

THE INFLUENCE OF ALUMINUM ON IRON OXIDES. PART I. THE INFLUENCE OF Al ON Fe OXIDE FORMATION FROM THE Fe(II) SYSTEM

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Abstract—The influence of Al on the products formed by aerial oxidation at pH 5.5–7 and 20°C of Fe(II) chloride, sulfate and carbonate solutions, was examined. In all cases Al at levels $Al/Al + Fe = 0.09–0.30$ inhibited the formation of γ phases (lepidocrocite and maghemite) in favor of goethite under conditions where, in the absence of Al, these γ phases formed. The influence of Al in these laboratory studies was supported by field observations.

At higher levels of Al, ferrihydrite formation was favored. This effect of Al was seen to be the result of a slowing down in the hydrolysis/oxidation rate of the Fe(II) system.

The presence of Al not only changed the direction of mineral formation, but also caused the formation of Al substituted goethites which resembled in particle size and morphology the natural aluminiferous goethite extracted from a soil.

Key Words—Aluminum, Ferrihydrite, Goethite, Iron, Lepidocrocite, Maghemite.

INTRODUCTION

Divalent Fe liberated during the weathering of primary minerals is the original source of mobile Fe that is ultimately precipitated as soil iron oxides. In an attempt to approach more closely conditions that could be expected during pedogenesis of Fe oxides, Taylor and Schwertmann (1974a) synthesized goethite (α -FeOOH), lepidocrocite (γ -FeOOH), maghemite (γ -Fe₂O₃) and ferrihydrite (Fe₅(O₄H₃)₃), a precursor of hematite or goethite, from Fe(II) chloride solutions at pH 6–7 and 20°C simply by changing the Fe concentration and the rate of aeration.

This technique utilized temperature and pH ranges that could be expected in soils, but applied only to the chloride system, and the inhibitory or enhancing effects of foreign ions on mineral formation were not considered. Such influences have been studied by other workers e.g., Schellmann (1959), Krause and Borkowska (1963), Schwertmann et al. (1968), Inouye et al. (1972), Schwertmann and Thalmann (1976), using different synthesis techniques. However, it is often uncertain whether any specific influences found are the result of the experimental conditions used, or if these conditions produce samples that have different morphologies, particle sizes and chemical properties. For example, Krause et al. (1970) found that Ca⁺⁺ and Mg⁺⁺ caused ferrihydrite to form from the oxidation of an Fe(II) carbonate system, and Detournay et al. (1975) found a specific influence of divalent Mn and Co in that they caused goethite rather than lepidocrocite to form from the oxidation of an Fe(II) system.

This present work was a study of the effect of Al on

the formation of Fe oxides from Fe(II) systems. Initially its effects were studied in a chloride medium under conditions previously studied (Taylor and Schwertmann, 1974a). The study was then extended to other anionic systems, particularly the carbonate, because of the frequent occurrence of this anion in soils, where it can exert its own specific influence on the direction of mineral formation. Schwertmann (1959) and Schwertmann and Fitzpatrick (1977) showed that this anion strongly favors the formation of goethite at the expense of lepidocrocite in the oxidation of an Fe(II) chloride system and possibly also in soils.

It was considered important to examine the effects of Al, because it occurs in nearly all soils and is often incorporated into the structure of the common soil Fe oxides, resulting in a change in their morphology and a possible modification of the properties that they impart to a soil. Part I of this paper discusses the influence of Al on Fe oxide formation from the Fe(II) system, while in a companion paper its influence in a pure Fe(III) system is examined.

EXPERIMENTAL

Fe(II) chloride and sulfate solutions were made by adding weighed amounts of the respective salts to N₂ saturated distilled water and dissolving under N₂. Weighed amounts of AlCl₃·6H₂O or Al₂(SO₄)₃·18 H₂O or measured volumes of an 0.24 M AlCl₃ solution were added to the above solutions in a Radiometer 200-ml titration vessel. The pH was then adjusted to the required value, in most cases while N₂ was still flowing, and the solutions were stirred magnetically using a 3.5 ×

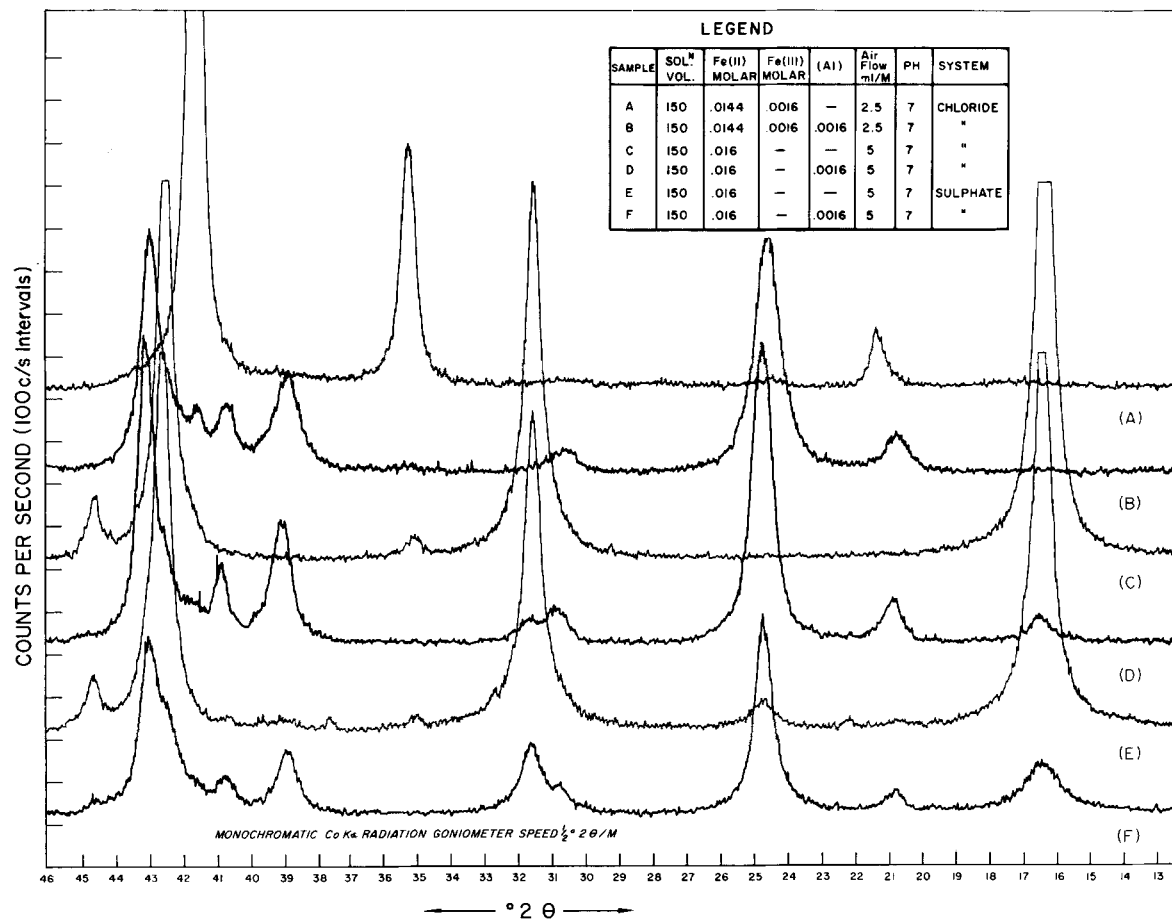


Fig. 1. X-ray powder diffractograms showing the effects of Al (Al/Al + Fe = 0.09) on the oxidation at pH 7 of 90% Fe(II)-10% Fe(III) and pure Fe(II) chloride and sulfate solutions.

0.9-cm magnetic follower* rotating at 180 rpm. When the required pH was attained by slow addition of 2.3 M NaOH the N₂ was switched off, and a controlled measured rate of air was passed into the solution via a Radiometer titrant delivery tube. The pH was then controlled at the preset value by additions of the alkali using a Radiometer TTT2 automatic titrimeter, and the base consumption (rate of oxidation/hydrolysis) was recorded on an SBR3 titrograph. When the reactions had finished (no further base consumption) the suspensions were centrifuged, washed and dried with acetone. Where Al had been added, the centrifuged washed precipitates were washed in cold 5 N NaOH for 2 min to remove as much as possible any of the Al not incorporated into the Fe oxides that were formed.

For the bicarbonate system Fe(OH)₂ was precipitat-

* The minor details concerning the reaction vessel used, the size and rotational speed of the magnetic stirrer are important as they influence the rate of aeration of the solution by the controlled air flow. This in turn influences the rate of oxidation of the Fe(II) species and can alter the form and crystallinity of the end product, especially in the pure systems.

ed from a solution of FeSO₄, with NH₄OH. The precipitate was centrifuged and washed, during which time some oxidation had occurred, and was then added to N₂ saturated distilled water. Solid CO₂ was added to the green suspension which was stirred to enable the CO₂ to form carbonic acid and dissolve the Fe(OH)₂. The solution was then filtered through a Whatman 41 filter containing solid CO₂ into a measuring cylinder into which further solid CO₂ had been added. A clear solution with a Fe(II) concentration of 0.02–0.03 M and a pH 5.8–6.1 generally formed. This solution was transferred to 100-ml volumetric flasks under a slight CO₂ pressure and stored in a refrigerator. When required these solutions were refiltered as above under CO₂ to remove any precipitate that had formed and an aliquot of the filtered solution taken for Fe determination by atomic absorption.

Similar techniques were used for the oxidation of these Fe(II) bicarbonate solutions except the pH adjustment to a preset value was not always done, nor was N₂ introduced into the system. In some cases the pH was controlled between narrow limits by using a second

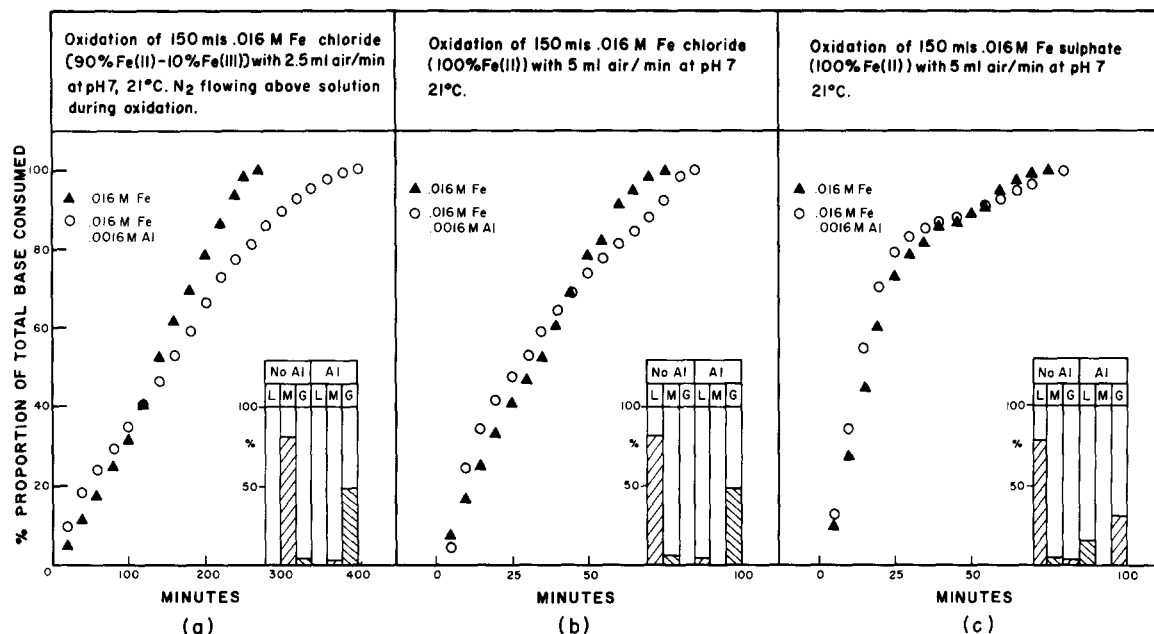


Fig. 2. Base consumption-time curves for Fe(II) and Fe(II)-Fe(III) chloride solutions oxidized at pH 7 in the presence and absence of added Al (Al/Al + Fe = 0.09).

automatic titrimer which controlled addition of HNO_3 .

The final products were examined by X-ray powder diffraction using monochromated $\text{CoK}\alpha$ radiation, 30 kV, 40 mA, with pulse height analysis and proportional counter techniques. A scanning speed of $1/2^\circ 2\theta$ -min and a time constant of 2 s were used to record the diffraction pattern between 12 – $45^\circ 2\theta$. After dissolution, samples were also analysed, for Al and Fe by atomic absorption, and electron micrographs were taken of selected samples. For accurate determinations of d spacings of the goethites approximately 10% by volume lead nitrate was added and step counting for 100 s was done at 2θ intervals of 0.05° over the (110), (130), and (111) goethite and the associated (200), (220), and (311) peaks of lead nitrate. Corrections were then applied to the measured 2θ values of the goethite peaks and corrected d spacings calculated.

RESULTS AND DISCUSSION

The chloride system

In general accordance with earlier experiments (Taylor and Schwertmann, 1974a) 0.016 M Fe solutions (both 100% Fe(II) and 90% Fe(II)–10% Fe(III)) yielded on oxidation with 2.5 ml air min^{-1} predominantly maghemite with traces of goethite and/or lepidocrocite (Figure 1A). If, however, Al is added at a mole ratio of Al/Al + Fe = 0.09, Al substituted goethite is formed instead, with only trace amounts of maghemite and/or lepidocrocite (Figure 1B).

Doubling the aeration rate in the Al-free system (5 ml air min^{-1}) gave predominantly lepidocrocite (Figure

1C), which was again replaced by goethite and only minor amounts of lepidocrocite on addition of Al at the same mole ratio 0.09 (Figure 1D). These small amounts of lepidocrocite which still formed are generally very poorly crystalline indicated by broad X-ray diffraction peaks where the major (020) reflection is often weaker than the (120).

At higher Al concentrations (Al/Al + Fe = 0.29) and

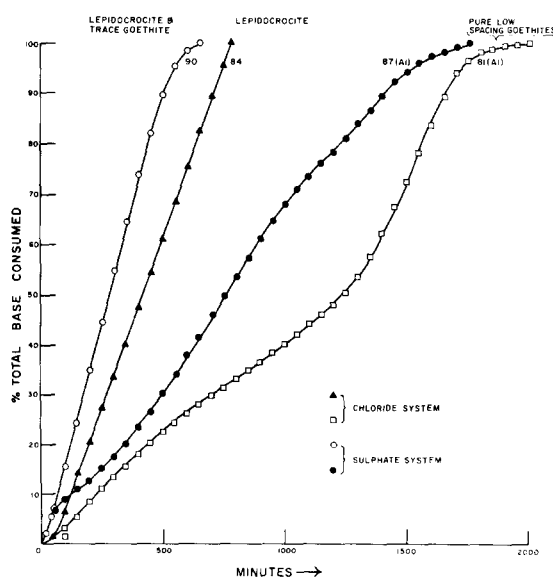


Fig. 3. Base consumption - time curves for Fe(II) chloride and sulfate solutions oxidized at pH 5.5 in the presence and absence of added Al (Al/Al + Fe = 0.29).

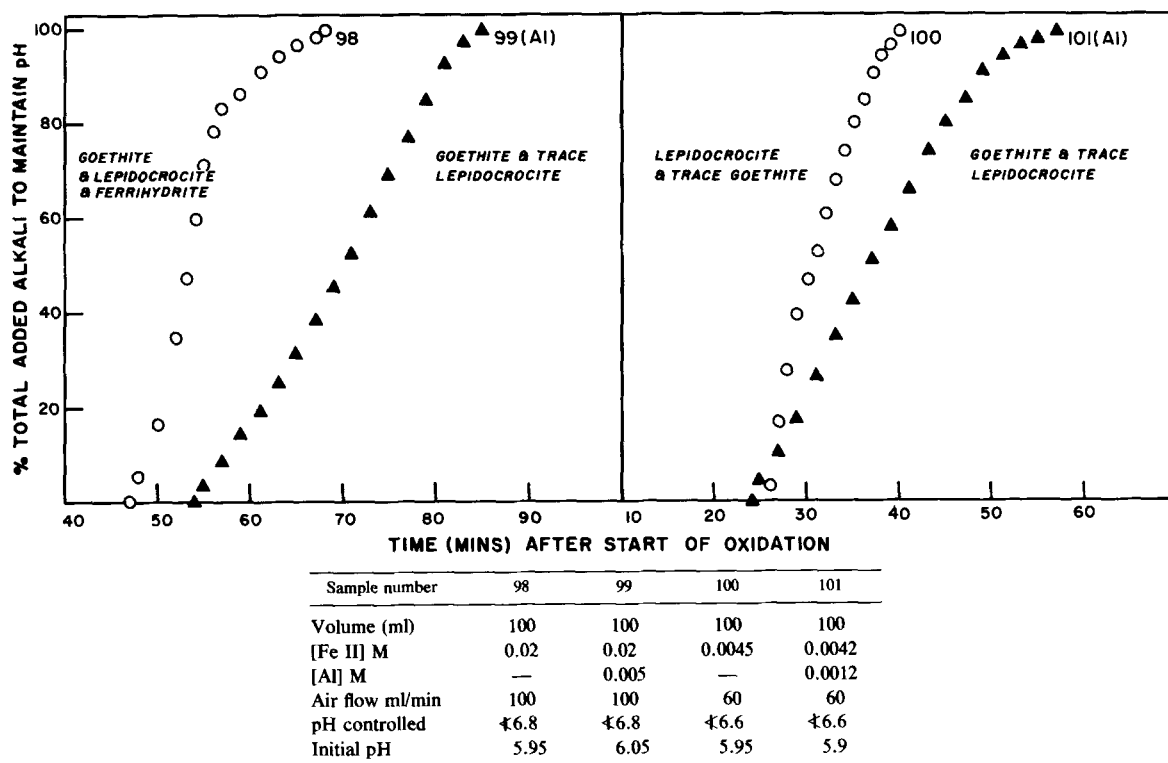


Fig. 4. Base consumption-time curves for Fe(II) carbonate solutions oxidized at pH 6.6 in the presence and absence of added Al (Al/Al + Fe \approx 0.2).

lower pH values, 5.5, the influence of Al was more marked as *only* Al substituted goethite was detected in the final product, irrespective of large changes in the rate of aeration (1.5–40 ml air/min), whereas lepidocrocite occurred either pure or as the dominant phase in the Al-free system.

At an even higher Al level (Al/Al + Fe \approx 0.55) crystallization was inhibited, and only very poorly crystalline goethite and ferrihydrite were formed. This ferrihydrite appeared to be an aluminous form as indicated from the formation of Al-hematite on refluxing (see also Part II). Details of these preparations are given in Table 1.

The base consumption-time curves as an indication

for the rate of oxidation show that at Al/Al + Fe = 0.09 the reaction time compared to a pure Fe(II) solution is not changed by Al (Figure 2B), but was nearly doubled in a Fe(II), (III) solution (Figure 2A). At pH 5.5, however, where the oxidation is generally much slower, Al at an Al/Al + Fe = 0.29 almost tripled the reaction time in respect to the Al-free pure Fe(II) solution (Figure 3). Figure 5C shows the very small crystals of Al-goethite resulting from addition of Al (Al/Al + Fe = 0.29) to an Fe(II) system which, in the absence of Al, gave well crystalline lepidocrocite (Figure 5A). The goethites prepared in the presence of Al under these conditions lack the marked acicular morphology commonly exhibited by goethites prepared under

Table 1. Oxidation products of Fe(II) chloride solutions and the effects of added aluminum.

Sample	Fe(II) conc. (molar)	Added Al Al/Al + Fe (molar ratio)	Total initial vol ml	pH controlled at	Air flow ml/min	Products	Al in final mole %
63	0.064	0.33	75	6.5	2.5	G + trace L	23.5
84	0.032	—	150	5.5	1.5	well crystalline L	—
81	0.032	0.29	150	5.5	1.5	G	11.4
86	0.032	—	150	5.5	40	L + trace M	—
92	0.032	0.29	150	5.5	40	fine grained G	12.8
82	0.032	0.55	150	5.5	1.5	F + little G \rightarrow G + H refluxing	—

G = goethite; L = lepidocrocite; F = ferrihydrite; H = hematite; M = maghemite.

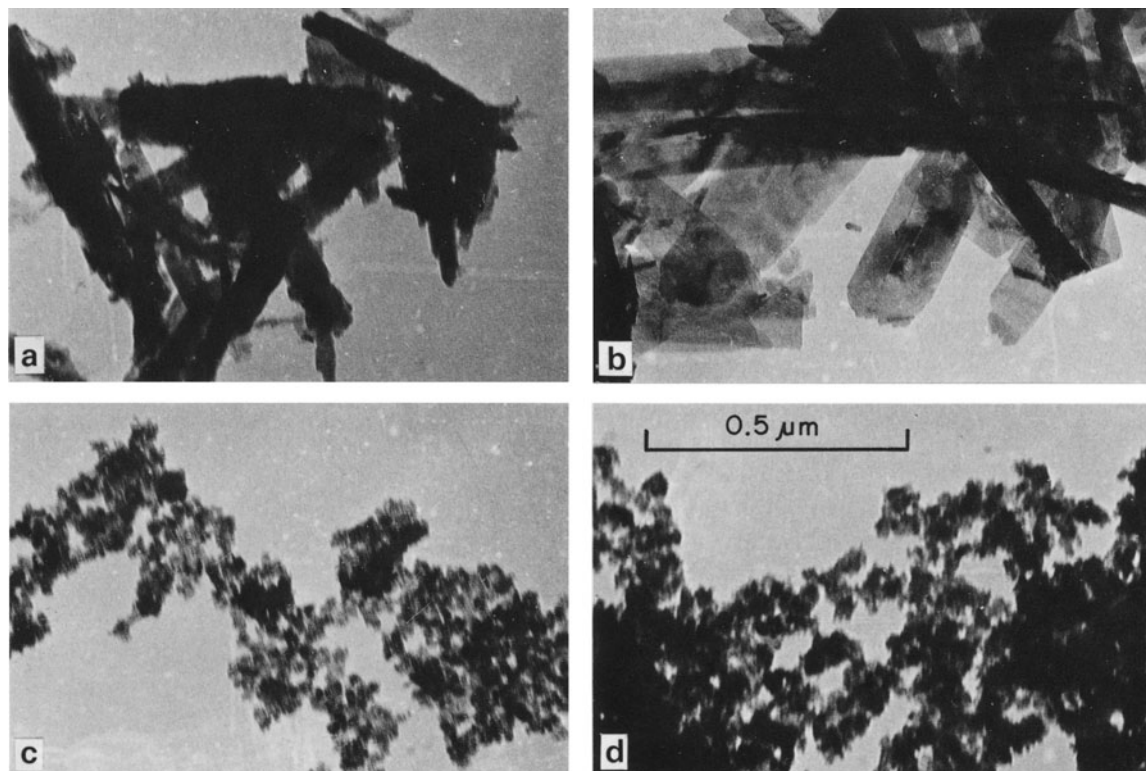


Fig. 5. Electron micrographs of lepidocrocite formed from the oxidation at pH 5.5 of Fe(II) chloride (A) and sulfate (B) solutions and the Al-substituted goethites formed instead from the chloride (C) and sulfate (D) system in the presence of Al (Al/Al + Fe = 0.29).

strongly alkaline conditions. On the other hand, they are very similar to Al-goethites extracted from soils, an example of which is shown in Figure 7 (see also Schwertmann and Taylor, 1977).

Sulfate system

The products formed during the oxidation of Fe(II) sulfate solutions were similar to those produced from the chloride system. Lepidocrocite generally dominated the Al-free systems under the oxidation conditions used. Addition of Al again caused goethite rather than lepidocrocite and Figure 1E and 1F show the change in the X-ray powder diffraction pattern caused by the addition of Al (Al/Al + Fe = 0.09) to a solution oxidized at pH 7 (See also Figure 2C). Oxidation of the pure sys-

tem at pH 5.5 with 1.5 ml air min⁻¹ gave lepidocrocite with trace amounts of goethite and maghemite. Addition of Al (Al/Al + Fe = 0.29) caused only well crystalline Al substituted goethite to form. Details of these experiments are given in Table 2.

Again, similar to the chloride system, the base consumption-time curves were not affected by the presence of Al at pH 7 and an Al addition of Al/Al + Fe = 0.09 (Figure 2C), whereas at the higher Al addition (Al/Al + Fe = 0.29) at pH 5.5 its presence again almost tripled the reaction time (Figure 3).

The lepidocrocites still present in the Al system oxidized at pH 7 (Figure 2C) had their crystallinity reduced and their X-ray diffraction patterns again showed weak (020) reflections. Electron micrographs of the

Table 2. Oxidation products of Fe(II) sulfate solutions and the effects of added aluminum.

Sample	Fe(II) conc. (molar)	Added Al Al/Al + Fe (mole ratio)	Total initial vol ml	pH controlled at	Air flow ml/min	Products	Al in final product mole %
65	0.064	0.33	75	7	2.5	G	14.0
78	0.032	0.29	150	6	2.5	G + trace L	9.8
85	0.032	—	150	5.5	1.5	L + trace G + M	—
90	0.032	—	150	5.5	1.5	L + trace G + M	—
87	0.032	0.29	150	5.5	1.5	well crystalline G	11.6

G = goethite; L = lepidocrocite; M = maghemite.

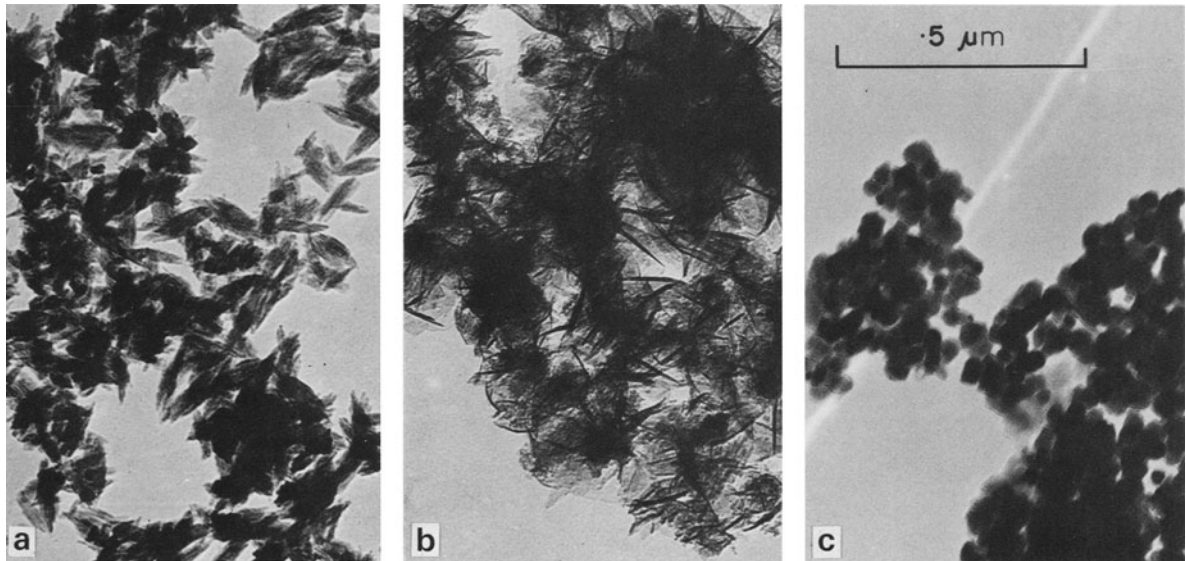


Fig. 6. Electron micrographs of iron oxides formed from oxidation of Fe(II) carbonate solutions. (A) Goethite from oxidation of 100 ml 0.019 M Fe(II) carbonate with 60 ml air/min pH 6.8–7.2, 20°C (sample 34); (B) lepidocrocite from oxidation of 125 ml 0.005 M Fe(II) carbonate with 100 ml air/min pH 6.8–7.0, 20°C (sample 37); (C) hematite from refluxing for 16 hr in distilled water ferrihydrite formed from oxidation of 100 ml 0.02 M Fe(II) carbonate with 100 ml air/min and fast stirring, pH 7, 20°C (sample 97).

products formed at pH 5.5 show the transition from very well crystalline lepidocrocite in the Al-free system (Figure 5B), to very small nonacicular particles of Al-goethite (Figure 5D), when Al is added. These resemble the Al-goethite from the chloride system (Figure 5C), and the natural Al-goethite (Figure 7).

Carbonate system

The carbonate system behaved rather differently. The initial pH of the Fe(II) solutions was between 5.9

and 6.4. Whereas oxidation in the chloride and sulfate system caused an immediate fall in pH as oxidation and hydrolysis occurred, the carbonate system generally showed an initial rise in pH due to the expulsion of CO₂, and then remained constant or dropped slightly depending on the initial Fe(II) concentration and aeration rate. As seen from the following equation the system is strongly buffered:



Table 3. Oxidation products of Fe(II) carbonate solutions and the effects of added aluminum.

Sample	Fe(II) conc. (molar)	Added Al Al/Al + Fe mole ratio	Total initial vol ml	pH controlled at	Oxidation commenced at pH	Air flow ml/min	Products	Al in final product mole %
34	0.019	—	100	6.8–7.2	6.4	60	G	
37	0.005	—	125	6.8–7	6.4	100	L	
40	0.028	—	100	≧6	6.4	5	G	—
73	0.021	0.125	200	≧6	6.4	5	G	5.4
93	0.020	0.2	100	≧6	6.2	100	G & F	
94	0.017	—	100	≧6	6.3	100	G & L	
96	0.005	0.7	100	≧6	6	1.5	F	
95	0.005	—	100	≧6	6	1.5	very fine grained G & L	
98	0.02	—	100	≧6.8	6.1	100	L & G & F	
99	0.02	0.19	100	≧6.8	6.2	100	G & trace L	5.6
97	0.02	—	100	≧7	7	100+ fast stirring	F → H on refluxing	—
101	0.0042	0.22	100	≧6.6	5.9	60	G & F	ND
100	0.0045	—	100	≧6.6	5.9	60	L & trace G → trace L + increased G on refluxing	—
103	0.02	0.15	100	5.7	6.1	1.5	G + trace L	6.4
76	0.028	0.31	100	≧6	6.1	5	G + trace L	8.4
67	0.017	0.42	115	≧6	6.0	10	F	ND

L = lepidocrocite; G = goethite; F = ferrihydrite; H = hematite.

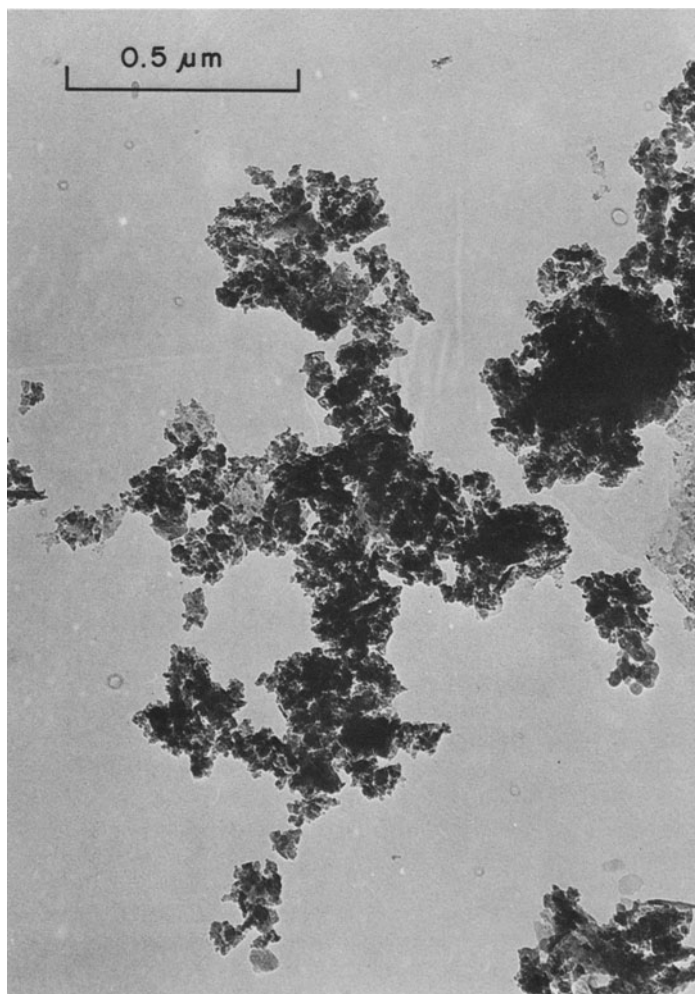


Fig. 7. Electron micrograph of an Al-substituted goethite ($H\ 165/10 < 2\ \mu m$; see Norrish and Taylor, 1961), extracted from a soil.

Another difference lies in the end product. Goethite was formed already *without Al addition* particularly at low rates of aeration and/or higher Fe(II) concentrations whereas lepidocrocite is favored at higher aeration rates and/or lower Fe(II) concentrations. At a very high aeration rate and a higher pH (7.0) only ferrihydrite was formed. Details of these syntheses in the carbonate system are given in Table 3. Electron micrographs of the three end products formed by variations in these parameters are shown in Figure 6. These results are in accordance with experiments (Schwertmann, 1959; Schwertmann and Fitzpatrick, 1977) which showed that the carbonate anion favors goethite production. The faster the aeration and the lower the initial carbonate concentration the faster would the CO_2 be expelled from the system and the influence of carbonate to favor goethite is reduced. Maghemite was also suppressed in the carbonate system under conditions which would have caused its formation in the chloride system.

As in the chloride and sulfate system, Al ($Al/Al + Fe \approx 0.2$) again caused lepidocrocite to be replaced by goethite (Table 3, samples 98 and 99; 100 and 101) and a significant increase in the reaction time (Figure 4). Goethite formed from a carbonate system in the absence of Al displayed the typical acicular morphology (Figure 8A) which was not evident in the much smaller particles formed when Al was present (Figure 8B). At much higher Al additions ($Al/Al + Fe = 0.42$) only ferrihydrite was formed (Figure 8C).

General discussion

The results in the three anionic systems suggest that minor amounts of Al favor the formation of the α -oxides under conditions that, in the absence of Al, lead predominantly to production of the γ -forms. Also at higher concentrations it will lead to ferrihydrite formation.

The Al-substituted goethites produced in the three different anionic systems ranged from 5.4–23.5 mole

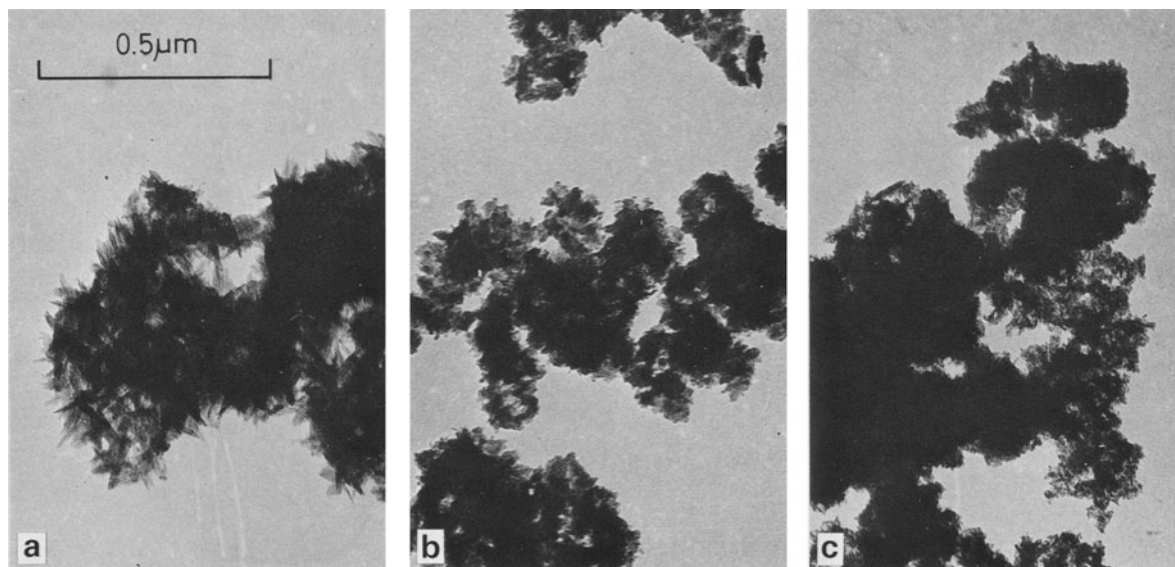


Fig. 8. Electron micrographs of iron oxides formed from oxidation of Fe(II) carbonate solutions, showing effects of added Al. (A) Goethite from oxidation of 100 ml 0.028 M Fe(II) carbonate with 5 ml air/min, pH 6; (B) goethite from oxidation 200 ml 0.02 M Fe(II) carbonate plus Al (Al/Al + Fe = 0.125) with 5 ml air/min, pH 6; (C) ferrihydrite from oxidation of 115 ml 0.017 M Fe(II) carbonate and Al (Al/Al + Fe = 0.42) with 10 ml air/min, pH 6.

% Al substitution and showed reduction in cell volumes and lattice parameters with increasing substitution (Figure 9). The existence of Al-substituted goethites in ooids (Correns and Engelhardt, 1942) and its common occurrence in soils (Norrish and Taylor, 1961) may be due not only to the abundance of Al in almost every soil, but also to the fact that in the presence of Al, goethite is strongly favored if formed from the oxidation of Fe(II). Additionally, the presence of carbonate anions also favors goethite rather than lepidocrocite whose less frequent occurrence is reasonable in view of the limited range of conditions under which it can occur. The general conclusion that, in the oxidation of mobile Fe(II), the presence of Al promotes goethite rather than lepidocrocite or maghemite is strongly supported by observations on natural samples. Taylor and Schwertmann (1974b) in an examination of ferruginous concretions from a variety of Australian soils, observed that the magnetic samples containing maghemite (commonly in association with hematite) generally contained much lower amounts of layer lattice silicate clay minerals (sources of Al) than morphologically similar nonmagnetic concretions with which they were associated. In other concretions from red and grey earth horizons† from soils in Queensland, Australia, a similar result was obtained, where the magnetic samples contained maghemite with either no kaolin or much less

than occurred in the morphologically similar nonmagnetic samples from the same horizon.

De Villiers and van Rooyen (1967) synthesized lepidocrocite in the presence of Al using a technique that is far removed from soil conditions. They obtained lepidocrocites with reduced peak intensities but no observable shifts in the X-ray diffraction spacings. From the present work it is acknowledged that any lepidocrocite associated in small amounts with goethite in the Al system had their diagnostic (020) X-ray diffraction reflection reduced in intensity, so that diluted in a soil, any such poorly crystalline lepidocrocite may not be detected by diffraction. Because of the development of magnetism in B horizon material from South African soils on heating, they suggested that lepidocrocite with an amorphous character may be present in these soils. However, because of the depression by Al, of lepidocrocite in favor of goethite and the ability of either goethite or ferrihydrite to transform to maghemite on heating in the presence of organic matter (Schwertmann, 1959), the observations of de Villiers and van Rooyen could equally well be interpreted as indicating goethite below the limits of detection, or ferrihydrite, which generally can not be detected in soils by X-ray techniques (Schwertmann and Taylor, 1977). This is not meant to deny that Al lepidocrocites can form. Certain synthesis techniques may utilize conditions that override the inhibiting influence of Al which was found only under the conditions used in these experiments.

The reasons why goethite is preferred over lepidocrocite in an Al-containing Fe(II) system are not clear

† R. M. Taylor and R. A. Coventry, CSIRO Division of Soils, Glen Osmond, South Australia, unpublished data.

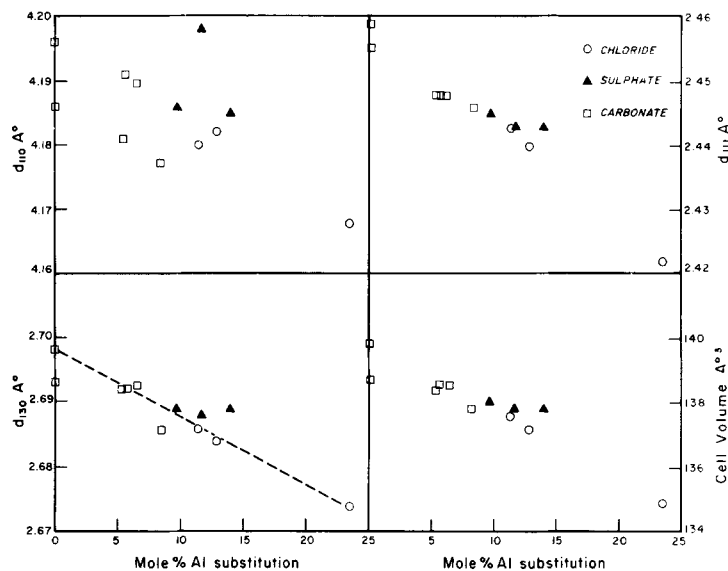
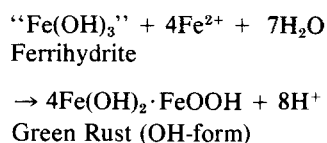


Fig. 9. Variation in X-ray diffraction spacings and cell volume with Al substitution.

yet. If the suggestion is correct that goethite although thermodynamically more stable than lepidocrocite is however kinetically disfavored, then any factor which in an Fe(II) system slows down the formation of Fe(III) species will favor goethite. The observation that the rate of base consumption during oxidation (which reflects the oxidation rate) is reduced in the presence of Al supports this hypothesis. The idea that goethite is favored through the slowing down of the rate of oxidation due to the presence of Al has also been proposed by Stauffer and Lovell (1968) in an investigation into the oxidation of Fe(II) in relation to coal mine drainage. They also noted that Al depressed the formation of ferromagnetic material.

The conclusions of Detournay et al. (1975) that the presence of divalent Co and Mn also caused goethite rather than lepidocrocite formation from Fe(II) systems by slowing down the oxidation rate further supports the observations on the effect of Al in this present work.

The manner in which Al retards oxidation is not clear but appears to be related to the intermediate precursor stages which form during oxidation of the Fe(II) solutions at pH 5.5–8, i.e., the so-called "Green Rust" (Bernal et al., 1959). This compound originates from a reaction of ferrihydrite formed from the oxidized iron with the still unoxidized Fe^{2+} ions in solution (Feitknecht and Keller, 1950; Feitknecht, pers. comm.):



Further oxidation of the Green Rust lead to lepidocrocite or maghemite depending on the conditions (Ber-

nal et al., 1959; Taylor and Schwertmann, 1974a; Schwertmann and Thalmann, 1976). In the present experiments at pH 7 a dark green phase was observed regardless of whether or not Al was present. If present, Al is precipitated with the Fe(III) ions as an Al-ferrhydrite from which an Al-substituted Green Rust can then form. In a system with only traces of Fe(III) Al might almost completely occupy the Fe(III) position in the Green Rust. This was suggested in an experiment[‡] carried out under N_2 saturation in which precipitated Al(OH)_3 caused added Fe(II) to be precipitated and hydrolyzed at pH 6–7, i.e., at a much lower pH than in the absence of Al(OH)_3 . The resulting Green Rust gave lower X-ray powder diffraction spacings, indicative of Al substitution and appeared to be much more resistant to oxidation both in air and under water, than the Al-free material. Such a material could lead to a slower production of Fe(III) through dissolution and oxidation, and would therefore tend to favor goethite rather than lepidocrocite.

An analogous example in which Al favors a certain iron oxide through its influence on the kinetics is given in Part II of this series. Here the ferrihydrite is stabilized by incorporation of Al and thereby hematite is favored against goethite because the hematite forms from the ferrihydrite aggregate (Fischer and Schwertmann, 1975) whereas goethite formation requires the dissolution of ferrihydrite and this appears to be slowed down by Al incorporation.

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[‡] To be reported elsewhere by Taylor, Schwertmann et al.

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Резюме— Исследовалось влияние алюминия на продукты, образующиеся при воздушном окислении Fe(II) хлоридного, сульфатного и карбонатного растворов при pH 5,5–7, 20°C. Во всех случаях на уровнях Al/Al+Fe=0,09–0,30 алюминий препятствовал образованию γ фаз (леpidокрокит и маггемит), способствуя образованию гетита, в таких условиях, когда при отсутствии Al, формируются эти γ фазы. Это влияние Al, обнаруженное в лабораторных условиях, было подтверждено полевыми наблюдениями.

На более высоких уровнях Al образовывался гидрит окиси железа. Было замечено, что такое воздействие Al является следствием замедления гидролизно-окислительного процесса в системе Fe(II).

Присутствие Al не только изменяло направление образования минералов, но также вызывало образование гетита с замещенным Al, который напоминал по размерам частиц и морфологии натуральный алюминий-железистый гетит, экстрагированный из почвы.

Kurzreferat— Der Einfluß von Al auf die Produkte, welche durch Luftoxydation von Fe(II) Chlorid-, Sulfat- und Karbonatlösungen bei pH 5,5–7 und 20°C formen, wurden untersucht. Bei Al/Al+Fe Werten von 0,09–0,30 verhindert Al in jedem Fall die Bildung von γ Phasen (Lepidokrokite und Maghemite) zu Gunsten von Goëthitbildung, unter Bedingungen, bei denen in Abwesenheit von Al diese γ Phasen normalerweise formen. Der Einfluß von Al, der in diesen Laboratoriumsuntersuchungen gesehen wurde, konnte in Feldbeobachtungen bestätigt werden. Bei höheren Al Werten wurde Ferrihydritbildung begünstigt. Dieser Effekt des Al wurde als Resultat einer Verlangsamung in der Hydrolyse/Oxydationsgeschwindigkeit des Fe(II) Systems angesehen. Die Anwesenheit von Al ändert nicht nur die Richtung der Mineralbildung sondern bewirkt auch die Formation von Al-substituierten Goëthiten, welche in Teilchengröße und Morphologie den natürlichen Aluminiumferro-Goëthiten ähnlich sind, die aus Erde extrahiert werden können.

Résumé-L'influence de l'Al sur les produits formés par l'oxidation à l'air de chlorure de Fe(II), de solutions de sulphate et de carbonate à un pH de 5.5-7, et à 20°C, a été examinée. Dans tous les cas, aux niveaux $Al/Al+Fe=0.09-0.03$, l'Al a réprimé la formation des phases γ (lepidocrocite et maghemite) en faveur de goethite sous des conditions sous lesquelles ces phases γ auraient été formées en l'absence d'Al. L'observation au laboratoire de cette influence de l'Al est soutenue par des observations sur le terrain.

A des niveaux plus élevés d'Al, la formation de ferrihydrite était favorisée. Cet effet de l'Al est considéré comme étant le résultat d'un ralentissement de l'allure du rapport hydrolyse/oxidation du système Fe(II).

La présence d'Al a non seulement changé la direction de la formation du minéral, mais a aussi causé la formation de goethites substitués à l'Al qui ressemblaient au point de vue de la morphologie et de la taille des particules à la goethite naturellement aluminifère extraite d'un sol.