

THE INFLUENCE OF ALUMINUM ON IRON OXIDES. VI. THE FORMATION OF Fe(II)-Al(III) HYDROXY-CHLORIDES, -SULFATES, AND -CARBONATES AS NEW MEMBERS OF THE PYROAURITE GROUP AND THEIR SIGNIFICANCE IN SOILS

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Abstract—In the absence of oxygen, Fe(II) chloride, sulfate, and carbonate solutions react at pH 6.5 to 7 with aluminum hydroxide suspensions to form new Fe(II)-Al(III) hydroxy anion compounds of the pyroaurite group. The Fe(II)-Al(III) hydroxy-chloride and -sulfate compounds are isostructural with Fe(II)-Fe(III) “green rust” compounds with Al essentially substituting for Fe(III). Where CO_3^{2-} is the only anion in the system, an Fe(II)-Al(III) compound isostructural with hydroxalcalite is formed. Either in the dried or wet state, these compounds are unstable in air due to oxidation of Fe(II). Oxidation of the dried sample in air yields akaganite or aluminous ferrihydrite, whereas, if the sample is maintained in a moist condition and oxidized by air under water, lepidocrocite or aluminous goethite is produced along with small amounts of ferrihydrite. On X-ray powder diffraction, the lepidocrocite so formed commonly shows no diagnostic (020) basal reflection, or one with a markedly reduced intensity. The products of oxidation, and the rapidity of their formation, appear to be dependent on the composition of the initial double hydroxy compound and the conditions under which the oxidation is carried out.

The green colored compounds commonly observed in gleyed soils also rapidly become yellow brown on exposure to air, and difficulty arises in the identification of the Fe oxide phases assumed to be present. Similar conditions and reactants to those involved in the formation of the compounds described above are expected in these soils, and it is suggested that Fe(II)-Al(III) members of the pyroaurite group may form in such an environment.

Key Words—Fe-Al hydroxycarbonate, Fe-Al hydroxychloride, Fe-Al hydroxysulfate, Green rust, Iron oxide, Pyroaurite.

INTRODUCTION

Taylor and Schwertmann (1978) reported that small amounts of Al present as hydroxy species in the pH range 5.5–7 inhibited the formation of γ -phase iron oxides from an Fe(II) system under conditions which normally lead to their formation (Taylor and Schwertmann, 1974a, 1974b). Instead of lepidocrocite and maghemite, goethite became the preferred end-product in the presence of Al. Al was influential only when the Fe(II) system was subjected to oxidizing conditions and was investigated only in the pH range 5.5–7.

Taylor and Schwertmann (1978) observed that the initial alkali consumption to maintain pH during the oxidation of an Fe(II) solution was faster when Al was present in the system. Moreover, the alkali required to bring a combined solution of Al^{3+} and Fe^{2+} to pH 7 was greater than the total amount required to adjust the pH of the two solutions separately. This suggested a reaction between the Al-hydroxy species present at this pH and the Fe(II) in solution. To investigate this reaction and its possible implications, a series of syntheses were conducted under anaerobic conditions to simulate those expected beneath the water surface of a stagnant gley soil.

EXPERIMENTAL

Ferrous chloride, sulfate, and carbonate systems were investigated.

Ferrous chloride and sulfate experiments

Solutions were prepared by dissolving the appropriate Merck AR grade Fe(II) salt in nitrogen-saturated distilled water in 100-ml volumetric flasks. The solutions were acidified with 25 ml of 0.08 M HCl or 20–40 ml of 0.3 M H_2SO_4 and stored at about 2°C until required. Acidified 0.24 M aluminum chloride and sulfate solutions were also prepared.

Measured volumes of the appropriate Al solution were added to 15–25 ml of nitrogen-saturated distilled water to give an Al content of 0.24 mmole (in a few cases larger amounts of Al were used, with essentially the same results). The solution was taken to pH 7 with 2.3 N NaOH using a Radiometer SBR2 automatic titrator. Independently, Fe(II) chloride or sulfate solutions containing approximately 0.5–11.5 mmole Fe were titrated under nitrogen to pH 7 with the standard NaOH. When equilibrium at pH 7 was attained, the Al hydroxide suspension was added to the Fe(II) solution while 150 ml/min nitrogen continued to flow into the enclosed 75-ml Radiometer titration vessel. The total initial volume was 50 ml + the volume of NaOH required to bring the two solutions independently to pH 7. In some experiments, the two solutions were adjusted to the same lower pH value before mixing, and this pH was maintained by alkali addition.

On addition of the Al-hydroxide suspension to the

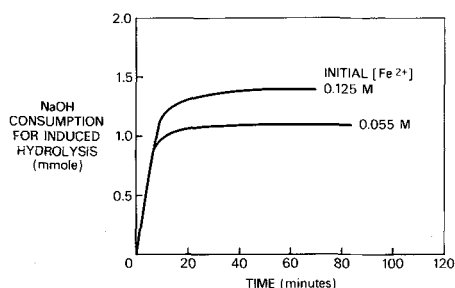


Figure 1. Rate of alkali consumption to maintain pH following the addition of FeCl_2 solutions at pH 7 to suspensions of 0.24 mmole $\text{Al}(\text{OH})_3$ under nitrogen.

$\text{Fe}(\text{II})$ solution there was an immediate drop in pH, and alkali was added automatically to maintain the pH until equilibrium was reached, generally within 2–4 hr. The volume of alkali needed to maintain the pH was measured to 0.001 ml, and the rates of consumption with time were recorded. After equilibrium had been reached, the resultant green-blue suspensions were centrifuged in stoppered tubes, and the equilibrium iron concentration was measured in the supernatant solution by atomic adsorption techniques. The precipitates were washed twice with a nitrogen-saturated water-ethanol mixture, and after a final acetone wash,¹ were dried under vacuum. An X-ray powder diffraction (XRD) photograph (5.73-cm diameter camera; $\text{CoK}\alpha$ radiation) was taken as soon as possible. In some samples, a portion of the final washed product was not dried, but put back into distilled water and oxidized with air at pH 7.

Ferrous carbonate system

$\text{Fe}(\text{OH})_2$ was precipitated from an FeCl_2 solution by the addition of excess NH_4OH . The suspension was centrifuged, washed 3 times with nitrogen-saturated distilled water, and added to a further volume of nitrogen-saturated water through which CO_2 was then bubbled for 15 min. The resultant green-brown suspension was filtered under CO_2 (solid CO_2 added to filter paper and receiving vessel). The clear filtrate was stored in stoppered flasks under CO_2 in a refrigerator until needed. Within 1 or 2 days, a slight yellow brown precipitate had generally formed. Before use, the solution was again filtered under CO_2 , with an excess of solid CO_2 in the 250 ml Radiometer flask. The $\text{Fe}(\text{II})$ concentration in these solutions was generally 0.02–0.03 M, and the pH value was about 5.8–6.1. Three milliliters of 0.23 M $\text{Al}(\text{NO}_3)_3$ was added to 20 ml of nitrogen-saturated distilled water and taken to pH 7. The suspension was

¹ It has been subsequently observed that by using two acetone washes instead of the nitrogen-saturated water-ethanol mixtures, less oxidation occurs and the compounds are a lighter shade of green.

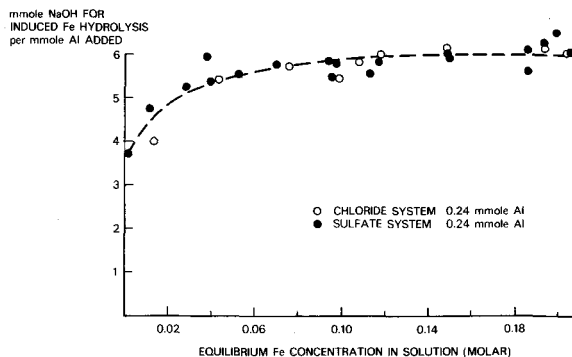


Figure 2. Induced hydrolysis of $\text{Fe}(\text{II})$ chloride and sulfate solutions at pH 7 in the presence of 0.24 mmole Al.

centrifuged and washed twice with nitrogen-saturated water and then added to the $\text{Fe}(\text{II})$ carbonate solution. The solution was stirred, and nitrogen was allowed to bubble at the rate of 150 ml/min into the solution for 10 min and then allowed to flow just above the surface. No pH control was used, and after a few hours the suspension became a blue-grey color. After about 24 hr a heavy blue-grey to blue-green suspension had formed which was centrifuged, washed, dried, and examined by XRD as described above for the chloride and sulfate systems.

RESULTS

The chloride system

$\text{Fe}(\text{II})$ hydroxide is not normally precipitated at pH 7 at $\text{Fe}(\text{II})$ concentrations below 0.18 M. The hydrolysis and dark-green colored material that forms immediately following the mixing of the Al and Fe compounds maintained at this pH appears to be due to an interaction between the respective soluble hydroxy species of the two cations. This reaction requires an excess of $\text{Fe}(\text{II})$ in solution, and the extent of the subsequent hydrolysis (called induced hydrolysis) is dependent on the concentration of $\text{Fe}(\text{II})$. A typical hydrolysis rate curve is shown in Figure 1.

The induced hydrolysis of $\text{Fe}(\text{II})$ (as measured by the alkali consumption to maintain the pH) showed an initial sharp increase with time, but reached a plateau value which was higher when the initial concentration of $\text{Fe}(\text{II})$ was greater. Figure 2 also shows that the NaOH consumption per mmole of Al initially increased with increasing $\text{Fe}(\text{II})$ in solution and reached a plateau value at the higher concentrations of iron.

With an initial concentration of 0.071 M $\text{Fe}(\text{II})$, hydrolysis and precipitation occurred at pH 7, and to a lesser extent at pH 6.5, but not at pH 6 (Figure 3). Precipitation still did not occur at pH 6 when the initial $\text{Fe}(\text{II})$ concentration was increased to 0.322 M, a level at which the $\text{Fe}(\text{OH})^+$ concentration would be greater

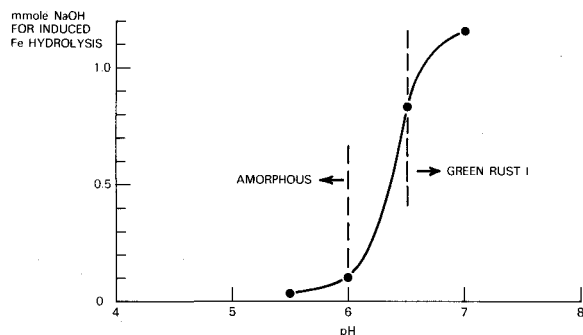


Figure 3. Effect of pH on the induced hydrolysis of an 0.716 M Fe(II) chloride solution by 0.24 mmole Al under N_2 .

than in the 0.071-M Fe(II) solution at pH 7. This suggests that the effect of pH is due to the lower concentration of $Al(OH)_4^-$, rather than that of $Fe(OH)^+$.

From Figure 2 it is seen that approximately 6 mmole of NaOH per mmole of added Al were required for the induced hydrolysis in both the chloride and sulfate system. This suggests that 3 mmole of Fe^{2+} have been fully hydrolyzed to $Fe(OH)_2$ giving an Fe/Al mole ratio of 3 in the final hydrolysis precipitate.

The green precipitates formed from the chloride system, if examined by XRD photography as soon as they have dried under a high vacuum, all showed the diffraction pattern of "green rust" I. The green rusts are

now recognized as belonging to the pyroaurite group of compounds (Taylor, 1973; Brindley and Bish, 1976). The spacings (Table 1) exhibit lower d values consistent with the substitution of Al(III) for Fe(III). These samples oxidized on exposure to air and changed from dark green or green-blue color to a yellow-brown color within a few hours. The rapidity of the oxidation appeared to be dependent on the conditions under which the sample was formed: Samples formed at a high Fe(II) concentration (in the plateau region of Figure 2) appeared to retain the basic structure of the double hydroxide for longer periods.

The diffraction lines for reflections other than the (003) reflection became more diffuse, shifted position, or became less intense during oxidation in air (Table 1). Storage of the samples under vacuum reduced the rate of this degradation, although the surfaces still underwent a color change. Samples formed at low Fe(II) concentration showed ferrihydrite diffraction lines, while the products from higher concentrations gave akaganeite (β - $FeOOH$) on aerial oxidation of the dried green compound (Table 1). The XRD pattern of the akaganeite became more intense and less diffuse after exposure to air for 7 months.

Oxidation products of the hydroxy chloride

Oxidation of the green precipitate in water at pH 7 before it had been dried under vacuum caused complete

Table 1. X-ray powder diffraction spacings of Fe(II)-Al(III) hydroxy chloride and its products of aerial oxidation.

Fe(II)-Al(III) hydroxy chloride (Sample 78/196)										
Green Rust I ¹			As soon as prepared				After 8 days in air		Akaganeite ²	
hkl	d (Å)	Int.	d (Å)	Int.	d (Å)	Int.	d (Å)	Int.		
003	8.02	vs	7.74	vs	7.44	s	7.40	vs		
006	4.01	s	3.85	s	3.73	w	5.25	m		
					3.30	s	3.70	vw		
10 $\bar{2}$	2.701	m	3.34	vw	3.30	s	3.311	vs		
			2.698	m (d)	2.54	s (d)	2.616	m		
10 $\bar{5}$	2.408	m	2.320	vw (d)	2.277	m-s	2.543	s		
							2.343	w		
							2.285	m		
							2.097	w		
							2.064	w		
10 $\bar{8}$	2.037	w	1.938	w (d)	1.938	w-m	1.944	m-s		
1010	1.805	vw					1.854	vw		
					1.747	w	1.746	m		
10 $\bar{1}\bar{1}$	1.716	vw					1.719	vw		
110	1.598	m-w	1.563	m (d)	1.629	w-m	1.635	vs		
113	1.567	m-w	1.535	w (d)	1.50		1.515	m		
							1.497	w		
							1.480	w		
					1.46	w (d)	1.459	vw		
							1.438	s		
					1.373	w	1.374	m		

v = very; s = strong; m = moderate; w = weak; d = diffuse.

¹ (hkl) indices based on rhombohedral cell after Bernal *et al.* (1959).

² d spacings for akaganeite after Bernal *et al.* (1959).

Table 2. X-ray powder diffraction spacings of Fe(II)-Al(III) hydroxy sulfate and its products of aerial oxidation.

Green Rust' II			Fe(II)-Al(III) hydroxy sulfate compounds								
			As soon as dried in vacuo						After 1 month in air		
			78/172 ²		78/187 ³		78/186 ⁴		78/186		
hkl	d (Å)	Int.	d (Å)	Int.	d (Å)	Int.	d (Å)	Int.	d (Å)	Int.	Oxidation products
001	10.92	vs	11.08	vs	10.90	vs	11.02	vs	9.32	w-m	Degraded original material
002	5.48	s	5.47	s	5.41	s (d)	5.455	s	—		
003	3.65	s	3.645	s	3.63	m (d)	3.65	s	4.10	vvw	Goethite (?)
			3.064	vvw	ND		3.073	vvw			
004, 100	2.747	m	2.744	vvw	ND		2.744	vvw			
101	2.660	m-s	2.650	m	2.65	m (d)	2.656	m	2.55	m-s	Ferrihydrite
102	2.459	m-s	2.437	m	ND		2.437	m	2.296	vvw	Ferrihydrite
005, 1013	2.195	m-s	2.171	w	2.175	vw	2.186	w			
104	1.938	m-s	1.938	w	1.948	vw	1.930	w			
105	1.712	w	1.702	vw	ND		1.708	vw			
110	1.587	w	ND		ND		1.583	w			
111	1.570	w	1.561	w	1.554	w	1.565	w	1.484	vvw	Ferrihydrite
112	1.525	w	1.512	w	1.506	w	1.515	w			
			1.362	vvw							

v = very; s = strong; m = moderate; w = weak; d = diffuse; ND = not detected.

¹ Indices based on hexagonal cell after Bernal *et al.* (1959).

² FeSO₄ solution from Merck FeSO₄·7H₂O and stored for 4 days before use. For sample preparation 16.4 mmole Fe(II) and 0.24 mmole Al were used.

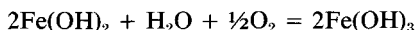
³ FeSO₄ solution made from dissolution of Fe powder in H₂SO₄. For sample preparation 0.1 mmole of Fe(II) and 0.14 mmole Al were used.

⁴ As in ³ above, but 9.1 × 10⁻⁴ mmole Fe(III) sulfate were also added.

transformation to a disordered form of lepidocrocite, giving no diagnostic (020) spacing, or one much less intense than the normally weaker (120) line. Oxidation at pH 6 and 5.5 yielded ferrihydrite.

Composition of hydroxy chloride compound

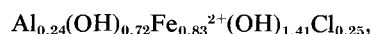
Theoretically, the aqueous oxidation of fully hydrolyzed Fe(OH)₂ will proceed without a decrease in pH according to the equation:



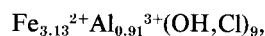
However, during the oxidation of the undried washed compounds from both the chloride and sulfate system in water, the pH dropped slightly, and alkali was needed to maintain the pH at 7. This is no doubt due to the replacement of the small amounts of Cl⁻ or SO₄²⁻ ions necessary for the respective green rust structures by OH. For each system the additional alkali consumed during the aqueous oxidation stage was approximately equal to a constant proportion of the consumption during the induced hydrolysis when no oxidation occurred. For the chloride system this value was approximately 17%, so that for every mole of OH used for the induced hydrolysis of the Fe(II), an additional 0.17 mole of chloride was associated with the compound. On this basis, for every two moles (OH + Cl) in the compound, the presence of Al caused the induced hydrolysis of one mole of Fe(II).

Thus, for example, with sample 79/1, 0.24 mmole of

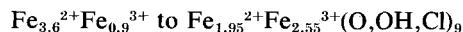
AlCl₃ was taken to pH 7, and the addition of 5.63 mmole of FeCl₂ also at pH 7 caused the consumption of a further 1.411 mmole of NaOH to bring the system to equilibrium. Subsequent oxidation of the washed green precipitate required a further 0.248 mmole of NaOH to maintain the pH at 7. This leads to an approximate formula of:



which can be rewritten as



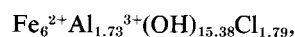
which is within the range



for 20% and 57% oxidation levels of Feitknecht and Keller's (1950) green rust I (Bernal *et al.*, 1959). If the formula is recast in the form of hydrotalcite,



one obtains



which is a good agreement, especially if a small amount of the Fe is present as Fe(III). To obtain the ideal M²⁺/M³⁺ ratio of 3 for the pyroaurite group, only 3.3% of the total Fe in the compound need be present in the trivalent state, giving a modified formula

Table 3. X-ray powder diffraction spacings of natural and synthetic hydrotalcites and the Fe(II)-Al(III) hydroxy carbonate compound.

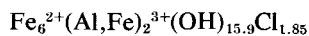
Hydrotalcite					Fe(II)-Al(III) hydroxy carbonate Sample 78/211 ³	
Natural ¹			Synthetic ²		d (Å)	Int.
hkl	d (Å)	Int.	d (Å)	Int.		
003	7.69	100	7.84	100	7.50	vvs
006	3.88	70	3.9	60	3.715	s
009, 012	2.58	20	2.60	40	2.578	vs
015	2.30	20	2.33	25	2.277	s
NI					2.090	vw
0.18	1.96	20	1.99	30	1.92	ms
NI	1.85	10	—	—	—	—
0012			1.95	6	—	—
1010	1.75	10	—	—	1.704	vw
0111	1.65	10	—	—	1.612	w
110	1.53	20	1.541	35	1.534	w
113	1.50	20	—	—	1.503	w
1013	—	—	1.498	25	—	—
0114	—	—	1.419	8	1.429	vw (d)

NI = not indexed; v = very; s = strong; m = moderate; w = weak; d = diffuse.

¹ ASTM card 14-191. Natural hydrotalcite. Data supplied by Neumann and Bergstol, Mineral Museum, Oslo, and indexed after Allmann (1968).

² Synthetic hydrotalcite from Ross and Kodama (1967) indexed on cell described by Allmann (1968).

³ Indices were assigned only on the basis of similarity with reflections indexed in standard samples.



which closely approximates the hydroxy-carbonate formula of hydrotalcite, further demonstrating that these "green rust" compounds are members of the pyroaurite group, as suggested by Brindley and Bish (1976).

The amount of Fe precipitated from solution by such induced hydrolysis cannot be accurately calculated since it is measured by a difference in Fe content of two concentrated solutions. An approximate value can, however, be obtained by using this difference calculation for the plateau region of Figure 2. For 4 chloride and 6 sulfate samples, an average of 0.9 mmole Fe was lost from solution due to the presence of 0.24 mmole Al, or 3.75 mmole Fe per mmole Al.

The sulfate system

For most Fe(II) concentrations studied in the sulfate system, the green precipitates that formed were isostructural with the "green rust" II described by Bernal *et al.* (1959). The diffraction spacings for typical samples are shown in Table 2. The reflections from samples prepared from freshly made nitrogen-saturated FeSO₄ solution showed a general lack of sharpness, and many of the spacings of "green rust" were not visible, even if the diffraction photograph was made as soon as the

sample had been dried in vacuo. A higher degree of crystallinity was obtained if the FeSO₄ solution had been stored for a few days, possibly allowing a very slight degree of oxidation to Fe(III) species to occur. This was demonstrated by preparing a Fe(II) sulfate solution from the dissolution of Fe powder in H₂SO₄ and comparing the diffraction results in the presence and absence of a small addition of Fe(III) sulfate, such that Fe(III)/Fe(II) = 10⁻⁴. The presence of this small amount of trivalent Fe resulted in a sharper XRD pattern with more discernible reflections (sample 78-186) than was obtained from an Fe(III)-free equivalent sample (78-187), as shown in Table 2. The green color of the final products in both the chloride and sulfate systems suggests that a small amount of Fe(III) might have been present, and that Fe(III) might even be necessary for crystal development. This effect may be due to the greater disparity between the ionic sizes of Fe(II) and Al(III) than exists between Fe(II) and Fe(III).

Products of oxidation of the hydroxy sulfate

On aerial oxidation, the basal spacing of the compound persisted for a long time even though the change of color from blue-green or dark green to yellow-brown was rapid, occurring in a few hours. In addition, diffraction lines indicative of ferrihydrite appeared. This transformation was accelerated by heating the samples for a few hours at 160°C. Reflections indicative of the original precipitate decreased in intensity or became diffuse and showed shifts to lower d values (Table 2). A comparison of the diffraction data of Tables 1 and 2 suggests that the presence of Al substituting for Fe(III) in the chloride system (green rust I) produced a greater shift to lower spacings than for the sulfate (green rust II) compounds.

When oxidized in water, the final products were variable and dependent on the previous treatments. For example, a washed and vacuum-dried sample, on subsequent oxidation in water at pH 7, gave a diffraction pattern in which only the two strongest lines of ferrihydrite (d = 2.50 Å and 1.45 Å) were detected. Washed, undried samples that were oxidized directly by stirring in water, whilst the pH was maintained at 7, gave products ranging from poorly crystalline goethite with ferrihydrite and possible traces of poorly crystalline lepidocrocite with no detectable (020) basal reflection, to well-crystalline, low spacing goethite (aluminous) with trace amounts of lepidocrocite which gave a very weak basal spacing. The identification of lepidocrocite in the absence of a diagnostic (020) reflection, especially when other mineral phases are dominant, cannot be made with certainty.

The carbonate system

As opposed to the chloride and sulfate systems, the hydrolysis of an Fe(II) carbonate solution in CO₂-

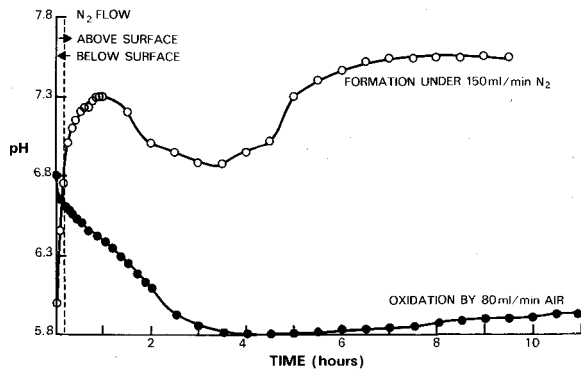


Figure 4. pH variation with time during formation and oxidation of Fe(II)-Al(III) hydroxy carbonate.

charged water did not necessarily require alkali addition to maintain the pH. The addition of a washed suspension of $\text{Al}(\text{OH})_3$ at pH 7 to the Fe(II) solution, which is normally around pH 6, caused an initial rise in pH due to the expulsion of CO_2 from the system by the nitrogen flow (Figure 4). The actual fluctuation in pH was dependent on the rate at which the CO_2 was lost and at which hydrolysis occurred. The presence of Al here also induced the hydrolysis of the Fe producing a tendency for the pH to fall in opposition to the rise produced by the loss of CO_2 . The start of hydrolysis was not clearly defined but after an induction period of 30–60 min, the whitish $\text{Al}(\text{OH})_3$ suspension became tinged with a pale green color. At this stage, the pH fell. If the CO_2 was expelled too quickly and the pH was allowed to rise to more than about 8, yellowish brown siderite precipitated.

After about 10 hr under the conditions given in Figure 4, the pH stabilized at about 7.4–7.5, and a heavy blue-grey precipitate formed. In comparison to the compounds formed from the chloride and sulfate systems, the carbonate compound is very well crystalline. It possesses a greasy, talc-like feel and is completely isostructural with hydrotalcite (see Table 3). The infrared spectrogram² closely resembles that of hydrotalcite published by Ross and Kodama (1967), although there are slight shifts in the peak positions.

There was no convenient technique to measure the amount of Fe hydrolysis that was produced by known amounts of added Al, as in the case of the chloride and sulfate experiments. Direct analysis of the compound, even though pure from XRD analysis, did not preclude small amounts of unreacted $\text{Al}(\text{OH})_3$ from being present and giving a lower value for the $\text{M}^{2+}/\text{M}^{3+}$ ratio. The compound is unstable at high and low pH values which would be necessary to remove excess Al. Analyses of

² The infrared analysis was carried out by Dr. W. R. Fischer, Lehrstuhl für Bodenkunde, Technische Universität München, while one of the authors (RMT) was on study leave.

Table 4. Variation in X-ray powder diffraction spacings of Fe(II)-Al(III) hydroxy carbonates on exposure to air.

Sample 78/123			Sample 78/124		Ferrihydrite ²	
Vacuum dried	12 hr in air	7 months in air	Vacuum dried	7 months in tube ¹	d (Å)	Int.
d (Å)	d (Å)	d (Å)	d (Å)	d (Å)	d (Å)	
7.66	7.49	7.33	7.445	7.44	—	
3.80	ND	ND	3.697	3.67	—	
2.578	2.498	2.493	2.584	2.465	2.52	m-s
2.282	2.231	2.231	2.284	2.205	2.23	m-s
1.925	ND	ND	1.915	1.866	1.98	vw
ND	ND	ND	1.709	ND	1.70	vw
ND	ND	ND	1.616	ND		
1.489	1.478	1.461	1.538	1.458	1.47	m

ND = not detected; m = moderate; s = strong; v = very; w = weak.

¹ Sample left in a sealed tube packed with tissue.

² Ferrihydrite data reported by Chukhrov *et al.* (1972).

a few preparations gave an Fe/Al ratio between 2 and 3, values which are apparently not uncommon for either natural (Allmann and Jepsen, 1969) or synthetic (Gastuche *et al.*, 1967) pyroaurite-group phases.

As with the chloride and sulfate systems, the very rapid oxidation of the hydroxy carbonate in air was manifested by a color change from the dark green or blue-grey to yellow-brown and the changes in the XRD pattern (Table 4). The initially sharp reflections showed measurable shifts to lower d values as well as marked changes in intensities. The basal (003) spacing changed to lower values and suffered a loss in intensity, but persisted much longer than the (006) reflection, which in some samples was not detectable after several hours. As the other spacings changed to lower values and the reflections became more diffuse, they approached the values for ferrihydrite. It is not certain whether the changed pattern represents a degraded initial structure, or, what is more likely, a new phase caused by a solid state transformation following oxidation of the hydroxy carbonate compound, see Table 4.

If the washed precipitate was not dried but allowed to oxidize directly in water, aluminous goethite resulted, similar to the end product obtained by Taylor and Schwertmann (1978) by the direct oxidation at a controlled pH of Fe(II) carbonate solution in the presence of Al. Figure 4 shows the variations in pH during the oxidation of the Fe(II)-Al(III) hydroxy carbonate by the passage of 80 ml of air/min through the aqueous suspension for 10 hr. The products of this oxidation were very fine grained goethite plus a small residual amount of the initial material as seen by a very weak (003) basal spacing. Ferrihydrite was also suspected from the intensity and diffuseness of lines in the $d = 2.5, 2.22,$ and 1.47 \AA regions (see Table 5). After an additional 11 days in water, goethite was enhanced, no residual hydroxy carbonate phase was evident, and the intensity and dif-

Table 5. Variation in X-ray powder diffraction spacings of Fe(II)-Al(III) hydroxy carbonate after oxidation in water.

Sample 78/211		
Vacuum dried	Oxidized in H ₂ O ¹ for 10 hr	Shaken further ² 11 days in H ₂ O
d (Å)	d (Å)	d (Å)
7.50	7.54	ND
	4.93	4.99
	4.14	4.16
3.715	ND	ND
	3.35	3.36
	2.676	2.676
2.578		2.557
	2.465	2.434
	2.231	2.238
2.277		2.196
2.090		
1.920		1.905
		1.797
	1.717	1.717
1.704		
1.612		1.597
		1.548
1.534		
1.503		1.494
	1.453	1.451
1.429		

¹ ND = not detected. Oxidized as described in Figure 6.

² All spacings recorded can be attributed to low spacing Al-goethite.

fuseness of the reflections attributed to ferrihydrite were reduced. The Fe and Al contents of the solutions used to prepare the samples described in Tables 1–5 are given in Table 6.

DISCUSSION

The experimental methods used preclude the possibility of coprecipitation of Fe and Al, and the large amount (2–3 mmole) of Fe removed from solution per mmole of Al added suggests that the products of the reaction were not formed by adsorption of an Fe(II) species by the already precipitated Al(OH)₃ phase. Rather, it is considered that the precipitates formed from soluble hydroxy species. The dominant hydroxy species of the reactants present at pH 7 are Fe(OH)⁺ and Al(OH)₄⁻, and a possible reaction mechanism is represented by the equations

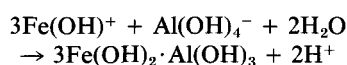
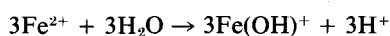
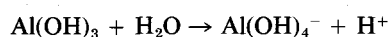


Table 6. Fe and Al contents of solutions used to form samples described in Tables 1–5.

Sample no.	Al added (mmole)	Fe(II) added (mmole)	Initial total volume ¹ (ml)
78/123	0.72	2.3	200
78/124	0.72	2.6	220
78/172	0.24	16.4	51.8 ²
78/186	0.24	9.1 ¹	51.6 ²
78/187	0.24	9.1	51.2 ²
78/196	0.24	10.4	51.2 ²
78/211	≈0.9	1.5	125

¹ In addition to this Fe(II) content, 0.09 mmole Fe(III) was present.

² For the sulfate and chloride samples this volume is the original 50 ml plus the alkali necessary to adjust the Al and Fe solutions independently to pH 7.

Pyroaurite-group compounds have been called "double hydroxides," and Taylor (1973) reported on the ease with which they formed. The basic structure of this group consists of brucitic layers containing both di- and trivalent cations with an interlayering of anionic groups and water. In general, there is no evidence for the ordering of cations in octahedral sites, although Gastuche *et al.* (1967) prepared synthetic samples which, because of the variable M²⁺/M³⁺ ratio, might indicate ordering or segregation. Taylor (1973) gave the general formula for the hydroxy carbonates as



where Δ is less than 0.125, and x is probably <0.33. However, he stated that for the group, CO₃²⁻, NO₃⁻, OH⁻, Cl⁻, Br⁻, or SO₄²⁻ may act as the anion in the interlayer position. A large number of divalent (Mg, Zn, Mn, Fe, Co, or Ni) and trivalent (Al, Mn, Fe, Co, or Ni) cations are also present which can take part in these reactions and give rise to a large range of possible combinations of either pure or mixed phases.

The present syntheses involved conditions and reactants that could be expected to occur in soils. The almost ubiquitous occurrence of Al minerals will always give rise to equilibrium concentrations of its hydroxy species, and the ability of these species to induce the hydrolysis and precipitation of Fe(II) near neutral pH values may influence the formation of Fe oxides over a large range of soil conditions (cf. Taylor and Schwertmann, 1978).

The double hydroxy-carbonate would be the most likely member of this group of compounds to occur in soils, as the CO₃²⁻ concentration is generally much higher than that of Cl⁻ or SO₄²⁻. Moreover, the system is self buffering during both its formation and oxidation stages, and therefore requires no stringent pH control

as is necessary for the chloride or sulfate system. The products of oxidation also give rise to iron oxide minerals commonly found in soils. For example, the upper limit of Al substitution in goethite is accepted as 33 mole % which is consistent with the compositional range M^{2+}/M^{3+} being between 2 and 3 found in these compounds. Additionally, ferrihydrite resulting from the aerial oxidation of this compound in the dried state is yellow-brown, resembling the naturally occurring soil material, as opposed to the red-brown synthetic ferrihydrite produced from rapid hydrolysis of Fe(III) solutions.

Further support for this compound as a likely pathway for soil iron oxide formation comes from the similar behavior of the dark green-blue compounds associated with gleyed horizons. In soils the CO_2 partial pressure is higher than in air (Hem, 1960), and anaerobic conditions lead to the presence of Fe(II) in the soil solution, producing the same conditions that were used in these present syntheses. On exposure to air, these green soil compounds commonly oxidize rapidly to a yellow-brown material whose identification is difficult. This would be expected as XRD can not detect small amounts of ferrihydrite in association with the other soil minerals. The formation of aluminous goethite, a common constituent of soils, would not be restricted to initially anaerobic conditions, but could occur whenever mobilized $FeCO_3$ is hydrolyzed by the presence of Al-hydroxy species also present in the soil solution.

Chloride is probably not the dominant anion in many soils, so that the "green rust I" compound or its Al analogue would not commonly be expected. Even if this compound did persist in small quantities, overlap of its diagnostic diffraction line with that of kaolinite would limit its detection. However, under certain conditions this compound could form and give rise to the rare occurrences of akaganeite. Akaganeite is not found in soils, and its conditions of formation have hitherto not been explained. Oxidation by an inflow of oxygenated water converts hydroxy-chloride compounds to disordered aluminous lepidocrocite (Taylor and Schwertmann, unpublished data) which to date has not been identified in soils. These transformations of the hydroxy-chloride supports the view that this compound is of little importance in soils.

Although hydroxy-sulfate also forms common soil Fe oxides on oxidation, e.g., ferrihydrite if oxidized dry in air or aluminous goethite if oxidized in water, it would not be expected in soils, except possibly in proximity to sulfide ore bodies or where prior anaerobic conditions had caused Fe sulfides to form. Here also, the rapid decomposition of the hydroxy-sulfate makes its identification by XRD rather difficult as its diagnos-

tic (003) basal reflection could be obscured by the reflections of mica and other aluminosilicates.

These reactions may be important in further pedological processes, for example, in the incorporation of foreign cations in soil iron oxides, or in the non-biological precipitation of Mn oxides. A more careful examination of the composition of the green horizons of certain gleys should lead to the identification of one of these phases as a metastable pedogenic mineral.

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REFERENCES

- Allmann, R. (1968) Magnesium aluminum carbonate hydroxide tetrahydrate: A discussion: *Amer. Mineral.* **53**, 1057–1059.
- Allmann, R. and Jepsen, H. P. (1969) Die Struktur des Hydrotalkits: *Neues Jahrb. Mineral. Monatsh.* **12**, 544–551.
- Bernal, J. D., Dasgupta, D. R., and Kackay, A. L. (1959) The oxides and hydroxides of iron and their structural interrelationships: *Clay Min. Bull.* **4**, 15–30.
- Brindley, G. W. and Bish, D. L. (1976) Green rust: a pyroaurite type structure: *Nature* **263**, 353.
- Chukhrov, F. V., Zvyagin, B. B., Ermilova, L. P., and Gorshkov, A. I. (1972) New data on iron oxides in the weathering zone: *Proc. Int. Clay Conf. Madrid, 1972*, 333–341.
- Feitknecht, W. and Keller, G. (1950) Über die dunkelgrünen Hydroxyverbindungen des Eisens: *Z. Anorg. Allg. Chem.* **262**, 61–68.
- Gastuche, M. C., Brown, G., and Mortland, M. M. (1967) Mixed magnesium aluminium hydroxides. I. Preparation and characterisation of compounds formed in dialysed systems: *Clay Miner.* **7**, 177–192.
- Hem, J. D. (1960) Restraints on dissolved ferrous iron imposed by bicarbonate, redox potential, and pH: *U.S. Geol. Surv. Water Supply Pap.* **1459-B**, 33–55.
- Ross, G. J. and Kodama, H. (1967) Properties of a synthetic magnesium-aluminum carbonate hydroxide and its relationship to magnesium-aluminum double hydroxide, manasseite, and hydrotalcite: *Amer. Mineral.* **52**, 1036–1047.
- Taylor, H. F. W. (1973) Crystal structures of some double hydroxide minerals: *Mineral. Mag.* **39**, 377–389.
- Taylor, R. M. and Schwertmann, U. (1974a) Maghemite in soils and its origin. II. Maghemite synthesis at ambient temperature and pH 7: *Clay Miner.* **10**, 299–310.
- Taylor, R. M. and Schwertmann, U. (1974b) I. Properties and observations on soil maghemites: *Clay Miner.* **10**, 289–298.
- Taylor, R. M. and Schwertmann, U. (1978) The influence of aluminum on iron oxides. Part I. The influence of Al on Fe oxide formation from the Fe(II) system. *Clays & Clay Minerals* **26**, 373–383.

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Резюме—В отсутствие кислорода, хлоридные, сульфатные, и карбонатные растворы Fe(II) реагируют при pH от 6,5 до 7 с алюминиевой гидроокисной суспензией, формируя новые гидрокси-анионные соединения Fe(II)-Al(III) пироауритовой группы. Гидрокси-хлоридные и-сульфатные соединения Fe(II)-Al(III) являются изоструктурными с соединениями зеленой ржавчины Fe(II)-Fe(III), где Al существенно замещен Fe(III). Там, где CO_3^{2-} является единственным анионом в системе, образуется соединение Fe(II)-Al(III), изоструктурное с гидроталькитом. В сухом или влажном состоянии эти соединения являются нестойкими в воздухе из-за окисления Fe(II). Окисление сухого образца в воздухе дает акаганеит или алюминиевый ферригидрит, тогда как если образец содержит во влажном состоянии и окисляется воздухом под водой, образуется лепидокроцит или алюминиевый гетит вместе с небольшим количеством ферригидрита. По данным порошкового метода рентгено-структурного анализа образовавшийся таким путем лепидокроцит обычно не дает диагностического (020) базального отражения, или оно имеет существенно ослабленную интенсивность. Продукты окисления и скорость их образования, по-видимому, зависят от состава первоначального удвоенного гидроксильного соединения и условий, при которых окисление происходит.

Соединения зеленого цвета, обычно наблюдаемые в глеевых почвах, тоже быстро становятся желто-коричневыми попадая в воздушную среду, что вызывает трудности в опозновании предположительно присутствующих окисленных фаз Fe. В этих почвах ожидаются условия и реагенты, аналогичные вовлеченным в образование выше описанных соединений. Предполагается, что Fe(II)-Al(III) члены пироауритовой группы могут образоваться в такой среде. [N. R.]

Resümee—Bei der Abwesenheit von Sauerstoff reagieren Fe(II)-Chlorid, -Sulfat und -Karbonatlösungen bei pH-Werten von 6,5–7 mit Aluminiumhydroxid-Suspensionen zu neuen Fe(II)-Al(III)-Hydroxy-Anionverbindungen der Pyroauritgruppe. Die Fe(II)-Al(III)-Hydroxychlorid und -Sulfatverbindungen sind isostrukturell mit Fe(II)-Fe(III)-"green rust"-Verbindungen, wobei das Al vor allem Fe(III) substituiert. Wo CO_3^{2-} das einzige Anion im System ist, bildet sich eine Fe(II)-Al(III)-Verbindung, die isostrukturell mit Hydrotalkit ist. Diese Verbindungen sind entweder im trockenen oder nassen Zustand an Luft aufgrund der Oxidation von Fe(II) zu Fe(III) instabil. Die Oxidation der trockenen Probe an Luft führt zu Akaganait oder Al-haltigem Ferrihydrit, während eine Probe, die feucht gehalten wird und unter Wasser mit Luft oxidiert wird, Lepidokrokit oder Al-reichen Goethit zusammen mit geringen Mengen von Ferrihydrit bildet. Nach der Röntgenpulverdiffraktometrie zeigt der so gebildete Lepidokrokit im allgemeinen keine typischen (020) Basis-Reflexion, oder eine mit einer merklich geschwächten Intensität. Die Oxidationsprodukte und die Geschwindigkeit ihrer Bildung scheinen von der Zusammensetzung des ursprünglichen Doppelhydroxy-Bestandteiles abzuhängen und von den Bedingungen, unter denen die Oxidation ausgeführt wird.

Die grün gefärbten Bestandteile, die häufig in vergleyten Böden beobachtet werden, werden ebenfalls schnell gelbbraun, wenn sie der Luft ausgesetzt sind, und es ergibt sich die Schwierigkeit der Identifizierung der angeblich anwesenden Fe-Oxidphasen. Ähnliche Bedingungen und Bildungsprodukte wie die bei der oben beschriebenen Bildung auftretenden Verbindungen werden in diesen Böden erwartet und es wird angenommen, daß Fe(II)-Al(III)-Glieder der Pyroauritgruppe sich in einem derartigen Milieu bilden. [U. W.]

Résumé—En absence d'oxygène, les solutions de chlorure Fe(II), de sulphate, et de carbonate réagissent avec des suspensions d'hydroxide d'aluminium aux pH 6,5 à 7 pour former de nouveaux composés d'anion hydroxy Fe(II)-Al(III) du groupe pyroaurite. Les composés hydroxy-chlorure Fe(II) et Al(III) et hydroxy-sulphate Fe(II) et Al(III) et les composés "rouille verte" Fe(II)-Fe(III) sont iso-structuraux, avec Al substituant essentiellement à Fe(III). Lorsque CO_3^{2-} est le seul anion dans le système, un composé Fe(II)-Al(III), de structure semblable à l'hydrotalcite, est formé. Que ce soit à l'état sec ou mouillé, ces composés sont instables dans l'air à cause de l'oxidation de Fe(II). L'oxidation à l'air de l'échantillon sec donne de l'akaganéite ou de la ferrihydrite alumineuse, tandis que si l'échantillon est maintenu dans une condition humide, et oxidé à l'air sous eau, de la lépidocrocite ou de la goéthite alumineuse est produite, avec des petites quantités de ferrihydrite. A la diffraction aux rayons-X, la lépidocrocite ainsi formée ne montre bien souvent pas la réflexion basale diagnostique (020), ou la montre avec une intensité fort réduite. Les produits de l'oxidation et la rapidité de leur formation semblent dépendre de la composition du composé hydroxy double initial et des conditions sous lesquelles l'oxidation se produit.

Les composés verdâtres souvent observés dans des sols gléifiés deviennent aussi rapidement jaunes-bruns après avoir été exposés à l'air, et il devient difficile d'identifier les phases d'oxide Fe que l'on suppose être présentes. On s'attend à des conditions et à des agents de réaction semblables à ceux inclus dans la formation des composés décrits ci-dessus, et il est suggéré que les membres Fe(II)-Al(III) du groupe pyroaurite peuvent être formés dans un environnement tel. [D.J.]