

Vapor transport in a porous smectite clay: From normal to anomalous diffusion

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Smectite clays are widely found on the Earth surface. They are porous materials possessing connected mesopores in the micrometer range, in-between mineral grains, and nanopores inside the grains. These grains are stacks of individual 1 nm-thick clay particles (the *layers*) and have the ability to swell by incorporating H₂O molecules (or other molecules such as CO₂) in-between the layers, depending on the ambient temperature and on the humidity present in the mesopores surrounding the grain. Imposing a gradient of relative humidity *RH* along a temperature-controlled dry sample of smectite clay, we investigate the diffusive transport of water molecules in vapor phase through the material. As water molecules diffuse through the mesopores, some of them intercalate into the nanopores, causing the grains to swell and causes a decrease in the mesoporous volume available for vapor diffusion. We monitor this process using space- and time-resolved X-ray diffraction. Water absorption into the nano-layered grains changes the interlayer repetition distance (*d*-spacing) of the stacks. A calibration experiment performed under controlled constant temperature and controlled humidity level all around the sample, varying *RH* by steps, has allowed us to map the monotonous evolution of *d* as a function of *RH*. By mapping *d* in space and time we obtain humidity *RH*(*x*) profiles along the direction of the initial humidity gradient, at different times *t*. To model the data we consider a one-dimensional effective diffusion process described by a fractional time diffusion equation with a diffusion coefficient that depends on humidity, and we show that it is possible to rescale the humidity profiles onto a single master curve as a function of the parameter $(x/t)^{\gamma/2}$, where γ is an exponent characterizing the diffusion process as normal ($\gamma=2$), subdiffusive ($\gamma<2$), or superdiffusive ($\gamma>2$). We observe that when the clay sample is prepared with sodium charge compensating cations intercalated in the nano-pores, then the vapor transport is normal ($\gamma=2$), while if the interlayer cation is lithium, the transport is strongly subdiffusive. We suggest that this is linked to the difference in time scales observed for the water adsorption dynamics by individual stacks for the two cation cases. The effective mechanism is reminiscent of retardation mechanisms known in other subsurface media, with a nanoscale trapping mechanism and a feedback effect of the mesoporous humidity on the local porosity of the medium.

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