

Influence of Layer Charge on the Hydration Properties of Synthetic Smectites

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Smectites are 2:1 phyllosilicates with a layer structure consisting of two siliceous tetrahedral sheets embedding an octahedral one. The occurrence of isomorphous substitutions within both tetrahedral and octahedral sheets induces a permanent negative layer charge, which is compensated for by the presence in the interlayer space of exchangeable cations whose hydration properties can strongly impact dynamical properties of interlayer species and thus the transfer/fate of H₂O and pollutants. Smectite crystal chemistry, and more especially the amount and location of smectite layer charge, has long been known to exert a pivotal control on smectite hydration. [1,2] The influence of charge location, however, remains incompletely documented. In this perspective, the present study is aimed at assessing the charge position influence on interlayer species organization by combining powder X-ray diffraction (PXRD) profile modeling and molecular modeling (Monte Carlo simulation in grand canonical ensemble).

A set of octahedrally charged trioctahedral smectites (hectorites), with a common structural formula $inter[Na_x, n H_2O]^{oct}[Mg_{6.0-x}Li_x]^{tet}[Si_{8.0}]O_{20}(OH)_4$ and a layer charge (x) varying from 0.8 to 1.6, was synthesized. Interlayer H₂O contents were measured as a function of relative humidity (RH) from H₂O vapor (de)sorption isotherms. The evolution in the proportions of mono- and bi-hydrated smectite layers and the distribution of interlayer species were then determined from PXRD profile modeling as a function of RH (Figure 1). Monte Carlo simulations were performed in the grand canonical ensemble to get additional details on the distribution of H₂O molecules and charge-compensating cations within interlayers.

The transitions between discrete hydration states occur at similar RH values, independent of the amount of layer charge. When normalized to the number of interlayer cations, the number of interlayer H₂O molecules decreases with increasing layer charge, and the proportion of these H₂O molecules hydrating interlayer cations increases. The influence of layer charge location on smectite hydration heterogeneity is also discussed based on the comparison with tetrahedrally charged smectites [1,2] with contrasting layer charge.

It is concluded that 1) the total amount of interlayer H₂O is about independent of layer charge amount and location; 2) the evolution of layer-to-layer distance with the layer charge amount differs for saponite and hectorite as the result of contrasting electrostatic interactions between the 2:1 layer and interlayer cations; 3) contrary to saponite, the RH domains for the different hydrates in hectorite are not modified by the amount of layer charge.

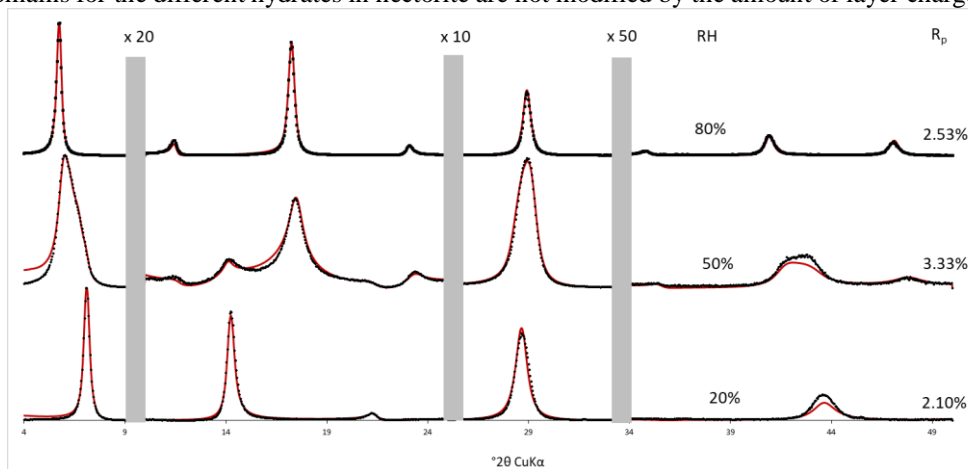


Figure 1. Comparison between experimental and calculated XRD patterns for Hectorite-1.0-OH. Experimental and calculated XRD patterns are shown as crosses and solid lines, respectively

[1] E. Ferrage *et al.*, J. Phys. Chem. C 114 (2010) 4515-4526

[2] B. Dazas *et al.*, J. Phys. Chem. C 119 (2015) 4158-4172