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IN SITU INFRARED SPECIATION OF ADSORBED CARBONATE ON ALUMINUM AND IRON OXIDES

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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 (γ-$Al(OH)_3$) and goethite (α-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-$Al(OH)_3$/aqueous solution at pH 4.1–7.8 when the solid was reacted with either $NaHCO_3$ or Na_2CO_3 solutions. Am-$Al(OH)_3$ was transformed to a crystalline sodium aluminum hydroxy carbonate, dawsonite [$NaAl(CO_3)(OH)_2$], and bayerite (α-$Al(OH)_3$) after reacting with 1.0 *M* Na_2CO_3 for 24 h. Gibbsite adsorbed much less carbonate than am-$Al(OH)_3$ 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-$Fe(OH)_3$ 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* $NaHCO_3$. 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.

INTRODUCTION

Dissolved inorganic carbon species such as $H_2CO_3^0$, HCO_3^- and CO_3^{2-} are ubiquitous in natural waters and soil environments. Yet their interaction with soil minerals such as Al and Fe oxides are not well understood. Information is lacking on *in situ* speciation of inorganic carbon species at the molecular level on soil mineral surfaces in aqueous suspension. An understanding of carbonate species adsorption mechanisms has practical applications in soil science, geochemistry and for the global carbon cycle.

Schulthess and McCarthy (1990) studied competitive adsorption of anions on an Al oxide (δ-Al_2O_3) and obtained an affinity sequence of the anions for the oxide: $OH^- > CO_3^{2-} >$ acetate $> Cl^-$. They stated that these ions adsorb competitively on the same Al sites, but not necessarily by the same mechanisms. Competitive adsorption also has been observed between CrO_4^{2-} and dissolved $CO_2(g)$ on amorphous Fe hydroxide (Zachara et al. 1987) and on goethite (Van Geen et al. 1994). In addition to surface adsorption, carbonate can also form discrete solid phases with Al such as dawsonite [$NaAl(CO_3)(OH)_2$]. The maximum adsorption of carbonate is at pH 6.5 on δ-Al_2O_3 (Schulthess and McCarthy 1990) and pH 6 on goethite (Van Geen et al. 1994), whereas the maximum content of dawsonite formed from precipitating Al hydroxide in the presence of solution carbonate species occurs at pH 8.5 (Scholtz et al. 1984). To explain increased solubility of hematite in the presence of $CO_2(g)$, Bruno et al. (1992) postulated the formation of a monodentate bicarbonate surface complex and its subsequent detachment from the hematite surface.

White and Hem (1975) precipitated an Al hydroxide gel (X-ray amorphous) by adding a solution of $AlCl_3$ to a mixed solution of $NaHCO_3$ and Na_2CO_3 until pH 6.5 was reached. They concluded from the IR spectroscopy of air-dried samples that an association exists between carbonate and Al cations in the Al hydroxide gel. Serna et al. (1977) also precipitated an X-ray amorphous Al hydroxide gel by adding $AlCl_3$ solution to a solution containing either $NaHCO_3$ or Na_2CO_3 until pH 6.5 was reached. They obtained the same IR results as White and Hem (1975). In both studies, monodentate carbonate bonding with Al was identified with no evidence for the presence of bicarbonate ion in the air-dried Al hydroxide gel. The IR spectra of air-dried Al hydroxide precipitates formed by mixing a solution of 0.5 *M* $AlCl_3$ with a solution of 0.75 *M* $NaHCO_3$ or 2 *M* Na_2CO_3 at pH 6–10 showed that daw-

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sonite formation occurred between pH 7.5 and 9.5 (Scholtz et al. 1984). Information on the speciation of adsorbed inorganic carbon species on Al hydroxide below pH 6 is lacking, and other common Al hydroxides such as gibbsite have not been studied in this regard. Additionally, the influence of air-drying from more acidic suspension on surface carbonate speciation has not been investigated.

The surface charge characteristics of Al hydroxide gel depend on both the surface hydroxyl density and the surface density of the specifically adsorbed anions. The wide range of point of zero net proton charge (PZNPC) values reported for Al hydroxide is thought to be due to the presence of specific adsorption of impurity anions such as carbonate (Feldkamp et al. 1981), and carbonate-containing crystalline solid phases such as dawsonite (Scholtz et al. 1984, 1985). The specifically adsorbed anion contributes additional negative charge to the surface, thereby displacing the PZNPC to lower pH values (Sposito 1984).

Russell et al. (1975) reported IR spectroscopic evidence for the formation of distorted carbonate molecules on the surface of moist goethite during CO_2(g)-adsorption experiments. Yapp and Poths (1990) also presented IR evidence for the existence of carbonate in the form of $Fe(CO_3)OH$ as a minor component in natural goethite. Lumsdon and Evans (1994) reported that goethite (α-FeOOH) suspensions purged with CO_2-free N_2(g) for up to 2 mo have a measured PZNPC in the range 9.0–9.3, which is close to the theoretical value of 9.4. Unpurged goethite samples showed PZNPC values in the range 7.4–8.8 (Evans et al. 1979; Zeltner and Anderson 1988; Lumsdon and Evans 1994).

The surface charge density of particles is an important factor affecting adsorption behavior. One of the most convenient techniques for monitoring the surface charge of dispersed particles is microelectrophoresis. The measurement of electrophoretic mobility (EM), which is related to the zeta potential and surface charge density of the particles, provides information on the nature of the surface of particles (Hunter 1981).

It is hypothesized that both bicarbonate and carbonate ions are adsorbed on Al and Fe oxides via ligand exchange and produce direct coordination to Al and Fe cations. *In situ* FTIR spectroscopy has been used to study surface-facilitated degradation of tetraphenylboron in smectite clay pastes (Hunter and Bertsch 1994), protonation of phosphate on goethite surfaces in aqueous suspension (Tejedor–Tejedor and Anderson 1986, 1990) and speciation of adsorbed boron on the surfaces of amorphous Al and Fe oxides and allophane in aqueous paste (Su and Suarez 1995). This technique should be useful in determining if the ligands are within the coordination sphere. Previous IR studies on carbonate interaction with Al oxide involved air-drying of samples. This method has its limitations as air-drying results in a more concentrated solution (higher ionic strength), and increasing alkalinity (with drying) shifts the pH to greater values. Both increased ionic strength and increased pH (constant H_2CO_3 concentration and increased alkalinity) result in an increase in the CO_3^{2-} concentration relative to the HCO_3^- concentration in solution. Because of these limitations it is preferred to utilize *in situ* examination in aqueous suspension for bicarbonate and carbonate adsorption with techniques such as ATR-FTIR spectroscopy.

The objectives of this study were to determine the bonding mechanisms of bicarbonate and carbonate with Al and Fe oxides and to elucidate the structure of surface-adsorbed species. We also seek to determine the relationship between the solution and interfacial species distribution.

MATERIALS AND METHODS

Synthetic X-ray amorphous Al hydroxide [am-$Al(OH)_3$] and Fe hydroxide [am-$Fe(OH)_3$] (hereafter called oxides) were prepared by the method of Su and Suarez (1995). A well-crystallized gibbsite (C-730) described by Kittrick (1966) was utilized. Synthetic goethite (α-FeOOH) was prepared with an OH/Fe molar ratio of 9.0 by the method of Schwertmann and Cornell (1991) using 1 *M* $Fe(NO_3)_3$ and 5 *M* KOH. The suspension was incubated at 70 °C for 60 h and centrifuged. The solids were resuspended in deionized water and the suspension pH was adjusted to 6.5 with HCl before centrifugation. The solids were washed repeatedly with deionized water until the supernatant electrical conductivity was <0.003 dS m^{-1}. The crystals were dried at 70 °C and gently ground.

The EM was determined for all minerals by microelectrophoresis using a Zeta-Meter 3.0 system (Zeta Meter, Long Island City, New York; mention of trade names is for the benefit of the reader only and does not indicate endorsement by the USEPA and USDA). Suspensions containing 0.2 g L^{-1} solid in 0.01 *M* NaCl were acidified to pH 3 with HCl and titrated with 0.01 *M* NaOH (CO_2-free) or 0.0033 *M* Na_2CO_3 to various pHs for EM determination. The PZC was obtained by direct observation or interpolating the data to zero mobility.

For the ATR-FTIR spectroscopic study, mineral suspensions (usually 100 g L^{-1} unless indicated otherwise) were prepared by adding the equivalent of 2 g of solids to 20 mL of CO_2-free water, 0.01, 0.1 and 1.0 *M* analytical grade $NaHCO_3$ or 0.01, 0.1 and 1.0 *M* Na_2CO_3 (Mallinckrodt, Paris, Kentucky) dissolved in CO_2-free water. The experiment was performed in the laboratory atmosphere. The CO_2-free water was prepared by boiling deionized water. The suspensions were shaken end-to-end for 24 h and centrifuged. Fifteen milliliters of the supernatant was removed and 3.5 mL of it was used as a "reference" for FTIR analysis. The solid was resuspended in the remaining 5 mL of

supernatant in the centrifuge tube and used as the "sample". This procedure yields a solid concentration of 400 g L^{-1} in the ATR reservoir. To avoid gel formation, 0.5 or 1.0 g of am-$Al(OH)_3$ was reacted with 20 mL of 1.0 *M* Na_2CO_3 for 24 h, and the suspensions were centrifuged; 10 mL of supernatant were removed so that the final solid concentration was 50 or 100 g L^{-1}. For the same reason, a final solid concentration of 200 g L^{-1} was obtained for goethite after the 2.0 g of goethite were redispersed in 10 mL of supernatant. The pH of supernatant of a subsample was determined using a combination pH electrode. Total inorganic C in both the supernatant and the final suspension was determined by the pressure-calcimeter method (Nelson 1982). The amount of inorganic C adsorbed was calculated as the total inorganic C in the suspension corrected for the total inorganic C in the supernatant using the particle density of 2.42 g cm^{-3} for gibbsite (Weast 1976) and am-$Al(OH)_3$, and 3.96 g cm^{-3} for am-$Fe(OH)_3$ and 4.26 g cm^{-3} for goethite (Schwertmann and Cornell 1991). All results reported were expressed on a moisture-free basis. Moisture of starting minerals was determined from weight loss after drying at 105 °C for 24 h.

Infrared spectra of the aqueous solutions of $NaHCO_3$ and Na_2CO_3, and carbonate-adsorbent suspensions were recorded in the 4000–700 cm^{-1} range with a Bio-Rad FTS-7 spectrometer and a deuterated triglycine sulfate detector (Digilab, Cambridge, Massachusetts). The sampling method was attenuated total reflectance (ATR) with a horizontal reservoir as a sample holder and a ZnSe crystal rod with a 45° angle of incidence as an internal reflectance element. The energy drop for the ZnSe internal reflection element is approximately 700 cm^{-1}. The sample holder is made of stainless steel and has a volume of 4 mL. Single beam IR spectra were developed from 2000 co-added interferograms with a 4 cm^{-1} resolution. Following the method of Tejedor–Tejedor and Anderson (1986) for free bicarbonate and carbonate anions in aqueous solution, all final solution spectra were obtained by subtracting the spectra of NaCl solution (adjusted for the ionic strength and pH) (reference), from spectra of the $NaHCO_3$ or Na_2CO_3 solution (sample). Likewise, all final spectra for the adsorbed carbonate species were obtained by subtracting the spectra of the equilibrating supernatant solution (reference) from spectra of the adsorbent suspension (sample). Both reference and samples spectra were corrected against empty ATR reservoir cell spectra. The subtraction factor was always unity in order to obtain true difference spectra instead of ratioed spectra.

Samples of starting minerals, minerals equilibrated with deionized water (control treatment) and water-washed minerals previously reacted with $NaHCO_3$ and Na_2CO_3 for 24 h were examined by X-ray diffraction. Washing with deionized water was necessary to remove excess sodium salts prior to X-ray examination. Packed powder mounts were scanned in 0.02 °2θ steps with a Philips model 12045 diffractometer (Philips Electronic Instruments, Mount Vernon, New York) using Cu*K*α radiation and a LiF crystal monochromator, all linked to a computer. Specific surface areas of adsorbents were determined using a single-point BET N_2 adsorption isotherm on a Quantachrome Quantasorb Jr. surface area analyzer (Quantachrome Corp., Syosset, New York).

RESULTS AND DISCUSSION

Surface Charge at the Shear Plane

The electrophoretic mobility data in Figure 1 show that the presence of carbonate lowered the mobility in the pH range 3.5 to 10 and reduced the PZC of all minerals, suggesting inner-sphere carbonate adsorption and a reduction of positive charge at the shear plane of adsorbents in aqueous suspension. Similar findings were reported for phosphate adsorbed on goethite (Tejedor–Tejedor and Anderson 1990), and for borate adsorbed on Al and Fe oxides, kaolinite and allophane (Su and Suarez 1995). It should be emphasized, however, that the electrophoretic mobility data only provide indirect information with regard to adsorption mechanisms. Direct molecular level adsorption information can be derived from spectroscopic study. Electrophoresis cannot distinguish between adsorption and surface precipitation. Electrophoretic mobility is, therefore, a complementary tool to the ATR-FTIR spectroscopy, which is relied on for direct information of molecular interactions.

Free Bicarbonate and Carbonate Ions in Aqueous Solution

Figure 2 shows the ATR-FTIR difference spectra (sample spectra minus reference spectra) of 0.01, 0.1 and 1.0 *M* HCO_3^-. The sample spectra were those of 0.01–1.0 *M* $NaHCO_3$ solutions, whereas the reference spectra were those of pH-adjusted NaCl solutions. IR adsorbance bands in Figure 2 were attributed to the free HCO_3^- anion because this anion is the predominant species at pH ≈8 (>97% of total C). There was essentially no neutral $H_2CO_3^0$ present as indicated by the absence of a band near 1730 cm^{-1} in the spectra for C = O stretching (Hage et al. 1993). The vibra-

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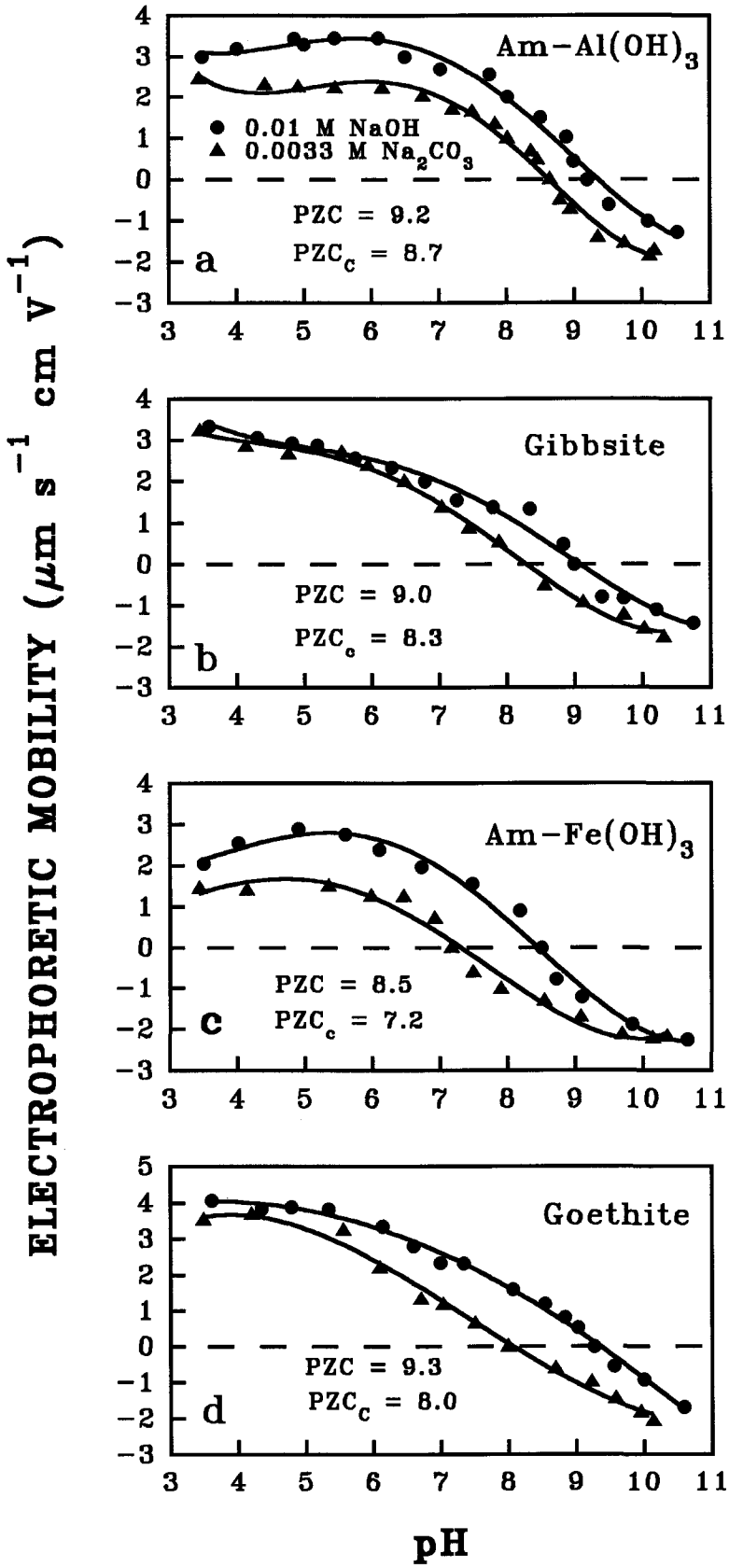
Figure 1. Electrophoretic mobility of Al and Fe oxides in 0.01 *M* NaCl titrated with 0.01 *M* NaOH and 0.003 *M* Na_2CO_3. Initial solid concentration was 0.2 g L^{-1}. The PZC_c stands for PZC of adsorbents titrated with 0.0033 *M* Na_2CO_3.


ELECTROPHORETIC MOBILITY (μm s⁻¹ cm V⁻¹)
Am−Al(OH)3
● 0.01 M NaOH
▲ 0.0033 M Na2CO3
PZC = 9.2
PZCc = 8.7
a
Gibbsite
PZC = 9.0
PZCc = 8.3
b
Am−Fe(OH)3
PZC = 8.5
PZCc = 7.2
c
Goethite
PZC = 9.3
PZCc = 8.0
d
pH

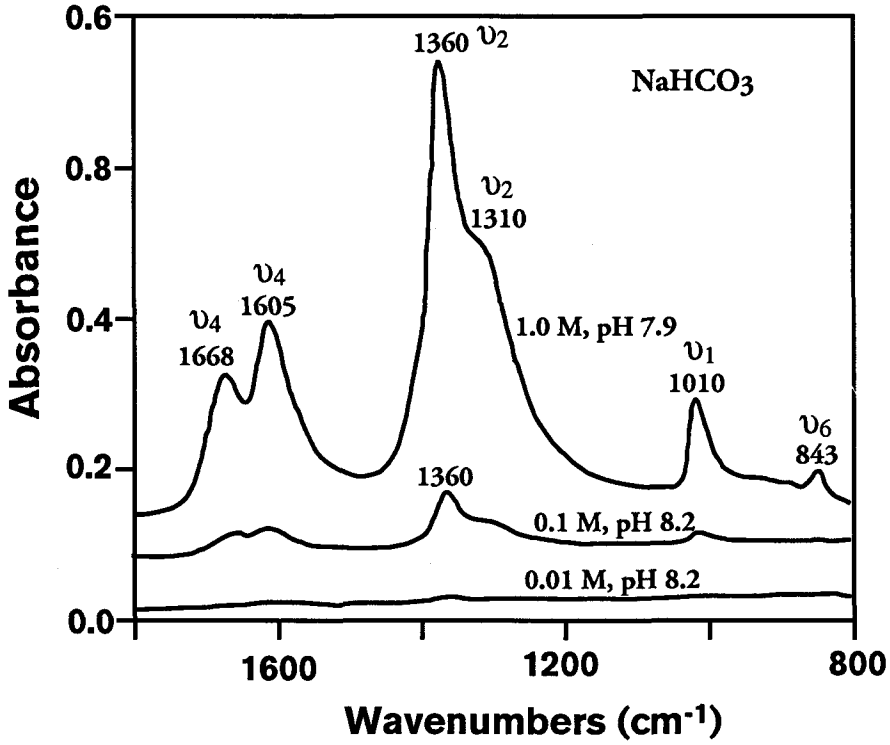


Figure 2. ATR-FTIR difference spectra of 0.01 (pH 8.2), 0.1 (pH 8.2) and 1.0 *M* $NaHCO_3$ (pH 7.9) solutions and 0.01 (pH 8.2), 0.1 (pH 8.2) and 1.0 *M* NaCl (pH 7.9) solutions, respectively. The spectrum of NaCl solution was subtracted from spectrum of $NaHCO_3$ solution. The subtraction factor was unity. The spectra are offset for clarity.

tional spectrum of the HCO_3^- anion can be interpreted on the basis of a planar tetratomic group $CO_2(OH)^-$, which has a C_{2v} symmetry (Ross 1972). By referring to the IR transmission spectra of alkali metal bicarbonate solids, bands for free HCO_3^- ion in aqueous solution (unavailable in the literature) were assigned as follows: ν_1 (stretching of C-OH) at 1010 cm^{-1}, ν_2 (symmetric stretching of CO_2) at 1360 and 1310 cm^{-1}, ν_4 (asymmetric stretching of CO_2) at 1668 and 1605 cm^{-1}, and ν_6 (out-of-plane bending of CO_3) at 843 cm^{-1}. The rest of the fundamental vibration modes, ν_3 (symmetric in-plane bending of CO_3) and ν_5 (asymmetric in-plane bending of CO_3) should appear below 800 cm^{-1}, a spectral region which could not be observed.

The ATR-FTIR difference spectra of uncomplexed Na_2CO_3 solutions are shown in Figure 3. At pH $\approx$11.2 in 1.0 *M* Na_2CO_3, only about 10% of total C is in the form of HCO_3^-, which exhibited ν_4 (asymmetric stretching) at 1680 and very weakly at 1560 cm^{-1}. Since the dominant carbonate species in Na_2CO_3 solution is the free CO_3^{2-} anion, which has a D_{3h} symmetry (trigonal planar) (Ross 1972), the IR absorption bands at 1065, 887 and 1383 cm^{-1} were assigned to the vibrational modes of ν_1 (symmetric stretching), ν_2 (out-of-plane bending) and ν_3 (asymmetric stretching), respectively.

Characterization of Carbonate/Al Oxide Surface Complexes

The spectra of chemical species at the solid/aqueous solution interface can be best observed by subtracting the bulk solution (supernatant) absorption from the spectrum of the corresponding suspension (Tejedor–Tejedor and Anderson 1986, 1990). The resulting difference spectra contain IR absorption bands due to both solid bulk and interfacial species. Figure 4 shows the difference ATR-FTIR spectra of am-$Al(OH)_3$ reacted with $NaHCO_3$ at various concentrations. The absorption bands of interfacial carbonate species in the spectral range 1800–800 cm^{-1} were examined.

Differences in position and number of absorption bands between the spectra of $NaHCO_3$ in aqueous solution (Figure 2) and spectra of carbonate species at the am-$Al(OH)_3$/aqueous solution interface (Figure 4) indicate carbonate species coordination with the surface Al atoms of the am-$Al(OH)_3$ particles. At all 3 $NaHCO_3$ concentrations, a split of ν_3 vibration for carbonate occurred to give a doublet near 1490 and at 1420 cm^{-1}. An additional band at 1028 cm^{-1} assigned to ν_2 vibration for carbonate was also observed for am-$Al(OH)_3$ reacted with 1.0 *M* $NaHCO_3$ (Figure 4). Since the characteristic doublet of ν_4 for the bicarbonate anion was not observed, it is con-

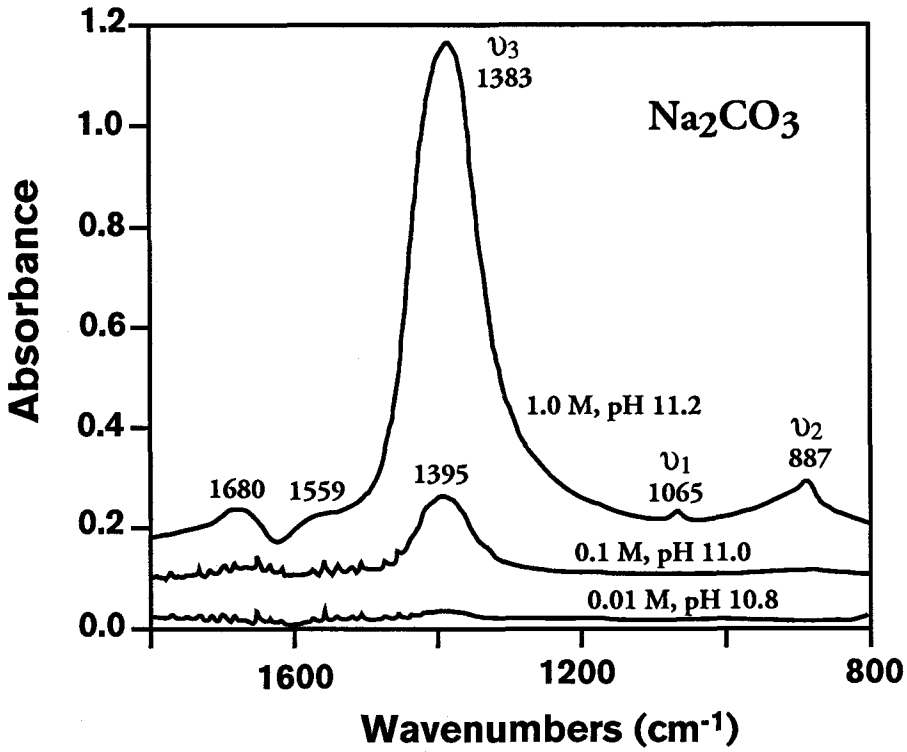


Figure 3. ATR-FTIR difference spectra of 0.01 (pH 10.8), 0.1 (pH 11.0) and 1.0 *M* Na_2CO_3 (pH 11.2) solutions and 0.03 (pH 10.8), 0.3 (pH 11.0) and 3.0 *M* NaCl (pH 11.2) solutions, respectively. The spectrum of NaCl solution was subtracted from spectrum of Na_2CO_3 solution. The subtraction factor was unity. The spectra are offset for clarity.

cluded that no detectable bicarbonate existed in the interfacial region of am-$Al(OH)_3$ suspension. Bands at 967 and 992 cm^{-1} are assigned to AlO_4 tetrahedra (Ross 1972), which exhibited a greater wave number in 1.0 *M* $NaHCO_3$, suggesting reduced symmetry of the AlO_4 tetrahedra. It is clear that the distribution of surface species on am-$Al(OH)_3$ does not correspond to the distribution of solution species of $NaHCO_3$ solution. At pH < 4.3, the neutral $H_2CO_3^0$ molecule is predominant in solution, whereas at pH 7.8, HCO_3^- anion is predominant; however, the only interfacial species of carbon detected is the complexed and distorted carbonate.

Spectra similar to that observed with $NaHCO_3$ and am-$Al(OH)_3$ was observed for am-$Al(OH)_3$ reacted with 0.01 and 0.1 *M* Na_2CO_3 (Figure 5). Again, after subtraction of spectrum of the supernatant from the spectrum of the am-$Al(OH)_3$ suspension, no evidence of bicarbonate was seen in the interfacial region. To further determine whether a mono- or a bidentate complex of carbonate with surface Al cation forms, we examine the magnitude of the splitting of the ν_3 vibration. When carbonate ion coordinates to a metal cation, the ν_3 vibration splits into 2 bands (Ross 1972; Nakamoto 1986). The frequency difference between the doublet in the model monodentate carbonate complex $[Co(NH_3)_5CO_3]Cl$ is 94 cm^{-1}, whereas it is 308 cm^{-1} in the bidentate carbonate complex $[Co(NH_3)_4CO_3]Cl$ (Table 1). A splitting of ν_3 vibration of a magnitude of about 70 cm^{-1} in am-$Al(OH)_3$ was observed in our study (Table 1). Therefore, we conclude that a monodentate carbonate complex exists in the interfacial region. This conclusion is in excellent agreement with that of Serna et al. (1977), who demonstrated that regardless of whether the precipitation of Al hydroxide gel is carried out with $NaHCO_3$ or Na_2CO_3, only carbonate ion is present in the air-dried gel. Air-drying thus does not seem to affect the carbonate speciation on the Al oxide surface.

After either 0.5 or 1.0 g of am-$Al(OH)_3$ was reacted with 20 mL of 1.0 *M* Na_2CO_3, dawsonite $[NaAl(CO_3)(OH)_2]$ formed, with traces of bayerite (α-$Al(OH)_3$), as indicated by the X-ray diffractogram (Figure 6). In addition, the difference ATR-FTIR spectra of the products (Figure 7) were in agreement with the IR absorption spectrum of a natural dawsonite in a dispersed KBr pellet examined by Frueh and Golightly (1967). The assignments for CO_3^{2-} in dawsonite are ν_1 (symmetric stretching) at 1096 cm^{-1}, ν_2 (bending) at 846 cm^{-1}, and ν_3 (asymmetric stretching) at 1560, 1497 and 1388 cm^{-1}. The band at 955 cm^{-1} is for Al-OH bending in dawsonite (Frueh and Golightly 1967) and at 1020 cm^{-1} for Al-OH bending in bayerite (Kodama 1985). Bayerite is shown to form in alkaline solutions with OH/Al molar ratios between

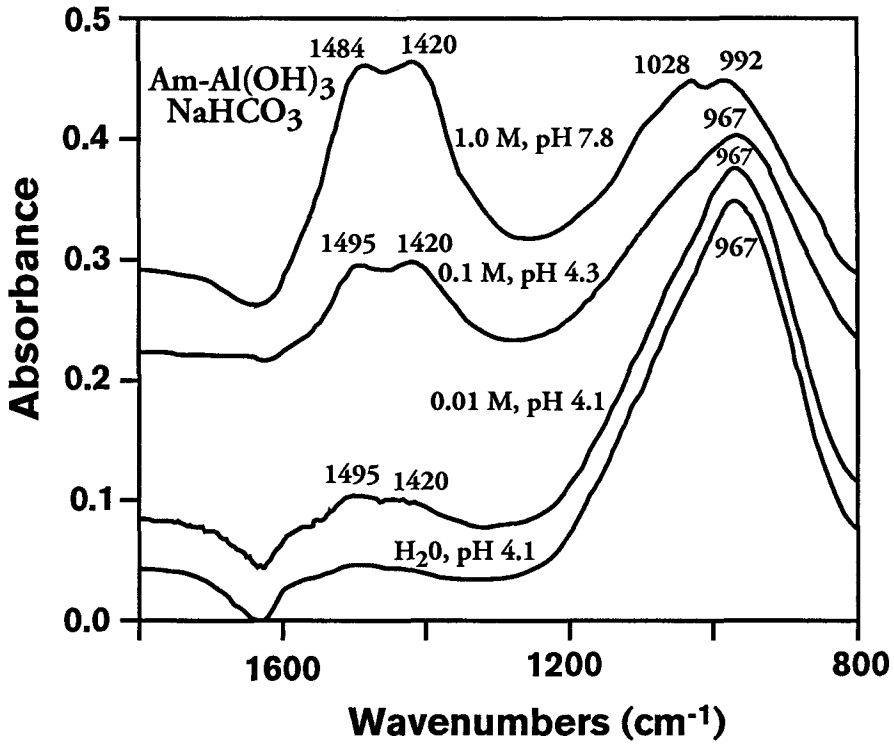


Figure 4. ATR-FTIR difference spectra of am-$Al(OH)_3$ (the spectrum of supernatant was subtracted from spectrum of solid suspension) as a function of $NaHCO_3$ concentration. Solid concentration in the ATR reservoir was 400 g L^{-1}. The amount of adsorbed C on am-$Al(OH)_3$ was 0.031, 0.051, 0.26 and 0.89 mol kg^{-1} in deionized water, 0.01, 0.1 and 1.0 *M* $NaHCO_3$, respectively.

3.0 and 3.3 (Hsu and Bates 1964; Hsu 1967). Apparently, CO_3^{2-} and OH^- compete for Al in am-$Al(OH)_3$ to form these 2 solid phases, as they do for Al in aqueous solutions of $AlCl_3$. Scholtz et al. (1984) found dawsonite in addition to amorphous carbonate-containing Al hydroxide when an $AlCl_3$ solution was titrated to pH 7.5–9.5 by separate solutions of $NaHCO_3$ and Na_2CO_3.

In comparison with am-$Al(OH)_3$, gibbsite was less reactive with $NaHCO_3$ and Na_2CO_3 as shown by their lower amounts of adsorption. The amount of adsorbed C on gibbsite was 0.001, 0.030, 0.10 and 0.27 mol kg^{-1} in water (equilibrium pH 4.7), 0.01 (pH 8.0), 0.1 (pH 8.6) and 1.0 *M* $NaHCO_3$ (pH 8.3), respectively. No detectable IR absorption bands were found for either carbonate or bicarbonate species in the interfacial region for aqueous concentrations of less than 0.1 *M*. The ν_3 vibration for CO_3^{2-} did not split in gibbsite reacted with 1.0 *M* $NaHCO_3$ and Na_2CO_3 (spectra not shown).

Characterization of Carbonate/Fe Oxide Surface Complexes

The ν_4 vibration doublet at approximately 1670 and 1590 cm^{-1} for the protonated complex, ≡Fe-O-COOH, were observed in am-$Fe(OH)_3$/aqueous solution of water, 0.01 *M* $NaHCO_3$ (Figure 8) and 0.01 and 0.03 *M* Na_2CO_3 (Figure 9). It is noteworthy that carbonate species on am-$Fe(OH)_3$ in deionized water gave as strong an IR absorption as did 0.01 *M* $NaHCO_3$ or Na_2CO_3 despite significant differences in the amounts of adsorbed carbon species. This may have been caused by the heterogeneity of the am-$Fe(OH)_3$ suspension as affected by differing ionic strength and pH in varying $NaHCO_3$ and Na_2CO_3 solutions. The native carbonate species in am-$Fe(OH)_3$ are derived from the NaOH reagent used to neutralize the $FeCl_3$ solution and adsorption of CO_2(g) from the laboratory atmosphere during the synthesis process. Zachara et al. (1987) showed that substantial CO_2(aq) remained in the amorphous Fe oxide suspension under N_2(g) despite sparging. We also noticed that am-$Fe(OH)_3$ gave stronger IR absorption for surface carbonate species than did am-$Al(OH)_3$ at similar adsorption levels. There may be 2 reasons for this difference. First, the penetration depth of the IR beam into the sample depends on the refractive index of the sample relative to that of the ZnSe crystal (Compton and Compton 1993). In the concentrated suspensions of adsorbents (400 g L^{-1}) in the ATR sampling reservoir, both water and the adsorbents determine the refractive index of the suspensions. We noticed that solids settled on the ZnSe crys-

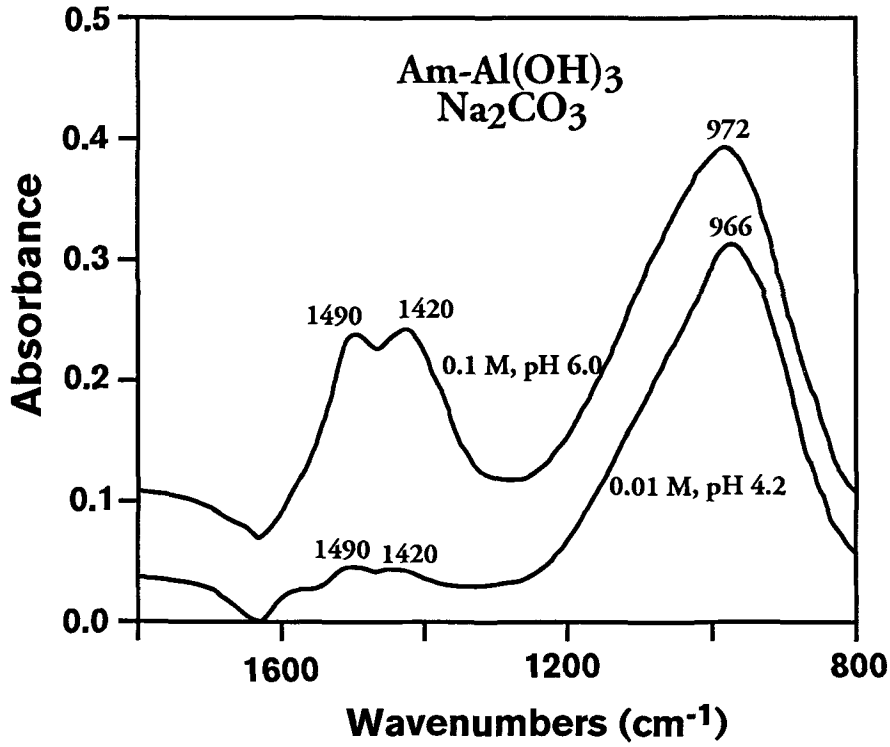


Figure 5. ATR-FTIR difference spectra of am-$Al(OH)_3$ as a function of Na_2CO_3 concentration. Solid concentration in the ATR reservoir was 400 g L^{-1}. The amount of adsorbed C on am-$Al(OH)_3$ was 0.058 and 0.52 mol kg^{-1} in 0.01 and 0.1 *M* Na_2CO_3, respectively.

tal during the 50-min IR scanning period; thus, they should determine the suspension refractive index for the most part. The higher refractive indices of 2.3–2.4 for Fe oxides, as compared to those of 1.6–1.7 for Al oxides (Weast 1976) result in greater depth of penetration into the Fe oxides. The IR band intensity increases due to the resulting deeper penetration. Second, am-$Fe(OH)_3$ had the highest surface area of the adsorbents studied [250 m^2 g^{-1} as compared to 128, 7.8 and 21.8 m^2 g^{-1} for am-$Al(OH)_3$, gibbsite and goe-

Table 1. Infrared absorption bands of bicarbonate and carbonate ions in aqueous solution (free state), on mineral surfaces (adsorbed form) and in dawsonite (structural form).

Anion	Symmetry	Frequency, cm^{-1}						
		ν_1	ν_2		ν_3		ν_4	
Free bicarbonate	C_{2v}	1010	1360	1310			1668	1605
Free carbonate	D_{3h}	1065	887		1383			
Monodentate carbonate†								
$[Co(NH_3)_5CO_3]Cl$		1062	877		1448	1354		
Bidentate carbonate†								
$[Co(NH_3)_4CO_3]Cl$		1043	865		1590	1282		
0.01 *M* bicarbonate + am-$Al(OH)_3$					1495	1420		
1.0 *M* bicarbonate + am-$Al(OH)_3$		1028			1484	1420		
0.01 *M* carbonate + am-$Al(OH)_3$					1490	1420		
1.0 *M* carbonate + am-$Al(OH)_3$‡		1095	1020		1560	1388		
1.0 *M* bicarbonate + gibbsite					1420			
0.01 *M* bicarbonate + am-$Fe(OH)_3$		1050			1477	1359	1667	1585
1.0 *M* bicarbonate + am-$Fe(OH)_3$		1070	950		1487	1335		
0.01 *M* carbonate + am-$Fe(OH)_3$		1020			1474	1358	1674	1586
1.0 *M* carbonate + am-$Fe(OH)_3$		1070	944		1485	1336		
1.0 *M* bicarbonate + goethite					1410	1335		

† From Ross (1972).
‡ The predominant reaction product was dawsonite with traces of bayerite.

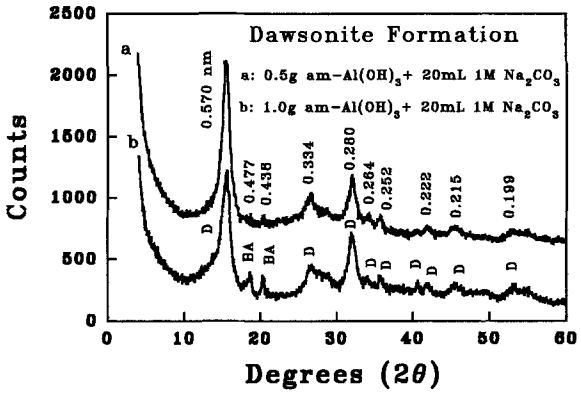


Figure 6. X-ray diffractogram of dawsonite (D) and bayerite (BA) formed when (a) 0.5 g of am-$Al(OH)_3$, and (b) 1.0 g of am-$Al(OH)_3$ reacted with 20 mL of 1.0 *M* Na_2CO_3 for 24 h. The solids were washed with deionized water 4 times and air-dried before X-ray examination.

thite, respectively], resulting in higher IR absorption for carbonate species. It is apparent that only qualitative information on carbonate speciation in the interfacial region can be obtained from this study.

There is a slightly larger splitting of the ν_4 vibration of the interfacial bicarbonate than the splitting of ν_4 vibration of the uncomplexed bicarbonate anion in aqueous solution (Table 1), suggesting a decrease in the symmetry of the surface complexed bicarbonate. In addition, the ν_1 vibration shifted from 1010 in solution to 1050 cm^{-1} in am-$Fe(OH)_3$ reacted with 0.01 *M* $NaHCO_3$. The ν_3 splitting for surface-complexed carbonate was observed in all am-$Fe(OH)_3$/aqueous solution systems and the frequency difference between the doublets increased with increasing initial concentration of both $NaHCO_3$ and Na_2CO_3, indicating increased distortion of CO_3^{2-} on the surface. The magnitude of the splitting suggests monodentate carbonate complexed to the am-$Fe(OH)_3$ surface. The ν_1 vibration for carbonate only slightly shifted upward from 1065 for the free species to 1070 cm^{-1} for the surface-complexed species. The band near 950 cm^{-1} may be a combination of ν_6 vibration for HCO_3^-, and ν_2 vibration for CO_3^{2-} on the surface (Figure 9). Failure to observe bicarbonate in an IR study of carbonate interaction with a freshly prepared Fe oxide by Harrison and Berkheiser (1982) is probably due to the air-drying and evacuation of their samples, which increases the pH, resulting in more carbonate relative to bicarbonate in the system. Apparently, the *in situ* ATR-FTIR method overcomes this problem and is able to detect bicarbonate surface complexation.

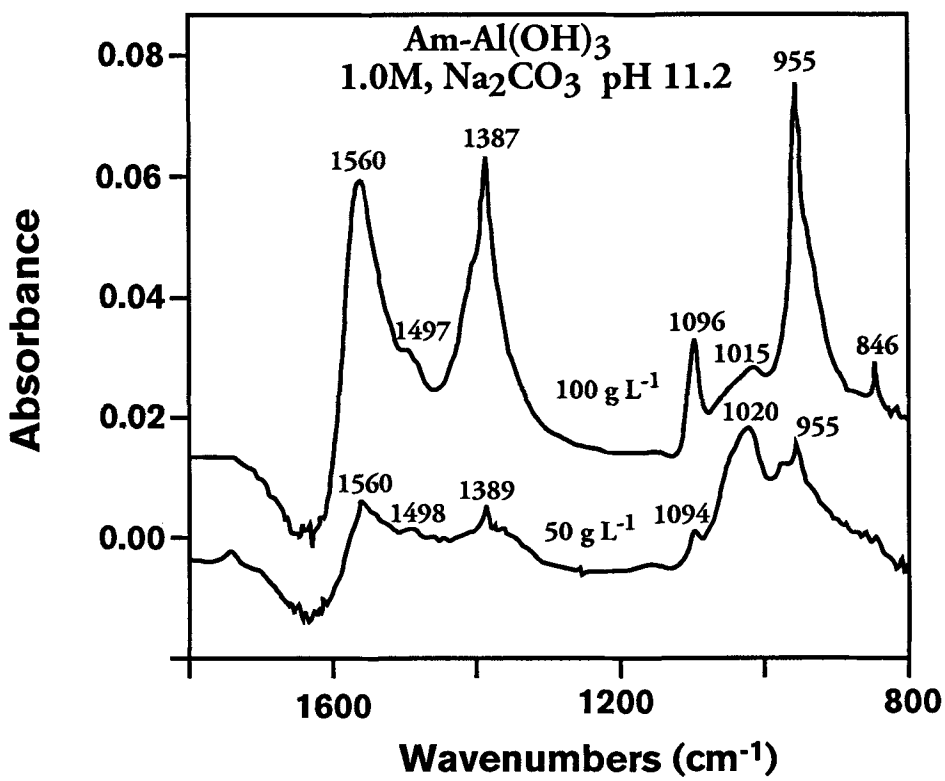


Figure 7. ATR-FTIR difference spectra of mineral solids after 1.0 (top spectrum) and 0.5 g (bottom spectrum) of am-$Al(OH)_3$ reacted with 20 mL of 1.0 *M* Na_2CO_3 for 24 h. Solid concentration in the ATR reservoir was 100 g L^{-1} for the top spectrum and 50 g L^{-1} for the bottom spectrum. The amount of sorbed C on am-$Al(OH)_3$ was 8.7 and 7.4 mol kg^{-1} for the top and bottom spectra, respectively.

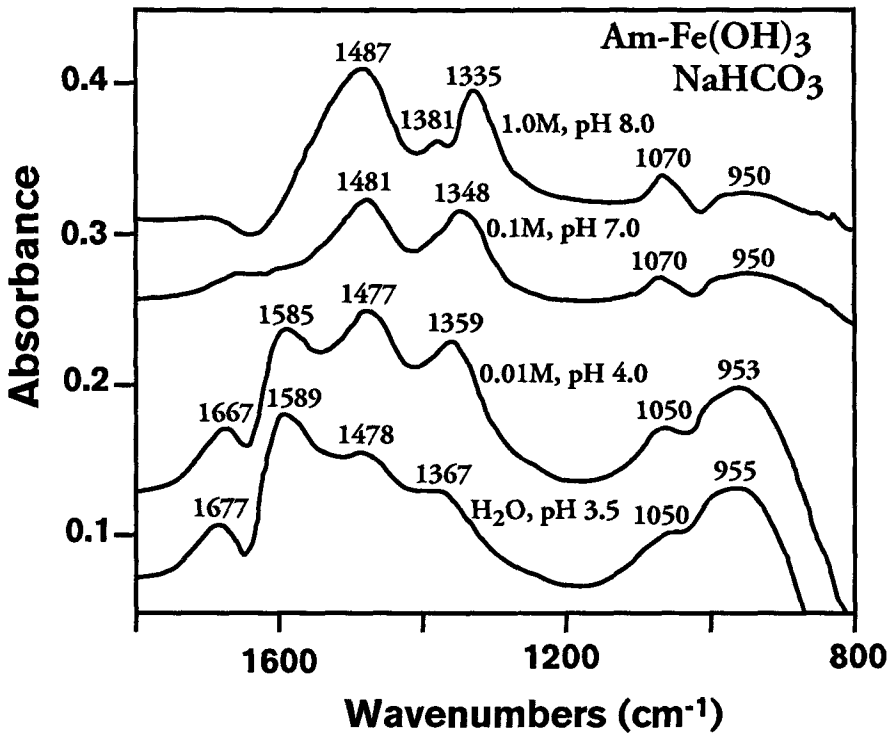


Figure 8. ATR-FTIR difference spectra of am-$Fe(OH)_3$ as a function of $NaHCO_3$ concentration. Solid concentration in the ATR reservoir was 400 g L^{-1}. The amount of adsorbed C on am-$Fe(OH)_3$ was 0.053, 0.074, 0.38, and 1.1 mol kg^{-1} in deionized water, 0.01, 0.1 and 1.0 *M* $NaHCO_3$, respectively.

The amount of adsorbed C on goethite was 0.005, 0.030, 0.070 and 0.23 mol kg^{-1} in water (equilibrium pH 5.9), 0.01 (pH 8.6), 0.1 (pH 8.6) and 1.0 *M* $NaHCO_3$ (pH 8.3), respectively. The ATR-FTIR difference spectra of goethite suspensions in water and various $NaHCO_3$ solutions (not shown) give a strong band at 893 cm^{-1} that is assigned to subsurface lattice goethite groups (Tejedor–Tejedor and Anderson 1986). Two bands at 1410 and 1335 cm^{-1} are assigned to monodentate carbonate on the goethite surface in 1.0 *M* $NaHCO_3$. These peaks are not observed at the lower $NaHCO_3$ concentrations. No peaks other than the one at 893 cm^{-1} for goethite were found in the goethite-Na_2CO_3 solution system, consistent with a negligible amount of carbonate adsorption.

Mechanisms of Carbonate Surface Complexes Formation

Any proposed mechanisms of the interaction between bicarbonate/carbonate and mineral surfaces have to explain 1) a lowering of electrophoretic mobility of adsorbent particles titrated by Na_2CO_3 as compared to NaOH at the same ionic strength, 2) a decrease of the PZC of adsorbents by carbonate adsorption, 3) the adsorption envelope as affected by pH from previous studies (such as Schulthess and McCarthy 1990; Van Geen et al. 1994) which show maximum adsorption at pH 6–6.5, and 4) distribution of interfacial species of bicarbonate and carbonate as affected by mineral type and pH detected by *in situ* ATR-FTIR spectroscopy (Table 1). The mass and charge balance also have to be maintained. The specific (inner-sphere) adsorption of anions on metal oxides is generally described as a ligand exchange reaction (Stumm 1986). That is, the surface OH groups of a metal cation (≡M) are exchanged by the aqueous anion (ligand L) as follows:

$$\equiv\text{M-OH} + \text{L}^- = \equiv\text{M-L} + \text{OH}^- \qquad [1]$$

The proposed reactions of bicarbonate and carbonate adsorption on am-$Al(OH)_3$ at pH 4.1–7.8 are:

$$\equiv\text{Al-OH}_2^+ + \text{HCO}_3^- = \equiv\text{Al-O-CO}_2^- + \text{H}_2\text{O} + \text{H}^+ \qquad [2]$$

$$\equiv\text{Al-OH} + \text{CO}_3^{2-} = \equiv\text{AL-O-CO}_2^- + \text{OH}^- \qquad [3]$$

and on am-$Fe(OH)_3$:

$$\equiv\text{Fe-OH}_2^+ + \text{HCO}_3^- = \equiv\text{Fe-O-COOH} + \text{H}_2\text{O} \quad \text{at pH 3.5–6.2} \qquad [4]$$

$$\equiv\text{Fe-OH} + \text{CO}_3^{2-} = \equiv\text{Fe-O-CO}_2^- + \text{OH}^- \quad \text{at pH 3.5–10.5} \qquad [5]$$

Changes in speciation of the carbonate surface com-

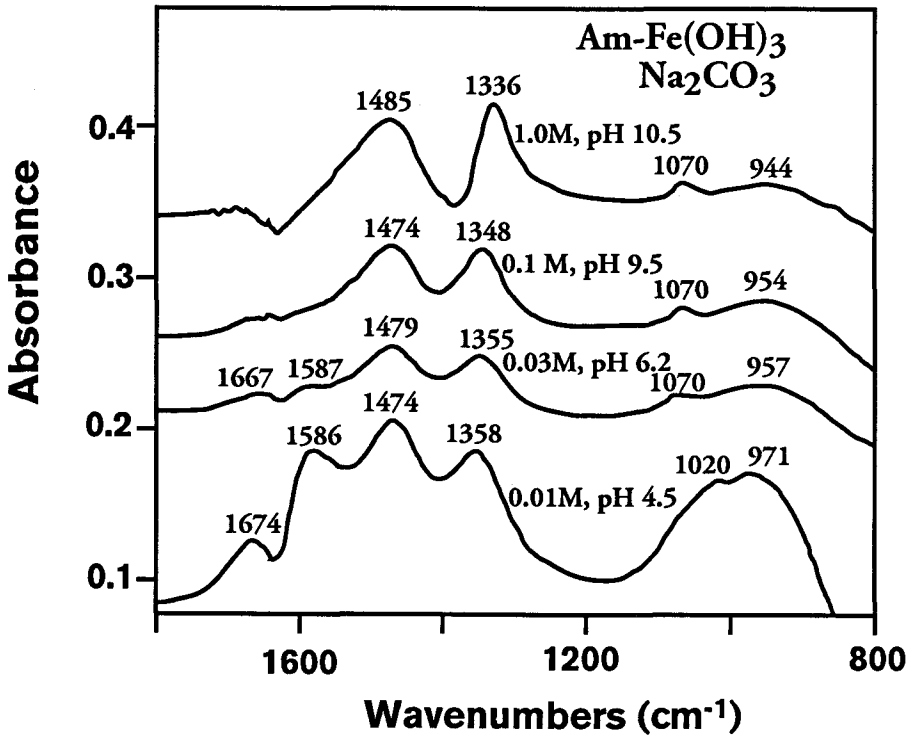


Figure 9. ATR-FTIR difference spectra of am-$Fe(OH)_3$ as a function of Na_2CO_3 concentration. Solid concentration in the ATR reservoir was 400 g L^{-1}. The amount of adsorbed C on am-$Fe(OH)_3$ was 0.060, 0.18, 0.31 and 0.81 mol kg^{-1} in 0.01, 0.1 and 1.0 *M* Na_2CO_3, respectively.

plexes on am-$Fe(OH)_3$ as a function of pH can be interpreted in terms of the following acid-base reaction:

$$\equiv\text{Fe-O-COOH} = \equiv\text{Fe-O-CO}_2^- + \text{H}^+ \qquad [6]$$

The apparent pK (the pH at which the concentration of the 2 surface species in equilibrium is equal) for this reaction is possibly between 4 and 6.

In summary, similar to phosphate and borate, carbonate lowered the electrophoretic mobility and decreased the PZC of Al and Fe oxides. The surface-complexed monodentate carbonate was the only identified interfacial species in am-$Al(OH)_3$/aqueous solution at pH 4.1–7.8. A discrete crystalline solid phase, dawsonite, formed with traces of bayerite when am-$Al(OH)_3$ was reacted with 1.0 *M* Na_2CO_3. Gibbsite adsorbed much less carbonate than am-$Al(OH)_3$ due to limited functional groups on the surface. Probably carbonate is also the complexed species on gibbsite. Both surface complexed bicarbonate and carbonate species were found in the interfacial region of the am-$Fe(OH)_3$-water system, depending on solution pH. Monodentate carbonate was identified on goethite in 1.0 *M* $NaHCO_3$ suspensions.

ATR-FTIR spectroscopy has been shown as a useful technique to yield qualitative if not semiquantitative information on the chemical structure of specifically adsorbed anions, providing increased understanding of the mechanisms of interfacial complexation of important species. Information on the reactions that occur at the solid-water interface at the molecular level will in turn lead to better predictive models of species behavior in soil environments.

REFERENCES

Bruno J, Stumm W, Wersin P, Brandberg, F. 1992. On the influence of carbonate in mineral dissolution: I. The thermodynamics and kinetics of hematite dissolution in bicarbonate solutions at T = 25 °C. Geochim Cosmochim Acta 56:1139–1147.

Compton SV, Compton DAC. 1993. Optimization of data recorded by internal reflectance spectroscopy. In: Coleman PB, editor. Practical sampling techniques for infrared analysis. Boca Raton, FL: CRC Pr. p 55–92.

Evans TD, Leal JR, Arnold PW. 1979. The interfacial electrochemistry of goethite (α-FeOOH) especially the effect of CO_2 contamination. J Electroanal Chem 105:161–167.

Feldkamp JR, Shah DN, Meyer SL, White JL, Hem SL. 1981. Effect of adsorbed carbonate on surface charge characteristics and physical properties of aluminum hydroxide gel. J Pharm Sci 70:638–640.

Frueh AJ, Golightly JP. 1967. The crystal structure of dawsonite $NaAl(CO_3)(OH)_2$. Can Mineral 9:51–56.

Hage W, Hallbrucker A, Mayer E. 1993. Carbonic acid: Synthesis by protonation of bicarbonate and FTIR spectroscopic characterization via a new cryogenic technique. J Am Chem Soc 115:8427–8431.

Harrison JB, Berkheiser VE. 1982. Anion interactions with freshly prepared hydrous iron oxides. Clays Clay Miner 30: 97–102.

Hsu PH. 1967. Effect of salts on the formation of bayerite versus pseudo-boehmite. Soil Sci 103:101–110.

Hsu PH, Bates TF. 1964. Formation of x-ray amorphous and crystalline aluminum hydroxides. Mineral Mag 33:749–768.

Hunter RJ. 1981. Zeta potential in colloid science. London: Academic Pr. 386 p.

Hunter DB, Bertsch PM. 1994. *In situ* measurements of tetraphenylboron degradation kinetics on clay mineral surfaces by IR. Environ Sci Technol 28:686–691.

Kittrick JA. 1966. The free energy of formation of gibbsite and $Al(OH)_4^-$ by solubility measurements. Soil Sci Soc Am Proc 30:595–598.

Kodama H. 1985. Infrared spectra of minerals: Reference guide to identification and characterization of minerals for the study of soils. Ottawa: Agriculture Canada. 197 p.

Lumsdon DG, Evans LJ. 1994. Surface complexation model parameters for goethite (α-FeOOH). J Colloid Interface Sci 164:119–125.

Nakamoto K. 1986. Infrared and Raman spectra of inorganic and coordination compounds. 4th ed. New York: Wiley. 543 p.

Nelson RE. 1982. Carbonate and gypsum. In: Methods of soil analysis. Part 2. Page AL et al., editors. Madison, WI: Agron Monograph. No. 9, 2nd ed. Am Soc Agron. p 181–197.

Ross D. 1972. Inorganic infrared and Raman spectra. London: McGraw Hill. 414 p.

Russell JD, Paterson E, Fraser AR, Farmer VC. 1975. Adsorption of carbon dioxide on goethite (α-FeOOH) surfaces, and its implications for anion adsorption. J Chem Soc, Faraday Trans. 71:1623–1630.

Scholtz EC, Feldkamp JR, White JL, Hem SL. 1984. Properties of carbonate-containing aluminum hydroxide produced by precipitation at constant pH. J Pharm Sci 73:967–973.

Scholtz EC, Feldkamp JR, White JL, Hem SL. 1985. Point of zero charge of amorphous aluminum hydroxide as a function of adsorbed carbonate. J Pharm Sci 74:478–481.

Schulthess CP, McCarthy JF. 1990. Competitive adsorption of aqueous carbonic and acetic acids by an aluminum oxide. Soil Sci Soc Am J 54:688–694.

Schwertmann U, Cornell RM. 1991. Iron oxides in the laboratory: Preparation and characterization. New York: VCH. 137 p.

Serna CJ, White JL, Hem SL. 1977. Anion-aluminum hydroxide gel interactions. Soil Sci Soc Am J 41:1009–1013.

Sposito G. 1984. The surface chemistry of soils. New York: Oxford University Pr. 234 p.

Stumm W. 1986. Coordinative interactions between soil solids and water—An aquatic chemist's point of view. Geoderma 38:19–30.

Su C, Suarez DL. 1995. Coordination of adsorbed boron: A FTIR spectroscopic study. Environ Sci Technol 29:302–311.

Tejedor-Tejedor M, Anderson MA. 1986. "*In situ*" attenuated total reflection Fourier transform infrared studies of the goethite (α-FeOOH)-aqueous solution interface. Langmuir 2:203–210.

Tejedor-Tejedor M, Anderson MA. 1990. Protonation of phosphate on the surface of goethite as studied by CIR-FTIR and electrophoretic mobility. Langmuir 6:602–613.

Van Geen A, Robertson AP, Leckie JO. 1994. Complexation of carbonate species at the goethite surface: Implications for adsorption of metal ions in natural waters. Geochim Cosmochim Acta 58:2073–2086.

Weast RT. 1976. Handbook of chemistry and physics. 57th ed. Cleveland, OH: CRC Pr. B86, B120.

White JL, Hem SL. 1975. Role of carbonate in aluminum hydroxide gel established by Raman and IR Analyses. J Pharm Sci 64:468–469.

Yapp CJ, Poths H. 1990. Infrared spectral evidence for a minor Fe (III) carbonate-bearing component in natural goethite. Clays Clay Miner 4:442–444.

Zachara JM, Girvin DC, Schmidt RL, Resch CT. 1987. Chromate adsorption on amorphous iron oxyhydroxide in the presence of major groundwater ions. Environ Sci Technol 21:589–594.

Zeltner WA, Anderson MA. 1988. Surface charge development at the goethite/aqueous solution interface: Effects of CO_2 adsorption. Langmuir 4:469–474.

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