# ALUMINUM-BEARING GOETHITE IN VENEZUELAN LATERITES

E. Mendelovici, Sh. Yariv,[1] and R. Villalba

Laboratorio Fisico-Química de Materiales, Centro de Ingeniería y Computación
Instituto Venezolano de Investigaciones Cientificas, Apartado 1827, Caracas, Venezuela

**Abstract**—The presence of Al-bearing goethites has been unequivocally established in Venezuelan laterite sediments by means of infrared spectroscopy (IR), chemical dissolution, and X-ray powder diffraction (XRD) methods. The composition of these samples ranges from $[Fe_{0.89}Al_{0.11}]O(OH)$ to $[Fe_{0.76}Al_{0.24}]O(OH)$. The data of dissolution experiments using a modified dithionite (CDB) treatment suggest a parallel behavior between Fe and Al; the gradual dissolution of Al is associated with the destruction of the Al-containing goethite. The interpretation of the CDB dissolution results for $SiO_2/Fe_2O_3$ is different; silica was only slightly extracted from phases other than goethite. Substitution of $Fe^{3+}$ by $Al^{3+}$ in these goethites was represented on the XRD patterns by a lowering of the (110) and (111) reflections corresponding to a reduction in size of the unit cell of goethite. IR spectroscopy showed the formation of such solid solutions by a shift of the 405 $cm^{-1}$ absorption band, assigned to $\nu$ (Fe–O) in synthetic goethite, to >460 $cm^{-1}$ in the spectrum of Al-bearing natural goethite. Moreover, this spectrum shows a shift of the 3140 $cm^{-1}$ absorption, due to $\nu$ (OH), to higher frequencies, indicating a H-bond weakening in $[Fe_xAl_{(1-x)}]O(OH)$ compared to FeO(OH).

**Key Words**—Al-goethite, Dithionite dissolution, Goethite, Laterite, Venezuela.

## INTRODUCTION

Solid solution of iron and aluminum in goethite, $\alpha$-FeOOH, was reported in the investigation of iron oxides and hydroxides in soils (Schwertmann and Taylor, 1977) and in bauxite ores (Janot *et al.*, 1971). Like many other ferruginous bauxite ores, Venezuelan lateritic sediments consist mainly of goethite, gibbsite, kaolinite, and quartz. The exact location and content of aluminum in various laterite minerals is of considerable importance in predicting whether or not aluminum can be economically extracted from such deposits. Normally, Al incorporated in the goethite structure is not extractable by conventional industrial treatments. In addition, the substitution of Al for Fe in the goethite structure may serve as a fingerprint for specific geochemical processes responsible for the formation of such deposits in weathering environments.

Because the determination of total $Al_2O_3$ by standard chemical analysis does not distinguish between Al incorporated in the structure of goethite from that in other laterite minerals, an alternative method for the determination of Al in goethite was developed based on selective chemical dissolution. A simple technique was also devised using infrared spectroscopy (IR) and well-established X-ray powder diffraction (XRD) to identify Al-bearing goethites in laterite samples.

## EXPERIMENTAL

### Materials

Three samples of Venezuelan laterites ($\leqslant$150 mesh) of variable composition were chosen for the study from

a residual profile in the Venezuelan Guayana (Mendelovici *et al.*, 1979). Locations, mineralogy, and total $Fe_2O_3$ contents of all samples are listed in Table 1.

Synthetic goethite was obtained by titrating $FeCl_3 \cdot 6H_2O$ with KOH at pH 13 and aging the precipitate at 60°C for at least 4 days (Landa and Gast, 1973). The crystalline goethite product was characterized by X-ray powder diffraction and infrared spectroscopic methods. The specific surface area was determined as 29 $m^2/g$ by the BET method.

### Methods

*Selective chemical dissolution with dithionite.* For the deferration of the Venezuelan laterite samples, the dithionite (CDB) method of Mehra and Jackson (1960) was adapted, with the following modifications: 2.5 g of sample was shaken with 20 ml of 0.3 M Na-citrate and 2.5 ml of 1 N $NaHCO_3$ in a water bath. When the temperature reached 75°C, 0.5 g of Na-dithionite was added, and the suspension shaken for 20 min. After this digestion period saturated NaCl solution was added to promote flocculation. The suspension was centrifuged, and Fe, Al, and Si were determined in the decanted clear supernatant by atomic absorption spectroscopy (AA) using a $N_2O$–$C_2H_2$ flame. The solids were analyzed for total iron in a fluoboric-boric acid matrix (La Brecque *et al.*, 1978). In order to remove completely the free iron oxides, 8 consecutive extractions with CDB were necessary for sample a and 15 for samples b and c. The amount of $Fe_2O_3$ dissolved after further extractions with CDB was <0.01%.

*NaOH treatment.* To identify and characterize the hydrous iron oxides by XRD and IR spectroscopy, gibbsite and part of the kaolinite were removed from

---

[1] On sabbatical leave from the Hebrew University of Jerusalem, Israel.

Table 1. Contents of major clay minerals and total $Fe_3O_2$ in Venezuelan laterite samples from an 11-m thick section in Los Guaicas (Edo. Bolívar).

| Sample | Depth (m) | Kaolinite[1] (%) | Gibbsite[1] (%) | Goethite[2] (%) | $Fe_2O_3$[3] (%) |
|---|---|---|---|---|---|
| a | 7 | 80 | traces | 11.1 | 13.22 |
| b | 6 | 40 | 40 | 22.0 | 27.21 |
| c | 3 | 5 | 70 | 21.5 | 24.90 |

[1] Approximate estimation by IR and XRD complemented by DTA.
[2] Estimated by the modified CDB treatment (this study).
[3] Determined by premanganometry, complexometry, and AA (La Brecque et al., 1978).



Figure 1. Percentages of $Al_2O_3$ extracted in a modified dithionite (CDB) treatment with respect to extracted $Fe_2O_3$ in samples a, b, and c.

the natural laterites by shaking them with 1.25 M NaOH at 75°C (Mackenzie and Robertson, 1961) for periods of 0.5 hr to 6 days. The resulting solids were washed by centrifugation with $H_2O$ to pH 7 and with spectroscopic grade acetone and then dried in air. For a comparative study the synthetic goethite was also treated with 1.25 M NaOH and further examined.

*X-ray powder diffraction.* Diffractograms of powdered samples were obtained on a Philips diffractometer using Mn-filtered FeK$\alpha$ radiation. The X-ray unit was operated at 36 kV and 20 mA (5-sec time constant). The scanning speed was 1° 2$\theta$/min.

*Infrared spectroscopy.* IR spectra were recorded on a Perkin-Elmer model 283 grating spectrophotometer at ambient beam temperature. The solids (0.5 mg) were examined in 200-mg KI disks, previously dried at 110°C. Preliminary experiments showed that better resolution can be obtained by using KI instead of KBr as a dispersant for the preparation of the disks.

## RESULTS AND DISCUSSION

### Dissolution of goethite by dithionite

The natural goethite contained in the Venezuelan laterites was only partially soluble in the buffered sodium dithionite solution used in the present study. However, by consecutive extractions with CDB practically all of the free iron oxide was dissolved. After 8, 15, and 15 extractions of samples a, b, and c, respectively, 10.0, 19.7, and 19.4% $Fe_2O_3$ was dissolved.

The degree of destruction of the goethite is inferred from the dissolution of iron. The pertinent results are presented in Figures 1 and 2, showing the amounts of $Al_2O_3$ and $SiO_2$ released into the CDB solutions as a function of the corresponding values of $Fe_2O_3$. The same series of extraction were used for dissolving all the elements. Each figure represents three series of extractions for each sample, and those points which are shown represent the maximum deviations from the plotted curves.

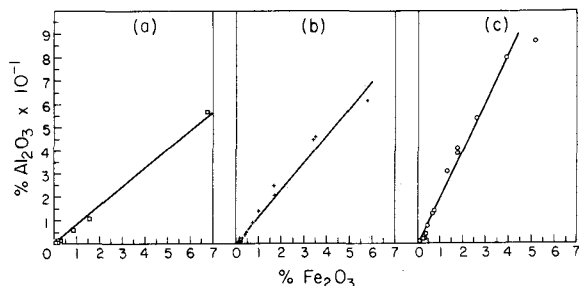The CDB extraction of the present study removes primarily free iron oxides and hydroxides as well as amorphous and poorly crystalline fractions of silica and alumina minerals (Kunze, 1965). After the exhaustive extraction of iron, practically no $Al_2O_3$ was dissolved (<0.01%). According to IR and XRD information, gibbsite and kaolinite persist in the residual sample. It is, therefore, inferred that under the present extraction treatment the contribution of gibbsite and kaolinite to the dissolved alumina can be neglected.

Thus, the linear relationship between the extracted $Al_2O_3$ and $Fe_2O_3$ (Figure 1) is independent of the extraction number and series, and suggests a parallel behavior between the aluminum and iron dissolved in CDB. Since, (1) the linear relationship holds until the complete dissolution of goethite, (2) gibbsite as well as kaolinite were practically unaffected by the present treatment, and (3) no amorphous $Al_2O_3$ was detected in the laterite samples examined (Mitchell et al., 1971), it may be assumed that the aluminum released by these CDB solutions comes chiefly from the goethite and was initially incorporated in the goethite structure.

The molar ratios $Al_2O_3/(Al_2O_3 + Fe_2O_3)$ in the various samples, obtained from Figure 1, are 0.11, 0.16, and 0.24 for laterites a, b, and c, respectively. According to Norrish and Taylor (1961), the substitution of Al for Fe in goethite decreases the solubility of this mineral. It is, therefore, expected that the goethite fraction with smaller Al content will be more soluble in dithio-
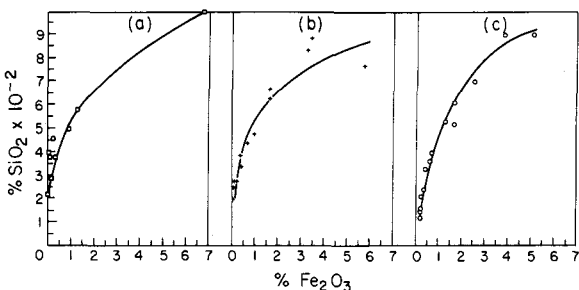


Figure 2. Percentages of $SiO_2$ extracted in a modified dithionite (CDB) treatment with respect to extracted $Fe_2O_3$ in samples a, b, and c.

Table 2.   Characteristic spacings of synthetic goethite and of goethites from Venezuelan laterites b and c after 15 hr of NaOH treatment.

| (hkl) | Synthetic goethite FeO(OH) (Å) | Laterite b[1] $(Fe_{0.84}Al_{0.16})O(OH)$ (Å) | Laterite c[1] $(Fe_{0.76}Al_{0.24})O(OH)$ (Å) |
|---|---|---|---|
| 110 | 4.195 | 4.18 | 4.164 |
| 111 | 2.454 | 2.434 | 2.427 |
| 121 | 2.254 | 2.238 | 2.242 |
| 140 | 2.190 | — | 2.167 |
| 221 | 1.720 | — | 1.717 |

Because of a relative high ratio of quartz/goethite in sample a, the reflections of goethite were overlapped by those of quartz.

[1] Formulae derived from Figure 1.



Figure 3.   Infrared spectra of disks of synthetic goethite, reground (I) and sample c, unground (II) after 15 hr of NaOH treatment.

nite. The percentages of $Fe_2O_3$ dissolved in the first CDB extractions are 6.78, 5.78, and 5.12% for samples a, b, and c, respectively. These numbers correspond to 68, 29, and 26% of the total free $Fe_2O_3$ and are inversely related to the Al contents of the correspondent goethites.

In the case of laterite c, the first extraction always gave smaller ratios of $Al_2O_3$ to $(Al_2O_3 + Fe_2O_3)$ compared to the further extractions, indicating the presence of goethite with an Al mole fraction lower than 0.24 (Figure 1c). This goethite material is the first to be extracted by the dithionite solution and is responsible for the relatively high solubility of iron during the first CDB treatment (26% of the total free iron oxide).

The $SiO_2$ that is extracted by dithionite is independent of the destruction of the goethite (Figure 2). The amount of extracted silica decreases only slightly with the number of the extractions and shows a different trend from extracted iron. Furthermore, the $SiO_2/Fe_2O_3$ ratio constantly increases with the number of extractions. The great difference in behavior between the dissolution of silica and alumina supports the assumption that the latter, whose content in solution is one order of magnitude higher than silica, is not extracted from aluminosilicate minerals to any considerable extent.

*X-ray powder diffraction*

Norrish and Taylor (1961) reported a shift of the (111) reflection of goethite from 2.452 to 2.426 Å in soil goethites. They showed that these goethites contain up to 30 mole % Al giving rise to a substantial reduction in the size of the unit cell. On the other hand, Janot *et al.* (1971) observed a decrease of the (140) reflection from 2.18 Å in synthetic goethites to 2.14 Å in natural Al-goethites. Smaller changes were also reported in their study for the (111), (121), and (221) reflections.

The decreased (110) and (111) spacings listed in Table 2 for the NaOH-treated laterites and the synthetic goethites can be rela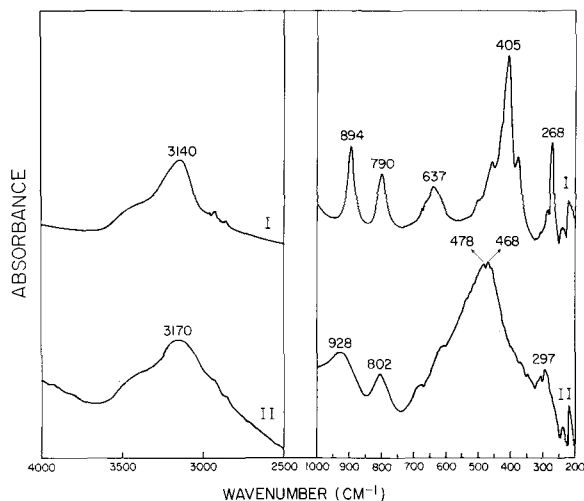ted to the amount of Al substitution in the goethites of these Venezuelan laterites, as estimated from the chemical dissolution data (Figure 1).

Aluminum minerals in laterites interfere with the identification and characterization of goethite. Such phases were mostly destroyed by treatment with 1.25 M NaOH, thus allowing the X-ray patterns to be inspected for goethite, which was unaffected by such treatment. At higher alkali concentrations, however, structural modifications of goethites have been reported (Petit *et al.*, 1964).

*Infrared spectroscopy*

Jonas and Solymar (1970) showed an increase in frequency for the 900 cm$^{-1}$ band of synthetic Al-goethite, which can be related to the degree of Al substitution. In the presence of kaolinite and aluminum oxide minerals it was not possible to identify goethite and Al-goethite in bauxites by IR methods. In fact, only one goethite band (800 cm$^{-1}$) was detected by Jonas *et al.* (1974) in red mud from the Bayer process.

The spectra recorded after various periods of treatment of the synthetic and lateritic goethites with 1.25 M NaOH show no changes in the positions of the absorption bands of goethite. This is in good agreement with the XRD observations, in the sense that no structural modifications of goethite are apparent. To detect the diagnostic $\nu$(OH) band of goethite (at about 3140–3170 cm$^{-1}$), which may be detected in the presence of large amounts of kaolinite, NaOH treatments for 15, 6, and 0.5 hr were necessary for samples a ($\sim$80% kaolinite), b ($\sim$40% kaolinite), and c ($\sim$5% kaolinite), respectively. However, to detect all of the goethite bands and therefore differentiate among various goethite varieties by IR, greater amounts of kaolinite must be removed by a longer NaOH treatment. Thus, 7-day, 15-

Table 3.   Infrared absorption bands of synthetic goethite and of goethites from Venezuelan laterites a, b, and c.

| Assignments (Ryskin, 1974) | Synthetic goethite FeO(OH) (cm⁻¹) | Laterite a $(Fe_{0.89}Al_{0.11})O(OH)$ (cm⁻¹) | Laterite b $(Fe_{0.84}Al_{0.16})O(OH)$ (cm⁻¹) | Laterite c $(Fe_{0.76}Al_{0.24})O(OH)$ (cm⁻¹) |
|---|---|---|---|---|
| $\nu$(OH) | 3140 | 3160 v.br. | 3160 v.br. | 3170 v.br. |
| $\delta$(OH) | 894 | 907 | 910 | 928 v.br. |
| $\gamma$(OH) | 790 | 793 | 798 | 802 br. |
|  |  |  | 690 w.sh. | 690 w.sh. |
| Fe–O | 637 | 610 w.sh. | 620 w.sh. | 620 w.sh. |
|  | 455 w. |  |  |  |
| Fe–O | 405 v.s. | 462 v.s. | 465 v.s. | 478 v.s. |
|  | 397[1] |  |  | 468[1] |
|  | 375 sh. | 365 w.sh. | 370 w.sh. |  |
|  |  |  |  | 305 v.w. |
| Fe–O | 268 | 280 w. | 283 w. | 297 w. |

s. = strong; v. = very; w. = weak; br. = broad; sh. = shoulder.
[1] Disappeared on grinding.

hr, and 3-hr treatments were needed for samples a, b, and c, respectively.

The IR spectra of laterite c after 15 hr of NaOH treatment as well as those of synthetic goethite, are shown in Figure 3. Much broader bands were exhibited by the natural goethites than by the synthetic goethite; in addition, the absorption maxima of the lateritic goethites are at higher frequencies (Table 3). The extent of these shifts are related to the amount of Al in the goethite, as estimated from the chemical dissolution results.

The most pronounced perturbation was the $\nu$(Fe–O) band. In synthetic goethite this band is at 405 cm⁻¹, while in the natural goethites, it is >460 cm⁻¹ and is very broad, overlapping with the 637, 455, and 375 cm⁻¹ absorptions. In the light of the information obtained from oxalic acid dissolution experiments (Schwertmann, 1973) the amount of amorphous iron in these laterites seems to be negligible and does not contribute to the development of the Fe–O vibrations mentioned above. Aluminum does not form an isolated phase, therefore no proper absorption bands can be identified as Al–O vibrations. Thus, it is concluded that the drastic changes displayed by the spectra of laterites in Figure 3 and Table 3 are due to partial substitution of Fe by Al in the goethite structure.

Substitution of Fe by Al should also change the acid strength of the hydroxyl groups, and therefore change the strength of the hydrogen-bonds between these hydroxyls (Heller-Kallai et al., 1975). In the goethite structure OH groups form intrahydrogen bonds with one another. The band at 3140 cm⁻¹ was assigned by Ryskin (1974) to hydrogen-bonded hydroxyls. Depending on the degree of substitution, this band shifts to higher frequencies in the Al-bearing goethites indicating a weakening of the hydrogen bonds compared to those in synthetic goethite. Because of the presence of a free d electron subshell in the Fe atom and its absence in the Al atom, one would expect a higher screening

effect in the Al–O–H group and a corresponding weakening of its H-bond compared to the Fe–O–H group. Therefore, it can be predicted that Al substitution for Fe will shift the $\nu$(OH) to higher frequencies, as has been observed.

## CONCLUSIONS

IR, XRD, and selective chemical dissolution data indicate that part of the $Fe^{3+}$ in the structure of the goethites of Venezuelan laterites is substituted by $Al^{3+}$. Infrared spectroscopy has proved to be a useful tool for discerning the existence of such solid solutions, represented by the general formula: $[Fe_xAl_{(1-x)}]O(OH)$. The substitution of Fe by Al shows that the precipitation of these goethites during lateritization occurred in an aluminum-rich milieu. The occurrence of this solid solution in the Venezuelan laterites portends difficulties in the separation of aluminum and iron by conventional methods.

## REFERENCES

Heller-Kallai, L., Yariv, Sh., and Gross, S. (1975) Hydroxyl-stretching frequencies of serpentine minerals: Mineral. Mag. 40, 197–200.

Janot, C., Gibert, H., de Gramont, X., and Biais, R. (1971) Etude des substitutions Al-Fe dans des roches latéritiques: Bull. Soc. Fr. Mineral. Cristollogr. 94, 367–380.

Jonas, K. and Solymar, K. (1970) Preparation, X-ray derivatographic and infrared study of aluminum substituted goethites: Acta Chim. (Budapest) 66, 383–394.

Jonas, K., Solymar, K., and Orban, M. (1974) Phase analysis of red mud by infrared spectrophotometry: *Acta Chim. (Budapest)* **81**, 443–453.

Kunze, G. W. (1965) Pretreatment for mineralogical analysis: in *Methods of Soil Analysis, Part 1,* C. A. Black, ed., American Soc. Agronomy, 568–577.

La Brecque, J. J., Mendelovici, E., Villalba, R. E., and Bellorin, C. C. (1978) The determination of total iron in Venezuelan laterites; the investigation of interferences of aluminum and silicon on the determination of iron in the fluoboric-boric acid matrix by atomic absorption: *Appl. Spectrosc.* **32**, 57–60.

Landa, E. R. and Gast, R. G. (1973) The evaluation of crystallinity in hydrated ferric oxides: *Clays & Clay Minerals* **21**, 121–130.

Mackenzie, R. C. and Robertson, R. H. (1961) The quantitative determination of halloysite, goethite, and gibbsite: *Acta Univ. Carol. Geol. Suppl.* **1**, 139–149.

Mehra, O. P. and Jackson, M. L. (1960) Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate: *Proc. 7th Nat. Conf. Clays & Clay Minerals,* 317–327.

Mendelovici, E., La Brecque, J., and Villalba, R. (1979) Cal-cium and magnesium determination in silicates and Venezuelan laterites by atomic absorption spectroscopy; interference studies in the fluoboric-boric acid matrix: *Chem. Geol.,* in press.

Mitchell, B. D., Smith, B. F. L., and de Endredy, A. S. (1971) The effect of buffered sodium dithionite solution and ultrasonic agitation on soil clays: *Isr. J. Chem.* **9**, 45–52.

Norrish, K. and Taylor, R. M. (1961) The isomorphous replacement of iron by aluminum in soil goethites: *J. Soil Sci.* **12**, 249–306.

Petit, J. M., Backer, L., and Herzog, E. (1964) Traitement alcalin de goethite substituée: *C. R. Acad. Sci.* **258**, 4993–4994.

Ryskin, Ya. I. (1974) The vibrations of protons in minerals: hydroxyl, water and ammonium: in *The Infra-red Spectra of Minerals,* V. C. Farmer, ed., Mineralogical Society, London, 137–181.

Schwertmann, U. (1973) Use of oxalate for Fe extraction from soils: *Can. J. Soil Sci.* **53**, 244–246.

Schwertmann, U. and Taylor, R. M. (1977) Iron oxides: in *Minerals in Soil Environment,* J. B. Dixon and S. B. Weed, eds., Soil Science Society of America, Inc., 145–180.

**Резюме**—Присутствие гетитов, содержащих Al, было определенно установлено в Венесуэльских латеритных осадках при помощи методов инфра-красной спектроскопии (ИК), химического растворения, и порошковым методом рентгеноструктурного анадиза. Состав этих образцов изменяется от [Fe$_{0,89}$Al$_{0,11}$]O(OH) до [Fe$_{0,76}$Al$_{0,24}$]O(OH). Данные экспериментов по растворению, использующие усовершенствованный дитионитный буфер (УДБ) указывает на параллельное поведение между Fe и Al; постепенное растворение Al связано с разрушением гетита, содержащего Al. Иначе интерпретируются результаты растворения с использованием УДБ для SiO$_2$/Fe$_2$O$_3$; кремний только слегка экстрагировался из фаз, не относящихся к гетиту. Замена Fe$^{3+}$ алюминием Al$^{3+}$ в этих гетитах была выражена на картинах РСА понижением отражений (110) и (111), соответствующих уменьшению в размере элементарной ячейки гетита. По данным ИК спектроскопии образование таких твердых растворов доказывается сдвигом абсорбционной полосы 405 СМ$^{-1}$, приписываемой $\nu$(Fe–O) в синтетических гетитах, к >460 см$^{-1}$ в спектре естественных гетитов, содержащих Al. Более того, этот спектр показывает сдвиг абсорбции 3140 см$^{-1}$, обусловленный $\nu$(OH), к более высоким частотам, что указывает на ослабление водородной связи в [Fe$_x$Al$_{(1-x)}$]O(OH) по сравнению с FeO(OH).

**Resümee**—Die Anwesenheit von Al-haltigem Goethit wurde in Laterit-sedimenten von Venezuela eindeutig mittels Infrarotspektroskopie, chemischer Zersetzung, und Röntgenpulverdiagrammen (XRD) nachgewiesen. Die Zusammensetzung dieser Proben geht von [Fe$_{0,89}$Al$_{0,11}$]O(OH) bis [Fe$_{0,76}$Al$_{0,24}$]O(OH). Die Werte für die Zersetzungsexperimente, wenn ein modifizierter Dithionit Puffer (CDB) benutzt wird, schlagen ein paralleles Verhalten zwischen Fe und Al vor; die langsame Auflösung von Al ist mit der Zerstörung von Al-haltigem Goethit verbunden. Die Interpretation der Resultate der CDB-Zersetzung für SiO$_2$/Fe$_2$O$_3$ ist anders; nur wenig Kieselerde wurde, mit Ausnahme von Goethit, von den anderen Phasen extrahiert. Austausch von Fe$^{3+}$ mit Al$^{3+}$ wurde in diesen Goethiten in den XRD Mustern gesehen in der Form einer Senkung der (110) und (111) Reflektionen, was einer Reduktion in der Größe der Goethit-Einzellen entspricht. IR-Spektroskopie von Al-haltigem, natürlichem Goethit zeigt die Bildung solcher festen Lösungen durch eine Verschiebung des 405 cm$^{-1}$ Absorptionsband, welches $\nu$(Fe–O) in synthetischem Goethit zugeschrieben wird, nach >460 cm$^{-1}$. Außerdem zeigt dieses Spektrum eine Verschiebung der 3140 cm$^{-1}$ Absorption, welche zu $\nu$(OH) gehört, zu höheren Frequenzen, was auf eine Verschwächung von Wasserstoffbrücken in [Fe$_x$Al$_{1-x}$]O(OH) verglichen mit FeO(OH) hindeutet.

**Résumé**—La présence de goethite contenant Al a été établie sans aucun doute dans des sédiments de latérite du Vénézuela au moyen de spectroscopie à l'infra-rouge (IR), de dissolution chimique, et de diffraction aux rayons X (XRD). La composition de ces échantillons s'étend de [Fe$_{0,89}$Al$_{0,11}$]O(OH) à [Fe$_{0,76}$Al$_{0,24}$]O(OH). Les donnés d'expériences de dissolution utilisant un tampon de dithionite (CDB) modifié suggère un comportement parallèle entre Fe et Al; la dissolution graduelle d'Al est associée avec la destruction de la goethite contenant Al. L'interprétation des résultats de la dissolution CDB de SiO$_2$/Fe$_2$O$_3$ est différente; la silice n'était que peu extraite des phases autres que la goethite. La substitution d'Al$^{3+}$ à Fe$^{3+}$ dans ces goethites est représentée sur les clichés XRD par une diminution des réflections (110) et (111) correspondant à une réduction dans la maille de la goethite. La spectroscopie IR a montré la formation de telles solutions solides par un déplacement de la bande d'absorption de 405 cm$^{-1}$, assignée à la goethite synthétique $\nu$(Fe–O) à >460 cm$^{-1}$ dans le spectre de la goethite naturelle contenant Al. De plus ce spectre montre un déplacement de l'absorption 3140 cm$^{-1}$, dû à $\nu$(OH) à des fréquences plue élevées, indiquant un faiblissement du lien H dans [Fe$_x$Al$_{(1-x)}$]O(OH) comparé à FeO(OH).