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Water vapor diffusive transport in a smectite clay: Cationic control of normal versus anomalous diffusion

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The transport of chemical species in porous media is ubiquitous in subsurface processes, including contaminant transport, soil drying and soil remediation. We study vapor transport in a multiscale porosity material, a smectite clay, in which water molecules travel in mesopores and macropores between the clay grains but can also intercalate inside the nanoporous grains, making them swell. The intercalation dynamics is known to be controlled by the type of cation that is present in the nanopores; in this case exchanging the cations from Na^+ to Li^+ accelerates the dynamics. By inferring spatial profiles of mesoporous humidity from a space-resolved measurement of grain swelling, and analyzing them with a fractional diffusion equation, we show that exchanging the cations changes mesoporous transport from Fickian to markedly subdiffusive. This results both from modifying the exchange dynamics between the mesoporous and nanoporous phases, and from the feedback of transport on the medium's permeability due to grain swelling. An important practical implication is a large difference in the time needed for vapor to permeate a given length of the clay depending on the type of intercalated cation.