

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

UDO SCHWERTMANN¹ AND EMILIA WOLSKA²

¹ Lehrstuhl Für Bodenkunde, Technische Universität München
8050 Freising-Weihenstephan, Federal Republic of Germany

² Adam Mickiewicz Universität, Grunwaldska 6, 60780 Poznan, Poland

Abstract—Lepidocrocite samples, γ -FeOOH, containing 0–10 mole % Al-for-Fe substitution were synthesized at 15°C and pH 8 by oxidizing mixed FeCl₂-AlCl₃ solutions. The unit-cell parameters *a*, *b*, and *c* were measured from step-counted X-ray powder diffractograms using seven lines and Si as an internal standard. With increasing Al substitution from 0 to 10 mole % the unit-cell edge lengths *a*, *b*, and *c* decreased regularly by 0.3, 0.8, and 0.6%, respectively. Furthermore, the crystals became smaller, but gained in thermal stability. Decrease in crystal size parallel to the *y* axis led to a significant increase of the OH-stretch vibration and a decrease of the out-of-plane OH-bending vibration due to a weakening of the hydrogen bond between the zig-zag layers in the structure.

Key Words—Aluminum, Infrared spectroscopy, Iron, Lepidocrocite, X-ray powder diffraction.

INTRODUCTION

Taylor and Schwertmann (1980) reported a shift of *d*(120), *d*(200), and *d*(231) to lower values for lepidocrocite samples synthesized at ambient temperature and pH 7 by oxidation of FeCl₂-AlCl₃ mixed solutions. These changes were interpreted as due to a decrease in the unit-cell size caused by some Al-for-Fe substitution in the lepidocrocite structure. The relation between *d*(200) and Al content of the samples was, however, only of low statistical significance, partly due to inaccurate measurement of *d*-values from highly broadened X-ray powder diffraction lines. In 1983, Childs and Wilson (1983) suggested some Al substitution in lepidocrocite from a soil of Tonga Island, again on the basis of a shift of *d*(200) from 1.935 to 1.92 Å. A low *d*(020) value at 6.24 Å for lepidocrocite in a soil from Tasmania was also interpreted as a possible result of Al-for-Fe substitution (Fitzpatrick *et al.*, 1985).

Because step-counting and curve-fitting procedures now enable line positions to be measured more accurately, a new attempt was made to ascertain the Al incorporation into the lepidocrocite structure by these techniques.

MATERIALS AND METHODS

The lepidocrocite samples were produced as follows: About 0.3 liter of a mixed FeCl₂ and Al(NO₃)₃ solution of about 0.1 M concentration was placed into a 0.6-liter glass beaker, and the pH was adjusted to 8.0 with a NH₃/NH₄Cl buffer (0.2 M NH₃ + 0.2 M NH₄Cl; 1:19). The solution was then oxidized with CO₂-free air at a constant flow rate of 0.5 liter/min while vigorously stirred with a magnetic stirrer. During oxidation the pH was kept constant at pH 8.0 ± 0.05 by adding M NH₃ solution dropwise. The temperature was kept between 13° and 15°C. After 3 hr the orange precipitate

was washed with doubly distilled water and dried in air at 30°C.

Samples for X-ray powder diffraction (XRD) were prepared by thoroughly mixing the air-dried samples with 10% w/w of powdered silica as an internal standard. A Philips PW1130 instrument utilizing monochromatic CoK α radiation was used to obtain XRD patterns by step scanning at 0.02°2 θ intervals for 10 s. The digitized scans were then fitted by the curve-fitting program of Janik and Raupach (1977). The 2 θ values were corrected against the internal standard applying a weighting scheme with tan θ (H. Stanjek, 1987, Lehrstuhl für Bodenkunde, Technische Universität München, 8050 Freising-Weihenstephan, F.R.G., unpublished) and were then converted into *d*-values. The unit cell was calculated using the program GITTER (W. Hummel, 1984, Institut für Mineralogie, Universität Tübingen, Tübingen, F.R.G., unpublished) using the tan θ -weighted 021, 130, 002, 151, 080, 200, and 132 reflections. Possible apparent line shifts due to broad lines could not be corrected because no quantitative data for the correction with lepidocrocite are available. We believe, however, that the general trends shown in Figure 1 would not have been altered by minor corrections.

Samples of the synthetic lepidocrocite materials were dissolved completely in HCl, and Fe and Al were determined by atomic absorption spectroscopy (AAS). The Al was also determined by the aluminon technique to obtain the Al/(Al + Fe) ratio for each sample.

Thermogravimetric analyses (TGA) were performed with a Linseis instrument using 60-mg air-dry samples and a heating rate of 10°C/min. Weights were recorded every 10°C and differentiated to obtain DTGA curves. Electron micrographs were taken with a Zeiss Elmiskop I instrument.

Infrared (IR) spectra were taken with 1:300 KBr pel-

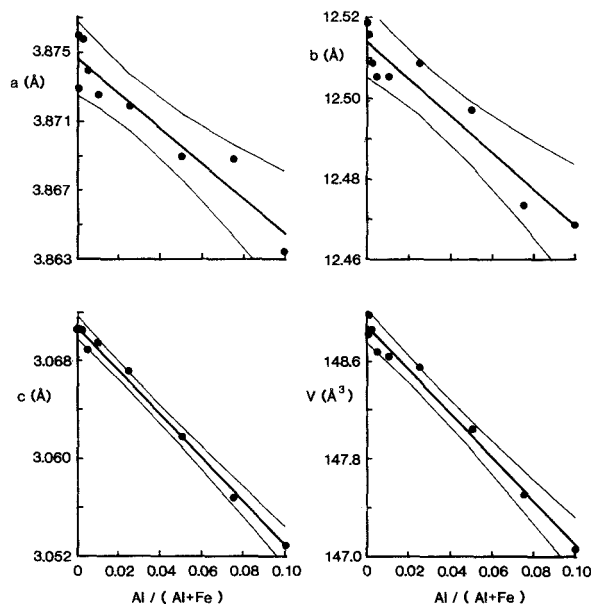


Figure 1. Relation between $\text{Al}/(\text{Al} + \text{Fe})$ and unit-cell edge length and volume. Solid lines indicate 95% confidence limits.

lets using a Beckman 4250 instrument at speeds of 150 and $20 \text{ cm}^{-1}/\text{min}$, the 906.9-cm^{-1} band of polystyrene serving as a standard.

RESULTS AND DISCUSSION

Figure 1 depicts the relation between the unit-cell edge lengths a , b , and c and its volume V and the $\text{Al}/(\text{Al} + \text{Fe})$ mole ratio of the initial solution. This relation assumes a complete precipitation of Fe and Al in the system at pH 8, which was justified by the relation $y = 0.21 + 1.031x$ ($n = 9$; $r = .998$), where y is the value $\text{Al}/(\text{Al} + \text{Fe})$ added and x is the value of the ratio determined by analyses.

The statistical parameters of the relations from Figure 1 are given in Table 1. Although highly significant for all four cell parameters, the scattering of a and b is much higher than that of c . This scatter is because the lines that influence a and b were broader than those that do not. For the least-squares program used for calculating the unit-cell parameters the scatter caused

Table 1. Statistical parameters of the relationship between $\text{Al}/(\text{Al} + \text{Fe})$ and unit-cell edge lengths a , b , c (Å) and unit-cell volume V (Å^3).

Unit-cell parameter	Intercept	Slope ¹	r
a	3.8746(6)	-0.102(13)	-.948
b	12.514(3)	-0.460(54)	-.954
c	3.0708(3)	-0.180(6)	-.997
V	148.89(4)	-18.1(8)	-.993

¹ Standard deviation of the last digit(s) given in parentheses.

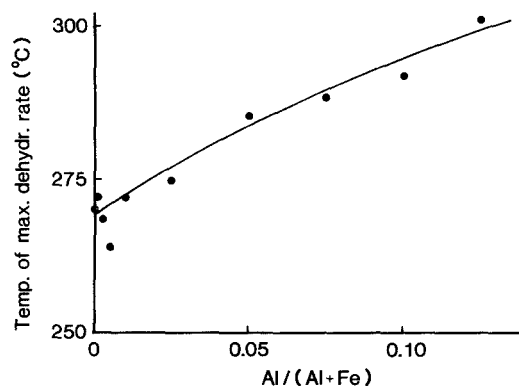


Figure 2. Temperature of maximum dehydration rate in thermogravimetric analyses as a function of $\text{Al}/(\text{Al} + \text{Fe})$.

a and b to deviate in opposite directions. Therefore, $a \times b$ and also the cell volume, V , scattered less than a and b alone (Figure 1). This increased scatter in the plots of the a - and b -edge length with substitution as against that for c -edge length has also been observed for natural (Schwertmann *et al.*, 1987) and synthetic (Schulze and Schwertmann, 1987) poorly crystalline goethites.

In addition to a contraction in unit-cell size, Al-for-Fe substitution in lepidocrocite also affected the thermal stability as determined by TGA. Figure 2 shows that the temperature of maximum dehydroxylation rate increased regularly from 270° to 300°C with increasing $\text{Al}/(\text{Al} + \text{Fe})$. An analogous increase in temperature of the endothermic dehydroxylation peak on DTA was recorded for Al-substituted synthetic goethite (Schulze and Schwertmann, 1987). This increase in the thermal stability of our samples is probably counteracted by a decrease in crystallinity as Al substitution increased so that the effect is weaker than expected.

The differential line broadening mentioned above reflects differential crystal growth. The 200 and 002 lines are always the sharpest, and the 020 and 080 lines are the broadest lines, indicating greater coherence *within* the zig-zag layer (crystallographic x - and z -direction), as opposed to much less coherence *between* the zig-zag layers bound together via H bonds (y -direction).

Electron micrographs (Figure 3) show the typical morphology of lepidocrocite consisting of plates having strongly serrated edges in the z -direction. With increasing Al substitution this morphology was less well expressed and the crystals were considerably smaller in length and width. For the thickness of the crystals which can not be seen from the micrographs, the mean crystallite dimension along the b -axis (MCD_b) was estimated from the width at half intensity of the 020 line using the Scherrer formula (Klug and Alexander, 1974). With increasing Al substitution from 0 to 12.5 mole % MCD_b decreased from 0.27 to $0.031 \mu\text{m}$ indicating

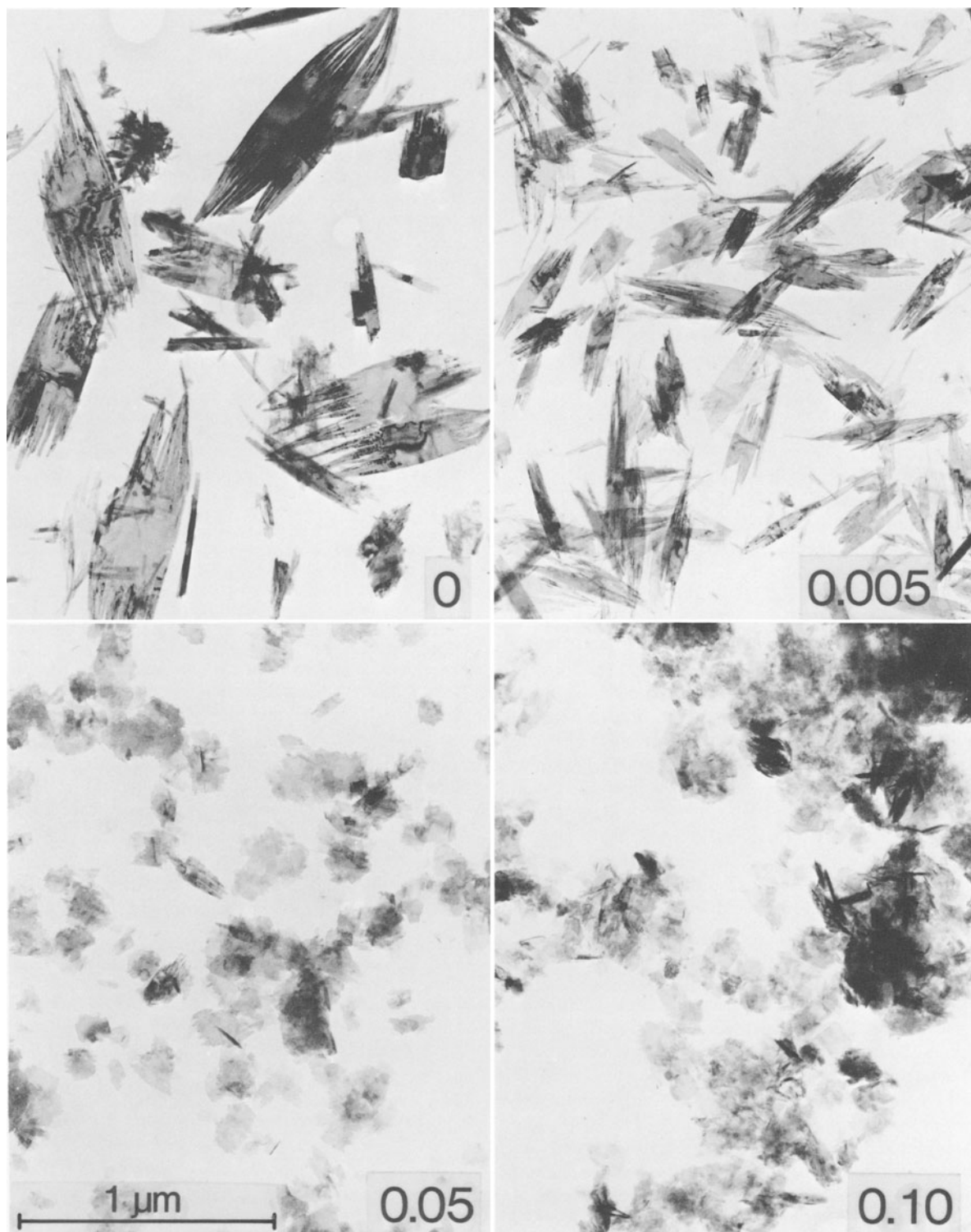


Figure 3. Electron micrographs of synthetic lepidocrocites with Al/(Al + Fe) ratios of 0, 0.005, 0.05, and 0.10.

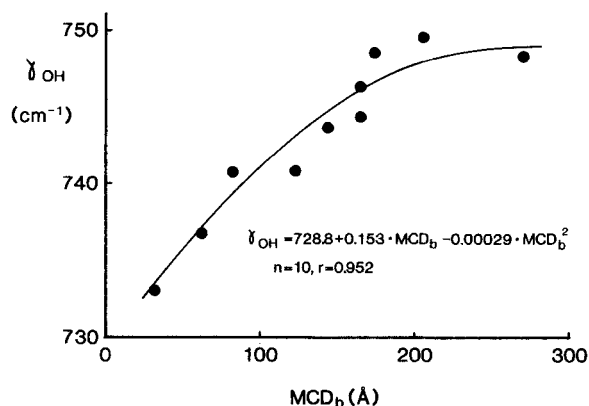


Figure 4. Relation between the mean crystallite dimension perpendicular to the y-axis direction (MCD_b) and the out-of-plane OH-bending vibration.

a very strong inhibitory effect of structural Al on crystal growth perpendicular to the zig-zag layers.

With increasing Al substitution the IR absorption spectra showed a shift of the OH-stretch vibration from about 3130 to 3200 cm^{-1} and of the out-of-plane OH-bending vibration (γ_{OH}) from 750 to 733 cm^{-1} whereas the in-plane vibration (δ_{OH}) remained essentially unchanged at about 1020 cm^{-1} . The changes are opposite to those observed with Al-substituted goethites (Schulze and Schwertmann, 1984, 1987), in which the shifts of OH-stretch and -bending were interpreted as an increase in the strength of the hydrogen bond as Al substituted for Fe. Schwertmann *et al.* (1985) also observed for goethites, however, that the two OH-bending modes were sensitive to crystal size, and shifted to lower frequencies (=weakening of the H bonds) as crystal size decreased. The increase of the OH-stretch frequency and the decrease of the out-of-plane bending frequency observed here are therefore interpreted as the weakening of the H bond (Hartert and Glemser, 1956) due to loss in crystallinity. This hypothesis is strongly supported by a highly significant non-linear correlation between γ_{OH} and MCD_b (Figure 4).

In contrast to Taylor and Schwertmann (1980), the present, more accurate measurements clearly indicate that lepidocrocite can incorporate Al into its structure. The reason why this is easier at pH 8 than at pH 7 (Taylor and Schwertmann, 1980) is not understood. One possibility is the difference in rate of oxidation. Carlson and Schwertmann (1989) recently showed that in a system in which lepidocrocite and goethite form simultaneously, lepidocrocite is favored as the rate of oxidation increases. Because the rate of oxidation of Fe^{2+} increases with increasing pH (Stumm and Lee, 1961), a pH increase from 7 to 8 might have favored lepidocrocite. At the same time, the formation of magnetite-maghemite, which is very likely at this pH, might have been suppressed by Al (Schwertmann and Murad, 1989; Taylor and Schwertmann, 1978).

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