

---

# *In Situ* Infrared Speciation of Adsorbed Carbonate on Aluminum and Iron Oxides

Chunming Su<sup>†</sup> and Donald L. Suarez

USDA-ARS, U.S. Salinity Laboratory, 450 West Big Springs Road, Riverside, California 92507-4617

<sup>†</sup> Present address: U.S. Environmental Protection Agency, National Risk Management Research Laboratory, 919 Kerr Research Drive, Ada, Oklahoma 74820.

**Abstract:** Surface adsorption mechanisms of dissolved inorganic carbon species on soil minerals are not well understood. Traditional infrared (IR) study of adsorbed species of inorganic carbon using air-dried samples may not reveal true species in the solid/water interface in suspension. The purpose of this study was to obtain information on interfacial carbonate speciation between solid and aqueous phases. The interaction of bicarbonate and carbonate ions with X-ray amorphous (am) Al and Fe oxides, gibbsite ( $\gamma$ -Al(OH)<sub>3</sub>) and goethite ( $\alpha$ -FeOOH) was examined by electrophoresis and *in situ* attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. The presence of carbonate lowered the electrophoretic mobility and decreased the point of zero charge (PZC) of all minerals, implying specific adsorption. Inner-sphere complexation of bicarbonate and carbonate was supported by a lowering in the anion symmetry due to the interaction with Al and Fe oxide surfaces. Only complexed monodentate carbonate was identified in am-Al(OH)<sub>3</sub>/aqueous solution at pH 4.1– 7.8 when the solid was reacted with either NaHCO<sub>3</sub> or Na<sub>2</sub>CO<sub>3</sub> solutions. Am-Al(OH)<sub>3</sub> was transformed to a crystalline sodium aluminum hydroxy carbonate, dawsonite [NaAl(CO<sub>3</sub>)(OH)<sub>2</sub>], and bayerite ( $\alpha$ -Al(OH)<sub>3</sub>) after reacting with 1.0 M Na<sub>2</sub>CO<sub>3</sub> for 24 h. Gibbsite adsorbed much less carbonate than am-Al(OH)<sub>3</sub> such that adsorbed carbonate on gibbsite gave weak IR absorption. It is probable that monodentate carbonate is also the complexed species on gibbsite. Evidence suggesting the presence of both surface complexed bicarbonate and carbonate species in the interfacial region of am-Fe(OH)<sub>3</sub> in suspension and the dependence of their relative distribution on solution pH is shown. Only monodentate carbonate was found in the interfacial region of goethite in 1.0 M NaHCO<sub>3</sub>. A ligand exchange reaction was proposed to describe the interaction of bicarbonate and carbonate with the surface functional groups of Al and Fe oxides.

**Key Words:** Attenuated Total Reflectance-Fourier Transform Infrared • Carbonate Adsorption • Electrophoretic Mobility • Infrared • Point of Zero Charge • Point of Zero Net Proton Charge • X-ray Diffraction

*Clays and Clay Minerals*; December 1997 v. 45; no. 6; p. 814-825; DOI: [10.1346/CCMN.1997.0450605](https://doi.org/10.1346/CCMN.1997.0450605)

© 1997, The Clay Minerals Society

Clay Minerals Society ([www.clays.org](http://www.clays.org))

---