

Mechanistic Thermodynamic Model for Zn^{2+} Uptake on Saponite

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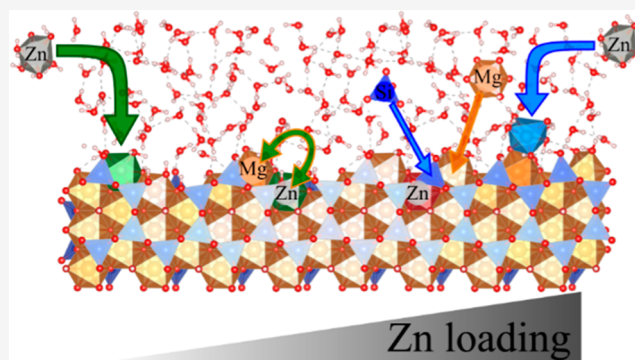


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Supporting Information

ABSTRACT: Zn uptake by the synthetic trioctahedral clay mineral saponite was investigated in batch sorption experiments over a wide range of conditions ($4.7 < \text{pH} < 9.6$; $2.3 \times 10^{-7} < [\text{Zn}_{\text{init.}}] < 3 \times 10^{-3} \text{ M}$) in 0.1 M NaCl. The pH- and concentration-dependent Zn^{2+} uptake follows the typical behavior previously reported for dioctahedral clay minerals and can be formally described by sorption on two types of surface sites. The sorption data were reproduced using the 2SPNE SC/CE model, which includes high-affinity/low-capacity “strong” sites and low-affinity/high-capacity “weak” sites. The protolysis constants of amphoteric oxygen sites were fixed based on the model available for montmorillonite, and only the site capacities and Zn complexation constants were optimized. Ab initio calculations, polarized EXAFS, and chemical constraints from solution-phase elemental analyses indicate that Zn is preferentially located on the edge surface attached to the octahedral sheet of saponite. The pronounced polarization dependency of the EXAFS spectra corroborates octahedral sheet-controlled Zn binding and rules out sorption on tetrahedral sites. The data sets consistently indicate a loading-dependent evolution of Zn coordination. At low surface loadings ($< 5 \text{ mmol/kg}$), Zn is predominantly taken up as a strongly bound inner-sphere complex at the octahedral edge sites, with 5-fold coordination by Mg. With increasing Zn concentrations, two additional Zn environments are identified and become dominant: (i) a weaker bound species with one-fold Mg coordination, consistent with the “weak” site complex predicted by the surface complexation model, and (ii) another strongly bound species with a 3-fold Mg coordination. The progressive consumption of dissolved Si and Mg with increasing Zn concentrations suggests the onset of an additional reaction pathway consistent with Zn–Mg phyllosilicate formation and agrees with the emergence of the highly coordinated species. Overall, the results show that, beyond the “strong” and “weak” surface complexes captured by the 2SPNE SC/CE model, an epitaxial Zn–Mg phyllosilicate phase likely forms at higher Zn concentrations.



INTRODUCTION

Clay minerals and clay-rich soils play a critical role in many geochemical environments due to their high reactivity.¹ The nanometer size of clay particles and their correspondingly large specific surface area renders them highly effective sorbents for toxic metals and potentially hazardous organic compounds.^{2–5} Due to their low hydraulic conductivity when compacted, such clays are used as geochemical barriers in environmental engineering applications, like the construction of landfills^{4,6,7} and deep geological repositories for radioactive waste.^{8–11} A mechanistic understanding of the sorption processes is essential for reliable long-term safety and performance assessments of such disposal systems.^{8,11}

The sorption capacity of clay minerals for cationic species is primarily governed by the negative structural charge of the clay platelets, which is compensated for by the interlayer cations. In swelling clay minerals, the cationic composition of the interlayer promptly equilibrates with an external solution. The cation uptake in the interlayer is termed cation exchange. Beyond the cation exchange, pH-dependent protonation and

deprotonation of surface hydroxyl groups at the edges of clay particles contribute to net cation uptake by surface complexation. Several models have been proposed to describe cation uptake by clay minerals across a wide range of geochemical conditions.^{12–15}

The 2 site protolysis nonelectrostatic surface complexation/cation exchange (2SPNE SC/CE) model^{15,16} has been successfully applied to describe the cation uptake by dioctahedral clay minerals such as montmorillonite and illite. This thermodynamic sorption model considers, besides cation exchange, surface complexation at two different sites on the clay mineral edge surfaces: the high-affinity, but low-capacity, “strong” sites and the low-affinity, but high-capacity, “weak”

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sites.^{17,18} The capacity of “weak” sites is derived from acid–base titration data, whereas the capacity of “strong” sites is typically estimated from sorption batch experiments, based on the extent of specific metal uptake. The affinities of both sites are characterized by distinct sorption constants, with the larger one for “strong” sites and the smaller for “weak” sites.

Although originally formulated from a purely thermodynamic perspective, the core assumptions of the 2SPNE SC/CE model have been corroborated by molecular-scale studies of Zn and Fe uptake on montmorillonite.^{19,20,23} The EXAFS studies¹⁹ and ab initio molecular simulations have shown that Zn^{2+} forms distinct sorbed complexes at edge sites, differing in coordination environment and binding strength.²⁰ These structural investigations confirmed that “strong” and “weak” sites postulated in the thermodynamic model indeed correspond to distinct structural complexes on the edge of montmorillonite with different site capacities and complexation strength. Results from Zn^{2+} sorption studies indicate that the “strong” sites governing uptake of Zn^{2+} at trace concentrations correspond to divalent cations located in structural defects and isomorphic substitution sites on the edge. The “weak” sites are better described as the inner-sphere Zn^{2+} complexes located on montmorillonite edge-surface. A similar combination of molecular simulations and EXAFS has been used to investigate the Fe^{2+} uptake and oxidation to Fe^{3+} on montmorillonite edge surface²¹ and the structure of iron incorporated into the bulk structure.^{22–24} These studies support the structural interpretation of the sorption sites previously proposed for Zn. Although numerous spectroscopic studies have been performed for other elements,^{25–32} they generally lack complementary ab initio modeling needed to resolve the individual surface species contributing to sorption.

Sorption models, in particular the 2SPNE SC/CE model, have been used to describe cation uptake in multimineral argillaceous systems.^{18,26,33} In such cases, a simplified component-additivity (bottom-up) approach has been developed to predict uptake using sorption models for the individual clay mineral phases.^{18,34–36} Uptake processes in mono- and polymineralic systems may involve not only sorption but also other processes such as neoformation, secondary-phase growth, or incorporation into mineral phases. Such processes are not properly accounted for in conventional sorption models. Although the model might be able to reproduce the overall uptake quantitatively, it cannot distinguish sorption from these nonsorption pathways. Under these conditions, the model no longer reflects the actual mechanism and, therefore, does not perform as expected across the full range of conditions.

Porewaters of complex systems typically contain multiple dissolved species, and it is therefore reasonable to expect mutual competition among different cations for the same sorption sites with limited capacity. A structural understanding of element-specific sorption is essential for evaluating such competitive effects.^{24,37–40} Previous sorption studies^{26–28,37,40,41} suggest that cations of the same valence and belonging to the same chemical group generally compete for the same sorption sites, whereas cations of different valence do not reveal mutual competition for the high-affinity sites. This behavior can be modeled by invoking structurally distinct, element-specific binding environments. For some pairs of elements (Pb–Ni, Pb–Co, Pb–Eu),⁴¹ partial competition has been observed and can be reproduced by assuming that only a subset of sorption sites is mutually exclusive. For example,

Tournassat et al.³⁹ showed that “strong” site like sorption can be described as an isomorphous substitution of Zn for Mg. Thus, the high-affinity sites can form through two different mechanisms: vacancy healing, where cations stabilize edge surfaces by filling coordinatively unsaturated sites, or isomorphous substitution, where cations with higher affinity replace Mg atoms on the edges.

The central goal of this study was to evaluate whether the 2SPNE SC/CE model developed for dioctahedral 2:1 clay minerals can be transferred to trioctahedral smectites. In both mineral groups, the octahedral sheet (O) is enclosed by two tetrahedral sheets (T), forming the characteristic TOT layered structure. In dioctahedral clays, two-thirds of the octahedral positions are typically occupied by trivalent cations (e.g., Al^{3+}), while one-third remains vacant. The structural charge of the TOT layer arises from divalent-for- Al^{3+} substitution in the octahedral sheet and Al-for-Si substitution in the tetrahedral sheets. In contrast, trioctahedral clays have all octahedral positions filled, usually by divalent cations such as Mg^{2+} . Their layer charge is primarily generated by Al-for-Si substitution in the tetrahedral sheets and, to a lesser extent, by monovalent-for-divalent substitution (e.g., $\text{Li}^+ \rightarrow \text{Mg}^{2+}$) in the octahedral sheet. These structural distinctions may influence sorption mechanisms on di- and trioctahedral clay minerals. Previous experimental studies on hectorite—a trioctahedral talc-like smectite, with Mg^{2+} – Li^+ substitutions in octahedral sheet, have indicated that Zn uptake can be hindered by phyllosilicate neoformation in the presence of additional dissolved Si.⁴² However, such epitaxial phyllosilicate growth has not been observed under natural conditions.^{42,43} Although trioctahedral clay minerals are less common than their dioctahedral counterparts, they provide an important contribution to the cation uptake^{26–30,43,44} and redox chemistry⁴⁵ in geochemical systems. Moreover, some dioctahedral clay minerals^{44,46} can recrystallize into or form trioctahedral clusters in dioctahedral clays at high temperature.

Since a reliable and robust description of cation uptake by these trioctahedral clays is not available, this study develops and tests a robust quasi-mechanistic model for cation sorption on trioctahedral clay minerals using saponite as the representative substrate and Zn as the proxy cation for divalent transition metals. Synthetic saponite was chosen for this work due to its high purity and crystallinity, which, as has been shown in our previous studies,^{47,48} provides a highly crystalline sorption matrix with well-controlled structural charge obtained by hydrothermal synthesis. The synthetic saponite used in this study maintains a TOT trioctahedral structure with Mg fully occupying the octahedral sheet and Al substituting for Si in the tetrahedral sheets.⁴⁸ The thermodynamic sorption model developed here based on wet chemical experiments is compared with those from previous studies on dioctahedral clay minerals. The molecular scale details of the sorption mechanism are investigated by using atomistic simulations combined with Zn EXAFS spectroscopy at different Zn loadings. Finally, we discuss the implications of our findings for sorption mechanisms in trioctahedral clays and the broader applicability of the 2SPNE SC/CE model.

■ MATERIALS AND METHODS

The details of the saponite synthesis are described in our previous studies.^{48,49} In short, the synthetic Mg-saponite was obtained through hydrothermal crystallization of calcined amorphous gel produced from a stoichiometric mixture of analytical grade reactants (Na_2CO_3 ,

$\text{Mg}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, $\text{Si}(\text{OC}_2\text{H}_5)_4$ aiming at an ideal $\text{Si}_{3.6}\text{Al}_{0.4}\text{Mg}_{0.4}\text{O}_{10}(\text{OH})_2\text{Na}_{0.4}$ formula unit, with a theoretical dry weight of 388 g/mol, similar to the Na0.8-Saponite prepared earlier.^{47,50} Hydrothermal synthesis was carried out for 1 month at 400 °C and ≥ 600 bar.⁵¹ The synthesized saponite was washed twice in an excess of 1 M NaCl to obtain a homoionic Na-saturated clay. The excess NaCl was removed in the final washing cycle with deionized water. The resulting paste was freeze-dried for 48 h to obtain a white solid powder. The saponite phase identity was confirmed by powder XRD measurements on oriented samples⁴⁹ (see Supporting Information Figure S5). Saturation of the samples with ethylene glycol showed the displacement of 00l reflections due to the swelling of the interlayer space that is typical of smectite structures such as saponite.^{52,53}

The cation exchange capacity (CEC) of Na–Mg-saponite was determined on two independent batches of synthetic saponite by the ¹³⁴Cs isotope dilution technique as described in ref 54. The average result was Cs-CEC = 0.92 ± 0.03 equiv/kg_{clay}. Detailed description of the CEC measurement procedure is given in Supporting Information.

Zn Sorption Experiments

Zn sorption on Na-saponite was quantified in two ways: (i) at trace Zn levels ($[\text{Zn}_{\text{init.}}] = 2 \times 10^{-7}$ M) over pH 4.6–9.7 in 0.1 M NaCl with an S/L ratio of 1.7 g/L (sorption edge) and (ii) at constant pH (6.8 ± 0.2) as a function of Zn concentration (2.3×10^{-7} – 3×10^{-3} M) using an S/L ratio of 0.52 g/L in 0.1 M NaCl (sorption isotherm).

All sorption experiments were conducted in a controlled N₂ atmosphere glovebox with CO₂ ≤ 1 ppm and O₂ ≤ 1 ppm to prevent changes in geochemical conditions (e.g., carbonate complexation, precipitation, oxidation). The pH was adjusted by using 1 M NaOH and 1 M HNO₃ without altering the ionic strength. Possible pH drift was prevented by adding 2 mM of one of the following buffers: acetate, MES, MOPS, TRIS, or CHES (BioChemika MicroSelect, Fluka). These buffers were selected for their weak complexation with divalent metal cations at the applied concentrations (Ferreira et al., 2015; Perrin and Dempsey, 1974). Zn sorption was quantified radiochemically using ⁶⁵Zn (*t*_{1/2} = 343.9 d; PerkinElmer, USA). For the EXAFS samples, stable Zn was used.

For each experimental series, the exact clay content was determined by drying to a constant weight at 105 °C and correcting for the salt content. All solutions were prepared from ultrapure deionized water (18.2 MΩ/cm at 25 °C) and analytical-grade chemicals. Well-characterized stock solutions of ⁶⁵Zn were used. The radiotracer was diluted from the stock solutions into the respective background electrolyte and equilibrated overnight. For the experiments, the tracer solutions were adjusted to the desired pH by addition of the buffer. In a subsequent step, a clay suspension was added to initiate sorption.

All experiments were performed in duplicate using 40 mL polyethylene centrifuge tubes, mounted on end-over-end shakers for 7 days. Sorption was quantified by measuring the activity of ⁶⁵Zn in the supernatant. Phase separation in the Zn experiments was achieved by centrifugation using a Beckman Coulter Avanti J30i High-Performance centrifuge (1 h at 108,000 g max). The pH of the equilibrated solutions was measured with a Metrohm combined electrode calibrated against Merck pH 4, 7, and 10 buffers. Aliquots of the supernatant were taken for radiotracer analysis (gamma line) of ⁶⁵Zn (β^+ emitter) using a Canberra Packard Cobra Quantum counter together with standard labeled solutions.

Four inactive sorption samples for the EXAFS measurements were prepared with stable Zn. The sorbed Zn concentrations were quantified by ICP-OES (Agilent 5110; Zn detection limit ~ 0.002 ppm $\approx 3.4 \times 10^{-8}$ M), along with total Si, Mg, and Al. The samples contained 1.1, 2.4, 29.4, and 38.2 mmol/kg of Zn (see Figure 2 and Table 5).

Sorption Modeling

The Zn²⁺ sorption data (sorption edge and isotherm) were modeled with the 2SPNE SC/CE model for montmorillonite,^{15,16,55} as no alternative sorption model specific to saponite is available and the 2SPNE SC/CE model has been successfully applied to 2:1 clays such

as montmorillonite and illite. The model and its parameters are described in detail in Table S1 (Supporting Information). Briefly, it accounts for cation exchange at planar sites (X–) and inner-sphere surface complexation (SC) at amphoteric $\equiv\text{SOH}$ groups, represented by one type of “strong” site ($\equiv\text{S}^{\text{SOH}}$) and two types of “weak” sites ($\equiv\text{S}^{\text{W1OH}}$, $\equiv\text{S}^{\text{W2OH}}$). The aim here is not to establish a full parametrization for Na-saponite but to test whether the commonly used “strong/weak” surface complexation framework in the 2SPNE SC/CE model is also applicable to trioctahedral saponite. The modeling also serves mechanistic interpretation of ab initio MD simulations and Zn EXAFS data. In the modeling, the protolysis constants were fixed to the values reported for montmorillonite ($\log_{10}K_{\text{app}} = 4.5$ and -7.9 for $\equiv\text{S}^{\text{S/W1OH}}$ and $\log_{10}K_{\text{app}} = 6.0$ and -10.5 for $\equiv\text{S}^{\text{W2OH}}$, respectively; see Supporting Information Table S1). The capacities and Zn surface-complexation constants were fitted to the experimental saponite data.

Sorption modeling was performed using the geochemical solver GEM-Selektor,^{56,57} following a procedure similar to that used in ClaySor, the GEMS-based implementation of the 2SPNE SC/CE model, for montmorillonite and illite.^{55,58} The aqueous speciation data for Zn were taken from the PSI/Nagra chemical thermodynamic database 2020.⁵⁹ Experimental sorption isotherm and pH edge data were used as input. The best-fit values and uncertainties of the apparent standard molar Gibbs free energy (G_{298}^0) of surface complexes and cation exchange species were determined using GEMSFITS,⁶⁰ a parameter optimization tool that employs the GEMS code to compute equilibrium states across all experimental data points simultaneously. Further details of the modeling procedure are listed in the Supporting Information.

EXAFS Measurements

The X-ray absorption measurements were performed at The Rossendorf Beamline (ROBL, BM20)⁶¹ at the European Synchrotron Radiation Facility (ESRF) in Grenoble. Detailed description of P-EXAFS sample preparation and measurement setup is given in the Supporting Information.

The Zn K-edge (9659 eV) fluorescence EXAFS spectra were collected using self-oriented clay films in a geometrical setup as described in refs 62 and 63. The accurate energy calibration of each scan was performed using a zinc foil standard measured in transmission mode. The quality of the fluorescence signal was improved through averaging several scans in the SixPack 1.4 software package.⁶⁴ Normalization of the measured XAS spectra and extraction of EXAFS converted from energy to *k*-space was performed using the WinXAS 3.2 code.⁶⁵ The Zn EXAFS shell fitting was carried out with the Artemis software package⁶⁶ based on scattering paths generated with FEFF 9.6,^{67–69} using the crystal structure of talc,⁷⁰ where one Mg in the octahedral position was replaced by Zn. Shell fitting of P-EXAFS was conducted from 2.0 to 10.5 Å^{−1} and limited to the first three coordination shells (Zn–O, Zn–Mg, and Zn–Si), following the procedure previously established for nontronite⁶³ and hectorite.³⁰ For instance, the Zn–O bond distance and Debye–Waller factors obtained at the 35° polarization angle were used as fixed value for the spectra obtained at the other angles, whereas Zn–Mg and Zn–Si distances and Debye–Waller factors were fixed to values obtained at 10° and 80°, respectively, i.e., at the angle where each of the backscattering pairs is most unambiguously expressed. Additionally, the Zn–Si coordination number at the 10° polarization angle (where the Zn–Si backscattering signal is largely suppressed) was fixed to zero. Some additional Debye–Waller factors needed to be constrained; namely, the Debye–Waller factors of the Zn–Mg and Zn–Si shell in high loading samples were fixed to the value obtained from the 2.4 mmol/kg sample shell fit. The amplitude reduction factor (S_0^2) was set to 0.9 for all shells.

Ab Initio MD System Setup

Based on the previous studies of dioctahedral clay minerals,^{20,21} we speculate that relevant sorption complexes could be represented either by inner-sphere complexes or by near surface structural sites on the edge facets of clay platelets. The stability and structure of possible edge facets have been revealed in our previous study using the talc

structure as a proxy for saponite⁴⁹ to avoid ambiguity regarding Al–Si substitutions in the tetrahedral sheets. Hence, talc and saponite mineral names are used interchangeably in the discussion of molecular simulation results and the comparison of theoretical predictions with spectroscopic data. The stable stoichiometry of (010) and (110) facets was obtained using the crystallographic structure C1, $a = 5.29$ Å, $b = 9.173$ Å, $c = 9.46$ Å, $\alpha = 90.46^\circ$, $\beta = 98.68^\circ$, $\gamma = 90.09^\circ$ of talc.⁷¹ Both the α and γ angles in the talc structure are very close to 90° , whereas the β angle primarily affects the relative shift of the neighboring TOT layers, which is controlled by weak dispersion interactions. As the primary focus of this work is the structure of edge surfaces controlled by the strong cation–oxygen bonds and hydrolysis, which are much stronger than the dispersive interactions between basal planes, the model setup was simplified by enforcing an orthorhombic supercell geometry. The simulations were performed in supercells composed by $4 \times 2 \times 1$ unit cells of talc with the interparticle space filled with water (see Figure 1). In the simulation setup, the edge surface is oriented normally to the a -dimension of the supercell.

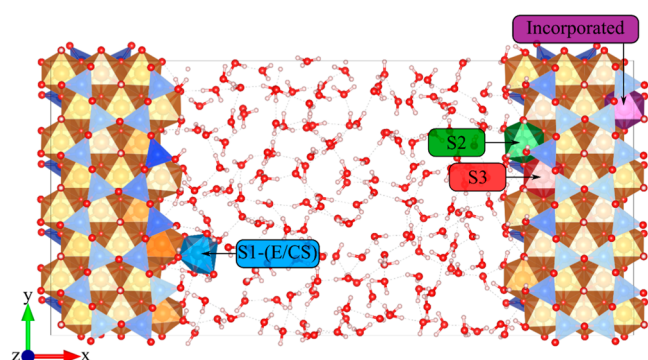


Figure 1. System setup for the ab initio MD simulations of Zn^{2+} sorption on the (010) and (110) edge surfaces. The “S1-CS” and “S1-ES” notations refer to mono- and bidentate inner-sphere surface complexes. Initial distribution of water at the edge surfaces was pre-equilibrated using classical MD simulations.

Potential structural sites considered for Zn uptake are indicated in Figure 1. The “S2” and “S3” sites are the octahedral near surface positions in the ideal edge surface of saponite. The “S1-ES” and “S1-CS” are bidentate octahedrally coordinated inner-sphere sorption complexes and a monodentate tetrahedrally coordinated Zn-complex on the ideal edge surface of saponite.

Prior to ab initio MD simulations, the distribution of water molecules in the interparticle space was pre-equilibrated using classical molecular dynamics simulations with the ClayFF force field⁷² using the LAMMPS code.⁷³ The number of water molecules and the inter particle pore size was optimized to obtain 1 g/mL water density in the middle of inter particle pore (see Supporting Information Figure S7). The system was annealed from 1000 to 300 K and then equilibrated for 1 ns at 300 K, while the clay particle atoms were kept fixed at the corresponding equilibrium positions obtained from ab initio structure optimization. The simulations were conducted in the NVT ensemble (i.e., constant number of particles, volume, and temperature), with the temperature controlled by a Nose–Hoover thermostat. Final structures ready for ab initio MD simulations contained 896 atoms and had the following dimensions: for (010), $a = 45.33$ Å, $b = 21.29$ Å, $c = 9.46$ Å; for (110), $a = 45.34$ Å, $b = 21.28$ Å, $c = 9.46$ Å.

Ab initio molecular dynamics simulations were performed based on the DFT approach using the CP2K open-source package. The electronic states were described using the Gaussian and Plane Wave (GPW) basis set.^{74–76} Goedecker, Teter, and Hutter scalar-relativistic norm-conserving pseudopotentials⁷⁷ were applied to avoid the explicit consideration of the core electrons. Following medium-core pseudopotentials were applied: [Ar] $4s^2 3d^{10}$ for Zn, [Ne] $3s^2 3p^2$ for

Si, [Ne] $3s^2$ for Mg, [He] $2s^2 2p^4$ for O, and $1s^1$ for H. The valence electron wave functions were described by a linear combination of contracted Gaussian-type orbitals using MOLOPT short-range basis sets.⁷⁸ The electronic charge density was expanded in an auxiliary basis set of plane waves by using a density cutoff of 450 Ry. The exchange and correlation (XC) functional of Perdew, Burke, and Ernzerhof (PBE)⁷⁹ in its spin-polarized formulation was used for all simulations. A dispersion correction DFT-D3 was applied according to refs 80 and 81. The energy in each self-consistent field (SCF) cycle was converged to 10^{-6} a.u. criteria. Conventional DFT is known to underestimate the Coulomb repulsion for the 3d-electrons, which leads to a delocalization of the 3d-states.⁸² Therefore, the so-called DFT + U method was applied to improve the description of 3d-states within the DFT formalism.⁸³ In this method, the DFT equation is augmented with the so-called Hubbard term (U_{eff}), which applies an additional potential enforcing element selective localization of the 3d-states. The Hubbard potential for Zn was fixed to 1.0 eV according to previous benchmarking studies.⁸⁴

After equilibrating the system, ab initio MD simulations were performed in the NVT ensemble (i.e., constant number of particles, volume and temperature) at 300 K by applying the canonical sampling velocity rescaling (CSVR) thermostat.⁸⁵ The relaxation time constant of the thermostat was set to 100 fs. The equations of motion were integrated using an MD time step of 0.5 fs. Overall, at least 16 ps long ab initio MD trajectories were obtained for each system studied, of which the last 10 ps were used for the calculations of structural and thermodynamic quantities. The modeling setup and the simulation parameters used in this study have been extensively tested and validated against spectroscopic data in our previous study of Zn- and Ni-doped saponite.⁴⁹

EXAFS Simulation

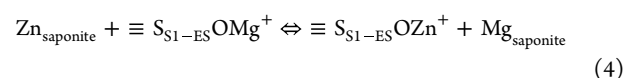
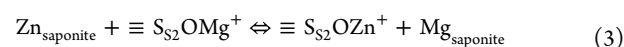
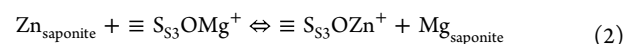
Theoretical EXAFS spectra were calculated based on molecular configurations obtained by ab initio MD simulations at 300 K using the FEFF 9.6 software.^{67–69} For each structural complex shown in Figure 1, at least 101 individual spectra, corresponding to statistically independent (i.e., separated by 100 fs) molecular configuration, were calculated using a global Debye–Waller factor (SIG2 parameter) set to zero. The spectra from instantaneous configuration were then averaged to obtain representative reference Zn^{2+} spectra for use in the component-specific analysis of the experimental data. Detailed description of the FEFF setup is provided in Supporting Information.

The linear combination fit of the experimental EXAFS spectra was performed within $k(\text{\AA}^{-1}) \in [2.5, 10.5]$ intervals to evaluate the contributions of different Zn complexes on (010) and (110) edge surfaces as a function of loading. The fit was performed according to eq 1 after max-min normalization to the value of the first oscillation of the calculated (see Supporting Information Figure S8) and the measured spectra

$$\|k^3(\sum_i a_i^2 \chi_i(k) - \chi(k)_{\text{exp}})\|^2 + \|a_i^2\|^2 \Rightarrow \min \quad (1)$$

where $\chi_i(k)$ and $\chi(k)_{\text{exp}}$ are the theoretical reference and the experimental EXAFS spectra, respectively; a_i^2 are the fitting parameters for the theoretical structures. The root-mean-square deviation (RMSD) of measured and simulated spectra was calculated using eq 1 without the regularization term ($\|a_i^2\|^2$).

Thermodynamic Integration. To evaluate the affinity of Zn for replacing Mg in various structural positions, the Helmholtz free energy of Zn–Mg exchange was calculated by using thermodynamic integration techniques for reactions:



The surface sites $\equiv\text{S}_{\text{SY}}$ are shown in Figure 1. The $\text{Zn}_{\text{saponite}}$ represents the Zn ion incorporated in the bulk structure of Mg-saponite at a Mg:Zn ratio equal to 47. The thermodynamic integration path is described by the λ -dependent Hamiltonian:

$$\hat{H}_\lambda = \lambda \hat{H}_0 + (1 - \lambda) \hat{H}_1 \quad (5)$$

where $\hat{H}_0$ and $\hat{H}_1$ are the DFT⁸⁶ Hamiltonians of the reactants and products in eqs 2–4, respectively.

Accordingly, the free energy of the exchange reaction is obtained by

$$\Delta A = \int_0^1 d\lambda \Delta E_{\hat{H}_\lambda} \quad (6)$$

where $\Delta E_{\hat{H}_\lambda}$ is the λ -specific vertical energy gap for ion exchange reactions (eqs 2–4) calculated for atomic geometry minimizing $\hat{H}_\lambda$ Hamiltonian defined in eq 5.

The integral in eq 6 was approximated by Simpson's rule for 11 equally spaced λ -points:

$$\begin{aligned} \Delta A &\approx \Delta \bar{A} \\ &= \frac{1}{30} [\Delta E_{\lambda=0} + 4(\Delta E_{\lambda=0.1} + \Delta E_{\lambda=0.3} + \Delta E_{\lambda=0.5} + \Delta E_{\lambda=0.7} \\ &\quad + \Delta E_{\lambda=0.9}) + 2(\Delta E_{\lambda=0.2} + \Delta E_{\lambda=0.4} + \Delta E_{\lambda=0.6} + \Delta E_{\lambda=0.8}) \\ &\quad + \Delta E_{\lambda=1}] \end{aligned} \quad (7)$$

The equilibrium constants of the simulated ion exchange reaction and thus the pK value were obtained using eq 8:

$$K_{\text{eq}} \approx \exp^{-\Delta A/RT} \quad (8)$$

where ΔA —Helmholtz free energy, J/mol, T —temperature, 300 K, R —gas constant, 8.314 J/(mol*K). The effective difference between the Helmholtz and Gibbs free energy calculations for the exchange reaction at ambient pressure is very small and can be neglected.

RESULTS AND DISCUSSION

Sorption Results and Modeling

The Zn sorption edge data and isotherm on Na-saponite are shown in Figure 2. The results of the Zn sorption measurements are expressed in terms of solid–liquid distribution ratios (R_d) plotted against pH, with R_d (L/kg) defined as eq 9:

$$R_d = \frac{[\text{Zn}_{\text{init.}}] - [\text{Zn}_{\text{equil.}}]}{[\text{Zn}_{\text{equil.}}]} \times \frac{V}{m} \quad (9)$$

where $[\text{Zn}_{\text{init.}}]$ is a total (active + inactive) initial aqueous metal concentration (M), $[\text{Zn}_{\text{equil.}}]$ is a total (active + inactive) equilibrium aqueous metal concentration (M), V is a volume of liquid phase (L), and m is a mass of solid phase (kg).

Zn sorption isotherm is plotted both as the amount of metal adsorbed, $[\text{Zn}_{\text{sorb.}}]$ expressed in mol/kg against the metal equilibrium concentration, $[\text{Zn}_{\text{equil.}}]$ (M) with eq 10:

$$[\text{Zn}_{\text{sorb.}}] = ([\text{Zn}_{\text{init.}}] - [\text{Zn}_{\text{equil.}}]) \times \frac{V}{m} \quad (10)$$

and in terms of R_d plotted against $[\text{Zn}_{\text{equil.}}]$. The relation between both is given by eq 11:

$$R_d = \frac{[\text{Zn}_{\text{equil.}}]}{[\text{Zn}_{\text{sorb.}}]} \quad (11)$$

Such a complementary representation of data allows a direct comparison of the log R_d values at trace concentrations between the isotherms and the sorption edges, while the

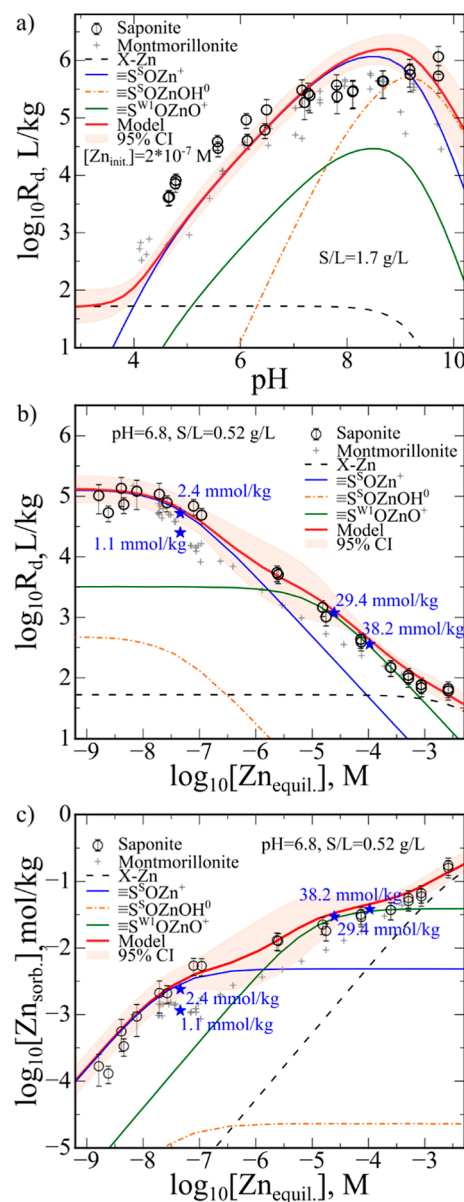


Figure 2. Zn(II) sorption modeling on synthetic saponite in 0.1 M NaCl: the red lines represent the modeling results with 2SPNE SC/CE model parameters tuned to the experimental data (see Table 1). The shaded band indicates the 95% confidence interval. Zn sorption data on montmorillonite¹⁶ are shown for comparison. The sorption isotherm was measured at pH 6.8 ± 0.2. Data shown as blue stars on the sorption isotherm correspond to the samples analyzed with EXAFS.

$[\text{Zn}_{\text{sorb.}}]$ versus $[\text{Zn}_{\text{equil.}}]$ plot highlights the presence of distinct site types and their respective capacities.

The pH-dependent sorption behavior of Zn on synthetic saponite exhibits the typical shape of the sorption edge common to other transition metals and lanthanides (e.g., Fe, Zn, Ni, Eu) on clay minerals^{16,17,19,33,36,87–90} and closely resembles that observed for Zn uptake on montmorillonite.¹⁶ The sorption on Na-saponite varies between log R_d values of 3.5 at pH 4.8 and increases up to pH 7.2 reaching a log R_d maximal value of ~5.5 L/kg. Significant precipitation of a solubility limited Zn-bearing solid can be excluded, as this would produce a sharp drop in dissolved Zn followed by a

Table 1. Cation Exchange and Surface Complexation Reactions of Zn(II) on Synthetic Saponite, along with Their Standard Gibbs Free Energy of Sorption Reaction $\Delta_r G_{298}^0$, Standard Gibbs Energy of Formation for Sorbed Species $\Delta_f G_{298}^0$, and Equilibrium Constants $\log_{10}K$

reaction	$\Delta_r G_{298}^0$, kJ/mol	$\Delta_f G_{298}^0$, kJ/mol	$\log_{10}K$	$\log_{10}K$ mont. ^{a,55}
$2X-Na + Zn^{2+} \leftrightarrow X_2-Zn + 2Na^+$	-0.013	-127.15 $\pm$ 0.86	0.00 $\pm$ 0.15 ^b	0.29
$\equiv S^S OH + Zn^{2+} \leftrightarrow \equiv S^S OZn^+ + H^+$	-6.28	-390.62 $\pm$ 0.66	1.10 $\pm$ 0.12	0.98 $\pm$ 0.15
$\equiv S^S OH + Zn^{2+} + H_2O \leftrightarrow \equiv S^S OZnOH^0 + 2H^+$	46.36	-575.13 $\pm$ 2.12	-8.12 $\pm$ 0.37	-
$\equiv S^{W1} OH + Zn^{2+} \leftrightarrow \equiv S^{W1} OZn^+ + H^+$	8.02	-376.33 $\pm$ 1.73	-1.40 $\pm$ 0.30	-2.36 $\pm$ 0.15
$Zn^{2+} + H_2O \leftrightarrow ZnOH^+ + H^+$	51.03	-333.31 $\pm$ 0.34	-8.94 $\pm$ 0.06	-8.94 $\pm$ 0.06
$Zn^{2+} + 2H_2O \leftrightarrow Zn(OH)_2^0 + 2H^+$	102.12	-519.37 $\pm$ 0.86	-17.89 $\pm$ 0.15	-17.89 $\pm$ 0.1
$Zn^{2+} + 3H_2O \leftrightarrow Zn(OH)_3^- + 3H^+$	159.71	-698.91 $\pm$ 0.57	-27.98 $\pm$ 0.1	-27.98 $\pm$ 0.1
$Zn^{2+} + 4H_2O \leftrightarrow Zn(OH)_4^{2-} + 4H^+$	230.32	-865.44 $\pm$ 1.26	-40.35 $\pm$ 0.22	-40.35 $\pm$ 0.22
$2Zn^{2+} + H_2O \leftrightarrow Zn_2OH^{3+} + H^+$	45.09	-486.45 $\pm$ 1.71	-7.9 $\pm$ 0.3	-7.9 $\pm$ 0.3

^aMontmorillonite equilibrium constants from a previous study⁵⁵ are given for comparison. Corresponding aqueous speciation data for Zn(II) are taken from the psi chemical thermodynamic database 2020.⁹¹ ^bThe cation exchange equilibrium constant is given in Vanselow convention.⁹²

Table 2. Structural Parameters of Zn²⁺ Adsorbed on Saponite as Derived from EXAFS Spectra Shell Fit Performed According to Refs 19, 48, 63, and 94 ($\alpha = 35^\circ$)^a

sample	Zn ²⁺ loading, mmol/kg	shell	CN ($\alpha = 10^\circ$), N	CN ($\alpha = 35^\circ$), N	CN ($\alpha = 55^\circ$), N	CN ($\alpha = 80^\circ$), N	<i>d</i> , Å	σ_{W}^2 , Å ²	ΔE_0 , eV
Zn ²⁺ sorption samples	1.1	Zn–O	5.6	5.7	5.5	5.2	2.07	0.012	1.3
		Zn–Mg	4.4	4.0	3.3	3.1	3.10	0.010	
		Zn–Si	0.0	1.7	2.9	4.7	3.25	0.009	
	2.4	Zn–O	5.5	5.2	5.0	4.8	2.08	0.011	2.5
		Zn–Mg	4.9	4.0	3.3	2.1	3.10	0.010	
		Zn–Si	0.7	2.0	2.9	3.8	3.25	0.008	
	29.4	Zn–O	5.6	5.1	5.0	4.8	2.08	0.011	2.7
		Zn–Mg	4.7	3.4	2.5	1.4	3.08	0.010 ^{<i>b</i>}	
		Zn–Si	2.7	2.9	3.2	3.4	3.27	0.008 ^{<i>b</i>}	
	38.2	Zn–O	6.0	5.3	5.4	4.9	2.08	0.012	1.9
		Zn–Mg	4.3	3.5	2.3	1.3	3.07	0.010 ^{<i>b</i>}	
		Zn–Si	2.8	3.3	3.2	3.4	3.27	0.008 ^{<i>b</i>}	
references									
Zn-doped saponite	200 ^{<i>c</i>}	Zn–O	5.8	6.0	5.4		2.09	0.007	8.46
		Zn–Mg	5.7	5.0	5.1		3.06	0.007	
		Zn–Si	2.5	2.5	4.2		3.29	0.015	
ZnKer3	79 ^{<i>d</i>}	Zn–O	-	6.0	-		2.07	0.010	−3.6
		Zn–Mg	-	6.0	-		3.08	0.010	
		Zn–Si	-	4.0	-		3.20	0.010	
ZnKer70	1715 ^{<i>d</i>}	Zn–O	-	6.0	-		2.07	0.010	−2.2
		Zn–Mg	-	4.6	-		3.07	0.010	
		Zn–Zn	-	1.4	-		3.10	0.010	
		Zn–Si	-	4.0	-		3.24		

^aData correspond to orientationally averaged bulk EXAFS measurements. Structural parameters derived from EXAFS fitting maintain an accuracy of ± 0.01 Å for interatomic distances and $\pm 25\%$ for coordination numbers. ^bMarked fit parameters were fixed in the shell fitting: σ_w^2 (Zn–Mg) and σ_w^2 (Zn–Si)—were constrained to the values obtained in the shell fit of 2.4 mmol/kg sample, respectively. ^cResults for Zn-doped saponite samples from ref 49 measurement was taken at $\alpha = 70^\circ$, i.e., almost parallel to the electric field vector. ^dZn²⁺ loading in mmol/kg was derived from ZnKer3 ($Si_4(Mg_{2.97}Zn_{0.03})O_{10}(OH)_2 \cdot nH_2O$) and ZnKer70 ($Si_4(Mg_{2.3}Zn_{0.7})O_{10}(OH)_2 \cdot nH_2O$) chemical formulas.⁴³ The shell-by-shell fit was performed by Schlegel et al.⁴³ with fixed coordination number and setting amplitude reduction factor (S_0^2) to 0.85.

constant Zn concentration fixed by the solubility of the precipitate, which is not observed.

The results of the modeling of Zn sorption on synthetic saponite as a function of pH are presented in Figure 2. The 2SPNE SC/CE model parameters for montmorillonite were used as initial guess and were optimized to fit the experimental Zn sorption data for synthetic saponite. In this model, the surface complexation is considered on “strong” and “weak” sites ($\equiv S^S$ and $\equiv S^{W1}$). The fitted standard Gibbs free energies of sorption and equilibrium constants for both cation exchange

and surface complexation, along with the corresponding aqueous speciation literature data, are summarized in Table 1.

The Zn isotherm (plotted as $[Zn_{sorb}]$ vs $[Zn_{equil}]$ in Figure 2c) measured for Na-saponite exhibits an overall nonlinear behavior and closely agrees with the isotherm obtained for Zn on montmorillonite. At low equilibrium concentrations ($[Zn_{equil}]$), the sorption follows a nearly linear trend consistent with the ideal (Henry’s Law) region of a Langmuir-type isotherm, whereas with increasing concentration, the isotherm becomes nonlinear, transitioning to a Freundlich-type behavior characterized by a log–log slope of less than 1. The observed

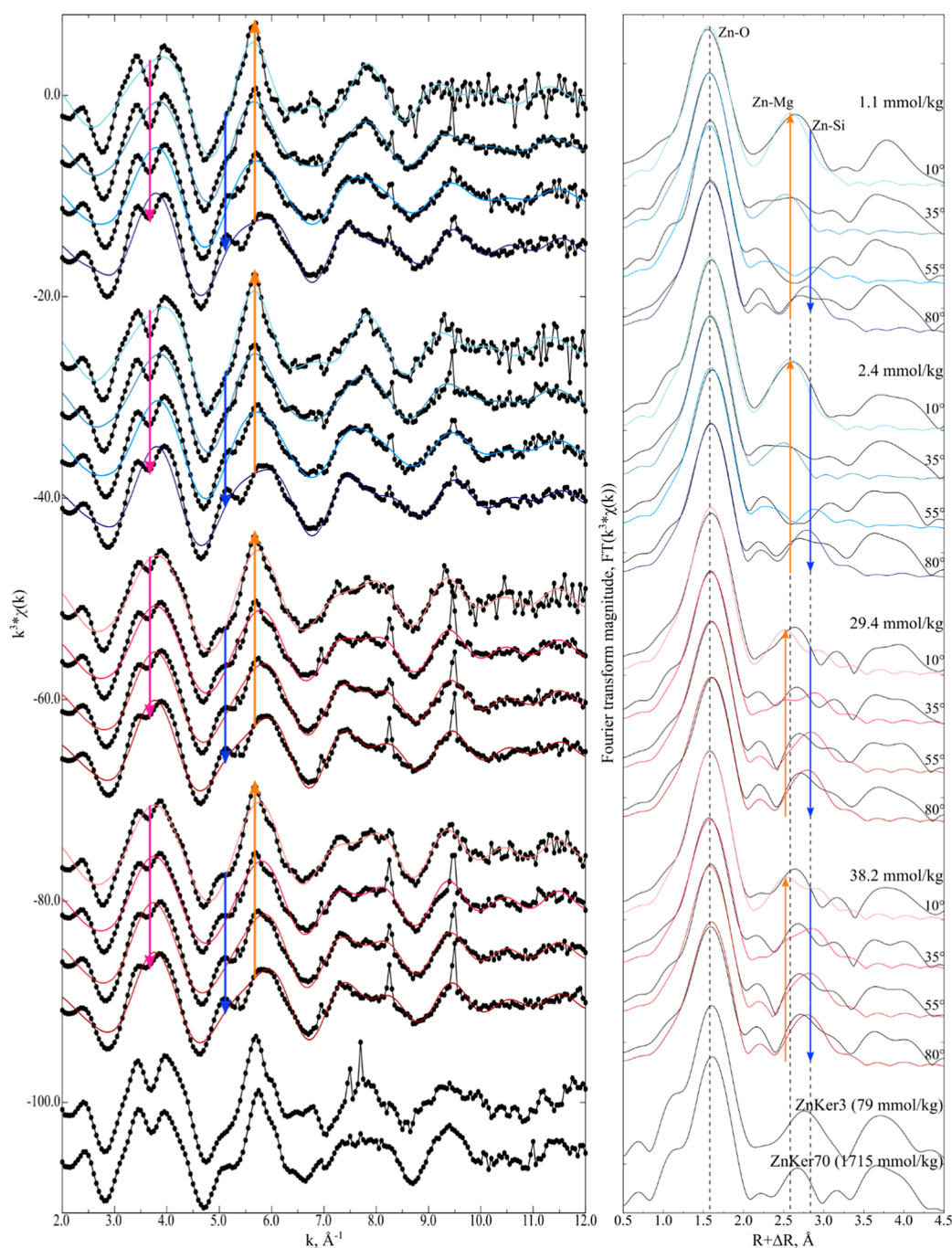


Figure 3. Polarized Zn K-edge EXAFS spectra of the four Zn-saponite sorption samples, grouped according to increasing Zn loading. Two Zn-kerolite reference spectra are shown at the bottom sorted in groups from top to bottom according to increasing Zn loading and reference Zn-kerolite samples.⁹³ k^3 -weighted $\chi(k)$ spectra are shown on the left; the corresponding magnitudes of Fourier-transformed $\chi(k)$ are shown on the right. Black dots connected with lines are the experimental data; blues and red lines are the shell fits (see Table 2). Shell fits of Zn-kerolite samples are marked in green. Shell fits were conducted in the Fourier transform space in the range from 1 to 3.25 Å and in the k -space from 2.0 to 10.5 Å⁻¹.

nonlinearity of the isotherm measured at pH value, where sorption becomes pH dependent (see Figure 2c), follows the expected concentration dependency and suggests the presence of at least two distinct sorption site types. Experimental data obtained at trace $[Zn_{\text{equil}}]$ are in good agreement with the Zn sorption edge data at the corresponding pH values, suggesting similarities in the mechanism of Zn uptake by montmorillonite and saponite. The capacity of the “strong” sites on saponite was fitted to the Zn isotherm and determined to be 5 mmol/kg, compared with 2 mmol/kg for montmorillonite. The

obtained sorption constants of Zn on saponite are comparable with those available for montmorillonite.

The pH edge data are fully accounted for by sorption on the high affinity sites. The model slightly underestimates the measured sorption at pH below 6 and overestimates the measurements between pH 8 and 9. The sorption isotherms have three distinct regions. At low loading ($[Zn_{\text{equil}}] < 10^{-6}$ M), the sorption equilibrium is fully accounted for by the capacity of “strong” sites. At higher Zn concentration in the equilibrium solution, the capacity of the “strong” sites is

Table 3. Coordination Numbers, Interatomic Distances, and Debye–Waller Factors (σ_T^2) for Zn–O, Zn–Mg, and Zn–Si Shells Derived from Atomistic Simulations^a

edge site	surface	shell	CN, N	$d(\text{Zn}) \pm 2\sigma, \text{\AA}$	$d(\text{Mg}) \pm 2\sigma, \text{\AA}$	$\sigma_T^2(\text{Zn}), 10^{-3} \text{\AA}^2$	$\sigma_T^2(\text{Mg}), 10^{-3} \text{\AA}^2$
incorporated ⁴⁹	-	Me–O	6.0	2.12 ± 0.02	2.09 ± 0.03	6.4	4.9
		Me–Mg	6.0	3.10 ± 0.05	3.11 ± 0.05	7.2	5.4
		Me–Si	4.0	3.27 ± 0.05	3.25 ± 0.05	6.6	5.1
S3 sites	(010)	Me–O	6.0	2.11 ± 0.08	2.09 ± 0.06	13.4	6.4
		Me–Mg	5.0	3.15 ± 0.13	3.12 ± 0.05	12.6	7.0
		Me–Si	4.0	3.23 ± 0.05	3.26 ± 0.03	15.3	7.0
	(110)	Me–O	6.0	2.11 ± 0.02	2.09 ± 0.05	9.3	6.8
		Me–Mg	5.0	3.12 ± 0.06	3.12 ± 0.06	8.5	7.1
		Me–Si	4.0	3.28 ± 0.05	3.27 ± 0.07	10.7	6.3
S2 sites	(010)	Me–O	6.0	2.07 ± 0.09	2.08 ± 0.01	25.8	14.5
		Me–Mg	3.0	3.15 ± 0.07	3.13 ± 0.04	17.4	10.8
		Me–Si	3.0	3.36 ± 0.10	3.36 ± 0.08	24.9	15.0
	(110)	Me–O	6.0	2.08 ± 0.06	2.10 ± 0.06	21.6	11.4
		Me–Mg	3.0	3.17 ± 0.12	3.14 ± 0.05	16.3	12.4
		Me–Si	3.0	3.36 ± 0.11	3.36 ± 0.05	21.9	12.4
S1-ES sites	(010)	Zn–O	6.0	2.08 ± 0.07	-	20.7	-
		Zn–Mg	1.0	3.19 ± 0.14	-	9.9	-
		Zn–Si	4.0	5.36 ± 0.11	-	146.0	-
	(110)	Zn–O	4.0	1.97 ± 0.08	-	6.2	-
		Zn–Mg	1.0	2.99 ± 0.13	-	8.2	-
		Zn–Si	3.0	4.65 ± 0.26	-	82.4	-
S1-CS sites	(010)	Zn–O	4.0	1.99 ± 0.03	-	7.8	-
		Zn–Mg	1.0	3.41 ± 0.13	-	13.2	-
		Zn–Si	1.0	4.69 ± 0.13	-	19.6	-
	(110)	Zn–O	4.0	1.96 ± 0.06	-	8.5	-
		Zn–Mg	1.0	3.46 ± 0.31	-	16.0	-
		Zn–Si	1.0	4.80 ± 0.30	-	37.1	-

^aThe shell radii reported in the table correspond to the position of maxima for Skewed Gaussian function fitted to the interatomic distance distribution. The uncertainty of the interatomic distances is reported within 95% ($\pm 2\sigma$) confidence interval calculated with respect to the mean interatomic distance as center of distribution.

exhausted and further uptake of the Zn by the saponite is accounted for by the “weak” sites. The cation exchange becomes relevant at equilibrium $[\text{Zn}_{\text{equil.}}] > 10^{-3} \text{ M}$.

Overall, the Zn sorption behavior on saponite can be adequately reproduced by a 2SPNE SC/CE model, considering two surface complexation sites and a cation-exchange site.

EXAFS Spectra Shell Fitting

The EXAFS spectra were collected for four samples, with Zn loadings carefully selected to represent the dominant signal from the two sorption sites suggested by the 2SPNE SC/CE model. According to the model in Figure 2, the Zn uptake in the 1.1 and 2.4 mmol/kg samples is predominantly controlled by sorption on the “strong” sites, whereas in the 29.4 and 38.2 mmol/kg samples, it is controlled by sorption on the “weak” sites. Results of shell fitting of the k^3 -weighted polarized EXAFS spectra are provided in Table 2 and Figure 3. All four measured spectra show polarization angle (α) dependency, namely, a decrease of the trough at 3.6 and shoulder intensity at $5.7 \text{ \AA}^{-1}$, and an increase of the shoulder intensity at $5.1 \text{ \AA}^{-1}$ with increasing polarization angle. Similarly, the Zn–Mg shell amplitude decreases, and the Zn–Si shell amplitude increases with the increase of polarization angle α in the Fourier transform magnitude (FTM) spectra. The described polarization angle dependency shows that Zn^{2+} uptake on the saponite happens on the octahedral sheet and follows the clay platelets orientation.

As expected,^{30,32,63} the Zn–O coordination numbers do not show significant dependency on the loading or polarization

angle. The spectra measured at the magic angle ($\alpha = 35^\circ$) correspond to the orientationally averaged bulk EXAFS signal. These spectra are used to derive the interatomic distances. The Zn–O and Zn–Si interatomic distances do not change with the loading, whereas the Zn–Mg interatomic distances gradually decrease with increasing loading (from 3.10 to 3.05 $\text{\AA}$). The Zn–Si coordination number increases from 1.3 at low loading to 3.3 at high loading. The obtained structural parameters at high loading are also well comparable with the data obtained for the Zn-doped saponite samples shown at the bottom of Table 2. The distances in high loading samples are very similar to the one in Zn-doped saponite.⁴⁹ A clear difference appears in the Zn–Mg coordination: the doped saponite shows a coordination number of ~ 5 , whereas the sorption sample shows only ~ 3 . The Zn–Si coordination number in the doped sample is slightly lower than that obtained for the high-loading sorption samples, although the large absolute uncertainty of the fitted values ($\pm 25\%$) limits direct comparison. The polarization dependence observed for the Zn–Mg shell indicates that sorbed Zn is located within or directly bound to the octahedral sheet of the saponite particles.

To further characterize the nature of Zn sorption complexes in saponite, EXAFS spectra and coordination environment are compared with Zn-doped kerolite samples synthesized as a reference material in a previous study.⁹³ “Zn-kerolite” refers to a poorly crystalline or even amorphous hydrous Zn–Mg-silicate phase with a talc-like local structure. The spectra obtained for Zn sorbed saponite closely resemble those of Zn-

kerolite (Figure 3). Specifically, the spectra of 29.4 and 38.2 mmol/kg samples match well that of kerolite with 25% Zn:Mg-substitution ratio. Due to poor crystallinity and destructive interference of Zn–Mg and Zn–Zn shells, Zn-kerolite does not display the typical EXAFS signatures of a well-ordered trioctahedral structure. Hence, an additional reference of Zn-doped saponite was synthesized with hydrothermal crystallization method.⁴⁹ Its structure resembles the structure of pure saponite, where approximately 2.5% of Mg atoms in the octahedral sheet were substituted by Zn. The structure of synthesized Zn-doped saponite was confirmed by XRD measurements and a satisfactory match of the theoretical EXAFS model with the experimental spectrum.

Interatomic Distances: Atomistic Simulations versus Spectroscopy

Interatomic distances and coordination numbers for Zn and Mg ions situated in the different structural positions at the edge surface of saponite particles (Figure 1) and their corresponding Debye–Waller factors are reported in Table 3. The Me–O distances are derived as the maximum of the pair distribution function smoothed with skewed Gaussians (Supporting Information Figures S9–S15), are in good agreement with the shell distances obtained by fitting experimental EXAFS data in Table 2. The strongly Mg coordinated coordination environment of S2 and S3 sites resemble the one of the surface-incorporated Zn. The local environment for surface S2 and S3 sites remained almost the same in the course of simulations due to structure rigidity of the TOT-framework. Furthermore, S2 and S3 complex geometries on (010) and (110) surfaces are nearly indistinguishable. Overall, simulation results systematically predict larger distances for the Zn–Mg and Zn–Si shells compared to the structural parameters derived from the shell fit of the experimental data (Table 2).

Contrarily, the coordination environment of the inner-sphere sorption sites (S1-ES/CS) is flexible and shows significant structural variations. The first coordination shell of this site has been fluctuating during the simulation, leading to spontaneous transitions between the bidentate edge-sharing complex (S1-ES) with an octahedral geometry and the corner-sharing monodentate complex (S1-CS) with a tetrahedral geometry. Structural parameters for the S1-ES and S1-CS sites deviate significantly from the S2 and S3 models. Notably, Zn–Si shells in the S1 sites show a noticeable expansion (up to 5.36 Å). However, Zn–O and Zn–Mg distances do not follow a uniform trend across all S1 sites. The Zn–O interatomic distances strongly correlate with the Zn–O coordination number, whereas the Zn–Mg distance controls the structural differentiation between the S1-ES and S1-CS sites. These variations underscore distinct coordination environments for (110) and (010) edge facets, particularly within the S1 sites.

In our previous study,⁴⁹ the ability of DFT calculations to reproduce the coordination environment of structurally incorporated Zn was clearly demonstrated. For the Zn sorption samples reported in this study, none of the simulated complexes matches the coordination environment derived from the experimental data, suggesting that Zn sorption is controlled by several surface complexes simultaneously coexisting in the samples.

EXAFS Linear Combination Fitting

A quantitative component analysis of EXAFS spectra as a function of loading was performed and independently validated

using two independent reference-based techniques. The first approach was based on a linear combination fit of experimental spectra using theoretical references obtained by molecular simulations. As an alternative approach, the Iterative Target Factor Analysis (ITFA) of the spectra was conducted using the reference spectrum of 1% Zn-doped kerolite.^{43,93} The results based on the atomistic simulations are discussed first.

Linear combination fitting of measured and simulated EXAFS spectra was performed with and without the consideration of monodentate complexes. Both fits provide equally good agreement with measured spectra (see Table S3 and Figure S1 in Supporting Information). Contributions of both S1-ES (bidentate) and S1-CS (monodentate) complexes strongly correlate with each other due to the structural similarity of both sites. Inclusion of monodentate species slightly reduces the Q-parameter but does not actually improve the quality of the fit as indicated by RMSD. This suggests a potential overfit. The XANES linear combination fit performed with experimental references (see Table S6 and Figure S4 in Supporting Information) suggests that the fraction of tetrahedrally coordinated Zn sorption complexes does not exceed 10% and, thus, negligible considering the XAFS experimental uncertainty. This is in line with the results of a previous Zn sorption study²⁰ suggesting a rather negligible impact of monodentate species on the EXAFS linear combination fit. For the sake of simplicity and considering the structural similarity of the complexes on (010) and (110) edges, the preferred model is described by the sum of S1-ES, S2, and S3 sites on (010) and (110) edges in Table 4. Full descriptions of all available individual components and separate fit with monodentate complexes are reported in the Supporting Information (see Table S3).

Table 4. Normalized Contributions of Different Structural Complexes to the Zn-Spectra Obtained at Different Loadings Obtained by Linear Combination Fitting in Range $k \in [2.5–12.5]$

	Zn ²⁺ loading, mmol/kg			
	1.1	2.4	29.4	38.2
ab initio spectral component				
total S1-ES, %	34.7	38.0	46.8	45.7
total S2, %	14.6	12.9	21.2	25.8
total S3, %	50.7	49.1	32.0	28.5
Q	0.99	0.93	0.91	1.03
RMSD	0.55	0.50	0.58	0.68
edge type (ab initio simulations)				
total (010), %	31	30	36	37
total (110), %	69	70	64	63
ITFA (experimental)				
Zn-Ker 1%(ZnKer3)	63	57	12	0
Zn sorbed	37	43	88	100

A very clear trend is observed as a function of the loading (see Figure 4). The contribution of S3 sites systematically decreases with the loading from 51 to 29%. The contribution of S2 and S1-ES systematically increases with the loading. Interestingly, the ratio of S2 and S1-ES appears to be nearly constant at all loading studied. It is worth stressing that due to the structural similarity of the sites, a qualitatively similar fit can be obtained using spectra of Zn-incorporated species instead Zn S3 sites. Overall, complexes on (110) and (010) edge surfaces appear to contribute 65% and 35% to the total

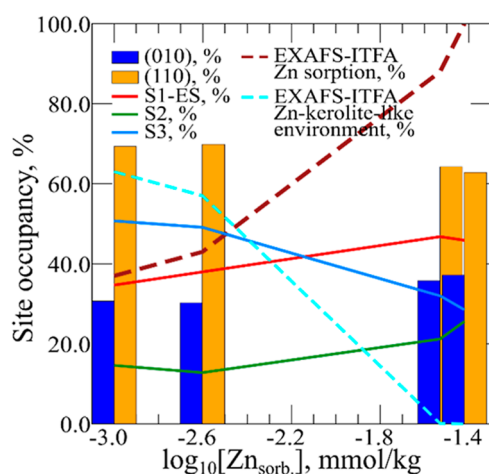


Figure 4. Relative surface (columns), surface complexes contributions derived from linear combination fits (lines), and EXAFS-ITFA quantitative speciation (dashed lines) of experimental EXAFS spectra. Linear combination fit was performed in $k \in [2.5-12.5]$. The EXAFS-ITFA quantitative Zn speciation was performed versus Zn-kerolite experimental reference provided by Schlegel et al.^{43,93}

spectra, respectively. The obtained surface ratio is in a close agreement with the first-principle surface morphology prediction reported in our previous work.⁴⁹

An alternative fit performed using the ITFA method and 1% Zn-doped kerolite^{43,93} reference indicate that experimental data can be described with two principal components. The kerolite-like component dominates at low loading and becomes negligible in the high loading samples, indicating strong correlations with the contributions of the strongly coordinated S2 and S3 sites. Consequently, at high loadings where S1-ES sites become more dominant, its presence vanishes. The high loading spectra are dominated by the sorption component. Based on these results, an alternative linear combination fits were performed by adding experimental reference spectra of ZnKer3, ZnKer70,^{43,93} and Zn-doped saponite⁴⁹ to the fit. These fits reduce the root-mean-square deviation but do not change principal conclusion about the site occupancy as a function of loading. The improvements, however, are mainly concentrated in a low k region from 3.0 to 4.5 Å⁻¹, where theoretical references struggle in reproducing trough. Therefore, the model with fewer parameters was preferred.

Solution Chemistry

Dissolved Zn, Mg, and Si concentrations were monitored by ICP-OES along the Zn sorption isotherm (Table 5). The data in Figure 5 illustrate the measured concentrations of Zn, Si,

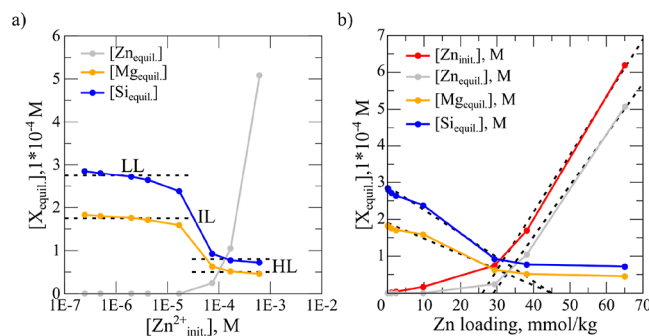


Figure 5. Solution chemistry monitoring showcasing $[Mg_{eq.}]$ and $[Si_{eq.}]$ uptake as a function of initial Zn concentration (a) and Zn loading on saponite edges (b). The data indicates 3 uptake domains: LL (low loading), where Zn uptake is unhindered by epitaxial phyllosilicate growth; IL (intermediate loading), where Mg and Si disappear from solution to form Zn–Mg phyllosilicate on the saponite edges; and HL (high loading), where Zn–Mg phyllosilicate growth slowly stops.

and Mg in the solution after 7 days of equilibration with saponite as a function of Zn loading; the baseline Mg and Si concentrations were defined by measurements at the lowest Zn loading. The $[Al_{eq.}]$, within uncertainty, remained constant across all loadings (below the ICP-OES detection limit of 2.22×10^{-7} M). For interpretation of the experimental data, it is useful to consider the sorption regions defined by the capacities of the $\equiv S^S$ and $\equiv S^{W1}$ sites. At Zn loadings below the capacity of the “strong” sites (~ 5 mmol/kg), the dissolved Si and Mg concentrations remain essentially constant and comparatively high (within the experimental variation). Once Zn loadings exceed the “strong” site capacity but remain below the capacity of the $\equiv S^{W1}$ sites (~ 40 mmol/kg), both Si and Mg concentrations decrease approximately linearly. At loadings beyond the $\equiv S^{W1}$ capacity, the available data indicate that Si and Mg concentrations begin to level off, although additional measurements in this range would be needed to confirm this trend. Below “strong” site capacity and above “weak” site capacity conditions, the aqueous Si/Mg ratio remains nearly constant at ~ 1.58 , slightly higher than the structural Si/Mg ratio of saponite (1.2–1.33 depending on Al content). In between, the Si/Mg ratio decreases to 1.48.

Table 5. ICP-OES Measurements

$[Zn_{sorb.}]$, mmol/kg	$[Zn_{eq.}]$, M	$[Zn_{init.}]$, M	$[Al_{eq.}]$, M	$[Mg_{eq.}]$, M	$[Si_{eq.}]$, M	$[Si_{eq.}]/([Mg_{eq.}] + [Zn_{eq.}])$	$[Si_{eq.}]/[Mg_{eq.}]$	at. per site, 1×10^{-3} N/nm ²	sorp. site occup., %
0.1	$<4.6 \times 10^{-8a}$	2.5×10^{-7}	4.4×10^{-7}	1.83×10^{-4}	2.85×10^{-4}	1.56	1.56	1.7	0.08
0.3	$<4.6 \times 10^{-8a}$	5.0×10^{-7}	4.3×10^{-7}	1.80×10^{-4}	2.80×10^{-4}	1.56	1.56	3.8	0.19
1.1 ^b	$<4.6 \times 10^{-8a}$	2.0×10^{-6}	5.2×10^{-7}	1.76×10^{-4}	2.72×10^{-4}	1.54	1.55	16.2	0.81
2.4 ^b	$<4.6 \times 10^{-8a}$	4.2×10^{-6}	3.7×10^{-7}	1.71×10^{-4}	2.64×10^{-4}	1.54	1.54	34.4	1.72
9.8	1.8×10^{-7}	1.7×10^{-5}	6.7×10^{-7}	1.59×10^{-4}	2.38×10^{-4}	1.50	1.50	139.2	6.96
29.4 ^b	2.5×10^{-5}	7.5×10^{-5}	$<2.2 \times 10^{-7}$	6.27×10^{-5}	9.25×10^{-5}	1.06	1.47	416.9	20.84
38.2 ^b	1.1×10^{-4}	1.7×10^{-4}	$<2.2 \times 10^{-7}$	5.15×10^{-5}	7.74×10^{-5}	0.50	1.50	541.7	27.08
65.1	5.1×10^{-4}	6.2×10^{-4}	$<2.2 \times 10^{-7}$	4.56×10^{-5}	7.20×10^{-5}	0.13	1.58	922.7	46.14

^aRegion with high uncertainty due to the ICP-OES detection limit. ^bEXAFS samples.

The constant Si/Mg ratio across all loading conditions indicates that the dissolved Si and Mg concentrations are controlled by a single solid phase. The simultaneous decrease of Si and Mg concentrations within the loading range corresponding to occupation of $\equiv S^{WI}$ sites with increasing dissolved Zn concentrations is consistent with the formation of a Zn–Mg saponite solid solution. Aqueous Zn concentrations near the “strong” site range approach the ICP-OES detection limit ($\sim 3.4 \times 10^{-8}$ M) and are therefore not fully reliable. A solid solution would have a solubility product lower than that of pure saponite, explaining both the decreased Si and Mg concentrations and the preserved Si/Mg ratio. As mentioned before, precipitation of a separate Zn-bearing solid can be ruled out, as this would produce a sharp drop in dissolved Zn followed by a concentration fixed by the solubility of the precipitate. Such a behavior is not observed in the experimental data.

The difference in dissolved Si and Mg concentrations between the high- and low-loading regimes allows an estimate of the amount of Zn–Mg saponite formed. By assuming a saponite stoichiometry of 1.33, approximately 4.4×10^{-5} moles saponite form in the 38.2 mmol/kg sample (Si:113.2 and Mg:70.9 mmol/kg, respectively). Considering these values together with the $\equiv S^{WI}$ site capacity (40 mmol/kg), the calculated stoichiometry of the formed Zn–Mg silicate is close to that of saponite. According to the sorption model, the Zn concentration range over which Si and Mg couptake occurs and corresponds to the occupation of $\equiv S^{WI}$ sites. This suggests that Zn associated with $\equiv S^S$ sites is accompanied by couptake of Si and Mg, consistent with the epitaxial (P-EXAFS dependency) formation of a thin (Zn–Mg) saponite solid solution layer along the Mg octahedral sheet. AFM data indicate that the combined uptake of Zn and Mg does not exceed the capacity of a single octahedral monolayer, which may correspond to the crystallographic distinction between the S2 and S3 sites.

At higher Zn loadings, where dissolved Si and Mg remain constant, further Zn uptake occurs without an additional Si/Mg release. This transition indicates a shift to simple sorption of mononuclear Zn complexes or to cation-exchange processes rather than continued incorporation into a Zn–Mg silicate phase.

Mechanistic Interpretation of the Sorption Process

To consolidate the interpretation of Zn sorption on saponite, the key experimental observations are summarized below for convenience:

- The sorption behavior of Zn on saponite follows the characteristic pattern observed for divalent cations on montmorillonite. Both experimental data sets are well described by the 2SPNE SC/CE model, which combines two surface-complexation reactions, one high-affinity, low-capacity site and one low-affinity, high-capacity site, together with a cation-exchange component. It should be noted that thermodynamic sorption models such as 2SPNE SC/CE treat sorption as a reversible, mass-conserving reaction between aqueous species and predefined surface sites; they assume no net mineral dissolution or precipitation, a constant number of reactive sites, and full reversibility of the surface reactions.
- However, the solution chemistry data clearly show that Si and Mg are removed from solution in a constant

stoichiometric ratio in agreement with saponite at higher Zn concentrations, demonstrating a net mass increase of the solid phase and suggesting the formation of a saponite-like phase at the loading range associated with the low-affinity sites region ($\equiv S^{WI}$).

- Polarization-dependent EXAFS analysis confirms that sorbed Zn is located within, or directly bound to, the octahedral sheet of saponite particles. The EXAFS analysis of Zn samples under various conditions on the sorption isotherm indicates clear structural trends as a function of loading, which are consistent with the analysis of solution chemistry. Comparison of EXAFS spectra with reference materials reveals distinct structural trends. At low loading, the Zn samples resemble the structural environment of Zn-doped kerolite, suggesting partial structural incorporation of Zn into octahedral edges. At higher loadings, Zn–Mg phyllosilicate epitaxial growth leads to slight Zn–Si coordination increase, whereas the dominance of weakly bound sorption species at this loading leads to slight (within uncertainty) Zn–Mg coordination decrease.
- Interatomic distances and coordination numbers for Zn at different structural positions on saponite edge surfaces were derived from atomistic simulations and compared with EXAFS fits. Strongly coordinated S2 and S3 sites resemble surface-incorporated Zn and remain structurally invariant during the simulations, reflecting the stability of the TOT framework. In contrast, weakly coordinated inner-sphere sites (S1-ES/S1-CS) exhibit significant flexibility, with spontaneous transitions between bidentate edge-sharing octahedral complexes (S1-ES) and monodentate tetrahedral complexes (S1-CS). Clear structural differences also emerge between complexes on (110) and (010) facets. Overall, neither of individual simulated configurations fully matches the experimental EXAFS analysis, suggesting that Zn sorption is not controlled by a single configuration but rather by a mixture of surface complexes.
- Linear combination fits of EXAFS spectra using theoretical reference spectra confirm consistent trends: S3 site contributions decrease with loading, while S2 and S1-ES contributions increase. The ratio of S2 to S1-ES remains nearly constant across loadings. ITFA identifies two principal components: a kerolite-like component, dominating at low loading and vanishing at high, and sorption component increasing at high loading. Contribution of kerolite-like environment correlates with fraction of strongly coordinated S3 sites, whereas flexible S1-ES sites and less rigid strongly coordinated S2 sites prevail at high loadings.

The combined evidence from thermodynamic modeling, solution chemistry, EXAFS spectroscopy, and atomistic simulations reveals two distinct sorption regimes:

At low loadings ($\equiv S^S$ sites), Zn occupies octahedral positions that resemble structural S3-like sites, as shown by the polarization dependence in EXAFS. These sites are structurally similar to Zn-doped kerolite, indicating partial Zn incorporation into the saponite framework. A dissolution–recrystallization process at edge surfaces is possible, but there is no direct confirmation because the dissolved Si and Mg remain constant.

At high loadings ($\equiv S^{WI}$ sites), Zn uptake is accompanied by the stoichiometric removal of Si and Mg from solution, demonstrating a shift in mechanism. Structural data indicate two parallel processes. One is an inner-sphere complexation at edge sites ($S1-ES$ and $S2$), which binds Zn strongly without full incorporation into the TOT layers. The other is surface-driven growth of Zn–Mg silicate phases that are structurally indistinguishable from $S3$ sites or Zn-doped saponite. Mass-balance considerations show that this film is only a few atomic layers thick. In this regime, solution chemistry provides the clearest evidence of the process, while EXAFS and simulations define only the minor structural changes in the resulting complexes combination.

Free energy calculations for geometry optimized structures confirm a slight energetic preference for Zn structural incorporation over surface adsorption (see Table 6). The

Table 6. Thermodynamic Integration Results of DFT Geometry Optimization for Zn^{2+}

$Zn_{saponite} + \equiv S_{S3}OMg^+ \rightleftharpoons \equiv S_{S3}OZn^+ + Mg_{saponite}$		
surface	ΔA , kJ/mol	pK
(010)	2.19	0.38
(110)	2.80	0.49
$Zn_{saponite} + \equiv S_{S2}OMg^+ \rightleftharpoons \equiv S_{S2}OZn^+ + Mg_{saponite}$		
(010)	8.40	1.46
(110)	6.81	1.19
$Zn_{saponite} + \equiv S_{S1-ES}OMg^+ \rightleftharpoons \equiv S_{S1-ES}OZn^+ + Mg_{saponite}$		
(010)	13.64	2.37
(110)	14.69	2.56

lower ΔA values (≈ 2 and 3 kJ/mol) for $S3$ sites, on the other hand, indicate that incorporation is favored at trace concentrations over the conventional inner-sphere sorption (ΔA values ≈ 13 – 15 kJ/mol). Thus, under conditions of very long reaction time sufficient for complete recrystallization of clay particles, Zn would be entirely incorporated into the saponite structure. However, given the time-scale of the sorption experiment, only a few atomic layers of the edge surface can effectively participate in the re-equilibration process. These thermodynamic and kinetic constraints explain why Zn uptake at low loading can be described through surface incorporation, while at higher loading, kinetic and solubility constraints favor surface growth.

CONCLUSIONS

This study integrates sorption experiments, solution chemistry, spectroscopy, molecular simulations, and thermodynamic modeling. No single approach can resolve the multistage Zn uptake mechanism; only their combined use clarifies how Zn interacts with saponite across the full loading range and allows the model assumptions to be evaluated. The combined techniques also revealed epitaxial Zn–Mg phyllosilicate growth that would not be identified from sorption experiments or thermodynamic modeling data alone.

The 2SPNE SC/CE model reproduces the uptake data well. The strongest sites host tightly bound edge complexes resembling partial surface incorporation. The uptake assigned to $\equiv S^{WI}$ is, however, explained by weaker inner-sphere edge complexes together with limited Zn–Mg phyllosilicate growth. At the highest concentrations, once Si and Mg concentrations stabilize, uptake behavior shifts toward standard cation exchange. EXAFS and atomistic calculations confirmed that

Zn sorption occurs predominantly on three structurally distinct complexes on the saponite surface and that additionally a small neoformation pathway contributes at higher loadings, consistent with the depletion of Si and Mg. The structure of this neoformed Zn–Mg phyllosilicate is, however, practically undistinguishable from simulated strongly bound surface complexes or Zn-doped saponite.

The model captured the overall uptake trend but cannot fully separate sorption from nonsorption processes. Because the model treats the neoformation contribution as sorption, it slightly overestimates sorption at high loadings and compensates it by assigning higher stabilities to the fitted surface complexes on the “weak” sites. Despite these limitations, the model remained robust: although developed for pure sorption on dioctahedral montmorillonite, it described Zn uptake on a trioctahedral clay reasonably well.

Overall, the results showed that macroscopic sorption models need to be evaluated alongside structural evidence. Reliable interpretation required accounting for the dominant structural pathway in each loading regime, particularly in cases in which minor growth processes began to influence uptake.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.5c08267>.

Implementation of the 2SPNE SC/CE sorption model for synthetic saponite in GEM-Selektor; the procedure for model parameters optimization, uncertainty estimation, and its propagation for R_d uncertainty evaluation; alternative linear combination fits of EXAFS spectra; thermodynamic integration results of DFT geometry optimization for Zn^{2+} ; interparticle water density distribution profile; and Zn–Mg and Mg–Mg radial pair distribution functions (PDF)

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Notes

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REFERENCES

- (1) Bergaya, F.; Lagaly, G. Chapter 1 General Introduction: Clays, Clay Minerals, and Clay Science. In *Developments in Clay Science*; Bergaya, F., Theng, B. K. G., Lagaly, G., Eds.; Elsevier, 2006; Vol. 1, pp 1–18.
- (2) Xu, Y.; Liang, X.; Xu, Y.; Qin, X.; Huang, Q.; Wang, L.; Sun, Y. Remediation of Heavy Metal-Polluted Agricultural Soils Using Clay Minerals: A Review. *Pedosphere* **2017**, 27 (2), 193–204.
- (3) Zhu, R.; Chen, Q.; Zhou, Q.; Xi, Y.; Zhu, J.; He, H. Adsorbents Based on Montmorillonite for Contaminant Removal from Water: A Review. *Appl. Clay Sci.* **2016**, 123, 239–258.
- (4) Yuan, G. D.; Theng, B. K. G.; Churchman, G. J.; Gates, W. P. Chapter 5.1 - Clays and Clay Minerals for Pollution Control. In *Handbook of Clay Science*; Bergaya, F., Lagaly, G., Eds.; Elsevier, 2013; Vol. 5, pp 587–644.
- (5) Gu, C.; Li, H.; Teppen, B. J.; Boyd, S. A. Octachlorodibenzo-dioxin Formation on Fe(III)-Montmorillonite Clay. *Environ. Sci. Technol.* **2008**, 42 (13), 4758–4763.
- (6) Voudrias, E. A. The Concept of a Sorption Chemical Barrier for Improving Effectiveness of Landfill Liners. *Waste Manag. Res.* **2002**, 20 (3), 251–258.
- (7) Wagner, J.-F. Chapter 5.3 - Clay Liners and Waste Disposal. In *Handbook of Clay Science*; Bergaya, F., Lagaly, G., Eds.; Elsevier, 2013; Vol. 5, pp 663–676.
- (8) Hummel, W.; Schneider, J. W. Safety of Nuclear Waste Repositories. *Chimia* **2005**, 59 (12), 909.
- (9) Baeyens, B.; Marques Fernandes, M. Adsorption of Heavy Metals Including Radionuclides. In *Developments in Clay Science*; Elsevier Ltd., 2018; Vol. 9, pp 125–172.
- (10) Johnson, L.; Schneider, J.; Zuidema, P.; Gribi, P.; Mayer, G.; Smith, P.; Kunz, B.; Frei, C. *Project Opalinus Clay Safety Report. Demonstration of Disposal Feasibility for Spent Fuel, Vitrified High-Level Waste and Long-Lived Intermediate-Level Waste (Entsorgungsnachweis)*; NTB; Technical Report 02–05, 2002.
- (11) Churakov, S. V.; Hummel, W.; Fernandes, M. M. Fundamental Research on Radiochemistry of Geological Nuclear Waste Disposal. *Chim. Int. J. Chem.* **2022**, 74 (12), 1000–1009.
- (12) Hiemstra, T.; Van Riemsdijk, W. H. A Surface Structural Approach to Ion Adsorption: The Charge Distribution (CD) Model. *J. Colloid Interface Sci.* **1996**, 179 (2), 488–508.
- (13) Mathur, S. S.; Dzombak, D. A. Chapter 16 - Surface Complexation Modeling: Goethite. In *Interface Science and Technology*; Lützenkirchen, J., Ed.; Elsevier, 2006; Vol. 11, pp 443–468.
- (14) Tournassat, C.; Chapron, Y.; Leroy, P.; Bizi, M.; Boulahya, F. Comparison of Molecular Dynamics Simulations with Triple Layer and Modified Gouy–Chapman Models in a 0.1 M NaCl–Montmorillonite System. *J. Colloid Interface Sci.* **2009**, 339 (2), 533–541.
- (15) Bradbury, M. H.; Baeyens, B. A Mechanistic Description of Ni and Zn Sorption on Na-Montmorillonite Part II: Modelling. *J. Contam. Hydrol.* **1997**, 27 (3), 223–248.
- (16) Baeyens, B.; Bradbury, M. H. A Mechanistic Description of Ni and Zn Sorption on Na-Montmorillonite Part I: Titration and Sorption Measurements. *J. Contam. Hydrol.* **1997**, 27 (3), 199–222.
- (17) Bradbury, M. H.; Baeyens, B. Modelling the Sorption of Mn(II), Co(II), Ni(II), Zn(II), Cd(II), Eu(III), Am(III), Sn(IV), Th(IV), Np(V) and U(VI) on Montmorillonite: Linear Free Energy Relationships and Estimates of Surface Binding Constants for Some Selected Heavy Metals and Actinides. *Geochim. Cosmochim. Acta* **2005**, 69 (4), 875–892.
- (18) Bradbury, M. H.; Baeyens, B. Predictive Sorption Modelling of Ni(II), Co(II), Eu(III), Th(IV) and U(VI) on MX-80 Bentonite and Opalinus Clay: A “Bottom-up” Approach. *Appl. Clay Sci.* **2011**, 52 (1), 27–33.
- (19) Dähn, R.; Baeyens, B.; Bradbury, M. H. Investigation of the Different Binding Edge Sites for Zn on Montmorillonite Using P-EXAFS – The Strong/Weak Site Concept in the 2SPNE SC/CE Sorption Model. *Geochim. Cosmochim. Acta* **2011**, 75 (18), 5154–5168.
- (20) Churakov, S. V.; Dähn, R. Zinc Adsorption on Clays Inferred from Atomistic Simulations and EXAFS Spectroscopy. *Environ. Sci. Technol.* **2012**, 46 (11), 5713–5719.
- (21) Kéri, A.; Dähn, R.; Marques Fernandes, M.; Scheinost, A. C.; Krack, M.; Churakov, S. V. Iron Adsorption on Clays Inferred from Atomistic Simulations and X-Ray Absorption Spectroscopy. *Environ. Sci. Technol.* **2020**, 54 (19), 11886–11893.
- (22) Kéri, A.; Dähn, R.; Krack, M.; Churakov, S. V. Combined XAFS Spectroscopy and Ab Initio Study on the Characterization of Iron Incorporation by Montmorillonite. *Environ. Sci. Technol.* **2017**, 51 (18), 10585–10594.
- (23) Kéri, A.; Dähn, R.; Krack, M.; Churakov, S. V. Characterization of Structural Iron in Smectites—An Ab Initio Based X-Ray Absorption Spectroscopy Study. *Environ. Sci. Technol.* **2019**, 53 (12), 6877–6886.
- (24) Soltermann, D.; Marques Fernandes, M.; Baeyens, B.; Miehé-Brendlé, J.; Dähn, R. Competitive Fe(II)–Zn(II) Uptake on a Synthetic Montmorillonite. *Environ. Sci. Technol.* **2014**, 48 (1), 190–198.
- (25) Fernandes, M. M.; Scheinost, A. C.; Baeyens, B. Sorption of Trivalent Lanthanides and Actinides onto Montmorillonite: Macroscopic, Thermodynamic and Structural Evidence for Ternary Hydroxo and Carbonato Surface Complexes on Multiple Sorption Sites. *Water Res.* **2016**, 99, 74–82.
- (26) Schlegel, M. Polarized EXAFS Characterization of the Sorption Mechanism of Yttrium on Hectorite. *Radiochim. Acta* **2008**, 96 (9–11), 667–672.
- (27) Finck, N.; Dardenne, K.; Geckeis, H. Am(III) Coprecipitation with and Adsorption on the Smectite Hectorite. *Chem. Geol.* **2015**, 409, 12–19.
- (28) Finck, N.; Schlegel, M. L.; Bosbach, D. Sites of Lu(III) Sorbed to and Coprecipitated with Hectorite. *Environ. Sci. Technol.* **2009**, 43 (23), 8807–8812.
- (29) Finck, N.; Bouby, M.; Dardenne, K.; Geckeis, H. Characterization of Eu(III) Co-Precipitated with and Adsorbed on Hectorite: From Macroscopic Crystallites to Nanoparticles. *Mineral. Mag.* **2012**, 76 (7), 2723–2740.

- (30) Schlegel, M. L.; Manceau, A.; Chateigner, D.; Charlet, L. Sorption of Metal Ions on Clay Minerals: I. Polarized EXAFS Evidence for the Adsorption of Co on the Edges of Hectorite Particles. *J. Colloid Interface Sci.* **1999**, *215* (1), 140–158.
- (31) Dähn, R.; Scheidegger, A. M.; Manceau, A.; Curti, E.; Baeyens, B.; Bradbury, M. H.; Chateigner, D. Th Uptake on Montmorillonite: A Powder and Polarized Extended X-Ray Absorption Fine Structure (EXAFS) Study. *J. Colloid Interface Sci.* **2002**, *249* (1), 8–21.
- (32) Dähn, R.; Scheidegger, A. M.; Manceau, A.; Schlegel, M. L.; Baeyens, B.; Bradbury, M. H.; Chateigner, D. Structural Evidence for the Sorption of Ni(II) Atoms on the Edges of Montmorillonite Clay Minerals: A Polarized X-Ray Absorption Fine Structure Study. *Geochim. Cosmochim. Acta* **2003**, *67* (1), 1–15.
- (33) Fernandes, M. M.; Vér, N.; Baeyens, B. Predicting the Uptake of Cs, Co, Ni, Eu, Th and U on Argillaceous Rocks Using Sorption Models for Illite. *Appl. Geochem.* **2015**, *59*, 189–199.
- (34) Payne, T. E.; Brendler, V.; Ochs, M.; Baeyens, B.; Brown, P. L.; Davis, J. A.; Ekberg, C.; Kulik, D. A.; Lutzenkirchen, J.; Missana, T.; Tachi, Y.; Van Loon, L. R.; Altmann, S. Guidelines for Thermodynamic Sorption Modelling in the Context of Radioactive Waste Disposal. *Environ. Model. Softw.* **2013**, *42*, 143–156.
- (35) Fernandes, M. M.; Marinich, O.; Miron, G. D.; Baeyens, B. Sorption of Cs, Ni, Eu, Th and U on Drill Core Samples of Opalinus Clay and Confining Geological Units from Deep Boreholes in the Potential Siting Regions Nördlich Lägern, Zürich Nordost and Jura Ost: Measurements and Predictive Sorption Modelling; NTB; Technical Report 23–01; Nagra, 2024.
- (36) Dähn, R.; Baeyens, B.; Fernandes, M. M. Zn Uptake by Illite and Argillaceous Rocks. *Geochim. Cosmochim. Acta* **2021**, *312*, 180–193.
- (37) Bradbury, M. H.; Baeyens, B. Experimental Measurements and Modeling of Sorption Competition on Montmorillonite. *Geochim. Cosmochim. Acta* **2005**, *69* (17), 4187–4197.
- (38) Orucoglu, E.; Grangeon, S.; Gloter, A.; Robinet, J.-C.; Madé, B.; Tournassat, C. Competitive Adsorption Processes at Clay Mineral Surfaces: A Coupled Experimental and Modeling Approach. *ACS Earth Space Chem.* **2022**, *6* (1), 144–159.
- (39) Tournassat, C.; Grangeon, S.; Leroy, P.; Giffaut, E. Modeling Specific pH Dependent Sorption of Divalent Metals on Montmorillonite Surfaces. A Review of Pitfalls, Recent Achievements and Current Challenges. *Am. J. Sci.* **2013**, *313* (5), 395–451.
- (40) Marques Fernandes, M.; Baeyens, B. *Competitive Adsorption on Illite and Montmorillonite: Experimental and Modelling Investigations*; NTB; Technical Report 19–05, 2020.
- (41) Fernandes, M. M.; Baeyens, B. Cation Exchange and Surface Complexation of Lead on Montmorillonite and Illite Including Competitive Adsorption Effects. *Appl. Geochem.* **2019**, *100*, 190–202.
- (42) Schlegel, M. L.; Manceau, A.; Charlet, L.; Chateigner, D.; Hazemann, J.-L. Sorption of Metal Ions on Clay Minerals. III. Nucleation and Epitaxial Growth of Zn Phyllosilicate on the Edges of Hectorite. *Geochim. Cosmochim. Acta* **2001**, *65* (22), 4155–4170.
- (43) Schlegel, M. L.; Manceau, A.; Charlet, L.; Hazemann, J. Adsorption Mechanisms of Zn on Hectorite as a Function of Time, pH, and Ionic Strength. *Am. J. Sci.* **2001**, *301* (9), 798–830.
- (44) Kaufhold, S.; Dohrmann, R.; Ufer, K. Interaction of Magnesium Cations with Dioctahedral Smectites under HLRW Repository Conditions. *Clays Clay Miner.* **2016**, *64* (6), 743–752.
- (45) Manceau, A.; Bonnin, D.; Stone, W. E. E.; Sanz, J. Distribution of Fe in the Octahedral Sheet of Trioctahedral Micas by Polarized EXAFS. *Phys. Chem. Miner.* **1990**, *17* (4), 363–370.
- (46) Petit, S.; Righi, D.; Decarreau, A. Transformation of Synthetic Zn-Stevensite to Zn-Talc Induced by the Hofmann-Klemen Effect. *Clays Clay Miner.* **2008**, *56* (6), 645–654.
- (47) Ferrage, E.; Lanson, B.; Michot, L. J.; Robert, J.-L. Hydration Properties and Interlayer Organization of Water and Ions in Synthetic Na-Smectite with Tetrahedral Layer Charge. Part 1. Results from X-Ray Diffraction Profile Modeling. *J. Phys. Chem. C* **2010**, *114* (10), 4515–4526.
- (48) Di Lorenzo, F.; Stotskyi, V.; Scheinost, A. C.; Rossberg, A.; Lanson, M.; Lanson, B.; Churakov, S. V.; Fernandes, M. M. Ni Retention Mechanisms by Trioctahedral Smectite (Saponite) Investigated by Polarized x-Ray Absorption Spectroscopy and Implications for Surface Complexation Modelling. In Preparation **2026**.
- (49) Stotskyi, V.; Di Lorenzo, F.; Marques Fernandes, M.; Krack, M.; Scheinost, A. C.; Lanson, M.; Lanson, B.; Churakov, S. V. Local Crystal Structure of Ni²⁺- and Zn²⁺-Doped Saponite Determined by EXAFS Spectroscopy and Ab Initio MD Modeling. *J. Phys. Chem. C* **2025**, *129* (30), 13691–13704.
- (50) Hamilton, D. L.; Henderson, C. M. B. The Preparation of Silicate Compositions by a Gelling Method. *Mineral. Mag. J. Mineral. Soc.* **1968**, *36* (282), 832–838.
- (51) Bergaoui, L.; Lambert, J.-F.; Franck, R.; Suquet, H.; Robert, J.-L. Al-Pillared Saponites. Part 3.—Effect of Parent Clay Layer Charge on the Intercalation—Pillaring Mechanism and Structural Properties. *J. Chem. Soc. Faraday Trans* **1995**, *91* (14), 2229–2239.
- (52) Szczerba, M.; Kalinichev, A. G. Intercalation of Ethylene Glycol in Smectites: Several Molecular Simulation Models Verified by X-Ray Diffraction Data. *Clays Clay Miner.* **2016**, *64* (4), 488–502.
- (53) Morida, K.; Fukushi, K.; Sakuma, H.; Tamura, K. Systematic Comparison of the Hydration and Dehydration of Na⁺, K⁺, and NH₄⁺-Saturated Montmorillonite, Nontronite, Hectorite, Saponite, and Fe-Saponite by in Situ X-Ray Diffraction Measurements. *Appl. Clay Sci.* **2023**, *237*, 106898.
- (54) Baeyens, B.; Bradbury, M. H. Cation Exchange Capacity Measurements on Illite Using the Sodium and Cesium Isotope Dilution Technique: Effects of the Index Cation, Electrolyte Concentration and Competition: Modeling. *Clays Clay Miner.* **2004**, *52* (4), 421–431.
- (55) Marinich, O.; Miron, G. D.; Kulik, D. A.; Fernandes, M. M.; Baeyens, B. ClaySor 2023: Implementation of the 2SPNE SC/CE Sorption Model and Database for Deep Geological Repository Safety Assessment. *Appl. Geochem.* **2025**, *191*, 106510.
- (56) Kulik, D. A.; Wagner, T.; Dmytrieva, S. V.; Kosakowski, G.; Hingerl, F. F.; Chudnenko, K. V.; Berner, U. R. GEM-Selektor Geochemical Modeling Package: Revised Algorithm and GEMS3K Numerical Kernel for Coupled Simulation Codes. *Comput. Geosci.* **2012**, *17* (1), 1–24.
- (57) Wagner, T.; Kulik, D. A.; Hingerl, F. F.; Dmytrieva, S. V. Geochemical Modeling Package: TSolMod Library and Data Interface for Multicomponent Phase Models. *Can. Mineral.* **2012**, *50*, 1173–1195.
- (58) Kulik, D. A.; Fernandes, M. M.; Baeyens, B. The 2SPNE SC/CE Sorption Model in GEM-Selektor v.3.4 Code Package (ClaySor): Implementation, Tests, and User Guide. *Nagra Work Rep. NAB* **2018**, *18–27*, 152.
- (59) Thoenen, T.; Hummel, W.; Berner, U.; Curti, E. *The PSI/Nagra Chemical Thermodynamic Database 12/07*; PSI, 2014.
- (60) Miron, G. D.; Kulik, D. A.; Dmytrieva, S. V.; Wagner, T. GEMSfits: Code Package for Optimization of Geochemical Model Parameters and Inverse Modeling. *Appl. Geochem.* **2015**, *55*, 28–45.
- (61) Scheinost, A. C.; Claussner, J.; Exner, J.; Feig, M.; Findeisen, S.; Hennig, C.; Kvashnina, K. O.; Naudet, D.; Prieur, D.; Rossberg, A.; Schmidt, M.; Qiu, C.; Colomp, P.; Cohen, C.; Dettona, E.; Dyadkin, V.; Stumpf, T. ROBL-II at ESRF: A Synchrotron Toolbox for Actinide Research. *J. Synchrotron Radiat.* **2021**, *28* (1), 333–349.
- (62) Dähn, R.; Scheidegger, A.; Manceau, A.; Schlegel, M.; Baeyens, B.; Bradbury, M. H. Ni Clay Neof ormation on Montmorillonite Surface. *J. Synchrotron Radiat.* **2001**, *8* (2), 533–535.
- (63) Manceau, A.; Chateigner, D.; Gates, W. P. Polarized EXAFS, Distance-Valence Least-Squares Modeling (DVLS), and Quantitative Texture Analysis Approaches to the Structural Refinement of Garfield Nontronite. *Phys. Chem. Miner.* **1998**, *25* (5), 347–365.
- (64) Webb, S. M. SIXpack: A Graphical User Interface for XAS Analysis Using IFEFFIT. *Phys. Scr.* **2005**, *2005* (T115), 1011.

- (65) Ressler, T. WinXAS: A Program for X-Ray Absorption Spectroscopy Data Analysis under MS-Windows. *J. Synchrotron Radiat.* **1998**, *5* (2), 118–122.
- (66) Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: Data Analysis for X-Ray Absorption Spectroscopy Using IFEFFIT. *J. Synchrotron Radiat.* **2005**, *12* (4), 537–541.
- (67) Ankudinov, A. L.; Ravel, B.; Rehr, J. J.; Conradson, S. D. Real-Space Multiple-Scattering Calculation and Interpretation of x-Ray-Absorption near-Edge Structure. *Phys. Rev. B* **1998**, *58* (12), 7565–7576.
- (68) Ankudinov, A. L.; Nesvizhskii, A. I.; Rehr, J. J. Dynamic Screening Effects in X-Ray Absorption Spectra. *Phys. Rev. B* **2003**, *67* (11), 115120.
- (69) Rehr, J. J.; Kas, J. J.; Vila, F. D.; Prange, M. P.; Jorissen, K. Parameter-Free Calculations of X-Ray Spectra with FEFF9. *Phys. Chem. Chem. Phys.* **2010**, *12* (21), 5503–5513.
- (70) Gruner, J. W. The Crystal Structures of Talc and Pyrophyllite. *Z. Für Krist. - Cryst. Mater.* **1934**, *88* (1–6), 412–419.
- (71) Perdikatsis, B.; Burzlaff, H. Strukturverfeinerung Am Talk $\text{Mg}_3[(\text{OH})_2\text{Si}_4\text{O}_{10}]$. *Z. Für Krist. - Cryst. Mater.* **1981**, *156* (1–4), 177–186.
- (72) Cygan, R. T.; Liang, J.-J.; Kalinichev, A. G. Molecular Models of Hydroxide, Oxyhydroxide, and Clay Phases and the Development of a General Force Field. *J. Phys. Chem. B* **2004**, *108* (4), 1255–1266.
- (73) Thompson, A. P.; Aktulga, H. M.; Berger, R.; Bolintineanu, D. S.; Brown, W. M.; Crozier, P. S.; in 't Veld, P. J.; Kohlmeyer, A.; Moore, S. G.; Nguyen, T. D.; Shan, R.; Stevens, M. J.; Tranchida, J.; Trott, C.; Plimpton, S. J. LAMMPS - a Flexible Simulation Tool for Particle-Based Materials Modeling at the Atomic, Meso, and Continuum Scales. *Comput. Phys. Commun.* **2022**, *271*, 108171.
- (74) VandeVondele, J.; Krack, M.; Mohamed, F.; Parrinello, M.; Chassaing, T.; Hutter, J. Quickstep: Fast and Accurate Density Functional Calculations Using a Mixed Gaussian and Plane Waves Approach. *Comput. Phys. Commun.* **2005**, *167* (2), 103–128.
- (75) Hutter, J.; Iannuzzi, M.; Schiffmann, F.; VandeVondele, J. Cp2k: Atomistic Simulations of Condensed Matter Systems. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2014**, *4* (1), 15–25.
- (76) Kühne, T. D.; Iannuzzi, M.; Del Ben, M.; Rybkin, V. V.; Seewald, P.; Stein, F.; Laino, T.; Khaliullin, R. Z.; Schütt, O.; Schiffmann, F.; Golze, D.; Wilhelm, J.; Chulkov, S.; Bani-Hashemian, M. H.; Weber, V.; Borštnik, U.; Taillefumier, M.; Jakobovits, A. S.; Lazzaro, A.; Pabst, H.; Müller, T.; Schade, R.; Guidon, M.; Andermatt, S.; Holmberg, N.; Schenter, G. K.; Hehn, A.; Bussy, A.; Belleflamme, F.; Tabacchi, G.; Glöß, A.; Lass, M.; Bethune, I.; Mundy, C. J.; Plessl, C.; Watkins, M.; VandeVondele, J.; Krack, M.; Hutter, J. CP2K: An Electronic Structure and Molecular Dynamics Software Package - Quickstep: Efficient and Accurate Electronic Structure Calculations. *J. Chem. Phys.* **2020**, *152* (19), 194103.
- (77) Goedecker, S.; Teter, M.; Hutter, J. Separable Dual-Space Gaussian Pseudopotentials. *Phys. Rev. B* **1996**, *54* (3), 1703–1710.
- (78) VandeVondele, J.; Hutter, J. Gaussian Basis Sets for Accurate Calculations on Molecular Systems in Gas and Condensed Phases. *J. Chem. Phys.* **2007**, *127* (11), 114105.
- (79) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865–3868.
- (80) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132* (15), 154104.
- (81) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.* **2011**, *32* (7), 1456–1465.
- (82) Dudarev, S. L.; Botton, G. A.; Savrasov, S. Y.; Humphreys, C. J.; Sutton, A. P. Electron-Energy-Loss Spectra and the Structural Stability of Nickel Oxide: An LSDA+U Study. *Phys. Rev. B* **1998**, *57* (3), 1505–1509.
- (83) Dudarev, S. L.; Nguyen Manh, D.; Sutton, A. P. Effect of Mott-Hubbard Correlations on the Electronic Structure and Structural Stability of Uranium Dioxide. *Philos. Mag. B* **1997**, *75* (5), 613–628.
- (84) Bocharov, D.; Pudza, I.; Klementiev, K.; Krack, M.; Kuzmin, A. Study of High-Temperature Behaviour of ZnO by Ab Initio Molecular Dynamics Simulations and X-Ray Absorption Spectroscopy. *Materials* **2021**, *14* (18), 5206.
- (85) Bussi, G.; Donadio, D.; Parrinello, M. Canonical Sampling through Velocity Rescaling. *J. Chem. Phys.* **2007**, *126* (1), 014101.
- (86) Sulpizi, M.; Sprik, M. Acidity Constants from Vertical Energy Gaps: Density Functional Theory Based Molecular Dynamics Implementation. *Phys. Chem. Chem. Phys.* **2008**, *10* (34), 5238–5249.
- (87) Soltermann, D.; Fernandes, M. M.; Baeyens, B.; Dähn, R.; Miehe-Brendlé, J.; Wehrli, B.; Bradbury, M. H. Fe(II) Sorption on a Synthetic Montmorillonite. A Combined Macroscopic and Spectroscopic Study. *Environ. Sci. Technol.* **2013**, *47* (13), 6978–6986.
- (88) Soltermann, D.; Baeyens, B.; Bradbury, M. H.; Fernandes, M. M. Fe(II) Uptake on Natural Montmorillonites. II. Surface Complexation Modeling. *Environ. Sci. Technol.* **2014**, *48* (15), 8698–8705.
- (89) Bradbury, M. H.; Baeyens, B. Sorption of Eu on Na- and Ca-Montmorillonites: Experimental Investigations and Modelling with Cation Exchange and Surface Complexation. *Geochim. Cosmochim. Acta* **2002**, *66* (13), 2325–2334.
- (90) Bradbury, M. H.; Baeyens, B. Modelling Sorption Data for the Actinides Am(III), Np(V) and Pa(V) on Montmorillonite. *Radiochim. Acta* **2006**, *94* (9–11), 619–625.
- (91) Hummel, W.; Thoenen, T. *The PSI Chemical Thermodynamic Database 2020; NTB; Technical Report 21–03*, 2023.
- (92) Vanselow, A. P. The Utilization of the Base-Exchange Reaction for the Determination of Activity Coefficients in Mixed Electrolytes. *J. Am. Chem. Soc.* **1932**, *54* (4), 1307–1311.
- (93) Manceau, A.; Lanson, B.; Schlegel, M. L.; Harge, J. C.; Musso, M.; Eybert-Berard, L.; Hazemann, J.-L.; Chateigner, D.; Lamble, G. M. Quantitative Zn Speciation in Smelter-Contaminated Soils by EXAFS Spectroscopy. *Am. J. Sci.* **2000**, *300* (4), 289–343.
- (94) Dähn, R.; Scheidegger, A. M.; Manceau, A.; Schlegel, M. L.; Baeyens, B.; Bradbury, M. H.; Morales, M. Neoformation of Ni Phyllosilicate upon Ni Uptake on Montmorillonite: A Kinetics Study by Powder and Polarized Extended X-Ray Absorption Fine Structure Spectroscopy. *Geochim. Cosmochim. Acta* **2002**, *66* (13), 2335–2347.

Supporting Information for: Mechanistic Thermodynamic Model for Zn^{2+} uptake on Saponite

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Cation exchange capacity measurements

The cation exchange capacity (CEC) of Na-saponite was determined by the ^{134}Cs isotope dilution technique due to the higher selectivity coefficient of this element towards divalent cations¹. The first step was the preparation of a homo-ionic Cs-saponite; this process is often referred as clay conditioning. The Cs conditioning of the Na-saponite was achieved by placing in a polyethylene bottle ($V_{\text{tot}} = 0.1$ l) a dialysis membrane filled with $10 \cdot 10^{-3}$ l of saponite suspension ($11 < [\text{clay}] < 18$ g/l) and interacting it with an excess of CsCl solutions ($\approx 90 \cdot 10^{-3}$ l, $[\text{Cs}^+] = 0.1$ M). After 4 hours on an end-over-end shaker, the old CsCl solution was replaced with a fresh one and the bottle was put back on the shaker. After the second step, the CsCl solution was discarded, ultrapure water was added to remove the excess of Cs^+ . After 4 hours of end-over-end shaking with ultrapure water, the clay in the dialysis membrane was put in contact with $\approx 90 \cdot 10^{-3}$ l of a CsCl solution with relatively low concentration ($[\text{Cs}^+] = 5 \cdot 10^{-3}$ M). The conditioning with diluted CsCl was carried out 4 times, as explained for concentrated CsCl. After the fourth washing with diluted CsCl, the conductivity of the conditioning solution and the conductivity of the stock CsCl solution were compared to ensure that the excess of CsCl was washed out. At this stage, $20 \cdot 10^{-3}$ l of a radiotracer solution containing ^{134}Cs was put in contact with the dialysis membrane containing the conditioned clay suspension. After 1 day on an end-over-end shaker, the solution outside the membrane was sampled and measured on a gamma counter (Packard, COBRA II auto-gamma) together with a scintillator fluid (Ultima Gold XR). The cation exchange capacity was determined twice on two independent batches of synthetic saponite. The average result was $\text{Cs-CEC} = 0.92 \pm 0.03$ equivalents/kg_{clay} and the pH was 6.7 ± 0.1 .

EXAFS measurements setup

The X-ray absorption measurements were performed at The Rossendorf Beamline (ROBL, BM20)² at the European Synchrotron Radiation Facility (ESRF) in Grenoble. The storage ring was operating at 6 GeV in top-up mode with a ring current of 200 mA. The X-ray beam was monochromatized using a Si (111) double-crystal monochromator. Higher harmonics were suppressed by two, 1.4- and 1.2-meters long, silicon mirrors with a grazing incidence of 2.5×10^{-3} radians. The Zn K-edge (9659 eV) EXAFS spectra were recorded both in fluorescence and transmission modes. Simultaneously, a metallic zinc foil was measured in transmission mode to allow for an accurate energy calibration for each scan. The incoming and transmission signals were recorded with ionization chambers (Oxford Instruments). The fluorescence signal was collected using an 18-element Ge-detector (Mirion) with CMOS-based charge sensitive CUBE amplifiers (XGLab) and Falcon-X read-out spectrometers (XIA) allowing to significantly improve the signal to noise ratio of $\chi(k)$ spectra in high k

range. Polarized EXAFS (P-EXAFS) spectra were collected using self-supporting, oriented clay films in a geometrical setup as described in refs^{3,4}.

The oriented films were prepared by filtering the samples under low vacuum through a double filter: an Isopore Membrane (Millipore, $\phi = 0.4 \mu\text{m}$) on top and a Nitrocellulose Membrane (Sartorius, $\phi = 0.1 \mu\text{m}$) at the bottom. After drying, the filters were peeled from the clay film. The clay films were then cut and mounted on a plastic sample holder using Kapton tape. A rotating sample holder was used to perform the angular-dependent measurement with an accuracy of $\pm 5^\circ$ (α angle).

FEFF simulation setup

The FEFF 9.6 software⁵⁻⁷ was configured to consider clusters with up to 430'000 scattering paths. For each atomic configuration, the scattering potentials of the atoms were calculated self-consistently⁵ using a cluster with a radius of 5.0 Å around the absorbing atom. Multiple scattering paths up to 8 legs (NLEG 8) were collected for the cluster radius of 6.5 Å. The cluster radius was reduced in comparison to our previous study⁸ due to increased number of scattering paths mainly because of much smaller size and, hence, larger density of water molecules. The amplitude reduction factor (S_0^2) was set equal to 0.9, a value typically used for fitting experimental EXAFS data. The edge energy of the theoretical EXAFS spectra was aligned to that of the experimental spectra using a correction factor of -2.0 eV previously derived for Zn-doped saponite⁸.

FEFF input example:

TITLE Zn sorption on talc (010) S3 site

```

EDGE    K
S02     0.9
*      pot  xsph  fms  paths  genfmt  ff2chi
CONTROL 1    1    1    1    1    1
PRINT   1    0    0    1    0    0
RPATH   6.5
EXAFS   15
NLEG    8
SCF     5.0
CRITERIA 0.0 0.0
EXCHANGE 0 -2.0 0.0
FOLP 2 0.8
POTENTIALS
*      ipot  Z  element
0  30  Zn
1   8   O
2   1   H
3  12  Mg
4  14  Si

ATOMS
0.00000    0.00000    0.00000    0    Zn    0.0000
-1.27213    1.04170    1.14312    1    O_1   2.00254
0.48624    -1.68050    1.08528    1    O_2   2.05872
-1.27487    -1.12880    -1.21510    1    O_3   2.09188
0.37729     1.83910    -1.06727    1    O_4   2.15956
1.86458    -0.78820    -1.08405    1    O_5   2.29632
-0.72037     1.24400     1.92346    2    H_6   2.40128
2.11700     1.01380     1.17646    1    O_7   2.62555
1.90509    -0.63010    -2.05508    2    H_8   2.87224
-1.23930     2.76160     0.05304    3    Mg_9  3.02739
-1.35991    -2.71800    -0.03398    3    Mg_10 3.03941
1.85288    -2.49490    -0.00267    3    Mg_11 3.10768
-2.73116     0.82380     1.45147    2    H_12  3.20073

```

-1.22182	-0.98720	-2.81316	4	Si_13	3.22200
0.48139	1.68600	-2.71817	4	Si_14	3.23462
0.74465	-1.64880	2.70439	4	Si_15	3.25373
1.90631	2.65930	0.06092	3	Mg_16	3.27255
-0.26913	0.34110	-3.24438	1	O_17	3.27334
3.45841	0.09150	0.02611	3	Mg_18	3.45972
-1.99123	-1.92620	2.08146	2	H_19	3.46522
1.22133	-0.16650	3.24019	1	O_20	3.46673
-3.42596	-0.71930	-0.46576	2	H_21	3.53150
-3.11494	1.33700	-1.16206	2	H_22	3.58341
0.31897	-3.41240	-1.14535	1	O_23	3.61359
-2.71287	-2.02310	1.46067	1	O_24	3.68594
-2.70775	2.21710	-1.35174	1	O_25	3.75162
2.23332	1.06960	2.81855	4	Si_26	3.75180
0.43922	3.60660	1.11713	1	O_27	3.80111
-0.68724	-1.90850	3.41537	1	O_28	3.97233
3.45192	-1.83050	0.97144	1	O_29	4.02619
-3.97316	0.00100	-0.85993	1	O_30	4.06515
3.52791	1.76680	-1.14878	1	O_31	4.10943
-3.66476	0.67650	1.84529	1	O_32	4.15851
-0.52397	-2.37430	-3.40213	1	O_33	4.18167
1.98129	1.72150	-3.34434	1	O_34	4.25132
3.48639	-1.77320	1.93242	2	H_35	4.36273
1.70848	2.56930	3.28970	1	O_36	4.51025
-0.33939	2.98810	-3.36498	1	O_37	4.51298
-3.06557	-2.84270	1.82573	2	H_38	4.56201
0.41041	-3.63900	-2.74924	4	Si_39	4.57920
-1.03803	4.33050	-1.12485	1	O_40	4.59304
-3.52926	1.04620	2.76270	2	H_41	4.60247
-2.58150	-0.88950	-3.73175	1	O_42	4.62399
1.85754	-2.76110	3.24891	1	O_43	4.65076
0.62770	3.73100	2.74135	4	Si_44	4.67219
-1.10020	-4.41310	1.10292	1	O_45	4.67999
-4.71666	0.33460	-0.17030	2	H_46	4.73158
-3.46126	2.83480	-1.55326	2	H_47	4.73593
-2.84919	-3.70750	-1.11121	1	O_48	4.80606
-0.86559	-4.27180	2.03865	2	H_49	4.81182
-0.79471	3.28240	3.47654	1	O_50	4.84686
3.56458	1.78500	-2.76250	4	Si_51	4.85014
1.88076	-4.35280	1.10128	1	O_52	4.86795
-2.68567	3.96320	1.17863	1	O_53	4.93041
-0.70268	-2.16710	4.37983	2	H_54	4.93690
2.00609	4.41140	-1.07357	1	O_55	4.96361
-2.75462	-0.00640	-4.24355	2	H_56	5.05922
1.89117	-3.28610	-3.35592	1	O_57	5.06332
3.46022	-3.53390	-1.14032	1	O_58	5.07562
3.59184	3.61230	0.97404	1	O_59	5.18640
-3.64535	-3.66840	-0.50752	2	H_60	5.19647
3.77790	1.00950	3.43295	1	O_61	5.20353
-4.82866	1.61040	1.25217	2	H_62	5.24188
-2.15766	1.86690	4.41322	2	H_63	5.25522
-0.94920	4.37290	-2.75636	4	Si_64	5.25554
2.17769	4.37030	-1.99633	2	H_65	5.27515
-4.40096	-0.70290	2.83915	2	H_66	5.28425
3.49908	3.50850	1.97138	2	H_67	5.33287

5.16399	-0.82910	-1.04207	1	O_68	5.33293
5.15515	1.00270	1.08617	1	O_69	5.36290
0.52097	5.34740	-0.03789	3	Mg_70	5.37285
-0.55317	3.04140	4.40869	2	H_71	5.38448
0.34187	-5.45200	0.12687	3	Mg_72	5.46418
2.04573	-4.31800	2.71898	4	Si_73	5.49754
-2.27901	4.87900	1.18109	2	H_74	5.51303
4.36012	0.50950	-3.35980	1	O_75	5.52797
-3.59942	3.96260	1.43357	2	H_76	5.54195
-2.70647	-4.68180	-1.29761	2	H_77	5.56130
-0.70268	-2.16710	-5.08017	2	H_78	5.56760
-3.01756	1.39620	4.47696	1	O_79	5.57658
-4.71976	0.19830	-3.02047	2	H_80	5.60702
3.46024	-3.45340	-2.79648	4	Si_81	5.63201
4.22163	-2.07280	-3.16665	1	O_82	5.66977
5.03335	-2.70080	-0.12548	3	Mg_83	5.71355
5.03925	2.72320	-0.02586	3	Mg_84	5.72805
-2.15766	1.86690	-5.04678	2	H_85	5.79748
5.10282	-0.73930	-2.65553	4	Si_86	5.79976
-2.75462	-0.00640	5.21645	2	H_87	5.89910
-0.55317	3.04140	-5.05131	2	H_88	5.92215
5.22135	1.00870	2.71916	4	Si_89	5.97276
-3.01756	1.39620	-4.98304	1	O_90	5.99047
-0.19263	-5.08370	-3.26867	1	O_91	6.04693
-5.75906	1.93870	0.86333	1	O_92	6.13764
-5.16226	-1.12810	3.23790	1	O_93	6.19722
-4.48226	3.99741	-1.55369	1	O_94	6.20354
-2.07202	-3.78300	-4.47387	2	H_95	6.21449
-5.60956	-2.63990	0.46886	2	H_96	6.21740
-1.99939	-5.75010	1.27656	2	H_97	6.22019
1.17141	5.20360	3.20675	1	O_98	6.22358
-0.26913	0.34110	6.21562	1	O_99	6.23079
4.30564	3.11920	-3.25674	1	O_100	6.23493
-5.12006	-3.58980	0.42209	1	O_101	6.26736
-3.71066	2.04960	-4.68709	2	H_102	6.31971
3.48881	-5.29320	-0.00117	3	Mg_103	6.33954
1.22133	-0.16650	-6.21981	1	O_104	6.34077
-2.58150	-0.88950	5.72825	1	O_105	6.34572
-2.38290	4.65420	-3.60027	1	O_106	6.34836
-0.68724	-1.90850	-6.04463	1	O_107	6.37591
-5.62656	2.93150	0.68335	2	H_108	6.38113
-3.71066	2.04960	4.77291	2	H_109	6.38361
3.59935	5.33470	-0.07265	3	Mg_110	6.43581
-5.30066	-0.29060	-3.64333	1	O_111	6.43858
1.86357	-6.11761	-1.00791	1	O_112	6.47410
1.00056	-5.45000	3.35505	1	O_113	6.47765
-1.20898	6.28555	1.05656	1	O_114	6.48738
-1.21123	-6.29669	-1.05126	1	O_115	6.49773

END

Implementation of the 2SPNE SC/CE sorption model for synthetic saponite in GEM-Selektor software

Table S1. Summary of 2SPNE SC/CE model parameters (site types, site capacities and protolysis constants) for montmorillonite⁹ and sites capacities determined for synthetic saponite

Site type	Capacity (mol/kg) montmorillonite / saponite	
X^-	0.87 / 0.92	
$\equiv S^S OH$	$2.0 \cdot 10^{-3} / 5.0 \cdot 10^{-3}$	
$\equiv S^{W1} OH$	$4.0 \cdot 10^{-2}$	
$\equiv S^{W2} OH$	$4.0 \cdot 10^{-2}$	
Protolysis reactions	$\log_{10} K_{app}$	
	$\equiv S^{S/W1} OH$	$\equiv S^{W2} OH$
$\equiv SOH + H^+ \leftrightarrow \equiv SOH_2^+$	4.5	6.0
$\equiv SOH \leftrightarrow \equiv SO^- + H^+$	-7.9	-10.5

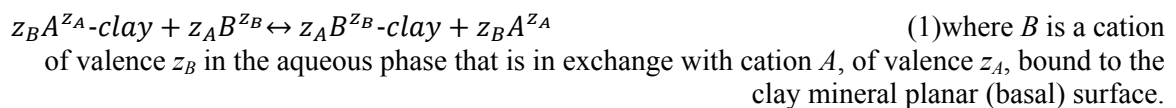
The 2SPNE SC/CE sorption model for synthetic saponite was implemented in GEM-Selektor^{10,11} (<https://gems.web.psi.ch/>) in line with a procedure, previously used in ClaySor model package – the GEMS-based implementation of the 2SPNE SC/CE model for montmorillonite and illite^{10,12,13}. The concepts of the implementation are detailed below.

The ion-exchange species for clay minerals are treated as endmembers of a separate ion-exchange phase, modelled as a solid solution with simple ideal mixing. Edge sorption species are assigned to another separate SC phase, also treated formally as a simple ideal solid solution¹².

Within the edge sorption phase, the mole amounts of surface complexes on strong, weak-1, and weak-2 sites are governed by mass balances based on the total mole amounts of independent components (ICs) for each site type, which are set in the input bulk composition of the chemical system.

In GEMS, chemical systems are typically expressed using an elemental stoichiometry basis, where the system bulk composition is defined by the mole amounts of ICs, usually representing chemical elements and electrical charge. In this work, as well as in ClaySor, sorption sites are represented as additional ICs, treated as “fictive elements”. The following ICs were set for synthetic saponite:

Clsa – permanent charge sites of valence (charge) -1 involved in CE reactions corresponding to the generic equation:

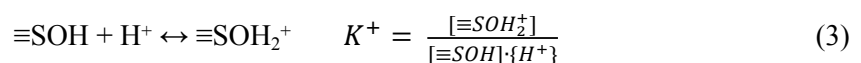


If ion exchange is treated as a phase-solution with simple ideal mixing, this reaction corresponds to a mass action equation with the equilibrium constant ${}^B_A K_V$, which in the Vanselow convention (Vanselow 1932) can be expressed as follows:

$${}^B_A K_V = \frac{(X_B)^{z_A}}{(X_A)^{z_B}} \cdot \frac{A^{z_B}}{B^{z_A}} \quad (2)$$

where $\{ \}$ denotes the activity of ions (A or B) in aqueous solution, X_A and X_B are the mole fraction occupancies. In GEMS, the equilibrium constants for cation exchange (CE) must be expressed using the Vanselow convention.

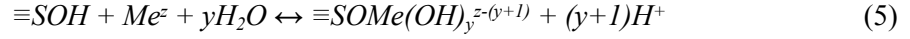
- Esss, Esvs, Esws – amphoteric edge sites on saponite: strong sites $\equiv S^S$, weak sites $\equiv S^{W1}$ and $\equiv S^{W2}$, respectively, all of valence +1. The protolysis reactions of these sites and the corresponding equilibrium constants are given as:



$$\equiv\text{SOH} \leftrightarrow \equiv\text{SO}^- + \text{H}^+ \quad K^- = \frac{[\equiv\text{SO}^-] \cdot \{H^+\}}{[\equiv\text{SOH}]} \quad (4)$$

where $[]$ denotes molar concentrations and $\{\}$ denotes activities of aqueous species.

The SC reaction of an aqueous cation Me^z on the amphoteric hydroxyl group of clay edge can be written as:



where Me^z denotes metal cation with valence z , and y is an integer.

The equilibrium SC constant for Equation (5) is given as:

$$K_y = \frac{[\equiv\text{SOMe}(\text{OH})_y^{z-(y+1)}]}{[\equiv\text{SOH}]} \cdot \frac{f_{\equiv\text{SOMe}(\text{OH})_y^{z-(y+1)}}}{f_{\equiv\text{SOH}}} \cdot \frac{\{H^+\}^{(y+1)}}{\{\text{Me}^z\}} \quad (6)$$

where f denotes activity coefficients of surface species, whose ratio is assumed to be unity.

Permanent charge sites (planar sites) are also assigned with the molar mass (in g/mol), roughly estimated as the mass (in g) of the respective (dry) clay with 1.0 eq permanent charge. This value derives from the CEC as follows:

$$M_{PS} = \frac{1000}{CEC} \quad (7)$$

where CEC is expressed in equivalent per kg clay. For synthetic saponite, the CEC was determined by Di Lorenzo et al.¹⁴ as 0.924 eq/kg, yielding a molar mass of Clsa of 1,082.251 g/mol.

Invention of this value is necessary in GEMS because the clay sorbent is represented not in the real elemental stoichiometry, but only in the amounts of sorption sites (“fictive elements”) proportionally to site capacities and the mass of (dry) clay. The molar mass of edge sites is arbitrarily set to 1 g/mol. These molar masses propagate into sorption species and are useful in setting compositions of clay systems in terms of solid/water mass ratios.

In GEMS, a chemical system is defined by its phases, which can include an aqueous electrolyte, gas mixture, pure condensed phases, liquid or solid solutions, and sorption phases. Each phase consists of one or more dependent components (DCs), also called chemical species, components, or endmembers. The activities and concentrations of a DC are defined within its phase based on appropriate standard-state convention and reference-state concentration scale (e.g., molality for aqueous species, mole fraction for a solid solution endmember). Each DC is represented by a chemical formula, expressed in moles of ICs per mole of the DC. The stability of each DC is set by its standard Gibbs energy per mole G°_{298} (of formation from ICs taken at the appropriate standard and reference states) at reference temperature $T_r = 298.15$ K (25 °C) and pressure $P_r = 1$ bar and, if necessary, corrected to temperature T and pressure P of interest.

The following reference DCs were established for synthetic saponite (the ‘@’ character represents zero charge):

ClsaNa@ – CE species representing Na^+ ion on the permanent charge site;

=sSsOH@, =sSvOH@, =sSwOH@ – representing amphoteric OH groups on edge site: strong sites $\equiv\text{S}^\text{S}\text{OH}$, weak sites $\equiv\text{S}^\text{W1}\text{OH}$ and $\equiv\text{S}^\text{W2}\text{OH}$, respectively.

The stoichiometries and the provisional standard-state thermodynamic properties of the reference DC species are set to be roughly consistent with those of related aqueous species, as listed in Table S2 and stored as DComp records in GEMS database.

Table S2: Provisional standard-state properties of ClaySor reference DC chemical species for Na-saponite at 1 bar, 25 °C

Species name	Formula	Molar mass, g/mol	G°_{298} kJ/mol	V°_{298} cm ³ /mol
ClsaNa@	ClsaNa	1,105.24	-251.92	428.47

where n is the number of data points. The nested GEMSFITS function was used to constrain pH in the system by titrating with acid or base until the experimental pH value was reached.

Typically, the G°_{298} boundaries of ± 10 kJ/mol were sufficient to locate the objective function's minimum.

During the optimization process, the composite scaled sensitivities (CSS) of the G°_{298} values were assessed, as described by Miron et al.⁸ and Hill & Tiedeman¹⁹. These metrics, available in the GEMSFITS results, represent the sum of all observation sensitivities for a given parameter. They indicate how well a parameter is constrained by the experimental data. Parameters with low sensitivity could then be excluded from the model.

Once the optimized G°_{298} values were determined, Monte Carlo simulations were conducted to estimate the uncertainty of the fitted parameters, expressed at 95% confidence level. The Monte Carlo sampling method²⁰ is particularly useful for evaluating error propagation and estimating parameter uncertainty when analytical propagation methods are not applicable. The parameter uncertainty at the 95% confidence level was approximated as twice the standard deviation of the parameter values, obtained from fitting the model to numerous (typically 1,000) synthetic experimental datasets. In Monte-Carlo simulations, the synthetic datasets were generated by perturbing the measured values with quantities randomly sampled from a log-normal distribution with a mean of zero and a data residual representing the data scatter Δ . In most cases, the scatter in the data was sufficient to produce data residuals that provided acceptable uncertainty in the values of G°_{298} . The data residuals were calculated as follows:

$$\Delta = |\log_{10} R_{d\text{ meas}} - \log_{10} R_{d\text{ calc}}| \quad (10)$$

where $R_{d\text{ meas}}$ and $R_{d\text{ calc}}$ refer to the measured and calculated best-fit R_d values, respectively.

Fitting against the synthetic datasets yielded 1,000 new sets of best-fit G°_{298} values. For the obtained G°_{298} values, their uncertainty at a 95% confidence level was approximated by:

$$Un_{G^\circ_{298}} = 1.96 \times \sigma \quad (11)$$

where σ is the standard deviation, 1.96 is the z-score corresponding to a 95% confidence level:

$$-1.96 \times \sigma < \overline{G^\circ_{298}} < 1.96 \times \sigma \quad (12)$$

where $\overline{G^\circ_{298}}$ is the mean of 1,000 best-fit G°_{298} values, and 95% of estimated parameter values lie within 1.96 standard deviations of the mean.

The fitted G°_{298} values of surface complexes and cation exchange species were converted into equilibrium constants of SC and CE reactions using the ReacDC module of GEM-Selektor via the standard Gibbs energy effect of reaction $\Delta_r G^\circ_{298}$ according to Equations (13) and (14).

$$\Delta_r G^\circ_{298} = \sum G^\circ_{298(\text{products})} - \sum G^\circ_{298(\text{reactants})} \quad (13)$$

where $\sum G^\circ_{298(\text{reactants})}$ is the sum of standard molar Gibbs free energies of formation of reactants in SC or the CE reaction in J/mol. Conversion to $\log_{10} K^\circ$ is then

$$\log_{10} K^\circ = \frac{\Delta_r G^\circ_{298}}{-R \cdot T^\circ \cdot \ln(10)} \quad (14)$$

where R is the gas constant in $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, and T° is the reference temperature, 298.15 K.

Uncertainties at a 95% confidence level of SC and CE reaction constants $Un_{K_{SC/CE}}$ were calculated as:

$$\log_{10} Un_{K_{SC/CE}} = \left| \frac{Un_{G^\circ_{298}}}{-RT \ln(10)} \right| \quad (15)$$

where $Un_{G^\circ_{298}}$ is the uncertainty at a 95% confidence level of best-fit G°_{298} values.

Based on the estimated uncertainties of the optimised parameters, the overall uncertainty of the sorption model (R_d value in pH edge or sorption isotherm) was propagated to a 95% confidence interval of the calculated R_d values, shown as shadowed bands in the thermodynamic modelling plots in the

main text. The propagation was performed for each selected experimental dataset with help of the in-house UpsaGEMS Python code (PSI LES 2022 annual progress report) combining the GEMS code with the polynomial chaos expansion method from the “Uncertainpy” toolbox²¹. For the calculated pH edges or isotherms, “Uncertainpy” samples many values for different parameter combinations from their normal distribution within respective uncertainty values. A spread of calculated pH edges or isotherms was generated through GEMS calculations encompassing all possible combinations and was subsequently employed to establish the band representing the 95% confidence interval that contained 95% of all model predictions.

Alternative LC fits of EXAFS spectra

Table S3. Normalized edge surface contributions obtained for Zn²⁺ sorbed samples through linear combination fitting with and without monodentate sorption complexes in range $k \in [2.5 - 12.5]$. Values reported for fit without monodentate sorption complexes presented in the concise way in the main manuscript.

Fit components	Surface	[Zn ²⁺] in sample, mmol/kg							
		With monodentate				Without monodentate			
		1.1	2.4	29.4	38.2	1.1	2.4	29.4	38.2
S1-CS,%	(010)	9.99	10.69	8.70	6.21	-	-	-	-
	(110)	9.34	11.06	12.48	11.97	-	-	-	-
S1-ES,%	(010)	2.33	3.13	15.48	16.50	5.46	6.64	19.06	19.59
	(110)	14.34	14.55	11.19	11.80	29.19	31.37	27.71	26.08
S2,%	(010)	4.80	3.54	7.09	9.78	5.85	4.63	8.10	10.65
	(110)	8.23	7.65	12.63	14.75	8.80	8.23	13.12	15.11
S3,%	(010)	19.78	19.38	9.20	7.49	19.39	18.96	8.71	7.07
	(110)	31.19	30.0	23.23	21.50	31.30	30.18	23.30	21.48
Total (010), %		36.9	36.7	40.5	40.0	30.7	30.2	35.9	37.3
Total (110), %		63.1	63.3	59.5	60.0	69.3	69.8	64.1	62.7
Total “S1-E/CS”, %		36.0	39.4	47.9	46.5	34.7	38.0	46.8	45.7
Total “S2”, %		13.0	11.2	19.7	24.5	14.6	12.9	21.2	25.8
Total “S3”, %		51.0	49.4	32.4	29.0	50.7	49.1	32.0	28.5
Q		0.89	0.82	0.81	0.95	0.99	0.93	0.91	1.03
RMSD		0.55	0.49	0.57	0.69	0.55	0.50	0.58	0.68

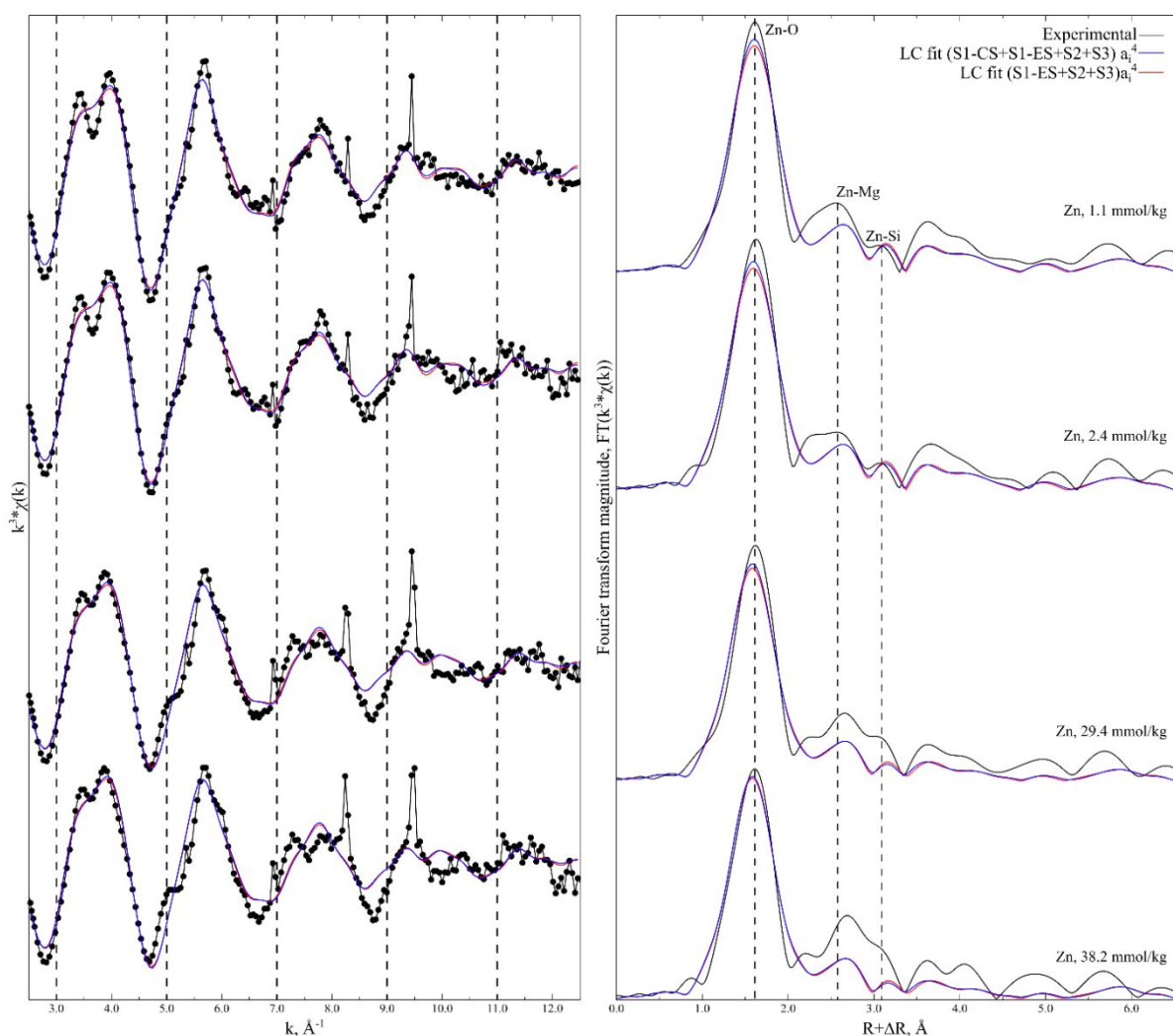


Figure S1. Graphical comparison of linear combination fits of experimental EXAFS spectra obtained with (blue lines) and without monodentate complexes (red lines). The EXAFS fit and Fourier transformation magnitudes were obtained in $k \in [2.5-12.5]$. Experimental measurements are indicated in black.

As it can be conveyed from Table S3 and Figure S1, monodentate sorption complexes have a rather negligible impact on the linear combination fit. Hence, it is sufficient to limit the fit to systems with bidentate (edge sharing) complexes only.

Theoretical EXAFS references struggled to accurately reproduce splitting of first oscillation peak even for simpler systems like Zn-doped saponite⁸. To assess its impact on linear combination fit of Zn sorption samples, linear combination fitting was additionally repeated using experimental Zn-doped saponite⁸ (2 mmol/kg) or Zn-kerolite²² as Zn incorporation reference. According to the fit results, root mean square deviation can be greatly reduced (almost by half) by more accurate reproduction of this feature and some experimental noise introduction. This, however, has practically no (within uncertainty) impact on individual components fractions.

The lowest contribution of inner-sphere sorption complexes (S1-E/CS) was observed for fits with Zn-kerolite samples, which potentially can indicate presence of surface-incorporated Zn on the kerolite edges that was exposed to solution especially at higher loading. This is reflected by RMSD reduction, where introducing Zn-kerolite spectra with higher loading and slightly larger decrease of S1-E/CS contribution. Detailed comparison of individual components indicates strong correlation between S3 site and incorporated Zn fractions.

Overall, linear combination fits obtained with Zn-doped saponite or Zn-kerolite reference spectra show no significant improvements except better reproduction of first oscillation splitting in comparison to theoretical fit with no “bulk” phase. Therefore, considering strong correlation in

contributions with S3 site, omitting them helps reduce the risk of overfitting experimental measurements.

Table S4. Normalized edge surface contributions obtained for Zn²⁺ sorbed samples through linear combination fitting in range $k \in [2.5 - 12.5]$ using experimental Zn-doped saponite spectrum⁸ (2 mmol/kg) as a reference of structurally incorporated Zn.

Fit components	Surface	[Zn ²⁺] in sample, mmol/kg							
		With monodentate				Without monodentate			
		1.1	2.4	29.4	38.2	1.1	2.4	29.4	38.2
S1-CS,%	(010)	9.61	10.34	8.25	5.62	-	-	-	-
	(110)	6.75	8.62	10.66	10.37	-	-	-	-
S1-ES,%	(010)	3.15	4.12	17.34	18.28	5.81	7.21	20.64	21.10
	(110)	8.06	8.90	6.28	7.15	20.11	22.98	20.48	19.28
S2,%	(010)	6.83	5.60	9.04	11.64	7.87	6.73	10.11	12.53
	(110)	7.82	7.35	12.82	15.02	8.38	7.92	13.31	15.37
S3,%	(010)	18.29	17.90	7.10	5.38	17.86	17.42	6.50	4.87
	(110)	14.47	14.05	9.70	8.88	13.82	13.26	8.78	8.03
Zn-doped saponite ⁸		25.03	23.12	18.80	17.65	26.16	24.48	20.18	18.82
Total (010), %		50.5	49.4	51.4	49.7	42.7	41.5	46.7	47.4
Total (110), %		49.5	50.6	48.6	50.3	57.3	58.5	53.3	52.6
Total "S1-E/CS", %		27.6	32.0	42.5	41.4	25.9	30.2	41.1	40.4
Total "S2", %		14.6	12.9	21.9	26.7	16.2	14.6	23.4	27.9
Total "S3", %		32.8	32.0	16.9	14.3	31.7	30.7	15.3	12.9
Q		0.45	0.42	0.57	0.71	0.50	0.49	0.63	0.77
RMSD		0.23	0.21	0.39	0.51	0.24	0.23	0.40	0.52

Table S5. Normalized edge surface contributions obtained for Zn²⁺ sorbed samples through linear combination fitting in range $k \in [2.5 - 12.5]$ using experimental Zn-doped kerolite spectrum²² (2 mmol/kg) as a reference of structurally incorporated Zn.

Fit components	Surface	[Zn ²⁺] in sample, mmol/kg							
		With monodentate				Without monodentate			
		1.1	2.4	29.4	38.2	1.1	2.4	29.4	38.2
S1-CS,%	(010)	5.91	6.96	5.53	3.25	-	-	-	-
	(110)	5.11	7.02	8.92	9.01	-	-	-	-
S1-ES,%	(010)	1.77	2.86	12.24	13.35	3.42	4.98	14.35	15.16
	(110)	8.82	9.79	7.76	8.37	16.47	19.58	18.42	17.55
S2,%	(010)	5.82	4.84	8.30	10.52	6.47	5.64	9.04	11.09
	(110)	7.75	7.39	11.56	13.62	8.05	7.72	11.77	13.71
S3,%	(010)	16.37	16.22	7.18	5.54	15.92	15.67	6.71	5.14
	(110)	19.25	18.71	11.41	10.87	18.52	17.77	10.55	10.11
Zn-doped kerolite ²² (ZnKer3)		29.20	26.20	-	-	31.14	28.64	-	-
Zn-doped kerolite ²² (ZnKer70)		-	-	27.09	25.46	-	-	29.16	27.25
Total (010), %		42.2	41.8	45.6	43.8	37.5	36.8	42.5	43.1
Total (110), %		57.8	58.2	54.4	56.2	62.5	63.2	57.5	56.9
Total "S1-E/CS", %		21.6	26.6	34.5	34.0	19.9	24.6	32.8	32.7
Total "S2", %		13.6	12.2	19.9	24.1	14.5	13.4	20.8	24.8
Total "S3", %		35.6	34.9	18.6	16.4	34.4	33.4	17.3	15.3
Q		0.55	0.52	0.50	0.67	0.57	0.56	0.54	0.70
RMSD		0.26	0.26	0.27	0.43	0.25	0.25	0.27	0.42

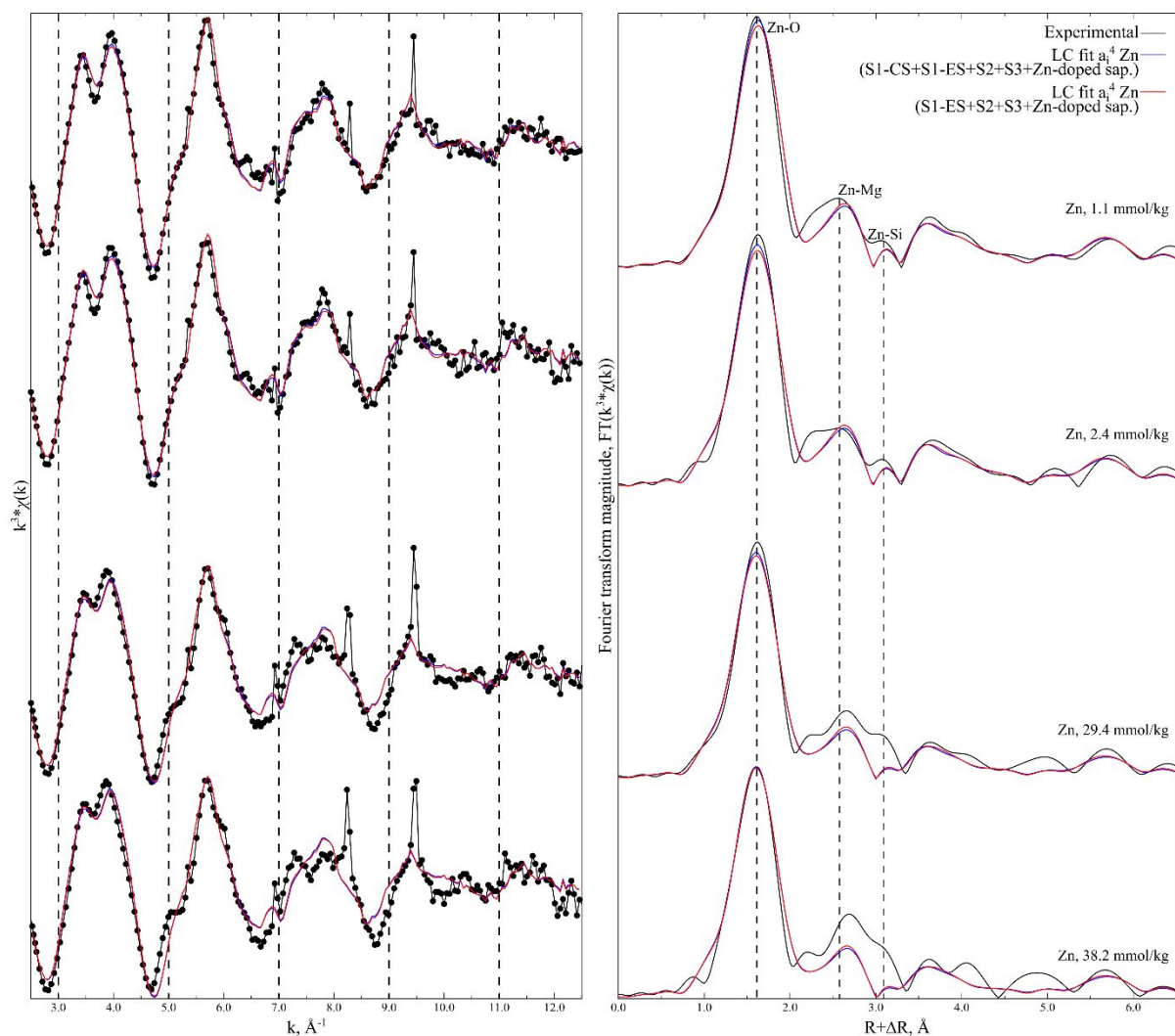


Figure S2. Graphical comparison of linear combination fits of experimental EXAFS spectra obtained with (blue lines) and without monodentate complexes (red lines) using experimental Zn-doped saponite spectrum⁸ (2 mmol/kg). The EXAFS fit and Fourier transformation magnitudes were obtained in $k \in [2.5-12.5]$. Experimental measurements are indicated in black.

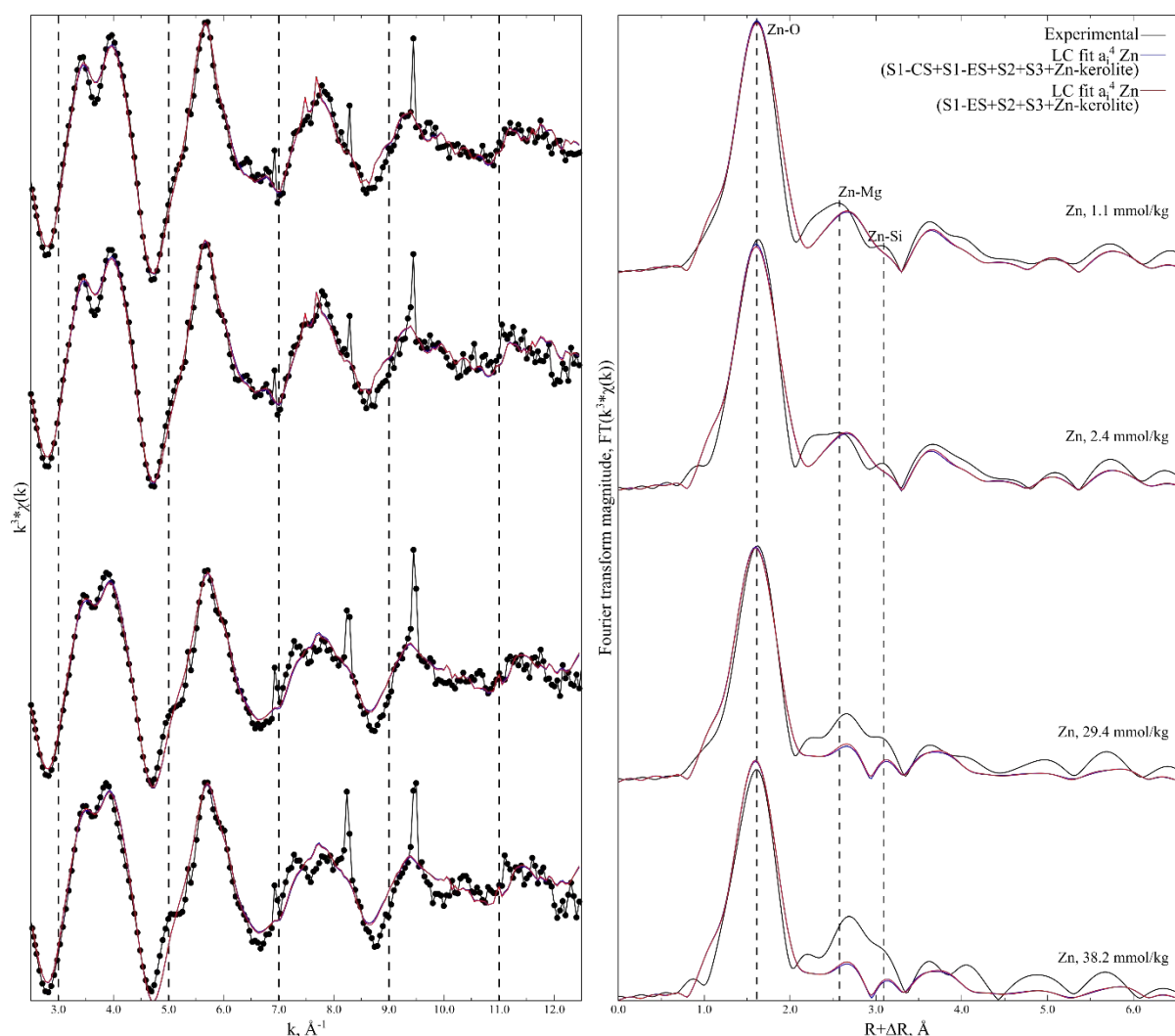


Figure S3. Graphical comparison of linear combination fits of experimental EXAFS spectra obtained with (blue lines) and without monodentate complexes (red lines) using experimental Zn-doped kerolite spectra (“ZnKer3” or “ZnKer70” as described in Table S4). The EXAFS fit and Fourier transformation magnitudes were obtained in $k \in [2.5-12.5]$. Experimental measurements are indicated in black.

XANES linear combination fit with experimental references

Table S6. Results of XANES linear combination fit with three experimental normalized XANES references: ZnAl-LDH, ZnO²³ and Zn-doped saponite⁸. The fit was performed in $E \in [9640-9700]$ eV.

Components fraction	1.1 mmol/kg	2.4 mmol/kg	29.4 mmol/kg	38.2 mmol/kg
Octahedral (ZnAl-LDH)	100.0%	100.0%	100.0%	100.0%
Tetrahedral (ZnO)	0.0%	0.0%	0.0%	0.0%
RMSD	0.0968	0.0974	0.0923	0.0898
Octahedral (Zn-doped saponite)	100.0%	100.0%	88.67%	91.30%
Tetrahedral (ZnO)	0.0%	0.0%	11.33%	8.70%
RMSD	0.0509	0.0532	0.0599	0.0594

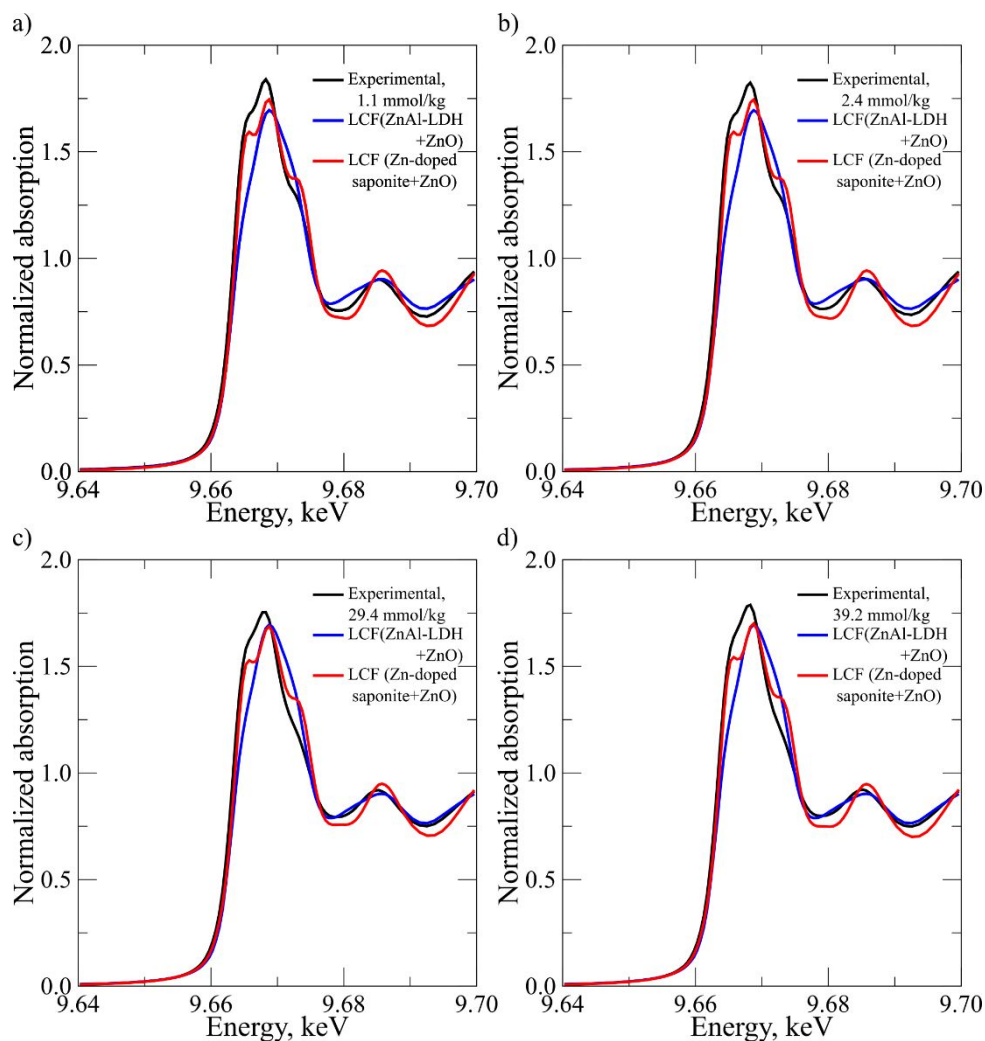


Figure S4. Graphical comparison of linear combination fits of experimental XANES spectra obtained using experimental references. The blue lines show the fit obtained with ZnAl-LDH and ZnO²³ (wurtzite), whereas the red lines show the fit obtained with Zn-doped saponite⁸ and ZnO²³ (wurtzite structural type). Individual component contributions are reported in Table S6). The XANES linear combination fit was obtained in $E \in [9640-9700]$ eV. Experimental Zn sorption samples are indicated in black.

Table S7. Free energy of reaction obtained by thermodynamic integration using DFT optimized geometries of Zn²⁺ complexes.

Surface	$\Delta E_{\lambda=x}$, kJ/mol											ΔA , kJ/mol	pK
	$\lambda=0$	$\lambda=0.1$	$\lambda=0.2$	$\lambda=0.3$	$\lambda=0.4$	$\lambda=0.5$	$\lambda=0.6$	$\lambda=0.7$	$\lambda=0.8$	$\lambda=0.9$	$\lambda=1.0$		
$Zn_{saponite} + \equiv S_{S3}OMg^+ \Leftrightarrow \equiv S_{S3}OZn^+ + Mg_{saponite}$													
(010)	4.53	3.52	2.40	1.19	-0.64	-2.07	-4.00	-5.66	-6.78	-7.78	-8.87	2.19	0.38
(110)	6.07	4.14	2.39	-0.25	-2.53	-3.64	-4.78	-5.80	-7.11	-8.56	-9.53	2.80	0.52
$Zn_{saponite} + \equiv S_{S2}OMg^+ \Leftrightarrow \equiv S_{S2}OZn^+ + Mg_{saponite}$													
(010)	-0.77	-1.92	-3.06	-5.99	-7.69	-8.95	-9.38	-10.87	-12.84	-14.68	-15.67	8.40	1.46
(110)	2.47	0.99	-1.19	-3.46	-6.13	-7.12	-9.19	-10.45	-11.92	-13.55	-15.46	6.81	1.19
$Zn_{saponite} + \equiv S_{S1-ES}OMg^+ \Leftrightarrow \equiv S_{S1-ES}OZn^+ + Mg_{saponite}$													
(010)	-23.80	-21.89	-18.68	-17.52	-14.93	-13.25	-12.85	-9.07	-7.74	-6.62	-3.54	13.64	2.37
(110)	-22.39	-20.66	-19.59	-18.38	-15.89	-14.57	-12.12	-11.30	-9.87	-9.01	-7.79	14.69	2.56

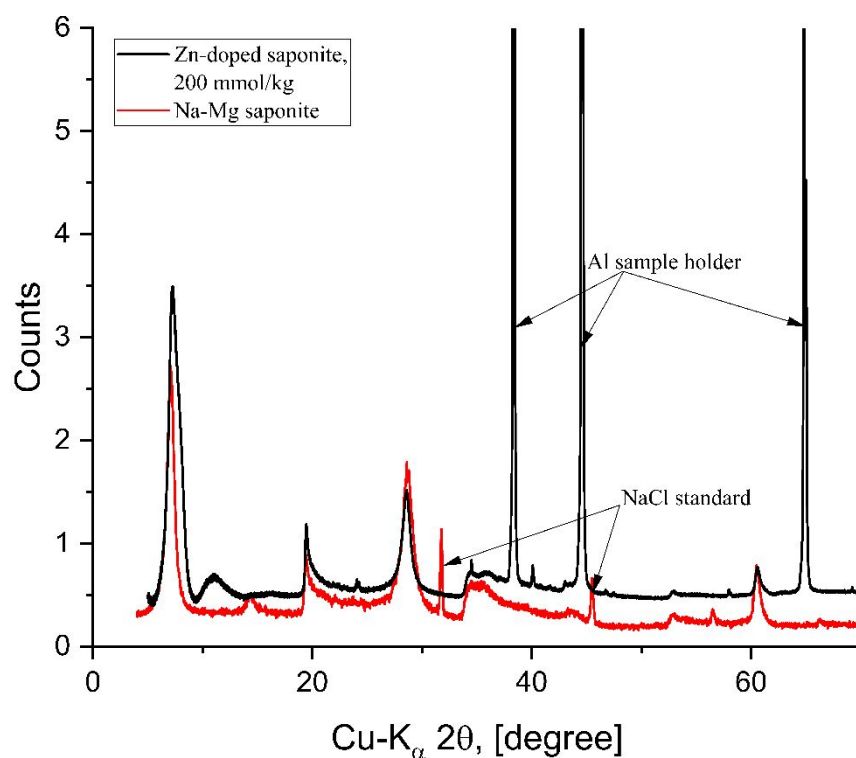


Figure S5. Powder X-ray diffraction pattern of pure synthetic saponite in comparison with powder pattern of synthetic Zn-doped saponite reported in ref⁸. Measurements were conducted at room temperature under atmospheric humidity conditions. The saponite diffraction pattern was measured on silicone sample holder using NaCl as standard, whereas Zn-doped saponite sample was placed on aluminium sample holder.

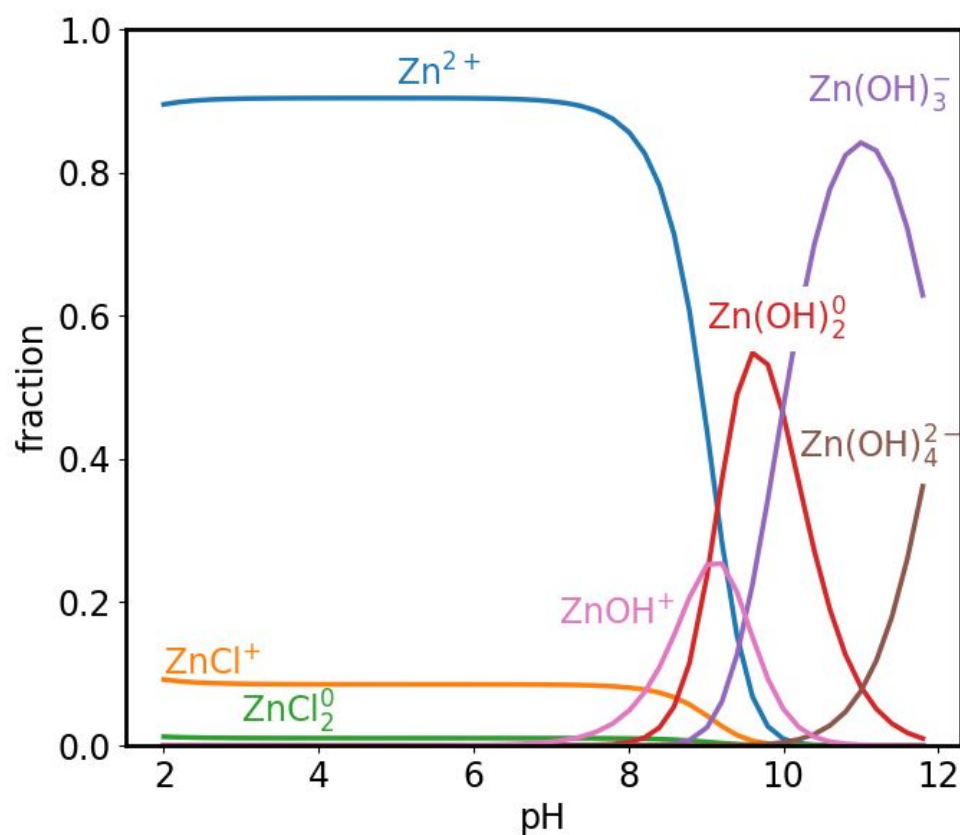


Figure S6. Speciation diagram depicting the fractional distribution of various Zn aqueous species as a function of pH in 0.1 M NaCl solution under inert atmosphere conditions.

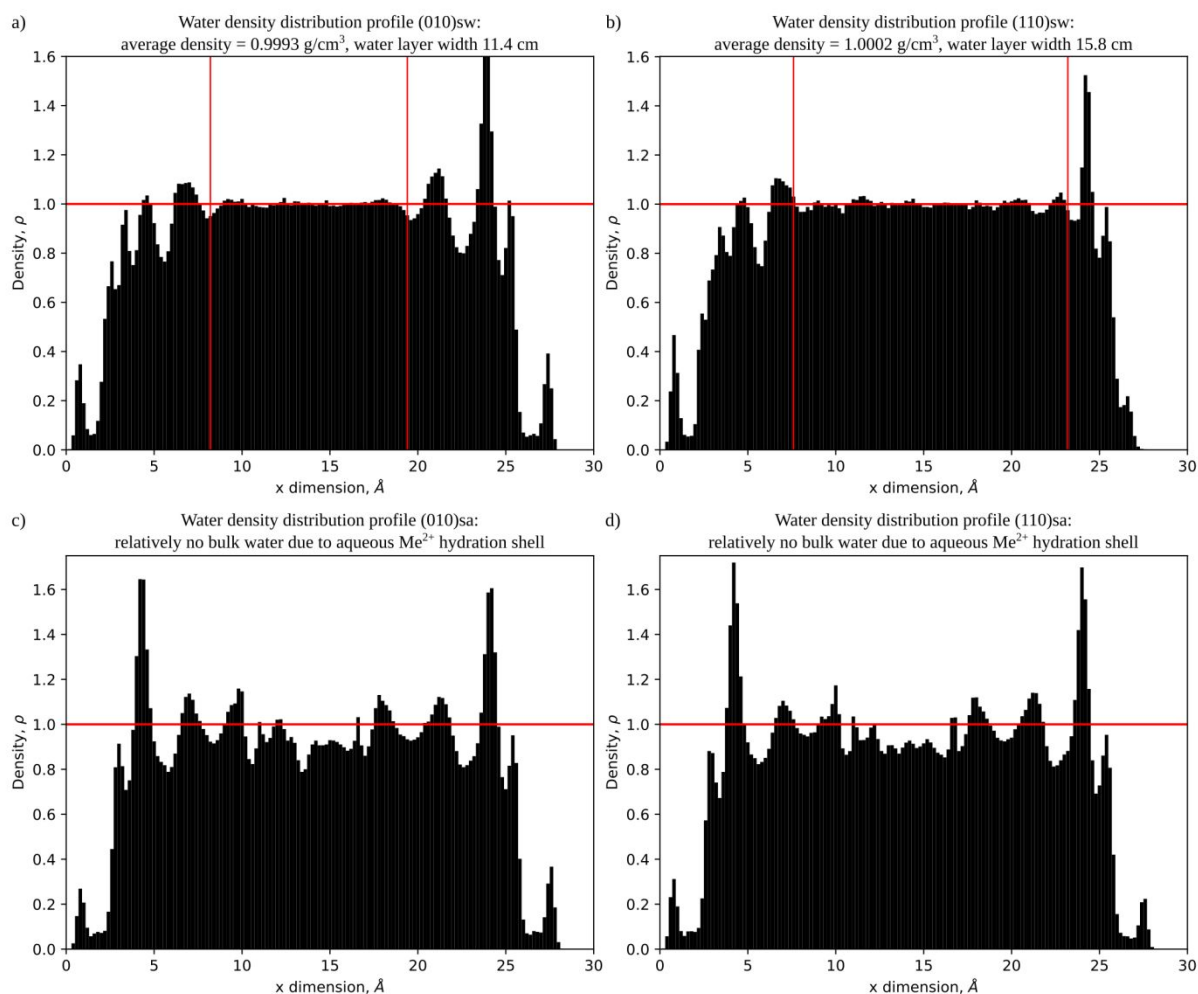


Figure S7. Inter particle water density profile derived for (010) and (110) S2 (*‘strong’*) and S1 (*‘weak’*) sites (a-b) exchange model of talc using classical MD simulations in LAMMPS. Red lines indicate borders of water filled inter particle space, where water molecules behave identically to bulk water. i.e. average water density close to 1 g/cm³. Water molecules outside of this cross section are either adsorbed on talc edge surface or are inherited parts of first and second hydration spheres around edge surface. Number of water molecules and inter particle spacing remains the same for cation exchange reaction between S2 (*‘strong’*) site and aqueous solution due to computational cost and size limitations. Therefore, water density profile changes due to aqueous cation hydration (c-d). It should be noted that water molecules and (OH)⁻ groups directly connected to aqueous Zn²⁺ considered as different water species and were not included in water density profile construction.

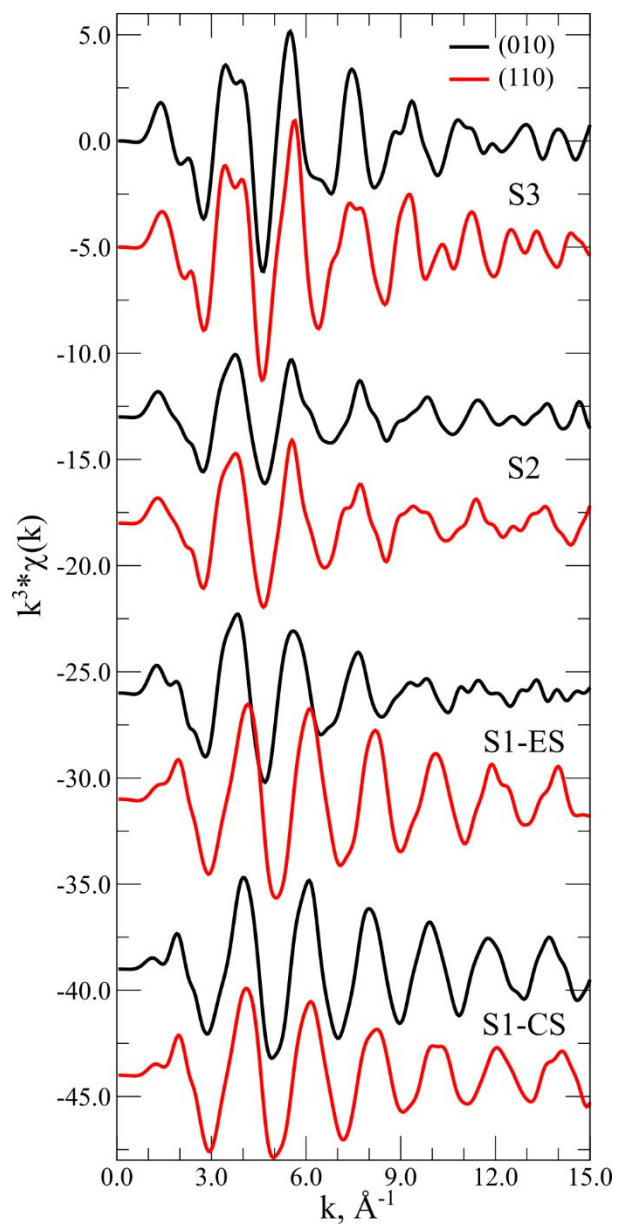


Figure S8. Graphical representation of individual theoretical Zn-sorption EXAFS references sorted in decreasing surface incorporation order. The (010) edge surface complexes are marked in black, whereas (110) complexes – in red.

Radial pair distribution functions

The radial pair distribution functions (RPDF) for Zn and Mg atoms in S3, S2, S1-ES and S1-CS sites were fitted with skewed Gaussian function (see Eq. 16) to accurately derive effective interatomic distances.

$$g_i(r) = \frac{2A_i}{\sigma_i\sqrt{2\pi}} e^{\left(\frac{(r-r_i)^2}{2\sigma_i^2}\right)} \Phi\left(\lambda_i \frac{r-r_i}{\sigma_i}\right), \quad (16)$$

where λ_i – is the parameter that controls skewness; A_i – amplitude of the Gaussian function describing RPDF; r_i – center of skewed Gaussian function; σ_i – the width of Gaussian function; Φ – standard cumulative distribution function. Hence, the maximum of fitted skewed Gaussian function (r_{max}) can be calculated using Eq. 17:

$$r_{max} = r_i + \sigma_i \lambda_i \frac{e^{\left(\frac{(r_{max}-r_i)^2}{2\sigma_i^2}\right)}}{\sqrt{2\pi}\Phi\left(\lambda_i \frac{r_{max}-r_i}{\sigma_i}\right)} \quad (17)$$

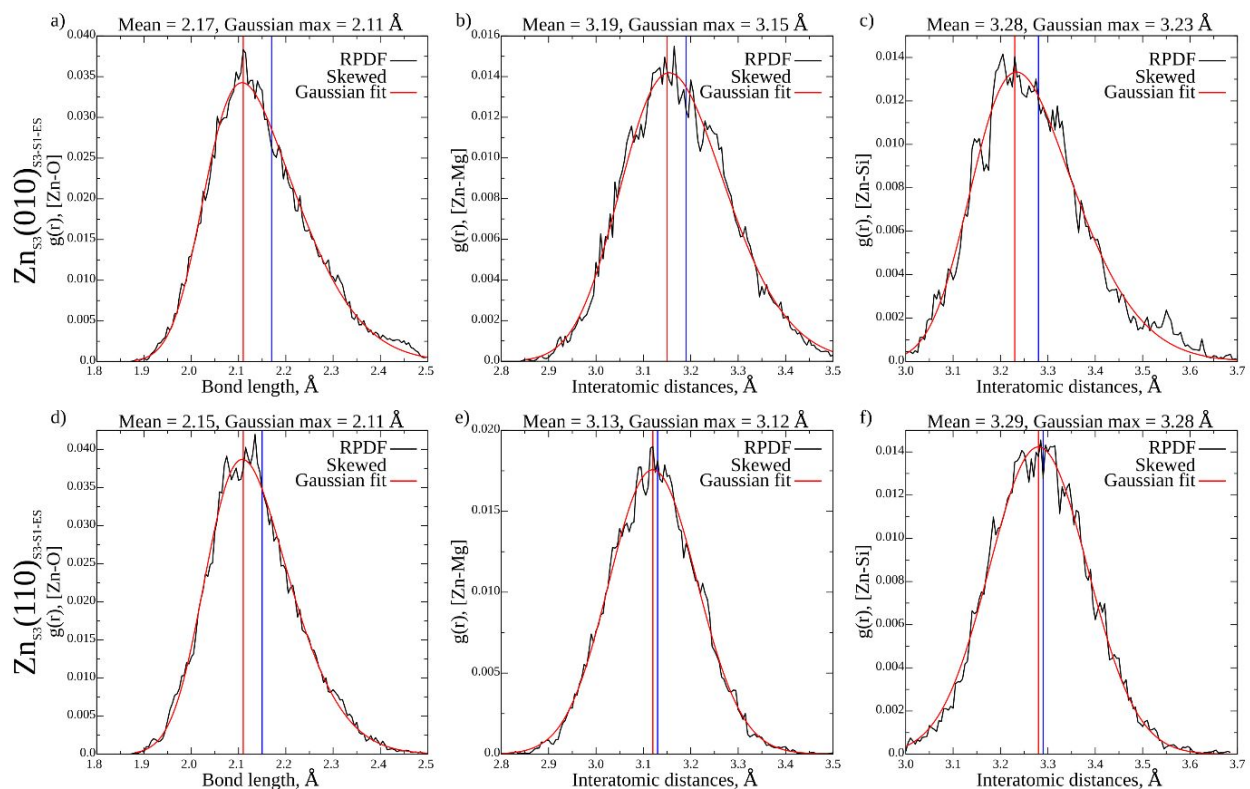


Figure S9. Radial pair distribution functions for first three coordination shells of Zn sorbed on S3 site on (010) (a-c) and (110) (d-f) surfaces: radial pair distribution function for Zn-O (a, d), Zn-Mg (b, e), and Zn-Si (c, f) pairs in a whole equilibrated 10 ps long ab initio MD trajectories used to simulate theoretical EXAFS spectra.

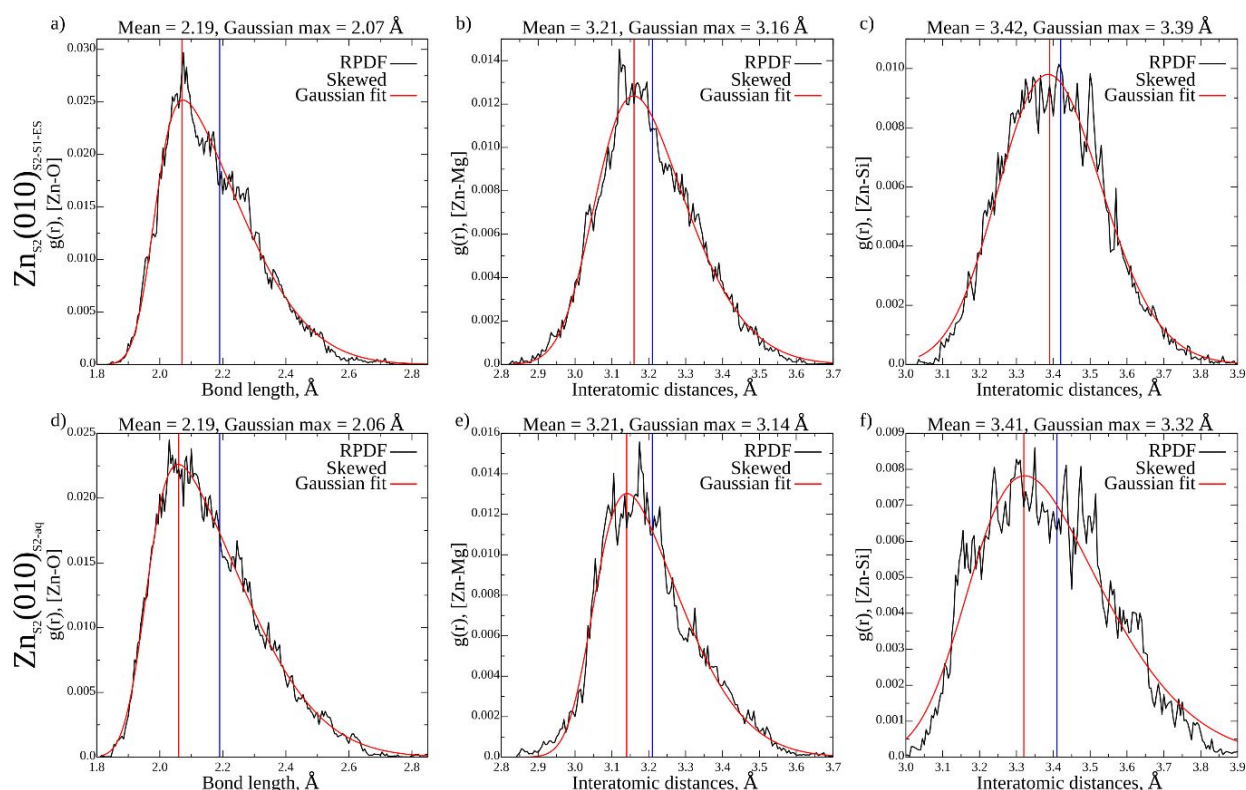


Figure S10. Radial pair distribution functions for first three coordination shells of Zn sorbed on S2 site on (010) saponite edge surface: radial pair distribution function for Zn-O (a, d), Zn-Mg (b, e), and Zn-Si (c, f) pairs in a two independently equilibrated 10 ps long ab initio MD trajectories used to simulate theoretical EXAFS spectra.

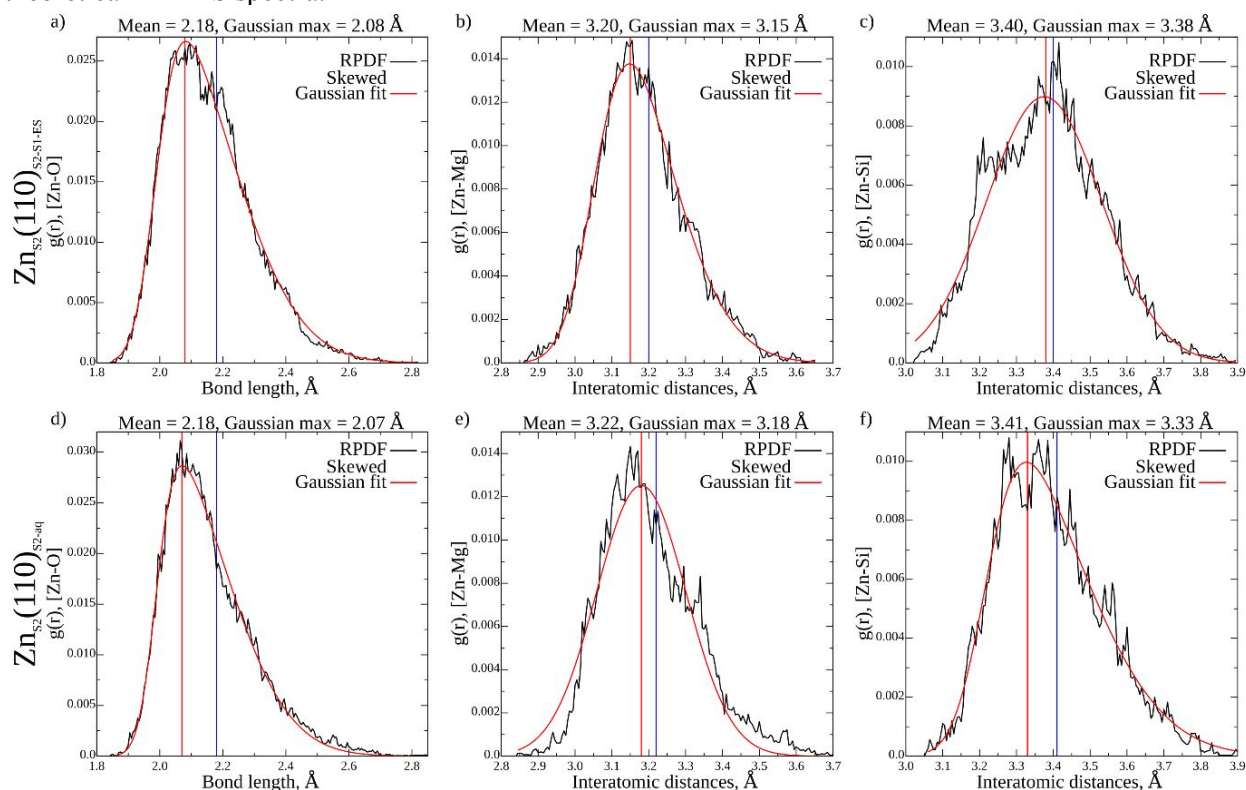


Figure S11. Radial pair distribution functions for first three coordination shells of Zn sorbed on S2 site on (110) saponite edge surface: radial pair distribution function for Zn-O (a, d), Zn-Mg (b, e), and Zn-Si (c, f) pairs in a two independently equilibrated 10 ps long ab initio MD trajectories used to simulate theoretical EXAFS spectra.

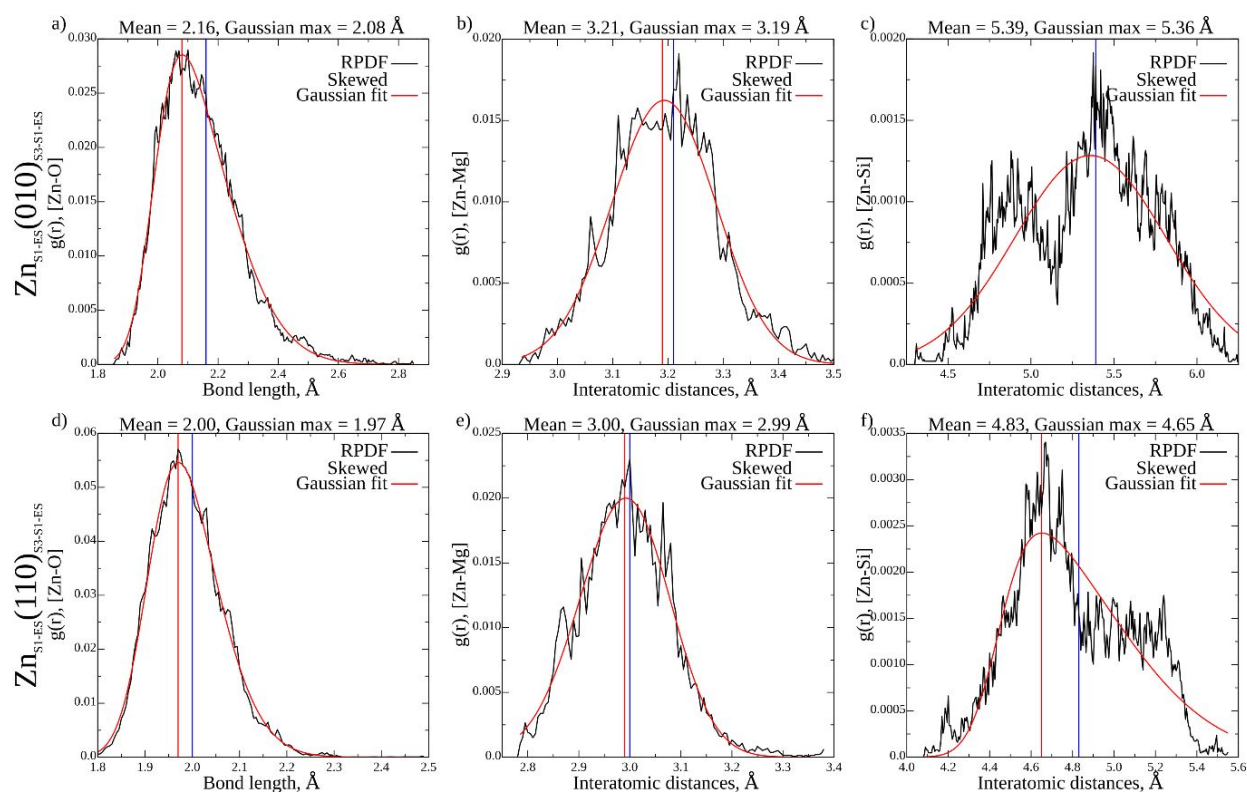


Figure S12. Radial pair distribution functions for first three coordination shells of Zn sorbed on S1-ES (bidentate) site on (010) (a-c) and (110) (d-f) surfaces: radial pair distribution function for Zn-O (a, d), Zn-Mg (b, e), and Zn-Si(c, f) pairs in a whole equilibrated 10 ps long ab initio MD trajectories used to simulate theoretical EXAFS spectra.

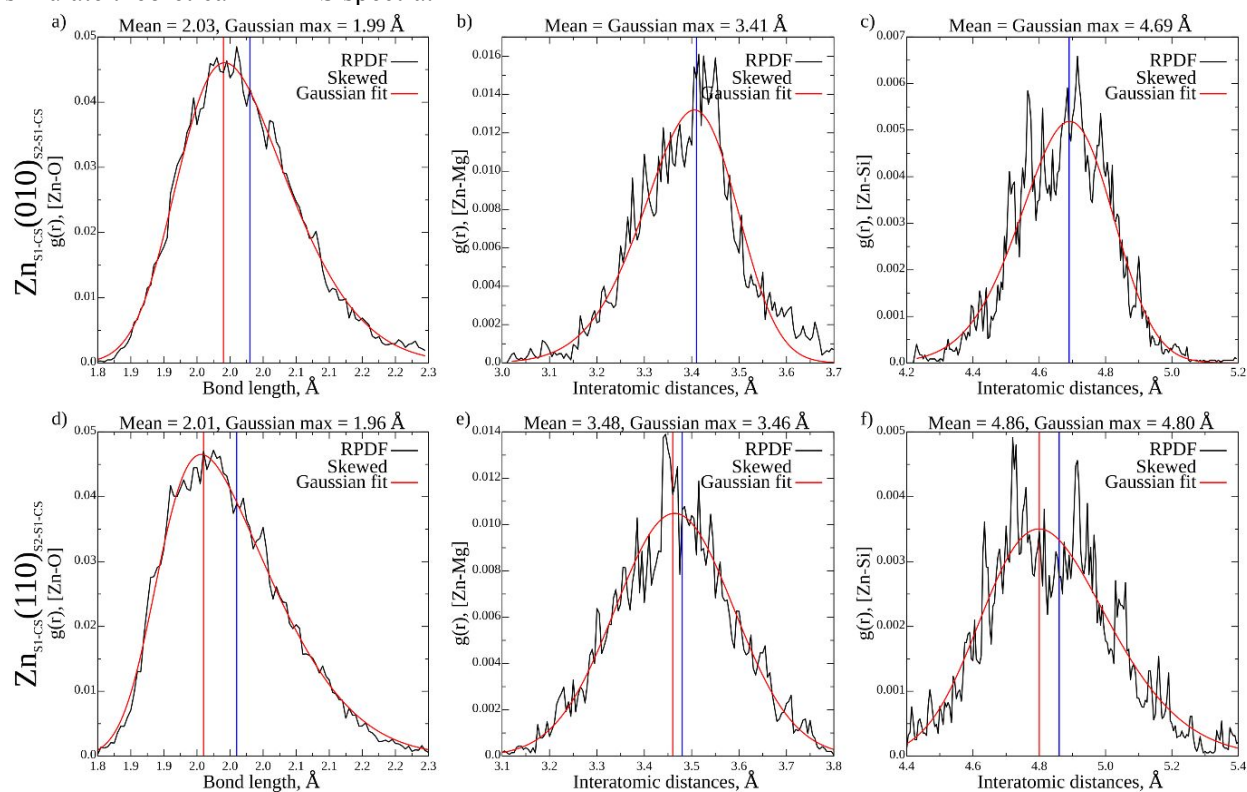


Figure S13. Radial pair distribution functions for first three coordination shells of Zn sorbed on S1-CS (monodentate) site on (010) (a-c) and (110) (d-f) surfaces: radial pair distribution function for Zn-O (a, d), Zn-Mg (b, e), and Zn-Si(c, f) pairs in a whole equilibrated 10 ps long ab initio MD trajectories used to simulate theoretical EXAFS spectra.

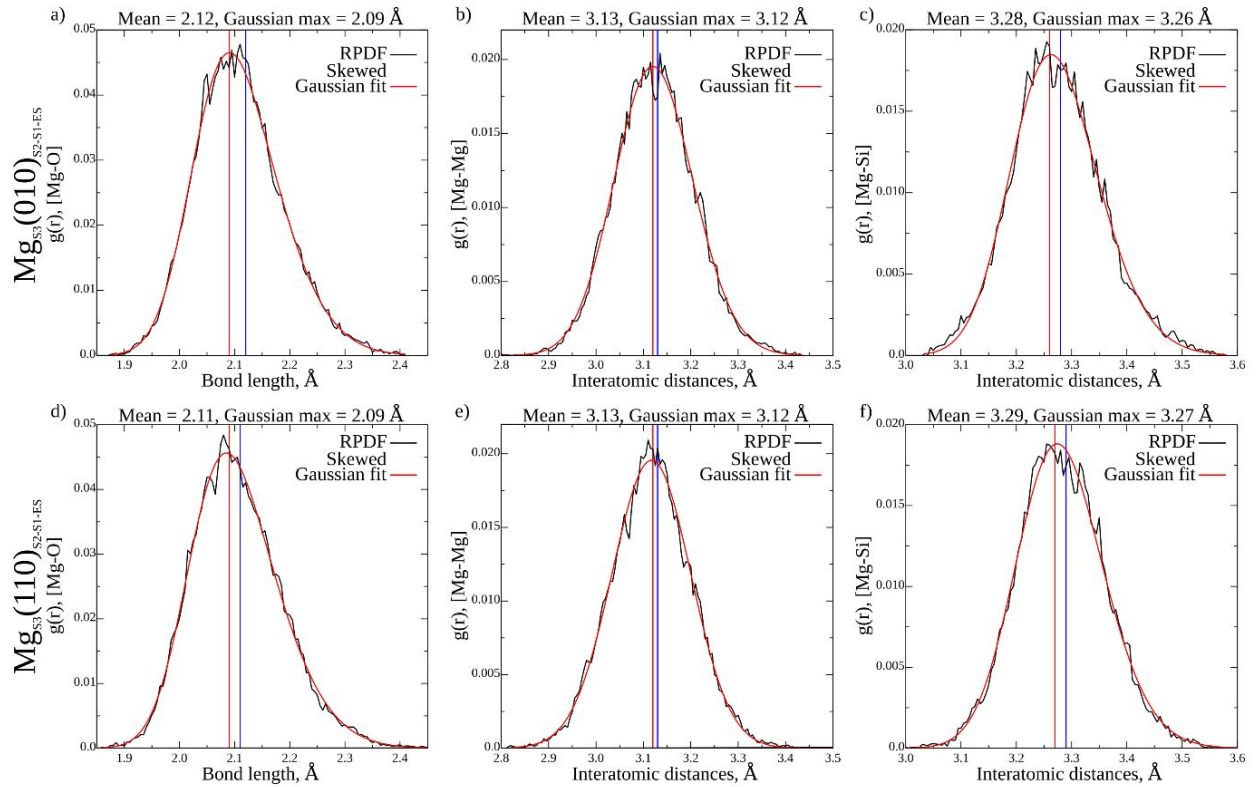


Figure S14. Radial pair distribution functions for first three coordination shells of structural Mg in S3 site position on (010) (a-c) and (110) (d-f) surfaces: radial pair distribution function for Mg-O (a, d), Mg-Mg (b, e), and Mg-Si (c, f) pairs in a whole equilibrated 10 ps long ab initio MD trajectories used to simulate theoretical EXAFS spectra.

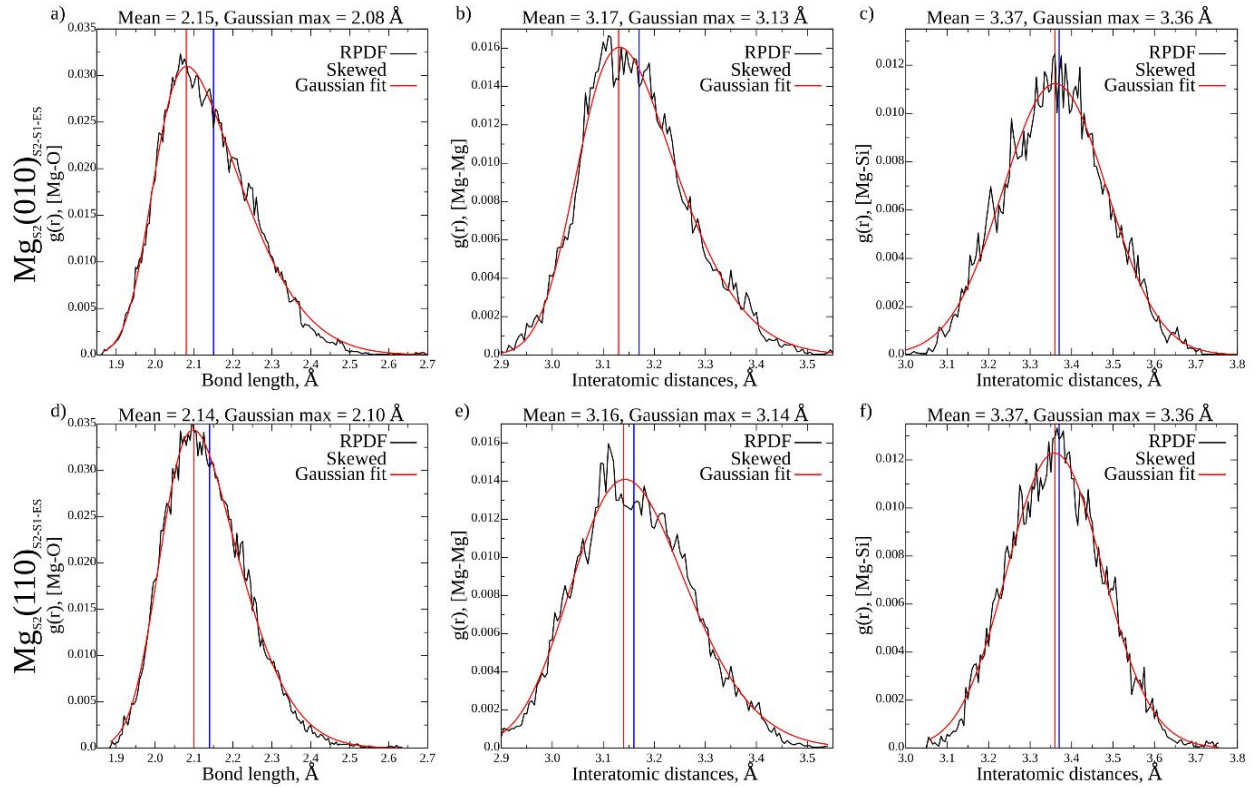


Figure S15. Radial pair distribution functions for first three coordination shells of structural Mg in S2 site position on (010) (a-c) and (110) (d-f) surfaces: radial pair distribution function for Mg-O (a, d), Mg-Mg (b, e), and Mg-Si (c, f) pairs in a whole equilibrated 10 ps long ab initio MD trajectories used to simulate theoretical EXAFS spectra.

References

- (1) Baeyens, B.; Bradbury, M. H. Cation Exchange Capacity Measurements on Illite Using the Sodium and Cesium Isotope Dilution Technique: Effects of the Index Cation, Electrolyte Concentration and Competition: Modeling. *Clays Clay Miner.* **2004**, *52* (4), 421–431. <https://doi.org/10.1346/CCMN.2004.0520403>.
- (2) Scheinost, A. C.; Claussner, J.; Exner, J.; Feig, M.; Findeisen, S.; Hennig, C.; Kvashnina, K. O.; Naudet, D.; Prieur, D.; Rossberg, A.; Schmidt, M.; Qiu, C.; Colomp, P.; Cohen, C.; Dettona, E.; Dyadkin, V.; Stumpf, T. ROBL-II at ESRF: A Synchrotron Toolbox for Actinide Research. *J. Synchrotron Radiat.* **2021**, *28* (Pt 1), 333–349. <https://doi.org/10.1107/s1600577520014265>.
- (3) Dähn, R.; Scheidegger, A.; Manceau, A.; Schlegel, M.; Baeyens, B.; Bradbury, M. H. Ni Clay Neoformation on Montmorillonite Surface. *J. Synchrotron Radiat.* **2001**, *8* (2), 533–535. <https://doi.org/10.1107/S0909049500017817>.
- (4) Manceau, A.; Chateigner, D.; Gates, W. P. Polarized EXAFS, Distance-Valence Least-Squares Modeling (DVLS), and Quantitative Texture Analysis Approaches to the Structural Refinement of Garfield Nontronite. *Phys. Chem. Miner.* **1998**, *25* (5), 347–365. <https://doi.org/10.1007/s002690050125>.
- (5) Ankudinov, A. L.; Ravel, B.; Rehr, J. J.; Conradson, S. D. Real-Space Multiple-Scattering Calculation and Interpretation of x-Ray-Absorption near-Edge Structure. *Phys Rev B* **1998**, *58* (12), 7565–7576. <https://doi.org/10.1103/PhysRevB.58.7565>.
- (6) Ankudinov, A. L.; Nesvizhskii, A. I.; Rehr, J. J. Dynamic Screening Effects in X-Ray Absorption Spectra. *Phys Rev B* **2003**, *67* (11), 115120. <https://doi.org/10.1103/PhysRevB.67.115120>.
- (7) Rehr, J. J.; Kas, J. J.; Vila, F. D.; Prange, M. P.; Jorissen, K. Parameter-Free Calculations of X-Ray Spectra with FEFF9. *Phys Chem Chem Phys* **2010**, *12* (21), 5503–5513. <https://doi.org/10.1039/B926434E>.
- (8) Stotskyi, V.; Di Lorenzo, F.; Marques Fernandes, M.; Krack, M.; Scheinost, A. C.; Lanson, M.; Lanson, B.; Churakov, S. V. Local Crystal Structure of Ni²⁺- and Zn²⁺-Doped Saponite Determined by EXAFS Spectroscopy and Ab Initio MD Modeling. *J. Phys. Chem. C* **2025**, *129* (30), 13691–13704. <https://doi.org/10.1021/acs.jpcc.5c01314>.
- (9) Bradbury, M. H.; Baeyens, B. A Mechanistic Description of Ni and Zn Sorption on Na-Montmorillonite Part II: Modelling. *J. Contam. Hydrol.* **1997**, *27* (3), 223–248. [https://doi.org/10.1016/S0169-7722\(97\)00007-7](https://doi.org/10.1016/S0169-7722(97)00007-7).
- (10) Kulik, D. A.; Wagner, T.; Dmytrieva, S. V.; Kosakowski, G.; Hingerl, F. F.; Chudnenko, K. V.; Berner, U. R. GEM-Selektor Geochemical Modeling Package: Revised Algorithm and GEMS3K Numerical Kernel for Coupled Simulation Codes. *Comput. Geosci.* **2013**, *17* (1), 1–24. <https://doi.org/10.1007/s10596-012-9310-6>.
- (11) Wagner T., Kulik D.A., Hingerl F.F., D. S. V. GEM-Selektor Geochemical Modeling Package: TSolMod Library and Data Interface for Multicomponent Phase Models. *Can. Mineral.* **2012**, *50*, 1173–1195.
- (12) Kulik, D. A.; Fernandes, M. M.; Baeyens, B. The 2SPNE SC/CE Sorption Model in GEM-Selektor v.3.4 Code Package (ClaySor): Implementation, Tests, and User Guide. *Nagra Work Rep. NAB 18–27* **2018**, 152.
- (13) Marinich, O.; Miron, G. D.; Kulik, D. A.; Fernandes, M. M.; Baeyens, B. ClaySor 2023: Implementation of the 2SPNE SC/CE Sorption Model and Database for Deep Geological Repository Safety Assessment. *Appl. Geochem.* **2025**, *191*, 106510. <https://doi.org/10.1016/j.apgeochem.2025.106510>.
- (14) Di Lorenzo, F.; Stotskyi, V.; Scheinost, A. C.; Rossberg, A.; Lanson, M.; Lanson, B.; Churakov, S. V.; Fernandes, M. M. Ni Retention Mechanisms by Trioctahedral Smectite (Saponite) Investigated by Polarized x-Ray Absorption Spectroscopy and Implications for Surface Complexation Modelling. *Prep* **2026**.
- (15) Hummel, W.; Thoenen, T. The PSI Chemical Thermodynamic Database 2020. Nagra Technical Report 21-03., 2023, 1–1253.
- (16) Shock, E. L.; Sassani, D. C.; Willis, M.; Sverjensky, D. A. Inorganic Species in Geologic Fluids: Correlations among Standard Molal Thermodynamic Properties of Aqueous Ions and

- Hydroxide Complexes. *Geochim. Cosmochim. Acta* **1997**, *61* (5), 907–950.
[https://doi.org/10.1016/S0016-7037\(96\)00339-0](https://doi.org/10.1016/S0016-7037(96)00339-0).
- (17) Miron, G. D.; Kulik, D. A.; Dmytrieva, S. V.; Wagner, T. GEMSIFTS: Code Package for Optimization of Geochemical Model Parameters and Inverse Modeling. *Appl. Geochem.* **2015**, *55*, 28–45. <https://doi.org/10.1016/j.apgeochem.2014.10.013>.
 - (18) Johnson, S. G. The NLOpt Nonlinear-Optimization Package, 2007.
<https://github.com/stevengj/nlopt>.
 - (19) Hill, M. C.; Tiedeman, C. R. *Effective Groundwater Model Calibration: With Analysis of Data, Sensitivities, Predictions, and Uncertainty*; 2007. <https://doi.org/10.1002/0470041080>.
 - (20) Motulsky, H.; Christopoulos, A. *Fitting Models to Biological Data Using Linear and Nonlinear Regression: A Practical Guide to Curve Fitting*; Oxford University Press, 2023.
<https://doi.org/10.1093/oso/9780195171792.003.0027>.
 - (21) Tennøe, S.; Haldnes, G.; Einevoll, G. T. Uncertainpy: A Python Toolbox for Uncertainty Quantification and Sensitivity Analysis in Computational Neuroscience. *Front. Neuroinformatics* **2018**, *12*. <https://doi.org/10.3389/fninf.2018.00049>.
 - (22) Manceau, A.; Lanson, B.; Schlegel, M. L.; Harge, J. C.; Musso, M.; Eybert-Berard, L.; Hazemann, J.-L.; Chateigner, D.; Lambelle, G. M. Quantitative Zn Speciation in Smelter-Contaminated Soils by EXAFS Spectroscopy. *Am. J. Sci.* **2000**, *300* (4), 289–343.
<https://doi.org/10.2475/ajs.300.4.289>.
 - (23) Voegelin, A.; Pfister, S.; Scheinost, A. C.; Marcus, M. A.; Kretzschmar, R. Changes in Zinc Speciation in Field Soil after Contamination with Zinc Oxide. *Environ. Sci. Technol.* **2005**, *39* (17), 6616–6623. <https://doi.org/10.1021/es047962g>.