

## Hydration, expansion, structure, and dynamics of layered double hydroxides

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### ABSTRACT

Water-vapor sorption isotherms, relative humidity (RH) controlled powder X-ray diffraction (XRD) data, and new and previously published multi-nuclear NMR spectroscopic data for a wide range of layered double hydroxides (LDHs) provide greatly increased understanding of the effects of hydration state on the structure and dynamical behavior of interlayer and surface anions and the factors controlling the expansion behavior of this group of minerals. Li,Al and Mg,Al LDH phases containing  $\text{SO}_4^{2-}$ ,  $\text{SeO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{MoO}_4^{2-}$ ,  $\text{ClO}_4^-$ ,  $\text{SeO}_3^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{OH}^-$ , and  $\text{NO}_3^-$  were examined. The phases studied can be grouped into three types based on basal spacing expansion, water sorption, and interlayer anion dynamics: Type 1, significantly expandable (1.5–3.0 Å); Type 2, slightly expandable (expansion <0.5 Å) and with significant interlayer water exchange; and Type 3, essentially non-expandable (0–0.2 Å) and with little interlayer water exchange. For Type 1, the fully expanded phases have a two-water layer structure, and the phase transition from one layer to two layers as determined by XRD consistently correlates with a significant step in the water sorption isotherm and with changes in the interlayer structure and dynamics as observed by NMR spectroscopy. For Type-2 phases, only one-water layer structures form, and the interlayer anions may undergo dynamical disordering with increasing RH, as observed by NMR. For both Types 1 and 2, the first water layer does not cause significant basal spacing expansion due to occupancy of vacant interstitial sites between the anions by the water molecules. For Type-3 phases, there is little interlayer water sorption because the interlayers are essentially closed due to the small size or planar shape of the anions and their strong electrostatic and hydrogen bonding interaction with the hydroxyl layers. RH has no effect on the structural environments and dynamics of the interlayer anions in this group.