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Hydration-Induced Transition from Site-Controlled to Diffusion-Controlled Ion Transport in Montmorillonite Interlayers

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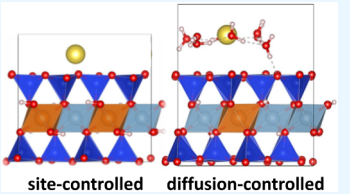
ABSTRACT: Ion transport in clay minerals is governed by hydration (interlayer water content), yet the underlying molecular mechanisms remain insufficiently understood. Specifically, it is unclear whether water simply reduces migration barriers or fundamentally alters the nature of transport. Here, we combine density functional theory (DFT) with two-dimensional potential energy surface (PES) mapping to investigate the mobility of Na^+ and K^+ in montmorillonite interlayers as a function of water content. In water-free conditions, the energy landscape is strongly corrugated, exhibiting pronounced minima and large migration barriers (~several eV) that localize ions at specific adsorption sites, defining a site-controlled regime. Upon hydration, migration barriers decrease nonlinearly, and the energy landscape progressively flattens. At sufficiently high water content, well-defined adsorption sites disappear, signaling a transition to a diffusion-controlled regime. We further demonstrate that the topology of the tetrahedral framework acts as a physical sieve, proving as decisive for ion localization as the electrostatic charge distribution. While Na^+ mobility remains sensitive to the local structural vacancy arrangement, the larger K^+ ion experiences a spatially averaged potential due to steric restrictions that decouple its transport from local lattice heterogeneity. These findings reveal that hydration does not merely enhance mobility but fundamentally alters the topology of the energy landscape, acting as a molecular "switch" between localized and delocalized ion behavior in confined nanoporous materials.



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1. INTRODUCTION

Interlayer water in montmorillonite (MMT), a 2:1 smectite clay, plays a critical role in controlling its swelling, mechanical, and transport properties. Water enters the interlayer space through the hydration of exchangeable cations (e.g., Na^+, Ca^{2+}), leading to discrete hydration states commonly referred to as 0W, 1W, 2W, etc., corresponding to monolayer or bilayer water coverage.[1,2] Basal spacing ($d001$) measured by X-ray diffraction (XRD), provides a direct probe of interlayer water content; idealized samples often exhibit stepwise expansions, whereas natural or heterogeneous samples display intermediate spacings due to interstratified layers or partial hydration.[2,3]

Molecular simulations and experimental studies further demonstrate that interlayer water is confined and structured around cations, forming hydrogen-bonded networks, with both discrete energetic minima and continuous density variations.[3,4] These hydration behaviors directly influence swelling pressure, shear strength, and permeability, which are critical in geotechnical applications, engineered barriers, and soil mechanics.[2,4] Understanding the interplay among hydration, cation type, and environmental conditions is therefore essential for predicting MMT behavior under practical conditions.

In these confined environments, the interplay between structure and interfacial interactions can lead to the formation of spatial patterns, which, in turn, strongly influence transport processes.[5−7] Ion and molecule transport in confined nanoporous systems, such as zeolites, has been extensively investigated using both experimental techniques and molecular simulations. In particular, classical simulation studies have provided detailed insights into adsorption, diffusion pathways, and shape-selective transport in well-defined pore networks. These systems have established the conceptual framework that links energy landscape topology to transport behavior in confined environments.[8,9] In contrast to rigid zeolitic frameworks, montmorillonite interlayers represent a dynamically evolving and hydration-dependent confinement, where both the accessible volume and the local electrostatic environment are strongly coupled to water content. As a result, the relationship between hydration, energy landscape topology, and ion transport remains less well understood at the molecular level, compared to processes in clay minerals, which provide complementary insights into transport behavior at larger time and length scales.[10] While it is widely recognized that hydration enhances ion mobility, the underlying mechanisms remain insufficiently understood at the molecular level. In particular, it remains unclear whether hydration (interlayer water content) simply reduces energy barriers or whether it induces a more fundamental transition in the

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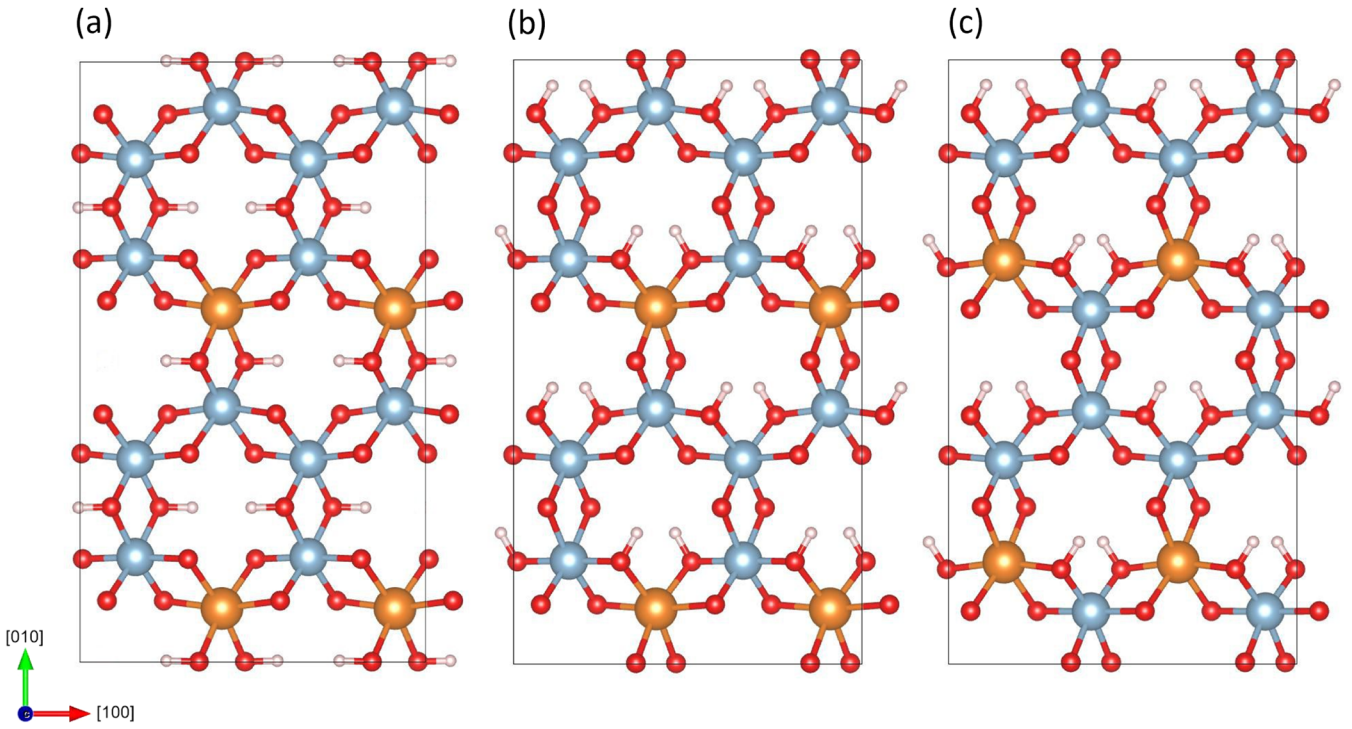

Figure 1. Top view of the montmorillonite octahedral sheet showing (a) trans-vacant, (b) cis-vacant1, and (c) cis-vacant2 configurations. Aluminum, magnesium, oxygen, and hydrogen atoms are shown in gray, orange, red, and white, respectively. The different vacancy arrangements define distinct electrostatic environments in the interlayer, which are expected to influence ion adsorption and migration.

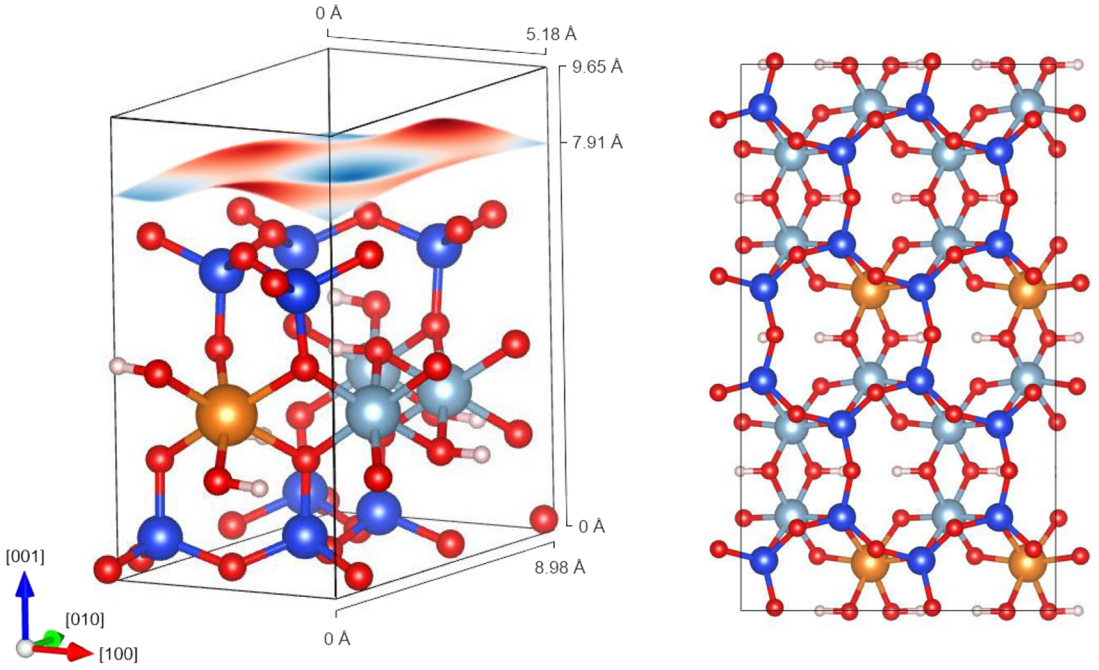

Figure 2. Representative position of a Na^+ ion in the interlayer of trans-vacant Na-saturated montmorillonite (1 unit cell, ξ = 0.500). The ion occupies specific adsorption sites defined by the underlying structure, indicating a site-controlled energy landscape in the absence of water.

topology of the energy landscape and the resulting transport mechanism.

In highly structured environments, strongly corrugated energy landscapes can impose localized states and suppress mobility, whereas a flattening of the landscape can lead to enhanced transport and delocalization. In this work, we address this question by combining DFT calculations with systematic two-dimensional potential energy surface (PES) mapping of interlayer cations in montmorillonite. By progressively increasing the water content, we are able to directly resolve how hydration acts as a molecular "switch", transforming the transport mechanism from a localized, site-controlled regime to a delocalized, diffusion-controlled regime. However, a direct molecular-level description of how hydration

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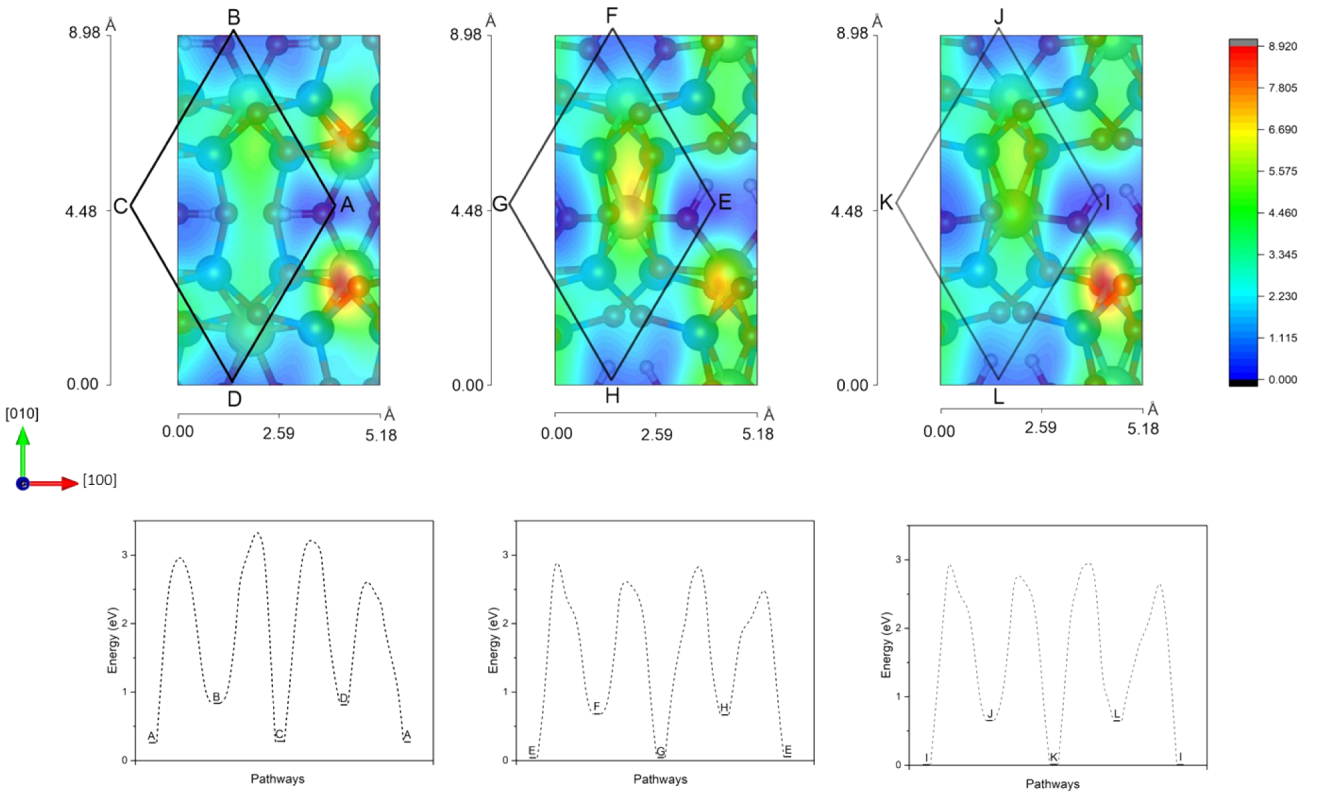

Figure 3. Two-dimensional potential energy surfaces and corresponding migration pathways for Na^+ in the interlayer of montmorillonite (1 unit cell, $\xi = 0.500$) under water-free conditions. (A–D) trans-vacant, (E–H) cis-vacant1, and (I–L) cis-vacant2 configurations. The energy landscapes exhibit pronounced minima and large migration barriers, indicating strongly localized ions and a highly corrugated energy landscape.

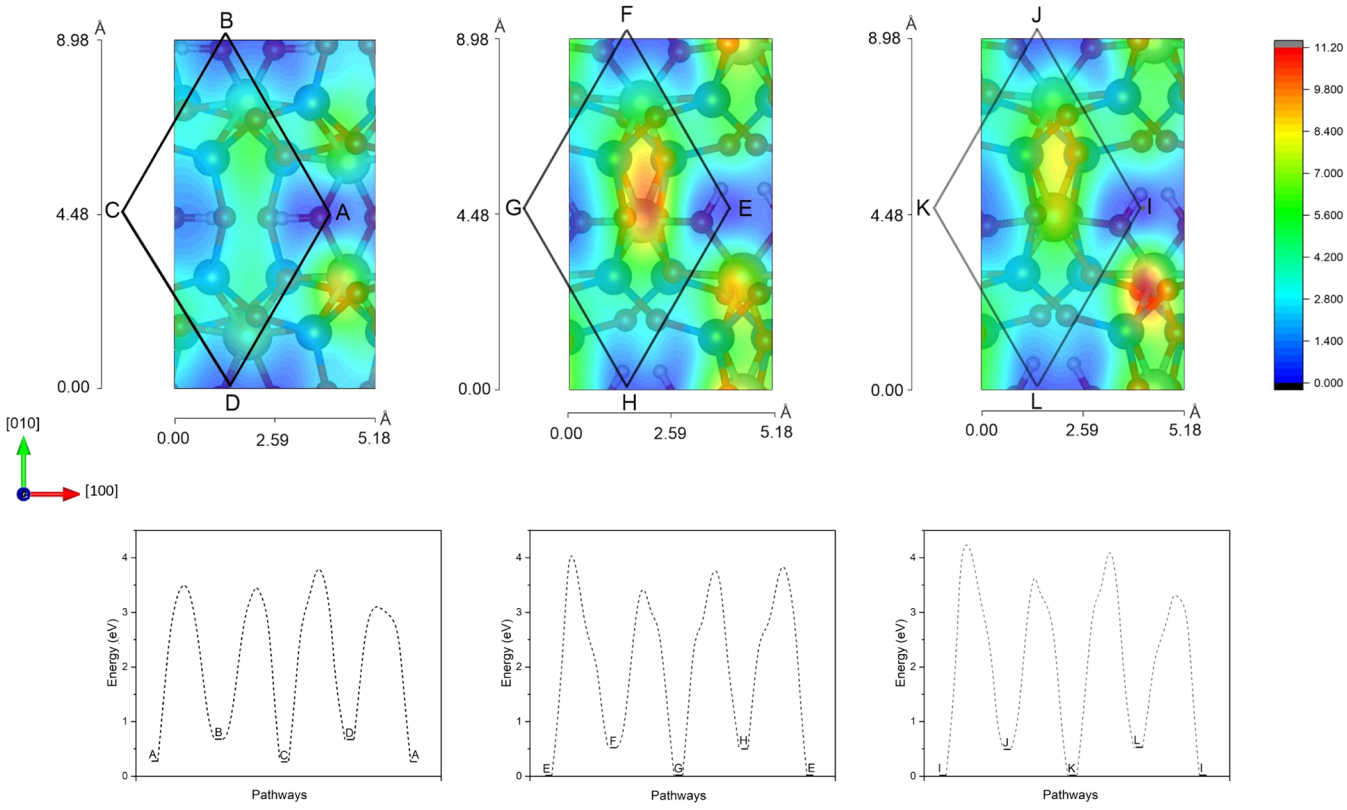

Figure 4. Two-dimensional potential energy surfaces and migration pathways for K^+ in the interlayer of montmorillonite (1 unit cell, $\xi = 0.500$) under water-free conditions. Compared to Na^+, K^+ exhibits a modified energy landscape with different barrier heights, reflecting ion-specific interactions within the interlayer.

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modifies the underlying energy landscape and induces transitions between distinct transport regimes is still lacking.

2. COMPUTATIONAL METHODOLOGY

The structural model for this study is based on a dioctahedral 2:1 montmorillonite framework.[11] Isomorphic substitutions were introduced in the octahedral sheet to create three distinct configurations: trans-vacant (tv), cis-vacant1 (cv1), and cis-vacant2 (cv2), with a fixed layer charge of ξ = 0.500, compensated by interlayer Na^+ or K^+ ions.

DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP). The projector augmented-wave (PAW) method[12] described core−valence electron interactions, while exchange-correlation functional effects were treated within the generalized gradient approximation (GGA) using the Perdew−Burke−Ernzerhof (PBE) form.[13] Dispersion interactions were accounted for using the D3 correction. A plane-wave energy cutoff of 400 eV was applied, and the Brillouin zone was sampled using a Γ-centered 1 × 1 × 1 k-point mesh. Structural relaxations were performed until forces were below 10^{-3} eV/Å.[12−17]

Potential Energy Surface (PES) mapping was performed by defining a regular grid in the x−y plane of the interlayer. At each grid point, the ion's lateral position was fixed, while relaxation was permitted along the *z*-direction to account for the local electrostatic environment. Water molecules were introduced incrementally, with full structural relaxations performed at each hydration level prior to subsequent PES mapping to resolve how hydration alters the landscape topology.

3. RESULTS AND DISCUSSION

To understand the origin of the observed energy landscapes, the structural features of the clay layers were analyzed in detail. Figure 1 shows the octahedral sheet, in which the negative layer charge arises from isomorphic substitution, whereas Figure 2 presents the tetrahedral sheet, which is in direct contact with the interlayer ions but does not carry the charge. It is commonly assumed that interlayer cations are primarily positioned above the charge-compensating sites because of electrostatic interactions. However, the calculated potential energy surfaces reveal a more complex picture. The preferred ion positions are not solely determined by the location of the charge but are strongly influenced by the geometry of the tetrahedral surface. In particular, the tetrahedral sheet defines the accessible volume and the local distance between the ion and the charged defect in the octahedral layer. As a result, the potential energy surface is effectively governed by geometric constraints that modulate electrostatic interactions.

To understand ion mobility in montmorillonite interlayers, two-dimensional potential energy surfaces (PESs) were first calculated under water-free conditions. In all investigated configurations, the energy landscape exhibits pronounced periodic minima, corresponding to well-defined adsorption sites imposed by the clay structure (Figures 3 and 4). These minima form a spatial pattern that effectively localizes interlayer cations. The calculated migration barriers are on the order of several electron volts, indicating that ion transport is strongly suppressed in the absence of water. This behavior defines a site-controlled regime in which ion mobility is governed by the strongly corrugated underlying energy landscape.

To investigate the effect of hydration, water molecules were systematically introduced into the interlayer region (Figure 5).

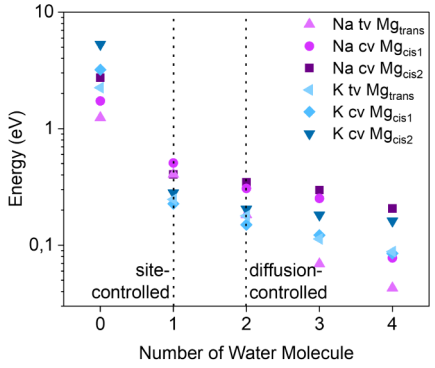

Figure 5. Migration energy barriers for Na^+ and K^+ as a function of interlayer water content. Hydration acts as a molecular switch, inducing a transition across three regimes: (i) site-controlled localization with high barriers (∼several eV), (ii) a nonlinear transition regime, and (iii) a diffusion-controlled delocalized regime. While Na^+ is sensitive to local structural vacancies, the larger K^+ ion experiences a spatially averaged potential due to steric restrictions.

This incremental increase in interlayer water content corresponds to the progression through discrete hydration states (0W, 1W, 2W), typically characterized by basal spacing (d001) in XRD experiments.[1,2] A pronounced and nonlinear decrease in migration barriers is observed with increasing water content. This nonlinear collapse of migration barriers corresponds to the progression through discrete hydration states—specifically the transition from the 0W to the 2W state—commonly observed in XRD characterization.[18] By linking the number of interlayer water molecules directly to the energy landscape topology, our results provide a molecular explanation for the "stepwise" expansion of basal spacing; the transition from a site-controlled to a diffusion-controlled regime suggests that the mechanical and transport properties of the clay are not just enhanced by water, but are fundamentally redefined at each hydration step. Even small amounts of water significantly reduce barrier heights. Based on this evolution, three distinct regimes can be defined. At low hydration levels, ions remain localized within well-defined adsorption sites, corresponding to a site-controlled regime. At intermediate hydration, a transition regime emerges, characterized by rapidly decreasing barriers and increased energy landscape connectivity.

The relevance of this hydration behavior is fundamental, as it dictates the macroscopic properties of the clay, including swelling pressure, shear strength, and permeability.[2,4] At higher water contents, the energy landscape becomes effectively flattened, and the periodic energy minima disappear. In this regime, ions are no longer confined to specific sites but can move more freely within the interlayer, indicating a transition to a diffusion-controlled transport mechanism. These results demonstrate that hydration does not merely enhance ion mobility but also fundamentally alters the topology of the energy landscape, acting as a molecular switch that induces a transition from localized, pattern-controlled ion behavior to delocalized diffusion. It is worth noting that the effect of water on transport in confined systems is not universally enhanced. While the present results demonstrate a strong increase in ion mobility at low to moderate hydration levels due to the

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flattening of the energy landscape, other studies have shown that at high degrees of saturation, transport can be hindered by crowding effects, increased viscosity, or pore blocking. These observations are not contradictory but rather reflect different hydration regimes, highlighting the complex and nonmonotonic role of water in confined transport phenomena.[19]

In the limit of full hydration, the interlayer environment approaches that of a confined aqueous phase, where dielectric screening and dynamic solvation are expected to further smooth the energy landscape. However, even under such conditions, geometric confinement imposed by the clay layers defines the accessible volume and is, therefore, likely to maintain a residual influence on ion transport. This suggests that, while localization effects vanish, structural constraints remain relevant even in highly hydrated states.

A notable difference between Na^+ and K^+ ions lies in the sensitivity of their energy barriers to the structural configuration of the clay layers (Figure 5). While Na^+ exhibits a clear dependence on the vacancy arrangement (trans- and cis-vacant structures), the corresponding energy barriers for K^+ collapse onto nearly identical curves. Because both ions carry the same charge, this behavior cannot be attributed solely to differences in electrostatic interaction. Instead, this behavior reflects the influence of ionic size and steric restrictions on the accessible configurational space within the interlayer. Due to its smaller ionic radius, Na^+ can access more confined regions defined by the tetrahedral framework, enabling a stronger sensitivity to local structural variations. In contrast, the larger K^+ ion is sterically restricted from these regions and consequently experiences a spatially averaged potential. This observation highlights geometric confinement as a key factor governing ion mobility in clay interlayers. While electrostatic interactions between cations and the negative layer charge are foundational, our results demonstrate that the tetrahedral sheet acts as a physical sieve. The energy mapping reveals that geometric constraints—defined by the accessible volume between oxygen triads—modulate the electrostatic attraction by forcing ions into specific heights relative to the charged defects. This implies that in confined nanoporous materials, the topology of the surface framework can be as decisive for ion localization as the charge distribution itself. The fact that K^+ energy barriers collapse onto nearly identical curves across different vacancy arrangements highlights a steric restriction mechanism. Because K^+ is larger, it remains "perched" higher above the tetrahedral cavities, effectively decoupling its transport from the local structural variations of the octahedral sheet. This explains why Na-saturated clays often exhibit more sensitive swelling and transport responses to mineralogical heterogeneity compared to their K-saturated counterparts. It should be noted that K-saturated montmorillonite is typically restricted to lower hydration states under experimental conditions. The inclusion of higher hydration levels for K^+ in the present study is therefore intended as a conceptual extension, enabling a systematic comparison of ionic size effects under controlled conditions rather than a direct representation of experimentally accessible states. The hydration states considered in this study (0W, 1W, 2W) correspond to well-established discrete swelling states observed experimentally by X-ray diffraction. The associated interlayer distances are consistent with typical basal spacings reported in the literature, supporting the physical relevance of the modeled configurations.

The potential energy surfaces (PESs) presented in this work do not directly correspond to free energy landscapes, as entropic contributions and thermal fluctuations are not explicitly captured in static DFT calculations. However, the PES provides direct access to the underlying energetic topology, governing ion localization and migration pathways. The pronounced corrugation observed under dry conditions and its systematic flattening upon hydration, therefore, represent robust trends that are expected to qualitatively persist under finite temperature conditions. In this sense, the present approach resolves the fundamental energetic origin of transport, which serves as the basis for the thermally activated diffusion processes.

While classical molecular dynamics (MD) simulations are well-suited to probe long-time diffusion and transport coefficients, the present DFT-based approach focuses on resolving the atomistic energy landscape that governs these processes. In this context, DFT provides the energetic framework, while MD samples the corresponding phase space. A combined DFT−MD approach would, therefore, represent a valuable extension, enabling a direct link between energy landscape topology and macroscopic transport properties. The periodic arrangement of energy minima observed in the calculated potential energy surfaces reflects the periodic boundary conditions inherent to the DFT model. Accordingly, no claim is made regarding the exact spatial pattern of ion positions in real systems. However, the presence of pronounced energy minima and large migration barriers unambiguously demonstrates that the energy landscape is strongly structured. This implies that ions are confined to preferred adsorption sites and that ion mobility is governed by a site-controlled mechanism in the absence of water. Importantly, the observed collapse of energy barriers upon hydration is independent of the imposed periodicity and reflects a fundamental change in the topology of the energy landscape. The disappearance of pronounced minima indicates that hydration removes the site-controlled character of the system, leading to a more homogeneous energy landscape for transport. Beyond clay systems, the observed hydration-induced modification of the energy landscape may have broader implications for confined chemical processes. In catalytic systems, water is known to strongly influence reactivity and transport by modifying local energetic environments. The transition from localized to more delocalized states identified here may, therefore, provide a conceptual framework for understanding how hydration affects the accessibility and mobility of reactive species in nanoporous catalytic materials.

4. CONCLUSIONS

In this work, we investigated the effect of hydration (interlayer water content) on ion mobility in montmorillonite interlayers by combining density functional theory calculations with systematic potential-energy surface mapping. Under water-free conditions, the calculated energy landscapes exhibit pronounced periodic minima and large migration barriers on the order of several electronvolts, demonstrating that ions are strongly localized within a site-controlled regime. While the periodic arrangement of minima reflects the modeling approach, the presence of a strongly corrugated energy landscape and high barriers provides robust evidence of suppressed ion mobility in dry clay systems.

Upon hydration, a pronounced and nonlinear decrease in migration barriers is observed. Increasing the interlayer water

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content progressively reduces the corrugation of the energy landscape, leading to the disappearance of the well-defined adsorption sites. At sufficiently high hydration levels, the energy landscape becomes effectively flattened, signaling a transition to a diffusion-controlled transport regime, where ions move in a delocalized manner.

Our findings further reveal that geometric confinement and ionic size play critical roles in this transition. We demonstrate that the topology of the tetrahedral framework acts as a physical sieve, proving to be as decisive for ion localization as the electrostatic charge distribution. While Na^+ mobility remains sensitive to local structural vacancy arrangements, the larger K^+ ion experiences a spatially averaged potential because of steric restrictions that decouple its transport from local lattice heterogeneity.

Ultimately, these results demonstrate that water does not merely enhance ion mobility but fundamentally alters the topology of the energy landscape. Hydration acts as a molecular switch between localized and delocalized ion behavior, providing a mechanistic basis for understanding macroscopic properties such as swelling pressure, mechanical strength, and permeability in hydrated nanoporous materials. This framework highlights the decisive role of the energy landscape topology in governing transport processes in confined mineral environments.

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Notes

The authors declare no competing financial interest.

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