

INTERACTIONS BETWEEN THE IRON AND THE ALUMINUM MINERALS DURING THE HEATING OF VENEZUELAN LATERITIC BAUXITES. I. INFRARED SPECTROSCOPY INVESTIGATION

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ABSTRACT

The thermal dehydroxylation of natural Al-bearing goethite was investigated by IR spectroscopy. Venezuelan lateritic bauxites (which in addition to goethite contain kaolinite, gibbsite, ilmenite and quartz), as well as chemically isolated samples of Al-goethites, were heated to 300, 600 and 1000°C. The spectral features of the iron oxides formed during the thermal treatment depend on the heating temperature, showing that the first dehydroxylation product is Al-bearing protohematite which at temperatures above 600°C is recrystallized to Al-bearing hematite. Part of the aluminum which is occluded in this hematite originates from the gibbsite and to a smaller extent from the kaolinite.

INTRODUCTION

The most important iron minerals in laterites and bauxites are goethite and hematite. Because of particle size, hematite is much more separable than goethite in the red mud resulting from the Bayer process (see e.g., Solymer et al. [1]). The technological disadvantages caused by the goethite content of the bauxites can be avoided by transforming goethite into hematite, i.e. by thermal treatment. Thermal transformation is also important in geochemistry as it may occur during the metamorphism of buried sediments.

The $\alpha\text{-FeOOH} \rightarrow \alpha\text{-Fe}_2\text{O}_3$ transformation in the absence of additives has been thoroughly investigated and reviewed (see e.g., Rooksby [2]). A polydomain with an imperfect structure of $\alpha\text{-Fe}_2\text{O}_3$ is obtained by heating goethite up to 600°C. This iron oxide variety is called protohematite [3]. At higher temperatures the protohematite recrystallizes to hematite. The various stages of the thermal transformation and the properties of the resulting hematite depend on the chemical environment as well as on the physical conditions in which the dehydroxylation reactions are carried out (see e.g., refs. 4–6). Although most natural goethites are actually Al-bearing goethites (see e.g., refs. 7 and 8), systematic research on the thermal transformation of

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iron oxides was carried out mostly with synthetic goethites barring a few exceptions (see e.g., Perinet and Lafont [9] and Schwertmann et al. [10]). During a study of the thermal reduction of goethite by alkali iodides (Mendelovici and Yariv [11]) and on the thermal transformation of goethite to maghemite in CsI disks [12], we showed that a natural goethite did not behave similarly to synthetic goethite.

The object of the present investigation is to study the thermal transformation of natural Al-bearing goethite as well as the effects of the presence of the various minerals found in Venezuelan lateritic bauxites on the reaction products. In the first part of the present investigation, the iron oxide reaction products are examined by IR spectroscopy; in the second part, the crystallinity of the resulting oxides will be determined by X-ray diffraction [17]. The first part of this work involves the following investigations.

(1) The thermal transformation of chemically isolated Al-bearing goethites and the formation of Al-bearing hematites is followed by IR spectroscopy; moreover the effects of initial Al substitution in the original goethite structure are correlated with band positions.

(2) The formation of corundum from the natural gibbsite by calcination of the lateritic samples after the removal of free iron oxides is followed by IR spectroscopy.

(3) The lateritic bauxites, either in their original forms or after a partial removal of free alumina, are heated to various temperatures, and their IR

TABLE 1

Content of minerals and thermal weight losses (in weight percentage) in the lateritic bauxite samples used in the present study

	Laterite			
	"a"	"b"	"c"	"d"
Content of:				
Quartz *	10	6	9	Trace
Kaolinite *	80	40	5	5
Kaolinite **	70	47	10	11
Gibbsite *	Trace	40	70	70
Gibbsite **	Trace	10	48	51
Gibbsite ***	Trace	16	44	52
Goethite †	11	22	22	26
Ilmenite **	7	7	8	13
Weight losses at:				
105°C	1.7	2.7	1.9	1.8
300°C	1.9	6.6	15.3	18.2
600°C	8.7	6.1	4.1	2.9
1000°C	0.3	0.1	0.1	0.8

* Approximate estimation by XRD and/or IR [14].

** Approximate estimation from total chemical analysis of the elements (kaolinite, calculated from total SiO₂ minus quartz SiO₂; gibbsite calculated from total Al₂O₃ minus kaolinite Al₂O₃; ilmenite calculated from total TiO₂).

*** Estimated by selective consecutive dissolutions with boiling 0.5 N NaOH.

† Estimated by the modified CDB treatment [14].

spectra are compared to those of synthetic hematite and corundum or to hematites and corundums obtained by the calcination of the natural goethites and gibbsite, respectively.

EXPERIMENTAL

Materials

Four representative lateritic samples (≤ 150 mesh) of different composition were used for this study from a residual profile in the Venezuelan Guayana [13]. Mineralogical contents of these samples are listed in Table 1. Goethite was synthesized in our laboratory [14]. Standard gibbsite was supplied by ALCOA and Georgia kaolinite by Wards. Corundum was obtained by calcination of gibbsite at 1000°C .

Methods

Four different groups of laterite samples were examined. The first group comprised the original ground samples. The second and the third groups were obtained by shaking the laterites with 1.25 M NaOH at 75°C for 20 min and 15 h, respectively. The gibbsite is only partly removed from the second group, whereas the third group is gibbsite-free [14]. A fourth group was obtained by selective dissolution of the iron in the natural laterite samples, by consecutive extractions (20 times) with citrate-dithionite-bicarbonate (CDB) until no iron was detected in the extracts [14]. Samples of the second, third and fourth groups were thoroughly washed before further treatment. The four different lateritic groups as well as synthetic goethite, gibbsite and Georgia kaolinite were heated at 300, 600 and 1000°C for 1 day at each temperature and weight losses were determined (Table 1).

Infrared spectra of the thermally treated samples were recorded on a Perkin-Elmer model 283 grating spectrophotometer at ambient beam temperature. For this purpose disks of 13 mm diameter were prepared by pressing a mixture containing 1.5 mg of sample and 200 mg of alkali halide (KI or CsI).

RESULTS AND DISCUSSION

Thermal treatment of lateritic Al-goethites (third group)

According to Schwertmann et al. [10] dehydroxylation of Al-goethites at 300°C results in poorly crystalline Al-protohematites which at higher temperatures are partly perfected. The difference in the thermal behavior between the pure goethite and the Al-bearing goethite is manifested at 600°C when the first is recrystallized, yielding a three-dimensionally ordered structure of hematite; whereas the latter is poorly ordered in the *c* direction. Schwertmann et al. [10] came to these conclusions from line broadening in

TABLE 2

Band maxima (in cm^{-1}) of O^{2-} displacements in hematite and Al-bearing hematites obtained after calcination of synthetic and natural goethites for one night at 300°C , 600°C and 1000°C

Heating Temp. ($^\circ\text{C}$)	Source of hematite			
	Synthetic goethite $\text{FeO}(\text{OH})$	Laterite "a" $(\text{FeO}_{0.89}\text{Al}_{0.11})\text{O}(\text{OH})$	Laterite "b" $(\text{FeO}_{0.84}\text{Al}_{0.16})\text{O}(\text{OH})$	Laterite "c" $(\text{Fe}_{0.76}\text{Al}_{0.24})\text{O}(\text{OH})$
300	308	z	330	340
	444	z	465	465
	530	z	538	535
600	308	320	325	335
	345 w.sh.			
	444	455	460	465
	475 w.sh.			
	525 m	537	543	545
1000	550 w			
	333	340 v.br.	332	340
	467	466	467	467
	545	546	550	560

m, Medium; w, weak; v.br., very broad; sh, shoulder; z, overlapping with bands of residual kaolinite.

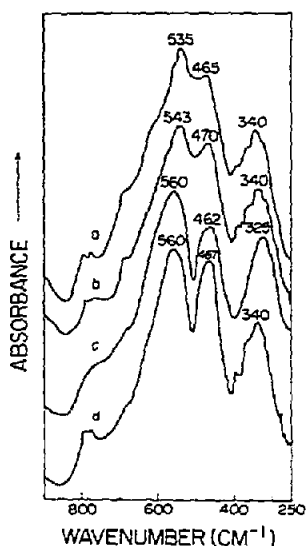


Fig. 1. Infrared spectra of Al-bearing goethite originated from laterite "c", heated for 1 day at the following temperatures: (a) and (b) 300 and 450°C, respectively, disks reground four times (Al-bearing protohematite); (c) and (d) 1000°C, disks unground and reground four times, respectively (Al-bearing hematite).

X-ray diffractograms and it seems reasonable to examine the effects of temperature on the IR spectra of these materials. It should be mentioned that the transformation of the pure protohematite to hematite at $>600^{\circ}\text{C}$ is demonstrated by drastic changes in the corresponding IR spectra [3]. The IR spectrum of synthetic $\alpha\text{-FeOOH}$ heated for 1 day at 600°C shows characteristic features of both varieties, protohematite and hematite (Table 2), although the X-ray diffractogram of the same sample is typical for hematite.

The thermal behavior of the Al-bearing goethites was investigated after the removal of gibbsite and part of the kaolinite from the natural laterites. The spectra of the $\alpha\text{-Fe}_2\text{O}_3$ obtained from goethite "c" after the thermal treatments at various temperatures are given in Fig. 1. Grinding during the preparation of the disks may affect the IR spectra of various minerals, (see e.g., Yariv [15]). No significant changes in the spectra of the Al-bearing protohematites formed at temperatures up to 600°C were observed in the present study if the disks were reground, apart from changes in the intensities of the absorption bands. On the other hand, grinding affected the spectrum of Al-bearing hematite obtained at 1000°C , in the sense that the low frequency absorption band was shifted to a higher value (Fig. 1, c and d). The differences in the behavior during the grinding process between Al-bearing protohematite and its analogous hematite are similar to the differences which were previously observed during grinding between synthetic pure protohematite and its analogous hematite, the latter showing a band displacement from 318 to 333 cm^{-1} upon repeated grinding of the disk [3].

The spectra of the Al-bearing protohematites (obtained from the natural goethites) heated between 250 and 600°C are only slightly affected by the temperature. For example, the spectrum of the protohematite obtained from

goethite "c" is characterized by three strong absorption bands assigned as O^{2-} displacements, at 335–340, 463–470 and 535–545 cm^{-1} ; the last of these shifts to higher frequency with increasing temperature. The most prominent effect of temperature on the IR spectrum was the increasing resolution of the 470–540 cm^{-1} absorption bands (Fig. 1), which may support the conclusion of Schwertmann et al. [10] that the degree of crystallinity of Al-bearing protohematite increases with temperature. At 1000°C, Al-bearing hematites are obtained and the three characteristic bands become very well resolved. The band maxima of the O^{2-} displacement of hematites obtained from the various goethites at 300, 600 and 1000°C, are collected in Table 2. From the Table it is obvious that Al affects some of the absorption bands, shifting them to higher frequencies. The most significant shifts are shown with the high frequency band in samples heated to 1000°C (hematites). It seems plausible that Al, initially present in the precursor goethite, isomorphically substitutes for Fe in the hematite. In conclusion, IR spectra seem to be reliable indicators of Al in the structure of hematite.

Thermal treatment of iron-leached laterites (fourth group)

The thermal behavior of the laterites at 1000°C was investigated after the removal of their goethite. The IR spectra of the calcined laterites are shown in Fig. 2. The weight ratios (Fe_2O_3/Al_2O_3 in the leached samples "a", "b", "c" and "d" are 0.09, 0.19, 0.11 and 0.08, respectively. No corundum was detected in the spectrum of sample "a" which initially did not contain gibbsite. Laterite "d" shows a spectrum typical of corundum. Laterites "b" and "c", on the other hand, which have higher Fe_2O_3/Al_2O_3 ratios, display perturbation of the 585 cm^{-1} peak which increases with the Fe_2O_3/Al_2O_3 ratios, and may be due to substitution of Fe for Al in the corundum structure.

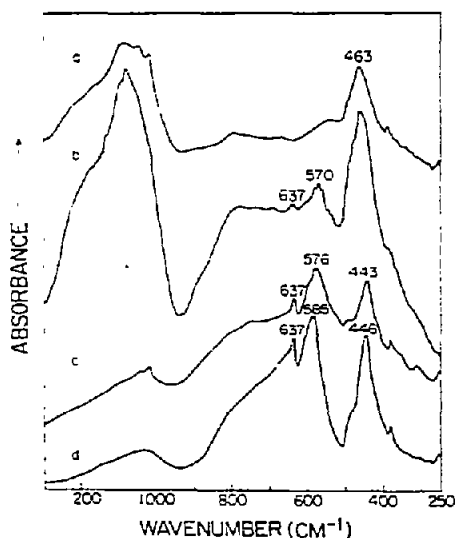


Fig. 2. Infrared spectra of iron-leached laterites calcined for 1 day at 1000°C: (a) laterite "a" (*meta-kaolinite*); (b) laterite "b" (*meta-kaolinite* with some corundum); (c) and (d), laterites "c" and "d", respectively (corundum with very little *meta-kaolinite*).

Thermal treatment of the original and partly aluminum-leached laterites (first and second groups)

Some selected spectra of the original laterites heated to 300°C and 600°C are shown in Fig. 3. Kaolinite persists at 300°C (Fig. 3, a). Its absorption bands overlap with those of hematite and it is thus impossible to estimate the maxima of the hematite bands in the spectra of laterites "a" and "b" heated at this temperature. Since the kaolinite content in laterites "c" and "d" is small, hematite bands are estimable in the spectra of the latter samples heated to 300°C (Fig. 3, d). The spectra of all samples heated to 600°C exhibit characteristic bands of hematite together with bands of metakaolinite; the latter bands appear at 465 and 1065 cm^{-1} and their relative intensities decrease in the order laterite "a", "b", "c" and "d" (Fig. 3, b, c and e). The 465 cm^{-1} band interferes in the accurate estimation of one of the diagnostic bands of the hematites in the spectra of laterites "a" and "b". The metakaolinite bands are considerably weakened after the thermal treatment of

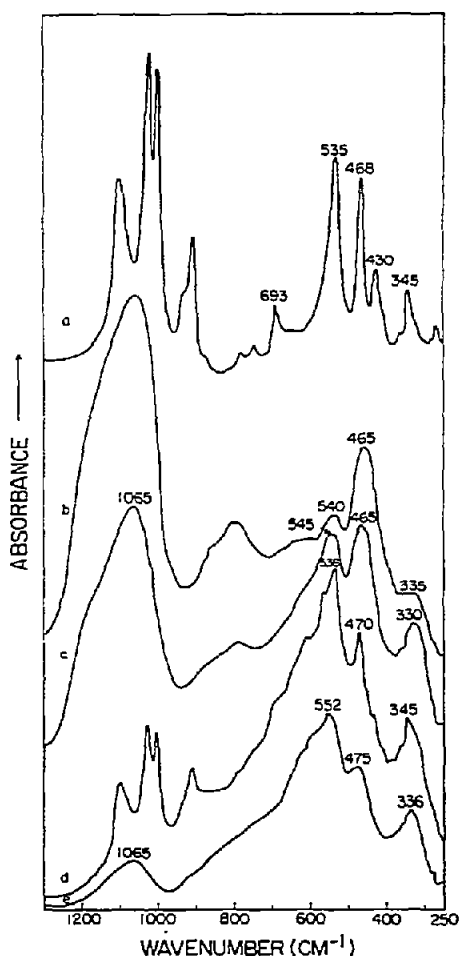


Fig. 3. Infrared spectra of laterites, heated for 1 day at 300 or 600°C: (a) laterite "a", 300°C; (b) laterite "a", 600°C; (c) laterite "b", 600°C; (d) laterite "d", 300°C; (e) laterite "d", 600°C.

TABLE 3
 Band maxima (in cm^{-1}) in the spectra of protohematites and hematites obtained after the calcination of laterites at 300, 600 and 1000°C

Heating temp. (°C)	Source of hematite											
	Laterite "a"			Laterite "b"			Laterite "c"			Laterite "d"		
	Original sample	NaOH treated	z	Original sample	NaOH treated	z	Original sample	NaOH treated	z	Original sample	NaOH treated	z
300°C	z	z	z	z	z	z	345	344	z	345	342 br	z
	z	z	z	z	z	z	468	470	z	470	470	z
	z	z	z	z	z	z	538	535 v.br	z	538	540 v.br	z
600°C	335 sh	338	330	330	330	330	340 br	336	330	336	335 br	330
	465	465	465	465	468 br	468 br	470 sh	470	468 br	475 v.br	478	465
	540 br	540 br	545	545	542 v.br	542 v.br	548	545	542 v.br	552	550	540 br
1000°C	335 sh	340 sh	335 v.br	335 v.br	330 br	330 br	344 br	335 br	330 br	340	340 br	335 c
	468	467	467	467	463	463	450	455	463	450	450	450
	557	557	572	572	550	550	580	564	550	587	580	580
							635 c.	634 v.w.c		637 c	637 c	

br, Broad; w, weak; v, very; sh, shoulder; c, band of corundum; z, overlapping with bands of residual kaolinite.

the original laterites at 1000°C, as a result of the partial recrystallization of the alumino-silicate.

The hematite band maxima of the various original laterite samples (first group), and of the samples whose gibbsite was partly removed with NaOH (second group) are summarized in Table 3. From the Table it is obvious that the band at about 540 cm^{-1} is highly sensitive to both factors, (1) the heating temperature of the laterite sample, and (2) the initial gibbsite content.

(1) Small increments in the band maxima (10–14 cm^{-1}) are recorded when the heating temperature changes from 300 to 600°C. Much larger increments in these maxima (17–37 cm^{-1}) are recorded on heating the laterites to 1000°C. Parallel increments were recorded during the thermal treatments of the chemically isolated Al-bearing goethite, suggesting that at 300°C Al-protoghematite is formed, which at 600°C is slightly recrystallized. Further recrystallization and Al-hematite formation occurs at 1000°C.

(2) The frequency of the band maximum increases with increasing Al content in the sample. The removal of gibbsite by 1.25 M NaOH solutions does not seem to have a significant effect on the location of the band maxima in the spectra of samples heated to 300°C. A slight effect of gibbsite removal is recognized in spectra recorded after heating the laterites to 600°C, but the

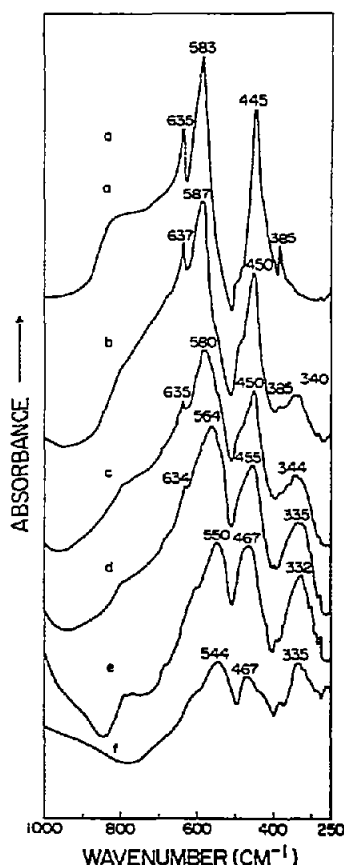


Fig. 4. Infrared spectra of synthetic gibbsite and goethite and of laterites heated for 1 day at 1000°C: (a) synthetic gibbsite (corundum); (b) laterite "d"; (c) laterite "c"; (d) laterite "c" treated for 20 min with NaOH; (e) laterite "b"; (f) synthetic goethite (hematite).

gibbsite removal is very significant if the samples are heated at 1000°C. No changes were detected in the location of this band at 540 cm⁻¹ in the spectra of laterite "a" before and after the 20 min NaOH treatment, because this sample initially does not contain gibbsite which should be removed during this short dissolution process. Alumina incorporation in the hematite of laterite "a" results from the interaction of the iron oxide with the thermal decomposition products of metakaolinite at 1000°C. Metakaolinite segregates into poorly ordered silica and alumina phases [16], and the latter interacts with the iron oxide to form Al-bearing hematite. Only prolonged treatments with NaOH, in which part of the kaolinite is removed, will affect the location of this absorption band (compare Tables 2 and 3).

Selected spectra of laterites heated to 1000°C and of synthetic corundum and hematite are given in Fig. 4. There is a progressive development from the spectrum of hematite to that of corundum with increasing amounts of gibbsite in the laterites. This is manifested by the decrease of the intensity of the 340 cm⁻¹ band relative to the intensities of the other bands. In addition, the 550 cm⁻¹ band shifts to higher frequencies, whereas the 470 cm⁻¹ band shifts to lower frequencies; at the same time these two bands are sharpened. With high Al content an additional band appears at 637 cm⁻¹. This band does not appear in the spectrum of laterite "a" and is very weak in that of laterite "b", after being heated to 1000°C. Furthermore, it is weakened after 20 min treatment with NaOH and does not appear at all if the samples have been treated for 15 h with NaOH before the thermal treatment (cf. Figs. 1 and 4). It is therefore obvious that the 340 cm⁻¹ band represents hematite whereas the 637 cm⁻¹ band represents corundum.

In Part II of this study [17] it will be shown from the X-ray diffractograms that these samples contain physical mixtures of two phases, Al-bearing hematite and Fe-bearing corundum. It is expected that such a mixture will be represented by an IR curve which is a combination of two traces. This combination curve should have two maxima in each of the ranges 550—590 and 440—470 cm⁻¹. However, only one maximum is recorded in each range. Since the corundum concentration is considerably smaller than that of hematite (inferred from X-ray and from the fact that the 637 cm⁻¹ band is weak compared to the other bands), it seems plausible that the maxima recorded in the two mentioned ranges correspond to Al-hematite.

In a previous study on the thermal transformation of goethite to hematite in the presence of additives such as K and Cs salts [6] we showed that during the goethite → protohematite dehydroxylation, the iron oxide became highly contaminated with K⁺ and Cs⁺. During the recrystallization of protohematite to hematite, the iron oxide became free of the alkali ions. However, in the present study it was demonstrated that in the presence of additives which are abundant suppliers of Al ions, such as gibbsite or kaolinite, enrichment of the resulting iron oxide by substituting Al³⁺ takes place during the protohematite → hematite thermal recrystallization process. This difference in affinity between the Al, on the one hand, and the alkali cations, on the other, for the isomorphic substitution of iron is due mainly to different ionic radii and charges. Thus, the affinity of aluminum to hematite — which is found so often in nature — must be considered when considering industrial

separation processes of aluminum from ferruginous bauxites, involving thermal treatments.

CONCLUSIONS

Hematites formed during the thermal transformation of goethites from Venezuelan laterites incorporate Al into their structure to an extent which depends on the initial gibbsite concentration of the samples. This incorporation takes place mainly at 1000°C, during the recrystallization of protohematite to hematite and of amorphous alumina to corundum. Small amounts of incorporated Al can be contributed by kaolinite which segregates at this temperature to poorly ordered silica and alumina phases. Infrared spectroscopy has been successfully employed for the study of isomorphic substitution of Fe by Al in hematites.

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