

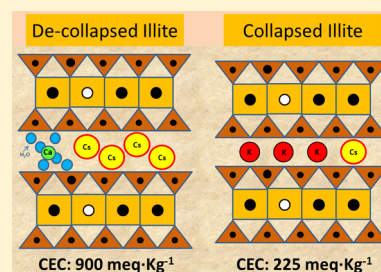
Interlayer Collapse Affects on Cesium Adsorption Onto Illite

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S Supporting Information

ABSTRACT: Cesium adsorption onto Illite has been widely studied, because this clay is especially relevant for Cs migration-retention in the environment. The objective of this study is to analyze how Cs adsorption onto Illite is affected by structural changes produced by the presence of different exchangeable cations—and specifically interlayer collapse. Cs sorption isotherms were carried out with Illite previously exchanged with Na, K, or Ca, at a broad enough range of ionic strength, for the determination of the possible effect of the electrolyte on the structure of Illite. In the presence of Ca, the maximum sorbed Cs was unexpectedly high (900 mequiv·kg⁻¹) given the cationic exchange capacity commonly accepted for Illite (near 200 mequiv·kg⁻¹). This was explained by the expansion of Illite layers (*decollapse*) induced by large hydrated cations such as Ca²⁺ that may facilitate cation uptake—especially Cs⁺, which is a highly selective cation. In the presence of Ca (and most probably of other divalent cations), Cs accessibility to exchange positions is increased. Both experimental evidence and the modeling of Cs sorption onto Illite supported the hypothesis of *decollapse*. Our results demonstrate the requirement of accounting for Illite *decollapse* especially for high Cs loadings, because of the potential prediction errors for its migration. Ignoring the Illite *decollapse* could lead the biased estimation of selectivity coefficients and consequently the erroneous prediction of sorption/migration behavior of Cs, and possibly other contaminants, in the environment.



INTRODUCTION

Cesium is widely studied by environmental scientists. The most common radioactive form of cesium is ¹³⁷Cs; other fairly common radioisotopes are ¹³⁴Cs and ¹³⁵Cs. However, ¹³⁷Cs is the most significant from an environmental point of view, being a major radionuclide of spent nuclear fuel and hence of the global radioactive waste inventory. ¹³⁷Cs has been introduced into soils and groundwater over the past decades by nuclear accidents and from nuclear weapons testing.¹ Recently concern about ¹³⁷Cs was elevated because it was (along with ¹³¹I) the primary radionuclide released from the Fukushima nuclear accident—both into the air and by water leakage.²

The migration-retention of this contaminant into soils and groundwater is controlled by clay minerals and it has been studied by different techniques.^{3–7} The presence of these minerals, with a large specific surface area and ubiquitous in natural systems, strongly affects ion adsorption processes. Micaceous clays, such as Illite, dominate Cs adsorption,^{8–11} especially at trace Cs concentrations.

¹³⁷Cs sorption on Illite is of interest for the geological disposal of radioactive waste, because Illite is a primary component of the argillaceous rock proposed as suitable host rock formations.^{12–14}

Cs adsorption onto Illite is generally accepted to occur by ionic exchange.^{11,15–17} Illite exhibits a lower cation exchange capacity (CEC) than other 2:1 type clays, because the permanent negative charge of Illite is usually balanced by potassium ions that are located at the planar surfaces of both the clay particles and at the interlayers.¹⁷ Yet those K ions at the interlayers, produce interlayer collapse and hinder Illite expansion and are unavailable for ion exchange.

The various reported values for Illite's CEC, from 120 to 600 mequiv·kg⁻¹, vary by the method and experimental conditions used for their determination. CEC values between 120 and 280 mequiv·kg⁻¹ were obtained by isotopic dilution or saturation with various index cations: Na, Ca, Sr, Ba, K, or Cs.^{8,15,16,18,19} Higher CEC values (approximately 600 mequiv·kg⁻¹) were obtained both by ammonium uptake with the standard method²⁰ and also for Illite previously depleted in K with sodium tetraphenylboron.⁸

Given these significant variations, Baeyens and Bradbury (2004) chose a reference Cs-CEC value of 225 mequiv kg⁻¹ and recommended Cs as the index cation for the determination of the CEC for Illite, because of Cs high capacity to access exchange locations. Yet previous studies did not consider the possible effects of the electrolyte used for CEC determination (or for other adsorption studies) on the structure of Illite—and that structural modifications could alter the availability of exchange sites. Regardless of the magnitude of Illite's CEC, the existence of various environments with varying selectivity for Cs exchange have been reported. These various sorption sites have been associated with both the frayed particles edges (frayed edge sites, FES),²¹ and also with the planar surfaces of Illite particles. At least two different types of environments for Cs interaction with Illite have been demonstrated with direct spectroscopic analyses;^{22–24} three types of FES, of increasing selectivity for Cs, were identified by sorption studies after

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masking planar ion exchange sites with the silver thiourea complex.²⁵

Three exchange sites are considered to explain Cs sorption behavior on Illite.^{11,15,16} These studies agree on the presence of a highly selective type of FES at low Cs loading that represents close to 0.1–0.5% of the CEC; and whose density can be relatively easily estimated with adsorption isotherms. However, the distribution of the remaining CEC between the two other sites is controversial and arbitrary.

The most common cations occupying exchange positions on natural Illite are Na⁺, K⁺, and Ca²⁺. The sorption selectivity sequence of Cs⁺ > K⁺ > Na⁺ > Ca²⁺ has been reported by refs 15 and 26. Selectivity coefficients have been estimated on the basis of experimental sorption data²⁷ and are essential for the modeling of Cs migration.

Much is known about Cs sorption onto Illite, but gaps remain: no experimental data are available for Cs–Na exchange at low ionic strengths (<0.1M), except for Cs trace loadings;^{11,16} the Cs–K exchange for Illite has been studied only at ionic strengths up to 0.02 M;^{11,15,28,29} and Cs–Ca exchange at high Cs loadings has been investigated only at low concentration of Ca in the electrolyte (<0.001 N).^{15,20}

Although Cs exchange at FES has been widely studied, adsorption onto planar sites has not; no previous studies considered the effects of the electrolyte and the exchanging cation on the structure of Illite—effects that could alter the degree of accessibility of the exchange locations for Cs and other selective alkali cations like, for example, Rb.

A specific feature of Illite, the collapse of the interlayers, determines Illite sorption behavior. K⁺ is the cation commonly responsible for this interlayer collapse, although other alkaline metals could have a similar effect.^{28,30} The presence of large hydrated cations may induce the expansion (*decollapse*) of the Illite layers and facilitate cation uptake—especially for Cs, because of its high selectivity.^{18,28}

The objective of this study is to understand the affect of the primary exchange cations on Cs adsorption—especially at the planar sites. Natural Illite was exchanged with Na, K, and Ca; and Cs sorption behavior was analyzed with Na-, K-, and Ca-Illite: Na⁺ was selected because it is the most studied exchange cation; K⁺ because it is a fixable cation with low hydration energy; and Ca²⁺ because it is a nonfixable cation with high hydration energy. The electrolytes were used in a wide enough range of concentrations to study the implication of the interlayers (de)collapse on Cs retention—implications previously not explicitly considered by adsorption studies.

MATERIALS AND METHODS

Materials. The Illite used for this study was natural “du Puy” Illite³¹ collected from within an 80 m thick Oligocene geological formation in the region of Le Puy-en-Velay (Haute-Loire, France) with a BET area of 97 m² g⁻¹.¹⁶

CEC measurements were performed using the copper(II) ion complex with triethylenetetramine [Cu(trien)]²⁺ as the index cation. With this method, CEC measurements for the three exchanged illites gave similar results: 213, 239, and 232 (±10) mequiv·kg⁻¹ for the K-Illite, Na-Illite, and Ca Illite, respectively.

The radionuclide ¹³⁷Cs (as CsCl in 0.1 M HCl, Isotope Products) was used for sorption experiments. In addition, stable Cs solutions in HCl 0.1 M were prepared from CsCl (Merck) for their use as a carrier for high Cs loading samples.

The electrolytes and suspensions were prepared using water according to EN ISO 3696:1987,³² grade I, free of organic

contaminants. The reagents were of analytical grade and used without further purification. All the experiments described below were at room temperature.

Preparation of Clay Colloidal Suspensions and Characterization. Stock colloidal suspensions of Illite, exchanged with the corresponding cation (Na, K, or Ca) were prepared as follows: 100 g L⁻¹ of clay in 1 M NaClO₄, KCl or CaCl₂ were stirred for 3 h and let depositing for 24 h; the supernatant solution was then replaced with fresh electrolyte 1 M. This process was repeated three times. Colloidal particles (size <500 nm) were obtained from this suspension by washing with deionized water and consecutive centrifugations at 600g for 7 min. Colloidal suspensions of 1 g L⁻¹ were finally prepared diluting the stock suspensions with the corresponding electrolyte at different ionic strengths. K, Na, and Ca in the supernatant after centrifugation (645 000g, 30 min.) were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Jobin-Yvon, JY38 Plus).

The three exchanged illites were analyzed by various techniques to identify possible structural changes caused by the different exchanging cations: a. infrared spectroscopy (FTIR) both in the midrange (4000–400 cm⁻¹) and the near-IR (NIR) region (10 000–4000 cm⁻¹); b. X-ray diffraction (XRD), and c. scanning electron microscopy equipped with a Link System energy dispersive X-ray microanalyser (SEM-EDX). The size of the particles in suspension was measured by photon correlation spectrometry (PCS): some results obtained by PCS are described in the Supporting Information (SI).

Sorption Experiments. Sorption isotherms were performed at pH 7 with Cs concentration varying from 6 × 10⁻¹⁰ M to 1 × 10⁻³ M. The procedure to carry out batch experiments was the following: an aliquot of 20 mL of the clay suspension, at the selected electrolyte concentration, was introduced into a polyethylene tube. MPS (3-mercaptopropyl-trimethoxysilane) (Sigma-Aldrich) buffer solution was added (2 × 10⁻³ M) to maintain constant the pH.

¹³⁷Cs was then added and for samples with higher Cs loading (>10⁻⁸ M), stable Cs (CsCl solution) was used in addition to the radiotracer. The pH was readjusted to 7, if necessary, using HCl or NaOH 0.1M.

The tubes were sealed and maintained with continuous stirring for 7 days (time enough to reach sorption equilibrium¹⁶). They were then ultracentrifuged (645 000g, 30 min.) and the activity of Cs in the supernatant solution was measured by γ -counting with a NaI detector (Packard Autogamma COBRA 2). No significant Cs adsorption in the tubes (below 0.5% of the total Cs) was measured with a total Cs concentration of 10⁻⁸ M after batch experiments. Thus, it was not specifically accounted for in the calculation of distribution coefficients.

The distribution coefficient, K_d (mL g⁻¹) was calculated with the following:

$$K_d = \frac{[Cs]_{tot} - [Cs]_{sol}}{[Cs]_{sol}} \frac{1}{[illite]} \quad (1)$$

[Cs]_{tot} is the total Cs concentration of the suspension (mol L⁻¹); [Cs]_{sol} is the Cs concentration in solution at equilibrium (mol L⁻¹); and [Illite] is the Illite concentration (g mL⁻¹). The maximum experimental error estimated for log K_d is ±0.2.

Modeling Background. Our modeling calculations were aided by CHESS v 2.4 code.³³

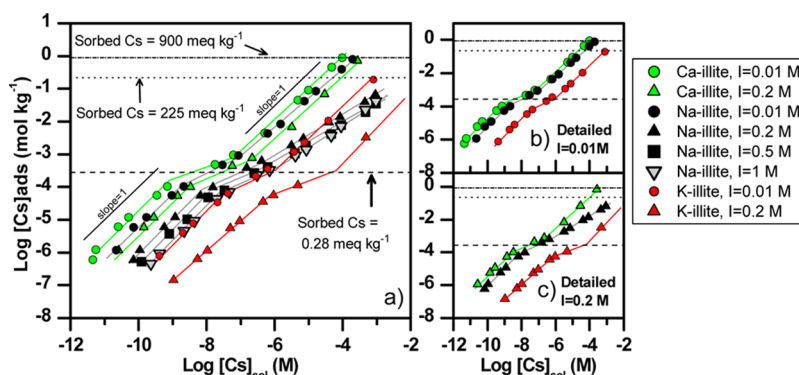
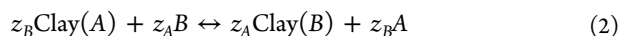


Figure 1. Cs sorption isotherms for Ca, Na, and K-illite at pH 7: (a) measured at different ionic strengths; (b) detailed at ionic strength of 0.01 M; and (c) detailed at ionic strength of 0.2 M (lines drawn to guide the eye).

The ionic exchange reaction between a cation B with charge z_B that exists in the aqueous phase and a cation A with charge z_A at the cationic exchange sites of the clay is expressed as follows:



The cation exchange reactions can be described with selectivity coefficients. Following the Gaines and Thomas³⁴ definition, the selectivity coefficient is expressed by

$${}^B_A K_{\text{sel}} = \frac{(N_B)^{z_A} (a_A)^{z_B}}{(N_A)^{z_B} (a_B)^{z_A}} \quad (3)$$

The terms a_A and a_B are the activities of the cations A and B , and N_A and N_B are the equivalent fractional occupancies. The equivalent fractional occupancy is defined as the sorbed quantities of the cations per mass (expressed in eq g^{-1}) divided by cationic exchange capacity CEC (expressed in eq g^{-1}). The maximum error estimated for $\log K_{\text{sel}}$ is similar to that of the experimental $\log K_d$.

RESULTS AND DISCUSSION

Characterization of the Exchanged Illites. The figures with the most relevant results, on the exchanged clay characterization are included in SI.

SI Figure SI.1 shows the FTIR spectra of the three illites for the MIR (SI Figure SI.1a) and NIR (SI Figure SI.1b) region. For both regions, the spectra did not show significant differences between the three illites; and showed the typical features expected for this clay.

SI Figure SI.2 shows the XRD spectra of the three exchanged clays and of the Ca-Illite in which Cs has been adsorbed ($[\text{Cs}] = 1 \times 10^{-3} \text{ M}$), which has been referred to as *Cs-Illite*. All the spectra presented the characteristics peaks of Illite clay mineral, but for Na- and Ca- exchanged illites, additional reflections appeared (region indicated by the arrow in the figure). Small peaks, corresponding to the dioctahedral mica Paragonite and brittle mica Margarite, were observed for Na- or Ca- exchanged Illite, respectively, indicating incipient changes with respect to the original structure of a raw Illite.

The existence of these differences upon the homoionisation process was also corroborated by both the SEM-EDX and the structural formulas derived by these analyses. SI Figure SI.3 shows the SEM image (left) and structural formulas with the calculated octahedral (O) and tetrahedral (τ) charge distribution (right) of the three exchanged illites. K-Illite shows the typical characteristics of Illite with a layer charge of

~ 1.6 ; Na-Illite presents a high replacement of potassium by sodium at exchange sites and a small increase in the octahedral charge; for the Ca-exchanged Illite, a significant increase of the total interlayer charge (~ 2.02) is observed. The Cs-Illite presents similar features to those of K-Illite.

The structural formula of Ca- exchanged Illite (SI Figure SI.3c), however, indicates a similar charge defect but less Ca content than that expected for Margarite. The results suggest that during the homoionisation process, Ca ions could substitute only a small proportion of the K interlayer cation, but as Ca is a hydrated and larger ion, these substitutions locally modified the Illite structure, probably causing the expansion (or *decollapse*) of Illite layers.

This mechanism must favor the exchange with selective cations, such as Cs, also considering the observed increase of the interlayer charge. Furthermore, solvated calcium ions occupy less ditrigonal cavities at interlayers than smaller solvated ions such as sodium, or dehydrated ions, such as potassium, that are accessible only to Cs or other selective cations.

The affects of these structural modifications on Cs adsorption onto Illite will be verified by detailed sorption experiments.

Qualitative Description of Cs Sorption on Illite. Cs sorption onto Na-, K-, and Ca-Illite was studied at different ionic strengths. The logarithm of Cs adsorbed per mass of Illite (mol kg^{-1}) is presented as a function of the logarithm of Cs in solution (mol L^{-1}) for K, Na, and Ca-Illite in Figure 1a. This format of illustration of the isotherms informs about the Cs cationic exchange capacity of Illite; and both the presence and density of various sorption sites. Because the sole aqueous specie is Cs^+ , linear segments with a slope of 1 for the isotherms presented in Figure 1a signifies that Cs sorption for each of these zones can be modeled given a unique sorption site. The decrease of slope indicates either saturation sorption sites, or the existence of more than one sorption site.

Figure 1a shows the greatest amount of Cs adsorbed ($900 \text{ mequiv kg}^{-1}$) was for Ca-Illite. Furthermore, the XRD structure of the Ca-Illite in which $1 \times 10^{-3} \text{ M}$ of Cs has been adsorbed (*Cs-Illite* in Figure SI.2), shows similarity with K-Illite; this probably means that after Cs adsorption, the clay collapses again leading to the fixation of large quantities of Cs.

A comparison of the three isotherms for Na, K, and Ca-Illite, at the same ionic strength of 0.01 M (Figure 1b) or 0.2 M (Figure 1c), shows Cs sorption higher for Ca and Na-Illite than for K-Illite; this clearly demonstrates K^+ to be much more selectively retained by Illite than Na and Ca, as reported

by.^{9,15,26,35} This selectivity order was observed among cations under a wide range of Cs loading.

Conceptual Model of Cs Sorption onto Illite. The maximum sorbed Cs, at lower ionic strength (0.01 M), varied for the three exchanged clays: 900, 800, and 192 mequiv·kg⁻¹ for Ca, Na, and K-Illite, respectively.

Therefore, when Ca²⁺ is the primary electrolyte cation (at ionic strength of 0.01 and 0.2 M) and of Na⁺ is at a low concentration (0.01 M)—Cs adsorption is significantly higher than that expected—if one considers either the CEC value given as a reference for Illite (225 mequiv kg⁻¹)³⁶ or the CEC measured in this work (Figure 1a) or in early studies.^{15,16,18,19}

Sorption results suggest either the presence of large hydrated cations Ca²⁺, or the low Na concentrations for the electrolyte are favoring the exposure of exchange positions on Illite; and thereby producing higher Cs retention than expected.

This phenomena is in agreement with the decollapse concept of Illite, in terms of the expansion of 2:1 layers stacks—causing an increase in Cs-accessible planar sites that is suggested by the analyses of the three exchanged materials presented in SI.

Comans et al. (1992)³⁷ and Wauters et al. (1994)¹⁸ already reported that the presence of large cations with a stable hydration shell, such as Ca²⁺, accelerates Cs fixation on micaceous clays by expanding their interlayers. Yet alkali metals, with a low energy of hydration, can favor the collapse of the interlayers,^{28,30} when they are present above specific concentrations. However, at lower alkali metals concentrations, Illite can remain (partially) decollapsed.

The quantification of Illite's decollapse and its affects, in terms of CEC, for use in Cs sorption modeling is not straightforward because of the following: 1. Illite's reference CEC must be determined with Cs as the index sorption cation,³⁶ as it is the more selectively retained cation, but high Cs concentrations would induce interlayer collapse because it is a very fixable alkaline cation; 2. Depending on the concentrations of the electrolyte, various alkaline metals such as Cs, Na, or K will induce interlayer collapse. As suggested by Koning and Comans (2004),³⁰ the higher the selectivity of the cation, the lower the concentration required for the collapse of Illite's interlayers (i.e., [Cs] < [K] < [Na]). This is a very important point that cannot be excluded for adsorption studies with Illite; and, 3. Is the collapse a gradual process, or are only two Illite states possible (decollapsed or collapsed). For these two possible Illite states, the Illite collapse would occur when the concentration of the electrolyte cation under consideration exceeded the critical concentration—referred to as the “critical level of collapse”.

Our experimental results, for Cs sorption modeling, were obtained by simplification to only two states (collapsed or decollapsed). A CEC value of 900 mmol·kg⁻¹ was used for initially *decollapsed* Illite (CEC_{decollapsed}), because this was the maximum adsorption capacity for Cs we observed; the reference CEC value of 225 mequiv kg⁻¹ for Illite³⁶ was used for *collapsed* Illite (CEC_{collapsed}). The CEC_{decollapsed} applies for all the Ca-batch systems (i.e., Ca-Illite in Ca²⁺ electrolyte). For Na-batch systems (i.e., Na-Illite in Na⁺ electrolyte), the CEC_{decollapsed} applies at [Na] ≤ 0.01 M and CEC_{collapsed} applies for Na-batch systems at [Na] ≥ 0.1M; this signifies that the critical level of collapse for Na⁺ is between 0.01 and 0.1 M. CEC_{collapsed} applies for all K-batch systems (K-Illite in K⁺ electrolyte), that is, the K⁺ critical level of collapse is <0.01 M.

In sorption isotherms, the variation of K_d with sorbate concentration or the slope changes in logCs(ads) vs logCs(sol)

curves, indicate the possible existence of different sorption sites. However, if these variations are small (within the experimental error) it is very difficult to draw any conclusion about the existence of multiple sorption sites. From our experimental data, the presence of three sorption sites (as previously reported in the literature^{11,15,16} could be assessed only for Na-Illite. This does not necessarily mean that three sites do not exist also in K- or Ca-Illite, but only two can be deduced from data in presented in Figure 1. However, as three sites exist in Na-Illite (and exchange coefficients must be defined for all three sites) the selection of a three site model is strictly necessary to be consistent with all the exchanged clays.

The density of highly selective FES (FES-I) was estimated directly from the isotherms—considering the point where the slope at low Cs loadings changes (0.28 mequiv kg⁻¹) (Figure 1). This value approximately coincides for the three illites (Figure 1a); but it is slightly lower, while in concordance, than those reported in the literature (0.4–1 mequiv·kg⁻¹).^{11,15,16,25}

The density of the second type of FES (FES-II), which cannot be deduced directly from the slope of the isotherms, was estimated by applying the rate of 2%–98% between FES-I and FES-II in agreement with Cremers et al. (1988)²⁵ and Brouwer et al. (1983).¹⁵ Both authors agree on this rate that was determined after masking the planar sites with silver thiourea by the former; and based on the capacity of the two types of FES to discriminate Cs and Rb by the latter. The value of FES-II estimated with this method was 14 mequiv kg⁻¹.

The remainder of the CEC was assigned to planar sites, that is, 884 mequiv·kg⁻¹ for initially *decollapsed* Illite and 210 mequiv·kg⁻¹ for *collapsed* Illite.

These densities for the three sorption sites summarized in Table 1 are established as fixed parameters for the modeling procedure.

Table 1. Summary of Parameters and Selectivity Coefficients Used for the Developed Cs Sorption Model on Illite (LogK_{sel} Values for Decollapsed = LogK_{sel} Values for Collapsed)^a

CEC _{decollapsed} (mequiv·kg ⁻¹)	900			
CEC _{collapsed} (mequiv·kg ⁻¹)	225			
surface area (m ² g ⁻¹)	97			
site density (mequiv·kg ⁻¹)	log Cs K K _{sel}	log Cs Na Na _{sel}	log Cs Ca Ca _{sel}	
FES-I	0.29	4.8	6.8	15.0
FES-II	14.49	1.1	3.9	5.4
planar sites	884 (decollapsed) 210 (collapsed)	1.1	1.7	5.4

^aThe maximum error on the logarithm of selectivity coefficients is ±0.2. ^bCa-Illite is considered *decollapsed*; Na-Illite is considered *decollapsed* at I ≤ 0.01 M and collapsed at I ≥ 0.1M; K-Illite is considered collapsed.

The selectivity coefficients for Cs–K were estimated first, because the electrolyte could contain trace levels of other cations released from either Illite or impurities.^{16,36} These cations can compete both with Cs and with the primary cation of the electrolyte, either of which could affect the estimation of the selectivity coefficients. K is much more selectively retained by Illite than Na and Ca.^{9,15,26,35} Although trace levels of K are expected to influence Cs sorption of Na and Ca-Illite systems,³⁸ the competition of Ca²⁺ or Na⁺ for K-Illite system sorption sites is presumably negligible. We therefore modeled Cs sorption on

K-Illite first; and estimated the Cs–K selectivity coefficients—dismissing the possibility of traces of other cations in the electrolyte.

After Cs–K selectivity coefficients were obtained, Cs–Na and Cs–Ca selectivity coefficients were estimated—always accounting for the Cs–K exchange. Small amounts of K^+ in solution can greatly influence Cs sorption. K concentrations of $2\text{--}6 \times 10^{-5}$ M were measured in the electrolyte of Ca and Na-Illite (1 g L^{-1}) at pH 7 and ionic strength 0.01 and 0.2 M. The mean K concentration of 4×10^{-5} M in solution was used for calculations. The K–Cs exchange reactions were accounted for in the fitting procedure using the Cs–K selectivity coefficients estimated previously.

The fit of the experimental data required the prior determination of the K_{sel} values for both FES-I ($\log \text{Cs–K } K_{\text{sel}} = 4.8$) and planar sites ($\log \text{Cs–K } K_{\text{sel}} = 1.1$), which are directly calculable, because K_d values and the site densities are known.

Because of the superposition of the sorption contribution for FES II and planar sites, a relatively wide range of $\log K_{\text{sel}}$ values for FES-II could fit the experimental data well. As explained above, three exchange sites are necessary to develop a model consistent with the three illites considered by this study (Na, K, and Ca-Illite). Nevertheless, two sites would be enough to explain Cs sorption on K-Illite, as the two linear segments in the isotherms indicate. Therefore, we assumed the same K_{sel} for FES-II as those for planar sites ($\log \text{Cs–K } K_{\text{sel}} = 1.1$ in FES-II); and the same for Ca-Illite (Table 1).

For Na-Illite, two different exchange capacities (for *collapsed* Illite or *decollapsed* Illite) were used as a function of ionic strength. It is interesting to note that the selectivity coefficient determined both for the collapsed and the decollapsed Illite are identical ($\text{Cs–Na } \log K_{\text{sel}}$ in collapsed planar sites = $\text{Cs–Na } \log K_{\text{sel}}$ in decollapsed planar sites = 1.7). These identical selectivity coefficients imply that the reduction/increase of the number of planar sites caused by the collapse/decollapse of the interlayer does not imply a change in their sorption properties.

All the parameters, reactions and selectivity coefficients used in the model are reported in Table 1.

The K_d values (eq 1) predicted with the developed model are plotted together with the experimental values in Figure 2. The K_d illustration is preferred for the modeling because it emphasizes the differences among experimental data.

Figure 2 shows that K_d values are reasonably well predicted at both the wide ranges of ionic strength studied for Ca, K, and Na-Illite, and also accounting for the (de-) collapse.

Generally, in clayey rocks, Illite dominates Cs adsorption for the presence of selective sites (FES) while the presence of smectite starts to be relevant at high Cs loadings. This is true for “collapsed” Illite. Yet, in the cases in which Illite is initially “de-collapsed”, at high Cs loadings, sorption onto Illite became very similar (or even higher) than that observed in smectite.³

Environmental Implications of the (De)Collapse Concept. The required application of the (de)collapse concept for Cs sorption modeling of Illite is justified by the variation of the maximum sorbed Cs of the various exchanging cations (Ca, Na, or K). This experimental evidence must not be ignored; the (de)collapse consideration is required because the fit of the experimental data over such a wide range of conditions—is not possible if only a single CEC value is considered.

To elucidate this concept in Figure 3, we will show several examples of (*false*) simulations obtained starting from the wrong hypothesis. Figure 3a shows an example of *false*

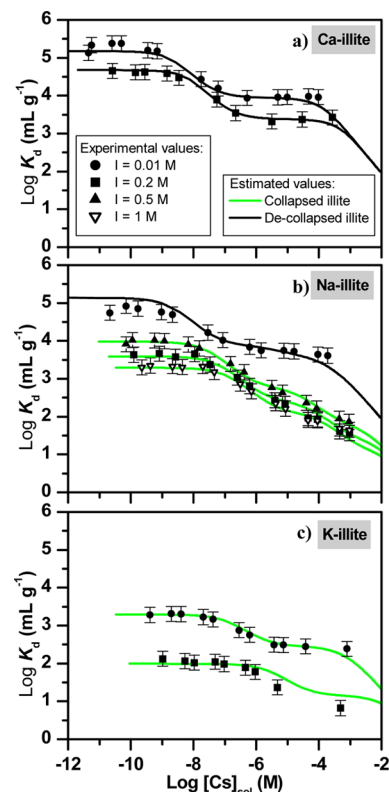


Figure 2. Cs sorption isotherms for (a) Ca-Illite, b) Na-Illite and (c) K-Illite at pH 7 and various ionic strengths. (Symbols represent experimental data and lines represent calculated values).

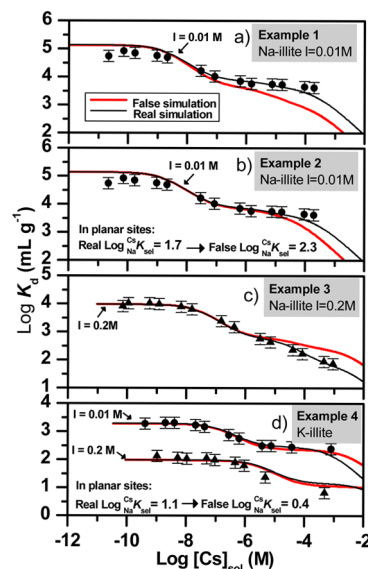


Figure 3. Examples of (*false*) simulations of Cs sorption on Illite without accounting for the decollapse of Illite (for conditions of simulation see Environmental Implications of the (De)Collapse Concept section).

simulation (*Example 1*), in which Cs sorption for Na-Illite at ionic strength 0.01 M is predicted with the parameters used for the collapsed Na-Illite (same $\log K$ values and same CEC value of $225 \text{ mequiv kg}^{-1}$). It can be seen that $\log K_d$ values are clearly underestimated at high Cs loadings (at $\log [\text{Cs}]_{\text{sol}} = -3.68 \text{ mol L}^{-1}$: real $\log K_d = 3.62 \text{ mL g}^{-1}$ and *false* $\log K_d = 2.66 \text{ mL g}^{-1}$).

Thus, neglecting the decollapse can lead to predictions of the sorbed Cs amounts up to 8 times higher than the actual (at $\log[\text{Cs}]_{\text{sol}} = -3.68 \text{ mol L}^{-1}$; experimental $[\text{Cs}]_{\text{sorbed}} = 0.80 \text{ mol kg}^{-1}$, and from false simulation: $[\text{Cs}]_{\text{sorbed}} = 0.11 \text{ mol kg}^{-1}$).

Figure 3b. (Example 2) illustrates the predicted K_d values for Na-Illite at 0.01 M ionic strength with the CEC value of collapsed Illite ($225 \text{ mequiv kg}^{-1}$). For this simulation, the selectivity coefficients $\log K$ were varied to fit the experimental data; producing a Cs–Na $\log K$ for planar sites ($\log K = 2.3$). This value is 35% higher than actual (Cs–Na $\log K = 1.7$).

Figure 3c. (Example 3) shows K_d values for Na-Illite at ionic strength of 0.2 M (expected to be collapsed) that was predicted using the developed model for the decollapsed Na-Illite, i.e., CEC of $900 \text{ mequiv kg}^{-1}$ and $\log K$ values indicated in Table 1. The predicted Cs sorbed at high Cs loadings would be highly overestimated.

Finally, Figure 3d (Example 4), illustrates the Cs sorption simulation on K-Illite given a decollapsed Illite (CEC of $900 \text{ mequiv kg}^{-1}$). Although the K_d values can be well predicted, the selectivity coefficient for the planar sites had to be decreased by 63%.

Even a perfect fit of experimental data can be misleading: the use of the erroneous calculated values of selectivity coefficients can give a false prediction of Cs sorption under different conditions. Furthermore, these errors in predicted values—without taking into account the decollapse factor—may be also extrapolated to the sorption behavior of other contaminants on Illite.

Because the (de)collapse mechanism involves the planar sites directly, it therefore must be considered—especially when high Cs concentrations are present.

For the illustration of the affect of the Illite collapse on the specific contribution of each site type see Figure 4 that shows the sorbed Cs corresponding to FES-I, FES-II, and planar sites on Na-Illite at ionic strength of 0.01 M (Figure 4a) and 1 M (Figure 4b).

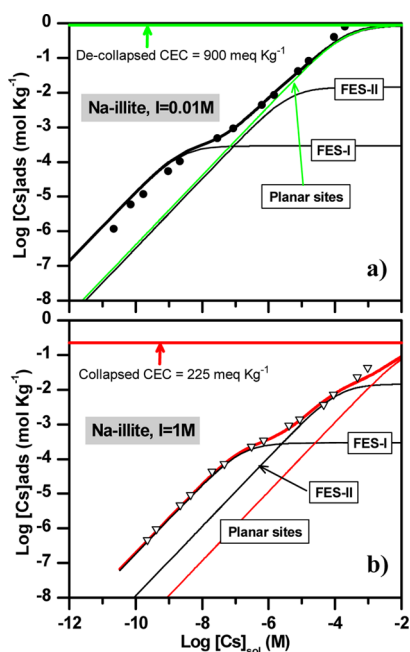


Figure 4. Contribution of the different types of sorption sites to the Cs sorption on Na-Illite, considering the (de)collapse concept at pH 7 and ionic strength of (a) 0.01 M and (b) 1 M.

(Figure 4b), as examples of *decollapsed* and *collapsed* Illite, respectively.

For both *decollapsed* and *collapsed* Illite (Figure 4a and Figure 4b), FES-I dominates the Cs sorption process at low Cs loadings (when $\log[\text{Cs}]_{\text{sorbed}} < -3 \text{ mol kg}^{-1}$). However, planar sites strongly contribute to Cs sorption at medium-high Cs loadings when Illite is decollapsed, but their contribution becomes negligible when Illite is collapsed, unless Cs loading is very high ($\log[\text{Cs}]_{\text{sorbed}} > -3.5 \text{ mol kg}^{-1}$).

Little contribution to Cs sorption, in previous studies, was attributed to the planar sites,^{11,16} because it was studied under conditions under which Illite is collapsed. However, planar sites play an important role in Cs sorption when Illite is *decollapsed*, that is, in the presence of bivalent ions, like Ca, Mg, or Sr quite common in natural waters, especially those with high hydration energy or low concentrations of alkaline cations.

Exchangeable cations and electrolyte concentrations affect the accessibility of Cs to the sorption sites of Illite: Nonfixable cations, such as Ca^{2+} , contribute to a local decollapse of Illite's planar sites and thereby, create more accessible sorption sites; whereas the Illite interlayer collapse, and hence the blockage of planar sites, is induced by a sufficiently high concentration of alkaline cations. The concentration effective for this collapse is associated with cation sorption selectivity of Illite (i.e., $[\text{Cs}] < [\text{K}] < [\text{Na}]$).

An underestimate of the contribution of planar sites to cationic exchange on Illite could lead to erroneous predictions of the sorption behavior and migration of Cs and other contaminants in the environment.

Sorbed Cs onto initially decollapsed Illite can be much higher than predicted by previous models based on Na-Illite^{11,15,16} with important implications for the understanding of Cs migration-retention. Furthermore, if, due to Cs adsorption, Illite collapses again, this will produce the fixation of high quantity of this ion. This higher sorption can imply higher retardation of Cs movement toward the geosphere because of Cs retention onto Illite surfaces.

But conditions favorable for *decollapsed* Illite, such as low concentrations of alkaline metals, are also favorable for clay colloid stability.^{39–41} The presence of clay colloids with higher Cs sorption onto *decollapsed* Illite—significantly increases the potential risk of colloid-facilitated transport of Cs.

The (de)collapse factor of Illite is also relevant for both the migration-retention of other contaminants and for other geochemical modeling, because the selectivity coefficients -- calculated on the basis of lower than actual Illite CEC values—will be biased and incorrect in their final application for transport modeling.

■ ASSOCIATED CONTENT

📄 Supporting Information

Additional information as noted in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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