Thermochimica Acta, 36 (1980) 25—38
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INFRARED STUDY OF THE THERMAL TRANSFORMATION OF GOETHITE TO MAGNETITE IN ALKALI-IODIDE DISKS

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(Received 20 June 1979)

ABSTRACT

Synthetic and natural goethites (0.5—1.5 mg) were heated up to 600°C in alkali-halide disks (400 mg). The thermal transformations occurring at different temperatures are found to depend on the preparation of the disks. For mixtures of alkali-halides and goethite not ground during the preparation of the disks, heating at >200°C resulted in protohematite, which persisted up to 600°C. However, disks which were subjected to repeated grinding—pressing cycles before thermal treatments gave rise to protohematite at >200°C, which on further heating at >330°C was transformed to a transitional iron oxide. In CsI disks, the transitional oxide derived from synthetic goethite can be further transformed to maghemite at 500°C; however, almost no maghemite could be obtained from natural goethite. At 600°C, both the transitional oxide and the maghemite resulting from the synthetic goethite in CsI disks were reduced to magnetite. On the other hand, in KI disks, transitional oxides obtained from both synthetic and natural goethites were reduced to magnetite upon re-pressing and gradual heating of the disks at 600°C. In KI disks, magnetite can be formed only if the reduction temperature is reached gradually, whereas in CsI disks magnetite is formed upon direct heating of the disks to 600°C. The iron oxides referred to above, including the transitional oxides resulting from thermal treatments, were studied by IR absorption spectroscopy.

INTRODUCTION

The oxidation—reduction reactions occurring between iron and iodine in aqueous systems have been thoroughly investigated (see, for example, a discussion by Kolthoff and Sandell [1]). The normal oxidation potentials for the systems Fe^{3+}/Fe^{2+} and $I_2/2\ I^-$ are 0.78 and 0.58 V, respectively, and it is therefore expected that the following reaction will be favored in aqueous systems

$$Fe^{3+} + I^- \rightarrow Fe^{2+} + 1/2\ I_2$$

The occurrence of the ferric ion in the hydrated form is essential in this reaction, and if it is transformed into a stable complex or a slightly soluble compound, the oxidation potential may change and the ferric ion will not be reduced. However, very little is known about the oxidation—reduction reac-

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tions which may take place in the solid state under thermal conditions.

In a previous publication [2] we studied the reactions which occur on heating very dilute concentrations of goethite in CsI disks (~0.25%). We found that at 250°C the goethite is dehydroxylated, forming the poor crystalline variety of α-Fe_2O_3 which we defined as protohematite; then, under very special conditions, thermal treatment at 500°C results in the transformation of protohematite to maghemite via a transitional oxide. It should be noted that thermal treatment of goethite in the temperature range 200—600°C usually results in protohematite, which is recrystallized at higher temperatures, forming the well-ordered crystalline variety of α-Fe_2O_3 known as hematite [3].

In the present paper we describe the effect of temperature on the iron oxides obtained by heating synthetic and natural goethites up to 600°C in KI and CsI matrices, and show that under very special conditions iron can be thermally reduced, giving rise to the formation of magnetite. For the sake of comparison, thermal transformations of goethite in NaCl, NaBr, KCl, KBr, RbCl, CsCl and CsBr disks are also described.

Infrared spectroscopy is a useful tool for the present investigation. It is preferable to X-ray methods as it can be used successfully to distinguish between protohematite and hematite [4], as well as between magnetite, maghemite and hematite [5], even in micro-quantities. Since the alkali-halide matrix does not absorb IR radiation in the region used for the study of iron oxides, there is no need to distinguish between the iron oxide and the alkali-halide for an IR study, as would be necessary if X-ray analysis were to be used for the same purpose.

EXPERIMENTAL

Materials

Synthetic goethite was obtained by titrating $FeCl_3 \cdot 6\,H_2O$ with KOH to pH 13 and aging the precipitate at 60°C for 4 days [6]. The crystalline goethite product was characterized by X-ray and IR methods. Natural goethite was obtained from Venezuelan laterites by shaking the ground sediment with 1.25 M NaOH [7] at 75° for 16 h. The resulting solid was washed by centrifuging with H_2O to pH 7 and then washed with acetone; finally it was air-dried. This goethite has previously been studied by X-ray diffractometry and IR spectroscopy. From a selective dissolution study [8], the chemical composition of the natural goethite was found to be $(Fe_{0.76}Al_{0.24})$-O(OH).

The alkali-halides were supplied by Merck. They were of a "suprapur" grade suitable for spectroscopic study.

Methods

Mixtures were prepared by hand-mixing 0.5 or 1.5 mg synthetic and natural goethites in 200 mg of all alkali-halides and in 400 mg KI or CsI.

Three parallel series of thermal treatments of the mixtures were carried out, two in disk form, unground and re-ground, respectively, and one in powder form. The unground disks (13 mm diameter) were prepared by pressing the hand-mixed mixture at 30 tons for 30 sec. The re-ground disks were prepared by repeatedly grinding and pressing the same disk at least three times. The powdery mixtures were obtained by re-grinding the ground disks.

The disks and powder mixtures were heated for 1 day in air at 250° C, followed by heating at 500° C, and then at 600° C for several days. Each day the disks were re-pressed and IR spectra were recorded at ambient temperature using a Perkin—Elmer 283 IR spectrophotometer. Some experiments were carried out by gradually heating the disks, from initial temperatures between 200 and 300°C up to 600°C. The disks were left for several days at each temperature (200, 230, 250, 300, 330, 360, 400, 450, 500, 550 and 600° C), and IR spectra were recorded every day after the disks had been re-pressed, until no significant changes in the spectra were recorded for each temperature. Parallel experiments were carried out by leaving the disks in the oven during the whole period of gradual heating until the oven reached the highest temperature (600° C). These disks were not re-pressed during the thermal treatment.

The magnetic activity of the various oxides obtained during the thermal transformations [9] was tested by examining whether or not the disks were attracted by a conventional small hand magnet.

RESULTS AND INTERPRETATIONS

The effect of grinding on the spectrum of goethite

Infrared spectroscopy is a useful tool in the study of ground mixtures of minerals and alkali-halides [10,11].

When the disk is repeatedly ground the Fe—O doublet at 397 and 405 cm^{-1} becomes a single band with a maximum at 407 cm^{-1} (Fig. 1). The number of re-grindings necessary for the disappearance of the 397 cm^{-1} band depend on the concentration of the disk. One re-grinding is sufficient if the disk contains 0.3 mg in 200 mg KI, but the 397 cm^{-1} band still appears after three re-grindings if the disk contains 1.5 mg goethite in 200 mg KI.

The intensity of this band compared to that of the other bands increases as a result of the repeated grinding—pressing cycles. The absorbance intensity ratio between the 405—407 cm^{-1} band and the 270 cm^{-1} band depends on the goethite concentration in the disk, and for a mixture containing 0.4 mg goethite in 200 mg KI the ratio is 1.1 for the unground sample and becomes 1.45, 1.72 and 1.84 after 1, 3 and 5 repeated grinding—pressing cycles, respectively. These values decrease upon increasing the concentration of goethite in the disks. After the sixth cycle this ratio begins to decrease. The band at 640 cm^{-1} is only slightly affected by the grinding—pressing cycles, becoming rather sharper. The absorbance intensity ratio between this and the 270 cm^{-1} band is 0.36, and does not change upon grinding. The difference between the behavior of the 407 cm^{-1} band and the other two bands

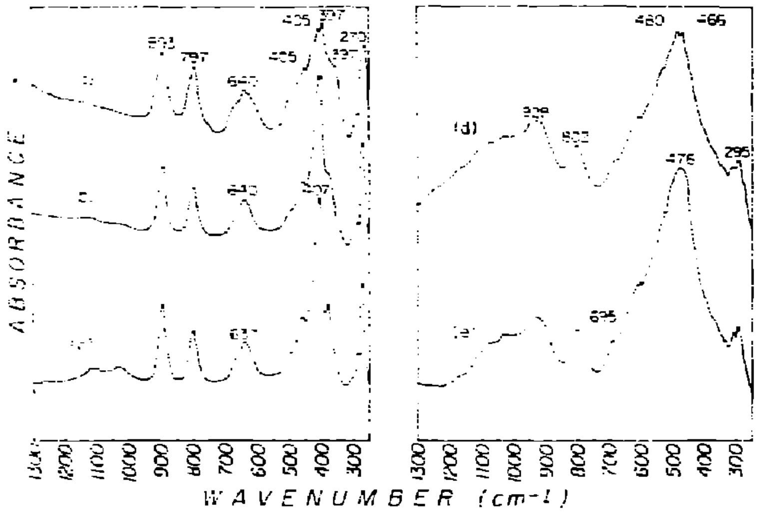

Fig. 1. IR spectra of synthetic goethite (0.4 mg) in KI disks (400 mg). (a) unground; (b) re-ground and re-pressed (one cycle); (c) re-ground and re-pressed (three cycles). IR spectra of natural goethite (1.0 mg) in KI disks (400 mg). (d) unground; (e) re-ground and re-pressed (three cycles).

may indicate that goethite crystals are cleaved in a certain definite direction during the grinding process, the 407 cm^{-1} band corresponding to a vibration perpendicular to the plane of cleavage. The intensity ratio between the δ(OH) band [12] at 890 and the 270 cm^{-1} band is 0.72, while that between the γ(OH) band [12] at 800 and the 270 cm^{-1} band is 0.49. No indication of decomposition was seen after five re-grinding—re-pressing cycles.

The natural goethite, like the synthetic mineral, is sensitive to grinding. An unground disk has a doublet at 466 and 480 cm^{-1} which becomes a single band at 476 cm^{-1} upon repeated grinding (Fig. 1d, e), but is very broad compared to the 407 cm^{-1} band of synthetic goethite. The absorbance intensity ratios between the 476 cm^{-1} band and the 295 cm^{-1} band is 3.4 for a non-ground disk and becomes 3.8, 4.1 and 4.7 after 1, 3 and 5 re-grinding—re-pressing cycles, respectively. A shoulder at ~690 cm^{-1} is only slightly affected by the grinding cycles, thus becoming sharper. The absorbance intensity ratio between this band and the 295 cm^{-1} band is 0.18 and does not change with grinding—pressing cycles. The difference between the behavior of the 470 cm^{-1} band and the other two bands may again indicate that, as a consequence of grinding, the goethite crystals are cleaved in a certain definite direction, the 470 cm^{-1} band corresponding to a vibration perpendicular to the plane of cleavage. This might mean that grinding results not only in disaggregation but also in a formation of thinner crystalline units. The intensity ratios of the 930 and 270 cm^{-1} bands and the 800 and 270 cm^{-1} bands are 0.68 and 0.80, respectively, and do not change upon re-grinding—re-pressing (up to five times).

Thermal treatments of synthetic goethite

The spectra recorded after heating the synthetic goethite powder mixtures or disks (unground and re-ground) in the presence of any of the alkali-halides, for 2 weeks at 200° C, 2 days at 230° C or for 1 day at 250—300° C, are characteristic of a multidomain of protohematite. The multidomain of protohematite has been characterized [4] by a doublet at 297 and 305 cm^{-1}. In the ground unaggregated form this doublet becomes a single band. located at 308 cm^{-1}. No significant changes were observed in the spectra of either the powder mixtures or the unground disks on heating to higher temperatures (up to 600° C). Disks of the starting material (goethite) or the resulting protohematite were not attracted by a magnet. The protohematite disks were reddish-brown in color. However, thermal treatments on the re-ground disks resulted in significant changes in the IR spectra, and also, in some cases, in the magnetic properties and color of the disks.

KI disks

The changes in the spectral and magnetic properties which occur during the gradual thermal treatment of re-ground KI disks of synthetic goethite can be summarized as follows. The spectrum obtained at temperatures between 200 and 300° C is that of protohematite (Fig. 2a). At this stage the reddish-brown disks do not show magnetic activity. At ~330° C the spectrum exhibits an additional absorption at 565 cm^{-1} and a shoulder at 348 cm^{-1}, with intensities which increase with the number of re-grinding and re-pressing cycles carried out on the goethite disk. When the disk is heated to higher temperatures (~400° C) it turns black in color and new bands predominate in the absorption spectrum, the bands which characterize protohematite disappearing. These spectra do not correspond to hematite [4], maghemite [5], magnetite [5] or wustite [13], and presumably represent a transitional oxide. Similar spectra are obtained from disks pre-heated at 250° C and then heated for 1 day at 500° C (Fig. 2b, h).

On prolonged heating at 500° C, the band at 348 cm^{-1} shifts to 360 cm^{-1}, and after a longer heating period a shoulder at 390 cm^{-1} develops very slowly; this may be diagnostic for magnetite. In addition to magnetite, very small bands characteristic of hematite appear at ~320 and 460 cm^{-1}(Fig. 2c, d). The relative intensities of the latter bands increase with increasing initial concentration of goethite in the KI disks, and if the temperature is raised to 550° C.

For an initial goethite content of 1.5 mg, the diagnostic absorption of magnetite, although very weak, could be detected after only 1 day's heating at 500° C; the same spectrum also shows the absorptions characteristic of the transitional oxide (Fig. 2n). At this stage the disk is strongly attracted by the magnet, whereas a KI disk containing 0.5 mg goethite heated for several days at 500° C is only slightly attracted by the same magnet.

On heating the ground disks gradually to 600° C, their spectra showed the diagnostic band of magnetite at 390 cm^{-1} after 1 day at 600° C; in addition, the 560 cm^{-1} band shifts to 575 cm^{-1}. The 390 cm^{-1} absorption appears whether the disks were pre-heated at 500° C for 4 days or 22 days. The intensity of this band increases with the length of time the sample was held at 600° C, whereas the converse is true for the intensities of the 348 and 360 cm^{-1} bands (diagnostic of the transitional oxide) (Fig. 2e, i, j, o, p).

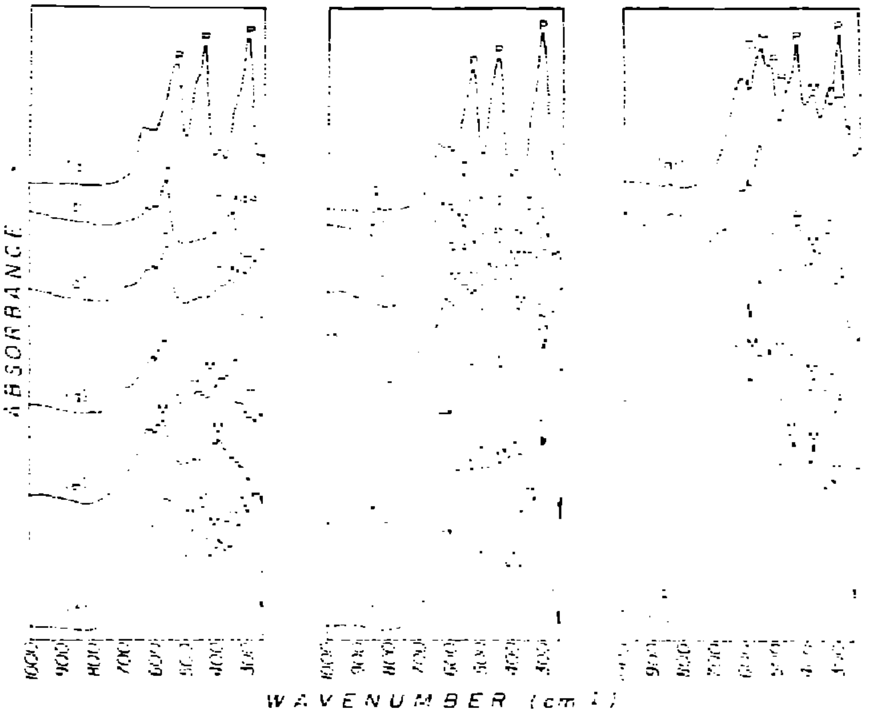

Fig. 2. IR spectra of synthetic goethite in KI disks (400 mg). (a) goethite (0.5 mg) in a re-ground and re-pressed (three cycles) disk, heated at 250°C, 1 day; (b) sample (a) heated at 500°C, 1 day; (c) sample (a) heated at 500°C, 14 days; (d) sample (a) heated at 500°C, 22 days; (e) sample (d) heated at 600°C, 14 days; (f) sample (a) heated at 500°C, 5 days and at 600°C, 7 days without being re-pressed during the thermal treatment; (g) goethite (0.5 mg) in a re-ground and re-pressed (one cycle) disk, heated at 250°C, 1 day; (h) sample (g) heated at 500°C, 5 days; (i) sample (h) heated at 600°C, 6 days; (j) sample (h) heated at 600°C, 10 days; (k) goethite (0.5 mg) in a re-ground and re-pressed (three cycles) disk, heated directly at 500°C, 4 days; (l) sample (k) heated at 600°C, 6 days; (m) goethite (0.5 mg) in a re-ground and re-pressed (three cycles) disk, heated directly at 600°C, 7 days; (n) goethite (1.5 mg) in a re-ground and re-pressed (three cycles) disk, heated at 250°C, 1 day and then at 500°C, 5 days; (o) sample (n) heated at 600°C, 6 days; (p) sample (n) heated at 600°C, 13 days. (P, protohematite; H, hematite; M, magnetite; T, transitional oxide.)

The diagnostic absorptions of hematite develop slowly and increase in intensity during heating at 600°C. They could be detected only after 10—14 days' heating and if the disks were highly concentrated in iron oxide (1.5 mg) or were partly ground. At this stage the color of the disks became brownish-grey with dispersed black points and stains.

When ground disks of goethite were heated directly at 500 or 600°C, protohematite was the main product (Fig. 2k, m). At this stage the brown disks did not show any magnetic activity. Magnetite was detected neither if the disk was pre-heated at 500°C nor if the same disk was then heated at 600°C (Fig. 2l).

The re-pressing of the disks several times during thermal treatment is essential for the formation of magnetite. A re-ground disk which was gradually heated up to 600°C without being re-pressed during thermal treatment gave rise to the formation of protohematite with minor amounts of magnetite (Fig. 2f).

CsI disks

At temperatures below 500° C, the changes taking place in the spectral and magnetic properties of the re-ground CsI disks of goethite during gradual thermal treatment are similar to those occurring in KI re-ground disks under the same conditions. At 500° C, however, a difference appears between the two groups of disks. This can be summarized as follows. The spectrum obtained at temperatures between 200 and 300° C corresponds to protohematite (Fig. 3a). At this stage the reddish-brown disk is not attracted by the magnet. At higher temperatures (300—450° C) the transitional oxide is gradually developed, giving rise to absorption maxima at 348 and 562 cm^{-1}, with intensities which increase with the number of re-grinding—re-pressing cycles to which the disks have been subjected. As shown previously [2], prolonged

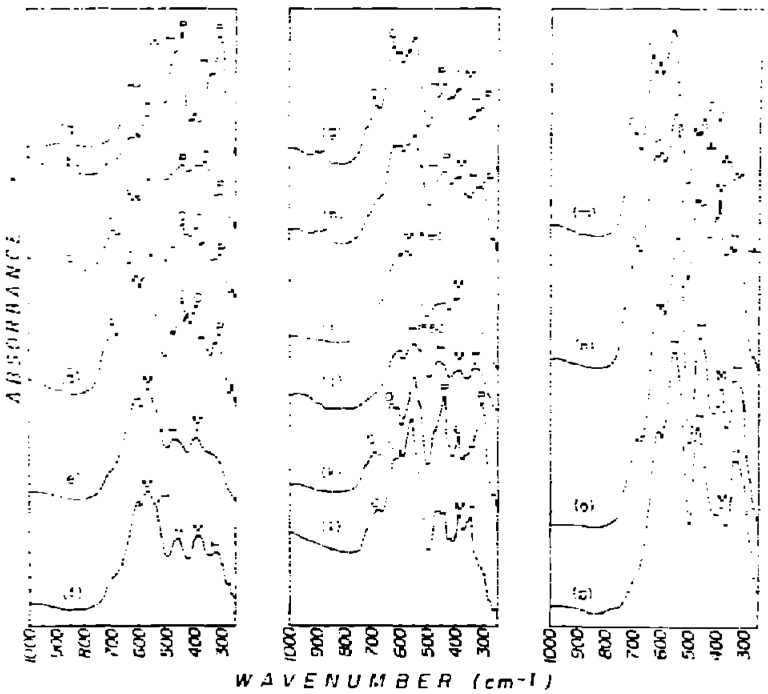

Fig. 3. IR spectra of synthetic goethite in CsI disks (400 mg), re-ground and re-pressed three times. (a) goethite (0.5 mg) heated at 250°C, 1 day; (b) sample (a) heated at 500°C, 1 day; (c) sample (a) heated at 500°C, 5 days; (d) sample (a) heated at 500°C, 22 days; (e) sample (c) heated at 600°C, 3 days; (f) sample (c) heated at 600°C, 6 days; (g) sample (d) heated at 600°C, 3 days; (h) sample (d) heated at 600°C, 6 days; (i) goethite (0.5 mg) heated directly at 600°C, 1 day; (j) sample (i) heated at 600°C, 9 days; (k) unground disk of goethite (0.5 mg) heated at 600°C, 1 day; (l) goethite (1.5 mg) heated at 250°C, 1 day and at 500°C; (m) sample (l) heated at 500°C, 5 days; (n) sample (m) heated at 600°C, 1 day; (o) sample (m) heated at 600°C, 6 days; (p) sample (m) heated at 600°C, 10 days. (P, protohematite; H, hematite; M, magnetite; O, maghemite (oxymagnite); T, transitional oxide.)

heating for several days at 500° C gives rise to the spectrum of maghemite (Fig. 3b—d, l—n), and hence the disk is attracted by a magnet.

At 600° C both magnetite and hematite are obtained, maghemite disappearing within a few days (Fig. 3e—h, n—p). It is difficult to identify magnetite spectroscopically in the presence of maghemite since both oxides show diagnostic absorptions at 390 cm^{-1}. The formation of magnetite in the presence of maghemite can therefore be deduced by comparing the relative intensities of the corresponding bands during the thermal treatment. Judging from the changes in the relative intensities of these bands, it seems plausible that magnetite is formed mainly during the first few days of the thermal treatment at 600° C and that formation of hematite occurs more slowly. As expected from the transformation of maghemite into hematite, there is a decrease in the magnetic attractability of the disk.

A transitional oxide is formed when a ground CsI disk of goethite is heated directly at 500° C for 1 day. This transitional oxide is transformed into maghemite on further heating at 500° C for several days; the reaction is similar to that occurring with disks pre-heated for 1 day at 250° C. However, the transformation is slower in the disk heated directly at 500° C. On heating the latter at 600° C, the maghemite disappears and some magnetite, together with more hematite, are obtained within several days.

When a ground disk of goethite was heated directly to 600° C, a spectrum characteristic of magnetite was recorded. This spectrum also showed the presence of small amounts of hematite. On prolonged heating, the magnetite content decreased, while that of hematite increased (Fig. 3i, j).

Alkali-chloride and bromide disks

Re-ground disks of goethite in alkali halides other than KI and CsI also give rise to protohematites, a transitional oxide, and hematite during thermal treatment. The results of the IR study are summarized in Table 1. Sodium bromide is the only salt which prevents the thermal transformation of protohematite into the transitional oxide. The cesium salts, including CsI (see previous section), show the greatest tendency to promote hematite formation at 600° C. It should be noted, however, that for highly concentrated alkali-halide disks of goethite (33%) the cesium salts showed the smallest tendency to promote formation of hematite at 430° C (paper in preparation).

Small amounts of magnetite were detected at 600° C in the CsBr disks only. In this case magnetite was obtained both in the disks which were heated gradually and in those which were heated directly at 600° C (as for the CsI disks). It should be noted that maghemite was not detected in any spectrum obtained from CsBr disks.

As a result of the thermal treatment, all the disks of protohematite were reddish-brown in color, whereas those of the transitional oxide were darker. The first were not attracted by a magnet, whereas the black disks were attracted slightly. When both products were formed, the disk was dark-brownish, or brownish-grey with black spots and stains if cesium salts were used as matrices.

TABLE 1

Protohematite (P), hematite (H), magnetite (M), and transitional oxide (T), obtained during the thermal treatments of disks of goethite (0.5—1.5 mg) in alkali halides (200 mg). Major component of iron oxide is underlined [a]

	NaCl	NaBr	KCl	KBr	RbCl	CsCl	CsBr
Gradual heating (250—600° C) and re-pressing of the disk every day during thermal treatment							
250° C, 1 day	$\underline{P}$, T(vl)	$\underline{P}$	$\underline{P}$	$\underline{P}$	$\underline{P}$, T(vl)	$\underline{P}$, H(l)	$\underline{P}$, H(vl)
500° C, 1 day	$\underline{T}$	$\underline{P}$	$\underline{T}$	$\underline{T}$	P(vl), T	P, H, T	P(l), $\underline{T}$
5 days	$\underline{T}$	$\underline{P}$	$\underline{T}$	$\underline{T}$	P(vl), T	P, H, T	P(l), $\underline{T}$
600° C, 1 day	$\underline{T}$	$\underline{P}$	$\underline{T}$	$\underline{T}$	P(vl), T	P, H	P(l), $\underline{T}$
600° C, 10 days	$\underline{T}$	$\underline{P}$	$\underline{T}$	$\underline{T}$	P(vl), H(vl)$\underline{T}$	$\underline{H}$	$\underline{H}$, M(l), T(vl)
Gradual heating (250—600° C) without re-pressing of the disk during the thermal treatment							
600° C, 10 days	$\underline{P}$	$\underline{P}$	$\underline{T}$	P, $\underline{T}$	P, H, $\underline{T}$	$\underline{H}$	$\underline{H}$, M(l)
Heating directly to 500° C							
500° C, 1—5 days	$\underline{T}$	$\underline{P}$	P, T	P, T	P, T	$\underline{P}$, H, T	P, T
600° C	$\underline{T}$	$\underline{P}$	P, T	P, T	P, T	H	$\underline{H}$, M(l)
Heating directly to 600° C							
600° C	P, T	$\underline{P}$	P, H, T	$\underline{P}$, H(vl)	P, H, T(vl)	$\underline{H}$	nr

[a] v, very; l, little; nr, non-reproducible results.

Thermal treatment of natural goethite

The thermal behavior of Al-goethite is similar to that of goethite, since Al-protohematite is obtained upon low temperature dehydroxylation (~300° C), the latter being recrystallized to Al-hematite at high temperatures (~1000° C) [14].

Al-protohematite obtained by heating Venezuelan natural goethites for 1 day at 250° C is characterized by a spectrum exhibiting three broad maxima at 340, 470 and 535 cm^{-1}. These maxima appear at 345, 470 and 560 cm^{-1} in the spectrum of Al-hematite obtained at 1000° C.

There are considerable changes in the spectral properties during the gradual thermal treatment of re-ground KI disks of natural goethite, but only slight changes in the magnetic properties. Figure 4 shows that the spectrum recorded after heating at 250° C is similar to that of Al-protohematite, and the disk is therefore not attracted by the magnet. At 500° C, there is evidence of slight magnetic activity, the spectrum indicating the formation of the transitional oxide. At this stage, the high frequency Fe—O stretching band sharpens and shifts to 565 cm^{-1}. The two other characteristic Fe—O bands are significantly broadened and shift to higher values.

When the disk is heated at 600° C a new spectrum is obtained, which shows distinctive bands characteristic of hematite (318, 330 and 460 cm^{-1}) and magnetite (390 and 580 cm^{-1}). However, the intensity ratios of the various peaks differ from those expected from a mixture of pure hematite and magnetite. The presence of the latter should cause magnetic activity; however, none is observed. It is therefore plausible to suggest that the presence of Al causes spectral changes and decreases the magnetic attraction

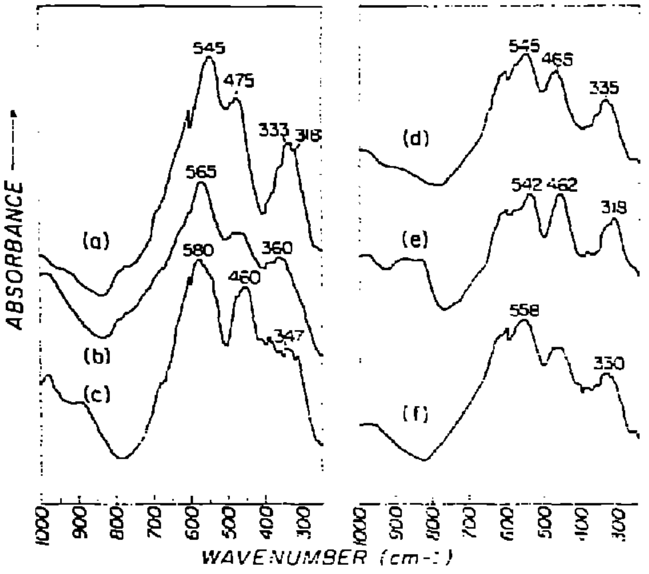

Fig. 4. IR spectra of natural goethite (1.5 mg) in KI disks (400 mg) re-ground and re-pressed (three cycles). (a) heated to 250°C, 1 day; (b) sample (a) heated at 500°C, 5 days; (c) sample (b) heated at 600°C, 5 days; (d) heated directly at 500°C, 5 days; (e) sample (d) heated at 600°C, 9 days; (f) heated directly at 600°C, 1 day.

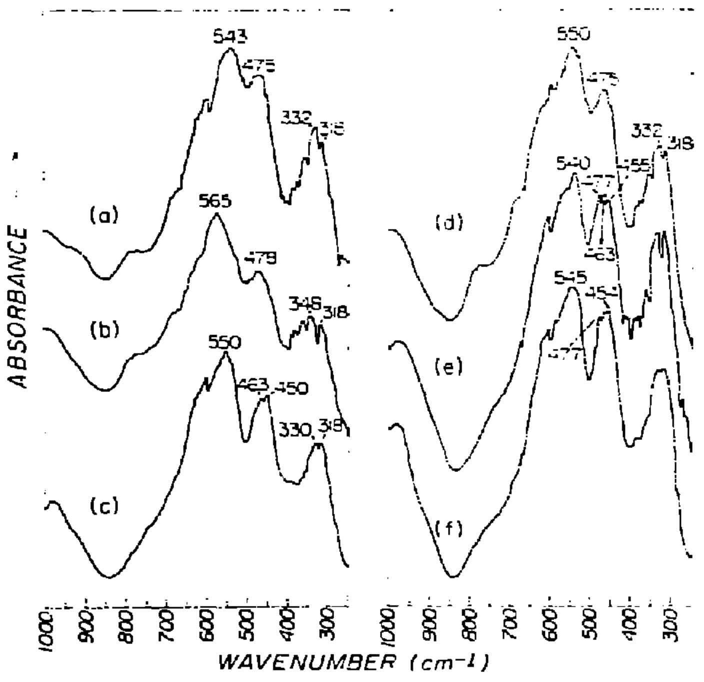

Fig. 5. IR spectra of natural goethite (1.5 mg) in CsI disks (400 mg) re-ground and re-pressed (three cycles). (a) heated to 250°C, 1 day; (b) sample (a) heated to 500°C, 4 days; (c) sample (b) heated to 600°C, 9 days; (d) heated directly to 500°C, 4 days: (e) sample (d) heated to 600°C, 9 days; (f) heated directly to 600°C, 5 days.

of the magnetite. Natural magnetites, especially titano-magnetites, containing inclusions, have much lower susceptibilities than pure magnetite [4].

The behavior of natural goethite in ground CsI disks differs from that in KI disks (Fig. 5) during the gradual thermal treatment. The transformations take place in two stages: at 500 and 600° C.

At 500° C, the high frequency Fe—O band shifts to 563 cm^{-1} and the other two Fe—O bands are broadened. These spectral changes are accompanied by the development of slight magnetism. Shoulders at ~630 and 690 cm^{-1} appear after 5 days of thermal treatment at 500° C, indicating the formation of trace amounts of maghemite. These shoulders do not develop into peaks even if the disk is left at this temperature for 22 days.

At 600° C, the magnetic activity of the CsI disk diminishes. The IR absorption peaks are sharpened and the maxima shift to lower values. The spectrum resembles that of pure hematite rather than that of Al-protohematite. The contribution of the 318 cm^{-1} peak to the low frequency Fe—O absorption increases and it is therefore assumed that Al-protohematite is recrystallized in the CsI disk at this temperature.

When ground disks of natural goethite in KI of CsI are heated directly to 500 or 600° C, Al-protohematite is the only product detected by IR spectroscopy. No other effects (spectroscopic or magnetic) are observed.

DISCUSSION

The transformation of goethite in alkali-halide disks has been followed by IR absorption spectroscopy, the following aspects being stressed:

(a) differences in the heating treatments, which may lead to the reduction of iron;

(b) effects of grinding and pressing the disks on this reduction process.

Grinding is one of the basic processes used in technology and industry. Nevertheless, the effects of grinding on the thermal products of mixtures of minerals have received little systematic attention. Mishirky et al. [15] have shown previously that the thermal reactions of mixtures composed of more than one solid phase are dependent on the interface reactions taking place during grinding. Different results were obtained in the thermal analysis, depending on whether the components of the mixture (kaolinite and calcined kaolinite, in the above-mentioned study) were ground together or separately. Yariv et al. [16] have shown that the type of diluent present in the mixture during the grinding process has significant effects on the thermal reaction. They have shown that these effects are manifestations of the interface and sorption reactions which occur during the grinding process.

The present investigation clearly indicates that the thermal reactions occurring during the treatment of alkali-halide disks of goethites depend on the method of preparation of the disks, and on the sequence of thermal treatment. We are therefore able to differentiate between two distinct types of disks: (1) disks prepared by avoiding the re-grinding process, and (2) disks prepared by repeated grinding and pressing.

The first group of disks behaves in a manner similar to powder mixtures, and only dehydroxylation reactions were observed at temperatures up to 600° C, resulting in protohematite. The second group shows the following thermal transformation sequence. In the first stage, at temperatures above 200° C, synthetic pure goethite gives rise to protohematite, while the sample containing natural Al-goethite gives rise to Al-bearing protohematite.

In the second stage, at temperatures above 330° C, the protohematite is transformed into a transitional oxide of unknown structure. It should be noted that the formation of this transitional oxide is not specific to alkali iodides and that a similar product is obtained with many other alkali halides, e.g. NaCl, KCl, KBr and RbCl. Since the probability of halide oxidation in these alkali salts is very low, the occurrence of considerable amounts of ferrous iron in the transitional oxide can be ruled out.

A third stage begins at 500° C, when the transitional oxide is transformed into maghemite. This stage is specific for CsI disks of synthetic goethite and does not occur in disks of KI or any other alkali halide. A fourth stage occurs at 600° C when part of the iron is reduced and magnetite is obtained. This reaction occurs with the synthetic goethite in both disks, though predominantly with KI; with the natural sample it occurs only in the KI disk. However, if the CsI disk is heated directly to 600° C, the temperature of the fourth stage, a higher fraction of the oxide appears in the form of magnetite. At the same temperature a slow recrystallization process gives rise to hematite. This recrystallization predominates in the CsI disks and is only minor in the KI disks. It is therefore concluded that maghemite tends to recrystallize to hematite at this temperature (600° C), whereas the transitional oxide is first transformed into magnetite and forms hematite only very slowly, hematite being the most stable iron oxide at 600° C under atmospheric oxygen. Of course, it is difficult to draw a line between the various transformation stages, and thus a very small amount of magnetite may be detected after heating the KI disks for several days at 500° C. The transitional oxide obtained from natural goethite is recrystallized to hematite in CsI disks but not in KI disks.

If the ground KI disks are heated directly at temperatures above 400° C, without any pre-heating at lower temperatures, the transitional oxide is not formed. Thus no magnetite is obtained at 600° C. The major product under these conditions is protohematite, indicating that only the first stage of the thermal transformation sequence occurs. The gradual heating of KI disks is critical for the appearance of the transitional oxide. However, this gradual heating is only of minor importance for other salts, especially KCl and KBr. The re-pressing of the disks, which is also critical in obtaining the transitional oxide and magnetite with the KI matrix, again is of secondary importance for disks of the other halides, except NaCl (see Table 1).

The formation of magnetite is associated with the reduction of ferric iron by the iodide, and implies a short distance between the two ions. From the present results it appears obvious that the transitional oxides are the phases largely responsible for the third- and fourth-stage reactions. The following suggest that the formation of a transitional oxide depends on interface reactions between the alkali halides and protohematite.

(a) Repeated grinding—pressing cycles are essential for formation of the transitional oxide. Moreover, the fraction of this phase in the salt matrix increases with the number of cycles. As shown in the Results section, the re-grinding—re-pressing process does not result in a random breaking of the goethite particles, but in a cleavage along a certain plane. In orther words, the re-grinding—re-pressing process results in thinner goethite particles and greater exposure of fresh surface Fe—OH groups.

(b) The transitional oxide is formed in alkali-halide disks, but not in the powder mixture obtained after the re-grinding of the same disk. This may indicate that good contact between the surfaces of particles in the two phases, achieved in the disk, is essential.

(c) No systematic effect (either acceleratory or inhibitory) due to any particular alkali or halide ion has influence on the formation of the transitional oxide. Table 1, however, shows that some salts, e.g. KBr or NaCl, do accelerate the formation of the transitional oxide, whereas others, like NaBr and to some extent KCl, behave as inhibitors. This suggests that these effects must be attributed to the whole salt and not to the individual ions. It may also be inferred that the reactions governing the second-stage process do not occur at interionic (or interatomic) level, but at the salt—iron oxide interface.

In a separate study of the thermal decomposition of goethite in concentrated disks (33%) of KCl, KBr, KI and CsI, we showed that the following interface reactions take place during the dehydroxylation of goethite (paper in preparation)

$$\mathrm{FeOOH + KI \rightarrow FeOOK + HI} \tag{1}$$

$$\mathrm{FeOOH + KI \rightarrow FeOI + KOH} \tag{2}$$

The same surface reactions may take place in the very dilute disks investigated here. Furthermore, since the re-grinding—re-pressing cycles increase the surface area of the goethite, the contribution of the latter reaction to the mechanism must be considered.

CONCLUSIONS

Synthetic goethite was reduced to magnetite in KI or CsI disks. In both cases, the disk must be re-ground and re-pressed at least three times during the thermal treatment for the reduction to occur. Gradual heating up to 600°C is optimal for obtaining magnetite in KI disks, whereas in CsI disks magnetite is detected upon direct heating at 600°C. Prolonged heating of the magnetite disk at 600°C gives rise to hematite, a process which is faster in CsI than KI disks. Magnetite was also obtained from a natural goethite (Al-bearing goethite) in KI disks but not in CsI disks. Infrared spectroscopy was successful in identifying the different compounds of iron produced in the thermal treatment of goethite in alkali-halide disks.

ACKNOWLEDGEMENTS

This project (52-23-30,CRH) was funded by CONICIT (Consejo Nacional de Investigaciones Científicas y Tecnológicas). One of us, S.Y., is grateful to

CONICIT for supporting his stay in Venezuela through this project. Mr. M. Cohen of the project Modificacion Fisico-Quimica de Lateritas de Venezuela y Minerales Asociados helped in the IR work.

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