



# Derivation of optical constants for nanophase hematite and application to modeled abundances from in-situ Martian reflectance spectra



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## ABSTRACT

Several studies have detected the presence of nanophase ferric oxide, such as nanophase hematite, across the martian surface through spacecraft and rover data. In this study, we used the radiative transfer method to detect and quantify the abundance of these nanophase particles. Because the visible/near-infrared spectral characteristics of hematite > 10 nm in size are different from nanophase hematite < 10 nm, there are not any adequate optical constants of nanophase hematite to study visible to near-infrared rover/spacecraft data of the martian surface. Consequently, we found that radiative transfer models based upon the optical constants of crystalline hematite are unable to reproduce laboratory spectra of nanophase hematite. In order to match the model spectra to the laboratory spectra, we developed a new set of optical constants of nanophase hematite in the visible and near-infrared and found that radiative transfer models based upon these optical constants consistently model the laboratory spectra. We applied our model to the passive bidirectional reflectance spectra data from the Chemistry and Camera (ChemCam) instrument onboard the Mars Science Laboratory rover, Curiosity. After modeling six spectra representing different major units identified during the first year of rover operations, we found that the nanophase hematite abundance was no more than 4 wt%.

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## 1. Introduction

### 1.1. The spectra of nanophase hematite

The red color of Mars has long been known to be due to the presence of ferric oxide, but with few exceptions the reflectance spectrum of Mars is inconsistent with the presence of crystalline ferric oxides. Ferric iron-bearing minerals typically exhibit a spectral shoulder near 700 nm and an absorption feature near 860 nm. However, in most spectra of Mars, this 860 nm absorption feature is absent (Singer et al., 1979; Bell et al., 2004). Analyses of in-situ data showed that nanophase ferric oxide particles, such as nanophase hematite, are ubiquitous on Mars. Various data sets (i.e., Mössbauer Spectrometer, Panoramic Camera, Alpha Proton X-ray Spectrometer) from the Spirit and Opportunity Mars Exploration Rovers showed evidence of nanophase ferric oxide at Meridiani Planum and Gusev Crater (Bell et al., 2004; Yen et al., 2005; Morris et al. 2006).

Morris et al. (1989) showed that nanophase particles of hematite are the likely coloring agent of Mars. They prepared samples with nanophase hematite with grain sizes < 10 nm suspended in silica and alumina matrices and found that the spectra do not exhibit the 860 nm absorption feature, unlike the spectra of bulk hematite. Based upon analysis of Mössbauer spectra, Morris et al. (1989) found that when nanophase hematite particles are > 10 nm, their visible to near-infrared spectra showed very distinct crystalline hematite bands reminiscent of spectra of pure bulk hematite powders. Morris et al. (1989) hypothesized that the absence of the 860 nm absorption in samples containing < 10 nm sized hematite particles was due to the compromised crystalline structure of hematite at these small sizes. In all hematite particles, the surface and near surface of a particle do not have a well-formed hematite crystalline structure resulting in a poorly defined ligand field, preventing the development of the 860 nm absorption feature. On the other hand, the core of a particle has a well-defined crystalline structure leading to a strong ligand field that produces the 860 nm absorption feature. In large hematite particles (> 10 nm), the ratio of core volume, which contains well-defined crystalline structure, to surface volume, which contains poorly defined crystalline structure, is high, resulting in spectra of these particles exhibiting the 860 nm absorption feature. Because

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small hematite particles with sizes < 10 nm have low core to surface volume, the 860 nm absorption feature is largely absent in the spectra of these particles.

An alternative hypothesis for the spectral differences between samples containing large and small nanophase particles (e.g., presence of the 860 nm feature) is the unusual scattering properties at the finest scale (e.g., Steyer, 1974; Marra et al., 2011). Hapke (2001) presented a formulation to model the optical effect of nanophase particles in a transparent matrix, while Lucey and Noble (2008) showed that the Hapke (2001) model successfully reproduced spectra of experimentally produced nanophase native iron (Fe<sup>0</sup>) within a silica host. However, the optical properties of native iron vary smoothly with wavelength, while hematite varies strongly, so the effects demonstrated numerically (Hapke, 2001) and experimentally (Noble et al., 2007) are not directly informative of the scattering influence on spectra of materials containing nanophase hematite. Nevertheless, the effect of size of nanophase particles on spectra of transparent hosts infused with this coloring agent is strong, so the optical effect of the nanophase size merits investigation.

In this paper we used the Hapke (2001) model and investigated its ability to reproduce the spectra of Morris et al. (1989) nanophase hematite particles, including modifications necessary to improve performance. We then applied our radiative transfer model to representative passive reflectance spectra obtained by the Chemistry and Camera (ChemCam) instrument during the first year of Curiosity Rover operations to estimate the nanophase hematite abundance near the landing site within Gale crater.

## 1.2. Radiative transfer model of nanophase particle spectra

Hapke (2001) developed a radiative transfer model to account for the strong optical effects associated with space weathering on airless objects within the inner solar system. Hapke (2001) attributed at least some of these effects to be due to tens of nanometer-sized native iron particles detected in lunar soils by ferromagnetic resonance techniques (Morris, 1976; 1978). Such particles were directly imaged by Keller and McKay (1997) and found to reside in rims on grains within lunar soils. Hapke (2001) presented a simple spectral model that to first order displayed the darkening and reddening of the visible to near-infrared reflectance associated with space weathering.

Lucey and Noble (2008) applied the Hapke (2001) model to visible and near-infrared spectra of a series of samples prepared by Noble et al. (2007) of porous silica matrices infused with nanophase native iron particles. The iron-bearing silica gels were ground and sieved to fixed size ranges followed by spectral measurements of each sample. The sample preparation methodology that they employed was that of Morris et al. (1989) with an additional step to reduce the ferric iron to native iron. These simple samples exhibited similar spectral properties found in nanophase native iron-bearing lunar soils, in which with increasing nanophase native iron abundance the samples displayed increasingly darkened and reddened reflectance spectra. Lucey and Noble (2008) found that for the sample series containing the smallest of the native iron particles (< 50 nm), Hapke's (2001) model was successful both at producing spectra that mimicked the empirical data and predicting the nanophase native iron abundance.

We will be applying the Hapke (2001) technique to hematite to determine if it can reproduce fine-grained hematite spectra. To do this, we need to find a suitable set of hematite optical constants. There are several hematite optical constants throughout the literature (e.g., Popova et al., 1973; Onari et al., 1977; Querry, 1985), but differ in spectral range and resolution. In addition several

**Table 1**

Sample names with their associated ferric oxide abundance.

Sample	Fe <sub>2</sub> O <sub>3</sub> [wt%]
S6BLANK	0.0
S6FN14	0.2
S6FN3	0.3
S6FN18	0.5
S5FN29	0.7
S6FN1	1.3
S6FN4	3.4
S6FN10	5.2
S6FN10	5.2
S6FN11	6.0
S6FN24	8.3
S6FN28	11.0
S6FN27	16.7

optical constants derivations are based on bulk hematite (Steyer, 1974; Onari et al., 1977; Bedidi and Cerville, 1993; Glotch et al., 2006; Marra et al., 2005; 2011) or fine-grained hematite (Kerker et al., 1979; Gillespie and Lindberg, 1992), which include spectral coverage of the visible to mid infrared wavelengths. Similar to the findings by Morris et al. (1989), several previous optical constants studies were unable to use bulk hematite optical constants to match the spectra of fine-grained hematite (Steyer, 1974; Marra et al., 2011). In this work, we will use the Querry (1985) optical constants because it covers the same spectral range as the laboratory spectra in Morris et al. (1989) with high spectral resolution. Therefore, this work would provide a new set of nanophase hematite optical constants in the visible and into the near infrared, which contains important absorptions in these wavelengths to study Martian mineralogy, and would be able to properly match fine-grained hematite spectra.

We use the Hapke (2001) approach in this work because it provided a validated model to the study of absorbing nanophase particles in a transparent silicate matrix; the Hapke (2001) model is well suited to quantitatively reproduce the spectral effects of nanophase hematite (< 10 nm in grain size) in silica gel as prepared and observed by Morris et al. (1989). Nanophase hematite is an interesting case from a modeling standpoint because the absorption of native iron is high throughout the visible and near infrared, but the spectra of hematite shows strong absorptions at short wavelengths (i.e., imaginary index of refraction values of ~1 near 400 nm), relatively low absorptions at near-infrared wavelengths, and a strong decrease in absorption between 400 and 600 nm.

## 2. Methods

For this work, we used reflectance spectra of the Morris et al. (1989) "Type D" samples that were shown by analysis of Mössbauer spectra to contain only hematite particles with sizes < 10.2 nm (Fig. 1a). The weight fraction of hematite particles within the samples ranged between 0 and 17 wt% (Table 1). The silica gel host particles ranged in size from 35–74 μm in size. With the exception of an iron-free sample (i.e., S6BLANK), the spectra of the samples feature properties reminiscent of those of Mars, such as the strong drop off in reflectance toward the blue portion of the spectrum and the absence of crystalline hematite features that are only occasionally observed in martian spectra (e.g., McCord et al., 1977).

We modeled the Morris et al. (1989) sample spectra using the Hapke (2001) radiative transfer model that includes the Maxwell-Garnett method to model visible to near-infrared spectra of powdered material that are coated with particles smaller than the wavelength of light (e.g., nanophase particles). Therefore, this radiative transfer model is applicable to the Morris et al. (1989)

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