
Theses and Dissertations

Fall 2011

Investigation of the atmospheric processing of α -FeOOH containing aerosols with water and HNO₃: reactivity, fate, and consequences and the impact of particle size on surface adsorption and particle solubility

A. K. Lahiru Anuradha Wijenayaka
University of Iowa

Copyright 2011 A. K. Lahiru Anuradha Wijenayaka

This thesis is available at Iowa Research Online: <http://ir.uiowa.edu/etd/2789>

Recommended Citation

Wijenayaka, A. K. Lahiru Anuradha. "Investigation of the atmospheric processing of α -FeOOH containing aerosols with water and HNO₃: reactivity, fate, and consequences and the impact of particle size on surface adsorption and particle solubility." MS (Master of Science) thesis, University of Iowa, 2011.
<http://ir.uiowa.edu/etd/2789>.

Follow this and additional works at: <http://ir.uiowa.edu/etd>



Part of the [Chemistry Commons](#)

INVESTIGATION OF THE ATMOSPHERIC PROCESSING OF α -FeOOH
CONTAINING AEROSOLS WITH WATER AND HNO₃:
REACTIVITY, FATE AND CONSEQUENCES
AND THE IMPACT OF PARTICLE SIZE
ON SURFACE ADSORPTION AND PARTICLE SOLUBILITY

by

A. K. Lahiru Anuradha Wijenayaka

A thesis submitted in partial fulfillment
of the requirements for the
Master of Science degree in Chemistry
in the Graduate College of
The University of Iowa

December 2011

Thesis Supervisor: Professor Vicki H. Grassian

Copyright by

A.K. LAHIRU ANURADHA WIJENAYAKA

2011

All Rights Reserved

Graduate College
The University of Iowa
Iowa City, Iowa

CERTIFICATE OF APPROVAL

MASTER'S THESIS

This is to certify that the Master's thesis of

A. K. Lahiru Anuradha Wijenayaka

has been approved by the Examining Committee
for the thesis requirement for the Master of
Science degree in Chemistry at the December 2011 graduation.

Thesis Committee:

Vicki H. Grassian, Thesis Supervisor

Christopher M. Cheatum

Sarah C. Larsen

Dedicated to my loving parents, brother and all the teachers and peers
who have always been my inspiration. You have made me who I am today!
Thank you for believing in me, not for 'who you wanted me to be',
but for 'who I was'!

“Science can only ascertain what *is*, but not what *should be*, and outside of its domain value judgments of all kinds remain necessary.”

Albert Einstein (1879-1955)

ACKNOWLEDGEMENTS

I wish to thank my committee members Professor Vicki Grassian, Professor Christopher Cheatum and Professor Sarah Larsen. Your comments and feedback was valuable in making this thesis a possible outcome. A special thank goes to all Grassian research group members. The support and guidance given by Dr Larissa Stabounova, Dr. Andrew Ault, Gayan Rubasinghege, Charith Nanayakkara, Imali Mudunkotuwa as well as Jackie Jansen during the last two years are much appreciated. You, as well as all other group members made my stay a wonderful experience. I express my sincere thanks to all technical and support staff at the Department of Chemistry of the University of Iowa.

I wish to thank all my teachers from my childhood to date, especially all my teachers and faculty at the Royal College, Colombo and the University of Colombo. You have always been my inspiration and have guided me to where I am today. But above all, thank you for believing in me, not for 'who you wanted me to be', but for 'who I was'!

A special thank goes to my parents and my brother. You have always supported me throughout my life. So thank you for making me who I am today! Without your guidance, I am sure this journey would have never become a reality! I would not forget all my friends who have also been a massive part of this journey. I appreciate all the wonderful things you have done to make this journey memorable. You were there to encourage me when life wasn't what exactly what I wanted it to be. So thank you for being a part of this journey. Finally, I am greatly thankful to Thilinee for being by my side always. You have been there for me and given me the courage to strive to do what I believe. Your caring words kept the spirit alive whenever it was needed. So thank you for being a part of my life!

ABSTRACT

The atmosphere is a heterogeneous system which is rich in potential chemistry. The processes taking place within this system as well as at the interface of its constituents are of immense importance in understanding how the atmosphere in turn can impact the well-being of all living on the surface of earth. Thus, the heterogeneous chemistry of atmospheric aerosols has since long been subjected to extensive scientific investigation, in view of broadening our understanding of this imperative system.

In this study, the heterogeneous interactions of water vapor and gaseous HNO_3 on goethite ($\alpha\text{-FeOOH}$), a prominent component of mineral dust aerosol is investigated with quartz crystal microbalance (QCM) measurements and attenuated total reflectance - Fourier transform IR (ATR-FTIR) spectroscopy. Laboratory synthesized goethite samples of varying size (microrods of specific surface area $34 \text{ m}^2/\text{g}$ and nanorods of specific surface area $121 \text{ m}^2/\text{g}$) were used in order to identify the size dependent interaction of goethite with H_2O and HNO_3 .

The study revealed that the exposure of goethite to gas phase H_2O and HNO_3 results in the uptake of these gases via surface adsorption. Additionally, this novel combined approach of QCM and ATR-FTIR spectroscopy allowed for quantification of the amount of uptake while the spectroscopic data provided information on the speciation of adsorbed products. Thus, with the QCM and spectroscopic data in hand, a precise interpretation of the reactivity as well as its size dependence was sought.

In a general sense, the reactivity of a substance is believed to increase with decreasing particle size. The results of this investigation show that in the case of H_2O , both microrods and nanorods take up water while the total amount of adsorbed water,

when normalized to surface area, is similar for both particle sizes. However, for HNO₃, the saturation coverage of total and irreversibly bound HNO₃ on microrods was observed to be higher than that on nanorods. With supplementary analysis, this anomalous size effect was attributed to structural features such as the involvement of surface hydroxyl groups in determining the reactivity, which would be subjected to change as a function of particle size.

Furthermore, an investigation of the behavior of HNO₃ reacted goethite in aqueous media and the uptake of H₂O and HNO₃ at their mutual presence was carried out such as to better understand the effects of atmospheric processing upon dispersal within the hydrosphere. Further analysis is warranted before arriving at a general conclusion on the size-dependent reactivity of goethite. However, we may argue that goethite containing aerosols may indicate the same pattern of reactivity within the atmosphere as that observed here. Thus, the inference of this investigation proves to be significant in broadening our understanding of this atmosphere as well as the entire biosphere as a whole.

TABLE OF CONTENTS

LIST OF TABLES	ix
LIST OF FIGURES	x
CHAPTER 1 - INTRODUCTION.....	1
1.1 Structure and atmospheric reactivity of goethite.....	3
1.2 Chemistry of atmospheric gases.....	4
CHAPTER 2 - EXPERIMENTAL SECTION	8
2.1 Materials.....	8
2.2 Synthesis of goethite	8
2.3 Characterization of goethite	9
2.4 Uptake of H ₂ O on goethite.....	10
2.5 Uptake of HNO ₃ on goethite	12
2.6 Aqueous phase behavior of HNO ₃ reacted goethite.....	12
2.7 Coadsorption of water on nitric adsorbed goethite	13
CHAPTER 3 - RESULTS AND DISCUSSION	14
3.1 The structure and characterization of goethite	14
3.2 Uptake of H ₂ O on goethite.....	19
3.3 Uptake of HNO ₃ on goethite	29
3.4 Aqueous phase behavior of HNO ₃ reacted particles	50
3.5 Coadsorption of water on nitric adsorbed goethite	52
CHAPTER 4 - CONCLUSIONS AND ENVIRONMENTAL IMPLICATIONS	55
4.1 Water uptake on goethite containing aerosols.....	57
4.2 HNO ₃ uptake on goethite containing aerosols	59
4.3 Subsequent chemistry of nitrated goethite aerosols	61
4.4 QCM - a tool in probing solid-gas interactions.....	63
4.5 Directions and implications to the future	65
REFERENCES	68

LIST OF TABLES

Table 1	SSA measured from BET analysis and the length and width values determined from the TEM images for the two goethite samples	19
Table 2	Vibrational frequencies for adsorbed water on goethite	22
Table 3	Vibrational frequencies for adsorbed HNO ₃ on goethite	33
Table 4	Average saturation surface coverage for adsorbed HNO ₃ on nano and micro-goethite	40
Table 5	Average reversibly and irreversibly bound HNO ₃ percentages determined using QCM data	41
Table 6	pH, dissolved Fe content (ppb), zeta potential (mV) and the hydrodynamic diameter of aqueous medium suspended nitric adsorbed samples of nano and micro-goethite	51

LIST OF FIGURES

Figure 1	The cycling of aerosols within the biosphere. Mineral dust aerosols enter the atmosphere by terrestrial origin and once in the atmosphere, they may undergo reactivity with various atmospheric constituents. The chemically altered material may then reenter the biosphere through various processes such as suspension in marine water.	2
Figure 2	Schematic representation of the flow system for gas phase adsorption studies. The powdered sample to be analyzed is placed on the IRE crystal of the FTIR spectrophotometer and on the quartz crystal of the QCM.	11
Figure 3	The three types of hydroxyl groups present on the goethite surface. Note that the dashed lines indicate the surface plane.	14
Figure 4	Structure of goethite. Hypothetical termination of a goethite surface, with a geometry giving rise to three distinct types of hydroxyl groups, singly, doubly and triply coordinated to the central Fe atoms. Adapted from Rustad <i>et al.</i> ²⁶	15
Figure 5	Surface FTIR spectra of nano and micro-goethite samples. Inset shows the enlarged spectra between 3800 – 3400 cm ⁻¹ .	16
Figure 6	Characterization of goethite samples. (a) XRD patterns of the nano and micro goethite samples, and the TEM images of (b) nano and (c) micro-goethite.	18
Figure 7	FTIR spectra for the uptake of water on (a) nano and (b) micro-goethite at varying relative humidity as indicated by the arrow in increasing direction.	20
Figure 8	QCM curves for the uptake of water on (a) nano and (b) micro-goethite at varying relative humidity.	21
Figure 9	Variation of water uptake on nano and micro-goethite. (a) Raw and (b) surface area normalized integrated absorbance of the bending mode of adsorbed water at 1639 cm ⁻¹ , plot as a function of relative humidity.	24
Figure 10	Variation of surface molecular density of water adsorbed on nano and micro-goethite surfaces, calculated from the QCM behavior and plot as a function of RH.	27

Figure 11	FTIR spectra of adsorbed HNO ₃ on (a) nano and (b) micro-goethite at a flow of 250 SCCM of dry air through the acid chamber.	30
Figure 12	QCM curves for the HNO ₃ uptake on (a) nano and (b) micro-goethite at a flow of 250 SCCM of dry air through the acid chamber.	31
Figure 13	FTIR spectra of reversibly, irreversibly and total bound HNO ₃ on the nano-goethite surface obtained by appropriate processing, as identified by the QCM behavior. There were no significant differences in vibrational assignments based on particle size.	32
Figure 14	Temporal variation of HNO ₃ uptake on (a) nano and (b) micro-goethite. $\nu(\text{NO}_2)$ mode at 1674 cm ⁻¹ and $\nu_3(\text{high})$ mode at 1572 cm ⁻¹ was selected for probing reversibly and irreversibly adsorbed nitrates respectively.	37
Figure 15	Temporal variation of (a) reversible and (b) irreversible HNO ₃ uptake. $\nu(\text{NO}_2)$ mode at 1674 cm ⁻¹ and $\nu_3(\text{high})$ mode at 1572 cm ⁻¹ was selected for probing reversibly and irreversibly adsorbed nitrates respectively.	39
Figure 16	Temporal variation of the integrated absorbance of negative peaks observed at 3660, 3630 and 3490 cm ⁻¹ upon nitric acid uptake on (a) nano and (b) micro-goethite.	48
Figure 17	Sedimentation pattern of nitric adsorbed micro-goethite suspended in aqueous media. Nano-goethite indicates the same trend but was less apparent within a shorter time scale.	52
Figure 18	Water uptake on nitric adsorbed (a) nano and (b) micro-goethite samples.	53

CHAPTER 1

INTRODUCTION

Reactivity taking place in the earth's atmosphere has always been perceived to be of immense importance in determining the link between the different environments within the biosphere. Aerosols, suspended in the atmosphere deliver the essential basis for such processes to proceed by providing a solid-gas interface for heterogeneous reactivity. Origin of aerosols into the troposphere may take place from different sources of which the largest contribution is believed to be given by mineral dust produced mainly from wind-blown soils.¹

As a result of such terrestrial origin, elements and compounds present in aerosols reflects the crustal abundance of substances. In this sense, it is reasonable to look at the atmospheric composition in terms of the abundance of material on the surface of earth. Iron is the major transition element in dust,² and is present in the atmosphere in significant quantities and in various forms. Iron oxihydroxides, the most common form being goethite (α -FeOOH),³⁻⁵ is a strong absorbers of visible light, thus playing a critical role in determining the overall impact of mineral dust aerosols on climate forcing.²

It is also a reactive component of dust and a potential source of iron in the open oceans, while dissolved iron in ocean waters is believed to limit the primary productivity of these ecosystems. Thus, it is important to understand the heterogeneous atmospheric chemistry of goethite and its interactions with atmospheric gases, as to better understand the iron chemistry taking place within the biosphere, as illustrated in Figure 1.

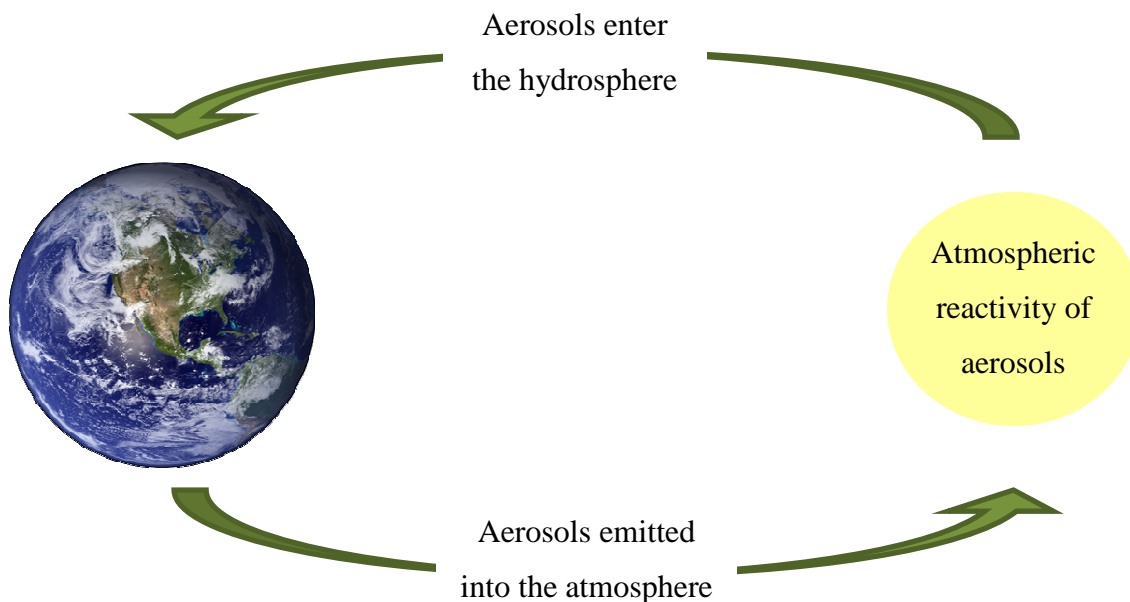


Figure 1 The cycling of aerosols within the biosphere. Mineral dust aerosols enter the atmosphere by terrestrial origin and once in the atmosphere, they may undergo reactivity with various atmospheric constituents. The chemically altered material may then reenter the biosphere through various processes such as suspension in marine water.

Until recently, most atmospheric models have assumed the iron oxide content in dust to be in the form of hematite. However, during recent investigations on a number of dust samples from Northern Africa and Eastern Asia, Lafon *et al* have found that goethite was present in higher concentrations than hematite in all samples concerned.^{4,5} Presently, there is evidence in literature for atmospheric models claiming goethite to be the most ubiquitous iron oxide in nature.³ Thus, goethite present in the atmosphere may have significant impact on atmospheric processes and it would be important to understand the atmospheric reactivity of goethite as a prominent aerosol component in order to be successfully incorporated into atmospheric chemistry models.

1.1 Structure and atmospheric reactivity of goethite

Adsorption reactions at mineral surfaces play an important role in determining the mobility, fate and consequences of the elements and compounds in the earth's surface as well as the atmosphere which surrounds it. These reactions typically involve different forms of surface hydroxyl groups that can undergo various consequences such as, protonation, hydrogen bonding or exchange reactions upon exposure to reactive atmospheric constituents.⁶ Thus, it can be said that the presence, absence as well as the nature of surface hydroxyl groups would be a key factor in determining atmospheric reactivity of aerosol components.

Goethite is one of the most extensively studied environmental interfaces,⁶ and it is considered to contain singly, doubly and triply coordinated hydroxyl groups within its structure, which will be discussed in more detail later. The presence of three distinct types of reactive centers gives interesting behavior to goethite reactivity, since the degree as to which each different type of hydroxyl would participate in reactivity will be distinct from each other.

With its hydroxylated structure, goethite provides an interface rich in potential reactivity and thus, as an atmospheric aerosol component, goethite would provide a substrate on which surface adsorption can occur. However, the exact nature through which adsorption and heterogeneous interactions with atmospheric gases on goethite proceed, thus driving its reactivity is still not clearly established.

The density of each type of hydroxyls on the goethite surface would depend on the size of the particles. In a recent study on nano- and micro-sized goethite, Cwiertny *et al.* have found that the density of singly coordinated surface hydroxyl groups, which were

suspected to play a dominant role in adsorption reactions, is greater on nano-sized goethite particles than on larger micro-sized goethite particles, indicating that a size effect on reactivity could potentially exist.⁷

Thus, with the knowledge that the three distinct types of hydroxyl groups may participate to different extents in adsorption processes, the uptake of substances on goethite may exhibit particle size dependence. However to date, any extensive investigation on the presence and participation of all three distinct hydroxyls in adsorption reactivity exists to be a missing link in understanding such reactivity of goethite and goethite containing aerosols.

1.2 Chemistry of atmospheric gases

Atmosphere, as far as this study concerns is the layer of gases which surrounds planet earth. This complex mixture of gases constitutes of many reactive species although some may be present only in trace amounts depending on altitude as well as other factors which may limit their existence. Water is a substance contained in significant and variable quantities within the atmosphere. Even though it is not highly reactive in nature, the association of water with various atmospheric constituents is believed to be responsible for notable atmospheric consequences such as tornados and typhoons.⁸

Intriguingly the adsorption and condensation of water on aerosols can liberate energy of high enough magnitude such as to result in these extreme weather conditions. Further, in a recent analysis, Makarleva *et al* have observed that water vapor condensation can also influence the atmospheric pressure and dynamics, thereby controlling the atmospheric wind patterns.⁹

Water vapor in the atmosphere plays a key role in the chemistry of mineral dust aerosols.^{1, 10, 11} Under certain atmospheric conditions of temperature, pressure and relative humidity, aerosol particles can serve as cloud or ice condensation nuclei, depending on the chemical composition of the aerosols and their solubility in water.^{1, 10, 11} There is also evidence that adsorbed water may enhance the uptake of trace atmospheric gases on aerosol surfaces.^{12, 13} Thus, assessment of the water uptake on aerosol surfaces would be important in understanding the atmospheric processing of mineral dust particles.

Additionally, various acidic gases present within the atmosphere can also play a crucial role in a wide range of atmospherically relevant heterogeneous processes. Nitric acid, HNO_3 present in the atmosphere is of high significance in terms of a number of potential reactivities.¹⁴ It is believed to be the main nitrogen oxide reservoir species in the atmosphere, while the ozone concentration in the troposphere is highly affected by NO_x and HNO_3 concentrations.¹²

Gaseous nitric acid can undergo reactivity at atmospheric interfaces, allowing the heterogeneous removal of HNO_3 from the atmosphere. Interestingly, it may also change the physiochemical properties of the aerosol itself, thus impacting its fate within the atmosphere, as well as the distribution of nitrated species into the hydrosphere.¹⁵ However, currently it is believed that the sources and sinks of atmospheric nitric acid are not entirely recognized and the amount of nitric is often over-estimated in atmospheric models. Therefore, it is important to identify the potential routes through which nitric can enter or leave the atmosphere, such as to successfully incorporate the insight into atmospheric chemistry models.

Many of the components present in aerosols can indicate reactivity towards atmospheric water vapor and nitric acid as have been extensively studied under various conditions.¹⁶⁻¹⁸ Goethite with its hydroxylated surface structure would also be capable of indicating reactivity towards such atmospherically relevant gases. Thus, understanding the interaction of goethite particles with water vapor and nitric acid would be of interest to many atmospheric chemistry models.

Furthermore, aerosols may be present within the atmosphere ranging in size from a couple of nanometers to a couple of micrometers, while many surface properties such as the type and density of surface functional groups may subject to variation depending on particle size. Hence, the type and density of surface hydroxyl groups on the goethite surface will effectively be a function of particle size. Having previously stated that not all surface hydroxyls are alike in reactivity and the density of the singly, doubly and triply coordinated surface hydroxyls of goethite depends on the surface area and plane exposed, goethite reactivity towards the above gases of concern is likely to indicate a particle size dependence. Thus, understanding the interaction of goethite particles with water vapor and nitric acid is of interest from a number of different perspectives.

1.3 Focus and scope of the study

This study focuses on understanding the atmospheric interactions of goethite with water vapor and nitric acid, with the focus on the possible particle size effects. Synthetic goethite preparations of two distinct sizes within the nanometer and micrometer size regimes have been selected for the investigation in view of observing the size effects and the size dependent reactivity of goethite have been observed under varying conditions.

Surface adsorption is often probed using infrared spectroscopic techniques to determine the speciation of adsorbed products, owing to the fact that adsorption would alter the native optical properties of the surface as well as the adsorbate. If such distinction is not visible or is not significant, spectroscopic techniques would fail to recognize and differentiate adsorbed species from those in their original state and quantitative information on uptake would become difficult to obtain.

However, gravimetric analysis would allow for quantitative measurements of adsorption, irrespective of the nature of the surface adsorption process, since adsorption is certain to be followed by a change in mass. Specially, techniques such as quartz crystal microbalance (QCM) would allow changes in mass of up to a couple of micrograms taking place on a surface to be measured accurately. However, due to this non-specific response, gravimetric analysis would not provide information on speciation.

Thus a combined approach of simultaneous measurements of attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy with QCM measurements had been employed here to investigate the interactions of goethite with atmospheric water vapor and nitric acid. To the best of our knowledge, there are not many attempts to utilize QCM in this manner and specially in distinguishing modes of adsorption as had been conducted within this study. However, the approach adopted is quite powerful when combined, so that quantitative measurements of reversible and irreversible adsorption along with the spectroscopic signatures that distinguish these different modes of adsorption can be easily obtained.^{19, 20}

CHAPTER 2

MATERIALS, METHODS AND EXPERIMENTAL DESIGN

2.1 Materials

All chemicals were reagent grade or better and were used as received. Ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Sigma Aldrich, $\geq 98\%$), sodium bicarbonate (NaHCO_3 , Sigma Aldrich, $\geq 99.5\%$), and potassium hydroxide (KOH, Sigma Aldrich, ACS reagent) were used for the synthesis of goethite (*vide infra*). Nitric uptake experiments were carried out with concentrated nitric acid (HNO_3 , Fisher Scientific, 69.3%). Water uptake experiments and solution preparation were done using optima water (Fisher Scientific). Sample preparation for FTIR and QCM application was done using a 1:1 mixture of optima water and methanol (CH_3OH , Fisher Scientific, 99.9%).

2.2 Synthesis of goethite

Goethite samples were prepared according to the method outlined by Anschutz and Penn²¹ as previously described elsewhere.²² Dropwise addition of NaHCO_3 to a solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was used in the synthesis, resulting in the formation of ferrihydrite nanoparticles. Subsequently, these nanoparticles were aged at pH 12 for 24 hours at a temperature of 90 °C to yield nano-scale goethite particles, which are referred to as nano-goethite. Method outlined by Schwertmann and Cornell was used as to prepare larger sized goethite particles, which are referred to as micro-goethite.²³

2.3 Characterization of goethite

The surface FTIR spectra of the nano and micro-goethite samples were obtained using a Thermo Scientific 6700 FTIR spectrophotometer, equipped with a liquid nitrogen-cooled, narrow-band mercury cadmium telluride (MCT) detector, and an amorphous material transmitting IR radiation (AMTIR), internal reflective element (IRE).

Specific surface areas of the samples were determined from a seven point N₂ - Bruauer-Emmet-Teller (BET) isotherm using a Quantachrome Nova 1200 surface area analyzer. Samples were outgassed overnight (~24 hours) at a temperature of 70 °C prior to the BET analysis. Higher temperatures were not used during outgassing, as to avoid the possible transformation of goethite into hematite. XRD patterns of the samples were obtained with a Rigaku Miniflex II diffractometer equipped with a Co source.

The dimensions of the goethite samples were determined from transmission electron microscopy (TEM) images obtained using a JEOL JEM-1230 transmission electron microscope operated at 100 keV accelerating voltage. Dilute suspensions of goethite were prepared in methanol followed by sonication, and a drop of the suspension was applied on a 40 mesh Cu TEM grid, as to be used for imaging. Digital images of the samples were acquired using a Gatan UltraScan CCD camera with the Gatan imaging software and the size of the goethite particles was determined by analyzing the images in software package Image J. The size distributions of the two samples were determined after the analysis of approximately 250 particles of the sample of concern.

2.4 Uptake of H₂O on goethite

Uptake studies were conducted in a custom built flow system as indicated in Figure 2, described in detail elsewhere.¹⁹ A Thermo Nicolette 6700 FTIR spectrophotometer and a QCM200, 5 MHz quartz crystal microbalance were integrated to the flow system in order for sample analysis.

A commercial attenuated total reflection (ATR) horizontal liquid cell apparatus (Pike Technology) was placed in the internal compartment of the spectrometer, alongside the optics attachment and the bottom portion of the liquid cell which were supplied by Pike Technology and used as is. The top portion of the liquid cell was redesigned to contain inlet and outlet ports for humidified air, reactive gases, and a Honeywell HIH-3602-L relative humidity sensor for the *in situ* measurement of relative humidity.

Dry air coming into the system was allowed to flow through a set of water bubblers at a controlled rate producing humidified air. This was then mixed and equilibrated with dry air inside the mixing chamber before being introduced to the samples contained in the FTIR spectrophotometer and the QCM.

The flow rate was held constant using flow meters throughout the experiment as to assure a steady humidity level during each step of analysis. The relative humidity was controlled by varying the flow of dry air through the system of water bubblers, while allowing the system to equilibrate for 30 minutes at each flow.

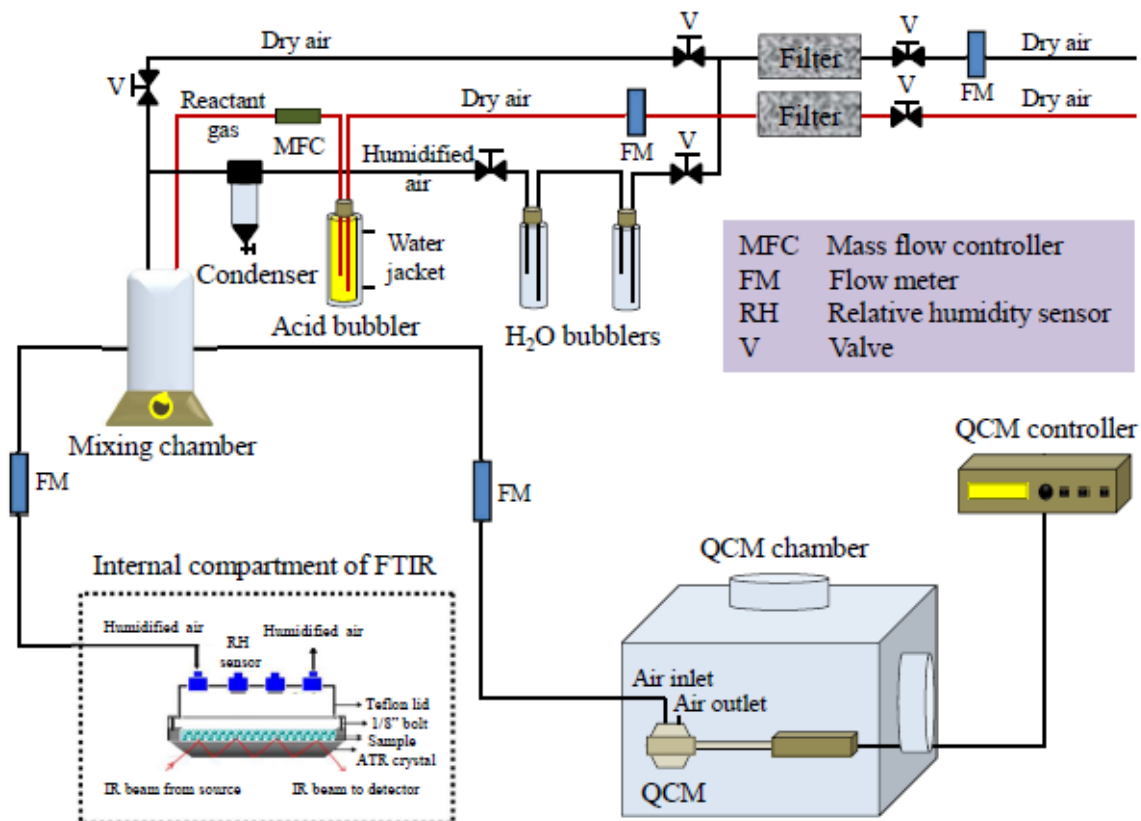


Figure 2 Schematic representation of the flow system for gas phase adsorption studies. The powdered sample to be analyzed is placed on the IRE crystal of the FTIR spectrophotometer and on the quartz crystal of the QCM.

The uptake of water at each humidity level was observed using FTIR and QCM measurements while the relative humidity was recorded using the humidity sensor and a custom-built digital readout. The experiment was continued at increments of relative humidity until saturation humidity was achieved, in order to observe the behavior of water adsorption. Then, the same procedure was continued while decreasing the humidity in steps, thereby observing the water desorption behavior.

2.5 Uptake of HNO₃ on goethite

HNO₃ uptake was conducted in a similar fashion to water but at single steady flow of 250 SCCM of dry air through the nitric acid solution. A calibration was done such as to convert the resulting nitric flow into units of pressure, with a Teflon coated reaction chamber being fixed on the FTIR spectrophotometer in place of the horizontal liquid cell apparatus. Using transmission IR spectra for HNO₃ at different flow levels collected here and the transmission IR spectra collected at varying pressures of HNO₃ obtained using another apparatus described elsewhere,²⁴ the relationship between HNO₃ flow and pressure was established.

While monitoring the uptake using FTIR and QCM measurements, the reversibly and irreversibly adsorbed HNO₃ components were analyzed using the QCM behavior and the corresponding ATR-FTIR spectra to quantify and characterize irreversibly vs. reversibly bound HNO₃ on the goethite surface.

2.6 Aqueous phase behavior of HNO₃ reacted goethite

To better understand the behavior of nitric acid reacted goethite particles upon deposition into water systems, goethite samples following exposure to HNO₃ were collected from the ATR element. After letting to sit overnight under a stream of dry air as to insure the removal of reversibly bound HNO₃, the reacted samples were deposited into optima water and diluted to produce a solution. The pH of the final 600 mg/L goethite-containing suspension was recorded and the amount of dissolved iron was determined using a Varian inductively coupled plasma - optical emission spectrometer (ICP - OES).

Additionally, the stability of these suspensions was measured using rates of sedimentation by measuring extinction measurements with a Perkin Elmer Lambda 20 UV-visible spectrometer at a wavelength of 510 nm. The size distribution of the aggregates present in aqueous media was determined using a Beckman Coulter Delsa Nano C particle analyzer in dynamic light scattering (DLS) mode, while the zeta potential of the samples was recorded using a Malvern Zetasizer Nano ZS instrument, equipped with a green laser at 532 nm.

2.7 Coadsorption of water on nitric adsorbed goethite

Nitric acid was allowed to react with goethite samples placed on the AMTIR crystal at a steady flow of 250 SCCM for a period of one hour and the samples were allowed to sit overnight. The uptake of water on these samples, at varying relative humidity was monitored using FTIR measurements on the following day, using a similar protocol as that adopted during the investigation of water uptake.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 The structure and characterization of goethite

Goethite is believed to exhibit a hydroxylated structure containing more than one type of hydroxyl groups within its structure. According to Parfitt *et al.*, goethite structure is built up from strips of condensed Fe(O, OH) octahedra, involving OH groups shared between three Fe³⁺ ions along its crystallographic [001] direction.²⁵ These give rise to the triply coordinated hydroxyl groups (μ_3 -OH) within the structure of goethite, thus being referred to as ‘bulk hydroxyls’. However, on the surface, two additional hydroxyl groups which are singly (-OH) and doubly (μ -OH) coordinated to Fe are present.²⁶ The three types of hydroxyl groups are illustrated in Figure 3 and their structural positioning is indicated in Figure 4 which follows.

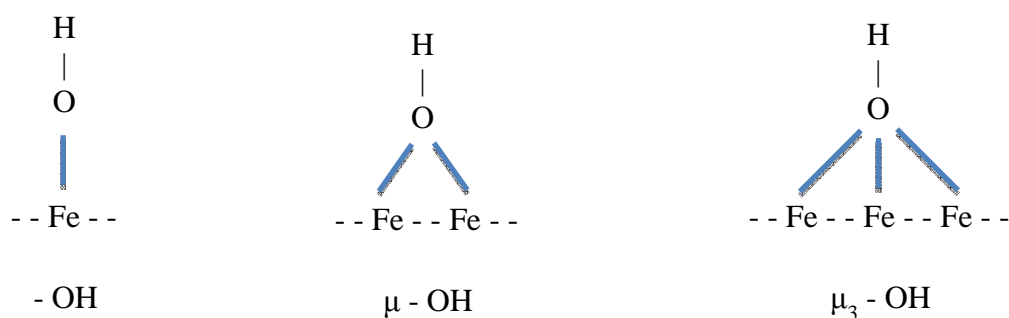


Figure 3 The three types of hydroxyl groups present on the goethite surface. Note that the dashed lines indicates the surface plane.

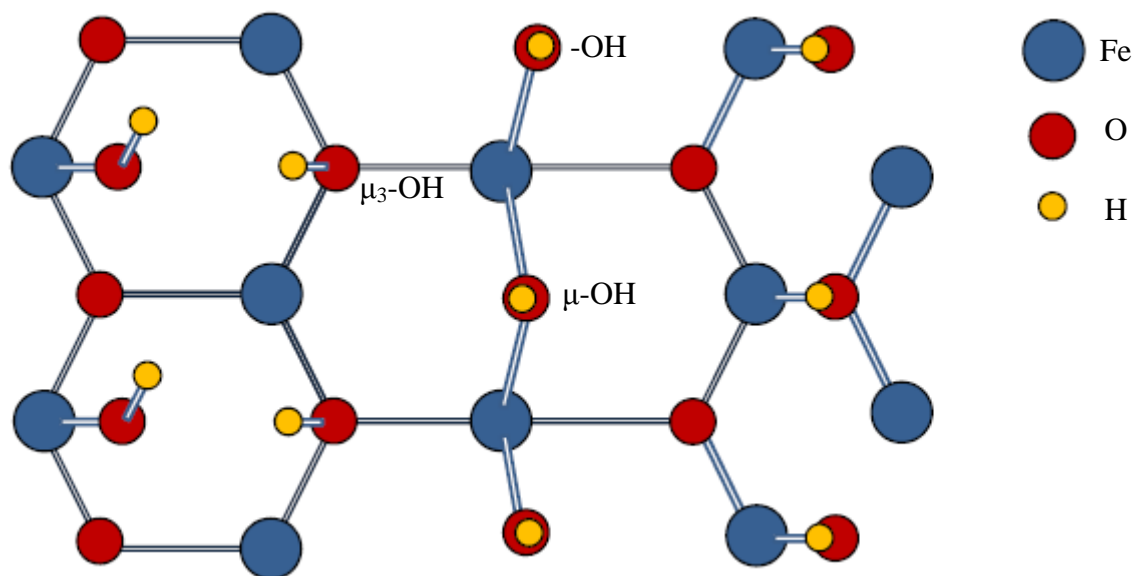


Figure 4 Structure of goethite. Hypothetical termination of a goethite surface, with a geometry giving rise to three distinct types of hydroxyl groups, singly, doubly and triply coordinated to the central Fe atoms. Adapted from Rustad *et al.*²⁶

These collectively give rise to a series of distinct peaks on the FTIR spectra as seen in Figure 5. Parfitt *et al.* has assigned the peak at 3660 cm^{-1} to the singly coordinated surface hydroxyls while the peak at 3486 cm^{-1} corresponds to the doubly coordinated surface hydroxyls.²⁵ The prominent peak at 3145 cm^{-1} had been assigned to bulk hydroxyls, which are the triply coordinated hydroxyls present in the bulk as well as on the surface structure of goethite.

In a more recent investigation by Boily and Felmy, it had been found that goethite can exhibit four distinct bands arising from; (1) -OH groups on the (110) plane, (2) -OH groups on the (021) plane, (3) μ-OH groups on the (110) plane, and (4) μ-OH groups on the (021) plane.⁶

Here a pair of bands at 3660 and 3490 cm^{-1} have been assigned to singly coordinated surface hydroxyl groups, whereas the $\mu\text{-OH}$ groups is said to be manifested through 3648 to 3578 cm^{-1} at greater levels of surface proton loading. Stretches arising from triply coordinated hydroxyl ($\mu_3\text{-OH}$) groups on the surface are proposed to be embedded within the dominant O-H band of bulk goethite.⁶

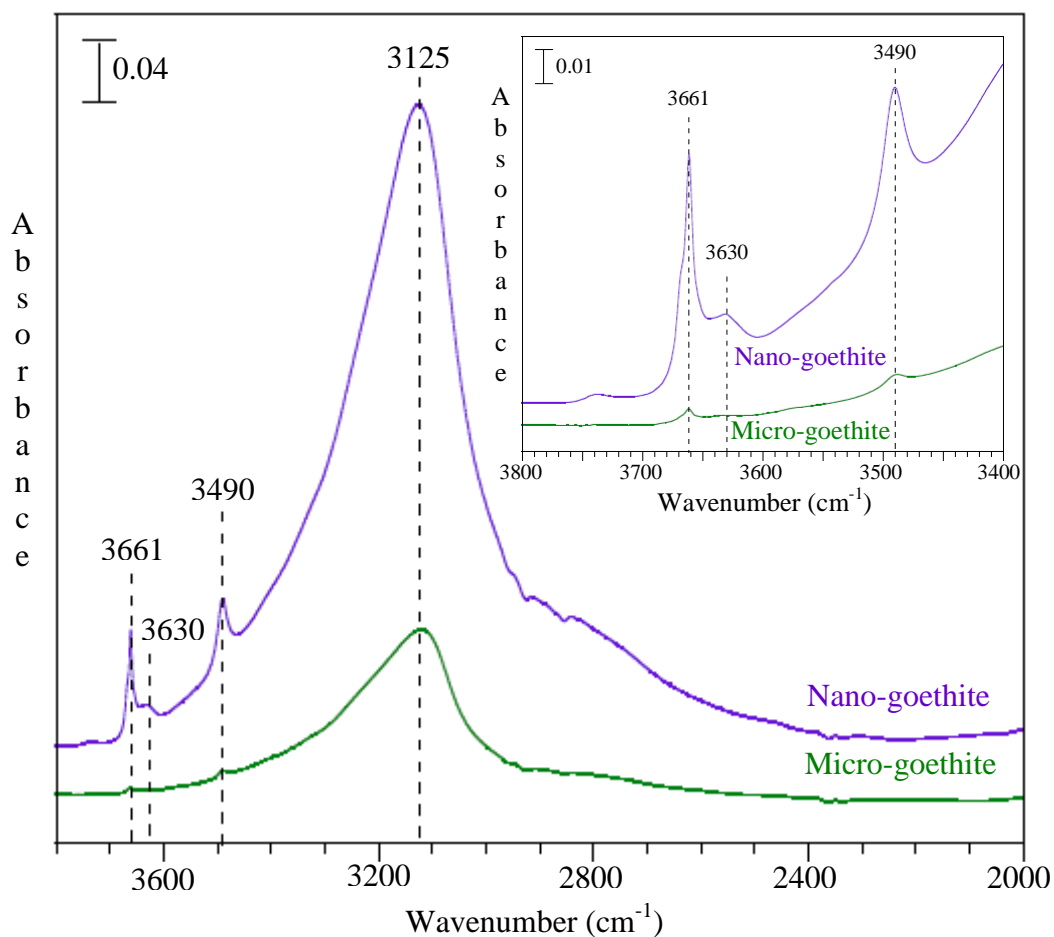


Figure 5 Surface FTIR spectra of nano and micro-goethite samples. Inset shows the enlarged spectra between 3800 – 3400 cm^{-1} .

Thus, for the goethite surface spectra indicated in Figure 5, the bands at 3661 and 3490 cm^{-1} can be attributed to -OH groups, whereas the weak absorption at 3630 cm^{-1} can be attributed to μ -OH groups. The peak at 3125 cm^{-1} would be a result of the bulk hydroxyl groups of goethite, while any absorption due to μ_3 -OH groups on the surface of goethite would be embedded within this prominent band.

X-ray diffraction (XRD) patterns and the TEM images of the nano and micro-goethite samples are shown in Figure 6. As seen, on Figure 6 (a), the XRD patterns of goethite samples indicated good agreement with the reference. However, the relative peak intensities indicate minor variations with size, suggesting that the crystallographic structure of goethite particles would be subject to change according to particle dimensions. Further, it is apparent that the XRD pattern for nano-goethite indicated peak broadening, as is expected with decreasing size.

TEM images of nano and micro-goethite as shown in Figure 6 (b) and (c) respectively indicate the elongated rod-like structure for goethite, as described in detail by Cwiertny *et al.*⁷ The particle length and width for the two goethite samples as determined by these images are set out in Table 1, alongside the measured BET specific surface areas of each sample.

It should be noted that goethite microrods were unstable upon sonication of a suspended solution. This eventually would lead to the damaging of the structure, as is evidenced by the large deviation in size observed from the micro-goethite TEM images, as visible on Figure 6 (c).

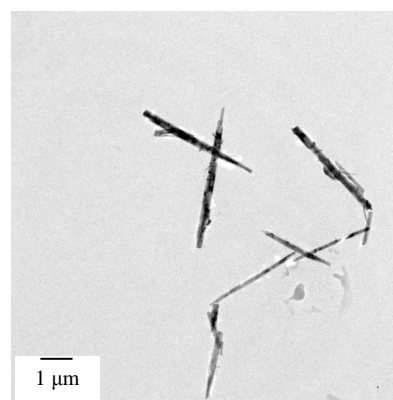
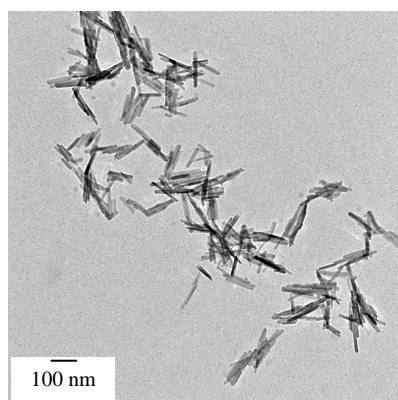
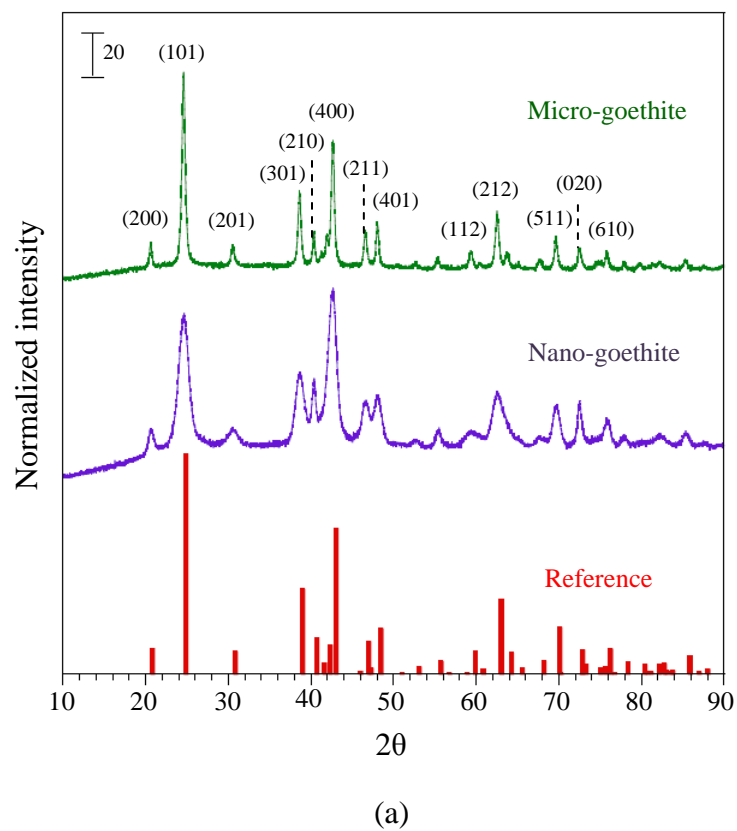


Figure 6 Characterization of goethite samples. (a) XRD patterns of the nano and micro goethite samples, and the TEM images of (b) nano and (c) micro-goethite.

Table 1 SSA measured from BET analysis and the length and width values determined from the TEM images for the two goethite samples.

	Nano-goethite	Micro-goethite
BET specific surface area (m ² /g)	121 ± 7	34 ± 1
Particle length (nm)	108 ± 23	2151 ± 590
Particle width (nm)	11 ± 3	131 ± 45

3.2 Uptake of H₂O on goethite

The FTIR and QCM behavior upon water uptake for goethite at varying relative humidity are indicated in Figures 7 and 8, respectively. Goethite indicates an increase in water uptake with increasing humidity as evidenced from the increasing FTIR spectral intensity. There is no direct evidence for the gas phase water uptake on goethite in literature. However, the vibrational assignments for adsorbed water on goethite have been given in Table 2, using similar studies conducted on metal oxide particles as a basis.

An additional weak adsorption band is apparent upon water uptake around 2100 cm⁻¹. This peak has been previously observed in literature and attributed to an association band (ν_a) which is a combination of the bending (δ), liberation (ν_L) and hindered translation (ν_T) modes of adsorbed water molecules.^{1, 27}

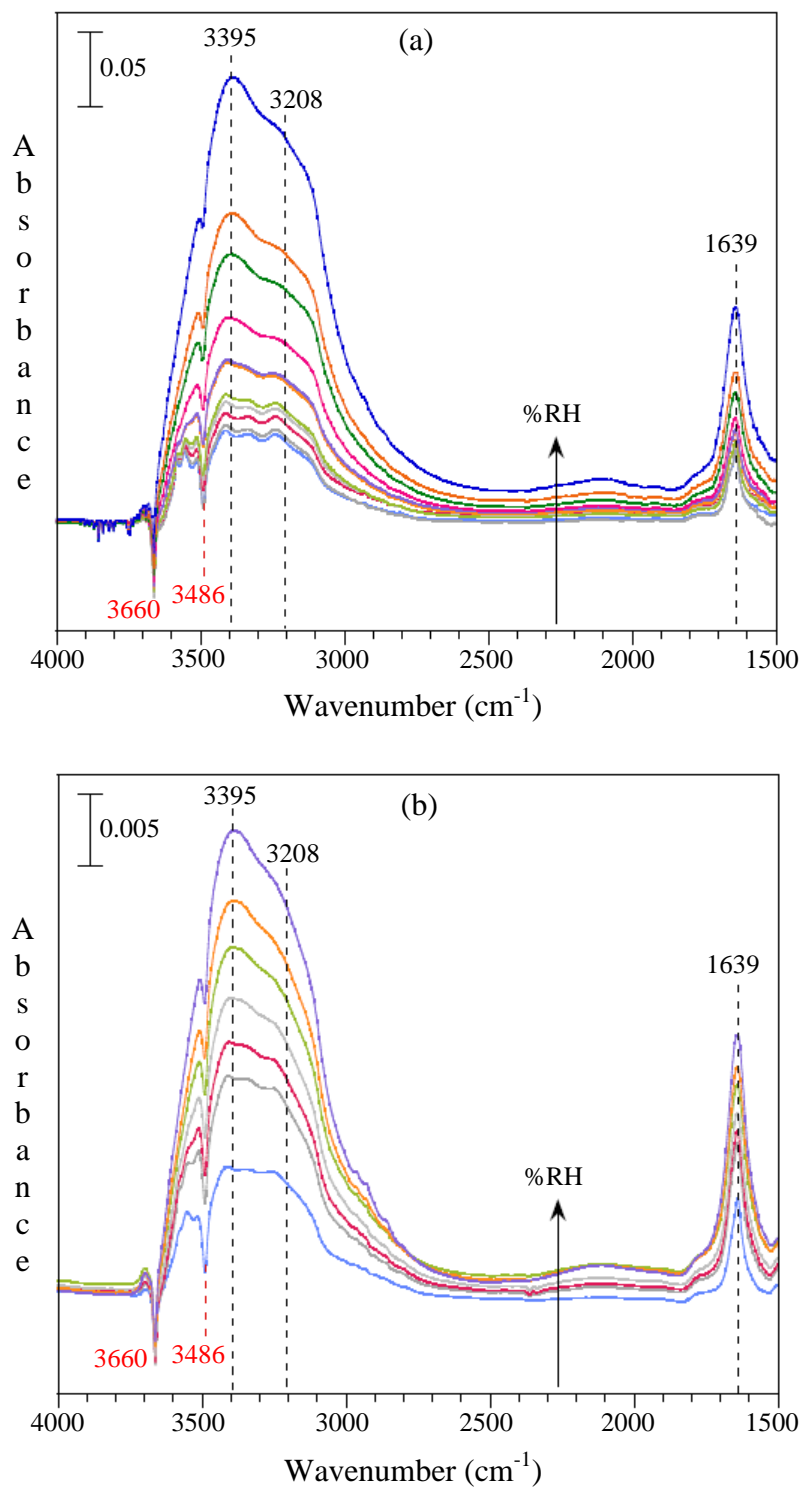


Figure 7 FTIR spectra for the uptake of water on (a) nano and (b) micro-goethite at varying relative humidity as indicated by the arrow in increasing direction.

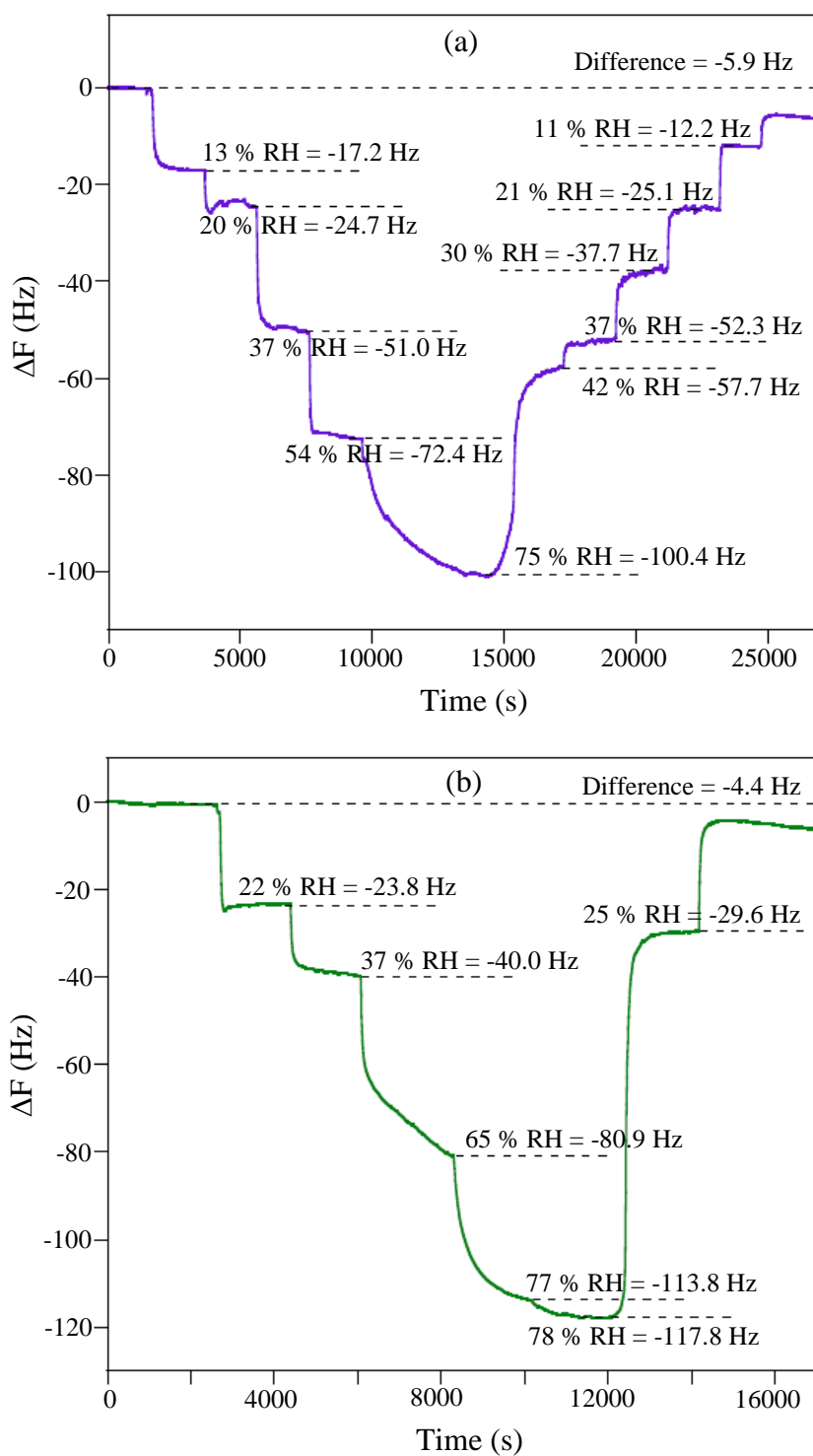


Figure 8 QCM curves for the uptake of water on (a) nano and (b) micro-goethite at varying relative humidity.

Table 2 Vibrational frequencies for adsorbed water on goethite

Wavenumber observed (cm⁻¹)	
O-H stretching	3395
	3208
H-O-H bending	1639
Association	2100

As in the case of many other metal oxides, water is adsorbed reversibly on goethite and can be desorbed from the surface upon evacuation of humidified air from the sample chamber. This fact was apparent from the decrease in spectral intensities when the relative humidity of the gas mixture was decreased. The broad peak in OH stretching region (ν_1 , ν_3) for adsorbed water which falls within 2800 - 3700 cm⁻¹ indicates a decrease in the structural features with increasing relative humidity. This has been previously explained by Al-Abadleh and Grassian as being a result of the condensation of water on the oxide surface upon uptake.¹

The first traces of water adsorbed on goethite will behave as a layer of ice, and when more water is adsorbed at higher humidity, which in turn will be on top of this initial layer, the adsorbed water will be in the form of liquid, thus tending to form hydrogen bonds. In general, it can be stated that more disordered the molecular environment, the broader the absorption band as stated by Al-Abadleh and Grassian, as well as the references therein.¹ Thus, due to the formation of hydrogen bonds and the

broadening of spectral features, the distinction between ν_1 and ν_3 becomes less apparent, eventually collapsing to a diffuse absorption band that is slightly red shifted from its initial value at higher humidity.

More interestingly, there appears to be two distinct negative bands that are centered at 3486 and 3660 cm^{-1} upon water uptake on both nano and micro-goethite. These features can be attributed to the singly coordinated hydroxyl groups on the goethite surface as seen on the goethite surface spectra in Figure 5. However, no loss of surface hydroxyls would be actually viable upon the reversible, molecular binding of water on the goethite surface. Thus, it can be stated that the appearance of these negative bands signifies the presence of isolated hydroxyl groups prior to water uptake, which may become hydrogen-bonded to molecular water, as have been previously observed in the case of other hydroxylated oxide surfaces.¹

However, the μ -OH or μ_3 -OH coordinated hydroxyl groups on the goethite surface do not show any significant contribution towards the uptake of water. For the μ -OH groups the initial spectral intensity was relatively low such that the appearance of a negative band might not be clearly evidenced. Therefore, in general it can be stated that water uptake on both nano and micro-goethite takes place with the association of gas phase water molecules with the singly coordinated hydroxyl groups on the goethite surface.

In order to understand the particle size effects on water uptake, the FTIR and QCM data were analyzed. Figure 9 (a) shows the integrated absorbance of the bending mode of adsorbed water at 1639 cm^{-1} , plot as a function of relative humidity. The graph indicates a BET type multi-layer adsorption of water on goethite.

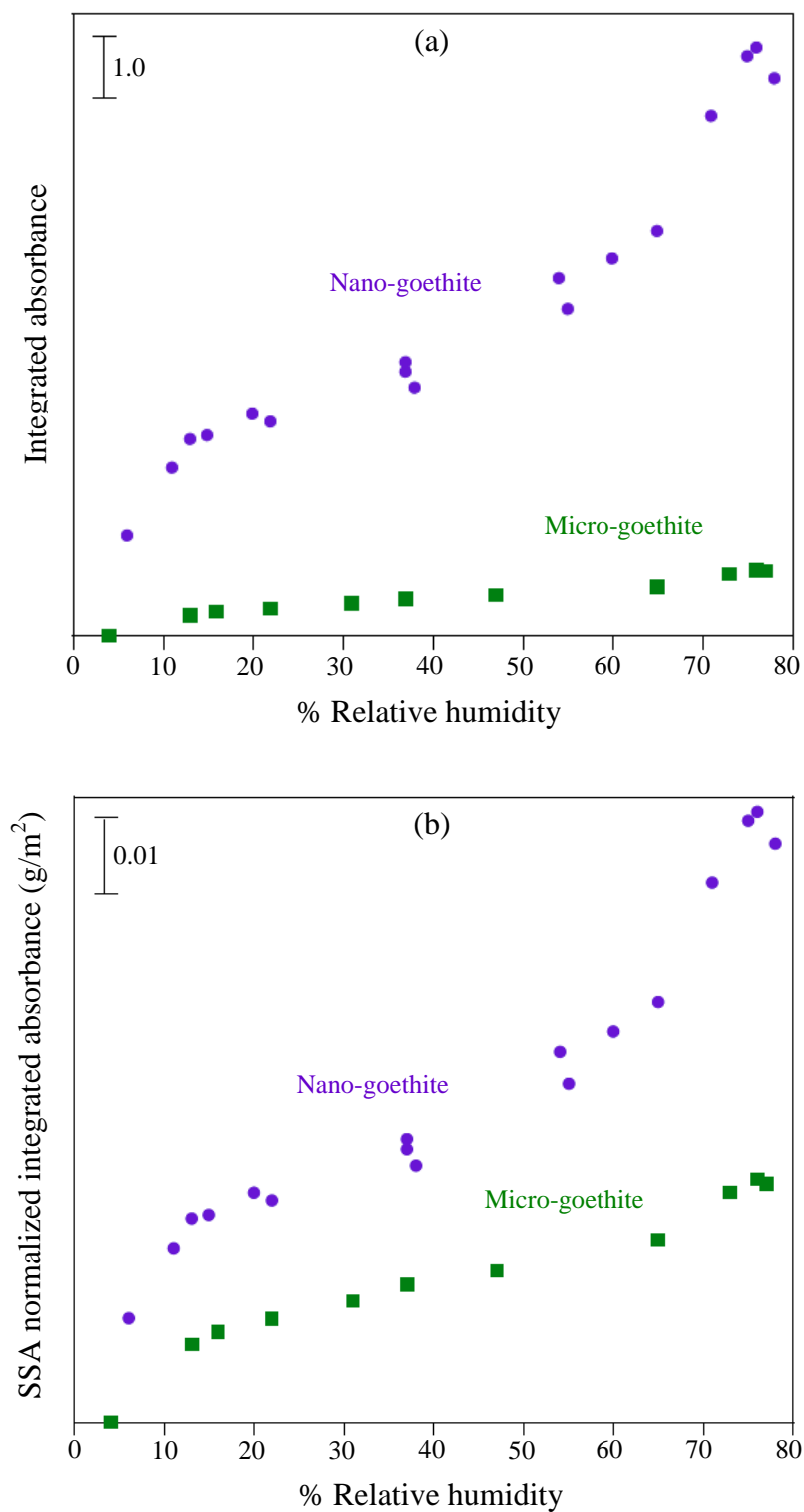


Figure 9 Variation of water uptake on nano and micro-goethite. (a) raw and (b) surface area normalized integrated absorbance of the bending mode of adsorbed water at 1639 cm^{-1} , plot as a function of relative humidity.

Since a mass of ~15 mg of sample was used on the AMTIR crystal in each case, the graph indicates the behavior on a per mass basis. Thus, it can be said that on a per mass basis, nano-goethite adsorbs more water than micro-goethite. This is in agreement with our conventional perception that surface area exposed would increase with decreasing size, thus allowing greater reactivity to be possible. However, although most models account for size dependence on a per mass basis, it might be important to visualize the phenomena on a per surface area basis, accounting for the possible surface driven reactivity.

On a per surface area basis, the water uptake on the two samples as observed from the FTIR data would follow the behavior indicated in Figure 9 (b). As can be seen, upon normalization to surface area, the enhancement of water uptake in nano-goethite over micro is still visible, but at a diminished ratio. This indicates that the enhancement in water uptake of nano-goethite cannot be entirely attributed to the greater surface area available for adsorption on nano-goethite as compared to its micro counterpart. Thus, the results suggest that there would be an effect beyond surface area on the water uptake on goethite of varying particle size and the uptake would generally indicate an increase with decreasing particle size.

Nevertheless, it is a known fact that the amount of edge sites exposed on a particle increases as particle size decrease. These edge sites are known to play an important role in determining the reactivity of the particles as seen in literature.^{28, 29} Therefore, the enhanced water uptake beyond surface area for nano-goethite as compared to its micro counterpart can be attributed to this reasoning.

Further, in a similar fashion QCM data can be employed in order to observe the adsorption of water on goethite. The QCM allows one to directly measure the mass of substrate adsorbed on a sample sprayed in a thin layer on a QCM crystal, by relating the mass on the crystal to the frequency of the resonator as given by the Sauerbrey equation indicated as equation 1.

$$\Delta f = -C_f \Delta m \quad (1)$$

Here, Δf is the change in frequency of the resonator, Δm is the change in mass related to the change in frequency ($\mu\text{g}/\text{cm}^2$), and C_f is the sensitivity factor which is a constant of $56.6 \text{ Hz cm}^2/\mu\text{g}$ for a 5 MHz AT-cut quartz crystal.^{19, 30} Adsorption or desorption of a substance onto or from a substrate would cause a change in mass. According to the Sauerbrey equation, this change would be coupled to a change in frequency of resonance of the quartz crystal resonator. Therefore, the mass of water adsorbed, or any other adsorbate for that matter can be probed by using QCM measurements.

As seen on the QCM curves in Figure 8 (a) and (b), a corresponding decrease in resonance frequency is observed at each step of increasing relative humidity and *vice versa* for decreasing humidity. These changes can be used to determine the mass of water adsorbed on the substrate at each corresponding relative humidity by using the Sauerbrey equation, which can eventually be converted into mass of water per unit area of sample ($\mu\text{g}/\text{cm}^2$), or in other words the surface molecular density of adsorbed water molecules. Therefore, this would once again result in surface area normalized data allowing us to conduct a direct comparison on particle size effects on the water uptake on goethite as indicated in Figure 10.

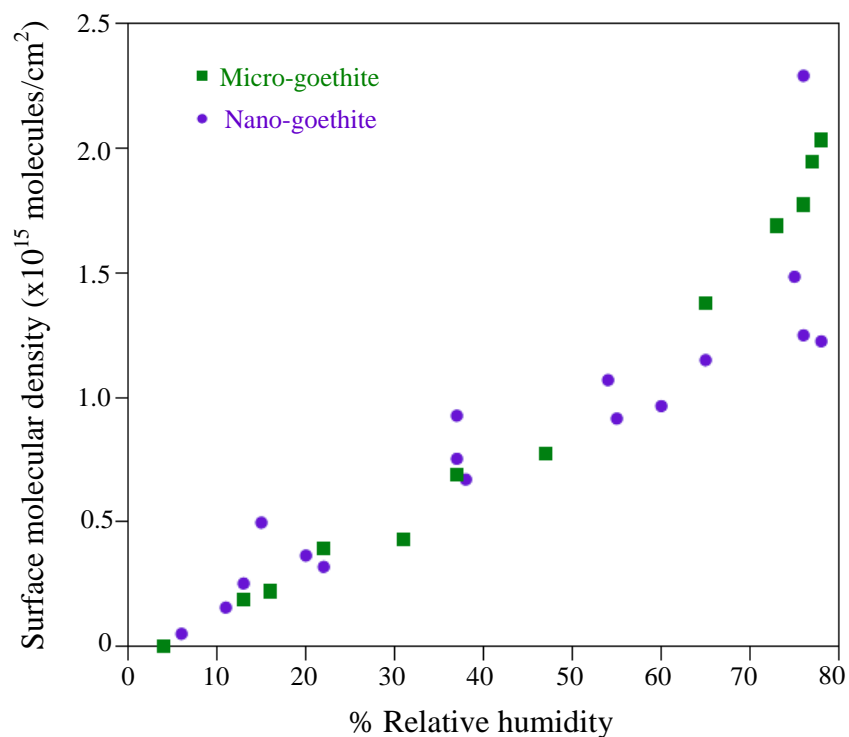


Figure 10 Variation of surface molecular density of water adsorbed on nano and micro-goethite surfaces, calculated from the QCM behavior and plot as a function of RH.

There is no distinct correlation between data points in this case, in contrast to the FTIR comparison which indicated a clear multi-layer formation behavior for both nano and micro-goethite. One of the inherent drawbacks of the QCM is the instrumental drift that indicates a decreasing relative frequency with time, which in turn is difficult to quantify. Especially, within a large time period as that considered for water adsorption and desorption, the drift would tend to become more significant and thus the anomaly observed above can be attributed to instrumental drift. However, it can be generally stated that there is no significant deviation for the water uptake on nano and micro-goethite as evidenced from this QCM comparison, in contrast to the observation previously discussed using the FTIR data.

As previously described it was found that only -OH groups are involved in water uptake. These hydroxyls being limited to the surface of the goethite structure, would be present to an extent limited by surface area of the particles. Thus, the reactivity of goethite towards water would be limited by particle surface area exposed and one would thus expect to see no effect between preparations of different size once surface area normalization is done. This justifies the QCM comparison making it more acceptable.

Nevertheless, water can easily be trapped between particles on a sample. Sample on the QCM crystal is generally well dispersed leaving a minimal room for such trapping, while that on the ATR is greater in density, thus allowing pores to be present. The contradicting conclusions obtained on water uptake, using FTIR and QCM measurements can thus also be attributed to this difference between sample preparations in each case.

Overall, it can be stated that FTIR and QCM measurements result in quantitative data that can be successfully utilized in conjunction such as to better understand the adsorption of water on different interfaces. It should be noted that the analysis conducted with FTIR data alone was competent to an extent to which a comprehensive size effect on water uptake can be evaluated.

However, such conduct would not be viable if the adsorbate in a given process would be infrared inactive, making it unable to be observed through FTIR spectroscopy. The viability of QCM in producing an alternative basis was clearly evidenced from the analysis conducted above. Thus, in such circumstances one may utilize QCM as a tool in order to probe the adsorption and desorption behavior on the substrate, since the QCM produces a universal signal which is independent of the nature of the adsorbate as well as the strength of the adsorbate-surface interaction.

3.3 Uptake of HNO₃ on goethite

The FTIR and QCM spectra for adsorbed HNO₃ on goethite at a flow of 250 SCCM (255 ± 1 mTorr in pressure terms as found from the calibration) are shown in Figures 11 and 12, respectively. It is found in literature that in contrast to water, which mostly adsorbs in a molecular fashion, HNO₃ uptake on most oxide surfaces is dissociative and irreversible, thereby forming surface nitrates.¹² This behavior was well evidenced by the QCM measurements, where a corresponding increase in relative frequency was observed after halting of the HNO₃ flow at the end of one hour, indicating a partly irreversible uptake.

In most occasions where both reversible and irreversible uptake may occur, it is not very straightforward to at once distinguish between the irreversible and reversible uptake components using spectroscopic data alone. However, it was observed here that the QCM behavior during the uptake process provides a relatively distinct picture of the irreversible vs. reversible binding *in situ*. To our knowledge, there had been no previous attempts to identify or quantify irreversible vs. reversible binding using QCM behavior as a basis. Here, with the complementary FTIR and QCM data in hand, the adsorption modes of HNO₃ on goethite were able to be analyzed relatively easily.

Here, the nature and extent of HNO₃ uptake on goethite was monitored using QCM, while simultaneous FTIR measurements were made to probe the adsorbed species. Eventually, FTIR spectra for the reversibly and irreversibly bound HNO₃ were obtained by appropriate processing of spectra acquired at suitable points in time, as indicated in Figure 13, allowing to easily distinguishing vibrational modes of reversibly bound HNO₃ on goethite, from those bound in an irreversible fashion.

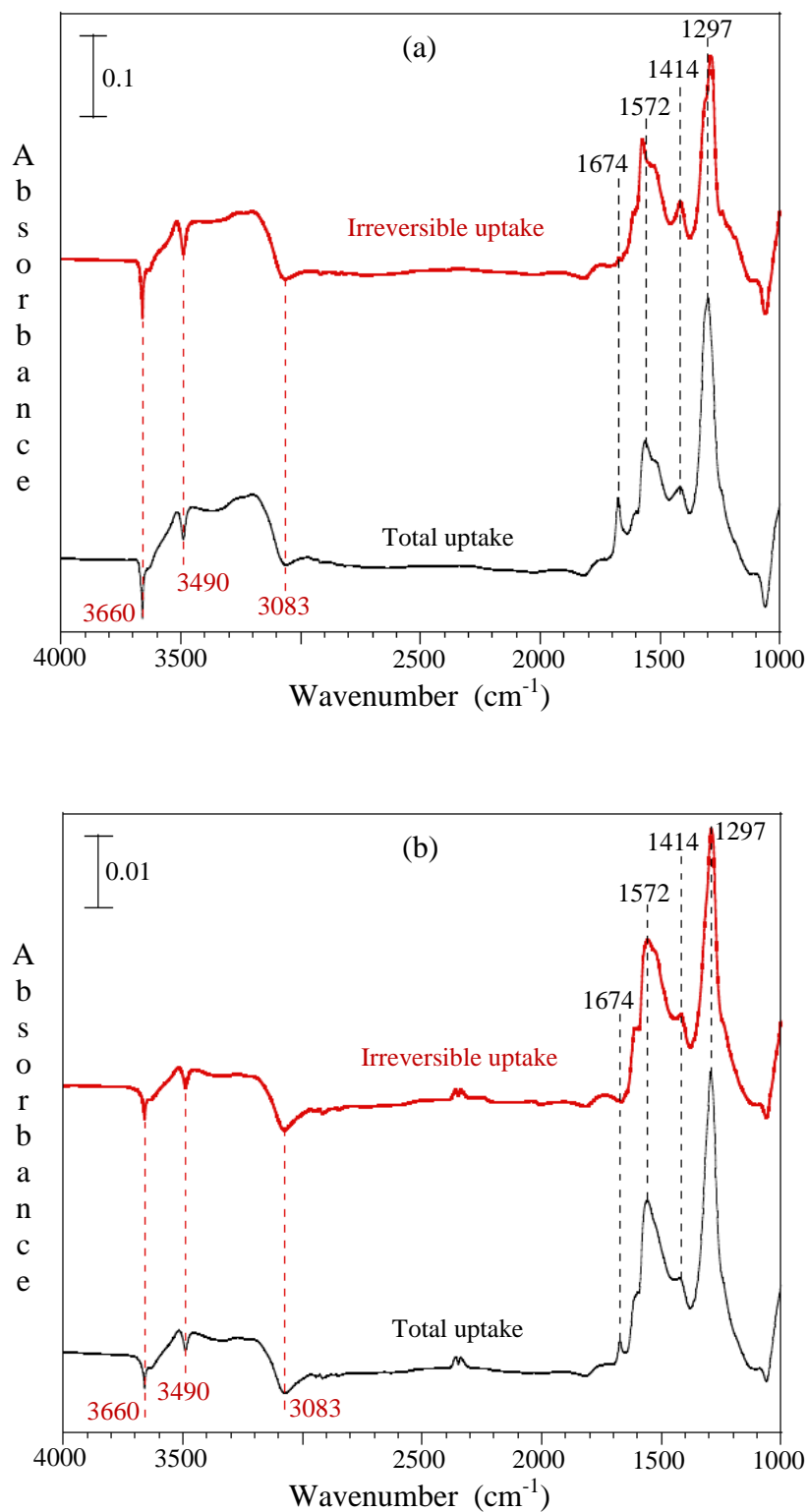


Figure 11 FTIR spectra of adsorbed HNO₃ on (a) nano and (b) micro-goethite at a flow of 250 SCCM of dry air through the acid chamber.

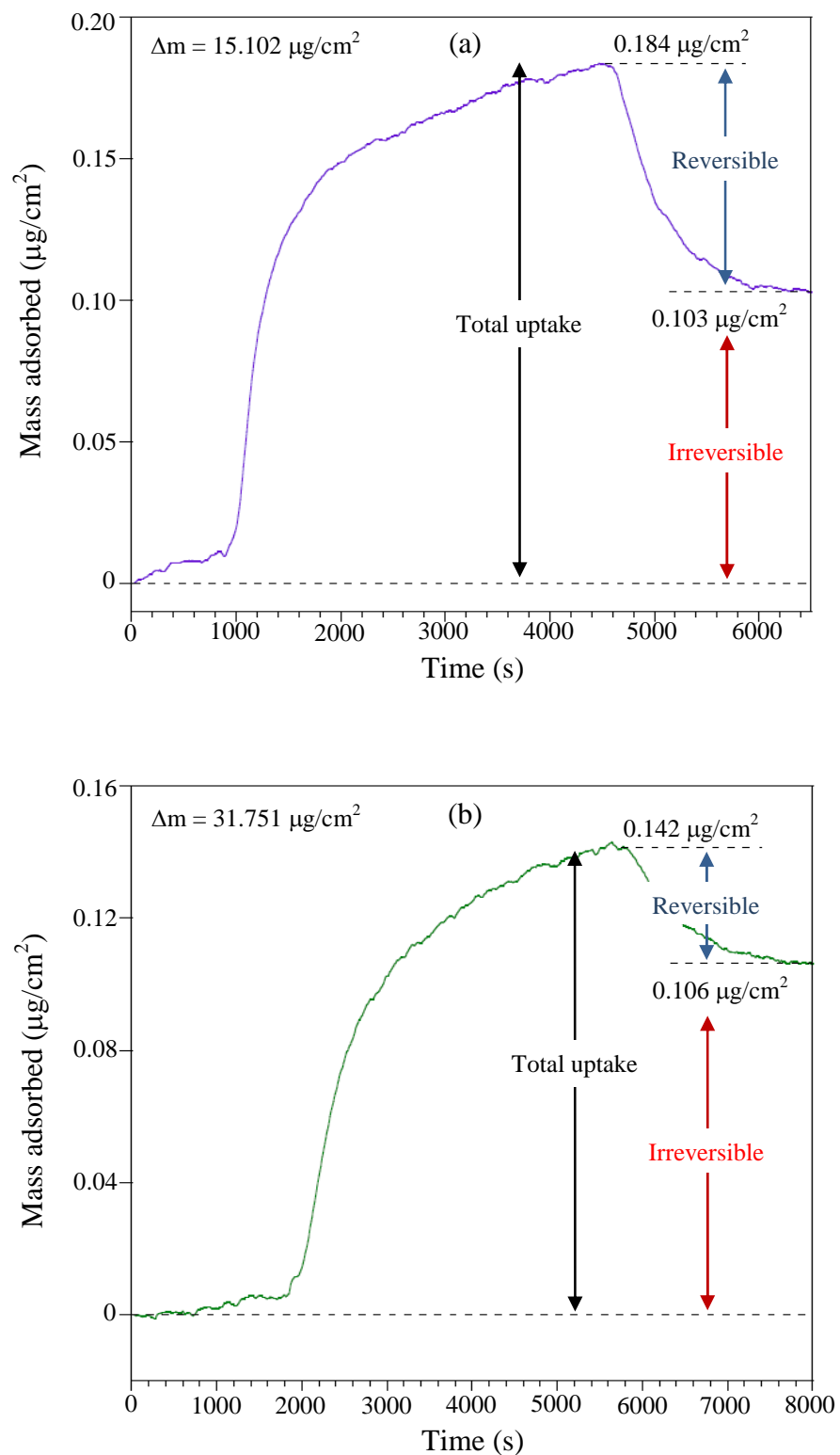


Figure 12 QCM curves for the HNO_3 uptake on (a) nano and (b) micro-goethite at a flow of 250 SCCM of dry air through the acid chamber.

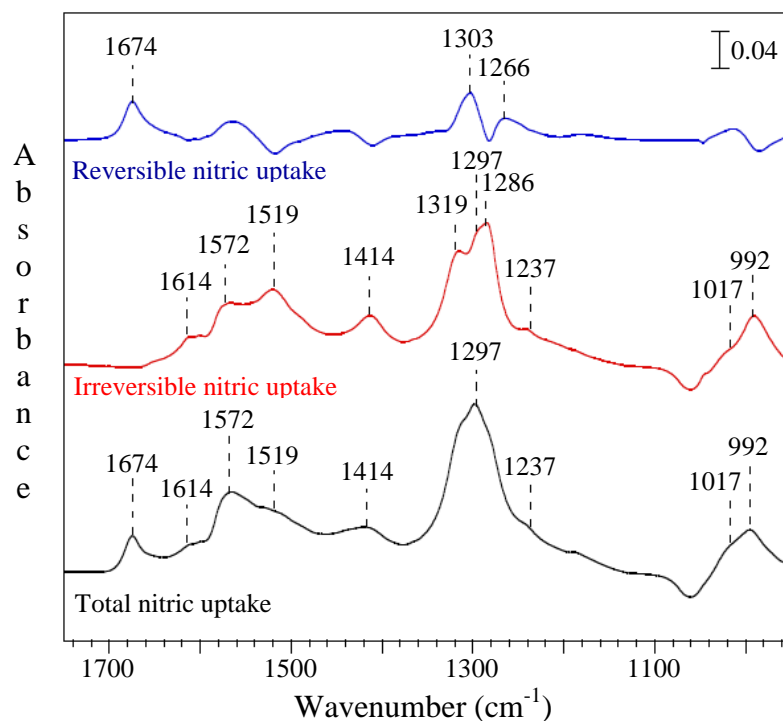


Figure 13 FTIR spectra of reversibly, irreversibly and total bound HNO₃ on the nano-goethite surface obtained by appropriate processing, as identified by the QCM behavior. There were no significant differences in vibrational assignments based on particle size.

From this, the peaks were assigned for molecularly adsorbed, oxide-coordinated, and adsorbed water-solvated nitrate on goethite upon gas phase HNO₃ exposure as set out in Table 3. However, no evidence was present in literature for the assignment of vibrational modes of HNO₃ adsorbed on goethite. Therefore, vibrational assignments for the HNO₃ uptake on γ -Fe₂O₃ were used as reference,¹² which in turn indicated good agreement with the values assigned here. It should be noted that only the FTIR spectra of nano-goethite have been indicated on Figure 13 since there were no significant differences between vibrational frequencies based on particle size.

Table 3 Vibrational frequencies for adsorbed HNO₃ on goethite

Description	Assignment	Wavenumber observed (cm ⁻¹)	Wavenumber for γ -Fe ₂ O ₃ (cm ⁻¹)
	ν (OH)		
Molecularly adsorbed HNO ₃	ν (NO ₂)	1674	1679
	δ (OH)	1303	1337
	ν_s (NO ₂)	1266	1297
	Monodentate		
	ν_3 (High)	1519	1555
	ν_3 (Low)	1286	1281
		1297	
Oxide-coordinated nitrate	Bidentate		
	ν_3 (High)	1572	1588
	ν_3 (Low)	1237	1229
	Bridging		
	ν_3 (High)	1614	1622
	ν_3 (Low)		1203
	ν_1	1017	993
Adsorbed water-solvated nitrate	ν_3 (High)	1414	1399
	ν_3 (Low)	1319	1346
	ν_1	992	814

Vibrational frequencies for γ -Fe₂O₃ have been included here as reference from literature¹²

In addition to the peaks corresponding to adsorbed nitrate species, the FTIR spectra indicated the appearance of negative bands upon HNO₃ uptake. Water uptake on goethite as previously discussed, indicated the appearance of only two negative bands. However, HNO₃ uptake on goethite was coupled to the appearance of three distinct negative bands, at wavenumbers 3660, 3490 and 3083 cm⁻¹. The former two negative bands are identical in value to that seen upon water uptake, and can once again be attributed to the involvement of -OH groups during the process of HNO₃ adsorption.

The third negative band appears at 3083 cm⁻¹. This is close in wavenumber to the bulk hydroxyls as visible at 3125 cm⁻¹ on Figure 5 and indicates a similarly broad nature. However, addition of the adsorbed nitrate spectra to the goethite surface spectra showed the complete diminishing of the peaks at 3660 and 3490 cm⁻¹, indicating that the -OH groups take part almost entirely in the HNO₃ uptake. In contrast, the surface peak at 3125 cm⁻¹ indicated no significant attenuation. Thus, the third negative peak observed at 3083 cm⁻¹ as on Figure 11 can be attributed to a surface feature which would have earlier been buried under the broad bulk hydroxyl peak.

During the recent assignment of vibrational frequencies for goethite hydroxyl groups Boily and Felmy have proposed the order of frequencies to be $\nu(-\text{OH}) \sim \nu(\mu\text{-OH}) > \nu(\mu_3\text{-O}_\text{I}\text{H}) > \nu(\text{OH}_{\text{Bulk}}) > \nu(\mu_3\text{-O}_\text{II}\text{H})$.⁶ Here, $\mu_3\text{-O}_\text{I}\text{H}$ and $\mu_3\text{-O}_\text{II}\text{H}$ denote hydrogen-bonded and non-hydrogen-bonded triply coordinated hydroxyl groups on the goethite surface respectively.

Thus, judging by the value, the negative peak at 3083 cm⁻¹ can be attributed to $\mu_3\text{-O}_\text{II}\text{H}$ groups, whose absorption would have been buried earlier under the broad peak for the bulk hydroxyl groups. This however was an interesting observation since these non-

hydrogen-bonded triply coordinated hydroxyl groups which seemed not to play any role during water uptake on goethite, indicated significant contribution during HNO₃ uptake, as evidenced from the results here.

Surfaces may contain differently coordinated hydroxyl groups, where each different type would indicate a varying degree of reactivity. In the case of goethite, the three distinct hydroxyl groups on goethite singly, doubly and triply coordinated to Fe atoms are likely to exhibit differences in reactivity. Parfitt *et al.* has observed that singly and doubly coordinated hydroxyls on goethite can be readily converted to OD, by brief (one minute) treatment with D₂O.²⁵

Rochester and Topham have done the same observation where surface hydroxyl groups underwent rapid isotopic exchange upon D₂O exposure to produce the corresponding surface deuteroyl groups, whereas the bulk hydroxyls did not indicate such reactivity.³¹ Parfitt *et al.* have also observed that goethite treated with 200 µmol/g H₃PO₄ or NaH₂PO₄ shows no infrared adsorption around 3486 cm⁻¹, indicating that these hydroxyl groups are replaced by phosphate groups, forming bridges between adjacent Fe³⁺ ions.²⁵

Thus, there is evidence in literature for the observation of marked differences between hydroxyl group reactivity at different coordination. At the same time there have been many attempts to model reactivity variations such as to predict the behavior of goethite preparations containing different hydroxyl group densities.^{3, 32, 33} However, at present there is no precise quantitative understanding as to how such reactivity differences can be directly correlated to the availability of differently coordinated hydroxyls, and thus the particle surface area exposed for reaction.

In order to attain a better insight of the process herein, the data obtained during the uptake process was analyzed further. Two distinct peaks corresponding to adsorbed nitrates, namely the $\nu(\text{NO}_2)$ mode of molecularly bound HNO_3 at 1674 cm^{-1} and $\nu_3(\text{high})$ mode of oxide-coordinated HNO_3 at 1572 cm^{-1} were selected for probing reversibly and irreversibly adsorbed nitrates respectively. Figure 14 indicates the temporal variation of reversible and irreversible HNO_3 binding on nano and micro-goethite by plotting the integrated absorbance of the above peaks as a function of time.

From these, it can be clearly seen that HNO_3 uptake, both reversible and irreversible, achieves saturation approximately within the first half hour of exposure, thus making it reasonable to assume complete surface saturation at the end of one hour HNO_3 exposure. It was also seen during analysis that upon the halting of HNO_3 flow at 60 minutes, the absorbance indicated by the peak due to molecularly adsorbed species gradually diminishes to near zero, while that in the case for oxide coordinated shows little or no considerable attenuation. This again justifies the assignment and selection of peaks for probing reversible and irreversible uptake.

Similar insight on surface saturation can be observed from QCM behavior, where the relative frequency should indicate a steady value upon achieving saturation. This behavior was observed during the water uptake as visible in Figure 8, where the relative frequency indicated a constant value under the equilibration at each RH. One would expect the same trend to be observed with change in mass since the two quantities would be directly proportional as given by the Sauerbrey equation.

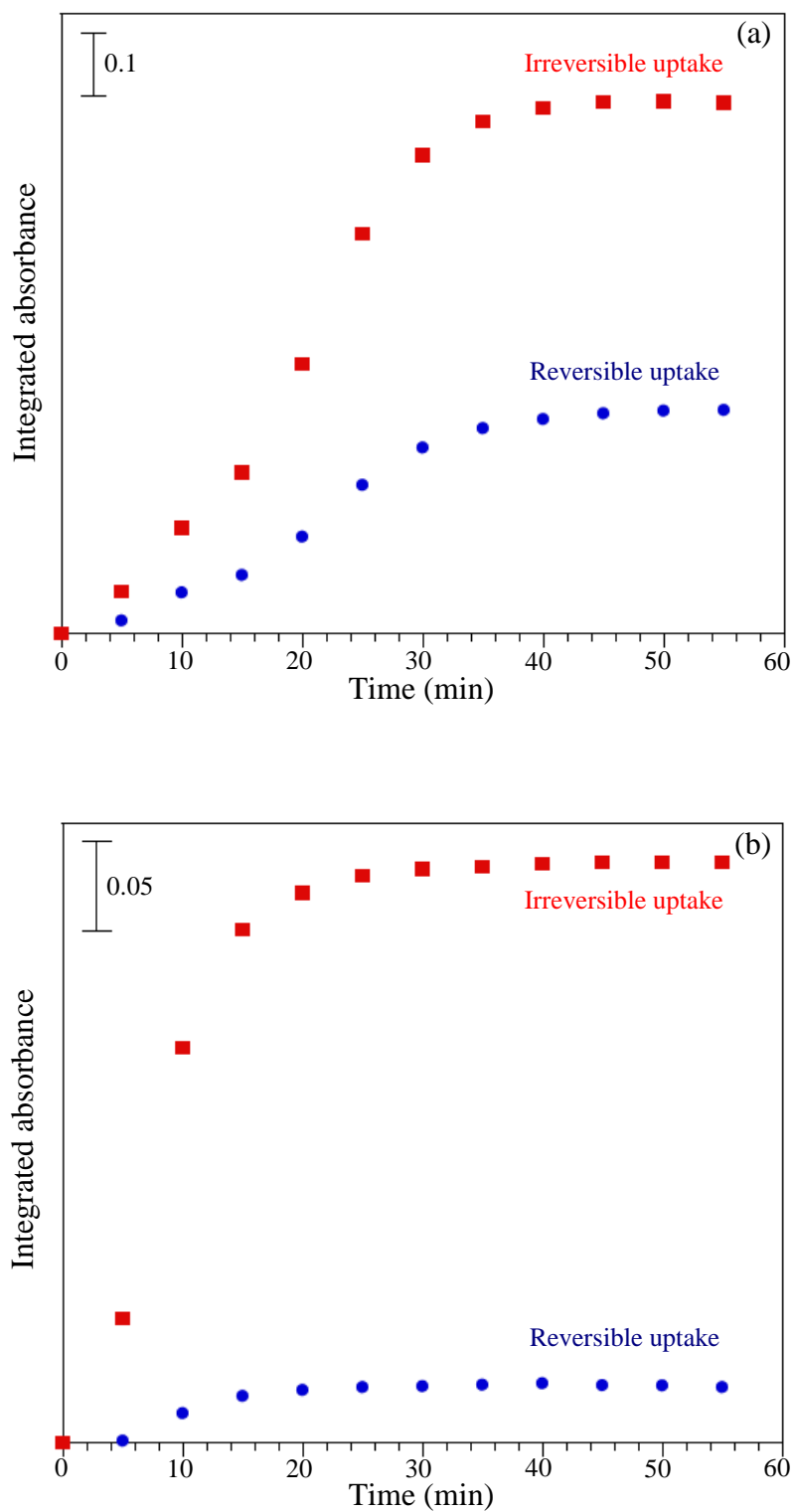


Figure 14 Temporal variation of HNO₃ uptake on (a) nano and (b) micro-goethite. $\nu(\text{NO}_2)$ mode at 1674 cm^{-1} and $\nu_3(\text{high})$ mode at 1572 cm^{-1} was selected for probing reversibly and irreversibly adsorbed nitrates respectively.

However, such behavior was not indicated during the QCM measurements on HNO_3 uptake, where the change in mass at each level of relative humidity did not achieve any constant value even after prolonged exposure as seen in Figure 12. QCM being a highly sensitive instrument, the frequency of vibration of the quartz crystal resonator is highly susceptible to changes in temperature. With such insight the non-leveling of relative frequency upon HNO_3 uptake can be said to be associated with the thermal energy liberated at the crystal surface by the adsorption and desorption of HNO_3 molecules, thus causing the local temperature to fluctuate.

As seen from Figure 14 (a) and (b), the irreversible uptake of HNO_3 on goethite is more pronounced than reversible uptake for both nano and micro-goethite. However, in order to observe the particle size effects upon HNO_3 uptake, the temporal variation of reversible and irreversible binding was plotted separately, indicating the behavior of nano and micro-goethite together on each graph as shown in Figure 15 (a) and (b). Since a constant mass of sample was used in each case the comparison conducted here was on a per mass basis. As seen, the reactivity of nano-goethite was greater towards both reversible and irreversible binding of HNO_3 than the larger micro-goethite.

The increase in surface area of nano-goethite, over micro-goethite is ~ 3.8 (121/34) folds. The enhancement of reversible HNO_3 uptake on nano-goethite as in Figure 15 (a), clearly indicates an enhancement inversely related to size, that is beyond the above surface area factor. But, for the same comparison under irreversible uptake, the enhancement in nano-goethite was apparently less than the factor of ~ 3.8 . It was also seen from the IR spectra that the surface hydroxyl groups on goethite are mostly associated with the irreversible uptake component, than with reversible uptake.

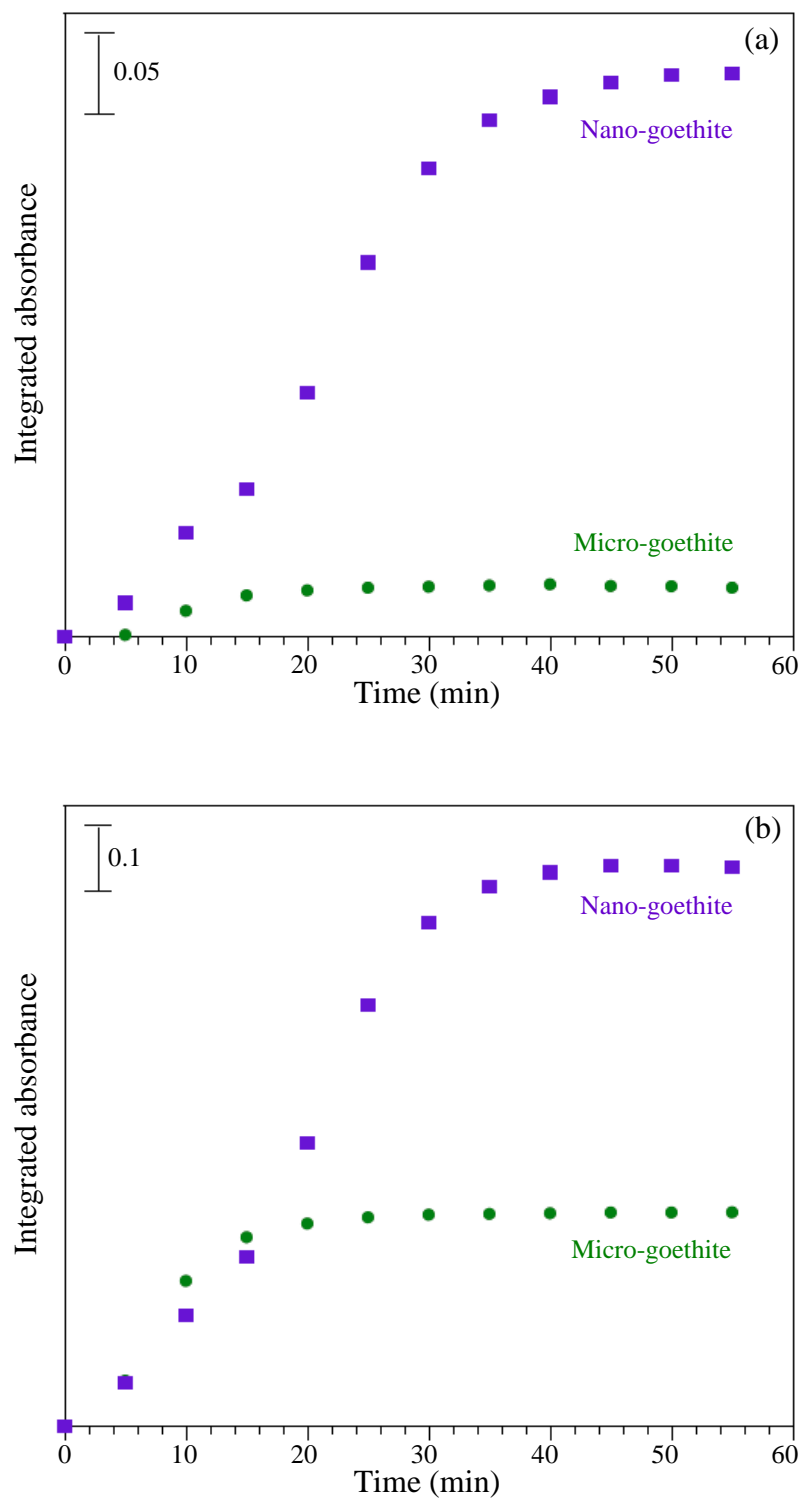


Figure 15 Temporal variation of (a) reversible and (b) irreversible HNO₃ uptake. $\nu(\text{NO}_2)$ mode at 1674 cm^{-1} and $\nu_3(\text{high})$ mode at 1572 cm^{-1} was selected for probing reversibly and irreversibly adsorbed nitrates respectively.

Thus, it can be stated that particle size has a greater effect on irreversible uptake of HNO₃, than on reversible uptake. At the same time QCM behavior also indicated a clear picture of the reversible and irreversible uptake components in terms of respective changes in relative frequency of oscillation. Thus, to obtain a quantitative view of size effects, the average saturation surface coverage of adsorbed HNO₃ were determined as given in Table 4. At this point it was apparent that contrary to the higher reactivity indicated by nano-goethite towards HNO₃ on a per mass basis, micro-goethite indicated higher saturation coverage of irreversibly bound HNO₃, than the smaller nano-goethite.

As supplementary analysis to further defend the above observation, nitric uptake on nano and micro-goethite was conducted using a transmission FTIR spectrophotometer setup as described elsewhere.²⁴ An initial pressure of 1 Torr was used as to assure saturation uptake within the period of analysis. The saturation coverage of total adsorbed HNO₃ on the goethite samples were then determined using the pressure differences taken place during the uptake process.

Table 4 Average saturation surface coverage for adsorbed HNO₃ on nano and micro-goethite

Sample	Surface coverage of irreversibly bound HNO₃	Surface coverage of total bound HNO₃ at a 1 Torr initial pressure
Nano-goethite	$(2.6 \pm 0.6) \times 10^{13}$ molecules/cm ²	$(3 \pm 1) \times 10^{14}$ molecules/cm ²
Micro-goethite	$(7 \pm 4) \times 10^{14}$ molecules/cm ²	$(9.3 \pm 0.6) \times 10^{14}$ molecules/cm ²

The rightmost column in Table 4 indicates the saturation coverage of total adsorbed HNO₃ determined using transmission FTIR measurements. Both the sets of results infer that micro-goethite would contain a higher density of adsorbed HNO₃ than nano-goethite, thus indicating an increased reactivity. Although one would expect the values in these two columns to coincide for each particle size, the observed variability observed can be attributed mainly to the differences between the two techniques adopted and the assumptions taken into consideration in carrying out the calculations in each of the separate techniques concerned.

Additionally, the average reversibly and irreversibly bound HNO₃ percentages were determined using QCM data and are set out in Table 5. From these calculations, it was visible that HNO₃ was predominantly bound in a reversible fashion on nano-goethite, whereas that on micro was mostly irreversible. So it becomes clear that both the extent as well as nature of adsorption of HNO₃ on goethite is particle size dependent.

Table 5 Average reversibly and irreversibly bound HNO₃ percentages determined using QCM data

Sample	Average percentage of reversible binding	Average percentage of irreversible binding
Nano-goethite	(65 ± 5) %	(35 ± 5) %
Micro-goethite	(14 ± 9) %	(86 ± 9) %

The rightmost column indicates the values obtained during the comparative transmission FTIR experiments

Although such relation between reactivity and particle size of goethite as inversely related to its specific surface area had previously been observed, very little convincing quantitative descriptions coupled to experimental observations are found in literature. Despite the general intuition that increasing surface area would allow reactivity to be enhanced, it has been previously recognized that goethite preparations of relatively large particle size (i.e. particles with SSA below ca. 60 m²/g) indicate considerable increase in reactivity towards protons,^{3, 34-36} as well as carbonates,^{3, 32} when normalized to surface area.

Additionally, there are examples for higher adsorption capacities of these particles towards anions such as phosphate and fluoride.^{37, 38} In some previous attempts to explain this observation, such anomaly had been attributed to morphological features of surface roughness that results from multi domain crystal formation, which in turn does not translate into an increase in the BET measured SSA.³

In a recent attempt to model this anomalous behavior in average adsorption capacities, Villalobos *et al.* have shown that a face contribution-site-density model of hydroxyl groups can adequately model the size dependent adsorption behavior of goethite.³² Considering the distribution of differently coordinated hydroxyls on different crystallographic planes and assuming that only singly and triply coordinated hydroxyl groups are reactive towards protons while only singly and doubly coordinated hydroxyl groups are reactive towards anions and cations, they have been able to successfully model the absorption of a number of species such as protons, carbonates, chromates, and Pb(II) on goethite preparations of varying SSA.

In terms of structural features, they have observed large topographic differences among goethite particles of varying size. Acoustic alternating current (AAC) mode atomic force microscopy (AFM) had revealed that smaller goethite particles with larger SSA are small acicular crystals with apparent smooth faces for which the simplified face-composition model with (101) and (001) faces with negligible contribution from capping faces are adequate. However, when particles become larger, more complex planes, such as (010) and (210) tend to become apparent as have been distinctly observed through AFM. Thus, in modeling the reactivity of larger goethite particles, the reactive site densities on these more complex surface planes would have to be taken into account.³²

With the information in hand, there are two major questions that would arise at this point. First, why is the saturation surface coverage of adsorbed HNO₃ greater on micro than nano-goethite, whereas no such pattern of reactivity was observed during water uptake. Second, why is HNO₃ mostly bound in a reversible fashion on nano-goethite, whereas that on micro-goethite is predominantly irreversible. Understanding the size dependent reactivity of goethite towards HNO₃ would therefore mean finding answers to these questions.

The range of SSA taken in to consideration by Villalobos *et al.* in this modeling approach has been 50 to 94 m²/g.³² With the sizes of goethite particles of concern in this investigation being 34 and 121 m²/g, and with an acicular structure been observed by TEM, the considerations on structural variation adopted by Villalobos *et al.* are deemed to be applicable here. However, with the complementary data obtained using FTIR and QCM measurements being at our dispense, we sought to understand this variable reactivity at a more precise level such as to visualize its molecular level picture.

The existing models on goethite surface reactivity, do not extensively describe the involvement of surface hydroxyl groups during the molecular binding of species including water. However, with the observations reported here, it can be postulated that molecular or reversible binding of water on goethite takes place with the involvement of the -OH groups as seen on Figure 7. The same behavior was observed for the reversibly bound HNO₃. However, with the majority of hydroxyl groups on goethite principally being involved in the dissociative, irreversible binding of HNO₃, the participation of -OH groups upon the molecular binding was much less apparent.

From the experimental evidence that we have, the first distinction between the uptake of water and HNO₃ on goethite is that during water uptake only -OH groups on goethite contributed towards reactivity, whereas the HNO₃ uptake was associated with -OH, μ -OH as well as μ_3 -O_{II}H groups at the goethite surface. The abundance of these hydroxyl groups on goethite surface planes would depend on the type of hydroxyl group as well as the nature of the crystallographic plane.

This fact has been previously postulated in describing goethite surface reactivity,⁶ and had also been taken into consideration during the modeling approaches.³² Thus, if the distribution of crystallographic planes would depend on particle size as have been previously observed by Villalobos *et al.*, reactivity of goethite should be a function of particle size, similar in trend to our experimental observation. Here, we may stipulate that the structure of nano and micro-goethite varies in character as experimentally observed by Villalobos *et al.*³² Thus, smaller sized nano-goethite particles would consist of (101) and (001) faces, while the larger micro particles would indicate additional significant contributions from more complex planes, such as (010) and (210).

Villalobos *et al.* have determined the density of each type of hydroxyl groups on the various crystal faces on goethite based on simplified polyhedral models of the predominant faces on the acicular goethite crystals, which are (101) and (001) (space group *Pnma*), with capping faces (010) or (210). Accordingly, it has been established that -OH and μ_3 -OH have comparable site densities of 3.03 sites/nm² on (101) and 3.34 sites/nm² on (001) main faces, while μ -OH indicates no significant presence.

-OH and μ -OH indicates the major composition on the capping faces with that for -OH being 9.1 sites/nm² on (010) and 7.5 sites/nm² on (210), while it being 4.55 sites/nm² on (010) and 3.75 sites/nm² on (210) for μ -OH. However, there seems to be no significant presence of μ_3 -OH on these capping faces according to Villalobos *et al.* It should be noted that there is no clear breakdown between μ_3 -O_IH and μ_3 -O_{II}H here.

We have observed the involvement of -OH, μ -OH as well as a part of the μ_3 -OH groups in driving the HNO₃ uptake on goethite. Coupling this insight into the model considerations, the total reactive hydroxyl group density towards HNO₃, on a goethite particle would be the sum of -OH, μ -OH and μ_3 -O_{II}H groups on its surface. So, in summary we can say that in going from smaller to larger goethite particle size, the face distribution ratio of main faces to capping faces decrease.

Note that there is a clear increase in terms of reactive hydroxyl group density in the larger sized goethite particles as compared to the nano-sized particles. Thus, assuming that the reactive μ_3 -OH group density given by Villalobos *et al.* only reflects μ_3 -O_{II}H groups, we can say that that the reactive hydroxyl group density would indicate a marked increase in going from smaller to large goethite particles.

This explains the anomalous variation in average saturation surface coverage for adsorbed HNO_3 on nano and micro-goethite observed in our experimental work. Thus, given the presence of three differently coordinated hydroxyl groups on the surface, the reactivity of goethite towards a specific reactant should be looked at in terms of its affinity towards each type of surface reactive groups. Then by coupling it to the variation of surface reactive site density, the particle size dependence of goethite towards the specific reactant could be effectively predicted.

This protocol had been outlined in detail for HNO_3 and has the potential to be extrapolated into other reactants of interest. So, we may conclude that the reactivity of goethite towards gas phase HNO_3 indicates a direct size dependence where goethite preparations of larger size (smaller SSA) would indicate a greater saturation surface coverage of adsorbed species than preparations of smaller size (larger SSA), as have been experimentally observed.

Having answered the first concern in terms of goethite- HNO_3 interaction, the next question to be answered is the variation of reversible and irreversible uptake between goethite preparations of varying size. With appropriate spectral processing it was visible that the involvement of surface hydroxyl groups on goethite was predominantly limited to dissociative, irreversible binding of HNO_3 on the goethite surface. Therefore, the reversible binding would be dependent on the surface area available for interaction, while the irreversible uptake would depend on the presence and density of reactive hydroxyl groups exposed on the surface.

In going from nano to micro-goethite, the amount of surface area exposed on the sample would decrease as a result of decreasing SSA, and this would result in a decrease

in reversible binding of HNO_3 . At the same time, the amount of reactive hydroxyl group density would increase in going in the same direction as explained previously, resulting in an increase in the irreversible binding. Thus, we would expect the ratio between irreversible and reversible binding of HNO_3 on micro-goethite to be significantly greater than that on nano-goethite.

This trend was evidenced from our experimental observations on the kinetics on HNO_3 uptake and is depicted on (a) and (b) of Figure 14. For the same reasoning, we expected a greater ratio between the reversibly bound species on nano and micro-goethite than those irreversibly bound. This pattern again was experimentally evidenced as seen on (a) and (b) of Figure 15. Thus, the FTIR observations are in agreement with the QCM inference as shown in Table 5.

In order to further understand how each type of hydroxyl would individually contribute towards reactivity, the loss of hydroxyl groups as observed from the negative FTIR bands upon HNO_3 uptake were used in further analysis. Figure 16 indicates the temporal variation of the integrated absorbance of the negative bands appearing at 3660, 3490 and 3083 cm^{-1} . Each value of integrated absorbance was obtained by peak fitting at the corresponding wavenumber. These values were then normalized to the integrated absorbance of the analogous peak on the surface spectrum for comparison purposes, expecting all values to be capped to a maximum of 1 or less, at maximum consumption.

However, interestingly some types of hydroxyl groups did not indicate such behavior. $\mu\text{-OH}$ peak at 3630 cm^{-1} indicated a saturation ratio larger than unity for both nano and micro-goethite, while -OH peak at 3490 cm^{-1} indicated a ratio much larger than 1 for micro-goethite.

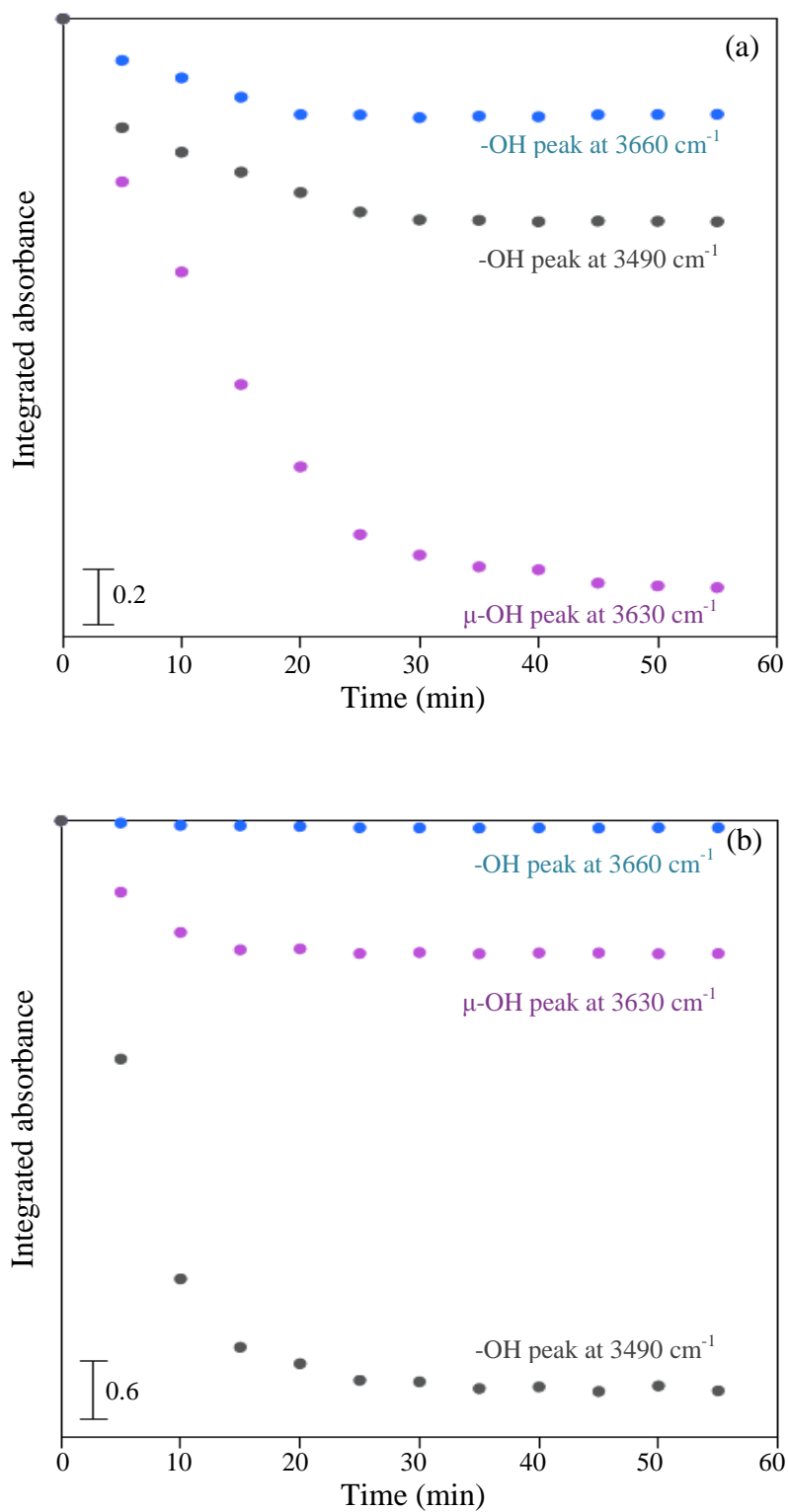


Figure 16 Temporal variation of the integrated absorbance of negative peaks observed at 3660, 3630 and 3490 cm⁻¹ upon nitric acid uptake on (a) nano and (b) micro-goethite.

The only rationale that could explain this observation is if we have more surface hydroxyls upon HNO₃ uptake than what was present on the surface initially. This would only be possible if HNO₃ uptake leads to the formation of these types of surface hydroxyl groups on the goethite surface.

Nevertheless, the irreversible adsorption of HNO₃ on goethite would mechanistically produce H₂O in the system which can be molecularly bound to the surface, as was evidenced from the FTIR data acquired during HNO₃ uptake. Thus we may postulate that these adsorbed water molecules may then dissociate such as to produce surface hydroxyl groups by binding to surface sites which would have initially been vacant. This would result in the formation of specific surface hydroxyl groups, thus justifying the observations done in Figure 16. The comparison however, could not be done with the peak at 3083 cm⁻¹, since no corresponding peak was apparent on the surface spectra at that region. But, in essence this observation can be used in further explaining the size-dependent reactivity patterns of goethite.

The reactivity of a substrate towards a specific reactant will be predominantly governed by the amount irreversible bound on the substrate surface. This fact can be specifically highlighted within an atmospheric context since these would be the reactants available for further reaction at prolonged exposure. Graphs on Figures 14 and 15 indicate raw FTIR data and demonstrate the comparison on a per mass basis. We saw that that the SSA ratio between nano and micro-goethite as measured here is ~3.8. However, the ratio of irreversible binding between nano and micro-goethite here is clearly less than this surface area enhancement factor, as evidenced from Figure 15 (b).

Thus, the reactivity of micro-goethite would be greater upon surface area normalization than its nano counterpart; a result that is once again congruent with that established via QCM observations. Therefore, we arrive at the conclusion that increasing particle size would increase the reactivity of goethite containing aerosols towards HNO_3 contained within the atmosphere; a size effect which is attributable to surface structural artifacts that becomes more pronounced with increasing particle size. At the same time, we have demonstrated that FTIR and QCM data produces complementary information, which are in good agreement with each other. Thus, QCM, similar in case to that indicated upon water uptake, has the potential to be adopted such as to successfully probe the reactivity of substances at a substrate of interest.

3.4 Aqueous phase behavior of HNO_3 reacted goethite

The summary of measurements made on aqueous medium suspended samples of nitric adsorbed goethite is listed in Table 6. Similar measurements made on control samples are listed on the same table for comparison. Surface adsorption of HNO_3 on goethite would result in surface bound protons which could be released upon suspension in aqueous media, causing the medium pH to decrease. Such trends were visible with both nano and micro-goethite as evidenced by the measured pH values set out in Table 6.

More interestingly, the liberation of bound protons into aqueous media would produce an environment in which dissolution is likely to be favored. This again was confirmed with the dissolved Fe contents determined using ICP-OES measurements. Thus, surface adsorption of HNO_3 would result in an enhancement of goethite dissolution upon the deposition into an aqueous environment.

Table 6 pH, dissolved Fe content (ppb), zeta potential (mV) and the hydrodynamic diameter of aqueous medium suspended nitric adsorbed samples of nano and micro-goethite

	Nano-goethite		Micro-goethite	
	Sample	Control	Sample	Control
pH	3.9 ± 0.1	6.9 ± 0.3	4.5 ± 0.1	7.8 ± 0.3
Dissolved Fe (ppb)	1764 ± 53	206 ± 17	50 ± 4	-
Zeta potential (mV)	41.9 ± 0.3	20 ± 1	37.0 ± 0.4	10.2 ± 0.8
Hydrodynamic radii (nm)	192 ± 18	494 ± 52	912 ± 196	4289 ± 423

The parameters for controls containing an equivalent weight of goethite have been listed for comparison

The presence of charged species, which are dissociatively bound HNO_3 is confirmed by the increase in zeta potential for HNO_3 adsorbed samples compared to the controls. This surface charge development in turn explains the variation of hydrodynamic diameter, where the particles would tend to aggregate less once the charged surface species are present, thereby resulting in smaller hydrodynamic diameter. Eventually, with lesser aggregation in place, the nitric adsorbed goethite samples would indicate a clear stability upon suspension in aqueous media, compared to the control samples and would thus indicate lower rates of sedimentation as opposed to their unreacted counterparts. This trend is clearly visible from the sedimentation patterns indicated in Figure 17.

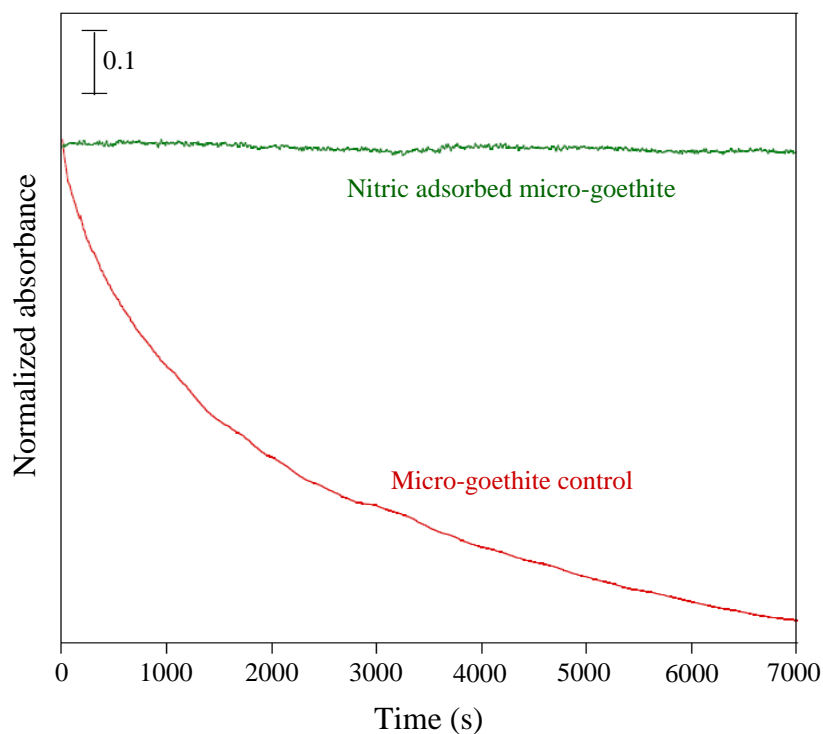


Figure 17 Sedimentation pattern of nitric adsorbed micro-goethite suspended in aqueous media. Nano-goethite indicates the same trend but was less apparent within a shorter time scale.

3.5 Coadsorption of water on nitric adsorbed goethite

The water uptake on HNO_3 adsorbed goethite samples were observed using FTIR spectroscopy in order of assessing the effects of coadsorption. Figure 18 indicates the FTIR spectra obtained at varying relative humidity for both nano and micro-goethite. For comparison, water was allowed to adsorb on each sample before and after HNO_3 uptake, while the initially adsorbed water was allowed to completely remove overnight under a steady flow of dry air prior to HNO_3 being introduced. The FTIR spectra for adsorbed water in the presence and absence of adsorbed HNO_3 were compared as to recognize how the mutual presence of the two reactants could affect the reactivity of goethite.

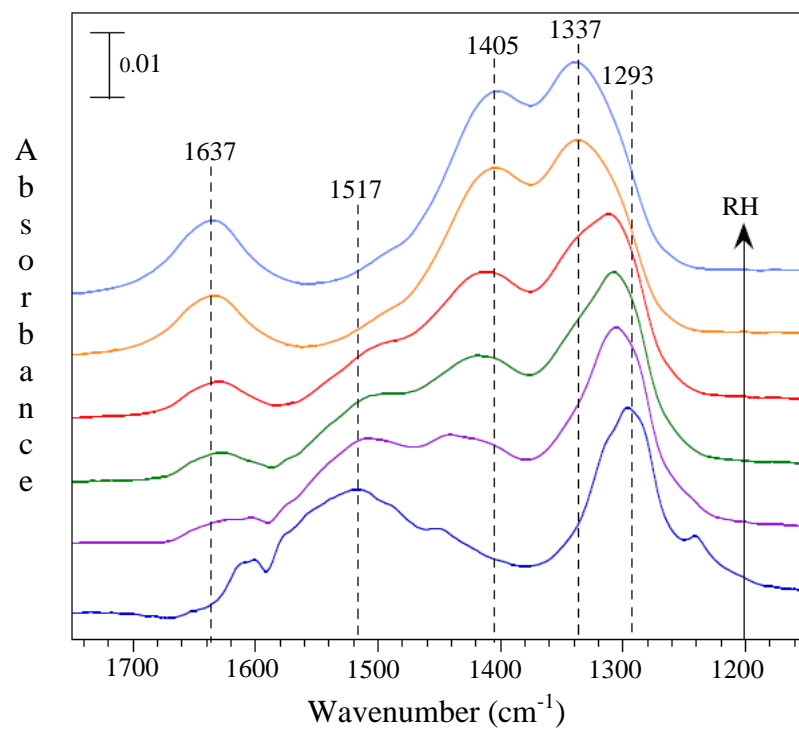
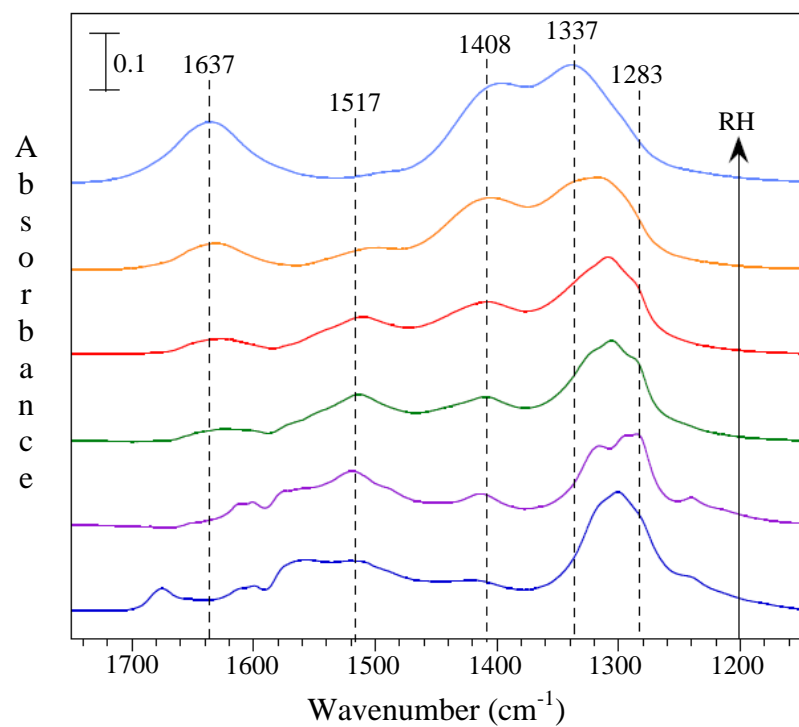


Figure 18 Water uptake on nitric adsorbed (a) nano and (b) micro-goethite samples.

Bending mode of adsorbed water on the samples was observed at 1637 cm^{-1} and indicated an increase with increasing humidity. The development of bands at $1408/1405\text{ cm}^{-1}$ and 1337 cm^{-1} was also clearly visible as humidity increased. These peaks can be attributed to $\nu_3(\text{high})$ and $\nu_3(\text{low})$ modes of adsorbed water-solvated nitrate species. At the same time, peaks at 1517 and $1283/1293\text{ cm}^{-1}$, which can be attributed to $\nu_3(\text{high})$ and $\nu_3(\text{low})$ modes of oxide-coordinated nitrate indicated a steady decrease in intensity when the humidity was increased, once again indicating the solvation of previously adsorbed species.

CHAPTER 4

CONCLUSIONS AND ENVIRONMENTAL IMPLICATIONS

Goethite is mainly used as an iron ore, while there are many other technological applications of goethite ranging from electronics to drug delivery.^{39, 40} At the same time it is also regarded as the most ubiquitous iron oxide in nature. This would imply that goethite could potentially enter the environment, and hence be present in the atmosphere via many anthropogenic sources and natural sources such as mineral dust, allowing it to be naturally as well as anthropogenically abundant in the atmosphere. This insight had made goethite to be considered as an important component of aerosols. As stated previously, atmospheric reactivity of aerosols is governed by the interactions taking place at the gas-solid interface, making it important to comprehend how goethite would behave in an actual atmospheric context.

However, the vast range of possibilities for goethite to end up in natural environments would mean that goethite would exist in a range of sizes, depending on its source of origin. Nevertheless, a particle classified as an aerosol may range in a vast range of sizes and the size distribution of aerosols, together with their composition, sources and sinks is believed to be a key element in understanding and managing aerosol effects on health, visibility and climate.⁴¹ A number of adverse effects of particulate matter, such as respiratory irritation, pulmonary and pulmonary function have already been confirmed, while some laboratory studies have shown that for a given mass concentration, the reactivity would be larger for the smaller sized particles.⁴¹

However, the structure reactivity relationship in reality would be characteristic to the compound of concern and thus it would be important to be looked at specifically than generally with regard to the substance of concern. The inverse relationship of structure and reactivity is often arrived at by considering the frequently crude assumption that surface area would increase as particle size decrease, neglecting the structural variations which may also occur as a function of particle size. Thus, the reactivity of goethite as well as its size-dependent nature would be important in understanding how goethite containing aerosols may impact the processes that may occur within the atmosphere.

It is true that goethite is only a single component of aerosols and in reality they would consist of various substances depending on the origin of the aerosol. Nevertheless, iron is regarded to play a key role in determining many processes taking place within the biosphere and thus any process impacting its distribution and availability within biological systems would be important to be looked at, making goethite a viable candidate to study atmospheric consequences.

Thus, the conducted study of the size-dependent reactivity of goethite in the presence of water vapor and gas phase nitric acid would add to our knowledge base, broadening our understanding on how goethite containing aerosols may impact atmospheric processes as well as how these processes may alter the distribution and bioavailability of iron from goethite containing aerosols. Within this current study, the experimental evidence explains the interaction of goethite with water vapor and gaseous HNO_3 , in a laboratory simulated atmospheric environment. Thus, if goethite is present within the atmosphere as a component of aerosols, we may expect it to follow the same pattern of reactivity as that observed here.

But more importantly, the study had indicated that the above interactions would be particle size dependent, and thus the reactivity of goethite or goethite containing aerosols in the atmosphere would not be identical across the boundaries of varying particle size, indicating a clear particle size dependence. Therefore, these results hold importance given the significance of goethite within the atmosphere, and its role in driving climate forcing as discussed previously.

4.1 Water uptake on goethite containing aerosols

In this study water was well evidenced to become adsorbed onto both nano as well as micro-goethite surfaces reversibly, using FTIR as well QCM observations. However, comparison of the reactivity of the two specimens of goethite required a clear definition of the basis adopted. To be more precise, it was observed that since the reactivity of substances can be incorporated into atmospheric models on a per mass or per surface area basis, the size-reactivity relationship of goethite would clearly depend on the basis of comparison. Thus, given the range of sizes of particles which may enter the atmosphere, it may be important to define a clear basis as for reactivity to be looked at under further investigation.

However, with the information in hand it can be said that on a per mass basis, nano-goethite adsorbs more water than micro-goethite, which is in agreement with our conventional perception that surface area exposed would increase with decreasing size, thus allowing greater reactivity to be possible. However, structural artifacts which are size dependent may again play an important role in driving reactivity.

In order to visualize such variations, a surface area normalization was adopted and upon normalization to surface area, the enhancement of water uptake in nano-goethite over micro was still visible, but at a diminished ratio. This indicates that the enhancement in water uptake of nano-goethite cannot be entirely attributed to the greater surface area available for adsorption on nano-goethite as compared to its micro counterpart. Thus, the data suggests that there would be an effect beyond surface area on the water uptake on goethite and the uptake would generally indicate an increase with decreasing particle size.

At this point, it might be important to consider why the water uptake by aerosols is important within the atmosphere. Water uptake or the affinity of a substance towards water would dictate the hygroscopicity of the substance. Thus, the water uptake of a substance would be an indicator of the hygroscopicity of aerosols composed of that specific substance. With this, we may say that nano-goethite or nano-goethite containing aerosols would indicate a higher hygroscopicity than its micro counterpart within the atmosphere.

Hygroscopicity holds much importance in atmospheric processes since as described by the Köhler theory, the hygroscopicity of atmospheric aerosol particles is a key factor regulating their cloud condensation nuclei (CCN) activity.⁴² Formation of clouds would eventually lead to many atmospheric consequences and also would play a pivotal role in driving the climatic and weather patterns within the atmosphere. Thus, we may conclude from the study of that nano-goethite containing aerosols would be higher in hygroscopicity and thus in CCN activity, eventually allowing them to have a higher atmospheric reactivity than those bearing micro-goethite.

4.2 HNO₃ uptake on goethite containing aerosols

HNO₃ is a substance that is highly corrosive as well as a toxic strong acid, regardless of the environment in which it is present. Thus, HNO₃ present within the atmosphere would tend to be highly reactive with aerosols mutually present within the system. Typical sources of nitrogen oxides (NO_x), which are the main precursors of HNO₃, include fossil fuel combustion, soils and biomass burning.⁴³ At the same time, HNO₃ at present is a commonly used oxidizing agent in many industrial applications, allowing it to enter the atmosphere in significant quantities.

Upon reaction at aerosol surfaces, HNO₃ may produce nitrate aerosols, which are aerosols containing nitrated substances. These in turn have been found to demonstrate interesting behavior within the atmosphere. Recently, nitrate aerosols have attracted more attention with regard to its perceived importance in relation to global as well as local air quality.⁴³ This had led to the investigation of the reactivity of HNO₃ in the presence of many different compounds which may be present within the atmosphere.^{44, 45} Thus in a similar fashion, the specific focus in relation to HNO₃ reactivity in this study was to understand the production of nitrate aerosols by the HNO₃-goethite reactivity which would take place within the atmosphere, and to observe how this in turn would alter the native reactive properties of the aerosol species.

Based on our experimental observations, we arrived at the conclusion that increasing particle size would increase the reactivity of goethite containing aerosols towards HNO₃ contained within the atmosphere. This in fact was a size effect which is attributable to surface structural artifacts that becomes more pronounced with increasing particle size, as opposed to the trend observed upon water uptake.

In relation to previous attempts to model the reactivity of HNO₃ and the production of nitrate aerosols, the observed formation of nitrate aerosols with goethite containing aerosols may be expressed as given on equation 2. It should be noted that the water formed in this reaction might be liberated into the atmosphere in its vapor phase, or may alternatively be adsorbed onto the goethite surface as have been evidenced from the experimental observations here.



Following the formation of these nitrate species, aerosols may attain significantly different physiochemical properties than the original, resulting in aerosols that would differ in their climate impact, heterogeneous chemistry and photoactivity, and at the same time would demonstrate interesting atmospheric processing patterns as have been described in many previous studies.⁴³⁻⁴⁶ The important thing to note here is that the reactivity of the formed nitrate aerosols would be limited by the amount of nitrate species formed on the aerosol surface.

As stated previously, the experimental observations done in this study have indicated goethite to have reactivity towards HNO₃ which is directly correlated to its size. Thus, the extent of nitrate aerosol formation with micro-goethite containing aerosols would be greater than that with those containing nano-goethite. This would mean that the micro-goethite containing aerosols would indicate a higher atmospheric significance than its nano-sized counterpart, following the formation of nitrate species. Therefore, the changes in climate impact, heterogeneous chemistry and photoactivity of an aerosol, which may be brought about by the reaction of aerosols with HNO₃, would be more prominent for aerosols containing goethite of larger size.

This however, is counter in argument to the general intuition that the increasing particle surface area would result in enhanced reactivity. Within the present day, where miniaturization have become a pivotal part of industrial applications, such reactivity patterns as opposed to what one would generally expect would certainly hold high significance. The result allows us to demonstrate that the structure-size-reactivity relation of a substance cannot be looked at in a general sense, but would have to be looked at specifically in relation to the nature of the species of concern.

The formation of nitrate aerosols may be followed by various consequences, which in turn would alter the distribution pattern of goethite containing aerosols within the biosphere. Thus, iron being an important component of all living systems and goethite being the most abundant iron containing substance present in aerosols, the correlation between particle size and reactivity identified here would be highly significant. Therefore, these findings would add to our understanding of the structure and reactivity of goethite containing aerosols, while at the same time suggesting the need to look into the possibility of anomalous size-reactivity variations for other substances which in turn would be significant within an atmospheric context.

4.3 Subsequent chemistry of nitrated goethite aerosols

The atmosphere is in direct contact with the oceans and other water sources, which covers a large proportion of the earth surface, allowing atmospherically processed aerosols to easily enter the hydrosphere. However, although atmospheric reactivity has always been a major experimental concern, there seems to be no previous attempts to model the direct entry of atmospherically processed species into the hydrosphere.

Therefore, in this study the subsequent chemistry of nitrated goethite was looked at in terms of its HNO_3 -water coadsorption affinity as well as its possible distribution into the hydrosphere. From the experimental evidence, it was seen here that nitric acid adsorbed goethite could indicate significant differences in behavior upon suspension in aqueous media, which may eventually facilitate the entry of atmospherically processed particles into the hydrosphere. The measurements made on dissolution of nitrate reacted goethite provides a quantitative picture of this enhancement in the possible distribution into the hydrosphere.

At the same time, the supplementary measurements of pH, zeta potential and hydrodynamic radii provide insight into how the native properties of nitrate-reacted goethite containing aerosols may vary from those unreacted. Thus, the study would add experimental evidence to what we currently know on the subsequent reactivity of aerosols. Additionally, the experimental protocol adopted here, opens up a new area of investigation for the distribution of atmospherically processed aerosol within the hydrosphere, allowing us to visualize the subsequent chemistry of atmospherically reacted particles in an entirely novel perspective.

The other line of investigation on the subsequent chemistry was on the coadsorption of water on nitric acid reacted goethite. As stated previously, nitrate aerosols would indicate a number of interesting reactivity variation, out of which the water adsorption would be one of the most important, owing to previously discussed reasoning. This study was pertinent in identifying the consequences of HNO_3 -water coadsorption on nano and micro-goethite and provided evidence of the reactivity variations of these nitrate aerosols which may take place as a function of RH.

In relation to most atmospheric chemistry models as well as atmospheric chemistry investigations, subsequent reactivity of atmospherically processed particles have only been looked at within the perspectives of variations which may take place within the atmosphere itself, such as the photochemistry of a substance. Yet, the investigation on subsequent reactivity conducted here was focused on the examination of coadsorption and aqueous phase suspension behavior of nitrate reacted goethite particles. This in turn, resulted in the knowledge of some interesting aspects of the subsequent chemistry of atmospherically processed aerosols which were not looked at as being important under previous investigations.

Therefore the current study would contribute towards our understanding of atmospheric processing in a novel dimension. With the importance for such investigation indicated here, the study indicates the need that extensive studies on the aqueous phase behavior of atmospherically processed particles, as well as supplementary co-adsorption studies would be warranted under further investigation of the atmospheric processing of many other atmospherically relevant species.

4.4 QCM - a tool in probing solid-gas interactions

A major auxiliary goal of the conducted study was the development of the QCM as a tool in probing solid-gas interactions. This area once again was novel to atmospheric chemistry studies since there have been no previous attempts to utilize QCM such as to obtain a quantitative information on atmospherically relevant solid-gas interactions. However, in the studies conducted here on the water and HNO₃ uptake on goethite, QCM was used in conjunction with the FTIR measurements as have been previously discussed.

Similar to any other emerging strategy, the QCM also indicated inherent limitations in being used in analysis. However, it was evidenced in the study that the QCM data correlated to an acceptable degree with the FTIR information obtained in each instance. Although there were some occasions where the two sources inferred somewhat contradicting results, the two methods in general were in agreement to a substantial level.

Moreover, with careful data analysis the QCM data was able to be utilized to obtain quantitative information on the atmospheric process of concern. This in turn was a significant advantage over the conventional spectroscopic techniques which are adopted to probe solid-gas interactions. Looking at the entirety of the analysis conducted in the study, it can be stated that FTIR and QCM measurements result in quantitative data that can be successfully utilized in conjunction such as to better understand the atmospheric reactivity of different interfaces.

The significance of QCM measurements would become more significant in the event of the adsorbate being vibrationally inactive, thereby making it unobservable through spectroscopic techniques. The viability of QCM in producing an alternative basis was clearly evidenced from the analysis conducted here. Thus, in such circumstances one may utilize QCM as a tool in order to probe the adsorption and desorption behavior on the substrate, since the QCM produces a universal signal which is independent of the nature of the adsorbate as well as the strength of the adsorbate-surface interaction.

Overall, the QCM indicates significant competence towards being developed as a tool to probe solid-gas interactions. However, with the appreciation of the information obtained via the QCM measurements made here, it can be stated that QCM would hold promising potential to be applied to many other areas of scientific research.

4.5 Directions and implications to the future

One of the most prominent aspects of atmospheric processing of aerosols would be the assessment of the variations of their native photochemical behavior, resulting from atmospheric processing. For instance, nitrated goethite may exhibit interesting daytime and nighttime chemistry, as have been previously observed with many other aerosol components. Information on such chemistry would allow us to better understand the importance of atmospheric processing of goethite containing aerosols as well as the particle size effects therein.

Within this study, the subsequent reactivity of nitrate reacted goethite particles was looked at only with relation to the mutual presence of water vapor. However, the atmosphere in reality is a complex mixture of gases. Thus, in order to better understand the reactivity within an actual atmospheric context, it may be helpful to investigate the reactivity of goethite in the mutual presence of other reactive atmospheric constituents. This once again opens up a new set of investigations which can be conducted as to better understand the atmospheric chemistry of goethite-containing aerosols.

The behavior of nitrated goethite upon suspension in an aqueous medium was conducted here as to identify the aqueous phase behavior of HNO_3 reacted aerosol particles. However, in this analysis optima water was used as the suspension medium for the reacted goethite samples. Noting that the majority of the water covering the surface of the earth surface is open ocean waters, the actual conditions prevailing within an atmospheric context may be significantly different as well as highly influential towards the solid-liquid interaction which would lead to the suspension.

Thus, in order of obtaining a better representation of the aqueous phase suspension behavior, artificial samples of seawater may be used as suspension media for the reacted samples under future investigation. With the characteristics inherent to the saline ocean waters such as the presence of a high degree of dissolved ionic species, this might produce interesting deviation from those previously observed with optima water. Nevertheless, such a novel approach might even allow us to observe interesting reactivity patterns which may have not been previously observed, allowing one to successfully extrapolate the importance of atmospheric processing into the hydrosphere as well as the entire biosphere.

The QCM data obtained during the HNO_3 uptake were used in obtaining quantitative information of the reversible and irreversible adsorption of HNO_3 on the goethite surface. However, another use of the QCM data obtained here would be in the theoretical determination of the amount of acidic species adsorbed onto the solid substrate and thus the pH that would result by suspending the reacted solid in an aqueous media. Several of these calculations were made with the QCM data obtained here and it was visible that a clear correlation exists between the theoretical pH determined from the QCM data and the actual experimentally measured pH.

Thus, under future investigation the QCM data can be utilized such as to determine the theoretical pH in solution, and eventually by comparison of this with the experimentally determined pH, one would be able to identify the exact correlation of the two measurements, and perhaps even the reasoning for any possible deviations between the two modes of measurement, which would eventually allow the successful utilization of the QCM, while at the same time identifying and overcoming its practical limitations.

Atmosphere in reality is a highly complex system where the majority of the chemistry taking place within is still unaware to the present day science. Atmospheric chemistry covers a broad spectrum of species, processes as well reaction conditions that prevails within the atmosphere, which in turn may prove to be imperative in assessing the lifetime, fate as well as consequences of aerosols and other reactive species of the atmosphere. Thus, understanding the exact atmospheric consequences of a species would require extensive knowledge of the many possible behavioral patterns of that species within the atmosphere.

However, the focus here was limited to the atmospheric reactivity of goethite containing aerosols, subsequent reactivity of reacted particles and the association of qualitative and quantitative QCM measurements into the atmospheric chemistry investigation. Thus, with the results obtained in this detailed analysis concerning atmospheric goethite, a clear appreciation of the size-dependent reactivity of goethite was attained. Although, further investigation would be warranted such as to arrive at a more precise understanding, it can be stated that the reactivity of goethite revealed here would certainly add to our understanding of the atmosphere, thereby allowing us to broaden the understanding of the atmosphere, biosphere as well as the entire eco system.

REFERENCES

1. H. A. Al-Abadleh and V. H. Grassian, *Langmuir*, 2002, **19**, 341-347.
2. L. Deguillaume, M. Leriche, K. Desboeufs, G. Mailhot, C. George and N. Chaumerliac, *Chemical Reviews*, 2005, **105**, 3388-3431.
3. M. Villalobos and A. Pérez-Gallegos, *Journal of Colloid and Interface Science*, 2008, **326**, 307-323.
4. B. Meland, P. D. Kleiber, V. H. Grassian and M. A. Young, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 2011, **112**, 1108-1118.
5. S. Lafon, I. N. Sokolik, J. L. Rajot, S. Caquineau and A. Gaudichet, *J. Geophys. Res.*, 2006, **111**, D21207.
6. J.-F. Boily and A. R. Felmy, *Geochimica et Cosmochimica Acta*, 2008, **72**, 3338-3357.
7. D. M. Cwiertny, G. J. Hunter, J. M. Pettibone, M. M. Scherer and V. H. Grassian, *The Journal of Physical Chemistry C*, 2008, **113**, 2175-2186.
8. A. É. Pashitskii, *Journal of Experimental & Theoretical Physics*, 2010, **110**, 1026-1041.
9. A. M. Makarieva, V. G. Gorshkov, D. Sheil, A. D. Nobre and B.-L. Li, *Atmos. Chem. Phys. Discuss.*, 2010, **10**, 24015 - 24052.
10. B. Zobrist, C. Marcolli, D. A. Pedernera and T. Koop, *Atmos. Chem. Phys.*, 2008, **8**, 5221-5244.
11. S. Seisel, A. Pashkova, Y. Lian and R. Zellner, *Faraday Discussions*, 2005, **130**, 437-451.
12. A. L. Goodman, E. T. Bernard and V. H. Grassian, *The Journal of Physical Chemistry A*, 2001, **105**, 6443-6457.
13. J. Schuttlefield, G. Rubasinghege, M. El-Maazawi, J. Bone and V. H. Grassian, *Journal of the American Chemical Society*, 2008, **130**, 12210-12211.
14. S. Wang, R. Bianco and J. T. Hynes, *Computational and Theoretical Chemistry*, 2011, **965**, 340-345.
15. G. Rubasinghege, R. W. Lentz, M. M. Scherer and V. H. Grassian, *Proceedings of the National Academy of Sciences*, 2010, **107**, 6628-6633.

16. C. M. Carrico, M. D. Petters, S. M. Kreidenweis, A. P. Sullivan, G. R. McMeeking, E. J. T. Levin, G. Engling, W. C. Malm and J. L. Collett Jr., *Atmos. Chem. Phys.*, 2010, **10**, 5165-5178.
17. N. Good, D. O. Topping, J. D. Allan, M. Flynn, E. Fuentes, M. Irwin, P. I. Williams, H. Coe and G. McFiggans, *Atmos. Chem. Phys.*, 2010, **10**, 3189-3203.
18. A. Vlasenko, T. Huthwelker, H. W. Gaggeler and M. Ammann, *Physical Chemistry Chemical Physics*, 2009, **11**, 7921-7930.
19. J. Schuttlefield, H. Al-Hosney, A. Zachariah and V. H. Grassian, *Applied Spectroscopy*, 2007, **61**, 283-292.
20. J. G. Navea, H. Chen, M. Huang, G. R. Carmichel and V. H. Grassian, *Environmental Chemistry*, 2010, **7**, 162-170.
21. A. S. Madden, M. F. Hochella Jr and T. P. Luxton, *Geochimica et Cosmochimica Acta*, 2006, **70**, 4095-4104.
22. D. M. Cwiertny, R. M. Handler, M. V. Schaefer, V. H. Grassian and M. M. Scherer, *Geochimica et Cosmochimica Acta*, 2008, **72**, 1365-1380.
23. U. Schwertmann and R. M. Cornell, *Iron oxides in the Laboratory: Preparation and Characterization*, Wiley-VCH, New York, 2000.
24. T. M. Miller and V. H. Grassian, *Journal of the American Chemical Society*, 1995, **117**, 10969-10975.
25. J. D. Russell, R. L. Parfitt, A. R. Fraser and V. C. Farmer, *Nature*, 1974, **248**, 220-221.
26. J. R. Rustad, D. A. Dixon and A. R. Felmy, *Geochimica et Cosmochimica Acta*, 2000, **64**, 1675-1680.
27. D. Williams, *Nature*, 1966, **210**, 194-195.
28. F. Viñes, Y. Lykhach, T. Staudt, M. P. A. Lorenz, C. Papp, H.-P. Steinrück, J. Libuda, K. M. Neyman and A. Görling, *Chemistry – A European Journal*, 2010, **16**, 6530-6539.
29. F. Viñes, A. Desikusumastuti, T. Staudt, A. Görling, J. r. Libuda and K. M. Neyman, *The Journal of Physical Chemistry C*, 2008, **112**, 16539-16549.
30. I. Stanford Research Systems, *Operation and Service Manual*, Sunnyvale, CA, 2005.
31. C. H. Rochester and S. A. Topham, *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, 1979, **75**, 591-602.

32. M. Villalobos, M. A. Cheney and J. Alcaraz-Cienfuegos, *Journal of Colloid and Interface Science*, 2009, **336**, 412-422.
33. C. Salazar-Camacho and M. Villalobos, *Geochimica et Cosmochimica Acta*, 2010, **74**, 2257-2280.
34. T. Hiemstra, J. C. M. De Wit and W. H. Van Riemsdijk, *Journal of Colloid and Interface Science*, 1989, **133**, 105-117.
35. F. Gaboriaud and J.-J. Ehrhardt, *Geochimica et Cosmochimica Acta*, 2003, **67**, 967-983.
36. J.-F. Boily, J. Lützenkirchen, O. Balmès, J. Beattie and S. Sjöberg, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2001, **179**, 11-27.
37. T. Hiemstra and W. H. Van Riemsdijk, *Journal of Colloid and Interface Science*, 1996, **179**, 488-508.
38. T. Hiemstra and W. H. Van Riemsdijk, *Journal of Colloid and Interface Science*, 2000, **225**, 94-104.
39. X. Lou, X. Wu and Y. Zhang, *Electrochemistry Communications*, 2009, **11**, 1696-1699.
40. A. F. Rebolledo, O. Bomati-Miguel, J. F. Marco and P. Tartaj, *Advanced Materials*, 2008, **20**, 1760-1765.
41. C. O. Stanier, A. Y. Khlystov and S. N. Pandis, *Atmos. Environ.*, 2004, **38**, 3275-3284.
42. M. Mochida, M. Kuwata, T. Miyakawa, N. Takegawa, K. Kawamura and Y. Kondo, *J. Geophys. Res., [Atmos.]*, 2006, **111**, D23204/23201-D23204/23220.
43. M. Dall'Osto, R. M. Harrison, H. Coe, P. I. Williams and J. D. Allan, *Atmos. Chem. Phys.*, 2009, **9**, 3709-3720.
44. S. E. Bauer, D. Koch, N. Unger, S. M. Metzger, D. T. Shindell and D. G. Streets, *Atmos. Chem. Phys.*, 2007, **7**, 5043-5059.
45. S. Li, T. Wang, B. Zhuang and Y. Han, *Adv. Atmos. Sci.*, 2009, **26**, 543-552.
46. E. R. Gibson, P. K. Hudson and V. H. Grassian, *J. Phys. Chem. A*, 2006, **110**, 11785-11799.