

# Goethite as an alternative origin of the 3.1 $\mu\text{m}$ band on dark asteroids

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## ABSTRACT

**Context.** The reflectance spectra of some main-belt asteroids contain a 3- $\mu\text{m}$  band, which is explained by the presence of water or hydroxyl groups in minerals. Recent observations of 24-Themis have been found to display evidence of water ice.

**Aims.** We synthesize iron oxy-hydroxide materials and in the laboratory measure their near-infrared spectra under dry conditions to compare with asteroid observations.

**Methods.** The syntheses are performed using either the well-established titration method or a non-conventional hydrothermal method. Bi-directional near-infrared reflectance spectra are obtained using the spectrogonio radiometer available at LPG/IPAG. Spectra are measured in a vacuum to avoid contamination by adsorbed water.

**Results.** The reflectance spectra that we measure for synthesized goethite are consistent with published transmission spectra. The 3- $\mu\text{m}$  band in goethite has a minimum around 3.10  $\mu\text{m}$ , similar to observations of 24-Themis. Its overall shape matches well Themis's 3- $\mu\text{m}$  band; goethite-like oxy-hydroxydes are a viable alternative way of explaining 24-Themis near-IR spectra

**Key words.** meteorites, meteors, meteoroids – minor planets, asteroids: general – minor planets, asteroids: individual: 24-themis – minor planets, asteroids: individual: 1-Ceres

## 1. Introduction

There are clear lines of evidence for a protracted origin of water on Earth and terrestrial planets (Albarede 2009). Within this framework, interest is growing toward the study of small (and usually cold) Solar System bodies, since mass and isotopic balance calculations suggest that successive impacts of comets and asteroids might have contributed significantly to the Earth's hydrogen budget (Dauphas et al. 2000). While hydrogen is mostly present as water ice within comets, it is supposed to occur within mineral structures as hydroxyl groups (-OH) or water molecules in the case of asteroids. Recent observations have suggested that H<sub>2</sub>O ice might also be present at the surface of main-belt asteroids. This interpretation suggests the presence of a previously unknown water reservoir, which might also have contributed significantly to the Earth water budget.

The most direct identifications of H<sub>2</sub>O ice and hydrated minerals at the surface of asteroids are based on observations of a near-infrared absorption band centered around 3- $\mu\text{m}$ . This broad band (typically stretching over almost one micrometer) is due to the combination of -OH bending and stretching vibrational modes, which are active for both cation-bonded hydroxyl groups within minerals (X-OH where X is usually a transition metal) and the H<sub>2</sub>O molecule. In the latter case, it is active when H<sub>2</sub>O is present as ice, as adsorbed water (i.e., weakly bonded water stuck onto a mineral surface), or as structural water (H<sub>2</sub>O molecule present within the mineral structure).

This absorption has been detected on most C-type asteroids that are commonly related to the carbonaceous chondrite meteorite family (Hiroi et al. 1996). Although referred to systematically as the “3- $\mu\text{m}$  band”, both meteorites and asteroids display

a diversity of 3- $\mu\text{m}$  band shapes, which is not currently fully understood (Jones et al. 1990; Milliken & Rivkin 2009; Hiroi et al. 1996; Rivkin & Emery 2010; Beck et al. 2010b). Here, we show that, as for asteroids, a diversity exists within near-IR spectral signatures of -OH bearing minerals and that goethite-like minerals have a 3- $\mu\text{m}$  band extremely similar to that of water-ice absorption (i.e. with an absorption maximum at 3.1  $\mu\text{m}$ ). The presence of goethite on the surface of asteroids might explain the occurrence of a water-ice-like 3- $\mu\text{m}$  band (Rivkin & Emery 2010; Campins et al. 2010) in regions where surface ice stability is unexpected. We propose a formation mechanism for goethite, from the precursor phase ferrihydrite, that has been observed in carbonaceous chondrites.

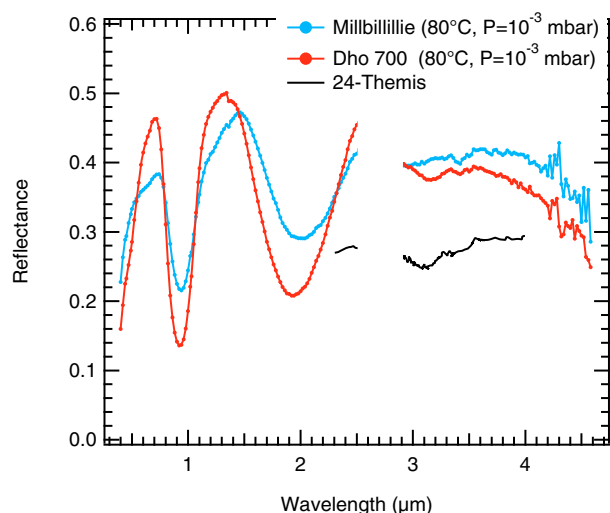
## 2. Methods

### 2.1. Syntheses of iron oxy-hydroxide

We synthesized the high-purity goethite material by means of an instantaneous chemical reaction between NaOH and Fe(NO<sub>3</sub>)<sub>3</sub> under hydrothermal conditions (70 °C). This non-conventional hydrothermal method allows the synthesis of high-purity goethite material as attested by scanning electron microscopy (SEM), X-ray powder diffraction (XRD), and transmission infrared spectroscopy (FTIR).

### 2.2. Sample preparation

The 3- $\mu\text{m}$  band of pure goethite is saturated when studied in reflectance geometry (reflectance close to 0 within the band). Thus, goethite was mixed at low concentration (“diluted”) in

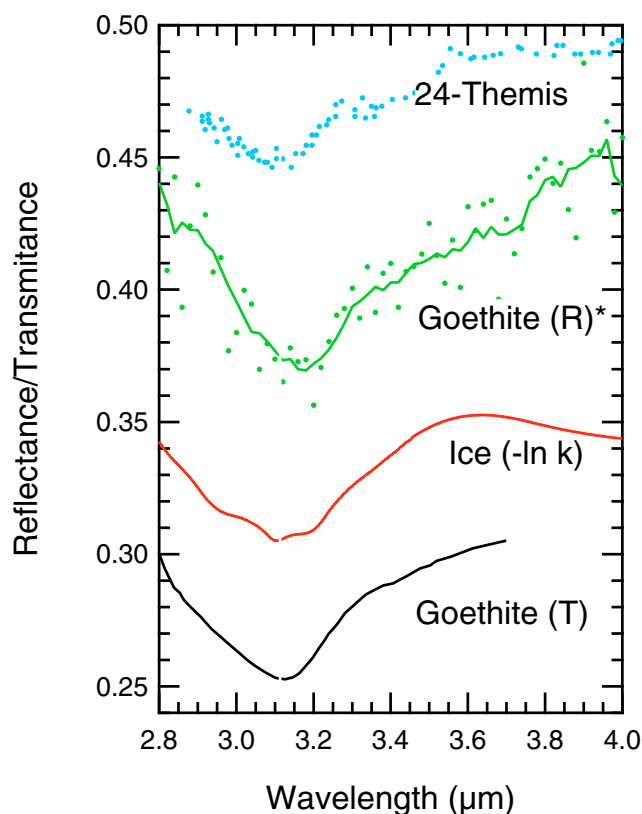


**Fig. 1.** NIR spectra of a eucrite (Millbillillie) and a diogenite powder (Dhofar700) showing the absence of significant H<sub>2</sub>O- related 3- $\mu$ m band upon heating to 80 °C and in a moderate vacuum ( $P = 10^{-3}$  mbar). Note the presence of a 3.1  $\mu$ m band in the spectrum of Dhofar 700. From its shape and position, this feature may be caused by a small amount of goethite produced by terrestrial weathering. The small absorption at 3.4  $\mu$ m is likely due to the presence of organic contamination.

a silicate component. A fresh basalt from the Massif Central (France) was used as the silicate component after being grinded in an agathe mortar and sieved below 100  $\mu$ m. Two mixtures were prepared with 5 and 10 weight percent of goethite, respectively. The average grain size of the goethite crystals is smaller than 5- $\mu$ m, as determined using secondary electron microscopy. Prior to our analyses, the mixtures were gently grinded to ensure efficient mixing. The samples were then put in a 25 mm wide and 1 mm deep holder for reflectance measurements. A sample holder was filled to the rim with sample powder and then very slightly packed until the surface appeared smooth.

### 2.3. Reflectance spectra measurements

Infrared reflectance spectra were measured using the spectrogonio radiometer available at the Laboratoire de Planétologie de Grenoble (Brissaud et al. 2004). This instrument enables bidirectional reflectance spectra measurements with a good photometric accuracy (below 1%). Spectra were measured in the 0.5–4.6  $\mu$ m range with a sampling interval of 20 nm. Because ambient atmospheric water might adsorb on the surface of the sample and perturb the 3- $\mu$ m band (especially for hydroxides that are strongly adsorbing materials), spectra were acquired within the SERAC environmental cell (Pommerol et al. 2009). Samples were heated up to 80 °C under moderate vacuum ( $P = 10^{-3}$  mbar), which enables the total removal of adsorbed water. Spectra were measured under normal incidence, and with an observation angle of 30°. To confirm that adsorbed water had been totally removed with our protocol, we measured the spectra of the Millbillillie meteorite. Millbillillie is a eucrite, which is amongst the driest rocky samples of the Solar System. As shown in Fig. 1, the spectrum measured in a vacuum and at  $T = 80$  °C, does not display any significant 3- $\mu$ m band. This testifies to the efficiency of our setup in removing adsorbed water.



**Fig. 2.** From top to bottom, the 3- $\mu$ m band in goethite, water ice, and as observed on Themis. The Themis spectrum has been digitized from Rivkin & Emery (2010). The green spectrum is the ratio between the two mixtures with different amounts of goethite, from Fig. 1. The black curve corresponds to the transmission spectrum of synthetic goethite from Ruan et al. (2002), obtained at 110 °C. The red curve shows the imaginary index of the optical constant of water ice (Schmitt et al. 1998) for comparison. Data have been offset and rescaled for clarity.

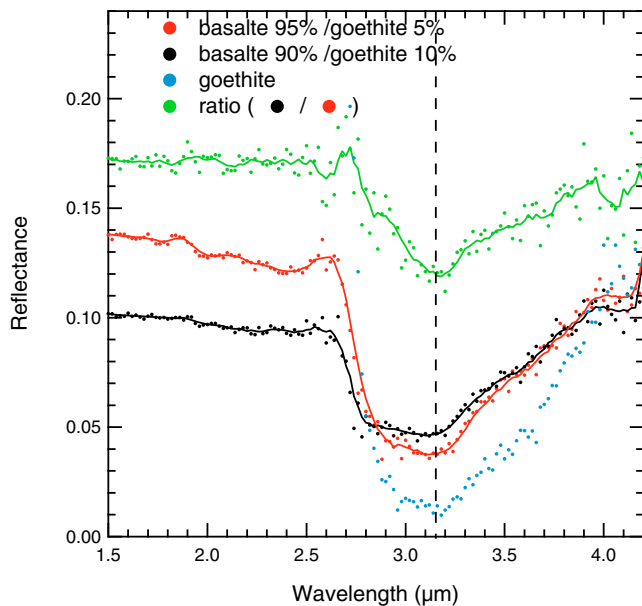
## 3. The near-IR spectrum of goethite

### 3.1. Transmission spectra

Goethite is an iron oxy-hydroxide, of structural formula FeO-OH. This mineral belongs to the *Pbnm* space group, and its structure is made of slightly distorted hexagonally packed FeO octahedra (Ruan et al. 2002). The near-IR spectrum of goethite contains a 3- $\mu$ m band that corresponds to the stretching mode of the hydroxyl groups. Although all the hydroxyl groups should be equivalent in this crystal group, the presence of two directions of hydrogen bonds induces a splitting of this stretching mode (Ruan et al. 2002). Two distinct bands are present and observed in the transmission spectrum of synthetic goethite (Fig. 2). These bands were modeled by two Gaussians by Ruan et al. (2002), located at 3450  $\text{cm}^{-1}$  (2.90  $\mu$ m) and 3210  $\text{cm}^{-1}$  (3.11  $\mu$ m). The goethite band is remarkably similar to the 3- $\mu$ m band of pure water-ice. For comparison, we also present the imaginary index of water ice in Fig. 2.

### 3.2. Reflectance spectra

The near-IR spectrum of pure goethite displays a strong 3- $\mu$ m feature, which is close to saturation in a large domain of the spectrum (Fig. 3). We note that most previously published reflectance spectra of goethite were measured under ambient conditions, where a significant amount of water might be present.



**Fig. 3.** Bi-directional (normal incidence and observation angle of  $30^\circ$ ) infrared spectra of pure synthetic goethite (blue dots) and synthetic goethite/basalt mixtures (red and black dots). Spectra were measured at  $T = 80^\circ\text{C}$  and under vacuum conditions. Because the  $3\ \mu\text{m}$  band of pure goethite is close to saturation, we calculated the ratio of the spectra of the two mixtures (green dots, offset and rescaled for clarity) to retrieve the shape of a “diluted” goethite. Solids lines correspond to moving averages.

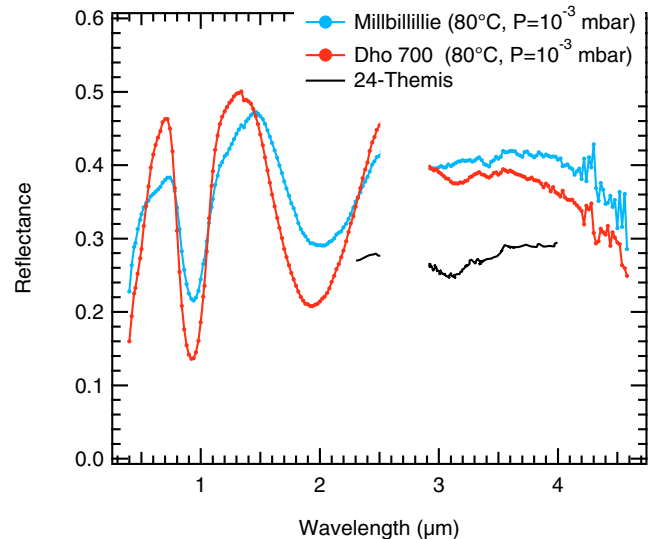
Goethite has a strong affinity for water molecules (since it can build H-bonds) and measurements under moderate vacuum ( $P = 10^{-3}$  mbar) and moderate temperature ( $80^\circ\text{C}$ ) are required. We mixed goethite in an almost neutral component, with two

different mixing ratios (5 and 10 weight %). Because a minor  $3\ \mu\text{m}$  band exists for the natural basalt, we divided the two spectra to retrieve the signature of pure goethite (Fig. 3). This ratio is in excellent agreement with the transmission spectra published previously (Fig. 2). Because of the low signal to noise ratio obtained, the band center of the smoothed near-IR spectra appeared to be shifted toward higher wavelengths than the transmission spectra (Fig. 2), but this difference is certainly within the margins of the analytical uncertainty.

## 4. Discussion

### 4.1. Diversity of the $3\text{-}\mu\text{m}$ band on asteroids

Determining the spectrum of the full  $3\text{-}\mu\text{m}$  band is challenging because of the presence of terrestrial atmospheric absorptions bands within the  $2.6\text{--}2.8\ \mu\text{m}$  range, and the thermal emission contribution at wavelengths above  $3.3\text{--}3.4\ \mu\text{m}$ . To date, the most clearly resolved asteroid spectra displaying a  $3\ \mu\text{m}$  band have been those of the largest asteroidal bodies. As well as on hydrated meteorites, this band shows some diversity (Beck et al. 2010b; Jones et al. 1990; Rivkin & Emery 2010) on asteroids. Three spectra that might be considered as end-members (Rivkin 2010) are presented in Fig. 4. In “Pallas-type” spectra, the band strength maximum is located below  $2.8\ \mu\text{m}$  and a general positive slope is present from  $2.8\ \mu\text{m}$  to  $3.6\ \mu\text{m}$ . This type of  $3\ \mu\text{m}$  band can be explained by the presence of hydroxyl groups within a phyllosilicate-like structure (Beck et al. 2010a). The 1-Ceres and 24-Themis spectra clearly differ from Pallas spectra because they display an absorption band centered at  $3.06\ \mu\text{m}$  for 1-Ceres



**Fig. 4.** Different types of  $3\text{-}\mu\text{m}$  band as observed on asteroids. 1-Ceres spectrum is from Milliken & Rivkin (2009), 2-Pallas spectrum is from Jones et al. (1990), and 24-Themis data are from Rivkin & Emery (2010). Spectra have been offset and rescaled for clarity.

and  $3.1\ \mu\text{m}$  for 24-Themis. A second absorption band appears to be present in the spectra of 24-Themis and 1-Ceres, around  $3.3\text{--}3.4\ \mu\text{m}$ , that has been attributed to the presence of carbonates (1-Ceres) or organic compounds (24-Themis) (Milliken & Rivkin 2009; Rivkin & Emery 2010; Campins et al. 2010).

### 4.2. The 1-Ceres case

Ceres is the most massive asteroid, and its surface reflects a well-defined  $3\ \mu\text{m}$  band (Fig. 4). This band differs from those in other asteroid observations because it contains an absorption band centered at  $3.06\ \mu\text{m}$ , superimposed on a general absorption slope with a maximum below  $2.8\ \mu\text{m}$ . Because the spectrum of natural brucite ( $\text{Mg}(\text{OH})_2$ ) also contains this absorption band at  $3.06\ \mu\text{m}$ , this mineral phase has been suggested as a possible component of Ceres’s surface material (Milliken & Rivkin 2009). In the spectra of natural brucite, this small band is superimposed on a stronger band with a maximum of absorption below  $2.8\text{-}\mu\text{m}$ , characteristic of  $\text{Mg}\text{-OH}$ , as expected from the brucite structure. The  $3.06\text{-}\mu\text{m}$  band is not expected for the theoretical brucite structure (Pascale et al. 2004), and it is not clear whether it is due to brucite, or to the presence of some impurities, which are common in natural minerals. That its spectrum contains a  $3\ \mu\text{m}$  band with increasing absorption down to at least  $2.8\text{-}\mu\text{m}$  implies that the surface of 1-Ceres might be covered by some  $\text{-OH}$  bearing phase in which the bounding cation might be  $\text{Mg}$ , but brucite might not be the only candidate surface material. Because of the small difference in the position of the  $3.06\ \mu\text{m}$  feature, pure goethite might not explain this feature. However, natural minerals can contain various amounts of impurities (Al can exist in the goethite structure as an example), which could produce some variations in the band position).

### 4.3. The 24-Themis case

High-resolution spectra of 24-Themis were reported by two different groups (Rivkin & Emery 2010; Campins et al. 2010). Both studies discovered significant absorption around  $3\text{-}\mu\text{m}$ , that was



attributed to water ice. A coating model was invoked to obtain a good fit to the observations (Rivkin & Emery 2010), in which a thin film of water ice is present at the surface of an anhydrous component. The 3- $\mu\text{m}$  band they reported differs from that typically observed in hydrated meteorites (Fig. 4) in terms of the shape and position of the absorption maximum, which seems to corroborate their interpretation as water-ice. However, as can be seen on Fig. 2, the presence of goethite might also be able to explain this observation. The spectra of 24-Themis differ from Pallas or Ceres-like spectra because their the band minima are observed at longer wavelength (3.1  $\mu\text{m}$ ). This absorption maximum is observed in the optical constants of water ice but also for goethite (Fig. 3). Closer examination of 24-Themis, goethite, and water ice IR signatures reveals that, within the 2.8–3.6  $\mu\text{m}$  region, it is not possible to discriminate between the presence of water-ice or goethite on the surface of 24-Themis. However, within the 3.6–4.0 range, water-ice shows a decrease of its absorption coefficient, which is not observed in 24-Themis nor in goethite. This implies that the 3.1  $\mu\text{m}$  band observed on 24-Themis could be due to the presence of a minute amount of goethite rather than crystalline water ice.

#### 4.4. Possible mechanism for the origin of goethite

Goethite is not a common mineral within the available meteorite collection (Papike 1996). It can be found as an alteration product in selected meteorite classes, but it is then likely to have formed during some terrestrial aqueous weathering event (see the small absorption band observed at 3.1  $\mu\text{m}$  in the spectra of the spectra of DHO700 in Fig. 1). However, a precursor for goethite, ferrihydrite, has been reported in the very primitive CI meteorites (Beck et al. 2010a; Tomeoka & Buseck 1988), which present fingerprints of an extensive aqueous alteration.

Ferrihydrite is a poorly crystalline iron (oxy)hydroxide, with nominal chemical formula  $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$  (Chuckrov 1973; Fleisher et al. 1975). This chemical formula can be expressed as  $\text{FeOOH}(0.4\text{H}_2\text{O})$  (Hiemstra & Van Riemsdijk 2009); to account for the  $\text{FeOOH}$  stoichiometry of the core of the dominant structures (Drits et al. 1993). This phase is highly disordered and its exact mineral structure is still a matter of active debate (Michel et al. 2007; Manceau 2009, 2010). Upon moderate heating (ex. 300 °C), ferrihydrite destabilizes toward the more stable goethite ( $5\text{Fe}_3\text{O}_3 \cdot 9\text{H}_2\text{O}$  gives  $10\text{FeOOH} + 4\text{H}_2\text{O}$ ), and at high temperature (above 500 °C) the ferrihydrite and/or goethite are completely dehydrated, leading to formation of a stable hematite mineral ( $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$  gives  $5\text{Fe}_2\text{O}_3 + 9\text{H}_2\text{O}$  and/or  $10\text{FeOOH}$  gives  $5\text{Fe}_2\text{O}_3 + 5\text{H}_2\text{O}$ ).

Thus, with sufficient heating, ferrihydrite might be a good precursor to the formation of goethite. Various heat sources can activate the transformation. A first candidate is the absorption of vis-NIR sunlight, which might be quite efficient for these low-albedo objects. However, this scenario might be applicable only to asteroidal bodies that experience close encounters with the Sun, i.e. near earth objects. For 24-Themis and members of the Themis family, with a subsolar point temperature of 210 K, an alternative can be found in the form of very localized energy deposition by recurrent micrometeorite impacts, which could favor the phase transition. The presence of a fine layer or recondensed iron metal spherules observed at the surface of the grains from the lunar regolith has suggested formation from a vaporization/recondensation process (Sasaki et al. 2001). The temperature required for the phase transition appears however to be easily accessible to this process. The micrometeorite impacts

on asteroids are likely to be less energetic than on the Moon because of the difference in impact velocity (on average 20  $\text{km s}^{-1}$  on the Moon vs. 5  $\text{km s}^{-1}$  on asteroids) but they are expected to be more frequent on asteroids than on the Moon. Finally, ferrihydrite might also transform to goethite upon exposure to the solar wind, although this has never been tested experimentally. Thus, although goethite-rich samples are absent in the meteorite collection, a fine surface layer of space-weathered CI-like material might provide an explanation of the observation of a goethite like 3- $\mu\text{m}$  band on some asteroids.

## 5. Conclusions

In this letter, we have reported on the near-IR spectrum of synthetic goethite, and the spectra of its various mixtures with a basaltic component, obtained under dry conditions. We have shown that the measured spectra agrees with published transmission spectra of goethite. Unlike most -OH bearing minerals, the 3- $\mu\text{m}$  band of goethite is broad and displays a maximum of absorption around 3.1  $\mu\text{m}$ , that resembles that of water ice. A similar spectral signature was observed on 24-Themis, and explained by the presence of water-ice. We have made the case here that the presence of a minute amount of goethite can also explain the shape of the 24-Themis 3.1  $\mu\text{m}$  band. This mineral phase might be a product of the thermal processing of ferrihydrite-bearing hydrated chondrites. Comparison with absorption features in the visible and at 0.9  $\mu\text{m}$  that are expected for goethite might help in distinguishing between water ice and goethite signatures.

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