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INTERACTIONS BETWEEN THE IRON AND THE ALUMINUM MINERALS DURING THE HEATING OF VENEZUELAN LATERITIC BAUXITES. II. X-RAY DIFFRACTION STUDY

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ABSTRACT

Four samples of Venezuelan lateritic bauxites were heated to 300, 600 and 1000°C and the thermal reactions were studied by X-ray diffraction (XRD) and by chemical extractability of silica and alumina. Gibbsite was converted to boehmite at 300°C, to an amorphous phase at 600°C and partly to corundum at 1000°C, with isomorphic substitution of Fe for some of the Al in the corundum structure. Goethite was converted to protohematite at 600°C and to hematite at 1000°C, with isomorphic substitution for Al for some of the Fe in both α-Fe_2O_3 varieties. Ti contributed by ilmenite is also occluded by the hematites. The occlusion of Ti takes place at 1000°C during the decomposition of the ilmenite and concomitant recrystallization of α-Fe_2O_3.

INTRODUCTION

Many investigators have shown that X-ray diffractograms of natural hematites differ from reference synthetic hematite in the following three aspects: (1) most reflections show some shift towards lower spacings; (2) most reflections are much broader, and (3) relative intensities between the various peaks differ from those of the reference synthetic hematite. These discrepancies are explained as resulting from Al replacing Fe in the hematite structure and from a low degree of crystallinity, both properties common among natural hematites (see e.g., refs. 1—3).

In the first part of the present study [4] we demonstrated with the help of IR spectroscopy that natural goethite from Venezuelan lateritic bauxites is converted to Al-bearing protohematite at temperatures up to 600°C and that at higher temperatures this protohematite is converted to Al-hematite. We also demonstrated that the Al content of the resulting hematite depends on the initial concentration of the gibbsite (and to a smaller extent on the kaolinite) in the laterite samples, rather than on the amount of Al which initially replaces Fe in the goethite structure of the starting material. Because

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of this phenomenon we concluded that Al-protohematite is converted via recrystallization to Al-hematite.

The purpose of the present investigation is to (1) determine whether the mechanism suggested for the transformation of goethite to hematite via protohematite in the natural laterites is supported by X-ray studies of these materials, and (2) gain information on other reactions taking place during the thermal treatment of the laterites, which were not detected by IR spectroscopy.

The extractability of alumina and silica with NaOH from the thermally treated laterites was also investigated and compared with extractability from thermally treated gibbsite and kaolinite. Such a comparison is useful to support conclusions drawn from IR spectroscopy and X-ray data on the location of Al in the various mineral phases. According to Janot et al. [2], aluminum incorporated in the iron oxide crystals is not extractable by NaOH. This is important information for the Bayer process when dealing with the extraction of alumina from lateritic bauxite ores.

EXPERIMENTAL

The preparation of the samples was described in Part I of this study [4]. X-Ray powder diffraction patterns were recorded on a Philips diffractometer, using Ni filtered CuK_α radiation. The X-ray unit was operated at 40 kV and 25 mA. The scanning speed was $1°\ 2\theta\ \mathrm{min}^{-1}$.

For the selective extraction of alumina and silica, 0.5 g of the original laterite samples, as well as kaolinite and gibbsite, were suspended in 2.5 ml of 1.25 N NaOH and the suspensions heated for 20 min at 75°C. Three consecutive extractions were carried out on the above samples, both before and after thermal treatment. After centrifugation the supernatants were analyzed for Al and Si by atomic absorption spectroscopy using a Varian 1200 spectrometer.

RESULTS

X-Ray diffractograms of corundum

From the X-ray diffractograms recorded after the thermal treatment of laterites "c" and "d", it is obvious that gibbsite decomposed at 300°C, giving rise to the appearance of characteristic peaks of boehmite at angles corresponding to *d* spacings of 0.611, 0.316 and 0.234 nm. The intensities of these peaks were weaker in cases where the laterites had been treated with NaOH before the thermal treatment. These characteristic peaks disappeared after heating the samples to 600°C, and no other peaks were detected which could be used to identify any aluminum oxide phase. However, if the samples were heated to 1000°C, characteristic peaks of corundum were identified. These peaks, which were not detected in the diffractogram of laterite "a", appeared broad in laterite "b" and very intense and sharp in laterites "c" and "d". The intensities of these peaks were very much weaker if the laterites had been treated with NaOH before the calcination. The weight ratios between corundum and hematite formed at 1000°C were calculated from the ratios between the intensities of the most intense peaks of these two minerals (the 113 and the 104 reflections in corundum and hematite, respectively) and are given in Table 1. The calibration curve for this purpose was prepared using diffractograms of artificial mixtures of synthetic corundum and synthetic hematite. By comparing these ratios with the initial gibbsite—goethite ratios from the laterites (table 1, ref. 4), it is obvious that only part of the alumina had been recrystallized to corundum under the present experimental conditions. The remainder probably forms amorphous alumina and silica—alumina phases.

Table 1 also presents the *d* spacings of the various corundums. From the Table it is obvious that all *d* spacings shift to higher values compared to those characteristic of the standard corundum. These shifts indicate that some isomorphous substitution of Fe for Al takes place in the corundum crystal [2]. This is in agreement with the band shifts observed in the corresponding IR spectra [4].

X-Ray diffractograms of Ti minerals

Ilmenite was detected in all the samples which were heated to 300 and 600°C. The peaks were more intense in the diffractograms of laterites which had been treated with NaOH before the thermal treatment. No ilmenite was detected in any of the samples which were heated to 1000°C. At this temperature ilmenite is usually transformed into pseudobrookite [5]. Ilmenite was identified by characteristic reflections at angles corresponding to 0.274,

TABLE 1

Characteristic *d* spacings (in nm) of corundums obtained during the thermal treatments of synthetic gibbsite and of the laterites heated at 1000°C and the weight ratios between corundum and hematite [calculated from ratios between the intensities of the (113) reflection of corundum and the (104) reflection of hematite $I(113)_C/I(104)_H$ *]

hkl	$I/I(113)$	Source of corundum			
		Standard gibbsite	Laterite "b"	Laterite "c"	Laterite "d"
012	75	0.346	0.347	0.349	0.347
104	90	0.254	0.255	0.256	0.255
110	40	0.237	n.d.	0.239	0.238
113	100	0.208	0.209	0.209	0.209
024	45	0.174	0.175	0.175	0.174
116	80	0.160	0.161	0.161	0.161
Corundum/hematite weight ratio *:			0.26	0.25	0.63

n.d. = Not detected.

* Calibration curve was prepared from pure synthetic hematite and corundum.

0.254, 0.233, 0.186 and 0.172 nm. Very small peaks of brookite, corresponding to 0.290, 0.248, 0.197 and 0.188 nm, were detected in diffraction patterns of samples heated at 1000°C.

X-Ray diffractograms of hematite

Characteristic *d* spacings calculated from the most intense peaks of diffractograms, recorded after heating the synthetic goethite and laterite samples to 300, 600 and 1000°C, are given in Table 2. From the Table it is obvious that most *d* spacings shift to lower values compared to those characteristic of the standard hematite. Such shifts normally accompany substitution of Fe by Al in the hematite lattice [6—9]. A weak peak, which corresponds to a (113) reflection, is extremely broad in the diffractograms recorded after heating the laterites to 300°C. The line is split into two peaks after heating the samples to 600°C.

The slight silica and alumina extraction by NaOH (20 min) before the thermal treatment did not cause any significant change in the characteristic spacings of the hematite or in the relative intensities and peak widths. This is in contrast to the significant change which this chemical treatment had on the location of the characteristic IR absorption bands of hematite [4].

TABLE 2

Characteristic *d* spacings (in nm) of protohematites and hematites obtained during the thermal treatments of synthetic goethite and Venezuelan laterites

Temp. (°C)	*hkl*	Source of hematite				
		Synthetic goethite	Laterite "a"	Laterite "b"	Laterite "c"	Laterite "d"
300	012	0.368	z	z	~0.367	0.367
	104	0.270 br	<0.270 *	<0.270 *	0.269	0.269
	110	0.252	0.249	0.250	0.250	0.251
	113	0.221				
		0.220	~0.219 br	~0.219 br	~0.218 br	<0.219 *
	116	0.170				
		0.169	0.169	0.169	<0.168 *	0.168 br
600	012	0.369	0.369	0.369	0.368	0.367
	104	0.270 br	0.269	0.269	0.269	0.269
	110	0.252 br	0.251	0.251	0.250	0.251
	113	0.220	0.220	0.220 sh	0.220 sh	0.220
			0.219 sh	0.218	0.219	0.218
	116	0.170	0.169	0.168	0.168	0.169
1000	012	0.368	0.366	0.364	0.365	0.365
	104	0.269	0.268	0.267	0.268	0.268
	110	0.252	0.251	0.249	0.250	0.250
	113	0.221	0.220	0.219	0.220	0.220
	116	0.169	0.168	0.168	0.168	0.168

* Extremely broad, impossible to determine the exact value.
br, Very broad; sh, shoulder; z, kaolinite interference.

Synthetic goethite is converted to protohematite at 300°C and almost completely to hematite at 600°C. The X-ray diffractograms of protohematite obtained from synthetic goethite differ from that of reference hematite (obtained at 1000°C) and from hematite formed at 600°C [10] in line broadening and in relative intensities as follows: (1) only lines associated with (110), (113) and (300) planes are sharp whereas the other lines are much broader than those of reference hematite (Table 3); (2) the relative line intensities *I*/*I*(104) are higher in the diffractograms of protohematite compared to those of reference hematite (Table 4). The diffractograms obtained from heating the natural laterite samples at 300—600°C also differ from that of reference hematite in line broadening and in relative line intensities (Tables 3 and 4). Moreover, most of the peaks are broader than those of the synthetic protohematite (obtained at 300°). This indicates that the resulting products of heating the natural laterites are more poorly crystalline than the synthetic protohematite.

Two drastic changes, which are diagnostic for the recrystallization of the iron oxide, are observed after heating the laterite samples to 1000°C: (1) most of the diffraction peaks become sharp and the widths at half height are equal to those of the standard hematite (Table 3), and (2) the intensity ratios of the various peaks relative to the (104) reflection decrease and approach the ratios obtained for the standard hematite (Table 4).

TABLE 3

Widths at half height (in 2θ units) of characteristic X-ray diffraction peaks of Fe_2O_3 obtained during the thermal treatments of synthetic goethite and of Venezuelan laterites

Source of hematite	Temp. (°C)	*hkl*				
		102	104	110	113	116
Synthetic goethite	300	0.80	0.70	0.30	0.45	0.55
	600	0.30	0.30	0.25	0.35	0.30
	1000	0.25	0.20	0.25	0.25	0.30
Laterite "a"	300	z	1.30	z	z	z
	600	0.60	0.90	0.50	0.50	0.65
	1000	0.20	0.30	0.30	0.55 *	0.25
Laterite "b"	300	z	<1.50	z	z	z
	600	0.60	1.00	0.65	0.90 *	0.70
	1000	0.25	0.25	0.25	0.25	0.30
Laterite "c"	300	z	0.80	z	<1.10	z
	600	0.60	0.95	0.70	1.50	0.55
	1000	0.25	0.20	0.25	0.30	0.30
Laterite "d"	300	0.65	0.90	0.65	1.05	1.00
	600	0.50	0.85	0.65	1.00 **	0.80
	1000	0.25	0.20	0.25	0.30	0.30

* This line is very broad because it comprises two maxima, see Table 2.

z, Overlapping with peaks of either kaolinite or quartz.

** Extremely broad, impossible to determine the exact value.

TABLE 4

Ratios of intensities (in percentage) of characteristic X-ray diffraction peaks of Fe_2O_3 obtained during the thermal treatments of synthetic goethite and of Venezuelan laterites, relative to (104) lattice plane $I/I(104)$

Source of hematite	Temp. (°C)	*hkl*				
		102	104	110	113	116
Synthetic goethite	300	30	100	105	35	50
	600	20	100	60	20	45
	1000	25	100	60	20	50
Laterite "a"	300	z	100	z	z	z
	600	50	100	110	65	65
	1000	30	100	70	40 *	50
Laterite "b"	300	z	100	z	z	z
	600	30	100	85	40 *	60
	1000	30	100	65	25	40
Laterite "c"	300	z	100	<100	<55	z
	600	35	100	95	30 *	45
	1000	30	100	65	25	45
Laterite "d"	300	45	100	90	45	55
	600	40	100	85	35 *	50
	1000	30	100	60	20	40

z, Overlapping with peaks of either kaolinite or quartz.

* Ratio determined for the more intensive of the two peaks (see Table 2).

Extractability of alumina from calcined laterites

The effect of the calcination temperatures on the extractability of alumina and silica by NaOH from synthetic gibbsite, standard kaolinite and the various lateritic bauxites is summarized in Table 5. The data of Table 5 represent the summation of three consecutive extractions. Regarding extractability of the silica, in most cases there was no clear decrease in the amount of dissolved SiO_2 during the three consecutive extractions, and in the few cases when we continued with the consecutive extractions more than three times, we found that the dissolution decreased only slightly. On the other hand, the extracted amount of alumina from the heated laterite samples decreased drastically with the number of extractions. In more than half of the cases extractability was already less than 1% in the third extraction. The extractability of alumina from kaolinite is similar to that of silica from this mineral, and there is no clear decrease in the amount of dissolved Al_2O_3 during the three consecutive extractions. It is clear that 20 min is not sufficient time to reach equilibrium in the solubility reaction and that the results presented in Table 5 do not give information on the absolute amounts of extractable alumina and silica, but merely represent a trend on their extraction.

Maximum extractability of alumina from gibbsite is achieved after the

TABLE 5

Extractability of Al_2O_3 and SiO_2 (in percentage) from standard gibbsite, Georgia kaolinite and laterites "a", "b", "c", and "d" by three consecutive extractions with an aqueous solution of NaOH (1.25 N)

Sample	Extracted oxide	Untreated sample	Calcination temp. (°C)		
			300	600	1000
Gibbsite	Al_2O_3	2.77	38.70	7.73	0.16
Kaolinite	Al_2O_3	1.32	1.12	12.33	0.66
	SiO_2	2.33	1.99	14.27	27.63
Laterite "a"	Al_2O_3	2.17	3.81	8.04	0.21
	SiO_2	2.07	7.81	9.77	5.62
Laterite "b"	Al_2O_3	5.80	10.04	7.12	0.26
	SiO_2	1.90	4.45	7.27	4.81
Laterite "c"	Al_2O_3	9.35	15.04	5.24	0.75
	SiO_2	0.73	0.90	2.03	1.50
Laterite "d"	Al_2O_3	12.22	15.87	4.81	0.37
	SiO_2	0.70	1.14	2.41	1.90

mineral has been heated to 300°C, and transformed to boehmite. Extractability decreases when the boehmite is dehydroxylated at 600°C and drastically falls when corundum results at 1000°C.

The effect of calcination temperature on the extractability of alumina and silica from kaolinite is different. Maximum extractability for both oxides is achieved only at 600°C, after the dehydroxylation of this mineral and its transformation to *meta*-kaolinite. At 1000°C, after the segregation of the *meta*-kaolinite into silica and alumina phases, the extractability of the silica decreases slightly, whereas that of the alumina is drastically reduced.

Regarding the extractability of silica from the laterites, all the samples show behavior characteristic of kaolinite, namely, a maximum in extractability is reached after the samples are heated at 600°C when the kaolinite is transformed to *meta*-kaolinite. On the other hand, the extractability of alumina depends on the sample's mineralogical composition. It is typical of kaolinite in laterite "a", and gibbsite in laterites "c" and "d" and seems to be controlled by both minerals in laterite "b". The alumina phases formed during the calcination of laterites "c" and "d" at 300 and 600°C are less extractable than the alumina phase which is formed from gibbsite at the same temperature. This is probably due to surface coatings by silica and iron oxide (protohematite), which results in the lowering of the solubility of the aluminum oxide. On the other hand, the alumina phases which are formed at 1000°C are more extractable than the pure corundum phase. This may be explained if we assume that the resulting alumina phase at this temperature is an iron-bearing corundum phase, whose existence was proved from the X-ray study. It seems plausible that such a solid solution phase, which forms very fine particles [2] and which is thermodynamically less stable than a pure corundum phase, may be more extractable by NaOH solution than the pure phase. Corundum from laterite “c” contains higher amounts of occluded Fe than that from laterite “d”, and is therefore more soluble than the latter.

DISCUSSION

The present investigation has clearly demonstrated that Al-bearing goethite is thermally transformed to Al-bearing hematite via the analogous protohematite. In this sense the natural Al-bearing goethite and the pure synthetic goethite behave similarly. However, the apparent minimum temperature at which a rapid transformation of protohematite to hematite begins is above 600°C; the latter being the minimum temperature necessary for the respective transformation of synthetic Al-free iron oxide to take place in the absence of additives. It may be concluded that in the Venezuelan laterites Al does not inhibit hematite formation unless a suitable temperature is applied. These results support the suggestions of Schwertmann et al. [3] and of Perinet and Lafont [11] that differential line broadening in the X-ray diffractograms of α-Fe_2O_3 from various soils and bauxites is due to the existence of iron oxides having a crystallographic character similar to that of protohematites in the natural samples.

Whereas lateritic hematite and protohematite can be unequivocally differentiated using the X-ray diffractograms, only one significant difference was ascertained between their IR spectra, namely a shift of the Fe—O high frequency band. On the other hand, there are drastic differences between the IR spectra of synthetic pure protohematite and hematite [12]. In addition to the shifts of the maxima of all three bands, the latter displays broad absorption bands whereas protohematite, which is of a very small particle size, exhibits very sharp absorption bands. The diffuse character of the absorption bands of the Al-bearing protohematite may indicate that this material is much more defective than the protohematite obtained from synthetic goethite; the latter has a fully ordered structure in the hematite *a* direction. This is in agreement with the fact that X-ray peaks are broader in the lateritic protohematites than those of the pure synthetic sample (Table 3).

There is some contradiction between the results of the X-ray and the IR studies of the above hematites. Shifts in the characteristic IR absorption bands of the hematite are correlated with the initial gibbsite/goethite ratio (or total Al_2O_3 content of the laterite) and were therefore suggested as indicators of substitution of Fe by Al in the hematite structure [4]. According to this assumption, hematite formed at 1000°C from laterite “d” has the highest ratio of substituted Al and this ratio gradually decreases in the order laterite “c”, “b” and “a”. On the other hand, many investigators showed that Al isomorphous substitution causes shifts in the *d* spacings to lower values, particularly the (012), (110) and (113) reflections. According to Table 2 it appears as if the hematite formed at 1000°C from laterite “b” has the highest ratio of substituted Al. This is neither in agreement with the IR data nor with what one would expect from the chemical composition of the system. It is therefore more plausible that in this multicomponent system other elements in addition to Al may substitute for Fe in hematite, causing the *d* spacings to shift either towards lower or higher values. Recently, Fitzpatrick et al. [13] showed that titanium can be incorporated in the iron oxide structures. Furthermore, the presence of titanohematite has been detected in soils. By comparing X-ray diffractograms of hematite and ilmenite one would expect that Ti occlusion in hematite will shift *d* spacings to higher values [5]. Laterite "b" has the lowest ilmenite content and is therefore the least affected by Ti occlusion. On the other hand, laterite "d" has the highest ilmenite content and the hematite formed at 1000° C will be highly contaminated by Ti ions. Values of *d* spacings corresponding to hematite "b" are therefore lower than those of hematite "d" formed in the more Ti-rich laterite, although from their IR spectra it was concluded that the former contains less occluded Al ions. The following two XRD observations may support this suggestion: (1) we did not find any significant difference between the X-ray diffractograms of either the NaOH extracted (20 min) samples before the thermal treatment or from the thermally treated samples which were not NaOH treated, and (2) ilmenite was detected by X-ray in the samples heated to 300° C and 600° C but disappeared after the samples were heated to 1000° C. Diffractograms of the latter show very weak and diffuse lines of brookite, and therefore it is suggested that during the thermal transformation of ilmenite to brookite some of the Ti ions diffuse into the hematite which at this temperature is recrystallizing.

The extractability experiments carried out with NaOH (Table 5) give some additional information about the character of the solid phases. Silica is extracted from a silica—alumina phase which seems to be uniform. This is inferred from the solubility of silica which is almost constant during the three consecutive extractions. Alumina, on the other hand, is extracted from several different solid phases, and its solubility decreases with the number of extractions. The extractability of alumina from the laterites heated at 300° C can be correlated with the total Al_2O_3 content initially present in the sample; the extractability increases with increasing alumina concentration. On the other hand, the extractability of alumina from the laterites heated at 600° C increases with the total SiO_2 content of the sample. The thermal reactions between the alumina and the iron oxide become critical at 1000° C and their effect on the extractability of Al becomes recognizable after heating the samples at 1000° C.

REFERENCES

1 Ch. Janot and H. Gibert, Bull. Soc. Fr. Mineral. Cristallogr., 93 (1970) 213.

2 Ch. Janot, H. Gibert, X. De Gramont and R. Biais, Bull. Soc. Fr. Mineral. Cristallogr., 94 (1971) 367.

3 U. Schwertmann, R.W. Fitzpatrick and J. Le Roux, Clays Clay Miner., 25 (1977) 373.

4 E. Mendelovici and S. Yariv, Thermochim. Acta, 45 (1981) 327.

5 R.W. Fitzpatrick and J. Le Roux, in S.W. Bailey (Ed.) Proceedings of the International Clay Conferenece, Mexico City, 1975, p. 585.

6 E. Pouillard, Ann. Chim., 5 (1950) 164.
7 S. Caillere, L. Gatineau and S. Henin, C.R. Acad. Sci. Fr., 250 (1960) 3677.
8 G. Shirane, G.E. Cox and S.L. Roby, Phys. Rev., 125 (1962) 1158.
9 G. Perinet and R. Lafont, C.R. Acad. Sci. Paris, Ser. C, 275 (1972) 1021.
10 H.P. Rooksby, in E. Brown (Ed.), The X-Ray Identification and Crystal Structures of Clay Minerals, London Mineralogical Society, 1961, p. 354.
11 G. Perinet and R. Lafont, C.R. Acad. Sc. Paris, Ser. C, 274 (1972) 272.
12 S. Yariv and E. Mendelovici, Appl. Spectrosc., 33 (1979) 410.
13 R.W. Fitzpatrick, J. Le Roux and U. Schwertmann, Clays Clay Miner., 26 (1978) 189.