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In situ FTIR study on the dehydration of natural goethite

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Abstract

Fourier Transform Infrared (FTIR) spectroscopy, thermal analysis -Differential Scanning Calorimetry (DSC) and Thermo-Gravimetry (TG-DTG) were used to study the dehydration behavior of synthetic goethite and two naturally occurring goethite samples (Natural 1 and Natural 2) from Banded Iron Formation (BIF), at C.S. Halli, Chitradurg district, Karnataka, India. Goethites and its dehydration products were also identified by powder X-ray Diffraction (XRD) method. The dehydration temperatures were at 538, 567 and 578 K for synthetic, Natural 1 and 2 goethite, respectively. On approaching the dehydration temperature, infrared active modes of the hydroxyl groups have shown distinct variations. The peak position for the stretching mode around 3150 cm^{-1} was shifted upwards, while that for in-plane-deformation mode around 890 cm^{-1} was down shifted indicating weakening of strength of the hydrogen bonding. No intermediate phase, so called hydro-hematite, was observed in these studies. The total absorbance (area under the peak) of these modes have shown the Arrehenius type behavior in the temperature range 500–600 K, using which the activation energy for the dehydration process was estimated as 71, 103 and 85 kJ/mol for synthetic, Natural 1 and 2 goethites respectively.

Keywords: Goethite; Hematite; Dehydration; XRD; DSC; TG-DTG and FTIR

1. Introduction

Iron oxides play important roles as adsorbents controlling the mobility of trace contaminants, supplying plant nutrients, soil aggregation, soil classification and pedogenesis. Among iron oxy-hydroxides, goethite (α-FeOOH) is abundant constituent of terrestrial soils, sediments, oolitic iron ores and major weathering product of all rock types. It is predominant in younger sedimentary deposits, giving the rocks a yellow colour. On the other hand, hematite (α-Fe_2O_3) is abundant in ancient deposits imparting a red colour (Goss, 1987). Thermodynamically, goethite is the most stable of the iron oxides and is an end member of many transformations (Schwertmann and Cornell, 1991). However, both particle size and kinetic effects are important for the crystallization and stability of goethite and hematite (Goss, 1987; Langmuir, 1971, 1972; Gonzalze et al., 2000; Walter et al., 2001). According to Langmuir (1971, 1972), goethite with particle size less than 0.1 μm is thermodynamically more unstable than hematite. However, goethite is the commonest phase in younger deposits, as the reaction kinetics is slow. The hematite/goethite ratio in soils is thus an indicator of the carbon regime and climate (Tite and Linington, 1975). Pollack et al. (1970a,b) studied the kinetics of the dehydration reaction and suggested that chemical equilibrium in the goethite-hematite system determine the time average abundance of water vapor on Mars.

The dehydration transformation, which is topotatic has been subjected to number of investigations. It has been suggested that the thermally induced transformation can either be a direct transformation from goethite to hematite

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(Walter et al., 2001; Watari et al., 1979),

$$2\,\alpha(FeOOH) \rightarrow \alpha(Fe_2O_3) + H_2O,$$

or a transformation with the formation of an intermittent super structure phase so called proto-hematite or hydro hematite, before the final formation of hematite (Lima-de-Faria, 1963; Gualtieri and Venturelli, 1999; Ozdemir and Dunlop, 2000; Wolska (1981,1988); Wolska and Schwertmann (1989),

$$2\alpha(FeOOH) \rightarrow \underset{\text{(super structure)}}{6/(6-x)\ \alpha Fe_{2-x/3}(OH)_xO_{3-x}} + (6-4x)/(6-x)H_2O \rightarrow \alpha(Fe_2O_3) + 3x/6-xH_2O.$$

There has been no general agreement on the mechanism of thermal transformation in goethite. In recent times, this solid state transformation has been subjected to experimental investigations. Gualtieri and Venturelli (1999) have studied this transformation by in situ synchrotron X-ray powder diffraction using pure, synthetic stoichiometric goethite with 1 μm long needle-shaped crystals. They reported that the dehydration of goethite started at 200 °C and concluded at about 270 °C; and the resultant phase is with non-stoichiometric composition called proto-hematite. This was eventually converted to hematite at around 800 °C. Ozdemir and Dunlop (2000), also reported an intermediate phase particularly in partially dehydrated goethite in the temperature range 238–402 °C. Wolska (1981,1988); Wolska and Schwertmann (1989) also reported the formation of a hydrohematite [$Fe_{1.83}(OH)_{0.5}O_{2.5}$] phase during the thermal dehydration of goethite in the range 180–250 °C, and this phase finally transforms into the hematite in the temperature range 800–1050 °C. On the other hand, mechano-chemical and thermal studies of the transformation by Gonzalez et al. (2000) using TEM and XRD reported a direct transformation of goethite to hematite. They also have reported conversion of goethite (original particle size 400–700 nm) to a hematite phase, when the average particle size was decreased to 19–25 nm, from goethite by mechanical grinding. Goss (1987) studied the kinetics of goethite to hematite transformation and suggested a direct transformation. Katoh et al. (2001); Walter et al. (2001) also reported a direct transformation to hematite, at approximately 220 °C. Ruan et al. (2001, 2002a,b) have studied the dehydration behavior of synthetic goethites and those from Australian bauxite using FTIR spectroscopy. Recently Frost et al. (2003) reported two-step phase changes during dehydration in naturally occurring and synthetic goethite samples using thermal analysis. Naturally occurring goethites are rarely stoichiometric and usually contain number of isovalent or heterovalent cations, like Ni^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Cr^{2+}, Ga^{2+}, V^{3+}, Mn^{3+}, Co^{3+}, Si^{3+}, Pb^{4+}, Ge^{4+}, Si^{4+}, and Ti^{4+}. These cations can partially replace the Fe^{3+} without a change in crystal structure (Huynh et al., 2002). It was reported that the dehydration temperature of Cu-substituted goethites decreases to 221 °C, while that of pure goethite is 238 °C (Huynh et al., 2002). On the other hand, the effect of Al and Cr was opposite and the dehydration temperatures increase (Ruan et al., 2002a).

Most of the above studies were on well-synthesized goethite and to the best of our knowledge the dehydration mechanism was not studied on natural samples. In this we report in situ Fourier Transform Infrared (FTIR) spectroscopic results of dehydration mechanism on two naturally occurring goethite samples from Banded Iron Formation (BIF), C.S. Halli, Chitradurg district, Karnataka, India, and the mechanism is compared with a synthetic sample. The main objective of this study is to get the FTIR signatures of hydro- (proto-) hematite, often observed in the literature as an intermediate product during the dehydration (Gualtieri and Venturelli, 1999; Wolska, 1989; Ruan et al., 2001).

2. Materials and methods

2.1. Sample description

Natural samples were extracted from a Banded Iron-Formation (BIF) occurring at C.S. Halli, Chitradurg district, Karnataka, India. This formation is the youngest among the several BIF bands in the Chitradurg schist belt, Ingaldahl copper mine. We have chosen samples within two patches spatially separated by about 4–5 mm, one dark brown in colour, another brown-yellow in colour, and in the latter has a width of about 3–4 mm. The material within the brown-yellow portion (Natural 1) could easily be removed by a sharp edge. Whereas, the material from dark brown portion (Natural 2) is more difficult to scratch. The sample contains bands of chert with hydrous alteration towards the formation of goethite. The goethites are of needle type and are embedded in chert.

The synthetic sample was prepared using the method of Schwertmann and Cornell (1991). A precipitate was formed by mixing 5 ml of 1 M ferric nitrate solution to 45 ml of 1 M KOH. This suspension of hydrous ferric oxide was then aged for one week at ambient conditions, and the formation of goethite was intermittently checked by FTIR spectra. The suspension was washed thoroughly with distilled water to remove residual KOH and nitrates before using it for dehydration studies. The residue was filtered and dried. IR and XRD confirmed the formation of mono-phase goethite.

2.2. X-ray diffraction

The X-ray diffraction patterns obtained were recorded using Phillips PW-1830 powder diffractometer with Ni-filter, θ–2θ scan. The radiation used was Cu Kα radiation. The 2θ scan was from 10–80°. The rate at which the sample rotates was 3 degrees/min.

2.3. Thermal analysis

The Differential Scanning Calorimetry patterns were recorded on 2010 TA-instruments. The sample was weighed using Metler AE 163. Aluminum pans were used to place the samples. The weight of the sample used was 8 mg and the rate of heat flow was 10 °C per minute. The thermogravimetric analysis (TGA and DTG) was on a Mettler Toledo Star^e TGA/SDTA 851 system using about 11.74 mg (Synthetic), 20.61 mg (Natural 1) and 14.84 mg (Natural 2) samples. Measurements were in the temperature range 300–1300 K with a heating rate of 20°/min.

2.4. Infrared spectroscopy

Infrared spectroscopic studies were carried out on a NEXUS FTIR spectrometer from Thermo-Nicolet, using a thermo-electrically cooled deuterated tri-glycene sulphate (DTGS) detector, extended range KBr (XT-KBr) beam splitter, capable of working in the wavenumber range 375–12,500 cm^{-1}. Spectra at above ambient temperatures were collected using specially fabricated environmental chamber. This chamber can be used to increase the temperature of the sample under study up to about 950° K with an accuracy of $\pm 2°$. Running tap water was used to cool the outer jacket of the chamber, which includes the infrared transparent windows. Conventional KBr pellet technique was followed to record FTIR spectra and the spectra reported are the resultant of 256 scans, resolution of 2 cm^{-1} and aperture of 25. Typical uncertainties in the peak positions are about 2 cm^{-1} for the sharper and stronger modes, while that for the weak and overlapping modes could be about 5 cm^{-1}.

3. Results and discussion

3.1. X-ray diffraction-characterization

Powder X-ray diffraction patterns of Natural 1, Natural 2 and Synthetic goethites were recorded. These samples were heated in air at about 650 K for about two hours (in a separate tubular furnace having maximum working

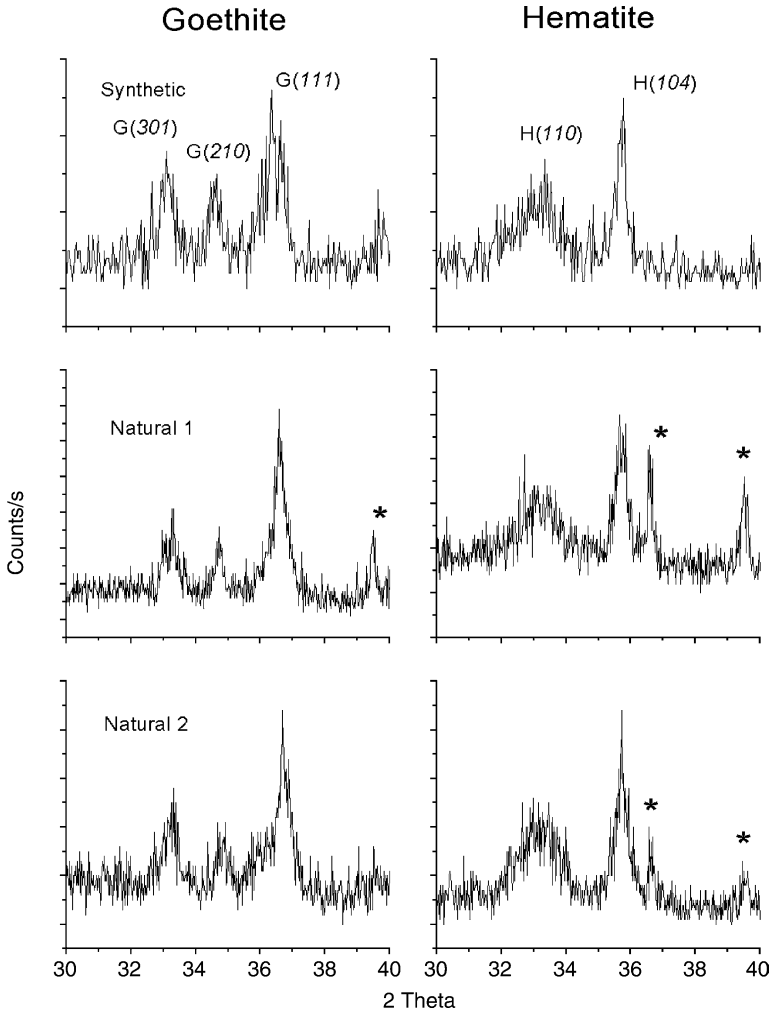

Fig. 1. Characteristic XRD patterns in 2θ range (30–40°) of goethite and their residue (heated at 625 K). The peaks with an asterisk mark of natural samples are from the quartz impurity.

temperature of 1000 °C), to allow it to dehydrate. Characteristic XRD patterns between 30–40 2θ of these goethites along with dehydrated samples are shown in Fig. 1. Three-peak behaviour transforming to two indicates the formation of hematite (Katoh et al., 2001; Gualtieri and Venturelli, 1999). Checkcell software was used to calculate the *hkl* planes of the virgin and dehydrated samples. Orthorhombic system, space group *Pbnm* with $a=4.608$, $b=9.956$ and $c=3.021$ Å for goethite (300 K) and hexagonal system, space group *R*-3*c* with $a=5.0356$ and $c=13.7489$ Å for hematite (650 K) are used (Gonzalez et al., 2000). Some of the intense peaks at around $d=0.420$, 0.270, 0.258, 0.246, 0.220, 0.172, 0.156 and 0.151 nm with *hkl* planes 110, 130, 021, 111, 121, 221, 151 and 002 respectively, of goethite are well comparable with the reported data of Gonzalez et al. (2000) and Wolska and Schwertmann (1989). And similarly intense peaks at around $d=0.368$, 0.269, 0.250, 0.220, 0.190, 0.169 and 0.145 with *hkl* planes 012, 104, 110, 113, 024, 116 and 300 respectively, of hematite are also comparable with the data reported by the same authors.

3.2. Thermal analysis study

The natural and synthetic goethite samples were analyzed by differential scanning calorimetry. Fig. 2A shows the DSC traces for synthetic (solid line), natural 1 (dashed line) and natural 2 (dotted line) goethites. The onset of dehydration is respectively at 526 K, 496 K and 498 K; while the transition temperature is about 538, 567 and 578 K, respectively, for Synthetic, Natural 1 and Natural 2 goethites. A single endothermic peak in all the samples suggests no intermittent phase during the transformation (Walter et al., 2001). Further, the observed thermo-gravimetry traces of these samples were shown in Fig. 2B (TGA), 2C (DTG). A total mass loss of about 11.56%, 8.10% and 9.02% was observed in our studies and this loss is predominantly in the temperature range 500–700 K and a negligibly small (<1%) mass loss is observed when heated to 1300° K. Observed mass loss in the initial temperature range 300–400° K may be due to the water adsorbed on to the surface of goethites as reported by Manceau and Gates, 1997. However, Gualtieri and Venturelli (1999), reported mass loss about 10.56% at around 573° K (299.6 °C) and this loss increased linearly to 13.5% upon heating to 1273° K (1000 °C).

3.3. Fourier transform infrared studies

Goethite to hematite phase transformation, though studied by many techniques over many years in situ but FTIR studies probing this transformation are limited. However, Ruan et al. (2001, 2002a,b) have extensively used FTIR spectroscopy to characterize various products of goethite. Kustova et al. (1992) and Russell and Fraser (1994), Ishikawa et al. (1986, 1992) characterized goethite and its dehydration products using IR. In view of the

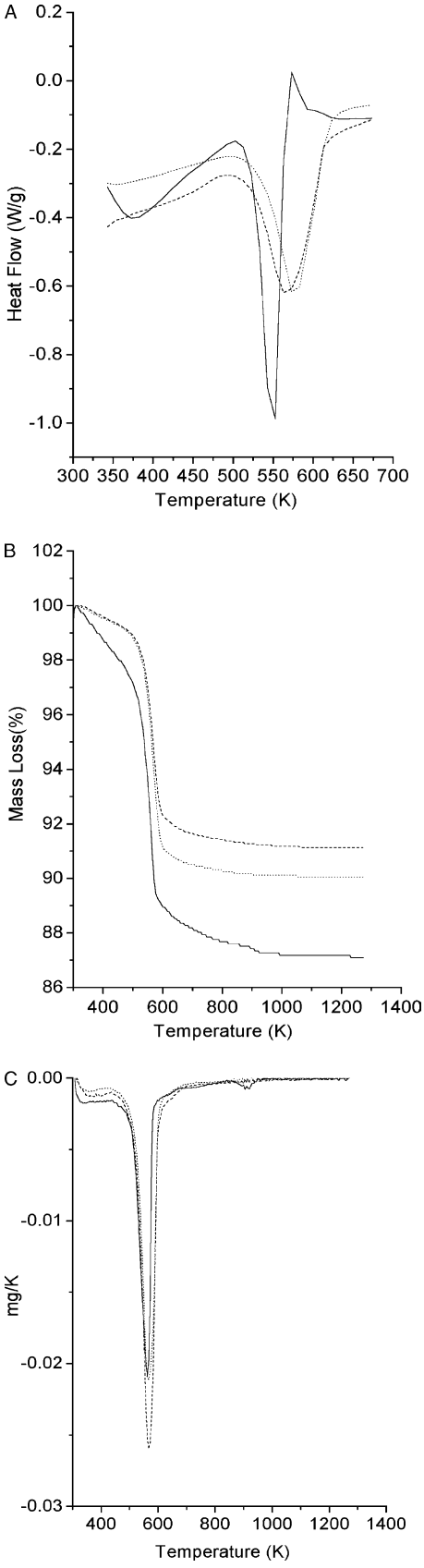

Fig. 2. Thermal analysis DSC (A), TGA (B) and DTG (C) plots of synthetic (—), natural 1 (- - -) and natural 2 (···) goethite samples.

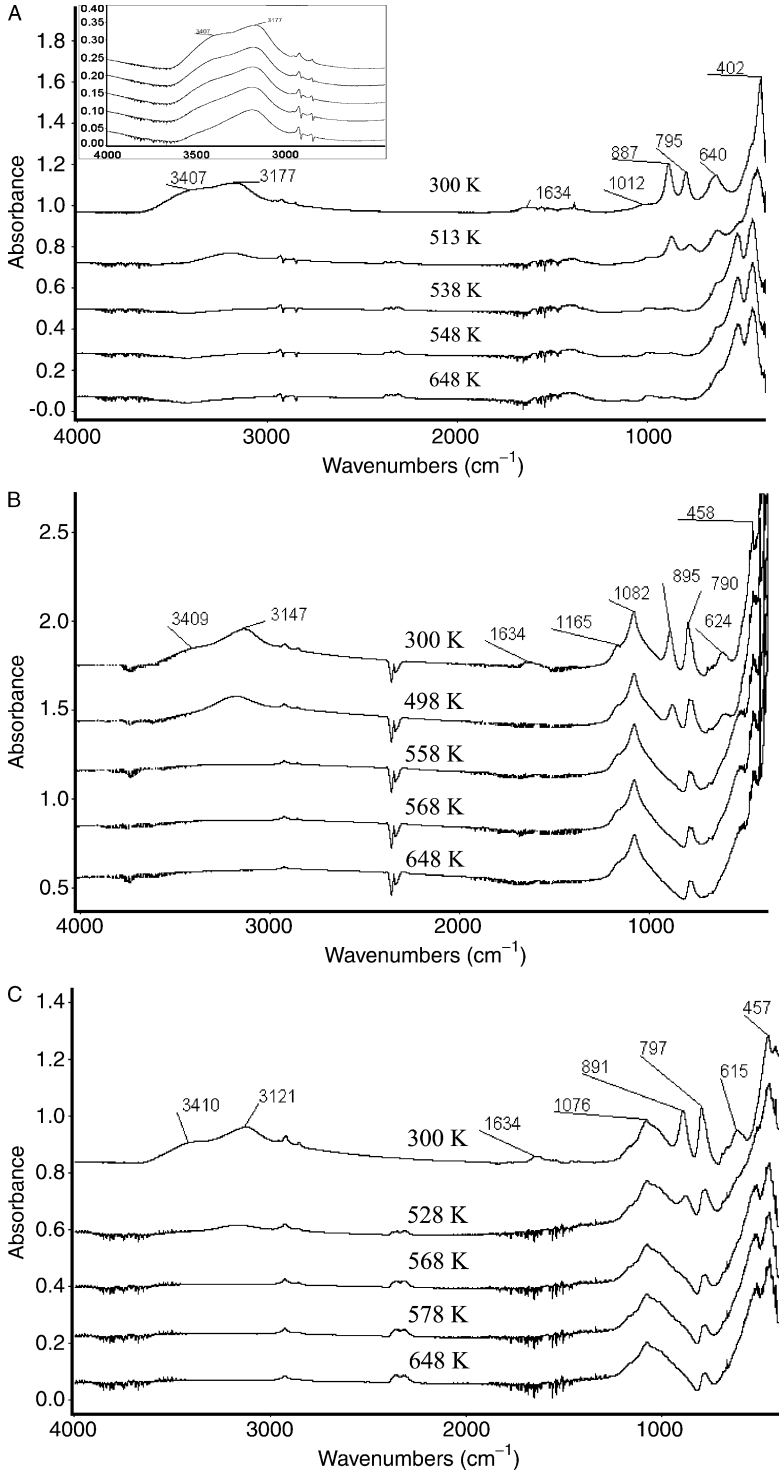

Fig. 3. (A) Background corrected FTIR spectra of synthetic goethite recorded at various temperatures. The inset shows the thermal evolution of IR modes in the wavenumber region 2500–4000 cm^{-1}. These traces (top to bottom) are recorded at 300, 328, 348, 373 and 398 K. (B) Background corrected FTIR spectra of goethite (Natural 1) recorded at various temperatures as indicated along with the spectra. (C) Background corrected FTIR spectra of goethite (Natural 2) recorded at various temperatures as indicated along with the spectra.

differences in the formation of hydro-hematite during the dehydration of goethite, we investigated this phase transformation using in situ FTIR spectroscopy.

Fig. 3 shows the recorded infrared spectra of Synthetic (A), Natural 1 (B) and Natural 2 (C) goethite at different temperatures. Additionally, the inset of Fig. 3A shows the thermal evolution of IR active modes in 2500–4000 cm^{-1} recorded at 300, 338, 353, 373, and 398 K. It is clear that the shoulder appearing at 300 K around 3407 cm^{-1} completely disappeared at around 398 K. In Table 1, observed infrared

Table 1
Observed peak positions of the infrared modes of goethite samples in the wavenumber region 400–4000 cm^{-1}

Present study			a	b	c	d	Assignment
Natural 1	Natural 2	Synthetic					
458	457	450	454		455,495,409	402,465	FeO_6 lattice
624	615	640	622		633	610,640	FeO_6 lattice
668	666	667			667	685–700	combination
694	694						SiO_2
780,790	797	795	800–798	799	794	800	δ_{deform}–OH
895	891	887	888–884	890	893	900	δ_{deform}–OH
1082,1165	1076						SiO_2
1634	1634	1634	1687–1643	1686,1637,1707			δ_{bend}–OH
3147	3121	3177	3206	3206	3153		ν(O–H)
3393	3410	3407	3450	3479			ν(H–O–H)

a: Ruan et al. (2001). b: Ruan et al. (2002a,b). c: Russell and Fraser (1994). d: Kustova et al. (1992).

active modes of these natural goethites and synthetic sample are compared with those reported earlier. The infrared modes due to hydroxyl groups are intense in goethite samples. In natural samples (1 and 2) we also observe infrared modes due to quartz grains occurring at 1082 and 1076 cm^{-1} respectively. Other modes of SiO_2 reported at 779 and 796 cm^{-1} as doublet; and 459 cm^{-1}, strongly overlap with infrared active modes of goethite. Low wavenumber lattice modes of FeO_6 are at 624, 615 and 640 cm^{-1} in Natural 1, Natural 2 and Synthetic goethites, respectively.

The next prominent modes around 780–797 cm^{-1} are assigned as out-of-plane deformational (γ) modes of hydroxyls. There is a strong overlap for this mode with matrix SiO_2 in the natural samples. In plane deformational (δ) mode, however, is clearly observed at 895, 891 and 887 cm^{-1} respectively in Natural 1, Natural 2 and Synthetic goethites, respectively. The bending modes of hydroxyl reported as triplet around 1639–1675, 1645–1613, 1693–1675 cm^{-1} have not been observed in the present study. The stretching mode region consists of a broad absorption peak around 3147 cm^{-1} and shoulder at 3393 cm^{-1} in natural 1, while those in natural 2 are at 3121, 3410 cm^{-1} and at 3177, 3407 cm^{-1} in synthetic goethite. Ruan et al. (2001), have reported the corresponding modes around 3206 and 3450 cm^{-1}, which were assigned due to stretching of hydroxyls of goethite and 'loosely bound water' adsorbed on the surface. Further, goethite is one of the strongly hydrogen bonded mineral with ν(OH) stretching mode around 3100–3150 cm^{-1} (Russell and Fraser, 1994; Libowitzky and Rossman, 1997). Temperature induced spectral variations of hydroxyl modes in this mineral are used to get an insight into the phase transition mechanism.

In situ infrared spectra of these samples were recorded at regular temperature intervals in the range 300–650 K. It is observed that, the stretching modes in synthetic, natural 1 and natural 2 has shown an upward wavenumber shift of 26, 107 and 66 cm^{-1}, in the temperature range 300–538, 300–568 and 300–578 K, respectively. The in-plane-deformational modes on the other hand have down shift by 18, 34 and 14 cm^{-1}, respectively. The temperature at which these modes disappear is assumed as transition temperature, and such temperature as detected by FTIR spectral variations at 538, 558 and 578 K are in good agreement with DSC

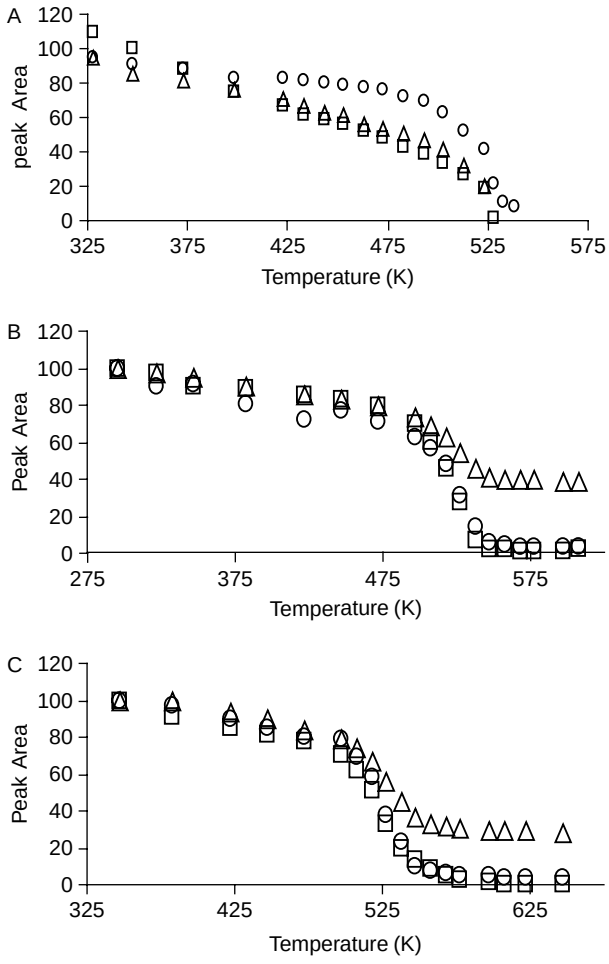

Fig. 4. Temperature induced variations in the peak area of hydroxyl stretching (□), in-plane (○) and out-of-plane (△) deformational modes of synthetic (A), natural 1 (B) and natural 2 (C) goethite samples. Peak areas were measured in the wavenumber region 3504–2970; 930–848 and 839–729 cm^{-1}, with a linear background.

studies. Such peak position shifts, namely upward shift for the stretching mode and downward shift for the deformation mode is a typical signature of weakening of strengths of hydrogen bonding (Novak, 1974; Beran and Libowitzky, 1998). Another shoulder mode in stretching mode around 3400 cm^{-1} assigned due to 'loosely bound water' in goethite has reported to show downward wavenumber shift and an increase in absorbance with increasing temperature (Ruan et al., 2001). However, we observe this mode diminishes fast (around 425 K) in all the samples (see inset of Fig. 3A). A similar behaviour was observed in all the three samples that we studied. We feel that this may be due to moisture adsorbed on to the KBr pellet. Similar spectral features were observed around 1634 cm^{-1}. Furthermore, one-stage dehydration behavior in these goethite samples inferred from FTIR studies corroborates TG and DSC results and is contrary to previous observations (Gualtieri and Venturelli, 1999; Walter et al., 2001; Ford and Bertsch, 1999).

Libowitzky and Rossman (1997) have shown that the use of integrated absorbance values (band areas) results in a linear correlation with water content, whereas, linear absorbance data (peak heights) is not. In Fig. 4, normalized integrated absorbance variations with the temperature are plotted for Natural 1(A), Natural 2(B) and Synthetic goethites. Integrated absorbance of the three-hydroxyl modes namely stretching, in-plane and out-of-plane deformational modes, measured in the wavenumber region 3650–2950; 930–839 and 860–750 cm^{-1}, with a linear background are included in this figure. Temperature induced variations of these parameters are more prominently seen in the temperature range 498–578 K for natural samples and 526–540 K for synthetic sample. On the either side of this temperature range, variations in the integrated absorbance are weakly dependent on temperature. However, variations in hydroxyl stretching modes in all these samples are stronger in the temperature range 300–425 K, and are due to the dehydration of water molecules adsorbed on to the KBr pellet. We believe that the IR mode observed around 3400 cm^{-1} is due to moisture adsorbed on to the KBr pellet. On the other hand, all the modes of hydroxyl groups namely stretching and deformation modes have abruptly became weaker in the temperature range 500–600 K. Variations in the integrated absorbency in this temperature range are like Arrehenius type. These spectral variations could be used to estimate the activation energies involved in the dehydration process. In the temperature range 500–600 K, the plots of the regression coefficient $r^2 = 0.9333$. From the slopes of (OH) deformational mode, activation energies for natural 1, natural 2 and synthetic goethites are 103, 85 and 60 kJ/mol, respectively. The activation energy for the dehydration process was reported by Lima-de-Faria (1963) as 82 kJ/mol for a crushed single crystal goethite; and by Goss (1987) 88 kJ/mol for a crushed single goethite and 154 kJ/mol for a recent sedimentary goethite.

3.4. Hematite transformation

The formation of intermittent proto-hematite, in which hydroxyl groups remain with the hematite phase, has recently been investigated. Gonzalez et al. (2000); and Gualtieri and Venturelli (1999) have reported that the dehydration of goethites at lower temperatures results into proto-hematite and this phase eventually converts into hematite at 1073 K (800 °C). The existence of this phase was characterized by the broadening of some XRD lines (Gualtieri and Venturelli, 1999). However, Pomies et al. (1998) have shown that the selective broadening of XRD peaks is not due to non-stochiometric proto-hematite but was due to cationic disorder. Infrared spectroscopic

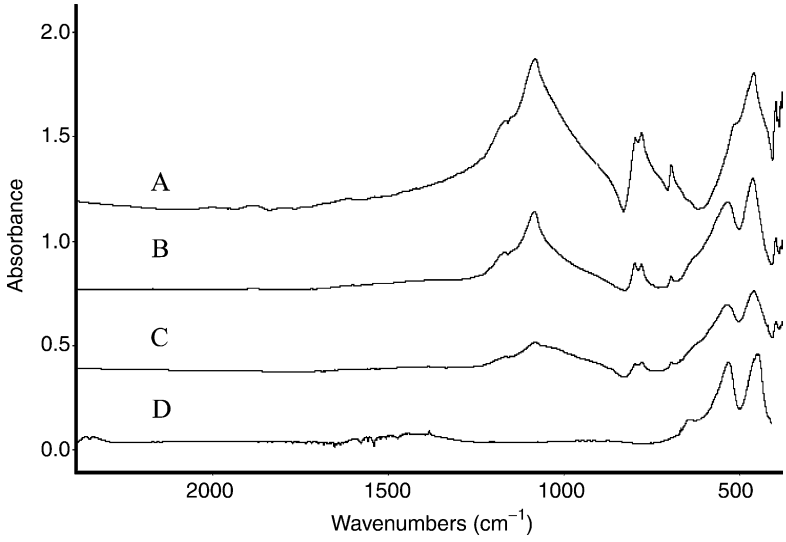

Fig. 5. Background corrected FTIR spectra of natural quartz (A), natural 1(B), natural 2(C) and synthetic (D) goethite's residues after heating to 648 K; collected at ambient temperatures.

Table 2
Observed changes in the normalized peak intensities of the infrared modes of goethite samples at 3400, 640 and 3150 cm^{-1}

Sample	Loss in peak area of 3400 cm^{-1}/K	Loss in peak area of 640 cm^{-1}/K	Loss in peak area of 3150 cm^{-1}/K
Synthetic	0.97 (±0.09)	0.16 (±0.04)	0.16 (±0.01)
Natural -1	0.96 (±0.13)	0.13 (±0.01)	0.28 (±0.07)
Natural -2	0.95 (±0.22)	0.13 (±0.01)	0.25 (±0.08)
Hematite	0.98 (±0.13)	0.16 (±0.37)	–
Pure KBr	0.90 (±0.17)	–	–

signatures of this phase are the bands around 950 and 630 cm^{-1} related to hydroxyl groups (Wolska, 1981). However, assignment of a band around 630 cm^{-1} is ambiguous (Kustova et al., 1992). Two possible assignments for this mode could be a stretching of Fe–O (ν_{FeO}) or out-of-plane bending of OH (γ_{OH}) (Kustova et al., 1992). Apart from this, stretching modes around 3200–3500 cm^{-1} could also be seen that are due to structural water or chemically adsorbed water is also another possibility (Ruan et al., 2001).

In Fig. 5, we show the recorded FTIR spectra of goethite residues, preserved in ambient conditions for duration more than 80 h. The absences of lower wavenumber IR modes around 950 cm^{-1} clearly demonstrate non-existence of the intermittent proto-hematite phase in these samples. A weak absorption around 3400 cm^{-1} and a shoulder mode around 649 cm^{-1}, observed in these residues show different variations with increasing temperature. The former abruptly disappears around 353 K, while the latter remain grossly unaltered till about 625 K, indicating that they originate from different molecular species. The band around 3400 cm^{-1} could be due to moisture adsorbed on to KBr and that around 640 cm^{-1} could be due to Fe–O stretching (ν_{Fe-O}) mode of hematite (Kustova et al., 1992). Further, to confirm temperature-induced changes in the integrated intensity of the modes around 3400, 640 and 3150 cm^{-1} of goethites samples were compared with the plain KBr pellet under similar experimental conditions. Overlapping ν_{OH} modes are deconvolved by GRAMS software as described by Prasad et al. (2005). The normalized peak intensities of deconvolved bands decrease monotonously in the temperature range 300–400 K. As observed from the Table 2 the rate of decrease for this parameter is more rapid for 3400 cm^{-1}, while that at 3150 and 640 cm^{-1} decrease slower. It is worth noticing that this rate for the mode at 3400 cm^{-1}, in all the samples matches well with that of the plain KBr pellet. Thus we feel that the band around 3400 cm^{-1} in all our samples is mainly due to moisture adsorbed on to the KBr. However, the contribution from the structural water adsorbed on to iron oxides, is difficult to rule-out completely (Frost et al., 2003). On the other hand, the rate of decrease for the modes at 640 and 3150 cm^{-1} is almost same (Table 2), indicating that these modes belong to the same structural component. We observed doublet around 790 cm^{-1} and the structures around 1100 cm^{-1} in natural samples that could be due to quartz particles that co-exist with goethites. Abundance of quartz is comparatively higher in Natural 1 goethite, where the dehydration is observed at lower temperatures in our studies.

In summary, the dehydration behavior of two naturally occurring goethite samples from BIF collected at C.S. Halli, Chitradurg district, Karnataka, India and a synthetic goethite were studied by DSC and in situ FTIR spectroscopy. Though these two natural samples are spatially separated by about 4–5 mm and they appear with different colours, they show similar dehydration mechanism compared with that of synthetic sample. The dehydration temperatures of Natural 1, Natural 2 and Synthetic goethites detected by FTIR and DSC studies are around 567, 578 and 538 K. Detailed FTIR analysis such as disappearance of υ(OH) and δ(OH) show that these samples dehydrate directly to hematite without an intermittent proto-hematite phase. Estimated activation energies for natural 1, natural 2 and synthetic goethites are 103, 85 and 60 kJ/mol.

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