Infrared study of $\text{FeO} \cdot \text{OH} \rightarrow \text{Fe}_2\text{O}_3$ thermal transformation

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Abstract. Infrared absorption spectroscopy has been applied for the identification of the minerals associated with natural goethite ($\alpha\text{-FeO} \cdot \text{OH}$) from Saudi Arabia. The thermal transformation of natural goethite as well as the effects of the presence of the associated minerals on the reaction products were investigated. The results revealed that at 300°C protohematite is formed which at 600°C is slightly crystallized. Further recrystallization and hematite formation takes place at 1000°C. It was also found that the presence of other minerals found in goethite samples has no effect on the reaction products.

Keywords. IR; DTA; goethite; thermal transformation.

1. Introduction

It is well known that most of goethites are Al-bearing goethite (Janot *et al* 1970, 1971). The incorporation of Al into goethite structure has been investigated by several authors (Jewur and Kuriacose 1976; Shimokawabe *et al* 1978; Yariv and Mendelovici 1980; Schwertmann *et al* 1977). Schwertmann (1977) stated that dehydroxylation of Al-goethite at 300°C results in poorly crystallized Al-protohematite which at higher temperatures is partly perfected. The difference in the thermal behaviour between pure goethite and 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. Mendelovici and Yariv (1981) investigated the dehydroxylation of natural Al-bearing goethite by IR spectroscopy. They concluded that 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.

The aim of the present study is to apply infrared absorption spectroscopy to investigate the thermal transformation of natural goethite into hematite.

2. Experimental

The samples used in this study were obtained from the collections of the Faculty of Earth Sciences, University of King Abdul Aziz. The localities are Bahra and Wadi Fatimah.

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Samples were ground in a hardened steel vial containing two hardened steel balls. The powder was then sieved and the fraction with particle sizes between 0.075 and 0.063 mm diameter was selected. Portions of the samples were shaken with 1 N of NaOH solution at 75°C for 10 hours. The powder either in the original form or after a partial removal of associated minerals was heated to different temperatures.

The infrared spectra (IR) were recorded on the PYE UNICAM full automatic double beam spectrophotometer model Sp 3-300. Samples for spectral runs were prepared from finely ground material. For all samples an amount of 3 mg was mixed with 197 mg of KBr and a pellet was made from the mixture.

For thermal analysis DTA instrument (Linsels, selb/Bay) with an automatic strip chart paper recorder was used in the present work to detect the endo- or exothermal reaction changes experienced by the tested samples from room temperature up to 1000°C.

3. Results and discussion

The minerals associated with natural goethite from Bahra and Wadi Fatimah were determined from their IR spectra. The IR spectra of these samples are shown in figures 1 and 2.

As can be seen from figure 1a the spectrum of the sample of Bahra exhibits absorption bands at the frequencies 3125, 890, 790, 660 *sh*, 580, 465 and 410 cm^{-1} . Farmer and Palmieri (1974) pointed out that the absorption of the Fe^{2+} OH ranges from 2900 to 3230 cm^{-1} in goethite and lepidocrosite. The main OH deformation vibrations of Fe^{2+} OH in goethite appear at the frequencies 810 and 910 cm^{-1} (Hartest 1956; Moenke 1962). The infrared spectra of amorphous hydrated iron oxides at the frequencies 3400 *s*, 1630 *w*, 1490 *w*, 1360 *w*, 690 *sh*, 580 *s* and 460 *s* cm^{-1} . Also the spectrum recorded by Estep (1973a) for the amorphous hydrated iron oxide showed

Figure 1.

Figure 2.

absorption bands at the frequencies 3400–3390 s ; 1600 w ; 1490 w ; 1370 w and 500 s cm^{-1} .

In addition to the characteristic bands of goethite the spectrum of the representative sample from Bahra shows a band of medium intensity at 3390 cm^{-1} and very weak absorption bands at the frequencies 1140, 1110, 1080, 1025 and 1000 cm^{-1} . It is unfortunate that the strongest stretching absorption bands of silicate, phosphate, and sulphate anions overlap to a considerable extent in the 1200 to 900 cm^{-1} region. The above absorption bands may be due to the existence of few trace amounts of silicate and sulphate minerals.

The spectrum of the representative sample of Wadi Fatimah in figure 2a is characterized by absorption bands at the frequencies 3110 w ; 910 m ; 795 m ; 590 sh ; 463 m ; 437 m ; and 400 sh cm^{-1} which are the diagnostic frequencies of the mineral goethite (Moenke 1962). Beside these bands other bands occur at the frequencies 3695 vw ; 3658 vw ; 3620 vw ; 3420 vw ; 1100 m ; 1028 m ; 1005 m ; and 530 s cm^{-1} . The structural assignments of these bands were carried out in comparison with literature reports of Alexanian *et al* (1966), Oinuma and Hayashi (1965) and Chester and Elderfield (1973), and with the spectrum of the pure material. It should be mentioned that the absorption bands at 1005, 1028 and 1100 cm^{-1} correspond to the Si-O stretching vibrations of kaolinite (Chester and Elderfield 1973). The absorption bands at 3695, 3658, 3620 and 3420 cm^{-1} are due to the presence of water and hydroxyls in the kaolinite mineral structure (Chester and Elderfield 1973). Accordingly, it could be concluded that kaolinite is associated with the goethite mineral of Wadi Fatimah. The samples from Bahra and Wadi Fatimah are hereafter referred to as goethite (A) and goethite (B) respectively.

It is clear from figures 1a and 2a that the spectral features of minerals associated with goethite (A) are not similar to those associated with goethite (B). The strong band appearing in the spectrum of the former at 580 cm^{-1} appears as a weak shoulder in the spectrum of the latter. In the absorption region from 400 to 500 cm^{-1} the spectrum of goethite (A) shows two absorption bands at 465 and 410 cm^{-1} , whereas the spectrum of goethite (B) shows two medium bands at 463 and 437 cm^{-1} and a shoulder at 400 cm^{-1} . It should be mentioned that the absorption at 463 cm^{-1} has some contribution from kaolinite.

The absorption bands at 3390 , 580 and 465 cm^{-1} are in close agreement with the absorption bands of hydrated iron oxide as reported by Van der Geissen (1968), suggesting that hydrated iron oxide minerals are associated with goethite (A).

In the present study the natural goethites (A) and (B) either in their original forms or after a partial removal of associated minerals were heated to various temperatures and their IR spectra were studied. The removal of part of the associated minerals was carried out by shaking the original ground samples with 1 N NaOH solution at 75°C for 10 hours.

The IR spectra of the original and treated samples after heating to 1000°C are shown in figures 1 and 2 for goethites (A) and (B). The frequencies of the recorded spectra are given in table 1.

It appears from figure 1 curve b that treatment of goethite with the NaOH solution causes no significant changes in the absorption bands of goethite apart from the changes in their intensities. On the other hand, it is clear that this treatment results in remarkable changes in the bands of the associated minerals. The silicate bands appearing in the spectrum of the original sample of goethite (A) at the frequencies 1140 , 1110 , 1080 , 1025 and 1000 cm^{-1} have disappeared from the spectrum of the treated one and the latter spectrum exhibits a broad band at 1035 cm^{-1} with a shoulder at 1070 cm^{-1} . Also, the kaolinite bands appearing in the spectrum of the original goethite (B) in figure 2 curve a at 3695 , 3658 , 3620 , 3420 , 1100 , 1028 , 1005 and 530 cm^{-1} are

Table 1. Frequencies of O^{2-} displacements in hematite obtained after calcination of goethite (A) and goethite (B).

Heating temperature ($^\circ\text{C}$)	Goethite (A)		Goethite (B)	
	Original sample	NaOH treated	Original sample	NaOH treated
300	328	325	318	318
	450	450	448	448
	525	530	532	535
	550 sh	550 sh		
600	330	330	313	312
	460	453	450	445
	540	540	533	532
	560 sh	560 sh		
1000	332	335	331	333
	467	468	475	470
	547	545	548	550

absent from the spectrum of the treated sample (figure 2 curve b). The spectrum of this treated sample shows a broad band at 1020 cm^{-1} and a shoulder at 1070 cm^{-1} .

The frequencies of goethites (A) and (B) after heating at temperatures 300°C and 600°C for 24 hours and at 1000°C for 3 hours are given in table 1. Examination of the recorded spectra of the heated samples revealed that the spectrum of the sample heated at 300°C is characterized by three broad absorption bands at 525 , 450 and 328 cm^{-1} and a strong shoulder at 550 cm^{-1} which are assigned as O^{2-} displacement. These bands shift to 540 , 460 and 330 cm^{-1} and to 547 , 467 and 332 cm^{-1} with temperature increasing to 600°C and 1000°C respectively. Also, it is evident from figure 1 that the bands become narrower with increasing temperature. Parallel changes were recorded during thermal treatment of samples treated with NaOH solution.

The spectrum of the sample of goethite (B) heated at 300°C exhibits the main three bands at frequencies 532 , 448 and 318 cm^{-1} . These bands occur at frequencies 533 , 450 and 313 cm^{-1} in the spectrum of the sample heated at 600°C and at frequencies 548 , 475 and 331 cm^{-1} in the spectrum of the sample heated at 1000°C . Figure 2 reveals also that the thermal behaviour of the sample treated with NaOH solution is similar to that of the original sample.

Mendelovici and Yariv (1981) mention that the band at about 540 cm^{-1} is highly sensitive to both factors (1) the heating temperature of the laterite samples, and (2) the initial gibbsite content. However, the IR spectra of the analyzed samples reveal that they are nearly free of gibbsite and contain considerable amounts of aluminium silicate minerals. Although the existence of these minerals is associated with natural goethite, the shifts in the peak maxima of the bands at 535 , 465 and 325 cm^{-1} are in good correlation with those reported in the literature for pure goethite (Mendelovici and Yariv 1981; Yariv and Mendelovici 1979).

Figure 3 illustrates the DTA curves of goethite (B) after heating at 300 , 600 and 1000°C . In figure 3 curve a the endothermic peak at 75°C is due to absorbed water but

Figure 3.

the small endothermic peak at 250–280°C is due to partial transformation of goethite to hematite (Todor 1976), which is not clear in the samples preheated at 600 and 1000°C, thus proving the complete transformation of goethite to hematite after firing at 600 or 1000°C.

The very clear endothermic peak at 525°C is due to the removal of the hydroxyl groups of kaolinite present with the goethite, which disappears by preheating at 600 and 1000°C as shown in figure 3 curves b and c.

The very small peak at 575°C, which is characteristic of the α - β quartz transformation, proves the presence of very small amounts of free silica with the goethite which is found to be repeated in the three samples owing to the fact that this transformation of the quartz modifications is a reversible one.

The above results lead to the conclusion that at 300°C protohematite is formed which at 600°C is slightly crystallized. Further recrystallization and hematite formation occurs at 1000°C. The presence of the various minerals found associated with goethite has no effect on the reaction products.

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