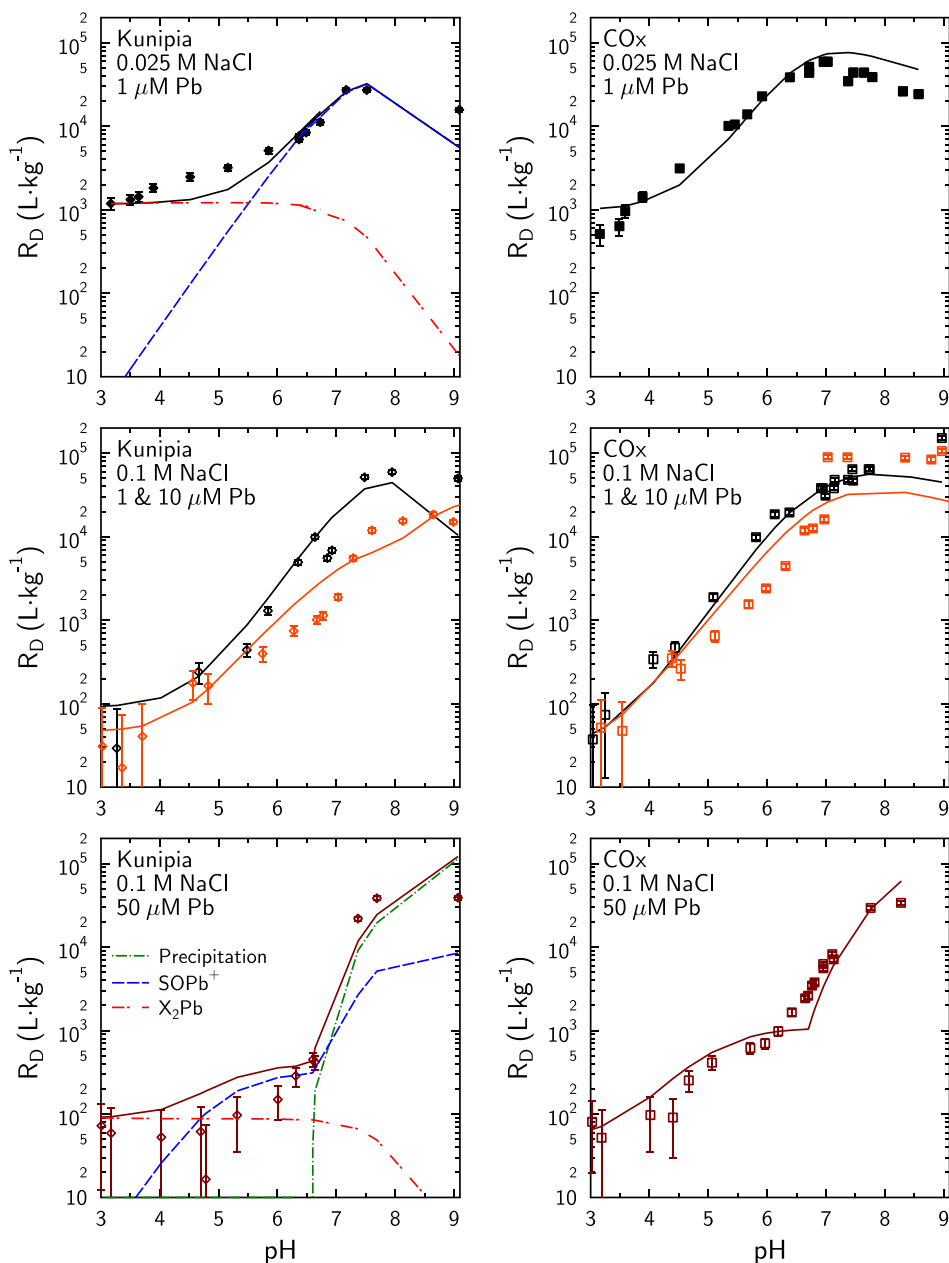
460 ⁽¹⁾(Bradbury and Baeyens 2002)

461 ⁽²⁾(Bradbury and Baeyens 2000)



462

463 Figure 5. Modeling of Pb adsorption and precipitation at room temperature according to the
 464 parameters given in Table 2 for MX-80 (left) and illite (right).



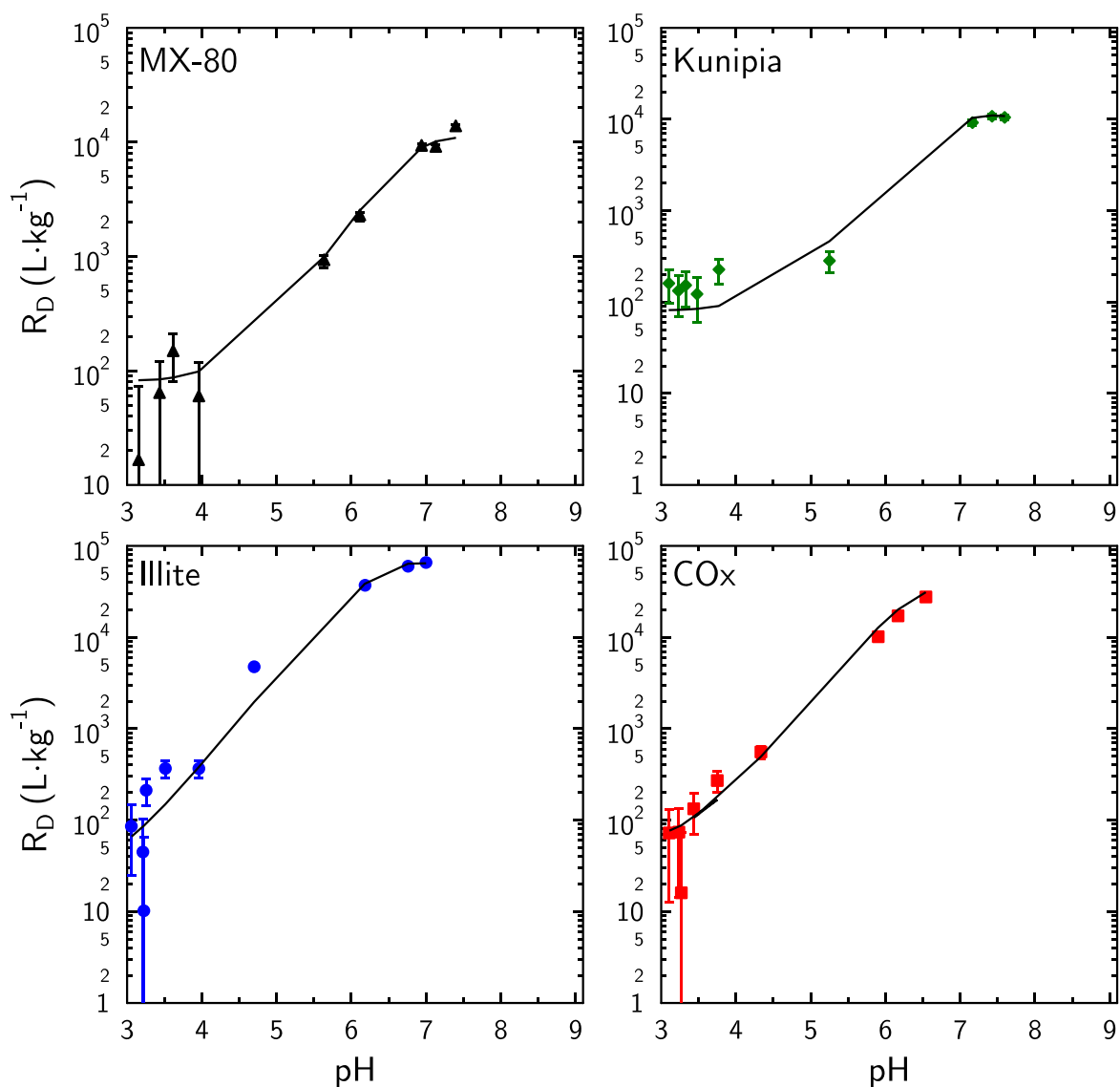
465

466 Figure 6. Model prediction for Pb adsorption / precipitation on Kunipia-P (left) and COx clay
 467 (right) at room temperature. Model parameters for Kunipia-P are the same as for MX-80. Pb
 468 adsorption on COx clay was modeled with an illite surface contribution of 50% and a smectite
 469 surface (montmorillonite) contribution of 50%.

470 *4.2.3. Modeling the data at 67°C*

471 A temperature increase at fixed pH and total Pb concentration values is responsible for a
 472 change in the $(\text{Pb}^{2+})/(\text{H}^+)$ activity ratio, which reflects the changes in Pb speciation in solution
 473 and the change of water dissociation constant as a function of temperature. This change
 474 should impact the equilibrium of the reaction $>\text{SOH} + \text{Pb}^{2+} = >\text{SOPb}^+ + \text{H}^+$. $(\text{Pb}^{2+})/(\text{H}^+)$
 475 changes can be tracked by looking at the value of $(\text{Pb}^{2+})/(\text{H}^+)$ at 67°C normalized to its value
 476 at 25°C at fixed pH and total Pb concentration (Figure S-3). Up to pH 6, the value of

477 $\frac{(\text{Pb}^{2+})/(\text{H}^+)_{67^\circ\text{C}}}{(\text{Pb}^{2+})/(\text{H}^+)_{25^\circ\text{C}}}$ is nearly constant and close to 0.85. For pH values above 6, the value of
478 $\frac{(\text{Pb}^{2+})/(\text{H}^+)_{67^\circ\text{C}}}{(\text{Pb}^{2+})/(\text{H}^+)_{25^\circ\text{C}}}$ decreases mostly because the abundance of Pb^{2+} compared to other Pb species
479 in solution decreases with increasing pH faster at 67°C than at 25°C . A temperature increase
480 from room temperature to 67°C had no significant effect on Pb adsorption on all four clay
481 samples up to pH 7 (Figure 3). Therefore, a slight log K change was applied in this surface
482 complexation model to compensate for the change in $(\text{Pb}^{2+})/(\text{H}^+)$ activity ratio in solution
483 from room temperature to 67°C (Table 2, Figure 7). The log K of surface complexation
484 reactions increased slightly with a temperature increase in agreement with previous
485 observations made on Ni adsorption (Tertre et al. 2005). It could be tempting to conclude that
486 a temperature increase is favorable to Pb adsorption on clay minerals. However, in a claystone
487 such as the Callovo-Oxfordian clay the pH value is expected to decrease from ~ 7.2 at 20-
488 25°C to ~ 6 at 80°C and the DIC concentration is expected to increase from ~ 3 mM at 20-
489 25°C to ~ 15 mM at 80°C (Beaucaire et al. 2012, Gailhanou et al. 2017). Overall, these
490 changes should be detrimental to Pb adsorption on clay mineral surfaces. Based on these
491 results, it can be estimated that Pb adsorption R_D value should drop by approximately one
492 order of magnitude if Pb is present at trace concentrations.



493

494 Figure 7. Model predicting Pb adsorption on the four clay samples at 67°C. Parameters are
 495 given in Table 2. Total Pb concentration: 1 μM . Solid/liquid ratio: 1 $\text{g}\cdot\text{L}^{-1}$. Background
 496 electrolyte: NaCl 0.1 M.

497 4.3. Comparison with literature data

498 The predictions of the model were tested with Pb adsorption literature data obtained with
 499 different montmorillonite, bentonite and illite samples in a range of experimental conditions
 500 (Table 3).

501 Table 3: Experimental conditions of Pb absorption experiments described in the literature

Clay Type	Clay material preparation procedure	pH	Background electrolyte (M)	$[\text{Pb}]_{\text{tot}}$ (μM)	R_{SL} ($\text{g}\cdot\text{L}^{-1}$)	Reference
SWy-2 Mont.	None	3–11	0.001–0.1 NaNO_3	0.1–50	0.5	(Akafia et al. 2011)
Fithian illite	< 2 μm NaNO_3 treated	3–8	0.001–0.1 NaNO_3	50	2.97	(Gu and Evans 2007)

MX-80 Mont Wyoming	None	1-12	0.01 NaNO ₃	48.3	0.2; 0.4	(Xu et al. 2008)
Mont. Chinese bentonite	< 2 μm NaNO ₃ treated	3-9	0.001 0.1 NaNO ₃	48.8	1.5	(Gu et al. 2010)
	< 2 μM 1.0 M NaCl treated	2-12	0.001-0.1 NaClO ₄	72.5	0.5	(Yang et al. 2010)

502

503 The data from Akafia et al. (2011), which were obtained with Swy-2 montmorillonite, were
504 adequately predicted with this very simple model (Figure 8). As for the modeling of the data
505 obtained in this study, the presence of a constant DIC concentration of 0.25 mM in all pH
506 range (due to atmospheric CO₂ contamination) and the possible precipitation of
507 hydrocerussite were also considered. Akafia et al.'s data at the highest total Pb concentration
508 (50 μM) and pH value above 6.5 were in quantitative agreement with a precipitation process
509 (Figure 8). Their data at low pH and low ionic strength (0.001 M NaNO₃ background
510 electrolyte) were reproduced, considering the presence of a low Mg²⁺ concentration
511 competing with Pb²⁺ for cation exchange sites. The Mg²⁺ concentration was fixed at 0.1 mM in
512 agreement with data reported in the literature in similar experimental conditions (Baeyens and
513 Bradbury 1995, Gu et al. 2010, Marty et al. 2011), and the same cation exchange selectivity
514 coefficient was attributed to Mg²⁺ and to Pb²⁺ (Fletcher and Sposito 1989, Tournassat et al.
515 2009). The presence of Mg²⁺ in solution (and on the exchanger at low background electrolyte
516 concentration) was due to the partial dissolution of the clay layers (Marty et al. 2011). The
517 competitive presence of Mg²⁺ for cation exchange sites cannot be avoided, and it cannot be
518 neglected in the modeling for data at low ionic strength (typically below 0.01) and low pH.
519 Finally, the data in the pH range 4 to 7 were very well fitted if the surface complexation site
520 density was increased from 0.01 to 0.02 mol·kg⁻¹ (Figure 8). Surface complexation site
521 density is related to the edge specific surface area of montmorillonite layers and not to the N₂-
522 BET surface area that lumps together external basal surface area and edge surface area (Metz
523 et al. 2005, Tournassat et al. 2015). According to Atomic Force Microscopy, Derivative
524 Isotherm measurements and potentiometric titration data, MX-80, Kunipia-P and Swy-2
525 montmorillonite have edge specific surface area values of ~7 – 12 m²·g⁻¹, ~5 m²·g⁻¹ and ~14 –
526 25 m²·g⁻¹ respectively (Duc et al. 2005, Yokoyama et al. 2005, Le Forestier et al. 2010,
527 Tournassat et al. 2015, 2016). This difference in surface area values is commensurable with
528 the modeled difference in site density between MX-80/Kunipia-P and Swy-2 samples.
529 Consequently, the agreement between the model predictions and the published data from
530 Akafia et al. (2011) indicated that three different reference montmorillonite samples – MX-
531 80, Kunipia-P, and Swy-2 – had similar Pb adsorption properties, MX-80 and Kunipia-P
532 having a smaller site density than Swy-2 because of their smaller edge specific surface area.

533 With the same modeling approach, the Pb adsorption data that were measured by Gu and
534 Evans (2007) with Fithian illite were predicted correctly up to pH 6.5 in the presence of
535 0.001-0.1 M NaNO₃ and of a 50 μM Pb total concentration. Above this pH value, the model
536 overestimated the measured adsorption values, but this discrepancy may fall in the range of
537 data uncertainty: first, it was difficult to estimate the uncertainty in the measurement itself,
538 and second, data digitization may have introduced some bias especially for data at retention
539 values close to 100%, for which the discrepancy is the largest. A better data fit was obtained if
540 the site density was reduced from 0.035 to 0.025 mmol·kg⁻¹ (Figure 9). Because this
541 difference in site density is small, it can be concluded that Fithian illite and IdP had similar Pb
542 adsorption properties.

543 Some other literature data were not compatible with this model prediction. Xu et al. (2008)
544 studied Pb adsorption on non-purified MX-80 bentonite, i.e. a material similar to the materials
545 used in this study, except that it contained additional mineral impurities such as quartz,
546 cristobalite, feldspar and calcite, which were partly removed during the sample preparation
547 procedure in this study. Xu et al. (2008) used a high Pb to clay ratio (total Pb concentration
548 was 48.3 μM and solid/liquid ratio was 0.2 or 0.4 $\text{g}\cdot\text{L}^{-1}$). In the experiment with 50 μM total
549 Pb concentration and a clay concentration of 1 $\text{g}\cdot\text{L}^{-1}$ and $I=0.01$ M NaNO_3 , a site (>S)
550 saturation effect was observed at $\text{pH} < 6.5$ that made it possible to refine a site density value
551 at ~ 0.01 $\text{mol}\cdot\text{kg}^{-1}$ (Figure 5). At pH values greater than 6.5, Pb precipitation occurred in these
552 experimental conditions. In the experiments of Xu et al. (2008), such site saturation did not
553 occur (Figure 10). If their data were modeled with a surface complexation model, the site
554 density should have been as high as 0.15 $\text{mol}\cdot\text{kg}^{-1}$. Because the edge specific surface area of
555 MX-80 is ~ 8 $\text{m}^2\cdot\text{g}^{-1}$, this site density would correspond to a surface occupancy of more than
556 11 atoms per nm^2 . This value is unrealistic and indicates clearly that additional processes such
557 as (co-)precipitation and/or surface precipitation must have occurred during their experiments.
558 The same conclusion can be made for the data of Yang et al. (2010), who reported similar
559 data for Pb retention on a Na-bentonite from Lin'an (from China) at different ionic strength
560 (0.001-0.1) with different background electrolytes and initial Pb concentration of 72.5 μM .
561 Why such processes occurred in their experiments and not in the experiments of this study or
562 those of Akafia et al. (2011) remains unclear. Based on extended X-ray absorption
563 fluorescence spectroscopy measurements (EXAFS), Strawn and Sparks (1999) suggested the
564 presence of Pb-Pb dimer on montmorillonite because of surface multilayer adsorption and/or
565 enhanced polymer formation due to nucleation from the clay. Surface precipitation of divalent
566 metals on clay mineral surfaces has been repeatedly observed with spectroscopic techniques,
567 especially with polarized EXAFS (P-EXAFS) (Scheidegger et al. 2001, Schlegel et al. 2001,
568 D'Amico et al. 2002, Schlegel and Manceau 2006). Polynuclear Pb species also formed at pH's
569 above 4.5 in the presence of high total Pb concentration sorbed on amorphous silica, a mineral
570 impurity that is frequently present in montmorillonite samples (Elzinga and Sparks 2002).
571 Therefore, the formation of polynuclear Pb species at the surfaces of clay minerals or of
572 mineral impurities may explain the results from Yang et al. (2010), and Xu et al. (2008).

573 The data from Gu et al. (2010) onto Na-montmorillonite could only be fitted with an increase
574 of the site density from 0.01 to 0.05 $\text{mol}\cdot\text{kg}^{-1}$ (Figure S-4). It is unclear if this increase in site
575 density may be justified or not: this site density corresponds to an edge specific surface area
576 of ~ 30 -40 $\text{m}^2\cdot\text{g}^{-1}$ according to the calculations explained above. Gu et al. (2010) used the <2
577 μm fraction of an Upton (Wyoming, USA) montmorillonite, and applied an acid treatment at
578 pH 3 for 5 h. This acid treatment could have formed new edge adsorption sites following the
579 partial dissolution of the clay, and/or new mineral impurities such as amorphous silica.
580 However, such a sample preparation effect was not apparent in the study carried out on
581 Fithian illite by the same authors and with the same sample preparation procedure (Gu and
582 Evans 2007).

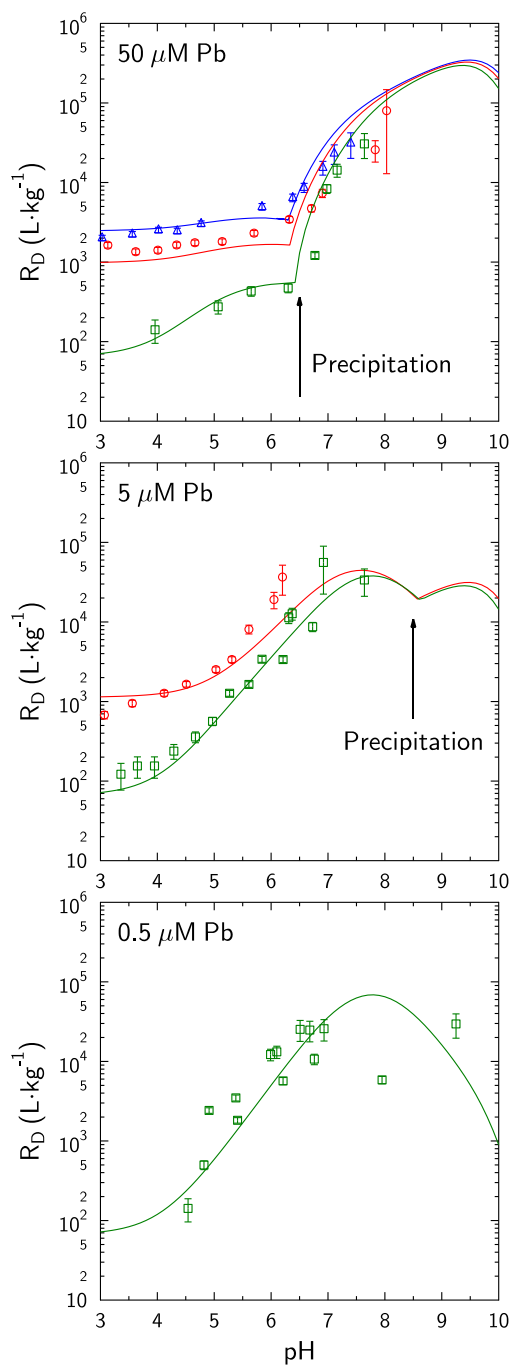
583 According to crystallographic data, clay mineral edge surfaces can adsorb a maximum Pb
584 monomer density of $d_{\text{mono}} = 2$ $\text{atom}\cdot\text{nm}^{-2}$ (Tournassat et al. 2018). Above this threshold value,

585 the presence of Pb dimers, polymers, or (co-)precipitation at the surface or in solution is
586 necessary to explain Pb retention values. SCM, for which only Pb monomer adsorption
587 reactions are considered, should then be restricted to the interpretation of data that do not
588 exceed this threshold value. The value of the edge specific surface area is however not well
589 known for most of the investigated clay minerals. This value is also subject to variability
590 because of the origin of the clay stock and/or on the clay preparation procedure. The specific
591 surface area measured by BET cannot help to determine the specific surface area of edges. It
592 is however possible to quantify a minimal edge specific surface area ($ESSA_{min}$ in $m^2 \cdot g^{-1}$) that
593 is necessary to explain the data according to:

$$ESSA_{min} = \frac{C_{ads} \cdot N_A}{1000 \cdot d_{mono} \cdot 10^{18}} \quad (5)$$

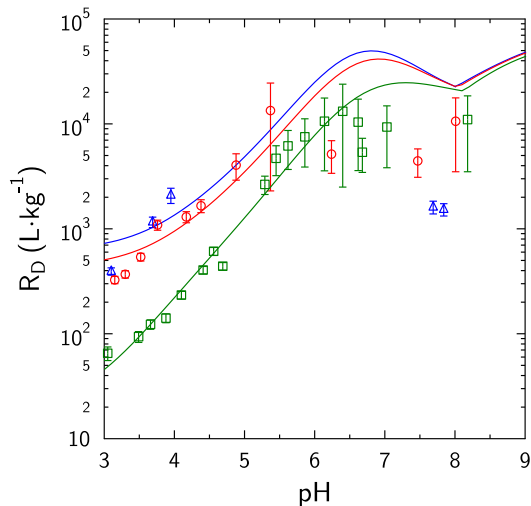
594 where N_A is the Avogadro number ($6.022 \cdot 10^{23} \text{ mol}^{-1}$). If $ESSA_{min}$ exceeds the maximum
595 reported value of edge specific surface area (i.e. $25 \text{ m}^2 \cdot \text{g}^{-1}$ for montmorillonite), or the BET
596 surface area value (which always exceeds the edge specific surface area) in the presence of
597 conditions where only surface complexation is expected, i.e. high electrolyte background
598 concentration to minimize cation exchange and $\text{pH} < 6.5$ to prevent hydrocerussite
599 precipitation, then it can be concluded that the data are not representative of surface
600 complexation processes.

601



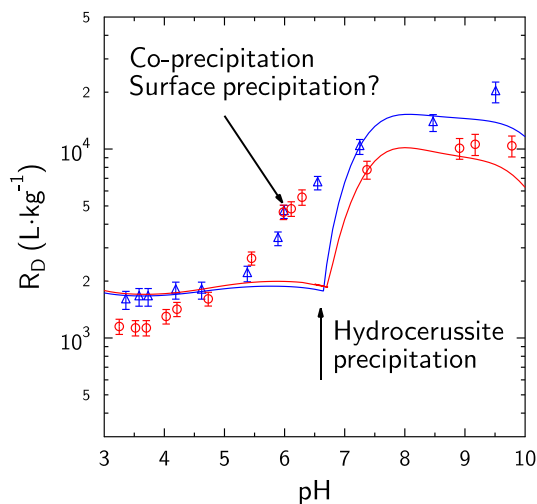
602

603 Figure 8. Prediction (lines) of the Pb adsorption data (symbols) on Swy-2 montmorillonite
 604 from Akafia et al. (2011), in the presence of a guessed DIC concentration of 0.25 mM, and of
 605 a guessed Mg concentration of 0.1 mM. Solid/ liquid ratio: $0.5 \text{ g}\cdot\text{L}^{-1}$. From top to bottom, Pb
 606 total concentration of $50 \text{ }\mu\text{M}$, $5 \text{ }\mu\text{M}$ and $0.5 \text{ }\mu\text{M}$. Blue triangles and line: 0.001 M NaNO_3
 607 background electrolyte. Red circles and lines: 0.02 M NaNO_3 background electrolyte. Green
 608 squares and lines: 0.1 M NaNO_3 background electrolyte. Error bands were calculated based
 609 on a digitization error of $\pm 1\%$ on the adsorbed Pb percentage (original data were reported as
 610 percentage of adsorption vs. pH). Data with error bands larger than their corresponding R_D
 611 value were discarded.



612

613 Figure 9. Prediction (lines) of the Pb adsorption data (symbols) on Fithian illite from Gu and
 614 Evans (2007), in the presence of a guessed DIC concentration of 0.25 mM, and of a guessed
 615 Mg concentration of 0.1 mM. Solid/liquid ratio: 2.97 g·L⁻¹. Pb total concentration = 50 μM.
 616 The site density was reduced to 0.025 mol·kg⁻¹ instead of 0.035 mol·kg⁻¹. Blue triangles and
 617 line: 0.001 M NaNO₃ background electrolyte. Red circles and lines: 0.01 M NaNO₃
 618 background electrolyte. Green squares and lines: 0.1 M NaNO₃ background electrolyte. Error
 619 bands were calculated based on a digitization error of ±1% on the adsorbed Pb percentage
 620 (original data were reported as percentage of adsorption vs. pH). Data with error bands larger
 621 than their corresponding R_D value were discarded.



622

623 Figure 10. Comparison of this model prediction with the data from Xu et al. (2008) on MX-80
 624 bentonite at I= 0.01 M NaNO₃. The initial DIC concentration was adjusted at 0.02 mM to fit
 625 the data at high pH. Total Pb concentration was 48.3 μM. Blue triangles and line: data
 626 obtained with a solid/liquid ratio of 0.2 g·L⁻¹. Red circles and line: data obtained with a
 627 solid/liquid ratio of 0.4 g·L⁻¹. Error bands were calculated based on a digitization error of ±1%
 628 on the adsorbed Pb percentage (original data were reported as percentage of adsorption vs.
 629 pH).

630 **5. Conclusion**

631 The determination of surface complexation model (SCM) parameters for direct or indirect use
632 in performance assessment calculations must be based on a critical review of the data
633 published in the literature. In this study, the experiments showed that many experimental
634 artifacts lead to misinterpretations of the processes underlying the measured R_D values. For
635 example, the order of reagent addition can influence the result. In addition, correct
636 interpretation of the data can be impeded by side reactions such as precipitation in the
637 presence of carbonated species in solution. Dissolved inorganic carbon concentrations are
638 seldom reported in the literature. This study revealed that most of the Pb adsorption data
639 measured at pH above 6.5 may indeed be representative of precipitating Pb carbonate
640 minerals (see data from Akafia et al. (2011) on Figure 8). This problem can be circumvented
641 by using low initial Pb concentration (typically below $5 \mu\text{M}$) so that hydrocerussite is not
642 saturated in the investigated pH range. Unfortunately, only a small set of published data were
643 obtained with initial Pb concentration below $5 \mu\text{M}$. Most of them had total Pb concentration
644 greater than or equal to $50 \mu\text{M}$. In these conditions, the possible presence of surface
645 polymerization/(co-)precipitation processes were highlighted. Inadequate experimental
646 procedures can be detrimental to quantitative interpretations with SCM and thus, many Pb
647 retention data that are published in the literature should not be used to calibrate SCM
648 parameters, because these data may not be representative of a true adsorption equilibrium, but
649 rather of (co-)precipitation or surface precipitation in conditions that can be barely met in a
650 waste storage environment (e.g. data from Xu et al. (2008) and some data of Akafia et al.
651 (2011)). This conclusion could be certainly extended to other divalent metallic cations for
652 which precipitation in the presence of carbonate in solution has not been considered. The
653 determination of surface complexation model parameters for PA should rely on preliminary
654 building of an adequate adsorption database, where adequate means that all experimental
655 conditions are met to quantify surface complexation only.

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660 LES laboratory for providing the IdP sample.

661 **Appendix A.**

662 **Supplementary information to this article can be found online. Supplementary**
663 **information contains Figures S-1 to S-4 and the experimental data in 26 tables.**

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Highlights:

- Retention of Pb^{2+} on clay mineral surfaces was modeled with a simple surface complexation model.
- Model calibration requires experimental data in well-defined and well-controlled conditions.
- All experimental conditions are met to quantify surface complexation only
- Experimental artifacts, especially the presence of carbonate in solution, cause misinterpretation of measured retention values.
- Fully controlled experimental conditions are necessary for calibrating models for performance assessment studies.

Table 1[Click here to download Table: Table 1.docx](#)

Initial Pb concentration (μM)	R_{SL} ($\text{g}\cdot\text{L}^{-1}$)	NaCl concentration (M)	pH range	T ($^{\circ}\text{C}$)
1	1	0.1	3-9	20*
10	1	0.1	3-9	20*
50	1	0.1	3-9	20*
1	0.5	0.025	3-9	20*
1	1	0.1	3-7	67

* Room temperature

Table 2

[Click here to download Table: Table 2.docx](#)

	Montmorillonite	Illite
Cation exchange		
CEC (X ⁻ site density) in mol·kg ⁻¹	0.78 ⁽¹⁾	0.2 ⁽²⁾
Reactions	log K	
$2 \text{XNa} + \text{Pb}^{2+} = \text{X}_2\text{Pb} + 2 \text{Na}^+$	0.6 (0.9)	0.7 (0.9)
$2 \text{XNa} + \text{Mg}^{2+} = \text{X}_2\text{Mg} + 2 \text{Na}^+$	0.6	0.7
$2 \text{XNa} + \text{Ca}^{2+} = \text{X}_2\text{Ca} + 2 \text{Na}^+$	0.5	0.5
Edge surface complexation		
Site density (>S) in mol·kg ⁻¹	0.01	0.035
Reactions	log K	
$>\text{SOH} = >\text{SO}^- + \text{H}^+$	-8.1	-6.6
$>\text{SOH} + \text{Pb}^{2+} = >\text{SOPb}^+ + \text{H}^+$	0 (0.2)	0.6 (0.9)
$>\text{SOH} + \text{Pb}^{2+} + \text{H}_2\text{O} = >\text{SOPb}(\text{OH}) + 2\text{H}^+$	Not necessary	-7.2 (-6.7)

⁽¹⁾(Bradbury and Baeyens 2002)⁽²⁾(Bradbury and Baeyens 2000)

Table 3[Click here to download Table: Table 3.docx](#)

Clay Type	Clay material preparation procedure	pH	Background electrolyte (M)	[Pb] _{tot} (μM)	R _{SL} (g.L ⁻¹)	Reference
SWy-2 Mont.	None	3–11	0.001–0.1 NaNO ₃	0.1–50	0.5	(Akafia et al. 2011)
Fithian illite	< 2 μm NaNO ₃ treated	3-8	0.001-0.1 NaNO ₃	50	2.97	(Gu and Evans 2007)
MX-80 Mont	None	1-12	0.01 NaNO ₃	48.3	0.2; 0.4	(Xu et al. 2008)
Wyoming Mont.	< 2 μm NaNO ₃ treated	3- 9	0.001 0.1 NaNO ₃	48.8	1.5	(Gu et al. 2010)
Chinese bentonite	< 2 μM 1.0 M NaCl treated	2-12	0.001-0.1 NaClO ₄	72.5	0.5	(Yang et al. 2010)

List of Figure Captions

Figure 1. Comparisons of experimental datasets for Pb retention at room temperature on MX-80, Kunipia-P, IdP and COx clay as a function of pH, ionic strength (0.025 M NaCl = closed symbols; 0.1 M NaCl = open symbols), and total Pb initial concentrations (triangle symbols: 1 μM ; circle symbols: 10 μM ; square symbols: 50 μM) (Details of the datasets are given in supporting information file).

Figure 2. Comparison of Pb retention on MX-80 (triangles), Kunipia (diamonds), IdP (circles) and COx clay (squares) at room temperature as a function of pH, in the presence of 0.1 M NaCl background electrolyte and a total Pb concentration of 1 μM .

Figure 3. Pb retention on MX-80 (triangles), Kunipia (diamonds), IdP (circles) and COx clay (squares) at room temperature (open symbols) and 67°C (closed symbols) as a function of pH, in the presence of 0.1 M NaCl background electrolyte and a total Pb concentration of 1 μM (Details of the datasets are given in supporting information file).

Figure 4. Top figure: Pb solid phase predominance as a function of pH and pCO_2 in the absence of adsorption processes. Minerals allowed to precipitate: cerussite (PbCO_3), hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$), cotunnite (PbCl_2), laurionite (PbClOH), paralaurionite (PbClOH) and $\text{Pb}(\text{OH})_2(\text{s})$: Total Pb concentration: 50 μM ($\log [\text{Pb}]_{\text{tot}} = -4.3$). Middle figure: Contour plot of calculated Pb concentration in solution (\log_{10} scale) as a function of pH and pCO_2 . The color change between two contour lines indicates a change of 0.25 \log_{10} scale units. Bottom figure: Contour plot of calculated DIC concentration as a function of pH and pCO_2 (\log_{10} scale). Symbols correspond to experimental measurements in the presence (triangles) or absence (circles) of clay and with sample preparation in contact with atmosphere (white symbols) or in the glove-box (black symbols). The background electrolyte concentration is 0.1 M NaCl for all figures.

Figure 5. Modeling of Pb adsorption and precipitation at room temperature according to the parameters given in Table 2 for MX-80 (left) and illite (right).

Figure 6. Model prediction for Pb adsorption / precipitation on Kunipia-P (left) and COx clay (right) at room temperature. Model parameters for Kunipia-P are the same as for MX-80. Pb adsorption on COx clay was modeled with an illite surface contribution of 50% and a smectite surface (montmorillonite) contribution of 50%.

Figure 7. Model predicting Pb adsorption on the four clay samples at 67°C. Parameters are given in Table 2. Total Pb concentration: 1 μM . Solid/liquid ratio: 1 $\text{g}\cdot\text{L}^{-1}$. Background electrolyte: NaCl 0.1 M.

Figure 8. Prediction (lines) of the Pb adsorption data (symbols) on Swy-2 montmorillonite from Akafia et al. (2011), in the presence of a guessed DIC concentration of 0.25 mM, and of a guessed Mg concentration of 0.1 mM. Solid/ liquid ratio: 0.5 $\text{g}\cdot\text{L}^{-1}$. From top to bottom, Pb total concentration of 50 μM , 5 μM and 0.5 μM . Blue triangles and line: 0.001 M NaNO_3 background electrolyte. Red circles and lines: 0.02 M NaNO_3 background electrolyte. Green squares and lines: 0.1 M NaNO_3 background electrolyte. Error bands were calculated based on a digitization error of $\pm 1\%$ on the adsorbed Pb percentage (original data were reported as percentage of adsorption vs. pH). Data with error bands larger than their corresponding R_D value were discarded.

Figure 9. Prediction (lines) of the Pb adsorption data (symbols) on Fithian illite from Gu and Evans (2007), in the presence of a guessed DIC concentration of 0.25 mM, and of a guessed

Mg concentration of 0.1 mM. Solid/liquid ratio: $2.97 \text{ g}\cdot\text{L}^{-1}$. Pb total concentration = $50 \text{ }\mu\text{M}$. The site density was reduced to $0.025 \text{ mol}\cdot\text{kg}^{-1}$ instead of $0.035 \text{ mol}\cdot\text{kg}^{-1}$. Blue triangles and line: 0.001 M NaNO_3 background electrolyte. Red circles and lines: 0.01 M NaNO_3 background electrolyte. Green squares and lines: 0.1 M NaNO_3 background electrolyte. Error bands were calculated based on a digitization error of $\pm 1\%$ on the adsorbed Pb percentage (original data were reported as percentage of adsorption vs. pH). Data with error bands larger than their corresponding R_D value were discarded.

Figure 10. Comparison of this model prediction with the data from Xu et al. (2008) on MX-80 bentonite at $I= 0.01 \text{ M NaNO}_3$. The initial DIC concentration was adjusted at 0.02 mM to fit the data at high pH. Total Pb concentration was $48.3 \text{ }\mu\text{M}$. Blue triangles and line: data obtained with a solid/liquid ratio of $0.2 \text{ g}\cdot\text{L}^{-1}$. Red circles and line: data obtained with a solid/liquid ratio of $0.4 \text{ g}\cdot\text{L}^{-1}$. Error bands were calculated based on a digitization error of $\pm 1\%$ on the adsorbed Pb percentage (original data were reported as percentage of adsorption vs. pH).

Figure 1
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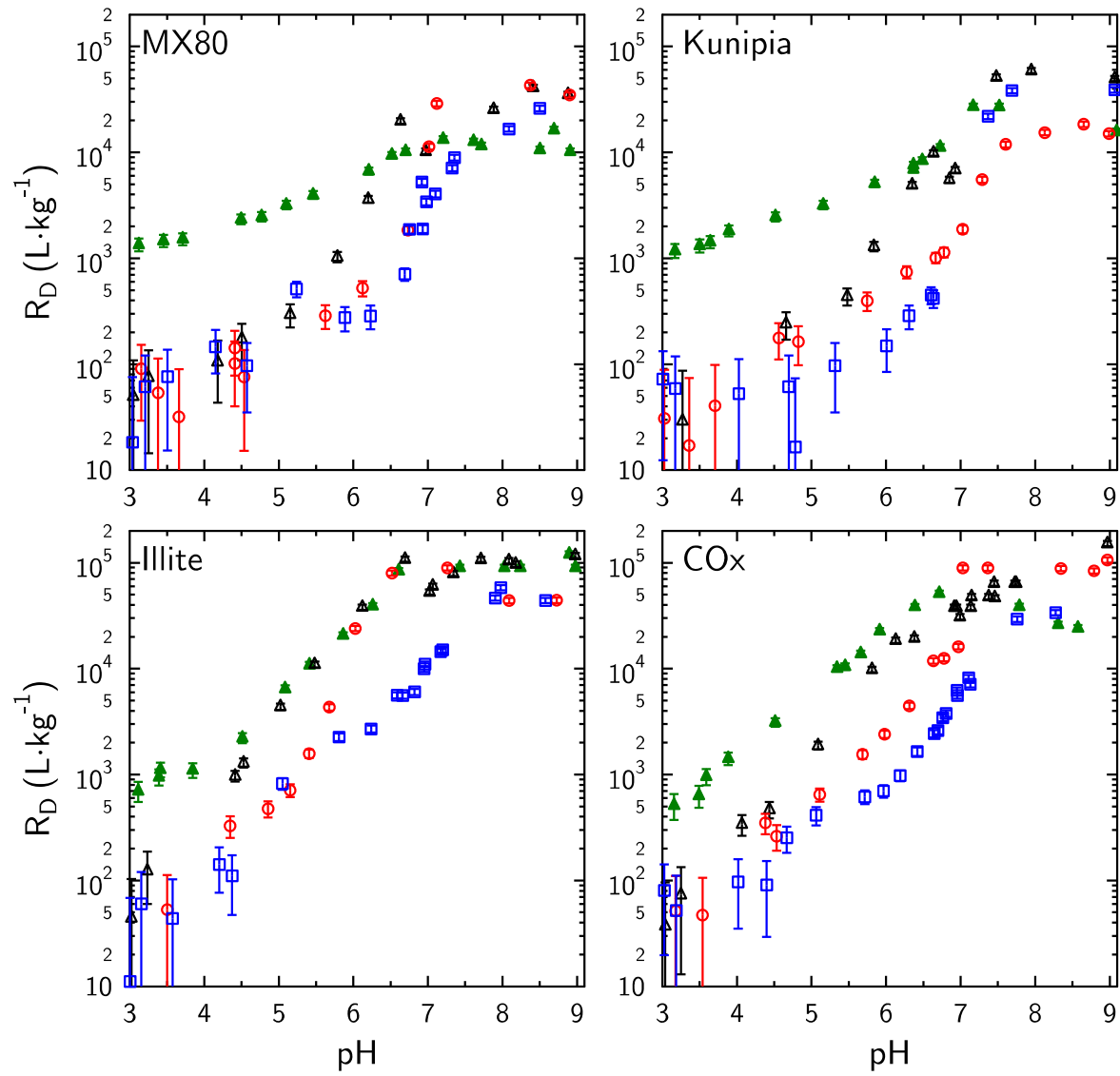


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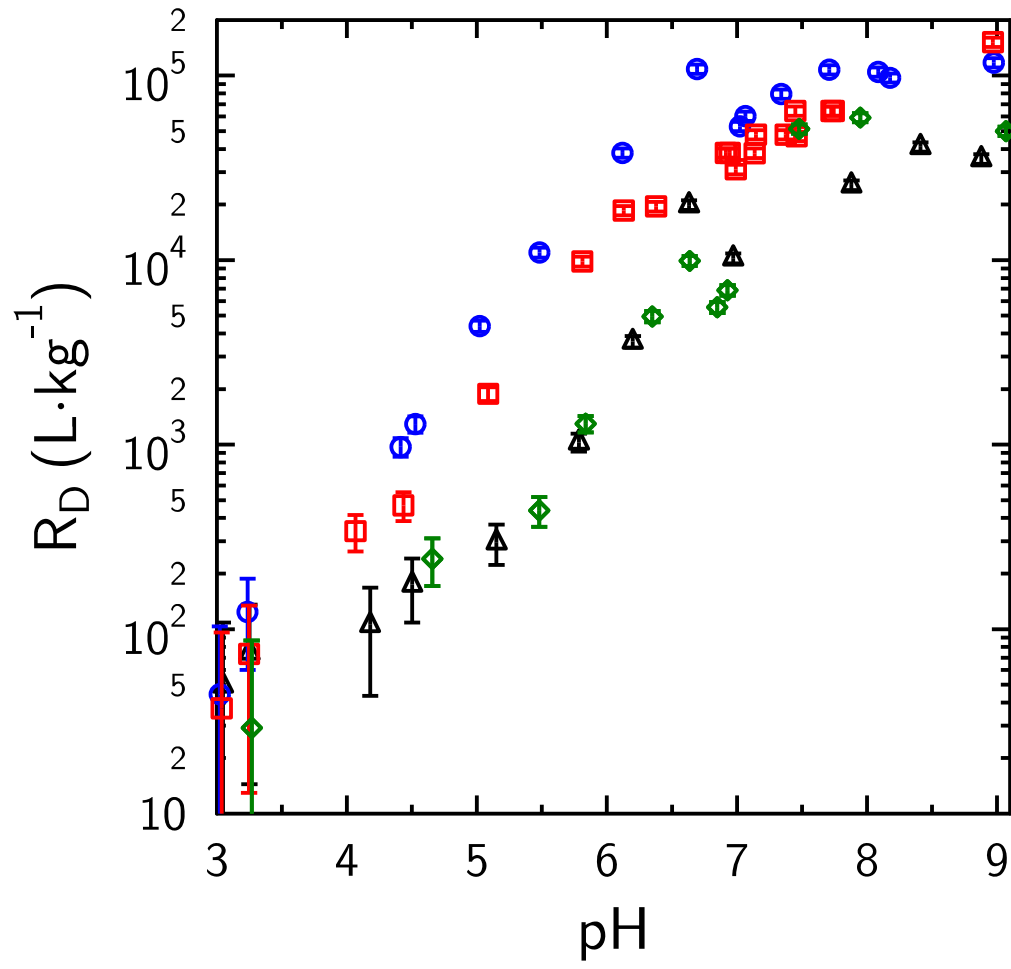


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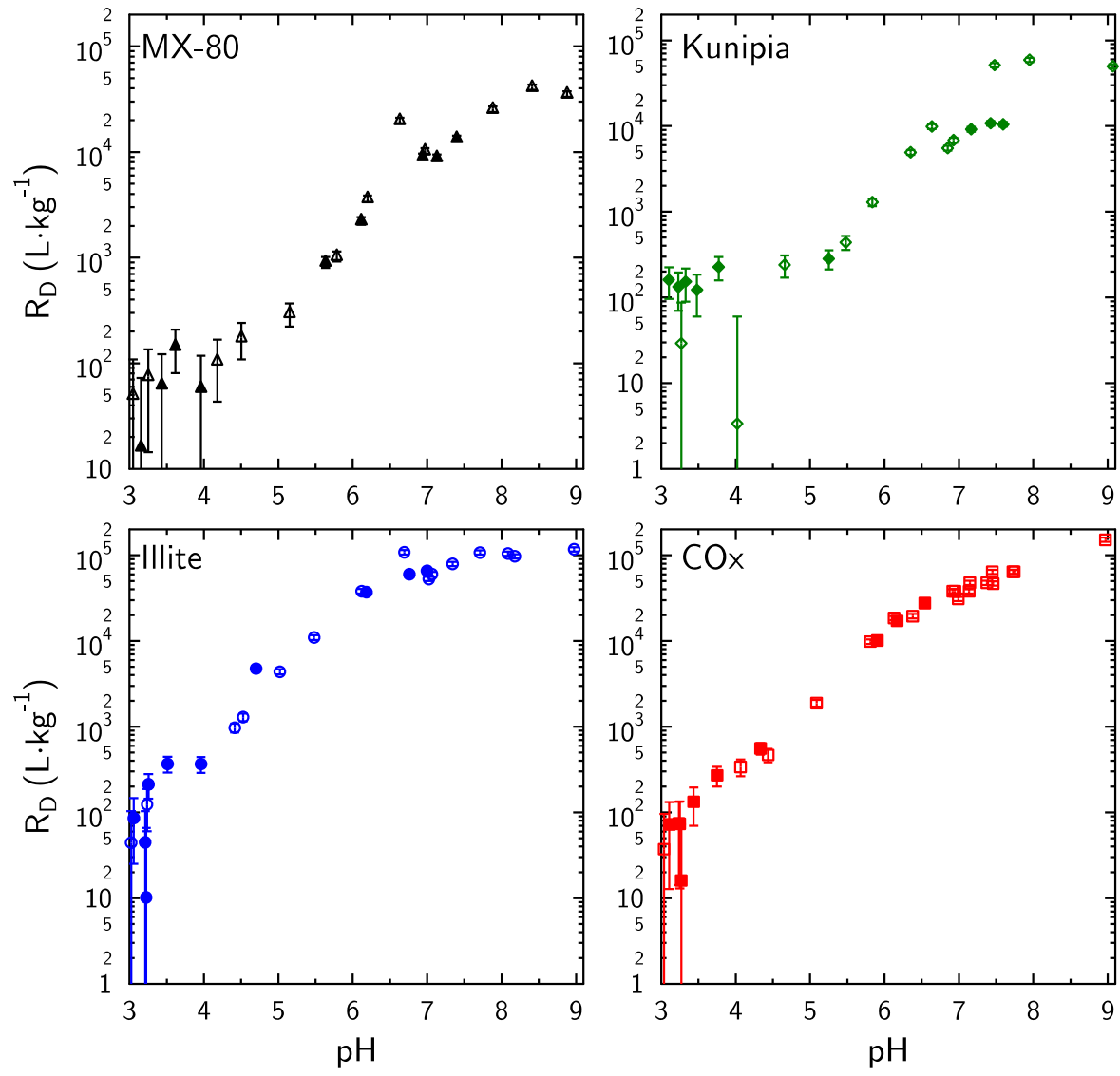


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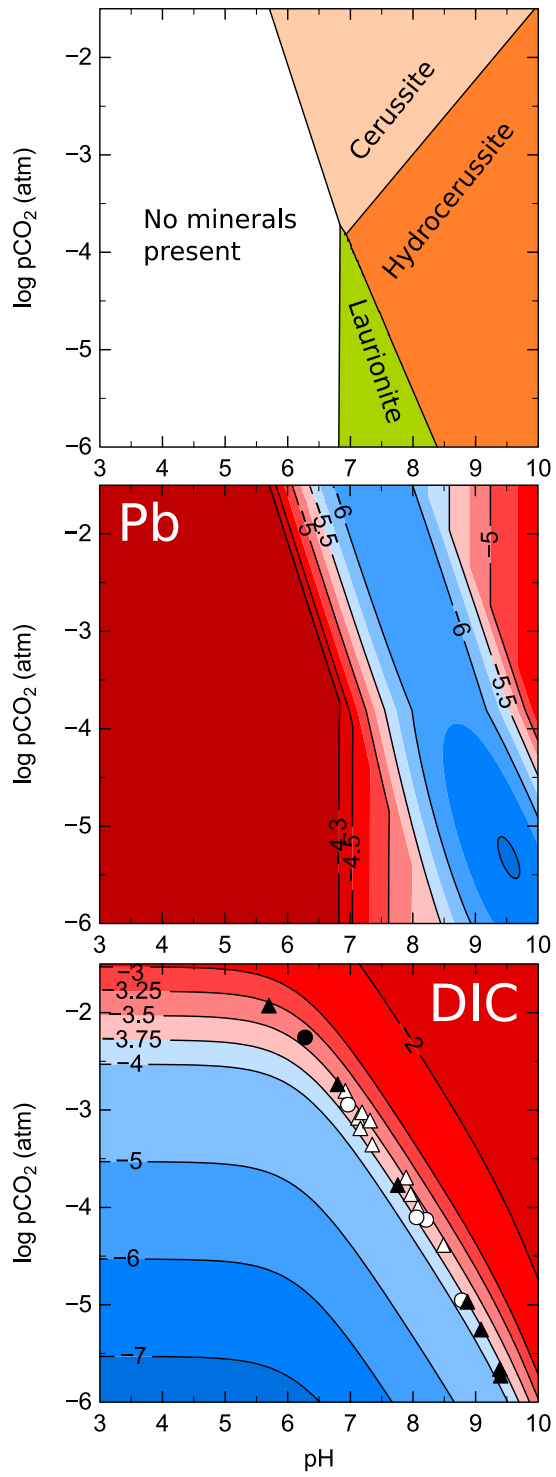
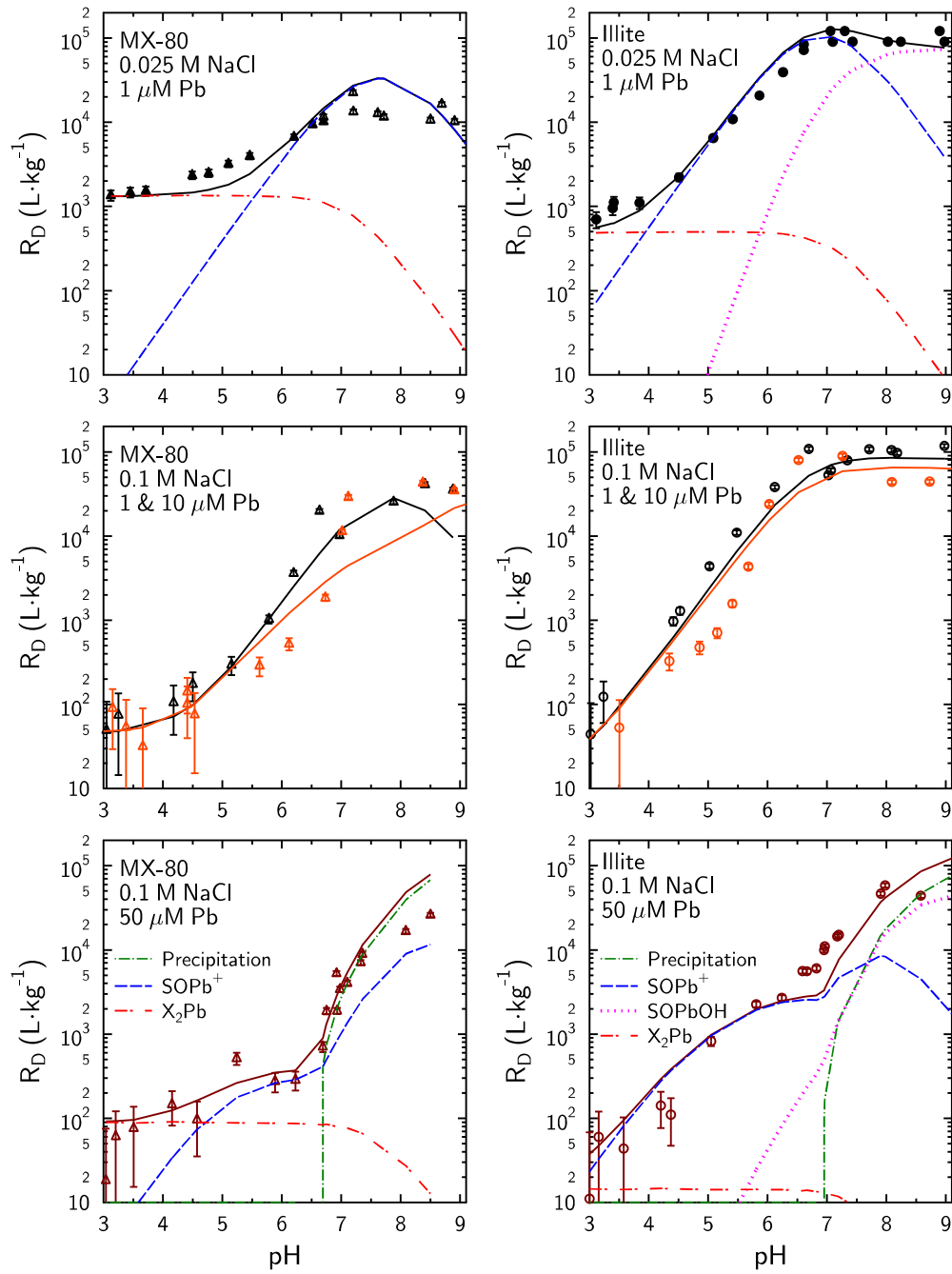
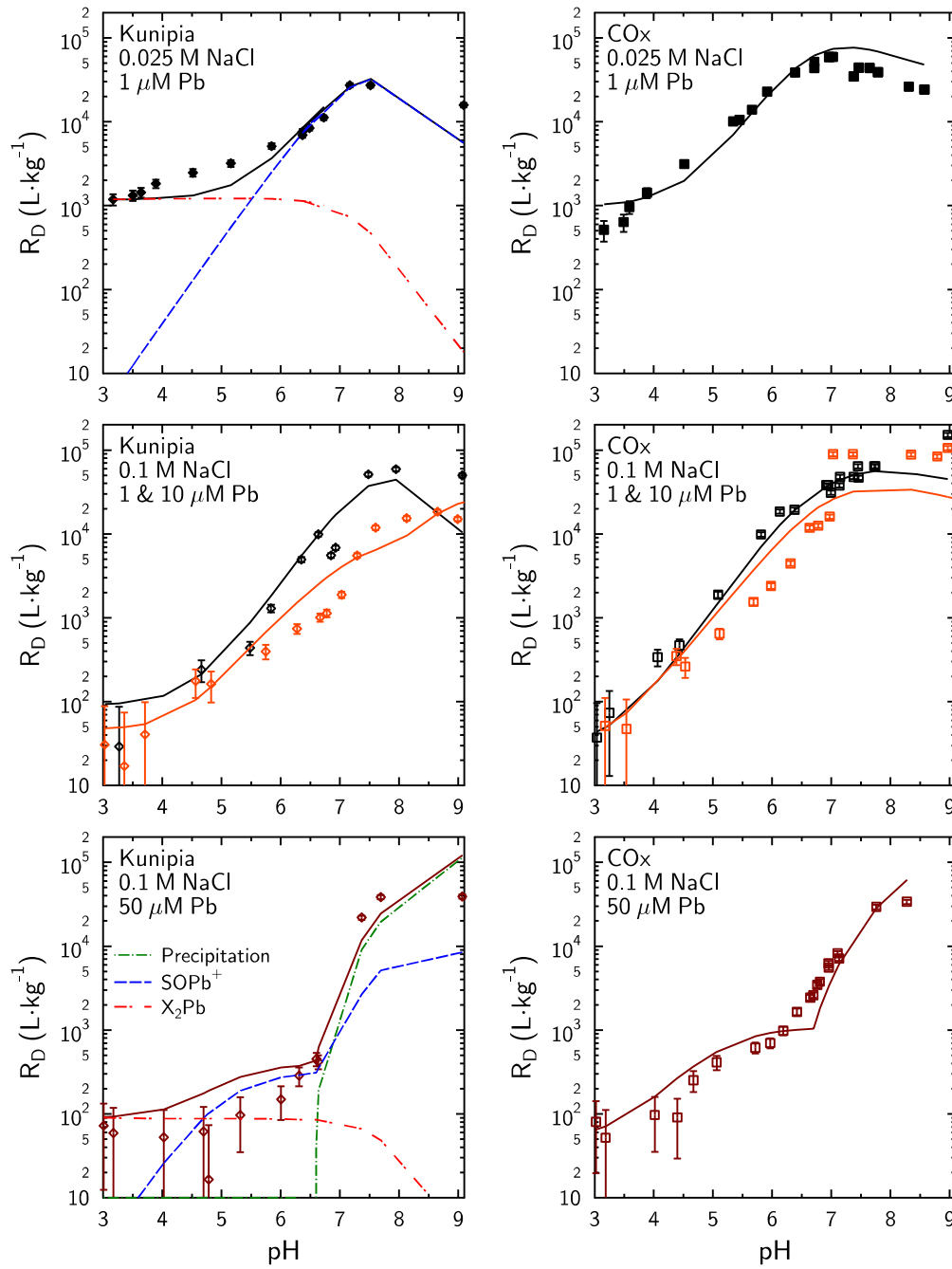


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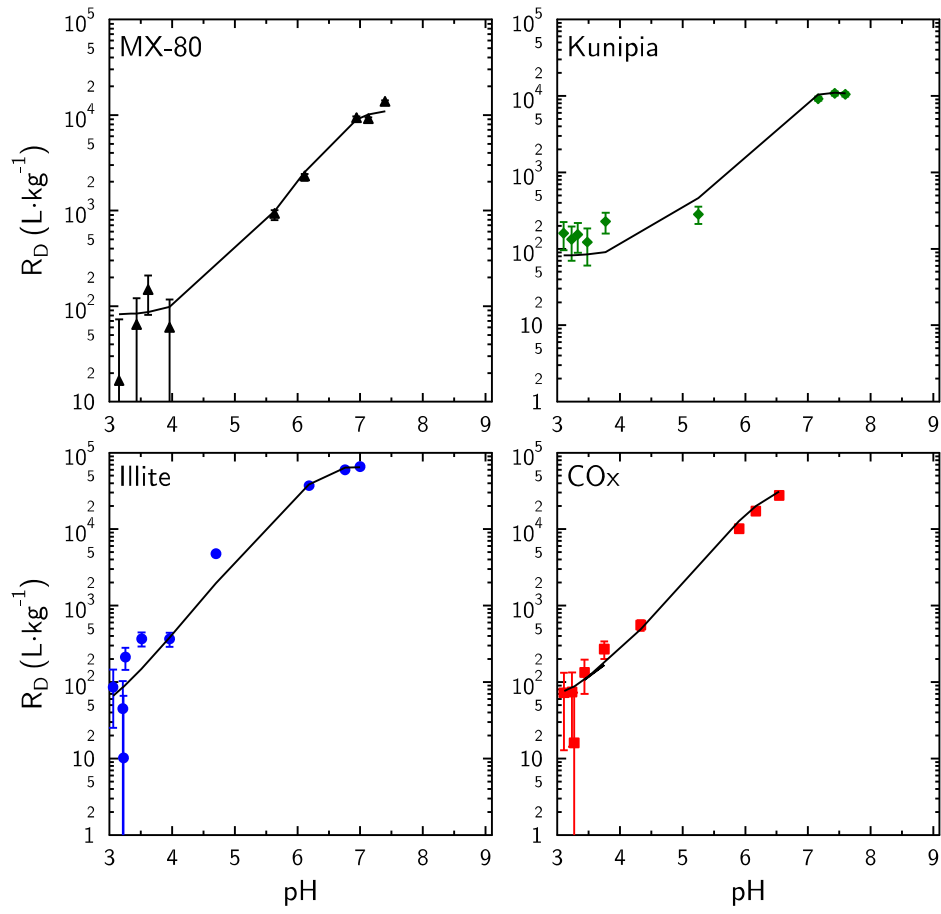


Figure 8

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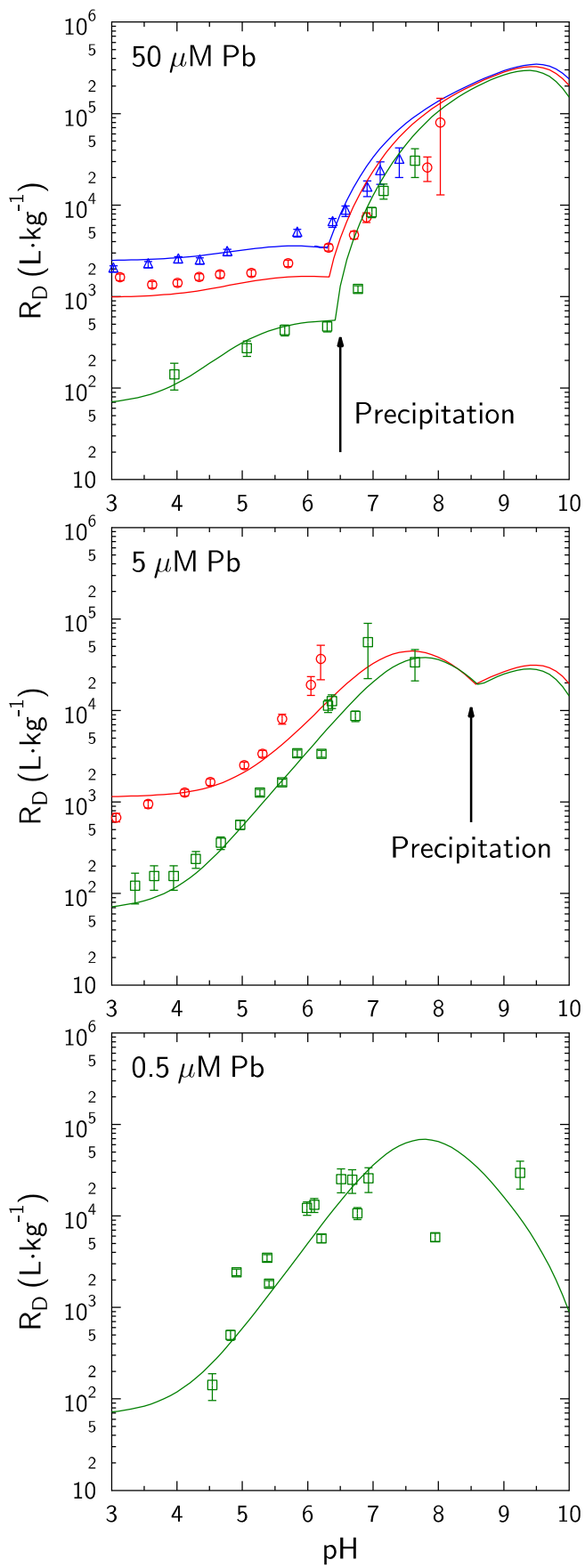


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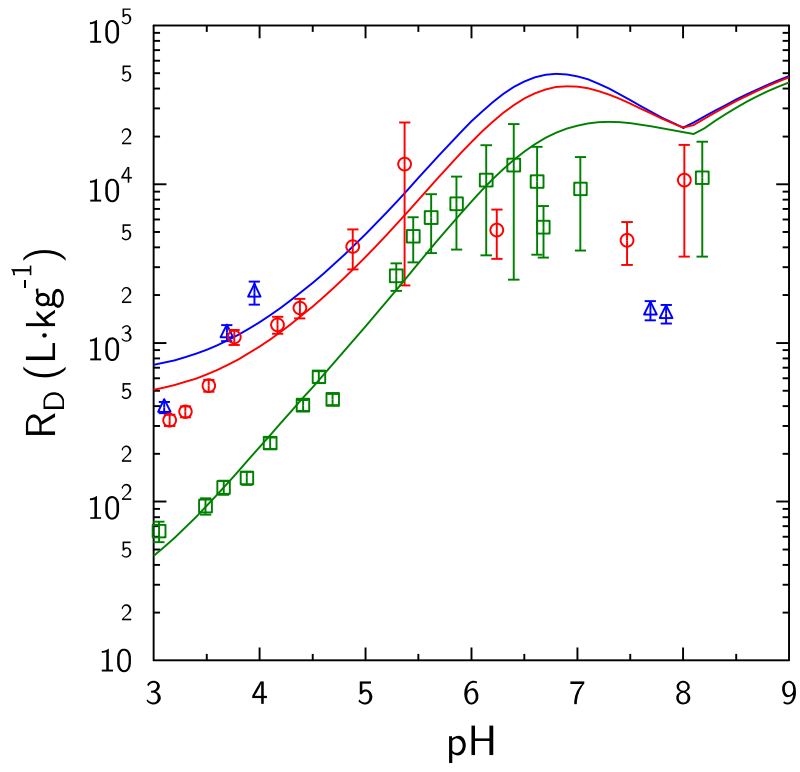
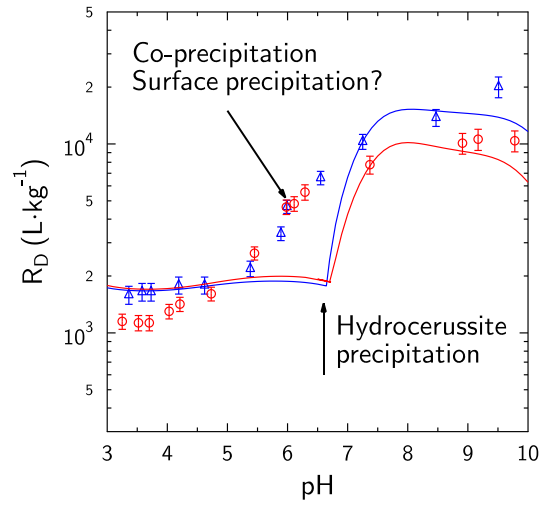


Figure 10
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Abstract

Surface complexation models (SCMs) have been developed in the last decades to describe metal ion sorption to clay minerals and especially to montmorillonite. In principle, these models can provide relevant information about sorption of radionuclides to be used in performance assessment (PA) of radioactive waste disposal systems. However, these SCMs have been developed in parallel with the acquisition of distinct adsorption datasets, which are not always consistent with each other. The objective of this study was to compare new experimental adsorption results with literature data to understand these discrepancies and to propose a SCM approach that could be amenable to determine sorption related retention parameters necessary for PA calculations. This study focused on lead (Pb) adsorption on montmorillonite, illite and in a natural clay (Callovo Oxfordian) as case studies of a strongly sorbing radionuclide that undergoes a range of retention processes depending on the chemical conditions. The experiments showed that many experimental artifacts lead to misinterpretations of the processes underlying the measured retention values. These include Pb precipitation in the presence of carbonate in solution. The determination of SCM parameters to provide sorption related information for PA of clay minerals should rely on preliminary building of an adequate adsorption database, where adequate means that all experimental conditions are met to quantify surface complexation only.

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