

Water Adsorption on Goethite: Experimental Infrared Measurements and Theoretical Adsorption Activation

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Abstract

The study of water adsorption on mineral surfaces is fundamental to soil and atmospheric science. The physiochemical effects of mineral aerosol influence atmospheric chemistry and climate as well as soil moisture. Iron-containing minerals are abundant on Earth as well as Mars, where the existence and location of surface water is uncertain. Experimental water adsorption measurements have been conducted as a function of relative humidity (RH) on goethite (α -FeO(OH)), a common component of atmospheric mineral dust and Martian crustal material. Water adsorption on goethite was monitored using Horizontal Attenuated Total Reflectance Fourier Transform Infrared (HATR-FTIR) spectroscopy equipped with a flow cell and quantified according to Beer's Law. Water content as a function of RH was analyzed using type II adsorption isotherms to model multilayer water adsorption. Brunauer Emmet and Teller (BET), Frenkel Halsey and Hill (FHH) and Freundlich adsorption isotherms were applied to model the experimental data. Monolayer water coverage was found to be 4.758×10^{13} molecules/cm² based on BET analysis. FHH Adsorption Activation Theory (AT) was used to predict cloud condensation nuclei (CCN) activity of goethite under Earth's atmospheric conditions. Results aid in the effort of climate prediction on Earth as well as locating liquid water on Mars' surface.

Introduction

Reported to account for nearly 50% of the total global aerosol load,^{1,2} atmospheric mineral dust is believed to contribute an overall cooling effect on the climate.³ Aerosol cooling is a direct result of the atmospheric effects particles have on the Earth's radiative balance and an indirect result of the role aerosols play in cloud formation, optical properties and lifetime. It has long been accepted that atmospheric mineral dust particles are efficient at nucleating ice crystals.⁴ More recently acknowledged is mineral aerosols' ability to influence warm cloud formation by acting as cloud condensation nuclei (CCN).⁵ Today, there exists a wide variety of methods used to determine CCN activation including direct measurements using a thermal gradient diffusion chamber or CCN counter, and indirect measurements of water adsorption followed by application of FHH Adsorption Activation Theory (FHH-AT). However, there are discrepancies between the methods which has resulted in a disconnect in results.^{2,6,7,8} Continued study of water adsorption on a variety of mineral dust surfaces will play a crucial part in correcting these discrepancies.

Mineral dust aerosol is comprised of a variety of metal oxides, carbonates and aluminosilicates. Iron oxides, which are abundant metal oxides, have been found in large quantities in igneous and metamorphic rocks as well as oceanic and volcanogenic Earth systems and are the most common components of natural rust.⁹ One common iron oxide is goethite, an iron oxyhydroxide which has been found to make up between 52 and 78% of aerosol iron oxide mass in certain regions of the world.¹⁰ The presence of goethite on planetary surfaces has been previously used as an indication of low-temperature weathering involving liquid water.¹¹ Furthermore, it has been recently discovered in high quantities on the surface of Mars.¹² Due to recent debate regarding liquid water on Mars,¹³ water adsorption on the surface of goethite has become a point of interest as it has implications as a potential reservoir for water on Mars.

Only in the past decade has the scientific community begun to acknowledge that slightly hydrophobic, insoluble aerosol particles can become CCN active and contribute to the cloud droplet number concentration (CDNC).^{1,2,5} Traditional Kohler Theory, used to simulate aerosol cloud activation, is based on particle curvature and water activity influenced by the presence of soluble material.^{4,14} Since mineral dust aerosol is insoluble and contains minimal soluble components upon initial atmospheric emission, it was previously believed to be a negligible contributor to the CDNC in the atmosphere as the soluble fraction tends to drive aerosol activation. However,

many studies have shown that mineral dust aerosol can be important CCN, especially if it contains a pre-adsorbed layer of water. Recent modifications of the Kohler Theory, also known as FHH-AT, can now predict CCN activation of mineral dust aerosol rather well.² However, FHH-AT requires accurate knowledge of FHH adsorption parameters obtained from water adsorption measurements.

In this study, surface-adsorbed water on goethite was quantified as a function of relative humidity (RH) through the use of a Horizontal Total Attenuated Reflectance Fourier Transform Infrared Spectrometer (HATR-FTIR) equipped with a flow cell (Thermo Fisher Scientific Inc.). The experimental results were applied to three type II adsorption isotherms, including Brunauer Emmet and Teller (BET), Frenkel- Halsey-Hill (FHH) and Freundlich adsorption isotherms. FHH adsorption parameters were used to predict CCN activation of goethite using FHH-AT.

Experimental Methods and Analysis

Goethite (Fluka) powder was used as received. The goethite powder was found to have a BET surface area of $9.20 \pm 0.04 \text{ m}^2\text{g}^{-1}$ using nitrogen (N_2) as the adsorbate and an average particle diameter of $0.320 \mu\text{m}$ calculated from SEM images. $18 \text{ M}\Omega$ water was generated by filtering deionized water through a Barnstead EASYpure LF (model 07381) compact ultrapure water system and used to generate humidified N_2 as described below. Approximately 12000 mg/L of goethite/ $18 \text{ M}\Omega \text{ H}_2\text{O}$ slurry was used to prepare the sample via deposition unto a germanium Internal Reflection Element (Ge IRE) (Pike Technologies) followed by drying for 24 hours in ambient air. The sample mass and geometric surface area were determined by averaging measurements collected before and after water exposure.

Experimental water adsorption measurement procedures have been reported previously.¹ Briefly, the sample in the flow cell was further dried by exposure to dry N_2 (Welsco) at a rate of 0.5 L/min , as measured at the outflow of the flow cell, for 24 hours prior to water exposure. The RH was varied by forcing a variable fraction of the dry N_2 through a humidification chamber. The humidified N_2 was allowed to mix and equilibrate with the remaining fraction of dry N_2 in a mixing chamber (minimum residence time = 2.5 minutes). The RH was measured using a hygrometer (Fisher Scientific 11-661-7a) inside the mixing chamber just prior to entering the HATR flow cell. FTIR spectra were collected at room temperature using a Nicolet 6700 spectrometer between 400 to 4000 cm^{-1} by averaging 250 scans at a resolution of 4 cm^{-1} .

Prior to exposure to water vapor, an FTIR spectrum (Figure 1a) was collected to ensure sample dryness.

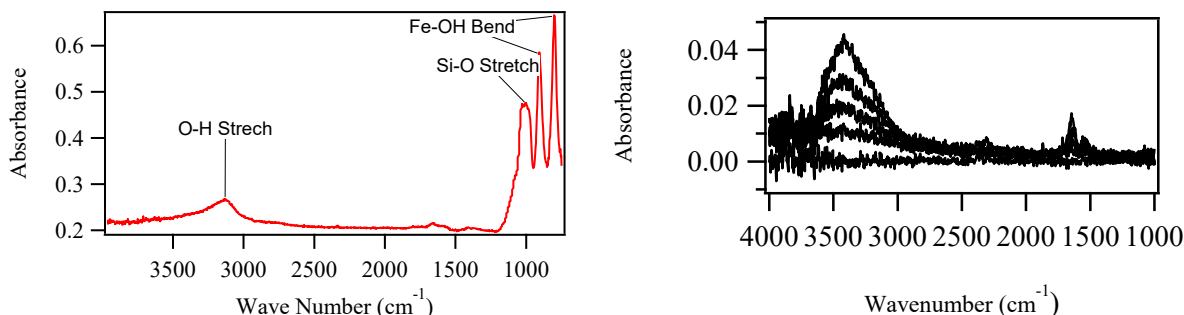


Figure 1a. Infrared spectrum of dry goethite prior to water vapor exposure (background = blank Ge IRE).

Figure 1b. Infrared spectra of goethite as a function of RH, collected at 0, 17, 56, 74 and 90% RH (background = dry goethite)

Condensed phase water occurs at $\sim 3300 \text{ cm}^{-1}$ and 1650 cm^{-1} representing the O-H stretching region and the H-O-H bending mode, respectively. Note that the H-O-H bending feature is not present in Figure 1a, suggesting that the sample was dry prior to water exposure. The O-H stretching mode observed is the result of goethite's surface hydroxyl groups, thus not an indication of adsorbed water. During exposure to water vapor, an IR background of the dry goethite was used such that the only observable FTIR absorption features during exposure are due to

adsorption of water. RH was increased or decreased incrementally, allowing for 45 minutes of equilibration time between each spectra collected to ensure steady-state water adsorption.

Figure 1b displays the results of steady-state water adsorption IR spectra collected while varying RH between 0-93%. As shown, the height of the H-O-H bending and O-H stretching regions increases with increased RH. Thus, the total amount of water adsorbed on the goethite sample increases with and is dependent upon RH. The H-O-H bending mode was used to quantify adsorbed water due to fewer spectral interferences compared to the O-H stretching region.

Water adsorption was quantified using Beer's Law and optical constants of bulk water, according to the literature.^{11,14,15} Figure 2 shows water content as a mass ratio ($\text{gram}_{\text{water}}/\text{gram}_{\text{Goethite}}$) as a function of % RH. The error bars for water content and percent RH represent one standard deviation from the mean of multiple data points collected at similar RH values. Figure 2 shows that at low RH values, goethite contains a small, yet significant, amount of adsorbed water which increases slowly and consistently until 70% RH. Above ~70% RH, a more rapid increase in adsorbed water is observed with increasing RH, suggesting that multilayer water adsorption is occurring on the surface. Notably, at 80% RH, goethite contains ~10% water by mass, similar to kaolinite clay a clay mineral with high surface density of hydroxyl groups.¹

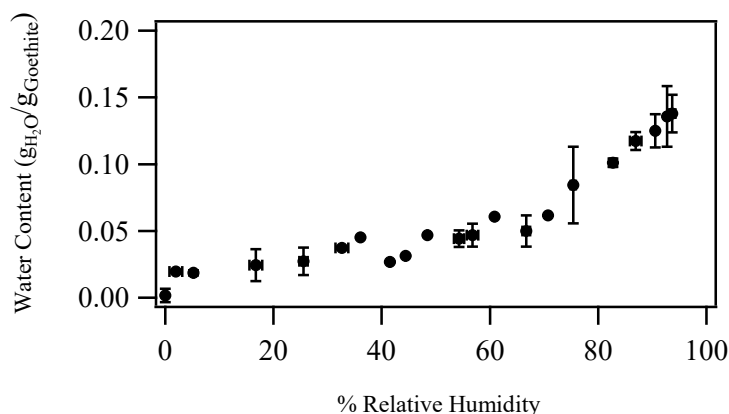


Figure 2. Mass ratio of water content on goethite as a function of percent RH.

Previous studies have shown that the water content on some minerals do not vary with temperature down to 212 K.¹⁴ If true for goethite, we would expect the results shown in Figure 2 to apply to Martian conditions, as goethite contains adsorbed water even at very low RH values. However, more studies on the temperature dependence of water adsorption on goethite should be conducted to validate the applicability of this study on both the notably colder Mars surface which typically ranges from -100° to -5° C and Earth's troposphere which ranges from -51° to 17° C.^{16 17}

Theoretical Methods

The experimental water adsorption results on goethite were analyzed by fitting with three unique type II isotherms, including BET, FHH and Freundlich, described in detail below. Results obtained from FHH analysis allowed for further assessment of goethite as a potential CCN in Earth's atmosphere using FHH-AT.

Brunauer Emmet and Teller (BET) Adsorption Isotherm

The BET adsorption isotherm is one of the most commonly applied multilayer adsorption isotherms. It is commonly used with an inert gas such as Ar or N₂ as a method for determining specific surface area upon identification of monolayer surface coverage and the size of the adsorbate molecule. Equation 1 shows the linear form of the BET model.¹⁸

$$\frac{\frac{P}{P_o}}{\left(1 - \frac{P}{P_o}\right)V} = \frac{1}{V_m c} + \frac{(c-1)}{V_m c} \left(\frac{P}{P_o}\right) \quad (1)$$

In Equation 1, $\frac{P}{P_o}$ represents RH, V is the volume of water adsorbed to the goethite surface (cm^3), V_m is the volume (cm^3) of water at which one monolayer covers the surface and c is a constant that is related to the enthalpy of adsorption for any layer of water.^{1,18} V was determined from the mass ratio of adsorbed water using Equation 2.

$$V = \frac{m_{H_2O} m_{sample}}{m_{sample} D_{H_2O}} \quad (2)$$

In Equation 2, m_{sample} is the mass (g) of sample, $\frac{m_{H_2O}}{m_{sample}}$ represents the experimental mass ratio of adsorbed water ($\text{g}_{H_2O}/\text{g}_{Goethite}$), and D_{H_2O} is the density of water at room temperature (3.34×10^{22} molecules/ cm^3).²⁰

The BET model was applied to both N_2 and water FTIR measurements to obtain the specific surface area and V_m for water, respectively.

Freundlich Adsorption Isotherm

The Freundlich adsorption isotherm was chosen as it has been shown to represent experimental water adsorption on mineral surfaces well, particularly in high RH conditions. Additionally, Freundlich provides parameters that represent adsorption capacity and strength that can be compared to other mineral surfaces. Unlike the BET model, the Freundlich isotherm assumes heterogeneity of adsorption sites and intermolecular interactions between the adsorbate and the mineral surface. The later assumption proves to be especially important due to the hydrogen bonding that occurs between adsorbed water and the surface hydroxyls of goethite. Equation 2 represents the linear form of the Freundlich model.¹⁹

$$\ln\left(\frac{x}{m}\right) = \ln(k) + \left(\frac{1}{n}\right) \ln\left(\frac{P}{P_o}\right) \quad (3)$$

In Equation 3, $\frac{x}{m}$ is the mass ratio of adsorbed water ($\text{g}_{H_2O}/\text{g}_{Goethite}$), $\frac{P}{P_o}$ is the RH, and k and n are Freundlich fit parameters associated with adsorption capacity and strength, respectively. A linear regression analysis of experimental data allows for determination of the Freundlich adsorption parameters.

Frenkel-Halsey-Hill (FHH) Adsorption Isotherm

The FHH adsorption isotherm is unique in that it accounts for both long and short-range interactions between the adsorbate and mineral surface as well as the interactions among adsorbate molecules. Equation 3 shows the FHH adsorption model.

$$S = \exp(-A_{FHH} \theta^{-B_{FHH}}) \quad (4)$$

In Equation 4, S represents the saturation ratio ($\frac{P}{P_o}$), θ is the relative number of adsorbed water layers and A_{FHH} and B_{FHH} are the FHH fit parameters. A_{FHH} represents the interactions between the surface of the goethite and the first monolayer of water and interactions among adsorbate molecules. B_{FHH} describes the long-range interaction between goethite surface and the subsequent water layers. In this study, A_{FHH} and B_{FHH} are experimentally determined by fitting the FHH model to FTIR water adsorption measurements.

In the FHH model, the θ term is determined by V/V_m , where V_m is the volume (cm^3) of adsorbed water at monolayer coverage from the BET fit to the experimental data and V is the volume (cm^3) of adsorbed water at steady-state for a particular RH calculated using Equation 2.

The resulting FHH adsorption fit parameters can be used along with FHH-AT to calculate the CCN activation of goethite as described below.

Frenkel-Halsey-Hill Activation Theory (FHH-AT)

FHH-AT was designed to describe heterogeneous cloud activation with respect to the change in droplet diameter (D_p) with saturation ratio under supersaturated water vapor conditions. FHH-AT is a modification of Köhler Theory²¹ whereby the water activity term has been replaced with the FHH adsorption isotherm featuring an expanded definition of θ as demonstrated in Equation 5,⁶

$$S = \frac{4\sigma_W M_W}{RT\rho_W D_P} A_{FHH} \left(\frac{D_P^3 - D_{dry}^3}{6D_{dry}^2 D_{H_2O}} \right)^{-B_{FHH}} \quad (5)$$

where D_{Dry} is the diameter of the dry particle, D_{H_2O} is the diameter of the adsorbed water molecule²⁰, and the A_{FHH} and B_{FHH} are the FHH adsorption parameters. The remaining constants are related to the Kelvin effect, where σ is the surface tension of water (0.072 J/m²),²² ρ is the density of water (997.0449 kg/m³)²⁰, M is the molar mass of water (0.01802 kg/mol), T is temperature (298.15 K) and R is the universal gas constant (8.314472 m³Pa/Kmol). For a given D_{Dry} , the critical supersaturation (S_{crit}) can be determined which represents the supersaturation above which the aerosol particles will be an active CCN. To the best of our knowledge, critical activation parameters for goethite do not exist in the literature. Thus, this study reports the first report of goethite CCN activation.

Theoretical Results

Brunauer Emmet and Teller (BET) Adsorption Isotherm

Figure 3 shows the BET fit to experimental data reported in Figure 2 between 1-99% RH. As expected, the BET model fits the experimental data quite well at low RH values, but deviates significantly above 80% RH. V_m and c were found by analyzing the linear region of the BET fit (5-25% RH). Monolayer coverage was found to occur at ~5% RH where a V_m of 0.0204 g_{H2O}/g_{Goethite} is adsorbed to the sample, corresponding to 4.76x10¹³ molecules/cm².

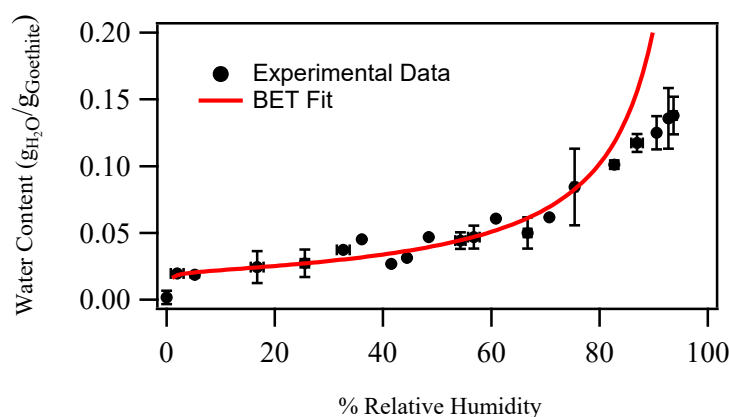


Figure 3. Adsorbed water content (g_{H2O}/g_{Goethite}) as a function of percent RH with the BET fit.

The BET model makes assumptions that are not entirely accurate for the system studied here, thus leading to a failure to accurately model experimental behavior, particularly at high RH values. The BET model assumes that all adsorption sites are uniform and that water adsorbs equally over the entire surface. Mineral aerosol particles typically exhibit surface microstructure and porosity, and thus non-uniformity of surface sites. Additionally, the

BET model assumes that the enthalpy of adsorption is equivalent for the first monolayer of adsorbed water and each successive water layer. The BET model fits exceptionally well in low RH conditions, which is essential to accurately determining the volume of water at monolayer coverage necessary for further theoretical analysis (i.e. the FHH isotherm).

Freundlich Adsorption Isotherm

Figure 4 shows the Freundlich fit to the experimental data. The Freundlich isotherm is best fit to the data in two distinct regions; 0-44 and 44-100% RH. This is consistent with the results obtained in a previous application of the Freundlich isotherm for water on kaolinite, illite and montmorillonite.¹ Each region was fit separately using the Freundlich equation. Freundlich fit parameters for both goethite's regions are reported in Table 1. For the 0-44% RH range the Freundlich parameters were found to be $k = 0.00397$ and $n = 4.764$. From 44-100% RH, $k = 0.1443$ and $n = 0.5825$. Strong adsorption is represented by n values greater than unity. Thus, the results indicate that adsorbed water is more strongly attracted to the goethite surface at low RH values. Multilayer adsorption at high RH values are based on weaker long range Van der Waals forces compared to the more strongly held water molecules in the first monolayer where hydrogen bonding interactions between adsorbed water and the structural hydroxyl groups of goethite govern adsorption. The adsorption strength exhibited by goethite is comparable to that reported for hydratable clay minerals such as illite and montmorillonite.¹

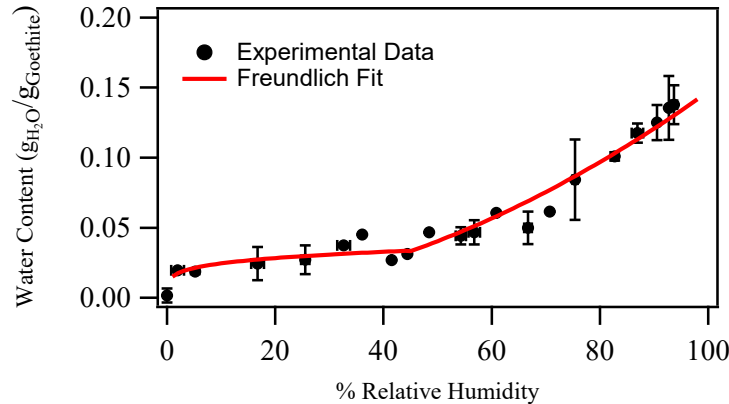


Figure 4. Graph of water content ($\text{gH}_2\text{O/gGoethite}$) as a function of % RH with Freundlich fit.

The adsorption capacity increases with increasing values of k . Similar to previously studied minerals,¹ water adsorption on goethite exhibits a larger adsorption capacity at high RH. However, the k values are much lower than those reported for hydratable clay minerals over the entire range of RH values studied.¹ Thus, goethite has a comparable adsorption strength and lower adsorption capacity than hydratable clay minerals.

Frenkel-Halsey-Hill (FHH) Adsorption Isotherm

BET analysis of the experimental water adsorption data provides the monolayer water content such that the volume of water adsorbed, V , for each RH value can be normalized to V_m in order to obtain the relative coverage (θ) necessary for FHH analysis. Figure 5 shows the relative coverage of adsorbed water representing the number of individual water layers as a function of percent RH. Upon fitting the FHH model we find FHH fit parameters of $A_{FHH} = 1.97$ and $B_{FHH} = 1.48$ for water adsorption on goethite as shown in Table 1.

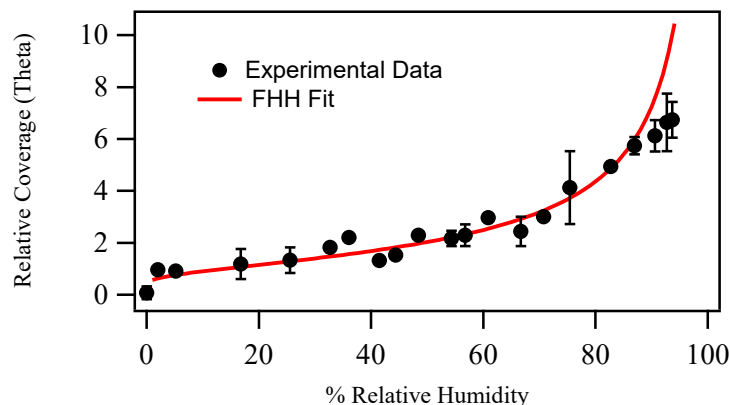


Figure 5. Relative water coverage (θ) as a function of percent RH with FHH fit to experimental data.

Isotherm Model	Parameter	Value
BET	% RH at monolayer coverage Water content at monolayer coverage (g)	5% 0.0204
Freundlich	k (0-44% RH) k (44-100% RH) n (0-44% RH) n (44-100% RH)	0.0397 0.144 4.76 0.529
FHH	A_{FHH} B_{FHH}	1.97 1.48

Table 1. BET, Freundlich and FHH fit parameters for goethite water adsorption.

As shown in Figure 5, the FHH fit models the experimental data well over the entire range of RH values studied. The FHH fit parameters are used below to predict the CCN activity of goethite under supersaturation water vapor conditions.

FHH Activation Theory

Adsorption activation curves were produced from FHH-AT by plotting the saturation ratio as a function of D_p according to Equation 5. Figure 6 shows the adsorption activation curves for five different dry particle diameters. The maximum of the curve represents the critical percent supersaturation ($\%S_{crit}$) and diameter, D_{crit} , required to be an active CCN. S_{crit} values must be lower than 1% to be relevant in the Earth's atmosphere.²³ Critical parameters resulting from FHH-AT are reported in Table 2. Results suggest that a 200 nm dry goethite particle must experience at least 0.69% supersaturation with respect to water vapor in order to become an active CCN. Lower S_{crit} values are required for larger particle sizes, typical of atmospheric mineral dust aerosol. Thus, goethite particles found in Earth's atmosphere can serve as potentially significant atmospheric CCN and should be considered in atmospheric cloud and climate models.

D_{dry} (nm)	D_{crit} (nm)	$\% S_{crit}$
100	140	1.3087
125	170	1.0642
150	205	0.8982
200	265	0.6874
250	330	0.5584

Table 2. Critical CCN parameters determined using FHH-AT for various D_{dry} values.

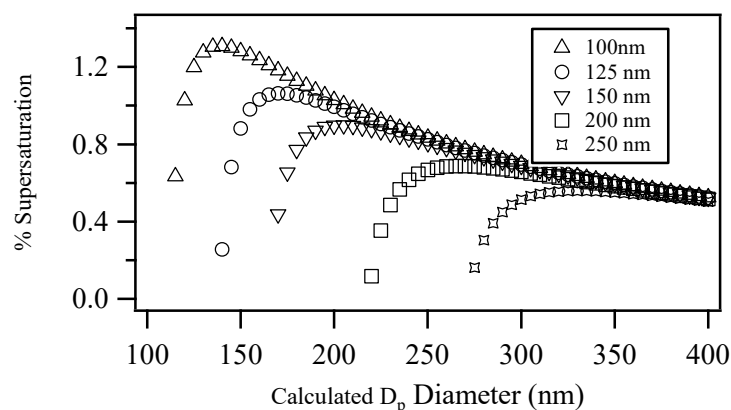


Figure 6. Percent supersaturation values as a function dry particle diameter (nm) for 5 unique D_{dry} values.

Discussion

The findings of this study indicate that goethite can take up significant amounts of water vapor and potentially impact overall climate effects through CCN activation. Calculated supersaturation conditions fall under 1% supersaturation for particles above 200 nm in diameter, indicating atmospheric relevance on Earth. This contributes further evidence to the growing movement that insoluble mineral dust holds an important role in cloud formation and climate as a whole. The results demonstrate the need to consider the role goethite and similar mineral dust particles plays when modeling atmospheric chemistry and climate.

The results of FHH-AT characterize goethite as being a less effective CCN compared to more hydratable clay minerals.¹ One possible explanation for this observation can be extracted from the results of the Freundlich isotherm. The values obtained for the k term, representing adsorption capacity for goethite, are notably lower in both high and low adsorption regimes compared to clay samples studied previously. We theorize that smaller adsorption capacity values may have a large effect on the value obtained for S_{crit} in the FHH-AT model by requiring a higher critical supersaturation to reach CCN activation. In the future, the results of the Freundlich model may prove as an indication of CCN effectiveness.

While the results of this study aid in the effort to create a clearer picture of atmospheric aerosol climate effects, significant questions remain. For example, goethite represents only a single component of mineral dust aerosol, thus further studies of water adsorption on authentic atmospheric dust samples are necessary. Additionally, the temperature dependence of water adsorption on the surface of goethite would be required to further assess applicability to Mars-like conditions.

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