

Characterization of Cd²⁺ surface complexes on kaolinite and gibbsite with experimental and theoretical XANES

MOLLY A. SMALL¹ HEATH D. WATTS²,
NIRANJAN GOVIND³ JAMES D. KUBICKI²
AND PEGGY A. O'DAY¹

¹University of California, Merced, CA, USA.

(*correspondence: msmall4@ucmerced.edu)

²Department of Geosciences, The Pennsylvania State University, University Park, PA, USA.

³Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA, USA.

Determination of energetically favorable surface complexes forming at the mineral-solution interface is important for understanding the surface reactivity of common minerals such as kaolinite and gibbsite. In addition to being a toxic pollutant, Cd²⁺ sorption is representative of divalent “hard” cations and thus a useful probe ion for surface complexation from solutions varying in metal and electrolyte concentration. In this study, experimental X-ray Absorption Near-Edge Spectroscopy (XANES) is combined with periodic density functional theory (DFT) and theoretical XANES calculations to characterize Cd²⁺ complexes sorbed to mineral surfaces. The Cd L_{III} XANES region exhibits a number of unique features which aid in the interpretation of the local bonding environment.

Spectra were collected for Cd²⁺ reference compounds, aqueous solutions, and sorption samples. Reference spectra include: CdCO₃(s), CdSO₄(s), Cd(OH)₂(s), Cd(OH)Cl(s), CdCl₂(s) and CdCl₂(aq). Cadmium sorption experiments were conducted with either kaolinite or gibbsite, Cd²⁺ (CdCl₂), and a constant background electrolyte (CaCl₂) concentration. Samples were equilibrated for 1 and 36 d periods at ~ pH 8 over a range of CaCl₂ background electrolyte concentrations (10-100 mM). Ground state DFT calculations were performed on reference and realistic complexes using VASP. Candidate structures from these simulations were used to calculate the XANES spectra with the NWChem computational chemistry program. Calculated spectra were compared with experimental spectra to verify known structures in crystalline compounds and assess the plausibility of theoretical surface complexes. Linear combination fits show that Cd²⁺ surface complexation can be described by a combination of a hydrated component, and mononuclear and binuclear inner-sphere complexes. Spectra show positive energy shifts with increasing ionic strength. Such experimental and theoretical combinations can characterize relevant surface complexes to support robust surface complexation models.