

On the disorder of hydrated cations in todorokite tunnels

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Todorokite is a tunnel-type Mn oxide found in diverse marine and terrestrial environments. The oxide, which contains various hydrated metal cations in the relatively large 1D nanopores, can impact the mobility and fate of metal contaminants. Compared to the lattice parameters, however, hydrated cation structures are unambiguously determined yet; conflicts exist as to the tunnel cation positions and their coordination configurations. We investigate the hydrated cation structures in todorokite tunnels using molecular dynamics (MD) simulation with the MnFn force field [1]. Here we report that the positions and coordination of the tunnel cations (Ni^{2+} , Zn^{2+} , Mg^{2+} , Ca^{2+} , Na^+ , K^+ , and Cs^+) strongly depend on water content in the tunnel. At high water content, divalent cations occupy the center sites of the tunnel as fully-hydrated outer-sphere complexes, but monovalent cations except Na^+ reside near the Mn octahedral sheet as inner-sphere complexes. Na^+ cations were outer-sphere complexes in Na^+ -todorokite at high water content, but they transform to inner-sphere complexes when mixed with divalent cations. We estimate the optimal water content that todorokite can accommodate for each cation and a mixed cation composition based on intercalation free energies calculated with the MD-based free energy perturbation method. We discuss disorder of the hydrated cation structure in todorokite tunnels.

**** References**

[1] Newton A. G. and Kwon K. D. (2020) *Geochim. Cosmochim. Acta* **291**, 92–109