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Water vapor binding on organic matter-coated minerals

W. Cheng^{1,2}, K. Hanna¹, J.-F. Boily²

¹Univ Rennes, École Nationale Supérieure de Chimie de Rennes, CNRS, ISCR – UMR6226, F-35000
Rennes, France

²Department of Chemistry, Umeå University, SE-901 87 Umeå, Sweden

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ABSTRACT

Atmospheric water vapor binding to soils is a key process driving water availability in unsaturated terrestrial environments. Using a representative hydrophilic iron oxyhydroxide, this study highlights key mechanisms through which water vapor (*i*) adsorbs and (*ii*) condenses at mineral surfaces coated with Leonardite humic acid (LHA). Microgravimetry and vibrational spectroscopy showed that liquid-like water forms in the three-dimensional array of mineral-bound LHA when present at total C/Fe ratios well exceeding ~240 mg C per g Fe. Below these loadings, minerals become even less hydrophilic than in the absence of LHA. This lowering in hydrophilicity is caused by the complexation of LHA water-binding sites to mineral surfaces, and possibly by conformational changes in LHA structure removing available condensation environments for water. An empirical relationship predicting the dependence of water adsorption densities on LHA loadings was developed from these results. Together with the molecular-level description provided in this work, this relationship should guide efforts in predicting water availability, and thereby occurrences of water-driven geochemical processes in terrestrial environments.

1. INTRODUCTION

Soil hydrophobicity is a key parameter that describes the extent to which water-based geochemical reactions can proceed, and can be used in environmental monitoring and soil quality assessment.¹ This concept is a manifestation of the ability to which water vapor flowing through unsaturated soils (*e.g.* vadose zones) can form thin water films and droplets at and between mineral grains. Knowledge of the propensity of formation of these aqueous environments is consequently essential for predicting water availability, as well as geochemical aqueous reactions taking place within the microscopic solvation environments of water films and droplets.

Understanding the fate of water binding to soils also requires knowledge of the intervening roles of natural organic matter (NOM). Of common occurrence in soils,²⁻⁴ NOM strongly reacts with mineral surfaces via chemical and/or physical adsorption reactions involving their hydrophilic functional groups (*e.g.* carboxylates, phenolates, amines), as well as by van der Waals hydrophobic interactions, and cation bridging.⁵⁻⁹ These organic coatings have a strong propensity to alter the hydrophilicity of mineral surfaces, the extent to which could be determined by the type and concentration of functional groups exposed at the mineral-organic/water vapor interface. Mineral-bound NOM can also alter surface properties of minerals,⁵ and have direct consequences on the mobility and fate of other contaminants, such as organic contaminants and heavy metals,¹⁰⁻¹⁴ through an interconnected network of water films/droplets localized on organic-coated mineral grains.

Although the concept of soil mineral hydrophobicity is well recognized and its influence on organic compound transport studied,^{1,11,15} its underlying mechanisms remain misunderstood. Still, strong correlations between soil hydrophobicity and soil organic matter¹⁶ or mineral-sorbed humic substances have been identified.¹⁵ Building upon our recent work on water vapor binding on minerals¹⁷⁻²² and the thermochemical stability of NOM mineral coatings,²⁰ this work uses microgravimetry and vibrational spectroscopy to explain and predict water vapor binding to mineral-NOM mixtures. This was achieved by focusing on a model system consisting of Leonardite humic acid (LHA), a representative hydrophilic NOM, and goethite (α -FeOOH), a nanosized mineral with key roles in NOM and contaminant mobility in terrestrial and aquatic environments.²³⁻

2. MATERIALS AND METHODS

2.1. Materials

Goethite was synthesized by hydrothermal conversion of a freshly precipitated ferric oxyhydroxide at 60 °C for 72 h.^{27,28} The starting material was made by drop-wise (1 mL/min) addition of 500 mL of a 0.5 M ferric nitrate solution ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) to a continuously stirred 400 mL of 2.5 M sodium hydroxide solution in a $\text{N}_2(\text{g})$ atmosphere. The resulting goethite was dialyzed (Spectra/Por membrane 2) against ultrapure water. The water was changed every day until its conductivity was lower than 1 $\mu\text{S}/\text{cm}$. The suspensions were stored in polypropylene containers at 4 °C for further use. Goethite purity was confirmed by X-ray diffraction (XRD) with a PANalytical X'Pert Pro X-ray diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 2θ range=10–65° (Figure S1). The B.E.T. specific surface area of the synthetic goethite (89.6 m^2/g) was determined on a Micromeritics AutoPore IV 9500 surface area analyzer, and was calculated from 90-point adsorption/desorption $\text{N}_2(\text{g})$ isotherms before degassing overnight at 105°C under a stream of dry $\text{N}_2(\text{g})$.

Leonardite Humic Acid Standard (1S104H) was purchased from the International Humic Substance Society. A LHA stock solution (2 g/L, 1276 mg C/L) was prepared by dissolving 2 g LHA in 100 mL of 1 M NaOH, then diluted to 1 L with ultrapure water.

2.2 NOM batch adsorption experiments

All NOM adsorption experiments were conducted in the absence of background electrolyte ions, and under an atmosphere of humidified $\text{N}_2(\text{g})$. This minimized any competitive adsorption reactions that would occur under dry conditions.

A 320 μL aliquot of a goethite (24.80 g/L, specific surface area: 89.6 m^2/g) aqueous suspension was mixed with 19.6 mL diluted LHA solutions (1.276 to 1276 mg C/L) in 50 mL polyethylene centrifuge tubes to achieve C/Fe (w/w) ratios in the 0.005–5 range. The suspensions were then adjusted to pH 5.0 with a pH meter by addition of small volumes of 1.0 M HCl or NaOH and equilibrated on an end-to-end rotator at $25 \pm 1 \text{ }^\circ\text{C}$ for 48 h. Next, the suspension was centrifuged at $\sim 2000 \text{ g}$ for 15 min, the supernatants were filtered (0.2 μm) and

the final soluble C concentrations were analyzed using a TOC analyzer (Shimadzu TOC-VCSH). The centrifuged wet pastes were analyzed by FTIR as described in Section 2.3.

2.3 Dynamic Vapor Sorption

The Dynamic Vapor Sorption (DVS) technique was used to trigger water vapor binding on initially dry LHA-goethite assemblages. Water binding was monitored in two sets of independent experiments using (1) Fourier Transform InfraRed (FTIR) spectroscopy, and (2) gravimetry by Quartz Crystal Microbalance (QCM).

For both experiments, water vapor was generated by mixing humid N₂(g) and dry N₂(g) in different proportions using mass flow controllers (MKS, 179A). The total flow rate was always 200 standard cubic centimeters per minute (sccm), and water vapor pressures were continuously measured using a Non Dispersible InfraRed device (LI-7000, Licor Inc). Preliminary FTIR and QCM experiments demonstrated that a 30 min equilibration period under a constant water vapor pressure was well sufficient to achieve equilibrium with respect to water vapor binding on the LHA-goethite assemblages.

2.3.1 FTIR

Centrifuged wet pastes were transferred onto a diamond window of an Attenuated Total Reflectance (ATR) cell (Golden Gate, single-bounce) and dried in the analytical chamber of a FTIR spectrometer under a flow of 200 sccm dry N₂(g). FTIR spectra were collected during the drying period until all O–H stretching and bending modes of free water disappeared. DVS experiments were then carried out on the resulting dry mineral film in a closed-loop flow-through reaction cell, and exposed to water vapor pressures from 0 to 19 Torr (80% R.H.) at 25 ± 1 °C.

FTIR spectra were continuously collected in situ with a Bruker Vertex 70/V FTIR spectrometer, equipped with a DLaTGS detector. All spectra were collected in the 600 – 4000 cm⁻¹ range at a resolution of 4.0 cm⁻¹ and at a forward/reverse scanning rate of 10 Hz. Each spectrum was an average of 250 scans. The Blackman-Harris 3-term apodization function was used to correct phase resolution.

2.3.2 QCM

A gold-coated quartz resonator operating at 10 MHz was used for QCM measurements (eQCM 10M, Gamry Instruments Inc.). The time-independent serial resonance frequency (f_s) of the quartz resonator exposed to a flow of 200 sccm dry $N_2(g)$ was first measured to obtain the correct baseline of the empty cell. A dilute aqueous suspension of the LHA-goethite assemblage was pipetted on the gold area of the resonator, then dried under the same flow of $N_2(g)$. The resulting f_s was used to obtain the mass of the dry sample. A DVS experiment was then initiated to expose the sample to water vapor pressures from 0 to 19 Torr.

Changes in frequency (Δf) of the quartz resonator were converted to changes in sample mass (Δm) using the Sauerbrey equation:²⁹

$$\Delta f = -\frac{2f_0^2}{A\sqrt{\rho_q\mu_q}}\Delta m \quad (1)$$

In this equation f_0 is the resonant frequency of empty cell, A is the piezoelectrically active crystal area of the gold-coated quartz crystal (0.205 cm²), ρ_q is the density quartz (2.648 g/cm³) and μ_q is shear modulus of quartz (2.947×10^{11} g/cm·s²).

2.3.3 Water Vapor Adsorption and Condensation Modeling

Water vapor uptake by goethite and LHA sites was modeled using an adaptation of the model of Do & Do³⁰, which we had previously³¹ shown to account for (i) *adsorption* and (ii) *condensation* phenomena in mineral powders:

$$C_\mu = S_0 \frac{K_f \sum_{n=1}^{\beta+1} n p_w^n}{1 + K_f \sum_{n=1}^{\beta+1} p_w^n} + C_{\mu s} \frac{K_\mu \sum_{n=1}^{\alpha+1} p_w^n}{K_\mu \sum_{n=1}^{\alpha+1} p_w^n + \sum_{n=1}^{\alpha+1} p_w^{n-1}} \quad (2)$$

This equation predicts the total water condensation (C_μ) as a function of the reduced partial pressure of water ($p_w = p/p_{sat}$; where p_{sat} is the saturation pressure) in terms of the aforementioned *adsorption* (left-hand term) and *condensation* (right-hand term) regimes. Parameters for each regime include water-binding site densities for *adsorption* (S_0) and *condensation* ($C_{\mu s}$) with their respective association constants (K_f , K_μ) and hydration numbers (β , α).

The *adsorption* term accounts for hydrogen binding of water molecules onto mineral and LHA surface sites. It is B.E.T.-type equation³² which is however forced to plateau at $p_w \rightarrow 0$ by setting $\beta=2$. This value denotes that a (hydr)oxo group can be involved in 2 (donating and/or accepting) hydrogen bonds, which is average hydration number that we retrieved in previous molecular modeling of water adsorption on various metal (oxy)hydroxides.³¹ The *condensation* pertains, in turn, to the condensation of water in the nano-/micro-porous environments of the mineral-LHA mixture. It is triggered only when a nominal population of water (nano)clusters (*e.g.* $\alpha = 8$) is exceeded³⁰. While the data on hand could not be used to unambiguously constrain *condensation* parameters of Eq. 2, the shape of the modelled curve nonetheless provide the possibility to extract the *adsorption* term, which is central for understanding the intrinsic affinity of water to LHA-bound goethite. Finally, we also used this equation to decompose the adsorption isotherm of LHA on goethite.

3. RESULTS AND DISCUSSIONS

LHA binding at goethite surfaces follows a Type II³³ adsorption isotherm loading (Figure 1), that can be characterized as an adsorption regime at low LHA concentrations, and a precipitation-like regime at high LHA. Maximal adsorption values under the adsorption regime are the equivalent of ~ 56 C atoms/nm², or ~ 3.7 times the total crystallographic oxygen site density (~ 15 sites/nm²)^{27,34,35}. From these results, we estimate that the goethite surface should be already covered in LHA at total C/Fe > 0.05. The highest LHA loadings (C/Fe=5; 220 adsorbed C atoms/nm²) suggest a precipitation-like regime possibly triggered by LHA-LHA interactions, and therefore in the establishment of LHA bulk environments entirely covering the goethite surface.

Figure 1. LHA binding on goethite after equilibration at pH 5. Total C/Fe ratios are expressed in terms of adsorption and precipitated LHA. The model was generated using Eq.2, here adapted for the case of LHA binding and precipitation on goethite.

Water vapor binding on goethite follows the characteristics of Type II³³ adsorption isotherms, and is strongly affected by LHA loadings (Figures 2a-b). LHA loadings in the C/Fe = 0.005 - 0.01 range decreased goethite hydrophilicity, while loadings above this this range increased hydrophilicity. Water uptake of unbound LHA is highest due to its heterogeneous structure and abundant hydrophilic functional groups. As a result, increasing excess LHA loadings promotes water uptake.

These changes can be appreciated further by decomposing these adsorption isotherms in terms of (i) *adsorption* and (ii) *condensation* regimes (Figure 2a), using Do & Do³⁰ theory (Eq. 2) presented in Section 2.3.3. In this framework, *adsorption* pertains to the attachment of water molecules to mineral surface and LHA functional groups via hydrogen bonding, followed by growth in the neighborhood of the adsorption site, very much in the manner described by B.E.T. theory.³² *Condensation*, on the other hand, pertains to water-water interactions leading to growth and coalescence of water (nano)droplets in (nano)/(micro)pores between goethite particles and within the LHA bulk.³³

Modeling of the water adsorption isotherms shows that maximal densities achieved under the adsorption regime on LHA-free goethite are equivalent to the total crystallographic O surface density ($\sim 15 \text{ H}_2\text{O}/\text{nm}^2$)^{27,31,32}, and therefore ~ 1 - $1.5 \text{ H}_2\text{O}$ monolayers. These loadings are however strongly affected by LHA loadings, as shown by the relationship of Figure 2c. This correlation expresses the decreased hydrophilicity of goethite at C/Fe below ~ 0.24 and of the increased hydrophilicity above these loadings. A mechanistic interpretation of these results can be developed by understanding the nature of organic-mineral interactions, and of hydrogen bonding of water on LHA-coated goethite. This can be gained by following the changes in the availability of the hydrophilic hydroxyl functional groups on goethite, as well as those of LHA (Figure 3), as will be detailed in the following paragraphs.

Figure 2. QCM-derived masses of water uptake by LHA and goethite. (a) Typical Type II water sorption isotherm on pure goethite. (b) Sorption isotherms for pure goethite, LHA and goethite-LHA, reported as total C/Fe (w/w). (c) Relationship between water site density (S_0 of Eq. 2) and total carbon loading on goethite (C/Fe). Values for pure goethite and LHA are shown for reference.

Figure 3. (a). Schematic representation of crystal habits of goethite (GT) particles under study, obtained from a selected portion of a snapshot of a Molecular Dynamics simulation from a previous study.¹⁸ (b-c) FTIR spectra of LHA-Goethite samples equilibrated at pH 5 then dried under N₂(g). (c) Difference spectra of the 1200-1800 cm⁻¹ region, with removed contributions from the goethite bulk ($\delta_{\text{OH}} + \gamma_{\text{OH}} = 1659 \text{ cm}^{-1}$; $\delta'_{\text{OH}} = 1794 \text{ cm}^{-1}$; cf. Figure S1 for raw data). Arrows in 1.3 adsorbed C atoms/nm² point to collection of bands.

Changes in the availability of hydrophilic hydroxo groups populating the goethite surface (Fig. 3a) can be revealed by vibrational spectroscopy (Fig. 3b), a detailed account of which is given in a series of articles from our group.^{17-19,22,36,37} Briefly, the dominant (110) crystallographic face of goethite populated by rows of singly-coordinated -OH, doubly-coordinated μ -OH, and triply-coordinated μ_3 -OH groups. About 50% of these -OH donate a hydrogen bond to a neighboring -OH, while all accept a hydrogen bond from an underlying μ_3 -OH, as in the goethite bulk.^{17-19,22,36,37} The intensities and positions of O-H stretching bands of -OH groups (3661 cm⁻¹) and of the less reactive μ -OH and μ_3 -OH groups (3648 cm⁻¹) are especially sensitive indicators of ligand exchange and hydrogen bonding reactions. Variations in the intensities of the triply-coordinated μ_3 -OH sites (3491 cm⁻¹) are, in turn, a direct response of the coordination changes in -OH due to the presence of a hydrogen bond between these two groups (μ_3 -OH...OH-). Finally, we note that while the minor (021) face also exposes -OH and μ -OH groups they are so strongly hydrogen-bonded that they generate no resolvable O-H stretch, as described in Song and Boily.¹⁷

The loss in intensity of these O-H stretching bands in the C/Fe 0 - 0.1 range confirms the loss of hydrophilic -OH groups via ligand exchanges and/or the loss of the hydrophilic activity of these groups via hydrogen bonding with LHA functional groups.^{25, 37-39} These changes correlate with the appearance of LHA functional groups in the range of 1200-1800 cm⁻¹ (Figure 3c), which we interpret as the appearance of a mixture of protonated ($\nu_{\text{C=O carboxyl}} = 1705 \text{ cm}^{-1}$, $\nu_{\text{C-O-H}} = 1261 \text{ cm}^{-1}$) and deprotonated ($\nu_{\text{COO}^-} = 1381 \text{ cm}^{-1}$) groups, as well as aromatic backbone of LHA ($\nu_{\text{C=C aromatic}} = 1600 \text{ cm}^{-1}$). They also reveal that the LHA-reacted

goethite surface exposes a mixture of -OH groups and of LHA. At C loadings greater than the crystallographic density of goethite surface oxygens ($> 26 \text{ C atoms/nm}^2$; $\text{C/Fe} > 0.1$), all intensities of the -OH band are lost due to direct ligand exchange with LHA and a red-shift in the stretching frequency of hydrogen-bonded group to a broad range of values below 3661 cm^{-1} . The O-H spectral signature is then characterized by a blue-shift in the band of $\mu_{3,\text{I}}\text{-OH}$ from the weakening of its hydrogen bond with -OH , as well as from the appearance of OH groups of sorbed LHA. Additionally, because LHA loadings increased under conditions where all -OH groups have been occupied, LHA binding must have been driven by additional mechanisms such as van der Waals-type hydrophobic bonding. This mechanism could be responsible for the precipitation of LHA at the highest loadings considered in this work (Fig. 1).

Figure 4. Baseline-subtracted FTIR spectra of $\text{C/Fe} = 0.005$ exposed to 0-60 % R.H. **(a)** O-H stretching region responding to -OH and $\mu_{3,\text{I}}\text{-OH}$ groups. The 3699 cm^{-1} band is likely from geminal water bound directly to Fe sites, but is outside the scope of this work. **(b)** The $1200\text{-}1900 \text{ cm}^{-1}$ region. This region shows the appearance of liquid-like water through the growth of the bending band of water (ν_2). The $\delta'_{\text{OH}} 1794 \text{ cm}^{-1}$ band is an bending overtone of the goethite bulk, and therefore not affected by water binding.

Figure 5. **(a-b)** Baseline-subtracted FTIR spectra of $\text{C/Fe} = 5$ exposed to 0-60 % R.H. **(c)** FTIR spectra of LHA first equilibrated at pH 5, then exposed to water vapor.

Exposure of water vapor to LHA-coated goethite (Fig. 4 & 5) also induced systematic changes in the vibration spectra of goethite and LHA functional groups, and generated bands strongly indicative of the formation of liquid-like water.^{41,42} While this can first be appreciated by the appearance of the bending (ν_2 ; Fig. 4b) and of the broad O-H stretching (Fig. 5c) bands of water deposited within the three-dimensional framework of LHA (see also Figs S3 & S4), the spectral signature of hydrophilic OH groups provide greater details on water condensation mechanisms.

Samples with the lowest LHA loadings ($C/Fe = 0.005$) provide insight into the mechanisms of water binding at goethite surfaces exposing a mixture of (i) non-reacted $-OH$ groups and (ii) adjacently-bound LHA molecules. While our results (Fig. 2) showed that water loadings were *lower* than on LHA-free goethite, vibration spectra (Fig. 4) suggest that water binding mechanisms were not altered by LHA-binding.¹⁸ This can be appreciated in the loss and red-shift of the 3661 cm^{-1} band of $-OH$ with water loading, as well as in the blue-shift of the 3490 cm^{-1} band of $\mu_{3,l}-OH$ to a triplet at 3512 , 3555 , and 3582 cm^{-1} , also seen in LHA-free goethite.¹⁸ We note that this triplet results from a weakening of the H-bonding strength between $\mu_{3,l}-OH$ and $-OH$ sites by water through the formation of hydrogen bonding networks of the type: $\mu_{3,l}-OH \cdots OH \cdots OH_2$ and/or $\mu_{3,l}-OH \cdots OH_2$. As water-binding mechanisms remain unchanged by LHA, lower water loadings are likely to result from the consumption of hydrophilic sites by LHA surface complexation, for example via ligand exchange and/or hydrogen bonding. This could also imply that the intrinsic LHA bulk structure (*e.g.*, intramolecular hydrogen bonding network) has undergone changes that, for example, expose hydrophobic sites to the outer portion of the macromolecules. This concept can be supported further in the $1200\text{-}1800\text{ cm}^{-1}$ region (Fig. 3c) revealing a combination of bands that is not manifested at larger LHA loadings. Previous work from our group even showed that these conformational changes could be responsible for increasing the thermal stability of mineral-bound NOM.

This scenario diverges starkly with water binding to samples of high C/Fe loadings which, again, promote greater water loadings than in LHA-free goethite (Fig. 2). In this case, the aforementioned triplet (Fig. 4a) is readily transformed to a broad singlet, which is characteristic of a broad distribution of hydrogen bonding environments (Fig. 5a). We also note that the water vapor pressure dependence of the $1200\text{-}1800\text{ cm}^{-1}$ region

is also considerably less sensitive than that of pure LHA (Fig. 5). This suggests that LHA functional groups directly bound to goethite remain largely unaffected by hydration. It also implies that while water condensation in the three-dimensional array of pure LHA facilitates high water loadings, LHA binding to goethite limits this intrinsic capability to accommodate water.

To summarize, we can explain the strong LHA-loading dependence on water binding in the following manner. LHA binding at low loadings ($1.3\text{-}26\text{ C atoms/nm}^2$; $\text{C/Fe} = 0.005 - 0.1$) involves a greater proportion of LHA moieties for ligand exchange or hydrogen bonding to goethite surfaces. This results in potentially important configurational changes in LHA structure, perhaps even exposing hydrophobic portions of the molecule to the goethite surface. This, with the decrease in accessible hydrophilic groups of the goethite surface, collectively lowers water binding on goethite reacted LHA loadings below $\sim 240\text{ mg C per g Fe}$. Water affinities become, in turn, substantially larger at high C/Fe loadings because a smaller fraction of the moieties is dedicated to binding with goethite, leaving excess LHA reacting with water in a similar manner to pure LHA.

Finally, we note that while this work on water condensation in NOM-reacted minerals was limited to a model system, we anticipate that its findings should be applicable to a wider range of representative systems. Recognition of the NOM loading dependency on the hygroscopic properties of solid materials in nature should not only be of importance to the study of terrestrial environments but also in the study of atmospheric clouds and rain formation phenomena^{43,44} Additionally, the molecular-scale knowledge of water vapor binding in organic-mineral assemblages should serve to consolidate our understanding of natural photocatalytic reactions⁴⁵ where co-adsorbed water is an essential ingredient in photodegradation processes.⁴⁶

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