

Local Crystal Structure of Ni^{2+} - and Zn^{2+} -Doped Saponite Determined by EXAFS Spectroscopy and Ab Initio MD Modeling

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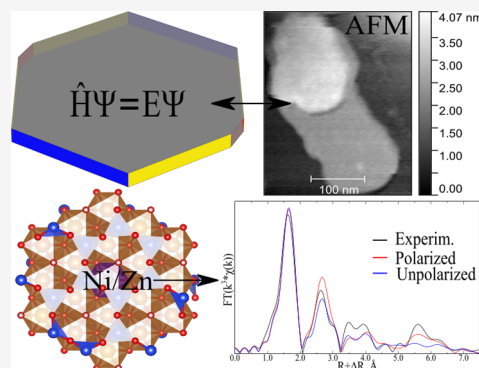


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Supporting Information

ABSTRACT: Due to their small particle size and high surface reactivity, clay minerals control geochemical conditions in soils. Particularly important are the sorption phenomena. In this work, the structure and speciation of the most stable edge surfaces of synthetic trioctahedral smectite saponite are measured by atomic force microscopy and modeled using molecular simulations based on density functional theory. The calculations predict that (110) and (010) are the most stable edge sites of saponite and dominate the particle shape at different degrees of hydration. The obtained theoretical results on the surface stability agree well with experimental observations and provide a basis for the further development of theoretical sorption complexation models. To address the thermodynamic driving force for the incorporation of trace metals into the structure of trioctahedral phyllosilicates, the free energy of Zn and Ni exchange reactions between the octahedral crystallographic site of saponite and the aqueous phase was obtained using the thermodynamic integration method. The obtained ab initio molecular dynamics trajectories were further used to derive theoretical X-ray absorption spectra of Zn and Ni incorporated into the saponite structure, which were compared with experimental X-ray absorption spectra of synthesized Zn- and Ni-doped saponite to validate the input parameters of the FEFF model.



INTRODUCTION

Clay minerals are formed by diagenesis and are ubiquitously present in both terrestrial and marine environments.¹ Due to their small particle size and highly reactive surface,² clay minerals control geochemical conditions and reactive transport phenomena in soil and argillaceous sediments (e.g., structure, permeability, swelling, buffering, cation exchange, retention of micronutrients and contaminants).^{3,4} The hydrophilic behavior⁵ of clay minerals arises from their crystal structure, in which two tetrahedral sheets (silica) sandwich an octahedral sheet (dioctahedral aluminum hydroxide or trioctahedral magnesium hydroxide). Heterovalent cationic substitutions in octahedral and/or tetrahedral sheets lead to the net negative structural charge of the TOT layer, which is compensated for by exchangeable cations in the interlayer.⁶ The high cation exchange capacity and minute crystal size of swelling clays leads to a high specific surface area per mass of material responsible for the pivotal role of swelling clay minerals in controlling pollutant behavior in natural soils and engineered barrier systems.^{7–10} Clay-based systems are commonly used as natural buffers to remediate contaminated soils and waters and to inhibit the migration of pollutants in disposal facilities for hazardous wastes (including high-level nuclear waste disposal).^{11,12}

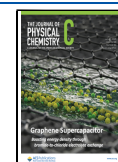
The adsorption properties of dioctahedral clay minerals (e.g., illite, montmorillonite) toward chemical elements with oxidation states from +I to +VI have been extensively addressed in the past decades by acid–base titrations, adsorption experiments, and thermodynamic modeling.¹³ Large body of available experimental data and well-defined experimental protocols allows a reliable quantification of the adsorption of a given element, the distinction of retention mechanisms (cation exchange on planar sites, surface complexation on edge sites, and surface-driven precipitation), and ultimately the derivation of thermodynamic data, which are key parameters for risk assessment. The particular success of current sorption models can be attributed to their quasimechanistic nature, which incorporates structure-related sorption sites and their respective capacities. The widely used and successful 2SPNE SC/CE model assumes the existence of two sorption sites namely high-affinity/low-capacity sites (“strong sites”) and a weak-affinity/high-capacity sites (“weak

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sites”), respectively.^{14,15} The structure of these sites has been investigated by molecular simulations and X-ray absorption spectroscopy (XAS).^{16,17}

Especially for surface complexation phenomena in phyllosilicates, true molecular scale understanding (i.e., identification of the specific crystallographic position on the surface) has not been provided for the entire range of clay mineral structures so far. Experimental and theoretical studies have been applied to investigate the structure of edge surfaces in dioctahedral clay minerals^{18–22} including the acid–base properties of the surface sites and the dissolution mechanism of the mineral surface.^{23–25} Spectroscopic measurements and ab initio simulation were applied to identify the molecular nature of high and low affinity sorption sites on dioctahedral swelling clays montmorillonite²⁶ as well as long-term entrapment of transition metals by structural incorporation.^{27,28} No detailed studies have been conducted for such trioctahedral systems so far.

Therefore, it remains to be shown whether sorption models developed and tested for dioctahedral smectites are transferable to trioctahedral clay minerals. This review aims to reveal structural and sorption properties of trioctahedral smectites by combining XAS and atomistic simulations. Natural clay minerals often contain traces of metals in their structure, making it difficult to discriminate the XAS signals originating from incorporated and adsorbed ions.^{27,28} Unlike their natural counterparts, synthetic clay minerals can be produced nearly free of impurities and with fine-tuned surface charges, which in turn make them ideal matrices for sorption experiments. This rationalizes the use of trioctahedral synthetic saponite to be the cornerstone of this study. Surface site capacity, structure, and stability of the adsorbed complexes are the key parameters in thermodynamic sorption modeling. In this study, ab initio simulations are used to determine the stability and morphology of the edge facets for the trioctahedral clay particle. The accuracy of the modeling approach is validated by spectroscopic characterization and atomic force microscopy (AFM). Finally, ab initio simulations at the level of density functional theory (DFT) were used to analyze the structure of the mineral–fluid interface and to evaluate the thermodynamic driving force for Zn and Ni incorporation in the trioctahedral clay minerals. The obtained results provide the basis for further development of thermodynamic sorption models for trioctahedral clay minerals.

MATERIALS AND METHODS

Experimental Synthesis and Samples. Natural clay minerals show a wide range of compositional impurities and structural defects. In this study, synthetic Mg-saponite was used to ensure structural homogeneity and chemical purity of the system.^{29,30} The Zn-doped saponite samples were obtained by a hydrothermal crystallization method using amorphous gel as a precursor. The synthesis conditions correspond to 400 °C and ≥ 600 bar^{30,31} and overall duration of one month. The amorphous gel used as precursor was prepared by calcination reaction of a stoichiometric mixture of analytical grade Na_2CO_3 , $\text{Mg}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, $\text{Si}(\text{OC}_2\text{H}_5)_4$ and $\text{Zn}(\text{NO}_3)_2$ at 600 °C.³² After crystallization, the obtained Zn-doped saponite was washed twice with an excess of 1 M NaCl to obtain homoionic Na-saturated saponite. The conditioning was followed by a third washing cycle with deionized water, centrifugation of the solids at 9600 rpm, and freeze-drying the

resulting hydrous paste for 48 h. The purity and crystallinity of the white Zn-doped saponite powder were confirmed by powder XRD measurements on oriented samples (see Supporting Information Figure S5). Ni-doped samples available from the previous study²⁹ were synthesized following the same synthesis methodology. Full list of synthesized samples measured using X-ray absorption spectroscopy is provided in Table 1.

Table 1. Ni- and Zn- Concentration in Doped Saponite Samples Used for Polarized XAS Measurements

sample name	[Me ²⁺] concentration, mmol/kg	measured polarization angles, °
NiSapD1	2	10, 35, 55, 80
NiSapD2	20	10, 35, 55, 80
NiSapD3	200	10, 35, 55, 80
ZnSapD1	2	10, 35, 70
ZnSapD3	200	10, 35, 70

XAS Measurements and Data Postprocessing. The X-ray absorption measurements were performed at the Rossendorf Beamline (ROBL, BM20) at the European Synchrotron Radiation Facility (ESRF) in Grenoble.³³ 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 m long silicon mirrors with a grazing incidence of 2.5×10^{-3} radians. Ni-(8333 eV) and Zn-(9659 eV) K edge XAS were recorded in both fluorescence and transmission modes. Simultaneously, a metallic nickel (or copper) foil was measured in transmission mode to allow for an accurate energy calibration of each scan. The 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 significantly improving 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 described in refs 34,35. 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 by using Kapton tape. A rotating sample holder was used to perform the angular-dependent measurement with an accuracy of $\pm 5^\circ$ (α angle). The fluorescence EXAFS spectra were averaged from 17 fluorescence signal channels and several scans using SixPack 1.4 software package.³⁶ Shell fitting was conducted from 2 to 12.0 Å^{−1}.

Normalization of the measured XAS spectra and extraction of EXAFS converted from energy to k space was performed using the WinXAS 3.2 code.³⁷ Similarly to the analysis of Ni K-edge measurements,²⁹ Zn EXAFS shell fitting was carried with the Artemis software package³⁸ based on scattering paths generated with FEFF 9.6.4,^{39–41} using the crystal structure of talc⁴² where one Mg in octahedral position was replaced by Zn. Shell fitting of P-EXAFS was limited to the first three coordination shells (Zn–O, Zn–Mg, and Zn–Si), following the procedure established for nontronite³⁵ and hectorite.⁴³ For

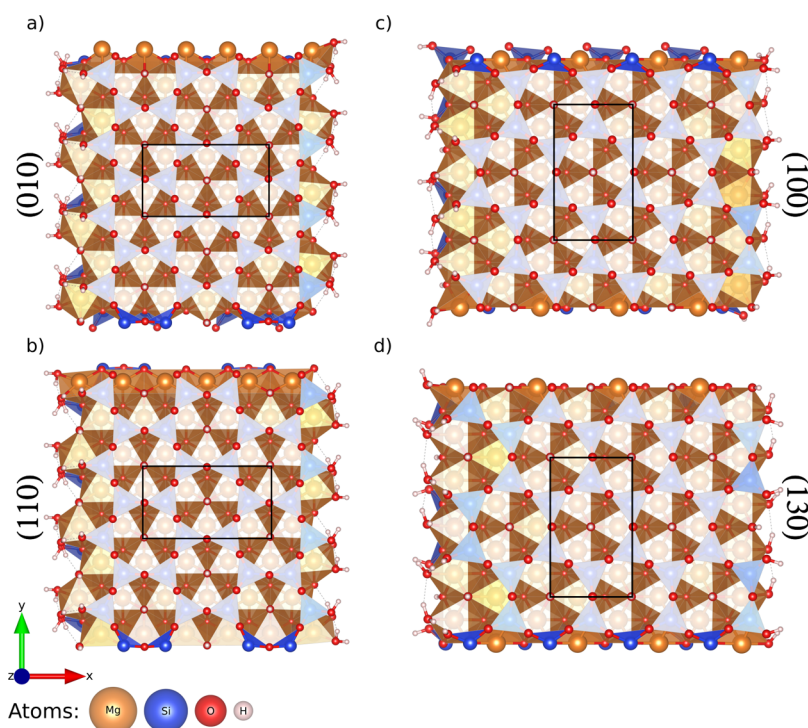


Figure 1. Water covered optimized edge surfaces of talc: (a) (010), (b) (110), (c) (100), and (d) (130). Each surface was modeled using $4 \times 2 \times 1$ talc unit cells with fixed interlayer distance and at least 10 Å vacuum along the x -axis. Black rectangles illustrate the dimensions of the talc unit cell.

instance, the Zn–O bond distance obtained for the 35° polarization angle was fixed for the spectra obtained at the other angles, whereas Zn–Mg and Zn–Si distances were fixed to values obtained at 10 and 70° , respectively, i.e., at the angle where each of the backscattering pairs is most purely expressed. Debye–Waller factors for Zn–O and Zn–Mg shells were constrained to $0.007 \text{ \AA}^2$, analogous to the values used in Ni spectra shell fitting performed by Di Lorenzo et al.²⁹ Based on previous studies of Zn containing clay minerals^{17,44,45} and own experience of fitting other Zn samples, this value was increased to $0.015 \text{ \AA}^2$ for the Zn–Si shell. The amplitude reduction factor (S_0^2) was set to 0.9 for all shells. The shell fitting results for the 35° (close to magic angle) polarization angle are reported in Table 4. For the sake of completeness, the coordination numbers and graphical representations of fits for other angles are reported in the Supporting Information (see Figure S9 and Table S2). Fourier transform magnitude (FTM) plots (see Figure 4) were obtained using full-length k^3 -weighted original $\chi(k)$ spectra measured at a 35° polarization angle.

System Setup for First Principle Simulations. Saponite is a swelling trioctahedral TOT-clay mineral with Al partially substituting for Si atoms in tetrahedral sheets, while octahedral sheets are fully occupied by Mg. The negative structural charge in the TOT layer is compensated for by Na ions in the interlayer. Structurally, saponite is similar to another uncharged clay mineral - talc. Talc is a trioctahedral TOT-phyllsilicate, with octahedral sheets fully occupied by Mg and tetrahedral sheets fully occupied by Si atoms. To avoid ambiguity in the simulation setup regarding Al–Si substitutions in the tetrahedral sheets, the structural model of talc⁴⁶ C1 , $a = 5.29 \text{ \AA}$, $b = 9.173 \text{ \AA}$, $c = 9.46 \text{ \AA}$, $\alpha = 90.46^\circ$, $\beta = 98.68^\circ$, $\gamma = 90.09^\circ$ was used as the proxy for saponite throughout all simulations. Accordingly, the names talc and saponite are used interchangeably in the discussion of molecular simulations and

comparison of theoretical results with spectroscopic data. 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 in talc by weak dispersion interactions. As the primary focus of this work is the structure of edge surfaces controlled by rearrangement of cation-oxygen bonds and hydrolysis, which are much stronger than the dispersive interactions between basal planes, the model setup was simplified by using an orthorhombic supercell. The simulations were performed in supercells composed by $4 \times 2 \times 1$ unit cells of talc (see Figure 1). Low-index surfaces (100), (010), (110), and (130) were simulated at different water coverages to reveal structure, stoichiometry, and preferential stability of edge sites. In the simulation setup the edge surface is oriented normal to the a -dimension of the supercell (see Figure 1). To avoid spurious interaction between periodic images, the edge surfaces used for surface energy determination were separated by at least 10 Å distance.

DFT-Based Simulations. Structural optimization and ab initio molecular dynamics simulations were performed using the DFT approach applying 3D periodic boundary conditions. The simulations were carried out with the CP2K open-source software using the Gaussian plane wave (GPW) method.^{47–49} Goedecker, Teter, and Hutter (GTH) scalar-relativistic norm-conserving pseudopotentials⁵⁰ were applied to avoid the explicit consideration of the core electrons. Following medium-core pseudopotentials were applied: [Ne] $3s^2 3p^6 4s^2 3d^8$ for Ni, [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.⁵¹ The electronic charge density was expanded in an auxiliary basis set of plane waves by using a density cutoff of 450 Ry. To validate the accuracy of

structural predictions and surface energy calculations, the geometry optimizations were performed using both 450 and 700 Ry density cutoff. The accuracy of the basis set convergence and the pseudopotential approximation was carefully analyzed and described in the section [Model Uncertainties](#). The exchange and correlation (XC) functional of Perdew, Burke and Ernzerhof (PBE)⁵² in its spin polarized implementation was used for all simulations. The electronic state of nickel Ni^{2+} was described with spin multiplicity $(2S + 1) = 3$. A dispersion correction DFT-D3 was applied according to refs [53](#) and [54](#). The energy in each self-consistent field cycle was converged to the 10^{-6} a.u. criterion. Conventional DFT is known to underestimate the Coulomb repulsion for the 3d-electrons, which leads to a delocalization of the 3d-states.⁵⁵ Therefore, the so-called DFT + U method was applied to improve the description of 3d-states within the DFT formalism.⁵⁶ In this method, the conventional DFT equations are augmented with the so-called Hubbard-term (U_{eff}), which impose an additional potential enhancing selective localization of the 3d-states. The value of U_{eff} is transferable between different systems but depends on the specific implementation (population analysis and, hence, basis set)⁵⁷ in the simulation code and has to be calibrated. The Hubbard potential of 1.545 eV was obtained for Ni atoms by fitting band gap value of an antiferromagnetic NiO ⁵⁸ (see SI [Figure S7](#)). The U_{eff} value for Zn was fixed at 1.0 eV according to previous benchmarking studies.⁵⁹

Surface Energies. Surface and water adsorption energies were calculated at different degrees of hydration using [eqs 1](#) and [2](#).

$$\Gamma_{hk0} = \frac{E_{(\text{surf}+m\text{H}_2\text{O})} - n(\text{bulk}) \times E_{(\text{bulk})} - m(\text{H}_2\text{O}) \times (E_{\text{H}_2\text{O}} + E_{\text{ZPE}} + \Delta\mu_{\text{H}_2\text{O}}^{298})}{A_{hk0}} \times N_A \quad (1)$$

where Γ_{hk0} , surface energy of respective $(hk0)$ surface, $\text{J}/\text{\AA}^2$; $E_{(\text{surf}+m\text{H}_2\text{O})}$ and E_{bulk} , energies of hydrated talc surface and one bulk talc unit cell, respectively, J/mol ; $n(\text{bulk})$, number of talc unit cells in bare surface; $m(\text{H}_2\text{O})$, number of water molecules adsorbed on the edge surface, $m \geq 0$; E_{ZPE} , the zero-point vibrational energy; A_{hk0} , total surface specific surface area, $\text{\AA}^2$; N_A , Avogadro's number.

$$\Delta E_{\text{ads}}(\text{H}_2\text{O}) = \frac{E_{(\text{surf}+m\text{H}_2\text{O})} - n(\text{bulk}) \times E_{(\text{bulk})}}{m(\text{H}_2\text{O})} - (E_{\text{H}_2\text{O}} + E_{\text{ZPE}} + \Delta\mu_{\text{H}_2\text{O}}^{298}) \quad (2)$$

where $\Delta E_{\text{ads}}(\text{H}_2\text{O})$, talc water adsorption energy per molecule, J/mol ; $E_{(\text{surf}+m\text{H}_2\text{O})}$, energy of system with $m(\text{H}_2\text{O})$ molecules, J/mol ; $E_{(\text{bare surf})}$, energy of bulk talc structure with n structural units, J/mol ; $E_{\text{H}_2\text{O}}$, energy of an isolated water molecule in gas phase, J/mol ; $\Delta\mu_{\text{H}_2\text{O}}^{298}$, water thermochemical correction term, J/mol . The thermodynamic properties of clay particles are approximated by cohesive energy, e.g., neglecting the thermal contribution to the free energy. This is an acceptable approximation for solids as this term is small. In order to account for the change in free energy of water between 0 K and standard thermodynamic conditions ($T = 298 \text{ K}$, $P_0 = 1 \text{ bar}$), a thermochemical correction term ([eq 3](#)) was added based on data reported in our previous study.⁶⁰ The zero-point

vibrational energy was obtained with Gaussian,⁶¹ whereas the chemical potential correction for bulk water from gas phase calculations was calculated using standard tabulated water thermodynamic data.⁶² The partial pressure of saturated water vapor at 298 K was set equal to 0.0314 bar.

$$\Delta\mu_{\text{H}_2\text{O}}^{298} = \Delta_f H_{\text{gas}}^{298}(\text{H}_2\text{O}) + T[298] \times S_{\text{gas}}^{298}(\text{H}_2\text{O}) - RT \ln \left(\frac{p_{\text{sat}}(\text{H}_2\text{O})}{P_0} \right) - \Delta H_{\text{gas}}^0(\text{H}_2\text{O}) \quad (3)$$

where $\Delta\mu_{\text{H}_2\text{O}}^{298}$, water thermochemical correction term, J/mol ; $\Delta_f H_{\text{gas}}^{298}(\text{H}_2\text{O})$ and $\Delta H_{\text{gas}}^0(\text{H}_2\text{O})$, formation enthalpies of gas phase at 298 and 0 K, J/mol ; T , temperature, K; $S_{\text{gas}}^{298}(\text{H}_2\text{O})$, entropies of water gas phase at 298 K, $\text{J}/(\text{mol K})$; $p_{\text{sat}}(\text{H}_2\text{O})$, partial pressure of saturated water vapor. P_0 , pressure at standard state, 1 bar; R , gas constant, 8.314 $\text{J}/(\text{mol K})$.

The equilibrium shape of clay particles at different degrees of hydration was obtained with Wulff constructions using the WulffPack Python package.⁶³

Molecular Dynamics Simulations. Surfaces with the lowest surface energies were used to construct cation exchange models for molecular dynamics simulations ([Figure 2](#)).

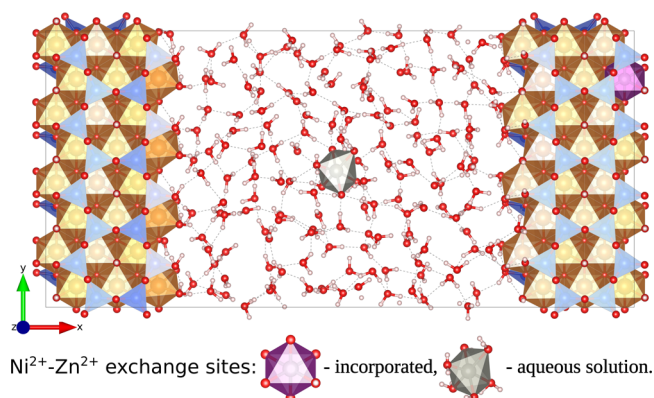
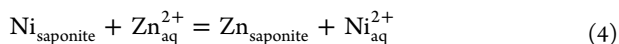


Figure 2. System setup for the simulation of cation exchange using the thermodynamic integration method: incorporated Ni^{2+} cation being exchanged with Zn^{2+} in aqueous solution. Initial distribution of water at the (110) edge surface was pre-equilibrated using classical MD simulations. Color coding for the atoms is described in [Figure 1](#).

Prior to ab initio MD simulations, the distribution of water molecules in the interparticle space was pre-equilibrated using classical molecular dynamics simulations with ClayFF force field⁶⁴ using LAMMPS code.⁶⁵ The number of water molecules and the inter particle pore size were optimized to obtain 1 g/mL water density in the middle of inter particle pore (see SI [Figure S6](#)). 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. Temperature of the NVT ensemble constrained system (e.g., constant number of particles, volume, and temperature) was controlled by a Nose-Hoover thermostat with a relaxation time constant of 1 ps. Final structures ready for ab initio MD simulations contained 896 atoms and had following dimensions: for (010) - $a = 45.33 \text{ \AA}$, $b = 21.29 \text{ \AA}$, $c = 9.46 \text{ \AA}$; for (110) - $a = 45.34 \text{ \AA}$, $b = 21.28 \text{ \AA}$, $c = 9.46 \text{ \AA}$ (see [Figure 2](#)).

Ab initio MD simulations were performed using structure model of (110) surface within the NVT-ensemble at 300 K by applying canonical sampling through velocity rescaling (CSVR) thermostat.⁶⁶ The system was thermostated every 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.

Thermodynamic Integration. Thermodynamic integration method was applied to calculate the free energy of ion exchange reactions between solution and the surface complexes according to eq 4.



The Helmholtz free energy of the reaction (eq 4) was calculated using thermodynamic integration method employing molecular dynamics simulations of a system described by a λ -dependent Hamiltonian at the DFT level of theory:⁶⁷

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

where $\hat{H}_0$ and $\hat{H}_1$ are Hamiltonians of the system describing reactants and products in eq 4, respectively. The free energy of the exchange reaction is obtained by

$$\Delta A = \int_0^1 d\lambda \langle \Delta E \rangle_{H(\lambda)} \quad (6)$$

where $\langle \Delta E \rangle_{H(\lambda)}$ is the potential energy for ion exchange (eq 4) averaged over the ensemble described by a λ -dependent Hamiltonian (eq 5). The same approach has been successfully used to describe cation exchange in calcium silicate hydrates.⁶⁸

The integral in eq 6 was approximated by Simpson's formula:

$$\Delta A \approx \Delta \bar{A} = \frac{1}{6} [\Delta E_{\lambda=0} + 4\Delta E_{\lambda=0.5} + \Delta E_{\lambda=1}] \quad (7)$$

The equilibrium constant of the simulated ion exchange reaction and thus the pK value was obtained using eq 8 and compared with experimentally derived data neglecting the volumetric change in the Gibbs free energy of the reaction.

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

According to eq 7 three independent trajectories are necessary to calculate the free energy. The length of the sampling trajectory was kept constant (10 ps), depending on the convergence of the target quantities, followed by at least 6 ps of equilibration. Standard deviations (σ) of thermodynamic properties were estimated using half of the equilibrated (10 ps long) trajectory:

$$\begin{aligned} \sigma &\approx |\Delta \bar{A}_{\text{half}} - \Delta \bar{A}| \text{ or} \\ &\approx |\Delta E_{\lambda_{\text{half}}} - \Delta E_{\lambda}| \end{aligned} \quad (9)$$

The initial configuration for the ab initio runs was taken from our previous DFT simulations of saponite edge surfaces.

EXAFS and XANES Simulation. The theoretical (Zn and Ni) EXAFS spectra and those measured for saponite doped with Zn and Ni were used to validate the simulation approach. Theoretical EXAFS spectra were calculated based on molecular configurations derived from ab initio MD simulations using the

FEFF 9.6 software.^{39–41} The software was configured to consider up to 430,000 scattering paths. For each atomic configuration, the scattering potentials of the atoms were calculated self-consistently³⁹ using a cluster with a radius of 5 Å around the absorbing atom. Multiple scattering paths up to 8 legs (NLEG 8) were collected for the cluster radius of 7.5 Å. The amplitude reduction factor (S_0^2) was set equal to 0.9, a value typically used for fitting experimental EXAFS data. The thermal disorder of EXAFS spectra was taken into account by averaging statistically independent (i.e., separated by 100 fs) molecular configurations from ab initio MD trajectories conducted at 300 K. In total 101 individual spectra for each molecular configuration were calculated using a global Debye–Waller factor (SIG2) of zero, which were then averaged to obtain theoretical spectra for the different Zn and Ni species. These were used for component-specific analysis of the measured experimental data. Based on the comparison of theoretical and measured spectra a correction factor of -7.0 and -2.0 eV was applied to align the SCF calculated and measured edge energy shift for Ni and Zn, respectively (see SI Figure S2). A relatively large ΔE_0 shift for Ni is applied to compensate for a large difference between the Fermi energy ($E_F = 8337.2$ eV) and experimental $E_0 = 8346.2$ eV derived as the edge inflection energy. A detailed description of the alignment of theoretical and experimental spectra is provided in the Supporting Information. The theoretical spectra were obtained for trace concentration of Zn and Ni in the structure (i.e., single atom Ni or Zn atom in the 7.5 Å cluster radius), and for Zn–Zn or Ni–Ni pairs located in the second nearest octahedral positions (i.e., 6 Å distance). The linear combination fit to the experimental EXAFS spectra was performed within a $k(\text{\AA}^{-1})$ interval of $\in [2.8, 12.5]$ to evaluate the possibility of Ni–Ni and Zn–Zn clustering in the doped samples. The fit was performed according to eq 10 after maximum normalization to the value of the first oscillation of the calculated and the measured spectra:

$$Q = \left\| k^3 \left(\sum_i a_i^2 \chi(k)_i - \chi(k)_{\text{exper.}} \right) \right\|^2 + \left\| a_i^2 \right\|^2 \Rightarrow \min \quad (10)$$

where $\chi(k)_i$ and $\chi(k)_{\text{exper.}}$ are the calculated and the experimental EXAFS spectra, respectively; a_i^2 are the fitting parameters for the theoretical structures.

The XANES spectra were obtained using two methods: (1) fully relativistic DFT with the local spin-density approximation (DFT-LSDA) implemented in FDMNES code⁶⁹ through finite difference method; (2) real space multiple scattering (RSMS) calculations implemented in FEFF9.6.^{39–41} The XANES specific input in FEFF is almost identical to setup described for EXAFS with the exception of substituting EXAFS specific input parameters by their XANES counterparts and absence of Fermi energy correction since, in contrary to EXAFS, XANES absolute energy alignment was achieved without aligning theoretical and experimental E_0 (see SI Figure S1). The scattering potentials of the atoms in FDMNES simulations were calculated self-consistently for each atomic configuration within 5 Å distance from absorbing atom. The total size of the molecular cluster used to obtain reference 101 XANES spectra for each element (separated by 100 fs time interval) was limited to 7.5 Å to eliminate any discrepancies between the FEFF and FDMNES generated XANES due to difference in system (absorption cluster) size. Convolved theoretical

Table 2. Surface Energies and Surface Areas of Bare and Water Covered Edge Surfaces of Talc^a

type	surface (<i>h</i> <i>k</i> 0)	<i>b</i> , Å	<i>A</i> _{<i>h</i><i>k</i>0} , Å ²	Γ _{<i>h</i><i>k</i>0} , J/Å ²	facet fraction	σ(H ₂ O), molec/nm ²	Δ <i>E</i> _{ads(H₂O)} , kJ/mol
bare	(100)	18.47	349.53	1.85	0.10	0	
	(010)	21.50	406.70	1.75	0.33	0	
	(110)	21.50	406.73	1.75	0.55	0	
	(130)	18.39	348.03	2.01	0.02	0	
water covered	(100)	18.46	349.21	1.30	0.07	5.73	−252.71
	(010)	21.29	402.82	1.20	0.34	5.96	−235.33
	(110)	21.29	402.73	1.20	0.59	5.96	−235.35
	(130)	18.44	348.90	1.49		5.73	−265.84

^aThe *a* dimension of the supercell was fixed at 40 Å or all of the structures to provide at least 10 Å of vacuum between periodic images of edge surfaces. The *c* dimension was kept at the experimental value of 9.46 Å. Facet ratios were obtained using the Wulff construction method,⁶³ where surface energies were used as the distance from facet to particle origin along its normal direction. Water coverage of (010) and (110) surfaces is slightly larger due to a larger surface area and slightly more intricate surface structure.

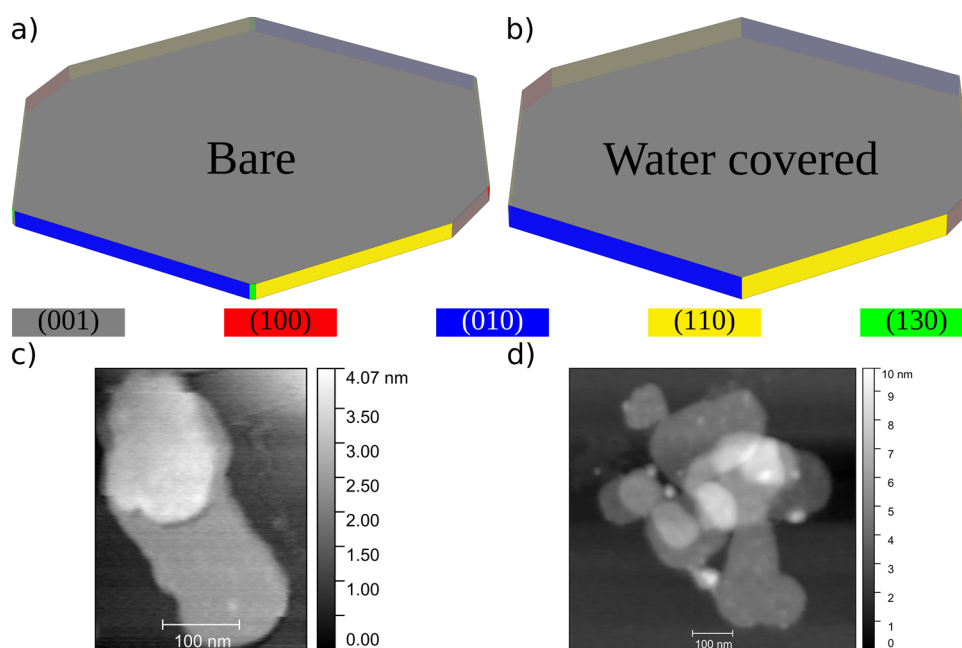


Figure 3. Most stable talc and saponite surfaces: (a) Wulff constructed model of talc particle with exposed (bare) edge surfaces: 55% of (110), 33% of (010), 10% of (100), and 2% of (130); (b) Wulff constructed model of talc particle with water saturated edge surfaces: 59% of (110), 34% of (010), 7% of (100), and 0% of (130); (c and d) AFM images of individual nanoparticle and nanoparticles agglomeration obtained for freeze-dried saponite. Measurement results are reported in Di Lorenzo et al.²⁹

XANES were normalized to the white line amplitudes. The comparison of FEFF and FDMNES generated XANES spectra and detailed examples of input parameters for both simulations are provided in the Supporting Information.

Model Uncertainties. The interpretation of the theoretical calculations and their comparison with experimental measurements should be done in the context of the modeling and experimental uncertainties. The major modeling uncertainties are related to the accuracy of the DFT approximation, statistical sampling uncertainty, and the ability of the simplified, idealized molecular model of talc to resemble potential structural disorder in synthetic saponite samples. Potentially, the largest uncertainties of the DFT calculations could be related to the accuracy of the pseudopotential (PP) approximation for the Mg ions and the exchange correlation potential. Mg is the most challenging element in the system because of its strongly localized 2s²2p⁶ states which can potentially contribute to the bonding. Explicit consideration of these states would require a very high density cutoff. For the sake of computational efficiency, a large-core [Ne] 3s² PP was

applied in the simulations. The accuracy of the PP was tested by calculating the cell parameter of MgO - periclase. The calculation showed an excellent agreement of predicted cell parameters of 4 × 4 × 4 supercell and experimental observation with only −0.004 Å (0.02%) and −0.016 Å (0.09%) difference for [He] 2s²2p⁶3s² and [Ne] 3s² PP, respectively. Thus, the small-core PP provides accuracy comparable to, or even better than, the experimental uncertainty of interatomic distance determination by XAS. Accuracy of the lattice energy calculations with the dispersion corrected PBE exchange-correlation functional is expected to be better than 0.5 kcal/mol.⁷⁰

The greatest structural uncertainty is likely associated with the idealized representation of the edge surface structure. Additionally, the calculations are performed for charge-neutral edge surfaces, representing the surface stoichiometry of talc and saponite at a pH of zero charge. Under the synthesis conditions, surface charge and surface speciation are controlled by the pH and ionic strength of the solution, while this calculated particle geometry represents the point of zero charge

which can be expected to be in a pH range from 2.5 to 4.6.^{71,72} The synthesis conditions correspond to a pH of 6.8, implying that saponite edge surfaces under experimental conditions are partially deprotonated.

The theoretical simulation of EXAFS spectra relies on several intrinsic parametrizations. As far as possible, the same set of parameters was used in the simulation and the theoretical modeling of the spectra. As described in the section “EXAFS and XANES Simulation”, the edge energy was corrected by 7 eV for Ni and 2 eV for Zn to achieve a good agreement between modeling and experimental results. Among the experimental uncertainties, the polarization angle accuracy should have the greatest impact. In P-EXAFS measurements, apparent coordination number depends on polarization angle and clay particle alignment in the sample.^{43,73} Quantitative texture analysis of Ni-doped samples²⁹ has shown that saponite clay films are well oriented ($I_{\text{ord}} = 0.79 \pm 0.05$), therefore, experimental uncertainty due to poor clay films alignment should be low. On the contrary, experimental polarization angle uncertainty is expected to be large ($\Delta\alpha = \pm 5^\circ$). Using equation derived by Schlegel et al.,⁴³ apparent coordination number uncertainties were estimated by using crystallographic coordination numbers and polarization angle uncertainty at $35^\circ \pm 5^\circ$ polarization angle. Although, it has practically negligible impact on the Zn–O shell, the Zn–Mg and Zn–Si can be under- or overestimated by 12.5 and 14%, respectively.

A large uncertainty is also related to the potential presence of structural defects in the synthetic materials compared with an idealized structure used in the simulations. On the contrary, the thermal disorder should be well described in the theoretical approach.

RESULTS AND DISCUSSION

Surface Energies and Nanoparticle Morphology. The calculated surface energies of bare and water covered surfaces for different facets of saponite are provided in Table 2. Based on the results presented in Table 2, (010) and (110) surfaces have the lowest energies and are likely to represent the most common edge surface geometry relevant for sorption studies. In contrast, (100) and (130) surfaces have significantly higher surface energies, suggesting that they should have negligible impact on stability and shape of saponite particles. Equilibrium particle shapes for different hydration states were reconstructed using Wulff construction method implemented in WulffPack⁶³ (see Figure 3). Based on surface ratios obtained for a fully water saturated particle, it was revealed that most of the edge surface area (93%) should be assigned primarily to (010) and (110) facets. The contribution of (100) surface is rather negligible, while (130) surface is not present at all. The negative value of the water adsorption energy indicates that water saturated talc surfaces are more stable than bare surfaces, hence, are showing hydrophilic behavior of edge sites. This agrees well with experimental studies of talc and other clay minerals solubility in aqueous solution at normal conditions.^{74,75}

Stability of talc and morphology of talc nanoparticles was also recently investigated by Toulhoat et al.⁷⁶ According to their study, (100) and (130) surfaces were revealed as the most stable edge surfaces for talc. This observation contradicts the results obtained in this study, as well as in situ experimental observations for saponite with AFM²⁹ and previous studies of dioctahedral smectites (Illite and montmorillonite^{16,77}). A direct comparison is given in Table 3. Similarly to Kraevsky et

Table 3. Comparison of Relative Facet Ratios Obtained by Theoretical Calculations for Talc (This Work) and Pyrophyllite⁷⁹ versus Experimental (AFM) Calculated Relative Ratios for Montmorillonite

edge	talc	pyrophyllite ⁷⁹	montmorillonite ⁷⁸
(100)	0.07	0.02	0.03
(010)	0.34	0.29	0.20
(110)	0.59	0.69	0.56
(130)			0.09

al.,⁷⁸ (110) is a dominant edge surface in saponite, whereas (010) is the second common edge surface. The theoretical surface morphology prediction is in a qualitative agreement with AFM observations of freeze-dried nanoparticles of synthetic saponite (see Figure 3) and in good quantitative agreement with results of Kraevsky et al. for montmorillonite:⁷⁸ the (110) is the most stable surface (59 vs 56%, respectively). Interestingly, the theoretical results are also in close agreement with another theoretical study conducted on pyrophyllite.⁷⁹

The reason for the discrepancies with the study of Toulhoat et al.⁷⁶ is not clear. Both studies (Toulhoat et al.⁷⁶ and this work) describe the system at the same level of theory. This suggests that the observed differences may be attributed to structural variations or, potentially, differences in the system size. An extra care has been taken in our study to ensure the inversion symmetric of opposing edge surfaces to avoid formation of surface dipoles and spurious interaction of periodic images in the system.

Zn–Ni Exchange Reaction between Bulk and Aqueous Solution. Zn–Ni exchange reactions between aqueous ions in the interparticle pore and structural position in the octahedral sheet were simulated for system setup shown in Figure 2. Helmholtz free energy of cation exchange with the outermost surface complex was obtained indirectly, using the cation exchange reaction between outermost and innersphere surface complexes as a proxy. Potential energies gap for the studied Ni–Zn exchange reaction (see eq 4), its running average, and other calculated thermodynamic integration results are reported in Supporting Information (see SI Table S3 and Figure S13).

Helmholtz free energy obtained through thermodynamic integration of three 10 ps long trajectories is equal to -42.72 ± 1.13 kJ/mol. Intrinsic cation exchange constant (pK) is -7.44 ± 0.20 , respectively. Due to its logarithmic nature, the pK parameter has asymmetric uncertainties. Therefore, the largest (in our case positive) deviation was reported for annotation simplification. The negative sign of the free energy indicates that Zn shows a higher affinity for incorporation into the saponite bulk structure than Ni.

Orientationally Averaged EXAFS Simulations. A comparison of the experimental and theoretical EXAFS spectra is provided in Figure 4 as a function of metal loading. The spectra obtained for different loadings are very similar, suggesting that the incorporation mechanism is the same for the range of investigated loadings.

The EXAFS simulations were carried out with FEFF code and based on ab initio MD simulations of the talc structure with trace quantities of Ni and Zn. The modeled spectra reproduce most of the features, but some of them underestimate the intensity (see Figure 4), which also impacts the peak magnitude of their Fourier Transform Magnitude (FTM)

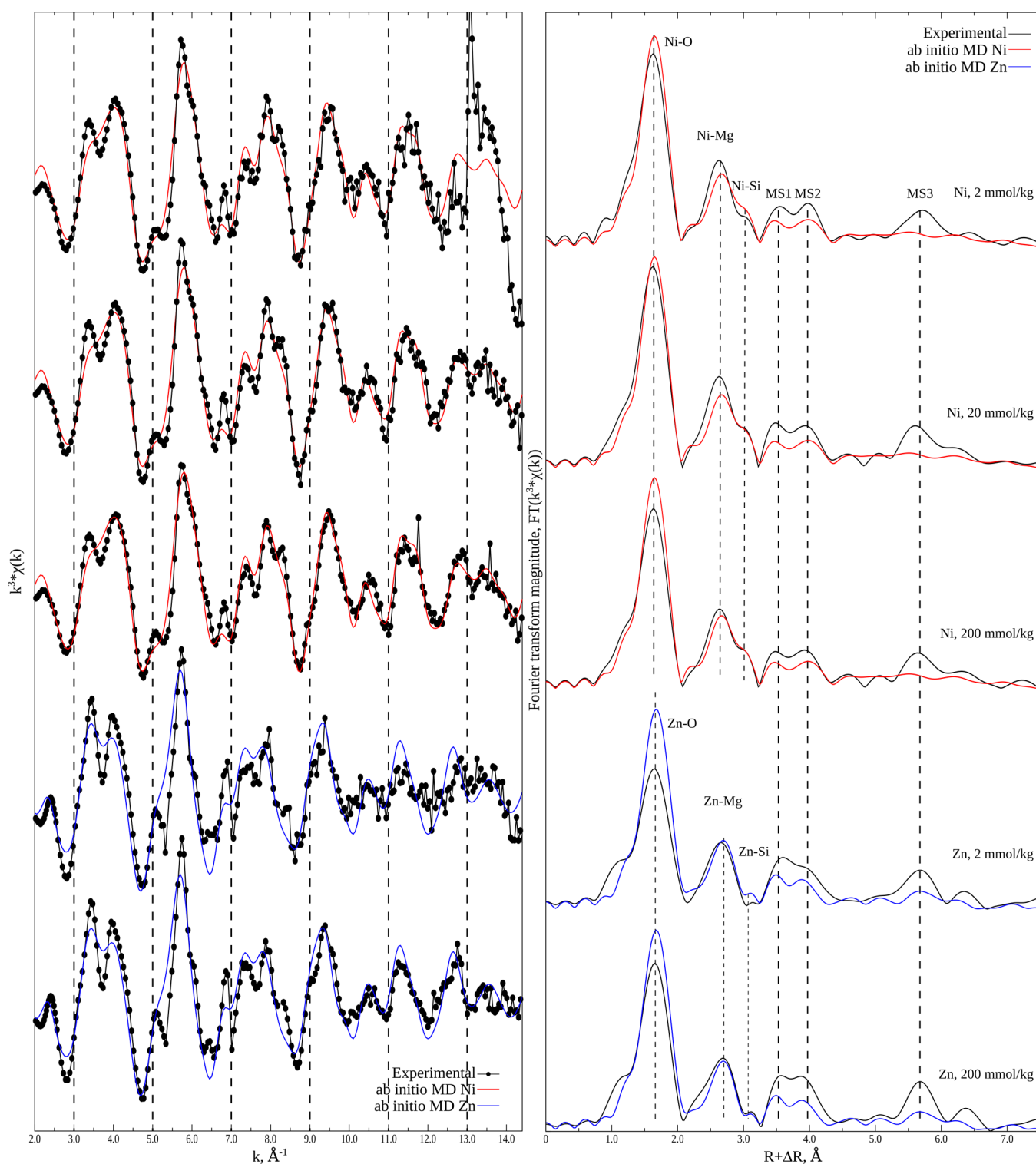


Figure 4. Orientationally averaged (nonpolarized) EXAFS spectra of Ni and Zn-doped saponite and their Fourier transform magnitudes, sorted along increasing loadings. Black lines are the experimental spectra measured at 35° polarization angle at room temperature, and red and blue lines are the FEFF-calculated nonpolarized spectra derived from the MD simulations at 300 K for Ni and Zn, respectively. The Fourier transformation was obtained for the k -range $\in [2.0\text{--}12.5]$. MS1, MS2 and MS3 labeled peaks are not exclusively MS dominated peaks. Such labels are used to indicate peaks where several single scatterings with multiple origins and multiple scatterings overlap. Only the last (MS3) peak shows strong MS dominance.

(see Figure 4). Theoretical spectra of Zn incorporated in saponite show a similar level of agreement (Figure 4). The differences observed for second and third shells in the most diluted Zn samples rise either from slightly longer theoretical

Zn–Mg bond (discussed later), significantly lower Si coordination number (obtained in shell fitting), or higher noise to signal ratio at high k -range. Considering that no shift was observed for the more concentrated sample, and the local

Table 4. Interatomic Distances and Coordination Numbers of Ni and Zn Obtained by Averaging Statistically Independent Atomic Configurations Spaced by 100 fs from Ab Initio MD Trajectory and EXAFS Measurements^a

sample	shell	CN	R, Å	σ_w^2 , 10^{-3} Å ²	ΔE_0 , eV	
NiSapD1	Ni–O	6.4	2.07(±0.01)	7.0	10.02	
	Ni–Mg	6.1	3.06(±0.01)			
	Ni–Si	2.7	3.27(±0.01)			
NiSapD2	Ni–O	6.8	2.07(±0.01)	7.0	9.75	
	Ni–Mg	6.9	3.06(±0.01)			
	Ni–Si	3.6	3.26(±0.01)			
NiSapD3	Ni–O	6.1	2.07(±0.01)	7.0	9.75	
	Ni–Mg	6.3	3.06(±0.01)			
	Ni–Si	3.8	3.26(±0.01)			
ZnSapD1	Zn–O	5.4	2.09(±0.01)	7.0	9.15	
	Zn–Mg	3.9	3.06(±0.01)	7.0		
	Zn–Si	0.6	3.28(±0.01)	15.0		
ZnSapD3	Zn–O	6.0	2.09(±0.01)	7.0	8.46	
	Zn–Mg	5.0	3.06(±0.01)	7.0		
	Zn–Si	2.5	3.29(±0.01)	15.0		
sample	shell	CN	avg. distance (±2σ), Å	σ_T^2 , 10^{-3} Å ²	median, Å	ΔE_0 , eV
Theorrtical (110)	Ni–O	6	2.09(±0.03)	5.3	2.085	−7.0
	Ni–Mg	6	3.08(±0.05)	6.8	3.080	
Ni _{incorp.}	Ni–Si	4	3.27(±0.02)	5.8	3.265	
Theoretical (110)	Zn–O	6	2.12(±0.02)	6.4	2.115	−2.0
	Zn–Mg	6	3.10(±0.05)	7.2	3.095	
Zn _{incorp.}	Zn–Si	4	3.27(±0.05)	6.6	3.265	

^aExperimentally derived atomic distances and coordination numbers of Ni are taken from Di Lorenzo et al.²⁹ Average interatomic distances are reported assuming normal distribution within 95% confidence interval (±2σ). Experimental Debye–Waller factors derived through shell fitting are reported as σ_w^2 , whereas theoretical thermal disorder - as σ_T^2 . The theoretical edge (reference) energy shift (ΔE_0) is determined by aligning theoretical EXAFS spectra to the experimental spectra; the experimental edge energy shift is determined by shell fitting.

structure of the incorporated cation should not depend on its loading (at least at such low loadings), differences observed for the most diluted Zn sample appear to be an artifact due to the quality of obtained spectra. This is further supported by similar Zn–Mg and Zn–Si distances obtained with shell fitting (see Table 4).

The experimental EXAFS spectra of Zn-doped saponite resemble the spectra of Zn-doped talc.⁸⁰ However, this sample was measured at 10–20 K, where thermal vibrations contributing to higher Debye–Waller components in the measured (or modeled) spectra are close to zero. Therefore, some features in this low-temperature spectra are more pronounced (for instance, peak at 6.5 Å^{−1}).

There have been a few studies investigating Ni incorporation in clay minerals.^{81,82} However, direct comparison of EXAFS is limited due to the variability of experimental conditions. For instance, in Noël et al.⁸¹ and Reinholdt et al.⁸² Ni-rich talc structures were analyzed. These EXAFS do not show characteristic peak splitting of oscillation at approximately 3.8 Å^{−1}, when a heavy atom is surrounded by much lighter elements like Mg. To some extent Ni incorporated saponite spectra resembles Ni poor serpentine measurements conducted by Noël et al.⁸¹ Serpentine is a TO trioctahedral clay mineral, which makes it structurally similar to talc (with an amendment that one tetrahedral Si sheet is missing). Therefore, its spectra matches well with Ni incorporated saponite, especially in region where first oscillation is split (approximately 3.8 Å^{−1}).

Prior to the detailed analysis of differences between the experimental data and model predictions, a few key observations should be summarized, and the limitations of the modeling approach should be clearly addressed to avoid

overinterpretation of the data. First, the theoretical FTM of the first shell (Me–O) is systematically more intense and narrower than the experimental ones. This suggests that the intensity of multiple scattering paths originating from Me–O pairs should also be somewhat overestimated. Contrary, certain features that strongly correlate with the first shell intensity (Me–O multiple scatterings) underestimate the peak intensity at distances ≥3.25 Å (discussed further). Second, the second (Me–Mg) and third (Me–Si) shells in the theoretical models are not as wide as those observed in the experimental data. This suggests that the theoretical thermal distortion for these shells is likely underestimated for both Mg and Si. This discrepancy may indicate the presence of structural defects, such as vacancies and substitutions, in the experimental samples, which are not accounted for in the ab initio MD models for Ni- and Zn-incorporated talc. Lastly, the experimental samples for both incorporated elements show quite similar differences with respect to the theoretical model, indicating a rather negligible or systematic nature of deviations between the theoretical and measured spectra. Consequently, it can be concluded that if similar features are observed for both elements experimentally, then they should be equally well reproduced by the theoretical models.

A splitting of the first EXAFS oscillation, observed on $\chi(k)$ -spectra between 3.0 and 4.5 Å^{−1}, is much less resolved in the theoretical spectra for both elements. The origin of this distinct feature comes from the longer distance, predominantly multiple scattering paths (more than 7.5 Å). Using ab initio MD structures, we were able to partially replicate this feature by using all available MS paths in a 7.5 Å absorption cluster. Expanding the cluster size was impossible due to FEFF code stability issues. The underestimation of the intensity in this

region can potentially be connected to the underestimation of the fifth and sixth peaks on Fourier transformation plots (3.5 to 4.5 Å, respectively). These peaks arise from a combination of several Me–O single and multiple scattering paths. Therefore, a low intensity in this region (in comparison to the experimental spectra) can be caused by the following factors: (1) theoretical simulations predict higher distortion of oxygen shell at this distance compared to natural samples; (2) experimental mean free paths as a function of k appear to be longer than those theoretically calculated using the default FEFF inelastic mean free path model, suggesting the need for a more accurate model. Attempts using the many-pole self-energy model showed slightly better agreement in this region but in turn caused an increase of the reference energy shift and worse agreement on the high energy part of the spectrum. Also, note that this feature strongly depends on the multiple scattering contributions. In the current (7.5 Å radii cluster) model, a substantial amount (approximately 38%) of all paths generated using ab initio MD structures correspond to multiple scatterings between 4 atoms (NLEG 5), whereas multiple scattering paths with 5 atoms contribute approximately to another 34% of all paths. Although the intensity/amplitude of these paths are much smaller, they still play a substantial role in reproducing all the features. For example, if theoretical spectra are calculated considering multiple scatterings only between 3 atoms, the characteristic differentiation of oscillation pattern/oscillation division will not be reproduced at all. Also, it should be noted that multiple scattering contributions are significantly dependent on temperature and polarization angle dependent. Therefore, Fourier transform peaks that occurred primarily due to multiple scattering phenomena can be challenging to reproduce.⁸³

Another feature, which has a slightly lower resolution, is located at approximately 5.2 Å⁻¹. Further analysis showed that this feature has a direct impact on the peak observed on Fourier transformation magnitude plots at approximately 5.8 Å. In the literature,^{35,80} this peak is commonly labeled as the combination of third and fourth order Me–Me multiple scattering paths, which can be observed only in trioctahedral clay minerals. Therefore, the appearance of this peak is indirect evidence of Ni and Zn incorporation in the (trioctahedral) saponite mineral structure. Although the simulated talc structure also belongs to the trioctahedral clay mineral class, the reason behind the weak intensity of the theoretical EXAFS in this region is rather unclear.

The low intensity in the region (R , Å $\in$ [5.2–6.7]) suggests partial Ni–Ni and Zn–Zn clustering. Previous studies show that such clusters form in natural clays^{28,84} or may form in course of recrystallization.^{44,45,85} However, since experimental EXAFS spectra do not resemble any structural similarity with previously investigated Ni⁸⁵ and Zn-phylosilicates,^{44,45} such neoformations can be ruled out. Contrary, considering a good agreement of experimental and theoretical Fourier transform magnitudes for second shell, Ni and Zn should form an isolated Me–Mg–Me clusters, following exclusion rule suggested by Vantelon et al.⁸⁴ for ordered Fe distribution in SWy2, with approximately 5.8–6.3 Å distance between Ni or Zn pairs. Considering relatively low metal loadings, such clusters must form randomly in rather small quantities; otherwise, oscillation belonging to a heavier atom would be clearly visible. Another potential argument in favor of considering Me–Mg–Me clusters, is based on XANES spectra (see SI Figure S1), which show a slight decrease in white line

intensity between Ni/Zn 20 and 200 mmol/kg samples. Although, it should be treated with caution since this had almost no impact on k^3 -weighted $\chi(k)$ spectra and practically negligible effect on Fourier transformed EXAFS. This effect was well described in studies of Kéri et al.,²⁸ which showed that incorporated metal loadings can be calculated by linear combination fitting of several dozens of theoretical spectra with varying Me–Me distances.

To test the validity of the clustering hypothesis, several Ni–Mg–Ni triplet configurations were modeled, taking various snapshots from the ab initio MD trajectory and replacing the neighboring Mg site with Ni. Next, structure geometry was optimized at the DFT + U level of theory and used to simulate theoretical EXAFS. Qualitative comparison of radial pair distribution functions of several individual atoms showed approximately 50% reduction in peak widths compared to initial ab initio MD structures. For structures obtained by geometry optimization, the global Debye–Waller factor (SIG2 = 0.003) was used. Obtained spectra were linearly combined with pure Ni-doped saponite spectra with respect to experimental data.

A linear combination fit (see SI Figure S3) shows unrealistically large (2/3 in sum) contributions of Ni–Mg–Ni clusters with almost equal contributions from structures with Ni–Ni distances of 5.8 and 6.3 Å for all experimental spectra. The FTM of combined spectra shows a more prominent increase in the amplitude of the second shell, rather than the peak at approximately 5.8 Å. Further linear combination fit analysis revealed that contributions from Ni–Mg–Ni shells strongly correlate with regularization with the a_i^4 term applied, which penalizes fits with too large (one-sided) spectra contributions. Applying weaker term a_i^2 resulted again in approximately 1/3 of pure Ni-doped talc and 2/3 of Ni–Mg–Ni with Ni–Ni interatomic distance 6.3 Å. The optimization without regularization parameter resulted in approximately equal (50:50) contributions from both structures, indicating that they are very similar. This agrees well with the initial uncertainty assessment due to Ni and Zn incorporation in different crystallographic sites (see SI Figure S10). It also explains why spectra with shorter Ni–Mg distances was omitted in linear combination fitting. Although Ni–Mg–Ni should have formed randomly, it would be expected to observe some linear dependency of Ni–Mg–Ni contribution on experimental Ni loading. However, no trend was observed and Ni–Mg–Ni structure inclusion did not result in any significant (primarily, 5.8 Å shell) fit improvement.

The last observation agrees well with previous analysis performed for diluted (4%) Zn-doped talc,⁸⁰ where the probability for the formation of Zn clusters was considered as low. In this study, probability of finding various local clusters was assessed using binomial law with respect to Zn by Mg substitution ratio (4000 ppm). However, fitting showed that pure Zn–Mg EXAFS spectra showed much better agreement than one with Zn–Zn_xMg_{6-x} clusters, indicating no significant clusterization. In comparison, the Ni and Zn concentrations in our doped saponite samples were mostly lower (100, 1000 and 10,000 ppm, respectively). Therefore, considering all indirect evidence and linear combination fit result, it is reasonable to assume that the discrepancies in the theoretical and experimental peak intensity at approximately 5.8 Å on Fourier transformed spectra can not be explained by Ni–Mg–Ni clustering.

The influence of the experimental errors can also be eliminated. In spite of slightly larger particle disorder ($I_{\text{ord}} = 0.79 \pm 0.05$) in saponite samples, quantitative texture analysis showed that strong preferential orientation of all self-oriented clay films was achieved.²⁹ Linear regression analysis also showed that recalculated spectra for a magic polarization angle of 35° are practically indistinguishable from the measured ones. Therefore, even if there would have been an error of $\pm 5^\circ$ in setting the polarization angle (α), it would have a negligible impact on intensity and would not eliminate this peak.

Comparing Ni and Zn spectra, the MS3 peak is practically indistinguishable from the background for Ni. As was mentioned before, if no significant differences are observed between the two elements in the experimental spectra, we expect that they both should show a similar level of agreement in theoretical models as well. Theoretical radial pair distribution functions for both elements also look rather similar (see SI Figures S11 and S12). Hence, since both elements do not form clusters and most of the experimental errors are rather insignificant, underestimated peak intensity should have another origin.

The last distinct high frequency feature, which was reproduced with underestimated amplitude, was an oscillation at approximately $6.8 \text{ \AA}^{-1}$. Considering its strength and frequency, it does not belong to a single heavy atom like Ni or Zn single scattering and is rather a result of interference of several different oscillations, including multiple scatterings. Although, most of Ni and Zn is in a bulk phase minor discrepancies in this region can raise due to partial exposure of Ni and Zn atoms to water on the surface. However, at this stage it is only a speculation. Linear combination fitting with Ni and Zn on the surface is needed to confirm such a possibility. Additionally, even if Ni or Zn surface complexes are responsible for observed differences, their contributions should be minor, especially since they cannot be responsible for the largest fit discrepancy - the low intensity of the trioctahedral (MS3) peak. Therefore, a reason behind the poor resolution of this EXAFS oscillation feature is also unclear.

Ni and Zn Local Environment. Experimental and theoretical atomic distances and coordination numbers are reported in Table 4. Given the typical uncertainties in experimentally measured atomic distances ($\pm 0.01 \text{ \AA}$), a good agreement between measurements and theoretical calculations could be achieved. At a closer look, theoretical bond lengths of the two first shells are slightly larger than the experimental ones (approximately $0.02 \text{ \AA}$ for Ni and $0.03\text{--}0.04 \text{ \AA}$ for Zn). Usually such variations are within GGA DFT method accuracy⁸⁶ and can be therefore neglected since similar discrepancies can be observed between different basis sets,⁸⁷ not to mention that simulations involving heavier atoms typically achieve $0.01\text{--}0.02 \text{ \AA}$ agreement with experimental data only using hybrid XC functionals.^{87,88} Remaining uncertainty can also be attributed to differences in the simulation temperature. Radial pair distribution functions (see SI Figures S11 and S12) show that some coordination shells exhibit slightly larger asymmetry than others. Consequently, it may be more appropriate to compare experimental bond lengths with the median of the distribution rather than the mean, as the median is less biased in cases where the distribution deviates from a Gaussian profile. Comparing both elements, Ni median values do not change much in comparison with mean bond lengths. This probably indicates a slightly more ordered positioning of Ni cations

inside the octahedral sheet compared to Zn, which has a smaller atomic radius. In the talc mineral structure, any structural disorder in the octahedral sheet is conditioned in the first place by the Mg framework. Therefore, the smaller Zn atom fits inside this framework easier. This also explains why thermodynamic integration results show that Zn incorporation is more favorable than Ni incorporation.

The coordination numbers derived from shell fitting of experimental spectra are known to have a large uncertainty, on the order of 25%. As a result, bond length accuracy is generally considered to be a more reliable metric in EXAFS analysis. The unpolarized theoretical EXAFS spectra fit experimental measurements quite well, without a substantial shift on the abscissa, as would be expected from a comparison of bond lengths, indicating that it probably has a very negligible impact on the overall EXAFS fit.

Potentially, variations in atomic distances could also have been explained by two structurally independent Mg positions in the talc mineral structure. Our comparison of EXAFS simulations using cell optimized structures of Ni and Zn incorporated in these two sites showed that they are almost identical (see SI Figure S10). This also agrees well with previous observations for Zn-doped talc model used by Juillot et al.,⁸⁰ where Zn atoms were distributed randomly. Moreover, even though we use a synthetic clay mineral, we cannot entirely exclude the presence of structural disorder within the clay films themselves. For instance, partial displacement of the absorbing atom toward the surface could occur due to structural defects in the tetrahedral sheet. Also, despite talc not containing any Al in tetrahedral sheet like saponite, no large discrepancies were observed for Zn–Si interatomic distance. Judging the agreement of distances for experimental and simulated third shells, it seems that partial substitution of Al by Si used in measured samples most likely had very limited impact on TOT trioctahedral structure. We can thus conclude that a very satisfactory mechanistic model was obtained for Ni and Zn incorporation in the saponite structure.

CONCLUSIONS

In this work, the theoretical talc nanoparticle surface morphology was determined by assessing the stability of each individual edge surface using cell optimized DFT simulations. According to the simulations and measurements, (010) and (110) surfaces appear to be the most stable and account for approximately 93% of all edge surface area. Comparing theoretical results obtained for talc with AFM measurements, we conclude that the talc structural model is a suitable proxy for saponite structure.

The structural incorporation of Ni and Zn into the saponite octahedral sheet was simulated using the ab initio MD method using the setup with a (110) edge interfacing water filled macropore. Additionally, thermodynamic integration method demonstrated that Zn shows higher affinity to incorporation than Ni, which aligns well with previous experimental studies on montmorillonite⁸⁹ (higher affinity of Zn to strong sites in competition reaction).

Theoretical EXAFS and XANES spectra were simulated from obtained equilibrated MD trajectories and further compared with experimental EXAFS and XANES spectra of Ni and Zn incorporation in saponite. Conventional theoretical calculations of unpolarized EXAFS and XANES underestimate key features attributed to third and fourth order Ni–Mg multiple scattering peaks. The formation of Ni–Mg–Ni

clusters was assessed and proven to be highly unlikely, and this could not explain the observed differences. The first three most important interatomic distances (Ni/Zn–O, Ni/Zn–Mg, and Ni/Zn–Si) obtained through ab initio MD simulations agree well with experimental fitting, although ab initio distances are constantly larger for Me–O and Me–Mg shells: by 0.02 Å for Ni and 0.04 Å for Zn. Theoretical Ni–Si shell distance agrees well with the shell fitting result.

The structural models for Ni and Zn incorporation in talc and saponite derived in this study provide a solid reference for future studies of Ni and Zn incorporation in clay mineral containing soils such as laterite or serpentine, whereas the obtained free energy of cation exchange between bulk and aqueous phases can be used to develop more efficient methods of Ni and Zn leaching from this soils.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.5c01314>.

Theoretical XANES simulations; linear combination fit results of experimental EXAFS spectra of Ni-doped saponite using theoretical unpolarized structures with Ni–Mg–Ni clusters; side projection of hydrated talc surfaces; water density distribution profile; effect of *U* on electronic Density of States (EDOS) in NiO; graphical and numerical results of Zn-doped samples EXAFS spectra shell fitting at various polarization angles; comparison of EXAFS spectra obtained for two Mg crystallographic sites in talc structure; radial pair distribution functions constructed for the first three shells of Ni- and Zn-doped structures; and thermodynamic properties obtained through numerical integration and cumulative average of potential energy gaps calculated coupled to λ parameter (PDF)

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Notes

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Supporting information for Local Crystal Structure of Ni²⁺ and Zn²⁺ Doped Saponite Determined by EXAFS Spectroscopy and *ab-initio* MD Modelling

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Supporting Information

XANES spectra measurements and simulation

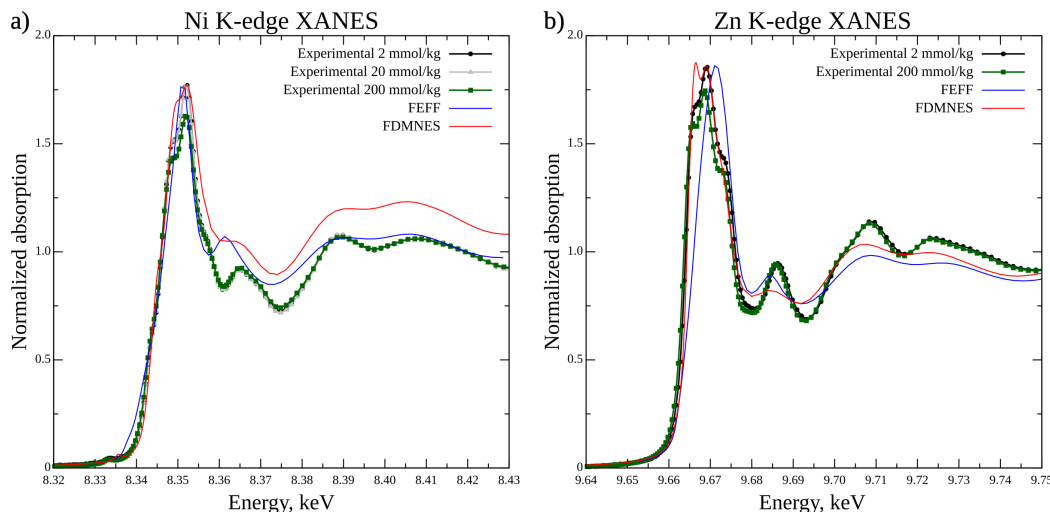


Figure S1: XANES spectra of Ni^{2+} and Zn^{2+} doped saponite measured at 35° polarization angle and corresponding theoretical simulations. Theoretical XANES were simulated using FEFF9.6 and FDMNES codes.

Although, EXAFS measurements can provide substantially more information about Ni and Zn local environment, XANES simulations were required to evaluate the need of the edge energy correction for Ni and/or Zn. Additionally, it provides a test for the ability of DFT simulations to reproduce XANES spectra, which usually can be well reproduced using only first (Me-O) coordination shell.

FEFF uses so-called muffin-tin approximation,¹ which assumes spherical symmetry for the potential around each atom to solve Kohn-Sham equations, and a real space multiple scattering (RSMS) method for XANES simulations that combines full multiple scattering Green's function calculations for the nearest neighbors (up to $5\text{\AA}$) and path extension formalism for high order paths above the edge. This simplifies the calculation but can limit accuracy for systems with strong anisotropy^{2,3} due to assumption that electron density is spherically symmetric for each atom. Obtained theoretical XANES spectra calculated for both Ni and Zn in FEFF 9.6 are practically featureless (see Fig. S1). Similar discrepancies

in simulated and measured Fe XANES spectra were reported using FEFF8.4 version in Kéri et al.². Although, theoretical FEFF XANES do not match well with the experimental data in edge region, they do align much better with experiment after the edge in the start of EXAFS region (low k space).

On the other hand, FDMNES⁴ utilizes fully spatially resolved DFT-based LSDA approach using finite difference method (FDM) for solving Kohn-Sham equations, which treats systems with inhomogeneity and anisotropic behavior more precisely. This approach however is much more computationally expensive. It is also possible to use a Green's function method in FDMNES, however, our own simulations have shown that XANES spectra obtained with Green's function method are less accurate in reproducing experimental results. XANES obtained with FDMNES FDM, on the other hand, provide much better agreement with experimental results in edge region. However, performing full EXAFS simulations with FDMNES is not really feasible considering computational costs. Based on obtained results, it is reasonable to assume that slightly worse performance of FEFF can be partially explained through differences between Green's function and FDM. XANES K -edge spectra of Ni (see Fig. S1a) using default parameters was reproduced almost perfectly, failing only to reproduce correct position of the pre-edge peak by approximately 3 eV (8.336 vs 8.333 keV). Appearance of this experimentally observed peak is typically explained by presence of inversion symmetry forbidden $1s \rightarrow 3d$ electron transition for octahedral symmetry.^{5,6} Since Zn $3d^{10}$ shell is fully occupied, such transition is impossible. However, this is not true for Ni. Hence, pre-edge peak can be present in XANES (see SI Fig.S1) due to the inversion symmetry breaking by various types of disorder. By default, FDMNES assumes that all states below Fermi level are fully occupied, hence, their cross section is set to zero. Observed pre-edge peak is below calculated Fermi level (see SI Fig.S2), hence, its cross section was also set to zero even if the $3d$ -orbitals are not fully occupied. Following recommendation of one of FDMNES developers (Dr. Yves Joly), this can be fixed by applying an additional parameter (E_cut -0.75 eV) that enables cross section calculations for negative energies (below Fermi

level). Similarly to Ni-spectra, the edge region of XANES for Zn-doped samples is better reproduced by FDMNES, whereas FEFF provide good description of the post edge features. Comparing with literature, the obtained experimental XANES show clear similarity to the Ni-rich talc and Ni-poor serpentine measured by Ratié et al.⁷. Absence of additional pre-edge peak typical for the tetrahedrally oriented Ni observed for trevorite also indirectly confirms octahedral symmetry of incorporated Ni²⁺ cation. To our best knowledge, no high resolution Zn-K edge XANES of Zn-doped trioctahedral clay minerals have been reported in literature so far.

Additionally, we would like to clarify, that ΔE_0 shift applied in FEFF for EXAFS alignment does not mean that theoretical Fermi energy was calculated incorrectly. Quite in contrary, XANES spectra calculated with $\Delta E_0 = 0$ reproduces experimental XANES very well (see SI Fig.S2). However, the real issue here is the way to select E_0 value. FEFF assigns E_0 value to the Fermi level (in case of Ni, for example, $E_0 = 8337.2$ eV), while experimentally E_0 value is derived as a root of second derivative of XAS spectrum (8346.2 eV). Since $k = \sqrt{2(E - E_0)}$, such large discrepancy in E_0 values will cause a large misalignment in EXAFS (see SI Fig.S8), while XANES plotted using absolute energies will align almost perfectly. In this work, we have derived applied ΔE_0 shift by aligning experimental and theoretical XANES using relative energies (see SI Fig.S2). This approach was chosen due to two main reasons: 1) absolute energies estimate in FEFF may be slightly inaccurate (few eV) due to the lack of solid-state corrections in the many-body relaxation energy; 2) alignment using absolute energies ($\Delta E_0 = -9.0$ eV) led to slightly greater misalignment for XANES too. Similar alignment, yet with slightly different implementation, was applied to XANES obtained with FDMNES. Theoretical K-edge XANES spectra were aligned to experimental measurements using a shift to the Kohn-Sham core state energies (Epsii) by approximately -9.84 eV for Ni and -6.01 eV for Zn.

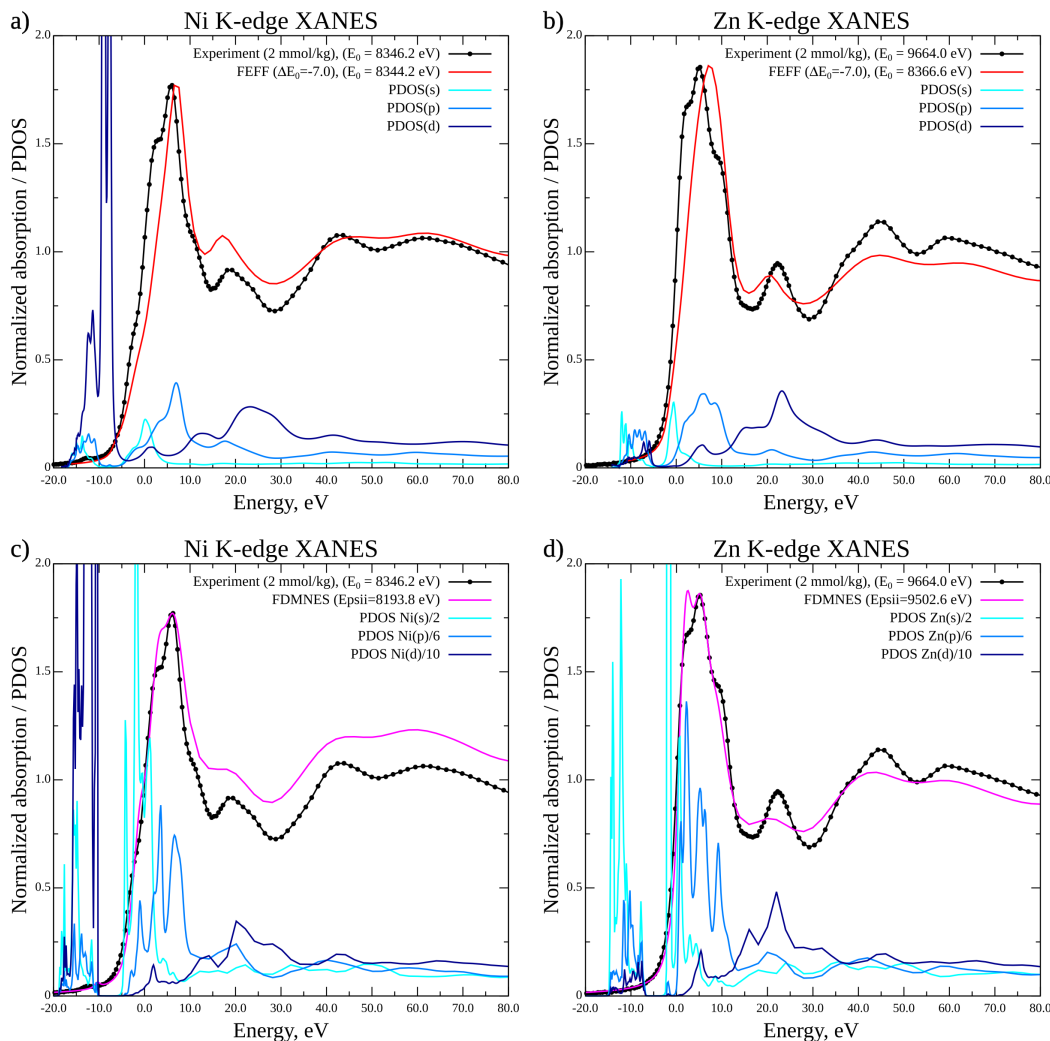


Figure S2: Theoretical XANES spectra for 2 mmol/kg Ni^{2+} and Zn^{2+} doped saponite samples and their calculated PDOS obtained with FEFF9.6 (a,b) and FDMNES (c,d) codes.

FEFF XANES and EXAFS input example

An independent routine was used to generate FEFF XANES due to E_0 alignment (see discussion above). No visible difference was observed by using ground state exchange potentials instead of Hedin-Lundqvist potentials, therefore, Hedin-Lundqvist potentials were used for consistency reason (FDMNES calculations used default Hedin-Lundqvist-Von Barth potentials). XANES and EXAFS input parameters are reported in table S1.

Table S1: FEFF9.6 input parameters used for XANES and EXAFS spectra generation.

XANES	EXAFS
TITLE Zn-Ni exchange on talc * Ni K edge energy = 8333.0 eV 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 SCF 5.0 CRITERIA 0.0 0.0	
XANES 5.0 FMS 5.0 MULTIPOLE 2 0 EXCHANGE 0 0 0	EXAFS 15 RPATH 7.5 NLEG 8 EXCHANGE 0 -7.0 0.0 or 0 -2.0 0.0 for Zn
LDOS -10 10 0.1 FOLP 2 0.8 POTENTIALS * ipot Z element 0 28 Ni or 0 30 Zn 1 8 O 2 1 H 3 12 Mg 4 14 Si ATOMS * this list contains 1378 atoms 0.00000 0.00000 0.00000 0 Ni 0.0000 -1.48114 -0.90110 1.07972 1 O_1 2.04244 -0.02200 -1.70190 -1.14502 1 O_2 2.05135 -1.47327 0.90080 -1.12656 1 O_3 2.06182 0.02200 1.82120 0.98408 1 O_4 2.07019 1.55520 -0.93090 1.02279 1 O_5 2.08118 1.59050 0.90360 -1.15701 1 O_6 2.16445 ***Atomistic structure of ab initio MD snapshot*** END	

FDMNES XANES input example

Comment

K edge of nickel/zink

Filout

./fdmnes

Range

-60. 10. -20 0.2 20 2.0 100

SCF

R_self

5.0

N_self

300

P_self

0.05

Delta_E_conv

0.1

Quadrupole

Edge

K

Radius

7.5

Density

Z_absorber

28 ! 30 for Zn

molecule

1 1 1 90. 90. 90. ! a, b, c, alpha, beta, gamma

28 0.00000 0.00000 0.00000

8 -1.48114 -0.90110 1.07972

8 -0.02200 -1.70190 -1.14502

8 -1.47327 0.90080 -1.12656

8 0.02200 1.82120 0.98408

8 1.55520 -0.93090 1.02279

8 1.59050 0.90360 -1.15701

!!!Atomistic structure of ab initio MD snapshot!!!

Convolution

E_cut ! only for Ni

-0.75

Epsii

8193.8 ! for Zn 9502.6

End

Linear combination fit results with Ni-Mg-Ni clusters

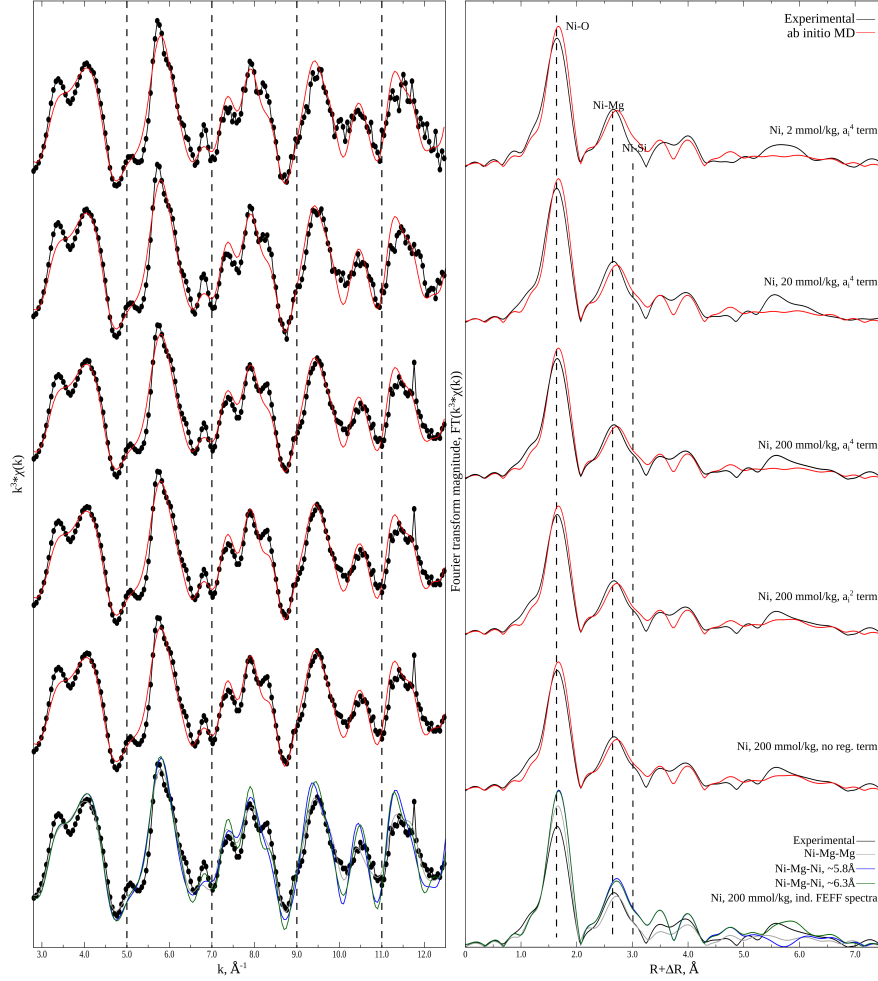


Figure S3: Linear combination fitting of experimental EXAFS spectra of Ni-doped saponite using theoretical unpolarized structures with and without Ni-Mg-Ni clusters and their Fourier transform magnitudes, respectively. Experimental spectra is indicated with black solid line and dots, whereas linear combination fit - with red solid line. The Fourier transformed spectra were obtained for linear combination fitting in the region ($k \in [2.0-12.5]$)

Fitting has shown that experimental spectra can be replicated with approximately equal contributions from all three (Ni-Mg-Mg, Ni-Mg-Ni 5.8 Å, and 6.3 Å) spectra. Decrease of regularization term suppress the contribution of Ni-Mg-Ni 5.8 Å spectra from fit probably due to significantly shorter Ni-Mg bond lengths. Linear combination fits obtained with no regularization show an almost equal contribution from both structures for all experimental samples. Considering that Ni concentration is 100 times larger between most diluted

and most concentrated samples, some tendency in Ni-Mg-Ni spectra contribution should be observed in presence of clusters Ni-Mg-Ni. All fits show a rather worse agreement with experimental data than ab initio MD Ni-talc structure with no Ni-Ni clustering at low distances and similar agreement at larger distances. Considering large contributions of clustering spectra and rather negligible fit improvement for trioctahedral peak at 5.8 Å, Ni-Ni clustering should be ruled out. It is likely that somewhat more pronounced shoulder feature appearing at approximately 8.3 Å is more intense due to reduced thermal motion after snapshots cell optimization (approximately 50%) than difference in structural positions. .

Additional figures and tables

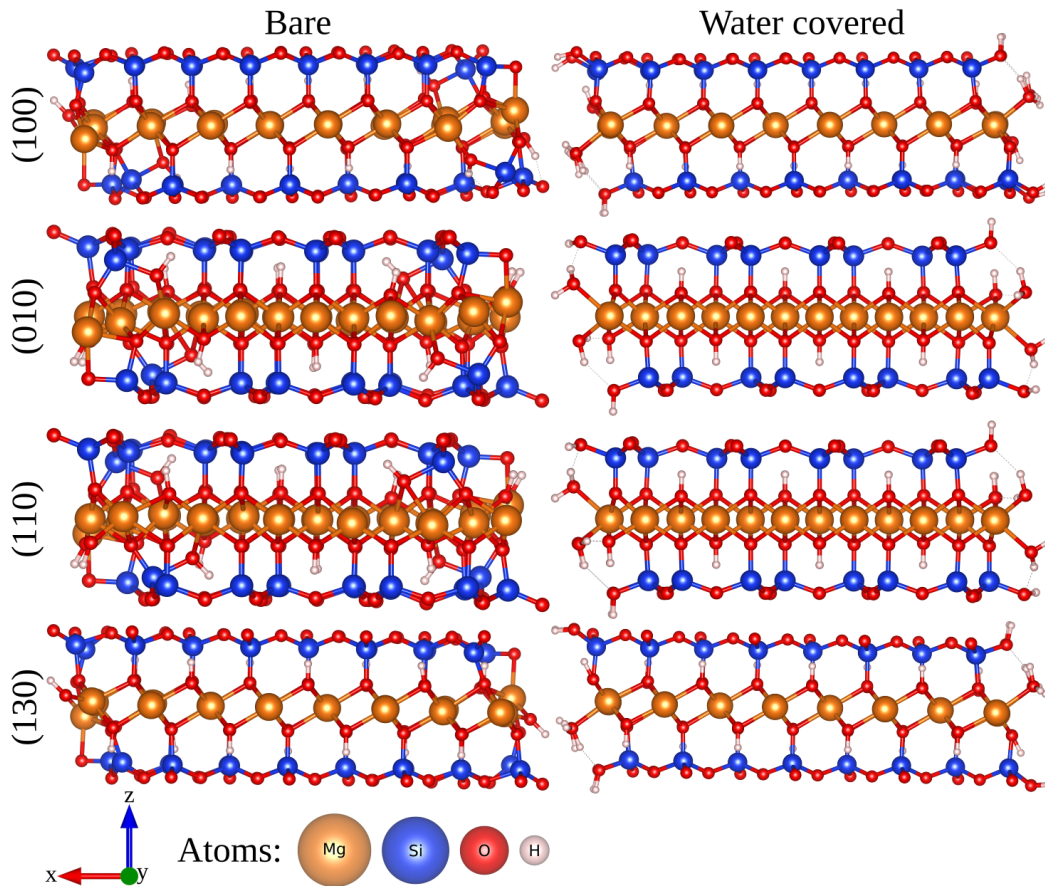


Figure S4: Bare and water covered optimized edge surfaces of talc: a) (010), b) (110), c) (100), d) (130). Each surface was modeled using $4 \times 2 \times 1$ talc unit cells with fixed (9.46 Å) interlayer distance and at least 10 Å vacuum along x-axis.

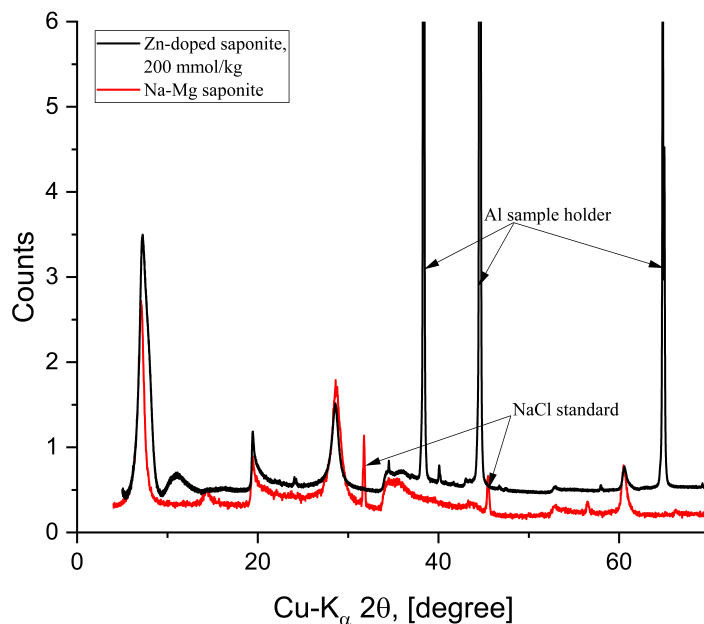


Figure S5: Powder X-ray diffraction pattern of Zn-doped saponite in comparison with powder pattern of pure synthetic Na-Mg-saponite reported in Di Lorenzo et al.⁸. Measurements were conducted at room temperature under atmospheric humidity conditions. Na-Mg-saponite diffraction pattern was measured on silicone sample holder using NaCl as standard, whereas Zn-doped saponite sample was placed on aluminium sample holder.

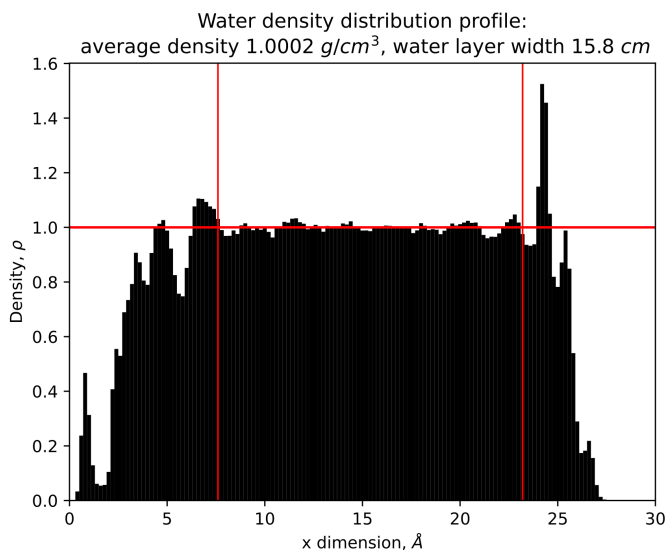


Figure S6: Inter particle water density profile derived for "strong"- "weak" sites exchange model of talc using classical MD simulations in LAMMPS. Red lines indicate borders of water filled inter particle space, where water molecules behave identically to bulk water. i.e. average water density close 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.

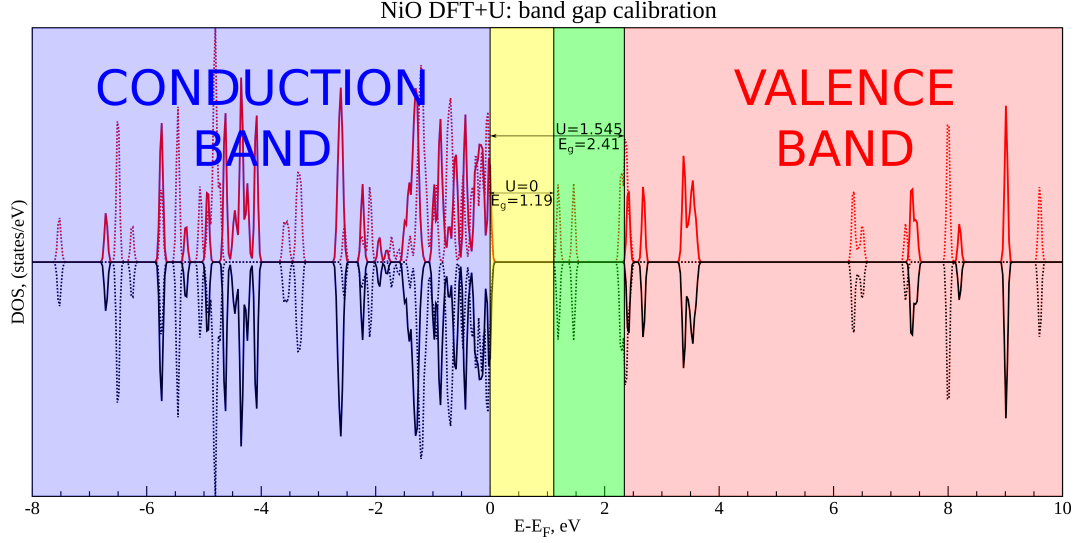


Figure S7: Density of states calculated for an antiferromagnetic NiO ($\text{Fm}\bar{3}\text{m}$, $a = 4.2166 \text{ \AA}$, $Z=4$) with (straight lines) and without (dotted lines) Hubbard potential. Application of additional 1.545 eV increased width of band gap between valance and conduction bands by 1.22 eV and raised it to the value reported in the Materials Project dataset.⁹ Calibration was performed using cell optimization with 1400 Ry density cutoff and no angular or symmetry constraints. Therefore, there are small differences in size of $2 \times 2 \times 2$ NiO supercell between both simulations: cell parameters decreased by approx. $0.0171 \text{ \AA}$, whereas angles - by 0.143° . Overall, thanks to applying Hubbard potential, cell volume decreased by approx. $3.54 \text{ \AA}^3$ compare to simulation without it, resulting in cell with $a=8.3080 \text{ \AA}$ and $\alpha=90.144^\circ$.

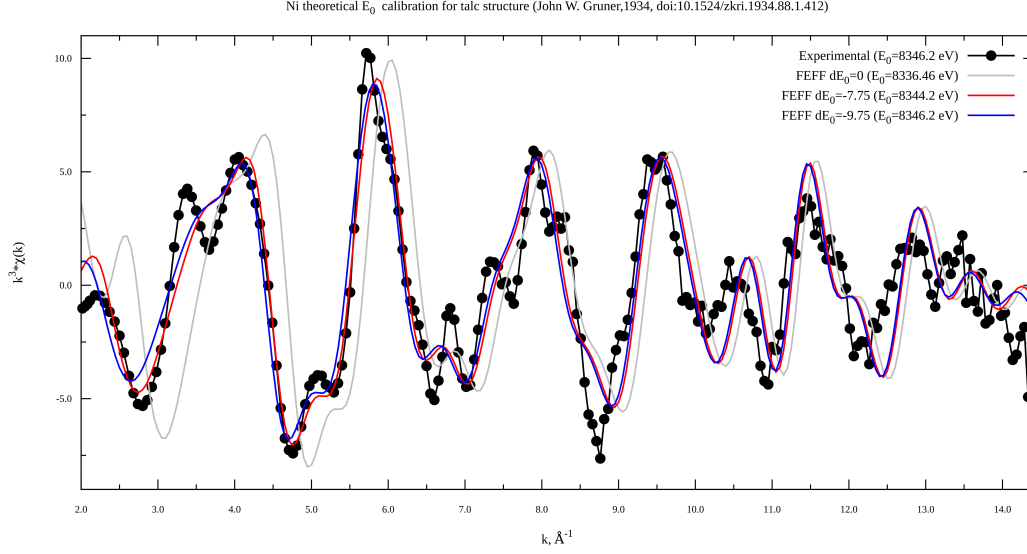


Figure S8: The ΔE_0 shift value for EXAFS spectra was initially pre-calibrated using experimental talc structure.¹⁰ As was also shown in XANES (see SI S2), relatively large E_0 shift for Ni is required to compensate for the difference between theoretical (Fermi energy) and experimental (the root of the second derivative of XAS spectrum) E_0 values. Initial alignment with talc structure¹⁰ suggested a slightly larger misfit when shift by absolute difference (approximately -9.75 eV) is applied. Hence, knowing that FEFF absolute energies may have a small error of few eV due to lack of accurate solid state correction, a slightly smaller shift was applied (-7.75 eV; $E_0 = 8344.2$ eV). This shift however has decreased slightly to -7.0 eV for ab initio MD simulations due to shift of average Fermi energy (8337.2 vs. 8336.46 eV). Although, Fermi energy should be temperature independent, we assume its slight fluctuation in FEFF must be connected to thermodynamic changes in ab initio MD structures simulated at 300 K ($\langle E_F \rangle = 8337.2$ eV). Because of observed fluctuations, theoretical spectra E_0 was aligned to experimental value with slight shift in energy (8344.2 eV).

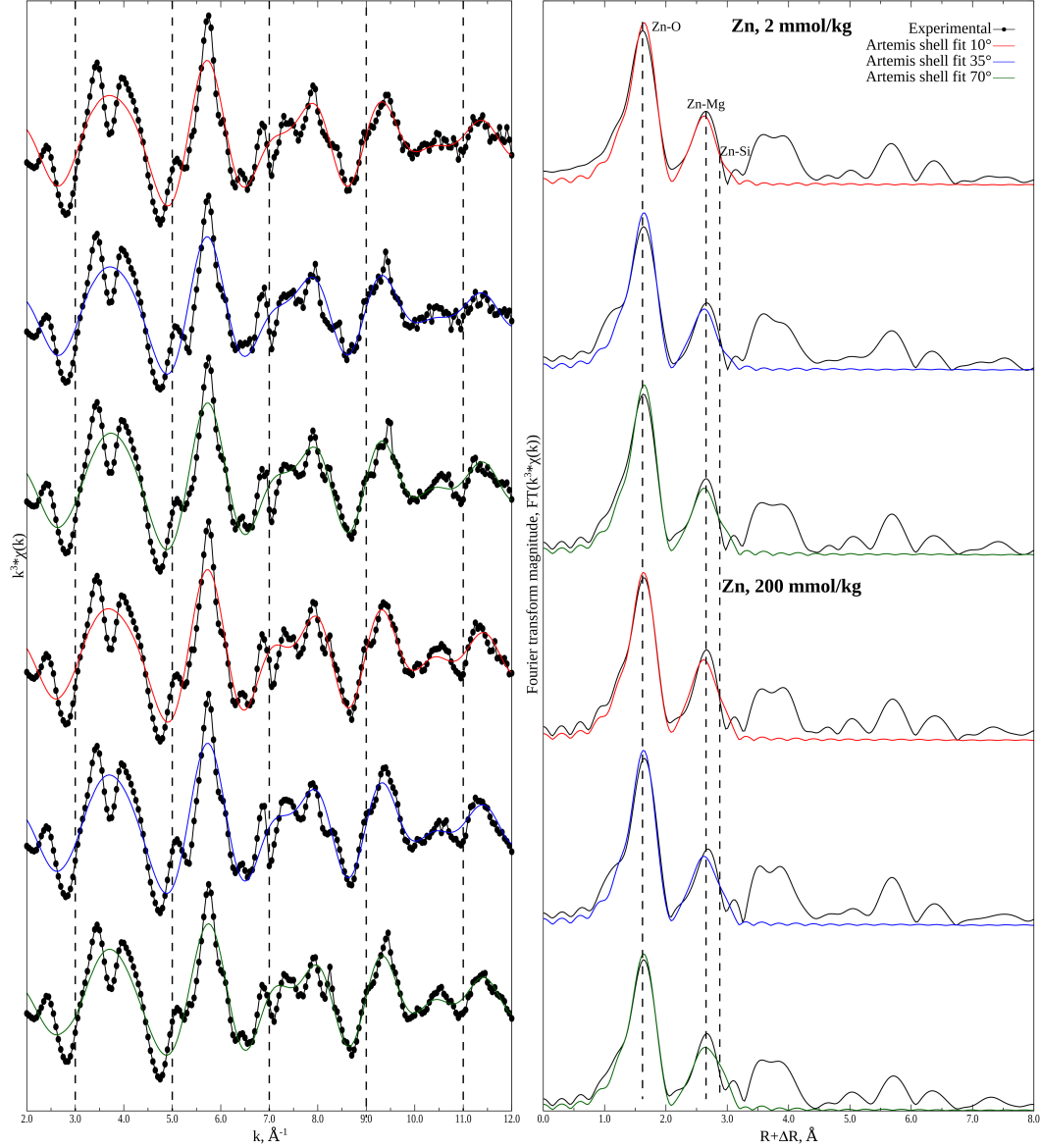


Figure S9: Graphical representation of shell fitting results obtained for polarized k^3 -weighted EXAFS spectra of Zn-doped saponite at 10° , 35° and 70° polarization angle, respectively. Corresponding experimental Fourier transformed spectra were obtained in k -range $\in [2.0-12.0]$, whereas fitting range was limited from 1 to 3 Å. Zn loadings are given above 10° shell fitting results for each sample.

Table S2: Shell fitting results of Zn doped saponite samples measured at pH=6.8 and room temperature. Bond lengths and Debye-Waller factors of polarization sensitive shells were fixed to the values measured at respective angle. Amplitude reduction factor set equal to 0.9 for all shells. E_0 shift is equal 9.15 eV for ZnSapD1 and 8.70 eV for ZnSapD3 samples. Debye-Waller factors were fixed to 0.007 for Zn-O and Zn-Mg shells and to 0.15 for Zn-Si shell. Experimental bond length uncertainty is ± 0.01 . The experimental edge (reference) energy shift (ΔE_0) is determined by shell fitting.

Polarization angle, α	Zn-O			Zn-Mg			Zn-Si			ΔE_0 , eV	R, %
	CN	d , Å	$\sigma_W^2, \text{\AA}^2$	CN	d, Å	$\sigma_W^2, \text{\AA}^2$	CN	d, Å	$\sigma_W^2, \text{\AA}^2$		
ZnSapD1											
10	5.6	-		4.3	3.06		0.5	-		9.15	2.5
35	5.4	2.09	0.007	3.9	-	0.007	0.6	-	0.015		3.7
70	5.8	-		4.9	-		2.5	3.28			2.3
ZnSapD3											
10	5.8	-		5.7	3.06		2.5	-		8.46	1.7
35	6.0	2.09	0.007	5.0	-	0.007	2.5	-	0.015		1.9
70	5.4	-		5.1	-		4.2	3.29			2.0

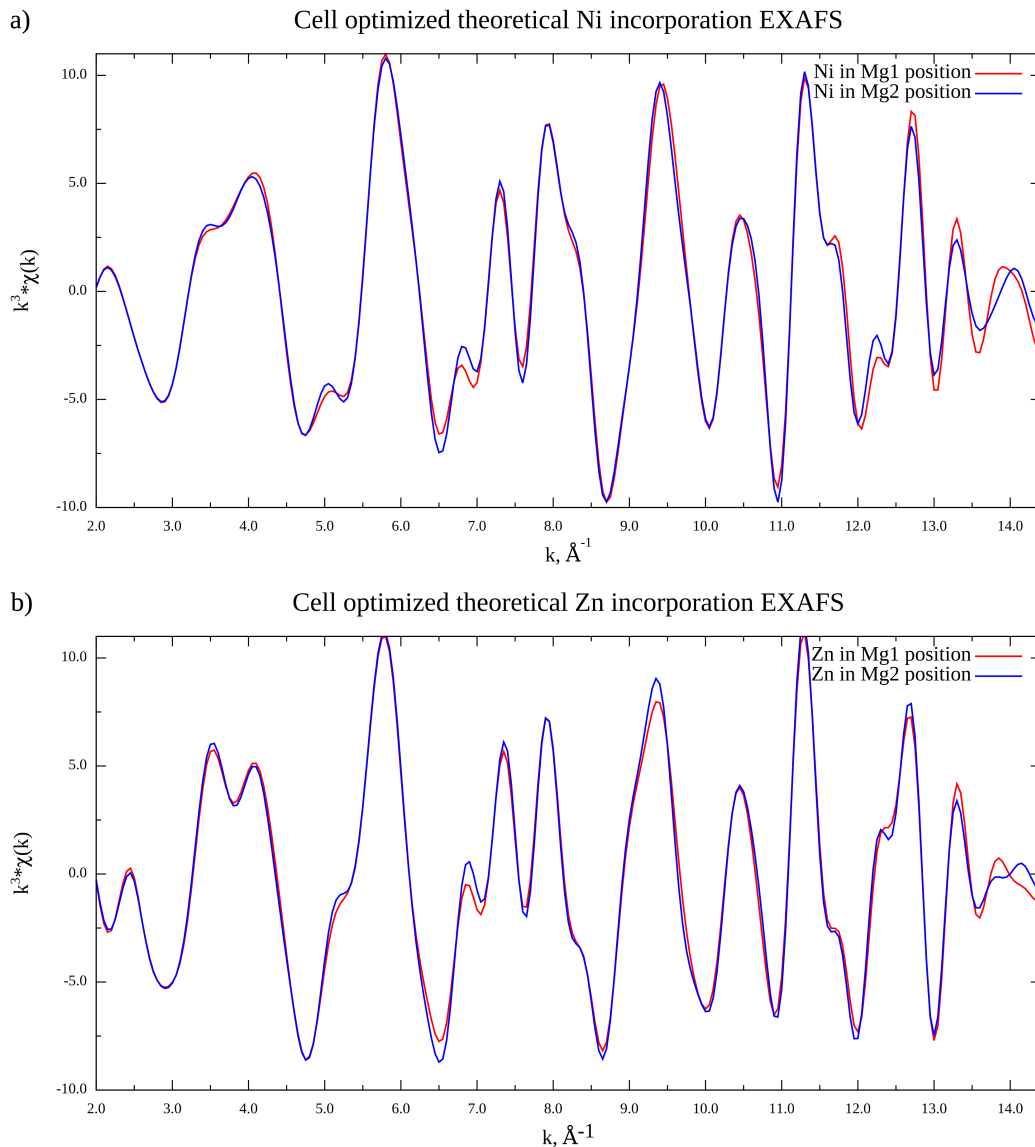


Figure S10: Theoretical EXAFS spectra simulated from cell optimized structures of Ni (a) or Zn (b) incorporation in talc bulk structure. Red spectra corresponds to incorporation in Mg1 position, whereas blue - in Mg2. Although, spectra from both positions are practically identical, it should be noted that position Mg1 exists is fully occupied only in trioctahedral clay minerals. Whereas, in dioctahedral clay minerals like montmorillonite - it is vacant.

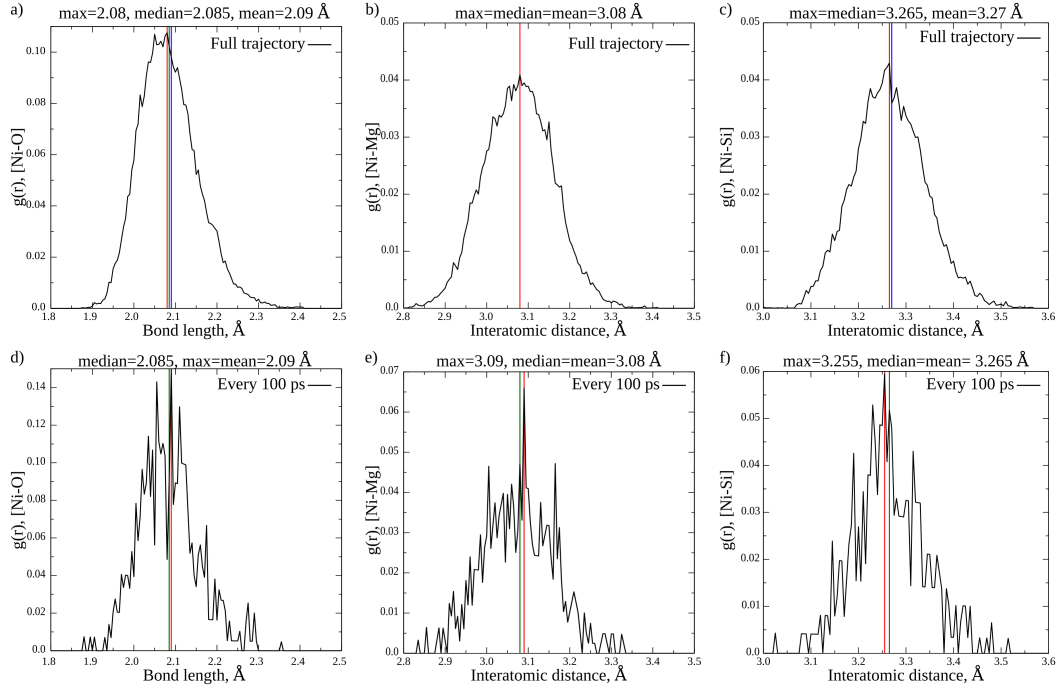


Figure S11: Radial pair distribution functions for first three coordination shells of Ni incorporated in saponite: a-c) radial pair distribution function for Ni-O (a), Ni-Mg (b), and Ni-Si(c) pairs in a whole equilibrated ab initio MD trajectory, 10 ps; d-f) radial pair distribution function of Ni-O(d), Ni-Mg(e), and Ni-Si(f) shells for 101 ab initio MD snapshot used to simulate theoretical EXAFS spectra.

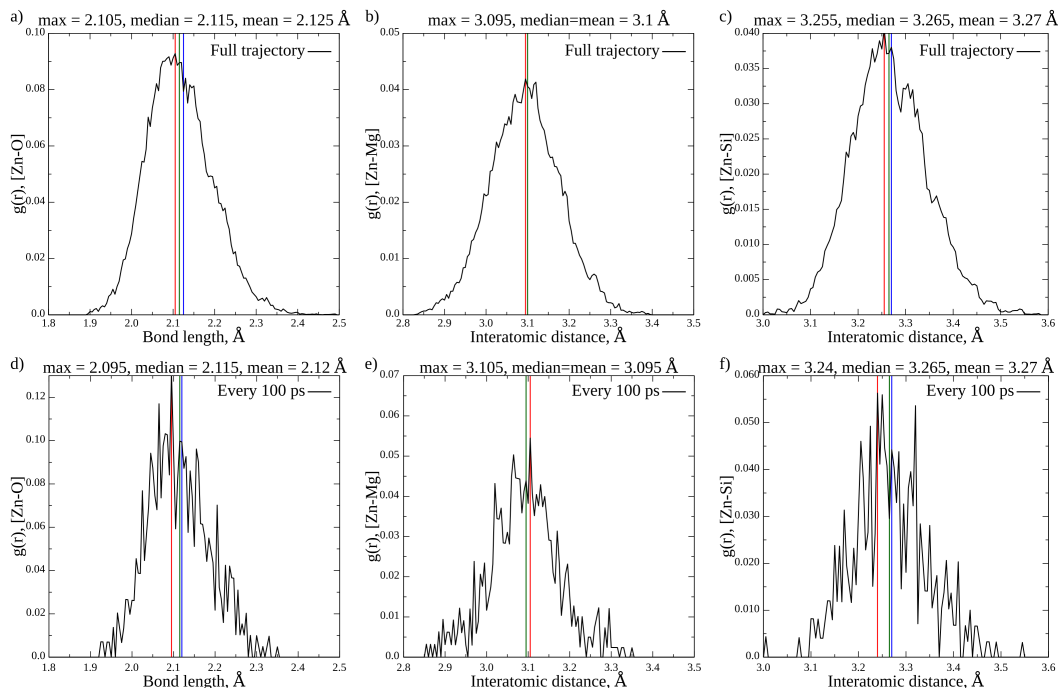


Figure S12: Radial pair distribution functions for first three coordination shells of Zn incorporated in saponite: a-c) radial pair distribution function for Zn-O(a), Zn-Mg(b), and Zn-Si(c) pairs in a whole equilibrated ab initio MD trajectory, 10 ps; d-f) radial pair distribution function of Zn-O(d), Zn-Mg(e), and Zn-Si(f) shells for 101 ab initio MD snapshot used to simulate theoretical EXAFS spectra.

Table S3: Results of thermodynamic integration for Ni-Zn cation exchange between bulk and aqueous phase. Helmholtz free energy and constants were calculated using 10 ps long ab initio MD trajectory. Uncertainties (σ) were estimated using half of the equilibrated (10 ps long) trajectory.

Thermodynamic property	Value
$\langle \Delta E_{\lambda=0} \rangle \pm 2\sigma$, kJ/mol	-1.70 $\pm$ 2.88
$\langle \Delta E_{\lambda=0.5} \rangle \pm 2\sigma$, kJ/mol	-43.93 $\pm$ 3.25
$\langle \Delta E_{\lambda=1} \rangle \pm 2\sigma$, kJ/mol	-78.89 $\pm$ 3.38
$\langle \Delta A \rangle \pm 2\sigma$, kJ/mol	-42.72 $\pm$ 1.13
pK $\pm 2\sigma$	-7.44 $\pm$ 0.20

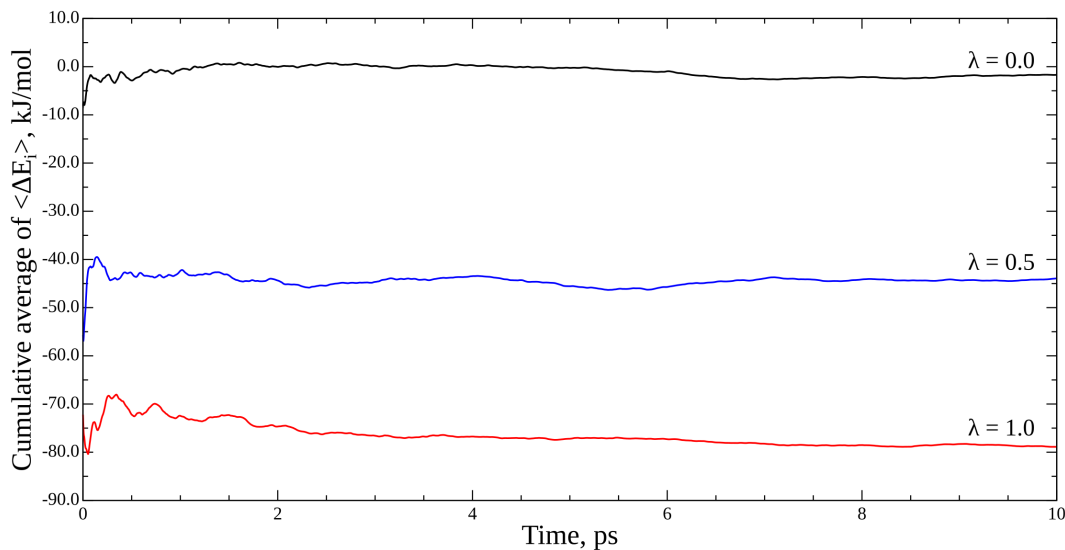


Figure S13: Cumulative average of $\text{Ni}^{2+}/\text{Zn}^{2+}$ cation exchange reaction between bulk and aqueous solution for three potential energy gap coupling λ parameters: 0.0, 0.5, and 1.0.

$$\text{Cumulative average of } \Delta E_i = \frac{1}{i} \sum_{j=1}^i x_j, \quad (1)$$

where x_j is the value at each data point and i is the current number of points.

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