

## IDENTIFICATION OF NONCRYSTALLINE (Fe,Cr)(OH)<sub>3</sub> BY INFRARED SPECTROSCOPY

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**Abstract**—Iron-chromium hydroxides are important solid phases governing the aqueous concentrations of Cr(III) in soils and fly ashes. Although direct identification of noncrystalline (Fe,Cr)(OH)<sub>3</sub> is difficult, the infrared spectra of noncrystalline Fe(OH)<sub>3</sub> and Cr(OH)<sub>3</sub>, coprecipitated (Fe,Cr)(OH)<sub>3</sub>, and physical mixtures of Fe(OH)<sub>3</sub> and Cr(OH)<sub>3</sub> can be distinguished on the basis of the asymmetric stretching doublet ( $\nu_3$ ) of structural carbonate anions. As the Cr mole fraction of the coprecipitated (Fe,Cr)(OH)<sub>3</sub> increases, the position of the low-frequency  $\nu_3$  peak ( $\nu_3''$ ) changes progressively to higher frequencies, and the carbonate  $\nu_3$  splitting decreases. No change in carbonate  $\nu_3$  splitting or  $\nu_3''$  location was observed for physical mixtures of Fe(OH)<sub>3</sub> and Cr(OH)<sub>3</sub>. The changes in  $\nu_3$  splitting are believed to be caused by different degrees of polarization of the carbonate ligand by the Fe and Cr cations.

Pure Cr(OH)<sub>3</sub> exhibits a strong affinity for carbonate and H<sub>2</sub>O and tends to remain noncrystalline even at very high pHs. In contrast, pure Fe(OH)<sub>3</sub> gradually converts to crystalline goethite at high pH, to the exclusion of much of the H<sub>2</sub>O and carbonate. The presence of Cr in (Fe,Cr)(OH)<sub>3</sub> solid solutions seems to inhibit the transformation to crystalline goethite. The strong association of carbonate with Cr and the kinetic inertness of Cr(III) inner-sphere complexes in general may account for the maintenance of noncrystalline solid-solution materials in lieu of transformation to a crystalline end product.

**Key Words**—Chromium hydroxide, Goethite, Infrared spectroscopy, Iron hydroxide, Noncrystalline, Solid solution.

### INTRODUCTION

Recently, Sass and Rai (1987) reported solubility data for a series of noncrystalline Fe and Cr hydroxide precipitates that provide strong evidence for the existence of an (Fe,Cr)(OH)<sub>3</sub> solid solution. Rai *et al.* (1988) have also shown by solubility studies that (Fe,Cr)(OH)<sub>3</sub> solids are important phases governing the aqueous concentrations of Cr(III) in soils and fly ashes. In light of their importance in natural environments, therefore, other more direct methods for identifying and distinguishing among the various (Fe,Cr)(OH)<sub>3</sub> solid solution members would be useful.

Direct identification of noncrystalline (Fe,Cr)(OH)<sub>3</sub> solids has proven elusive because X-ray and electron powder diffraction techniques cannot be used. Vibrational spectroscopy, however, is well suited to the analysis of noncrystalline solids because of its sensitivity to local bond energies, rather than to long-range structural order. Accordingly, in this paper we (1) show that infrared vibrational spectroscopy can be used to distinguish among the noncrystalline Fe- and Cr-containing hydroxides and (2) interpret the carbonate-stretching vibrations on which these distinctions are based.

### EXPERIMENTAL

Primary stock solutions of 0.8 M FeCl<sub>3</sub> and 0.8 M CrCl<sub>3</sub> were prepared by diluting the reagent-grade chemicals to a volume of 250 ml with 0.1 M HClO<sub>4</sub>. The solutions were treated with 1 ml of 30% H<sub>2</sub>O<sub>2</sub> and

heated for several minutes at 95°C to reduce trace amounts of Cr(VI) to Cr(III) and to oxidize any Fe(II) to Fe(III). Secondary (Fe,Cr)Cl<sub>3</sub> stock solutions were then prepared by combining the primary stock solutions in the desired molar ratios.

Hydroxide phases having different Fe:Cr molar ratios (100:0, 75:25, 50:50, and 0:100) were precipitated by titrating 10 ml of the appropriate (Fe,Cr)Cl<sub>3</sub> stock solutions with 1.25 M NaOH to pHs ranging from 5.5 to 13. Small amounts of carbonate were present in the NaOH and were incorporated into the phases during the precipitation. The resulting suspensions were diluted to 45 ml with H<sub>2</sub>O, aged overnight, washed three times with 10 ml of 0.01 M NaClO<sub>4</sub>, and then diluted to 30 ml with 0.01 M NaClO<sub>4</sub>. The pH of each washed suspension (pH 10 and lower only) was adjusted to the original level at which it had been precipitated. The samples (in loosely capped 50-ml polypropylene centrifuge tubes) were then shaken continuously and incubated for various periods at 25°C. Physical mixtures (prepared from pure Fe and Cr phases that had been precipitated and aged separately overnight) with Fe:Cr ratios of 75:25 and 50:50 were also prepared and incubated as above.

After 0, 4, and 18 days of incubation, the pHs of the suspensions were measured, the aliquots were filtered, and the resulting unwashed solids were freeze-dried. Subsamples of the dried solids (3 mg) were each mixed thoroughly with 300 mg of spectroscopic grade KBr, and placed in a 13-mm-diameter evacuable die. Vac-

Table 1. Composition of acidic solutions, initial and final pH levels of suspensions, and composition of (Fe,Cr)(OH)<sub>3</sub> solids after 18 days of incubation at 25°C.

Sample <sup>1</sup>	Acidic solutions		Suspension pH <sup>2</sup>		Final solids		
	X <sub>Fe</sub>	X <sub>Cr</sub>			X <sub>Fe</sub>	X <sub>Cr</sub>	CO <sub>3</sub> <sup>2-</sup>
	(mole %)		Initial	Final	(mole %)		(wt. %)
5.5A	100	0	5.50	5.02	100.0	0.0	0.5
5.5D	75	25	5.51	5.12	73.6	26.4	— <sup>3</sup>
5.5E	50	50	5.53	5.35	48.3	51.7	—
5.5F	0	100	5.51	5.48	0.0	100.0	4.8
5.5M25	75	25	5.6	5.10	86.9	13.1	—
5.5M50	50	50	5.44	5.43	69.6	30.4	—
7A	100	0	7.15	6.85	100.0	0.0	1.0
7D	75	25	7.05	6.71	73.5	26.5	—
7E	50	50	7.00	6.53	47.8	52.2	—
7F	0	100	7.00	6.54	0.0	100.0	3.6
7M25	75	25	7.02	6.56	68.3	31.7	—
7M50	50	50	7.01	6.59	50.6	49.4	—
8.5A	100	0	8.50	8.23	100.0	0.0	1.2
8.5D	75	25	8.50	8.03	73.4	26.6	2.8
8.5E	50	50	8.51	8.03	47.8	52.2	2.3
8.5F	0	100	8.50	7.66	0.0	100.0	3.8
8.5M25	75	25	8.56	7.99	74.6	25.4	2.6
8.5M50	50	50	8.49	7.80	50.7	49.3	3.6
10A	100	0	9.97	9.81	99.6	0.4	1.4
10D	75	25	10.00	9.82	73.4	26.6	—
10E	50	50	10.00	9.75	48.1	51.9	—
10F	0	100	10.01	8.97	0.0	100.0	2.9
10M25	75	25	10.00	9.63	73.5	26.5	—
10M50	50	50	9.99	9.60	48.9	51.1	—
12A	100	0	(12)	9.92	100.0	0.0	1.0
12D	75	25	(12)	10.43	73.4	26.6	—
12E	50	50	(12)	10.49	48.1	51.9	—
12F	0	100	(12)	10.25	0.0	100.0	4.4
12M25	75	25	(12)	9.97	74.0	26.0	—
12M50	50	50	(12)	—	48.4	51.6	—
13A	100	0	(13)	9.66	100.0	0.0	1.6
13D	75	25	(13)	10.81	73.9	26.1	3.7
13E	50	50	(13)	11.34	48.0	52.0	7.3
13F	0	100	(13)	11.33	0.0	100.0	7.2
13M25	75	25	(13)	10.03	74.3	25.7	2.7
13M50	50	50	(13)	10.47	48.1	51.9	5.1

<sup>1</sup> At each initial pH, samples A and F are end-member phases, D and E are coprecipitated phases, and M25 and M50 are physical mixtures of pure phases.

<sup>2</sup> Initial pH for pH 12 and 13 samples estimated from known additions of NaOH.

<sup>3</sup> — = not determined.

uum was applied to the die for 2 min and then continued as the KBr solid mixture was pressed into a pellet for infrared (IR) analysis. Pellets were stored in a desiccator until analyzed. Separate subsamples of the 18-day freeze-dried solids were analyzed for Fe and Cr content by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) after decomposition in an acid matrix. Selected subsamples were also analyzed for total C using a dry-combustion coulometric technique (Huffman, 1977).

IR spectra (0.25-cm<sup>-1</sup> resolution) were obtained on a Nicolet Model DB-7199 FT-IR spectrometer operating in single-beam mode with a Globar source, a Michelson interferometer (KBr-Ge beamsplitter), and a HgCdTe-B detector. To minimize interferences from

impurities in the KBr matrix, all spectra were ratioed to a background spectrum taken for a blank KBr pellet. The interferograms were deconvoluted with the aid of the Happ-Genzel apodization function (Griffiths and Dehaseth, 1986, pp. 17–23).

#### COMPOSITION OF SOLIDS

The mole fractions of Fe and Cr in the solids that had been incubated for 18 days are shown in Table 1. (Because pHs in the suspensions decreased during the incubation period, the solids are referred to below by the initial pH at which they were precipitated, rather than by the final pH of the suspension at the time of sampling.) A comparison of these mole fractions with those of the original solutions (Table 1) shows excellent

agreement in most instances and suggests that the precipitation from solution was stoichiometric.

The amounts of carbonate present in the solid phases varied from <1% to >7% by weight, depending on the Fe and Cr content of the solid and the pH of the suspension (Table 1). In general, more carbonate was present in the solids that contained Cr, with the most carbonate in the pure Cr(OH)<sub>3</sub> phases at pH 13. Even at pH 13, however, the maximum estimated mole ratio of carbonate (as CO<sub>3</sub><sup>2-</sup>) to hydroxyl in the noncrystalline Cr(OH)<sub>3</sub> solids after 18 days of incubation was relatively minor (~0.1).

## RESULTS OF INFRARED ANALYSES

### General aspects

IR absorbance spectra for pure Fe(OH)<sub>3</sub>, pure Cr(OH)<sub>3</sub>, and the two coprecipitated solids (25% and 50% Cr mole fractions) incubated at various initial pHs for 18 days are shown in Figure 1. All the spectra include a broad peak corresponding to coordinated or adsorbed H<sub>2</sub>O (near 1620 cm<sup>-1</sup>) and a sharp peak amidst a broad cluster of peaks (near 1120 cm<sup>-1</sup>), which can be assigned to adsorbed or coprecipitated ClO<sub>4</sub><sup>-</sup> anions.

In the spectra for pure Fe(OH)<sub>3</sub>, prepared at high pH (Figure 1a), the distinctive OH-bending doublet associated with goethite ( $\alpha$ -FeOOH) at 795 and 887 cm<sup>-1</sup> was seen along with well-defined peaks corresponding to Fe-O lattice vibrations at lower frequencies (646 and 476–463 cm<sup>-1</sup>). As a consequence of collecting spectra in single-beam mode and the abrupt decline in IR beam energy below 500 cm<sup>-1</sup>, the lattice vibration peaks were distorted by extraneous water vapor peaks and thus appeared at somewhat higher frequencies than normally observed for goethite (630 and 410 cm<sup>-1</sup>, respectively).

The pure Cr(OH)<sub>3</sub> spectra (Figure 1d) contained prominent peaks corresponding to coordinated or adsorbed H<sub>2</sub>O (near 1620 cm<sup>-1</sup>) and carbonate (1492 and 1375 cm<sup>-1</sup>). The carbonate in these samples was probably structural in nature, inasmuch as surface-adsorbed carbonate would have been completely removed by evacuation when the KBr pellets were pressed. The carbonate doublet was probably due to the asymmetric stretching of the C-O bonds [doubly degenerate  $\nu_3$  fundamental, in the notation of Nakamoto (1970, p. 62)]. The intensity of the carbonate doublet was greater at the higher pH, which was expected because of the greater CO<sub>3</sub><sup>2-</sup> content of these solutions. A broad peak at about 850 cm<sup>-1</sup> was due to the out-of-plane bending vibrations ( $\nu_2$ ) of carbonate, and the strong peak near 540 cm<sup>-1</sup> was due to the Cr-O lattice vibration. A comparison of the pure Fe and Cr spectra (Figures 1a and 1d) shows that considerably more H<sub>2</sub>O and carbonate were indicated in the spectra of Cr(OH)<sub>3</sub> than in those of the Fe(OH)<sub>3</sub> solids, a result that agrees with the chemical data in Table 1. The absence of sharp

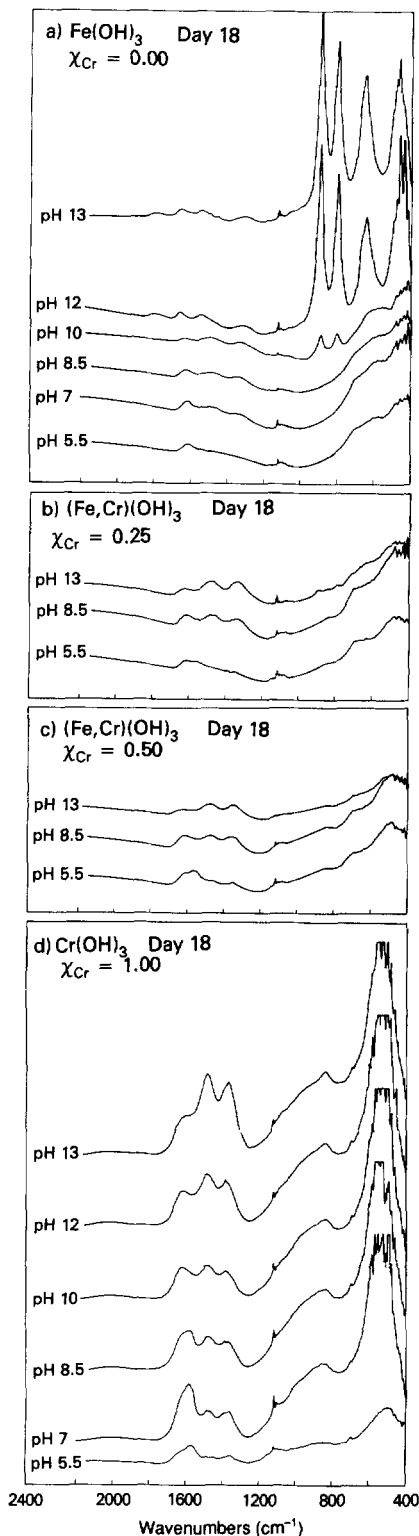


Figure 1. Infrared absorbance spectra of hydrous oxide phases having initial Fe:Cr mole ratios of (a) 100:0, (b) 75:25, (c) 50:50, and (d) 0:100 after 18 days of incubation at 25°C and several initial pH levels.

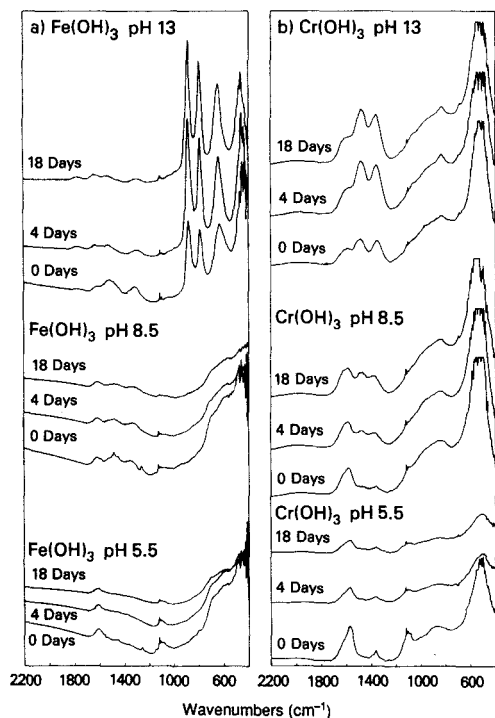


Figure 2. Infrared absorbance spectra of (a) Fe and (b) Cr hydroxide phases after incubation for 0, 4, and 18 days at 25°C and initial pHs of 5.5, 8.5, and 13.

peaks in the spectra of  $\text{Cr}(\text{OH})_3$  prepared at high pH also suggests that these solids were not as highly ordered as the  $\text{Fe}(\text{OH})_3$  phases (i.e., crystalline goethite), perhaps because of inclusions of  $\text{H}_2\text{O}$  and carbonate in the  $\text{Cr}(\text{OH})_3$ .

The spectra for the two coprecipitated solids (Figures 1b and 1c) were relatively featureless compared with the spectra of the pure phases, but peaks due to  $\text{H}_2\text{O}$  and  $\text{CO}_3^{2-}$  were clearly evident. Faint peaks due to hydroxyl and lattice vibrations were present in these spectra at frequencies of  $<1000\text{ cm}^{-1}$ . Weak peaks corresponding to the characteristic OH-bending doublet of goethite ( $\sim 890$  and  $800\text{ cm}^{-1}$ ) were present in the spectrum for the 25% Cr solid equilibrated at pH 13. The mole fraction of Cr in the goethitic phase is not known. Lim-Nunez and Gilkes (1985), however, observed an upper limit of about 14 mol % Cr in the substituted goethites they prepared. The same limit may apply to the samples prepared in this study as well.

#### Incubation period and pH

The effects of the length of the incubation period and the initial pH on the spectra of the pure Fe and pure Cr hydroxide phases are shown in Figure 2. At pH 5.5, very weak peaks due to adsorbed  $\text{HCO}_3^-$  (near  $1250\text{ cm}^{-1}$ ) were present in the spectra of the unincubated

samples but not in the spectra of samples incubated for 4 and 18 days. The intensities of peaks due to  $\text{ClO}_4^-$  also decreased with longer incubation periods, suggesting (1) that coprecipitated  $\text{ClO}_4^-$  may have been replaced by  $\text{OH}^-$  ions, or (2) that the amount of adsorbed  $\text{ClO}_4^-$  may have decreased because of a change in the extent and charge of the solid surfaces during the aging process. The initial intensity of the carbonate peaks ( $1500\text{--}1300\text{ cm}^{-1}$ ) of phases prepared at high pH was generally greater than that of phases prepared at lower pHs. With longer incubation periods, however, the intensity of these peaks decreased for the pure Fe phases and increased for the pure Cr phases.

The different trends in carbonate peak intensities for the Fe and Cr solids can be related to the degree of transformation of the noncrystalline phases to crystalline phases. For example, at high pH, the decrease in carbonate peak intensity for the pure Fe phases corresponded to an increase in the intensities of the goethite hydroxyl-bending peaks. Transformation to the goethite structure thus seems to have eliminated most of the carbonate anions that were coprecipitated with the noncrystalline  $\text{Fe}(\text{OH})_3$ . In contrast, the pure  $\text{Cr}(\text{OH})_3$  remained noncrystalline and continued to incorporate carbonate anions. As noted by Cotton and Wilkinson (1972, p. 652), the coordination sphere of Cr(III) [like that of Co(III)] is relatively inert to ligand-exchange reactions. In fact, ligand replacement reactions for the aquo ion may have half-lives of days or weeks at 25°C. This property of Cr(III) could have been responsible for the persistence of the noncrystalline state and the inhibition of the conversion to a crystalline goethite-like phase (e.g., brucewellite) by pure  $\text{Cr}(\text{OH})_3$ .

#### Evidence for solid solution

In Figure 3, the major features of the spectra of the pure end members (i.e.,  $\text{Fe}(\text{OH})_3$  and  $\text{Cr}(\text{OH})_3$ ) and the coprecipitated  $(\text{Fe,Cr})(\text{OH})_3$  solids are summarized, and spectra of physical mixtures of the two end members are presented. The latter spectra showed the prominent features associated with the end-member phases (e.g., goethite-OH and carbonate peaks), in contrast to the relatively featureless spectra of the coprecipitated solids. Indeed, the absence of strong goethite peaks in the coprecipitated-solid spectra is indirect evidence for a single  $(\text{Fe,Cr})(\text{OH})_3$  phase.

Close inspection of the portion of the spectra due to carbonate vibrations shows that the frequencies of these vibrations vary with the Cr mole fraction of the coprecipitated solids (Figure 4a). In contrast, no change in frequency was observed for the physical mixtures of the end member Fe and Cr solids at 25% and 50% Cr mole fractions (Figure 4b). Indeed, the carbonate spectra of the physical mixtures are essentially identical to that for pure  $\text{Cr}(\text{OH})_3$ , and suggest that carbonate was associated solely with the noncrystalline  $\text{Cr}(\text{OH})_3$ .

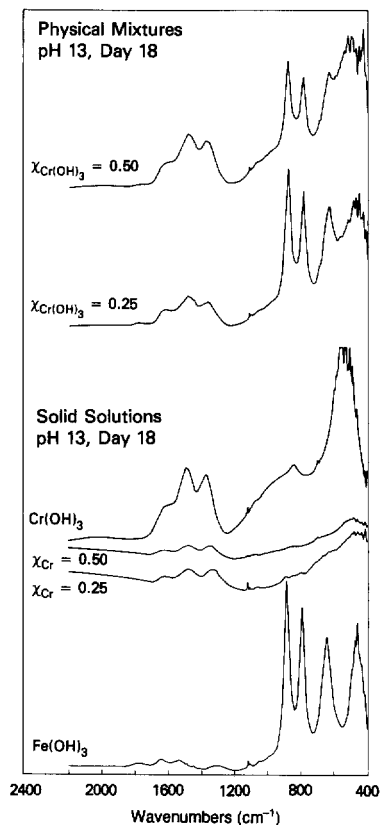


Figure 3. Infrared absorbance spectra of physical mixtures of end member phases and of coprecipitated and end member phases in the (Fe,Cr)(OH)<sub>3</sub> solid solution series after incubation for 18 days at 25°C and an initial pH of 13.

phase. These observations, therefore, show that the carbonate spectra can be used to distinguish the coprecipitated solids from the physical mixtures and that the coprecipitated solids can be distinguished on the basis of Cr mole fraction. In short, the spectra provide clear, independent evidence for the existence of an (Fe,Cr)(OH)<sub>3</sub> solid solution.

#### CO<sub>2</sub>-free atmosphere

To examine the relationship between the carbonate vibrations and the Cr mole fraction in the solid-solution (i.e., coprecipitated) phases further, (Fe,Cr)(OH)<sub>3</sub> solids having Cr mole fractions of 0, 1, 5, 10, 20, 33, 50, 75, and 100% were precipitated at an initial pH of 9.5. These materials, unlike the previous materials, were incubated in a CO<sub>2</sub>-free atmosphere at room temperature and sampled after 1 and 17 days. All carbonate in the samples, therefore, came from Na<sub>2</sub>CO<sub>3</sub> in the NaOH used to precipitate the solids.

Spectra for the 1-day samples (not shown) exhibited strong carbonate peaks similar to those obtained by Dvorak *et al.* (1969) for “amorphous basic iron carbonate” and by Serna *et al.* (1978) for “amorphous

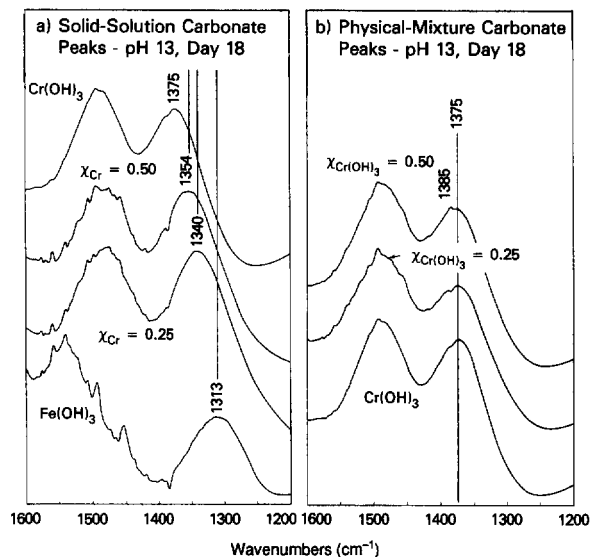


Figure 4. Infrared absorbance spectra showing the  $\nu_3$  vibrations of (a) the end member phases and coprecipitated phases, and (b) physical mixtures of the end member phases in the same proportions as the coprecipitated phases after 18 days of incubation at 25°C and an initial suspension pH of 13.

aluminum hydroxycarbonate.” Faint peaks due to OH-bending vibrations in goethite were found in the spectrum of the pure Fe(OH)<sub>3</sub> sample, whereas no evidence for goethite was found in the samples that contained Cr. The 1-day samples, therefore, were almost entirely noncrystalline. The 17-day samples yielded spectra (not shown) that were similar to those for the 18-day samples, which had been incubated in air (Figure 3), except that the carbonate peaks in the spectra of the 17-day samples were weaker. The carbonate peaks for the 17-day samples were also weaker than those obtained for the 1-day samples. The 17-day incubation period in the CO<sub>2</sub>-free atmosphere thus resulted in the formation of goethite in the samples having Cr mole fractions of 0%, 1%, and 10% and in a loss of carbonate from all samples.

## DISCUSSION

The relationship between the frequencies of the carbonate-stretching vibrations and the composition of the solids (Figure 4a) can be explained in terms of the symmetry and bonding environment of the carbonate ion. The free carbonate anion has D<sub>3h</sub> point group (trigonal planar) symmetry and is predicted by group theory to have a single fundamental *asymmetric* stretching vibration ( $\nu_3$ ). The fundamental *symmetric* stretching vibration ( $\nu_1$ ) is infrared inactive for the D<sub>3h</sub> point group. Coordination of the carbonate anion to a metal cation, however, results in a loss of symmetry, changes in the C–O bond lengths, and an increase in the number of C–O-stretching vibrations.

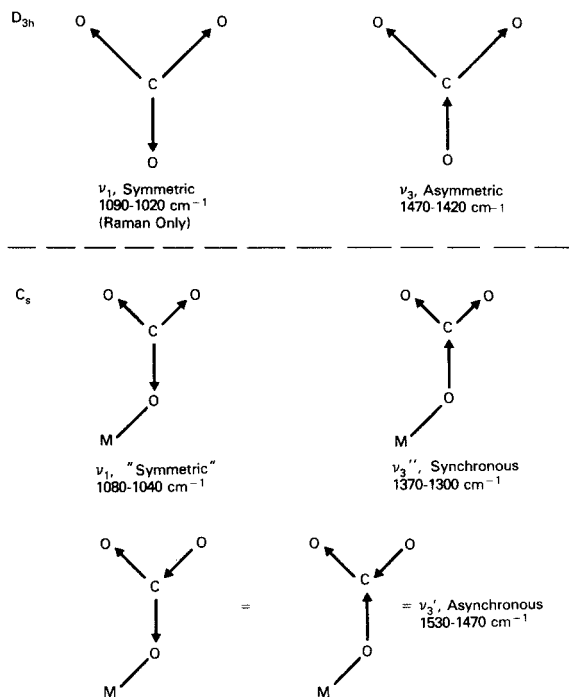


Figure 5. Vibrational modes and frequency ranges for the free carbonate anion ( $D_{3h}$  point group) and the unidentate coordinated carbonate anion ( $C_s$  point group) (after Little, 1966, pp. 76-77).

Consider, for example, the formation of an inner-sphere complex between a carbonate oxygen and a metal ion in the  $(\text{Fe,Cr})(\text{OH})_3$  structure. Such a complex is termed a "unidentate" complex and has  $C_s$  or  $C_{2v}$  point group symmetry (depending on the angle between the metal-oxygen bond and the carbonate anion). As the covalent character of the metal-oxygen bond increases, the oxygen is less able to satisfy the charge on the central carbon atom, causing a shift in electron density from the remaining oxygen atoms towards the carbon atom to compensate. The result is two different C-O bond lengths, one for the metal-coordinated oxygen and one for the remaining two oxygens. Furthermore, a correlation table for the fundamental vibrations associated with the  $C_{2v}$  and  $C_s$  point group symmetries (Nakamoto, 1970, p. 62) predicts that the  $\nu_1$  vibration is infrared active and that the  $\nu_3$  vibration splits into two vibrations ( $\nu_3''$  and  $\nu_3'$ ). Thus, unidentate coordination of the carbonate anion results in two C-O bond lengths and three C-O-stretching vibrations, rather than the single bond length and asymmetric stretching vibration ( $\nu_3$ ) observed for the free anion.

Theoretical calculations for the coordinated carbonate anion, based on earlier work by Nakamoto *et al.* (1957) and Gatehouse *et al.* (1958), were made by Fujita *et al.* (1962) and, after comparison with observed spectra, were used to make frequency assignments for

the three predicted vibrational modes. The possible C-O-stretching modes and the ranges in their frequency assignments for  $D_{3h}$  and  $C_s$  symmetry (Little, 1966, p. 76) are summarized in Figure 5. In the strict sense, all the vibrational modes for the coordinated carbonate anion are asymmetric. To distinguish among them, however, the  $\nu_1$  mode is referred to as the "symmetric" mode, because all three C-O bonds are stretching simultaneously. The two  $\nu_3$  stretching modes are distinguished by whether the vibrations of the two "free" C-O bonds are in phase (synchronous stretching) or completely out of phase (asynchronous stretching, i.e., one stretching and the other compressing). Thus, the higher-frequency peak in the  $\nu_3$  doublet ( $\nu_3'$ ) is due to the asynchronous stretching modes and the lower-frequency peak ( $\nu_3''$ ) to the synchronous stretching mode.

As shown by Brintzinger and Hester (1966), polarization of the carbonate anion is responsible for nearly all of the  $\nu_3$  splitting observed. Polarization arises from the electronegativity of the metal ion and therefore is expected to be slightly greater for Fe than for Cr. For a unidentate complex, the effect of polarization is to increase the bond length (and thereby decrease the strength) of the metal-coordinated C-O bond. Small differences in the electronegativity of the metal cations should have little effect on the bond lengths of the more distant free C-O bonds.

An effect, however, is seen in the vibrational frequencies of the  $\nu_3$  mode because of the contribution of the metal-coordinated C-O bond vibration to the synchronous stretching vibration ( $\nu_3''$ ) of the free C-O bonds. As polarization of the carbonate ion increases, the metal-coordinated C-O bond weakens and the frequency of the synchronous  $\nu_3''$  vibration decreases. In contrast, the frequency of the asynchronous  $\nu_3'$  vibration, which does not include a contribution from the metal-coordinated C-O bond (Fujita *et al.*, 1962), remains the same or increases slightly. Fujita *et al.* (1962), however, did note that the  $\nu_3'$  vibration seems particularly sensitive to changes in the amounts of adsorbed or crystalline  $\text{H}_2\text{O}$  in the complex, apparently through the influence of hydrogen bonding on the C-O-stretching modes. The net result of an increase in polarization, therefore, is a larger  $\nu_3$  splitting, with most of the change resulting from a decrease in the synchronous  $\nu_3''$  vibrational frequency. Calculations of polarization effects by Brintzinger and Hester (1966) support this interpretation in part, but they predict an equivalent increase in the  $\nu_3'$  frequency to match the decrease in the  $\nu_3''$  frequency.

The spectra for the coprecipitated  $(\text{Fe,Cr})(\text{OH})_3$  solids also support this interpretation of the  $\nu_3$  splitting. For solids incubated for 1 day at pH 9.5, the high-frequency peak ( $\nu_3'$ ) lies between 1518 and 1496  $\text{cm}^{-1}$ , and although the data exhibit some variability that can be attributed to interferences from water vapor peaks (e.g., Figure 4a), no trends in peak location are dis-

Table 2. Frequencies of vibration of the asynchronous ( $\nu_3'$ ) and synchronous ( $\nu_3''$ ) C–O-stretching modes of the carbonate ligand in noncrystalline (Fe,Cr)(OH)<sub>3</sub> phases after aging for various periods in the presence or absence of atmospheric CO<sub>2</sub>.

$X_{Cr}$ (mole %)	$\nu_3'$	$\nu_3''$	$\Delta\nu_3$
	(cm <sup>-1</sup> )		
1-day incubation in absence of CO <sub>2</sub> (coprecipitated phases, pH 9.5)			
0	1505	1334	171
1	1518	1335	183
5	1509	1339	170
10	1501	1333	168
20	1508	1343	165
33	1496	1350	146
50	1501	1359	142
75	1503	1370	133
100	1503	1375	128
17-day incubation in absence of CO <sub>2</sub> (coprecipitated phases, pH 9.5)			
0	1530	1322	208
1	1522	1323	198
5	1513	1326	188
10	1503	1328	175
20	1494	1329	164
33	1485	1335	150
50	1494	1351	142
75	1513	1360	154
100	1530	1371	158
18-day incubation in presence of CO <sub>2</sub> (coprecipitated phases, pH 13)			
0	1544	1313	231
25	1483	1340	143
50	1486	1354	132
100	1491	1375	117
18-day incubation in presence of CO <sub>2</sub> (physical mixtures, pH 13)			
25	1491	1375	117
50	1491	1375	117

cernible with changes in the Cr mole fraction (Table 2). Presumably, this consistency in  $\nu_3'$  frequency was observed because all phases were noncrystalline and have similar hydrogen bonding environments. For solids incubated for 18 days at an initial pH of 13 and in contact with atmospheric CO<sub>2</sub>, however, an abrupt shift in the  $\nu_3'$  frequency was found between the pure Fe phase (mostly crystalline goethite) and the noncrystalline Cr-containing phases (Figure 4a; Table 2). Apparently, hydrogen bonding of carbonate in the goethite structure was stronger than in the noncrystalline Cr-containing phases. Russell *et al.* (1975) noted strong hydrogen bonding of carbonate adsorbed to goethite surfaces; hence, carbonate incorporated in the goethite structure would probably form strong hydrogen bonds as well.

For solids incubated for 17 days at pH 9.5 in a CO<sub>2</sub>-free atmosphere, however, the  $\nu_3'$  frequencies were also high for phases having 75% and 100% Cr mole frac-

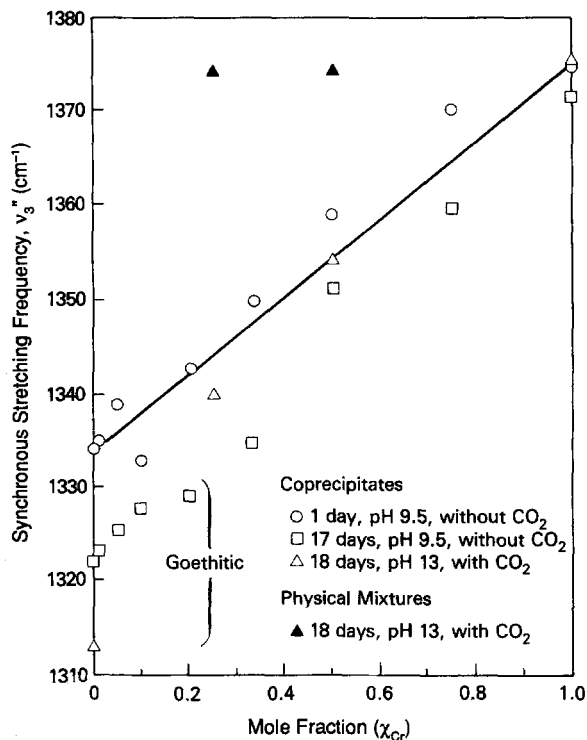


Figure 6. Relationship between the frequency of the synchronous  $\nu_3''$  vibration of the carbonate ligand and the Cr mole fractions of the coprecipitated Fe and Cr hydrous oxide phases and the physical mixtures of pure Fe and Cr hydrous oxide phases, after various incubation periods at 25°C in the presence or absence of atmospheric CO<sub>2</sub> and at initial pHs of 9.5 and 13.

tions (Table 2). Indeed, the pure Cr and Fe phases had identical  $\nu_3'$  peak locations despite their chemical and structural differences. The  $\nu_3'$  frequencies for the high-Fe phases can be explained by the formation of crystalline goethite; however, no evidence of transformation to a crystalline phase could be found in the high-Cr solids. The only treatment difference between the 17- and 18-day samples (other than initial pH) was the contact with atmospheric CO<sub>2</sub>. The 18-day, high-Cr samples, which were in contact with atmospheric CO<sub>2</sub>, gained carbonate, whereas the 17-day samples actually lost roughly a third of the original carbonate during the incubation. Perhaps this loss of carbonate resulted in an increase in the strength of the hydrogen bonds to the remaining carbonate ions.

In contrast to the abrupt shifts in the  $\nu_3'$  peak, the frequency of the  $\nu_3''$  peak for the 1-, 17-, and 18-day coprecipitated samples increased progressively as the Cr mole fraction of the solids increased (Figure 6). This behavior was expected from the assignment of this peak by Fujita *et al.* (1962) to the synchronous stretching mode (which includes contributions from the metal-oxygen bond) and, in part, from the predictions of

polarization effects by Brintzinger and Hester (1966). Indeed, the  $\nu_3''$  frequency shifts in these spectra were analogous to the Vegard's law shifts that are often observed in the X-ray powder diffraction patterns of crystalline solid-solution members. The presence of goethite in the samples, however, skewed the  $\nu_3''$  vibration to lower frequencies, suggesting that polarization by the metal-carbonate bond was stronger in goethite than in the noncrystalline phases.

The frequency of the fundamental  $\nu_1$  vibration should also have changed with the metal cation. The  $\nu_1$  vibration, however, was very weak relative to the  $\nu_3$  vibrations, and no  $\nu_1$  peak was observed for the 18-day samples. In the spectra of the 1- and 17-day samples, no change in the frequency of the  $\nu_1$  vibration was observed. This observation is contrary to intuition, but consistent with the calculations of Brintzinger and Hester (1966), which showed very little change in the  $\nu_1$  fundamental frequency as a result of changes in metal-oxygen bonding.

In addition to unidentate complexes, which involve one carbonate oxygen, other carbonato complexes involving two carbonate oxygens are possible. For example, two carbonate oxygens may coordinate to a single metal atom to form a bidentate complex, or they may coordinate to two separate metal atoms to form a bridging complex. The  $\nu_3$  splitting for bidentate and bridging complexes are generally larger than those for the unidentate complexes (Nakamoto *et al.*, 1957; Fujita *et al.*, 1962; Grigor'ev *et al.*, 1972) and can be as large as  $610\text{ cm}^{-1}$  for some organic carbonates (Nakamoto, 1970, p. 171). The  $\nu_3$  splittings observed in the present study (Table 2) compare well with those obtained for goethite and freshly precipitated  $\text{Fe}(\text{OH})_3$  by other workers (Russell *et al.*, 1975; Harrison and Berkheiser, 1982; Dvorak *et al.*, 1969) and are definitely smaller than the splitting expected for bidentate and bridging carbonato complexes ( $\sim 300\text{--}600\text{ cm}^{-1}$ ), if the data of Fujita *et al.* (1962) for Co(III) are used as a reference. We conclude, therefore, as did Russell *et al.* (1975) and Harrison and Berkheiser (1982), that a unidentate carbonato complex with at least  $C_s$  point group symmetry was formed with the metal cations in the  $(\text{Fe,Cr})(\text{OH})_3$  solids.

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