

THE INFLUENCE OF ALUMINUM ON IRON OXIDES. VII. SUBSTITUTION OF Al FOR Fe IN SYNTHETIC LEPIDOCROCITE

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Abstract—The presence of Al hydroxy species in solution during the synthesis of lepidocrocite had been previously found to influence the reaction towards goethite formation. However, under certain conditions, which are not unrealistic in terms of the natural soil environment, this influence does not occur, and Al appears to substitute for Fe(III) in the lepidocrocite structure. This substitution causes the unit-cell dimensions to decrease along the "a" direction and to increase along the "b." From the differential line broadening of X-ray powder diffraction peaks, the incorporation of Al was found to inhibit crystal growth preferentially in the b-axis direction, the hkl peaks being more broadened the higher the value of k relative to h and l. Al-substituted lepidocrocites have been suggested to occur in soils, and although they can be synthesized under conditions approaching those expected in soils, it is considered that their formation in nature is unlikely or restricted to unusual environments.

Key Words—Aluminum, Goethite, Iron, Lepidocrocite, Substitution, Synthesis.

INTRODUCTION

The similarity of ionic radii leads to frequent substitution of octahedrally coordinated Fe(III) by Al(III) in soil goethites and hematites. However, the incorporation of Al in natural lepidocrocites has not been definitely established, although it could be expected because of the similar coordination of the Fe(III). De Villiers and van Rooyen (1967) presented indirect evidence for the existence of aluminous lepidocrocite in soils. This mineral was not detected by X-ray diffraction, probably due to the limited crystal development and the consequent reduction in diffracted intensities resulting from Al incorporation, an effect they demonstrated in synthetic samples. Aluminum substitution was inferred on the basis of the higher temperatures required for dehydration to maghemite, a behavior also exhibited by their Al substituted synthetic lepidocrocites. Moreover, the resultant maghemites from their heated soil sample and synthetic material required higher temperatures for their transformation to hematite, an observation consistent with Al incorporation. However, both normal (van der Marel, 1951) and Al-substituted goethite (unpublished data by RMT) will transform to maghemite when heated in the presence of organic materials, e.g., humic acids, and this possibility was not apparently considered by these two workers.

Direct evidence of Al substitution for Fe in the crystal lattice can come from a change in the lattice param-

eters analogous to the observations on goethite (Correns and Engelhardt, 1941; Norrish and Taylor, 1961) and hematite (von Steinwehr, 1967; Schwertmann *et al.*, 1979), or from dissolution treatments that are specific only for lepidocrocite. The following work presents direct evidence for Al substitution in lepidocrocite synthesized under various conditions.

EXPERIMENTAL TECHNIQUES

Aluminous lepidocrocites were synthesized by two techniques. In the first technique (sample 79/13), 0.48 mmole of washed, freshly precipitated $\text{Al}(\text{OH})_3$ ¹ was added as a suspension to 200 ml of 0.006 M FeCO_3 solution saturated with CO_2 . Nitrogen was passed into the solution at the rate of 150 ml/min for 10 min, progressively expelling CO_2 and thus causing the pH to rise from the initial value of 5.5 to 7.2. The N_2 flow was then replaced by 100 ml/min of air while the suspension was constantly stirred. The pH was not controlled and gradually fell to and remained at 5.6. The yellow-brown precipitate was centrifuged, washed, and dried from acetone at 80°C. The second technique (samples 78/121A, 79/18, and 79/24) involved the oxidation under water of a dark-green, metastable member of the pyroaurite group, an Fe(II)Al hydroxy-chloride, which is isostructural with Fe(II)Fe(III) hydroxy-chloride, the

¹ The $\text{Al}(\text{OH})_3$ was prepared by titrating 0.48 mmole AlCl_3 in 20 ml H_2O to pH 7 with 2.3 M NaOH.

Table 1. Conditions for formation of Fe(II)Al(III) hydroxy-chloride and its subsequent oxidation to lepidocrocite.

Sample	Formation ¹		Oxidation	
	Al added (mmole)	Initial [Fe ²⁺] (molar)	Method	pH
78/121A	0.72	0.14	5 ml air/min into solution + stirring	7
79/18	0.72	0.31	5 ml air/min into solution + stirring	7
79/24	0.24	0.22	Stirring in contact with air	7 for 2 hr then 9.5 for 1 hr

¹ Initial total volume = 50 ml.

“green rust I” phase described by Bernal *et al.* (1959). This phase is produced by the induced hydrolysis at pH 7 under N₂ of an FeCl₂ solution by the addition of a N₂-saturated suspension of AlCl₃ previously adjusted to pH 7. During hydrolysis under N₂, the pH was maintained by the addition of 2.3 M NaOH by an automatic titrimeter (Taylor and MacKenzie, 1980). The varying conditions of formation of these intermediate phases and for their subsequent oxidation are given in Table 1. The final oxidized products were centrifuged, washed, and dried from acetone at 80°C. Two non-substituted lepidocrocites with varying degrees of crystallinity were used for comparison. Sample P23 was prepared by bubbling oxygen through a 0.15 M FeCl₂ solution at pH 7, and sample RMT 152 was prepared by the oxidation of 200 ml of a CO₂-saturated 0.0046 M Fe(II) carbonate solution by 100 ml air/min and fast stirring (Schwertmann and Taylor, 1979). Preliminary identification of the samples was made on X-ray powder diffraction (XRD) photographs (5.73-cm diameter camera, CoK α radiation). Peak positions and diffraction line widths were obtained using step scanning techniques involving 100-sec counts at 0.05°2 θ intervals with a Philips PW1130 instrument equipped with a monochromator before the detector stage. Differential thermograms (DTA) were made on a Linseis instrument using 20–25-mg samples and hematite as the inert material at a heating rate of 10°C/min. Fe and Al analyses were carried out after dissolution in HCl or acid ammonium oxalate (Schwertmann, 1964) by atomic ab-

sorption techniques. Infrared (IR) spectrograms were run on 0.3% KBr disks on a Beckman IR 20 instrument.

RESULTS AND DISCUSSION

All lepidocrocites prepared in the presence of Al gave XRD peaks which were broadened, presumably due to small particle size. The degree of line broadening varied for different reflections (Table 2). This differential broadening is indicative of reduced crystallite development in particular crystal-axis directions. The diagnostic (020) basal reflection was either not discernible, or possessed a much lower intensity than the normally less intense (120) reflection. For the samples prepared from the aqueous oxidation of Fe(II)Al(III) hydroxy-chloride compounds, the lowest rates of oxidation (sample 79/24) gave the relatively best crystallized lepidocrocite. The poor crystallinity of the samples is also indicated by their high degree of solubility in acid ammonium oxalate in the absence of light (Fe_{0/I}, Table 3). Differential line broadening of the various XRD peaks and reduced intensities of the (020) reflections were reported by Schwertmann and Taylor (1979) for nonsubstituted, synthetic (e.g., sample RMT 152) and natural lepidocrocite samples. Their results demonstrated that rapid oxidation during synthesis hindered crystal development, causing differential line broadening in the XRD pattern. The main inhibition of crystal growth was in the b-axis direction, resulting in very broad (020) peaks with markedly reduced intensities. These reflections were, however, shifted to lower 2 θ values, cor-

Table 2. Spacings and widths of X-ray powder diffraction peaks of Al-substituted and other synthetic lepidocrocites.

Sample	Al in system	d(020) (Å)	WHH ¹ (°2 θ)	d(120) (Å)	WHH ¹ (°2 θ)	d(031) (Å)	WHH ¹ (°2 θ)	d(131,060) (Å)	WHH ¹ (°2 θ)	d(051,200) (Å)	WHH ¹ (°2 θ)	d(231) (Å)	WHH ¹ (°2 θ)
79/24	+	6.338	1.45	3.294	0.92	2.466	1.15	2.081	1.05	1.932	0.80	1.520	1.75
79/13	+	6.822	4.1	3.295	2.65	2.478 ²	3.45	—	—	1.929	0.95	1.524 ²	—
79/18	+	6.448	3.2	3.289	1.58	2.460	2.10	—	—	1.926	1.09	1.517	1.475
78/121A	+	—	—	3.282	2.5	2.485	3.17	—	—	1.924	1.27	1.515 ²	—
RMT 152	—	6.7	≈4.5	—	2.5	—	3.6	—	—	1.937	1.09	—	—
P 23	—	6.281	0.39	3.297	0.50	2.475	0.50	2.089	0.55	1.940	0.63	1.530	1.10

¹ Width at half height.

² Measurement possibly influenced by trace amounts of ferrihydrite.

Table 3. Effect of Al substitution on some properties of synthetic lepidocrocites.

Sample	Al in system	% composition of end product ¹					d(200) (Å)	DTA ² (°C)	I.R. ³
		Fe _t	Fe _o	Fe _{o,t}	Al _t	Al (mole %)			
79/24	+	47.7	39.7	75.	3.08	11.8	1.931	293	0.28
79/13	+	35.6	n.d.	n.d.	6.04	25.0	1.929	n.d.	n.d.
79/18	+	43.8	44.4	100.	3.79	15.2	1.926	322	0.19
78 121/A	+	44.7	45.1	100.	4.64	18.0	1.924	284	0.12
RMT 152	-	52.1	50.3	96.	0	0	1.937	251	0.16
P 23	-	58.2	23.4	40.	0	0	1.940	268	0.73

¹ t = total, o = oxalate soluble, n.d. = not determined. The fact that the preparative conditions for the formation of the hydroxy chloride had lower mole percent Al content than the final oxidized products is due to not all of the Fe(II) in solution hydrolyzing and precipitating due to the presence of Al. (See Taylor and McKenzie, 1980.)

² Temperature of dehydroxylation peak.

³ Absorbance at 1020 cm⁻¹ per mg of Fe.

responding to an increase in the b-axis dimension of the unit cell. As seen from electron micrographs, the individual crystals were elongated laths. These were 2–10 unit layers thick in the direction perpendicular to the plates (b-axis). Because of the limited development in this direction, the hkl peaks were more broadened, the higher the value of k relative to h and l. Because the (200,051) reflection was generally the least broadened in the diffraction pattern of these poorly crystalline lepidocrocites, the (200) reflection may well be the major component of this peak, and the a-axis direction may be along the elongated lath.

In addition to the differential line broadening and reduced (020) intensity, samples produced in the presence of Al (present study) gave lower d(200) values, indicative of a contraction of the unit cell in the a-axis direction. This contraction is consistent with the substitution of the smaller Al(III) cation for Fe(III), but was not observed for the nonsubstituted lepidocrocites reported by Schwertmann and Taylor (1979). For example, sample RMT 152, produced in the absence of Al, exhibits marked line broadening, but shows no significant shift to lower values for the (200) reflection (Table 2.) The d(200) values measured on the three samples produced from the oxidation of Fe(II)Al(III) hydroxy-chloride compounds are negatively correlated with the mole percent Al given from the analyses of the HCl-dissolution extracts (Figure 1). Moreover, these values lie close to the theoretical relationship derived assuming a linear decrease in d(200) with Al content between the two isostructural end members, lepidocrocite and boehmite. These results suggest that the Al found by analyses was contained predominantly within the lepidocrocite structure, and that there is a progressive contraction in the a-axis of the unit cell with increasing Al incorporation. The three samples all give values above the theoretical lepidocrocite-boehmite relationship, i.e., they possess slightly higher d(200) values than would be expected from their measured Al contents. These increased values could possibly arise

from a slight bias towards lower 2θ values, due to the coincident (051) reflection being influenced by the observed increase in the b-axis dimensions (Table 2). However, because the influence of this peak is considered to be negligible (as discussed above), the departure from the theoretical relationship between d(200) and mole percent Al incorporation may be real and analogous to the similar variations observed for hematites (von Steinwehr, 1967; Schwertmann *et al.*, 1979) and for goethites (Norrish and Taylor, 1961) with isomorphous substitution of Al for Fe.

Sample 79/13 shows a much greater departure from the theoretical relationship (Figure 1) probably due to unreacted Al(OH)₃ being present as an impurity in the final solid phase. This sample was prepared by adding excess Al(OH)₃ (0.48 mmole) to 1.2 mmole of Fe(II) carbonate solution, and any alkali extraction of the unreacted solid Al(OH)₃ may have altered or dissolved the poorly crystalline lepidocrocite phase.

Al incorporation caused no measurable shift of the

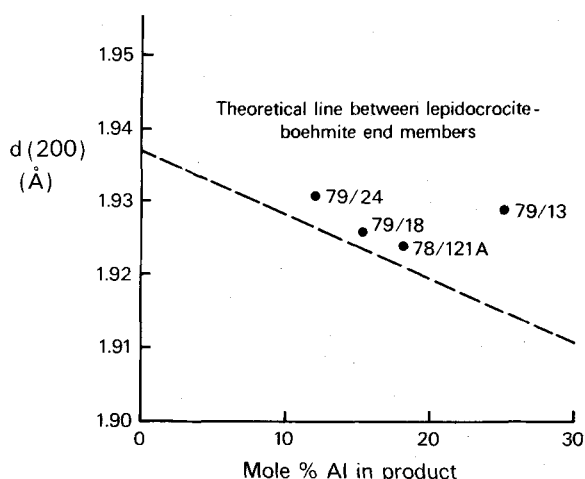


Figure 1. Relationship between d(200) X-ray powder diffraction spacing and mole percent Al in lepidocrocite samples.

Fe–OH mode at 1020 cm^{-1} in the IR spectrograms. This band is generally broad, and its intensity decreases with decreasing crystallinity (Table 3) as observed elsewhere by Schwertmann and Taylor (1979). After heating the Al substituted samples for 1 hr at 200°C , the peak at 1020 cm^{-1} did not alter, whereas it disappeared on similar treatment of pure lepidocrocite.

This higher thermal stability of Al-substituted lepidocrocite is also indicated by the higher temperatures of the DTA dehydroxylation peaks (Table 3) than are observed for pure lepidocrocites. However, a correlation between peak temperatures and the estimated degree of Al substitution was not observed. Higher thermal stability for synthetic Al-substituted lepidocrocite was also observed by de Villiers and van Rooyen (1967).

Although fast oxidation of an Fe(II) solution during synthesis (Schwertmann and Taylor, 1979), and Al incorporation within the crystal lattice (present study, Table 2), both impeded crystal development, there was a definite increase in the b-axis dimension in these poorly crystallized samples. This axis is in the direction of OH bonding between the double chains of octahedra. By analogy there appears to be a similar behavior in the poorly crystallized goethites produced by Al incorporation. From the $d(hkl)$ values of the synthetic aluminous goethites of Thiel (1963), the cell parameters can be calculated. Whereas the b- and c-axis dimensions show a marked linear dependence on the degree of Al substitution, there is a wide scattering, and even increased values for the a-axis. It is interesting that in these related compounds the possible departure from the Vegard rule is again essentially in the direction of OH bonding.

Possible occurrence in soils

De Villiers and van Rooyen (1967) suggested that Al-substituted lepidocrocites might be present in some Natal soils they examined. Their evidence was based on the similar magnetic behavior of the samples after heating to that of some Al-substituted lepidocrocite samples produced under conditions that could not be expected in nature. However, no positive identification of lepidocrocite could be made on the original soil material. In a study of lepidocrocite in numerous soils of Natal, Schwertmann and Fitzpatrick (1977) found that the mineral was generally well crystallized, and no shift in the $d(200)$ spacing, indicative of a contraction in the a-axis of the unit cell due to Al substitution, was observed. If an Al-substituted lepidocrocite was present in sufficient quantities in a soil, even though it would possess small crystallite size, there should be an observable detectable shift in the $d(200)$ spacing which, in the poorly crystalline samples, shows the least line broadening.

In its common association with goethite in soils, lep-

idocrocite is generally the more crystallized phase (Schwertmann and Fitzpatrick, 1977). This, together with the observation that Al incorporation tends to restrict the crystal development of lepidocrocite, and the fact that under conditions expected in soils the presence of Al inhibits lepidocrocite formation in favor of goethite (Taylor and Schwertmann, 1978), suggest that, at least in such associations of the two phases, Al substitution in lepidocrocite is unlikely.

Although Al-substituted lepidocrocite was formed in this present study from reactants at pH values and temperatures that could be expected in soils (e.g., sample 79/13 formed from an Fe(II) carbonate solution), its formation in soils via this mechanism is regarded as improbable because of the very high rates of oxidation required. Aluminum-substituted lepidocrocites were formed at lower rates of oxidation in suspensions of Fe(II)Al(III) hydroxy-chloride (samples 78/121A, 79/18, and 79/24), but again this reaction path is considered unlikely in most soils. Taylor and McKenzie (1980) showed that the analogous hydroxy-sulfate on oxidation gave only trace amounts of lepidocrocite (in which Al substitution was not confirmed), whereas the more probable compound in hydromorphic soils, the hydroxycarbonate, did not transform at all to lepidocrocite. Although this family of compounds can form under pH and temperature conditions expected in soils, the high chloride content necessary for the formation of the hydroxy-chloride makes the occurrence of Al-substituted lepidocrocites via these compounds improbable. Moreover, in view of the established influence of Al to favor the formation of goethite under conditions that would normally lead to lepidocrocite (Taylor and Schwertmann, 1978), the presence of Al-substituted lepidocrocite in soils is considered unlikely.

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Резюме—Ранее было обнаружено, что присутствие в растворе гидроксильных видов Al во время синтеза лепидокрокита оказывает воздействие на реакцию, приводящее к образованию гетита. Однако, при определенных естественных условиях среды, в которых могут находиться почвы, этого не происходит, причем Al, по видимому, замещает Fe(III) в лепидокрокитовой структуре. Это замещение вызывает уменьшение размеров элементарных ячеек вдоль направления «а» и увеличение вдоль направления «b». По дифференциальному линейному расширению дифракционных пиков порошкового метода рентгеноструктурного анализа было обнаружено, что включение Al препятствует росту кристаллов особенно в направлении оси b, причем пики hkl расширяются тем больше, чем выше значение k по отношению к h и l. Предполагается, что лепидокрокиты с замещающим Al присутствуют в почвах, и, хотя их можно синтезировать при условиях близких к условиям предпологаемым в почвах, считается, что их образование в природе мало вероятно или наблюдается только в необычных условиях. [N.R.]

Resümee—Es wurde früher gezeigt, daß bei der Oxidation von Fe(II) bei Gegenwart von Al-hydroxy-Ionen in der Lösung statt Lepidokrokit Goethit gebildet wird. Unter bestimmten Bedingungen kann man jedoch die Goethitbildung verhindern. Dann wandert Al in das Lepidokrokitgitter ein und ersetzt dort Fe(III). Dieser Ersatz verursacht eine Verkleinerung der Elementarzelle des Lepidokrokits in der a-Richtung. Dagegen ist die Elementarzelle in der b-Richtung leicht vergrößert. Aus der differentiellen Verbreiterung der Röntgenlinien (die hkl-Linien sind umso breiter, je höher der Wert von k relativ zu h und l) wird geschlossen, daß diese Vergrößerung auf der sehr geringen Kristallgröße in b-Richtung beruht, die einen leicht vergrößerten Abstand der Elementarschichten zur Folge hat. Al scheint also das Kristallwachstum besonders in der b-Richtung zu behindern. Al-substituierte Lepidokrokite sind in Böden zwar vermutet, jedoch bisher nicht nachgewiesen worden. Aus den Synthese-Bedingungen ist zu schließen, daß ihr Auftreten auch nicht sehr wahrscheinlich ist.

Résumé—On avait auparavant trouvé que la présence d'espèce hydroxy Al en solution pendant la synthèse de lépidocrocite influençait la réaction vers la formation de goéthite. Sous certaines conditions qui ne sont pas irréalistes en termes d'un environnement de sol naturel, cependant, cette influence n'apparaît pas, et Al semble se substituer à Fe(III) dans la structure de lépidocrocite. Cette substitution est la cause d'un décroissement des dimensions de la maille dans la direction "a" et d'un accroissement dans la direction "b". On a trouvé à partir de l'élargissement de bande différentiel des sommets de diffraction poudrée aux rayons-X que l'incorporation d'Al inhibait la croissance de crystal préférentiellement dans la direction de l'axe b, les sommets hkl étant plus élargis à mesure que la valeur de k par rapport à h et l était plus élevée. On a suggéré que la substitution par Al dans des lépidocrocites se passe dans des sols, et malgré qu'elles peuvent être synthétisées sous des conditions se rapprochant de celles auxquelles on s'attendrait dans des sols, il est considéré que leur formation dans la nature est peu probable ou restreinte à des environnements inhabituels. [D.J.]