

## ICE VS GOETHITE AS THE ORIGIN OF THE 3 MICRON FEATURE OF LOW ALBEDO ASTEROIDS

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**Introduction:** 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- $\mu$ m. This broad band (typically stretching over almost one  $\mu$ m) is due to the fundamental -OH stretching vibrational modes and combinations with bending 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 [1]. Although referred to systematically as the "3- $\mu$ m band", both meteorites and asteroids display a diversity of 3- $\mu$ m band shapes [2].

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- $\mu$ m band extremely similar to that of water-ice absorption (i.e. with an absorption maximum at 3.1  $\mu$ m). The presence of goethite at the surface of asteroids might explain the occurrence of a water-ice-like 3- $\mu$ m band [3-4] in regions where surface ice stability is unexpected.

**Sample synthesis and preparation:** 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). The 3- $\mu$ 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 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.

**Reflectance spectroscopy:** Infrared reflectance spectra were measured using the spectrogonio radiometer available at the Laboratoire de Planétologie de Grenoble [5]. This instrument enables bi-directional 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, spectra were acquired within the SERAC environmental cell [6]. Samples were heated up to 80°C under vacuum (P=10<sup>-3</sup> mbar) to remove of adsorbed water. Spectra were measured under normal illumination incidence, and with an observation angle of 30°.

**NIR spectra of goethite:** The near-IR spectrum of pure goethite displays a strong 3- $\mu$ m feature, which is close to saturation in a large spectral domain (Fig. 1). We note that most previously published reflectance spectra of goethite were measured under ambient conditions, where a significant amount of water might be present. Goethite has a strong affinity for water molecules (since it can build H-bonds) and measurements under moderate vacuum (P=10<sup>-3</sup> mbar) and moderate temperature (~80°C) are required. We mixed goethite with an almost neutral component, with two different mixing ratios (5 and 10 weight %). Because a minor 3  $\mu$ m band exists for the natural basalt, we divided the two spectra to retrieve the signature of pure goethite. This ratio is in excellent agreement with the transmission spectra published previously (Fig. 1 and 2).

**The 24-Themis case:** High-resolution spectra of 24-Themis were reported by two different groups [3-4]. Both studies discovered significant absorption around 3- $\mu$ m, that was attributed to water ice. A coating model was invoked to obtain a good fit to the observations [3], in which a thin film of water ice is present at the surface of an anhydrous component. The 3- $\mu$ m band they reported differs from that typically observed in hydrated meteorites 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. 1, 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 band minima are observed at longer wavelength (3.1  $\mu$ m). This absorption maxi-

mum is observed in the optical constants of water ice but also for goethite (Fig. 2). 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.

**Possible formation mechanism:** Goethite is not a common mineral within the available meteorite collection. 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. However, a precursor for goethite, ferrihydrite, has been reported in the very primitive CI meteorites [7-8], which present fingerprints of an extensive aqueous alteration. Ferrihydrite is a poorly crystalline iron (oxy)hydroxide, with nominal chemical formula  $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ . This phase is highly disordered and its exact mineral structure is still a matter of active debate [9-10]. Upon moderate heating (ex.  $300^\circ\text{C}$ ), ferrihydrite destabilizes toward the more stable goethite ( $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$  gives  $10\text{FeOOH} + 4\text{H}_2\text{O}$ ), and at high temperature (above  $500^\circ\text{C}$ ) 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 its formation from a vaporization/recondensation process [11]. The temperature required for the phase transition appears however to be easily accessible to this process. 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.

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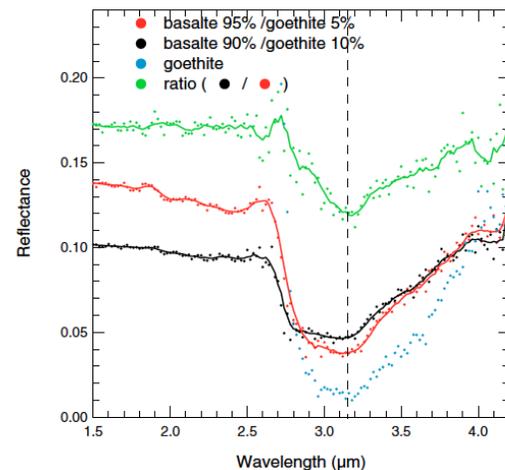


Figure 1: NIR spectra of pure goethite (blue) and goethite/basalt mixture.

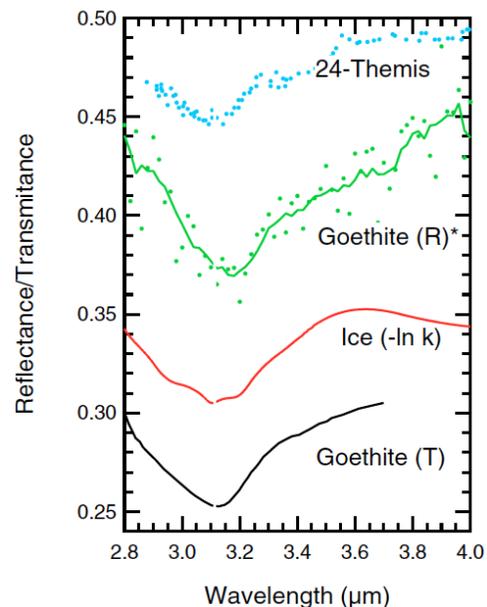


Figure 1: Spectra of 24-Themis [3], optical constant of water ice [12], the transmission spectra of goethite [13] and the reflectance spectra of goethite we obtained