Electrical Properties of Mineral Surfaces for Increasing Water Sorption

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Thin films of nanostructures alter the electrical properties of mineral surfaces and thereby affect reactions with charged species such as metal ions and biological cells. In this study, electric-force microscopy is used to probe the electrical properties of a heterogeneous layout of manganese oxide nanostructures grown as a film on a MnCO₃ substrate. The role of water sorption is examined by carrying out experiments for increasing relative humidity (RH). Electric-force images collected with a negative dc tip bias show that the apparent heights of the nanostructures decrease from +3.4 nm at 16% RH to +0.7 nm at 33% RH to −5.6 nm at 74% RH, although the topographic height is 2.3 nm regardless of RH. The apparent heights for a positive dc bias also decrease with increasing RH from −3.5 nm at 16% RH to −8.9 nm at 74%. The explanation for these trends is that the dominant electric-force transitions with increasing RH from an electrostatic force attributable to surface potential to a polarization force arising from hydrated, mobile surface ions including Mn⁷⁺ and CO₃²⁻. The positive-to-negative trend in apparent heights implies that either the density or the intrinsic mobility (or both) of mobile ions over the substrate exceeds that over the nanostructures, implying increased water sorption over the former compared to the latter. Ridges around the perimeter of the nanostructures also develop above 40% RH for images collected using a negative dc tip bias. A tip-induced gradient of net positive charge near the nanostructure edges, which implies the nonequivalence of cations and anions there, explain this observation. The findings of this study show that thin films of nanostructures on mineral surfaces have complex but measurable RH-dependent electrical properties.

Introduction

Mineral particles, which serve as reactive centers in soils, have complex, heterogeneous surfaces. Inorganic surface films composed of nanostructures are one important type of heterogeneity especially in aqueous or humid conditions. The nanostructures often have physicochemical properties that are very different from those of the underlying mineral substrates, and the overall effective reactivity of soil particles can be greatly affected. The nanostructures vary in thickness from several nanometers to a few micrometers and thus generally account for less than 0.5% of the mass of a millimeter-sized particle. Nevertheless, the nanostructures may regulate the rate of particle solubility as well as the surface sorption of inorganic and organic components. Cell adhesion and subsequent biofilm formation can be directed by the nanostructure properties rather than by those of the primary particle. Thin-film nanostructures also commonly serve as sources or sinks of minor element sequestration within natural systems. Any comprehensive quantitative model of mineral surfaces in natural systems must therefore account for the growth and physicochemical properties of thin-film nanostructures.

As a model system for the study of thin-film nanostructures, we have grown and investigated Mn oxide nanostructures on MnCO₃ in the presence of O₂. In addition to controlling Mn concentrations, the nanostructures sequester heavy-metal pollutants through sorption and coprecipitation reactions. Thin films of iron oxide have similar roles. The formation of nanostructures is a dynamic process. With changes in pH and oxygen levels, the nanostructures can dissolve and the associated toxic metals can be remobilized.

Nucleation, growth, and alteration of the nanostructures occur when minerals are exposed to humid air. For example, CaCO₃ reconstructs in response to surface hydration. The resulting nanostructures have structural and electrical properties that are distinct from the underlying substrates. Kendall and Martin report evidence in support of the presence of a hydrated film nanostructure. Mass repartitions among the CaCO₃ substrate, the hydrated nanostructure, and the surface water layer possibly provide an important dynamic pathway for the incorporation of toxic metals into carbonates. Surface-mediated diffusion of mobile ions is critical to mass transport under these conditions.

These phenomena can be investigated using surface-sensitive electrical techniques, one of which is electric-force microscopy. A polarization electric force arises from the long-range, attractive interaction between a voltage-biased tip of an atomic force microscope and the charge induced on the mineral surface by water adsorption increasing RH from an electrostatic force attributable to surface potential to a polarization force arising from hydrated, mobile surface ions including Mn⁷⁺ and CO₃²⁻. The positive-to-negative trend in apparent heights implies that either the density or the intrinsic mobility (or both) of mobile ions over the substrate exceeds that over the nanostructures, implying increased water sorption over the former compared to the latter. Ridges around the perimeter of the nanostructures also develop above 40% RH for images collected using a negative dc tip bias. A tip-induced gradient of net positive charge near the nanostructure edges, which implies the nonequivalence of cations and anions there, explain this observation. The findings of this study show that thin films of nanostructures on mineral surfaces have complex but measurable RH-dependent electrical properties.

commercial system for collection of dc micrographs is described in detail in our previous work. In a modification to that protocol, some images are collected using the tapping mode of the nanoscope software in a technique that we term tapping mode dc (TM-dc) electric-force microscopy. A dc-biased tip (Nanoprobe MESP tips, Digital Instruments, nominal force constant of 4 N m\(^{-1}\)) is mechanically oscillated near its first resonance frequency of 60 kHz. This technique is similar to the standard electric force microscopy (EFM) technique\(^\text{16}\) but with the important difference that no interleave trace to compensate for topography is used. TM-dc images contain apparent height information that is recorded by keeping constant the oscillation amplitude of the tip. Although similar results are obtained by both TM-dc and dc imaging, the former typically results in higher quality images because of increased stability in the feedback loop. Moreover, the images are collected in a shorter time period.

In a related technique, micrographs are also collected by applying an ac bias of frequency \(\omega\) to the tip (without forced piezoelectric mechanical oscillation) while recording the second harmonic of the mechanical position of the tip, which is deflected because of electric forces experienced during an \(x\)-\(y\) scan.\(^\text{17}\) The resulting 20\(i\) images track heterogeneities in the dielectric and the topographic properties of the sample. Heterogeneities in the excess surface potential, however, are filtered. Implementation of this technique on a Multimode AFM is described in the Appendix.

Relative humidity (RH) is controlled during imaging by introducing proportionated flows of dry \(N_2\) and \(N_2\) bubbled through water into a chamber housing the AFM. Capacitive sensors mounted inside the chamber are used to quantify RH. Additional description is provided in refs 1 and 10.

**Electric-Force Imaging: Extracting Chemical Information.** An extensive body of literature provides a detailed description of electric forces.\(^\text{13,14,17–20}\) Here, we briefly review the phenomena contributing to the instantaneous electric force \(F\), which has contributions from both polarization and electrostatic forces:

\[
F = -\frac{1}{2} \frac{\partial C}{\partial z} (V - \varphi) \approx 4\pi\epsilon_0 f(\epsilon) \frac{R}{z^3} (V - \varphi)^2 \tag{1}
\]

where \(V\) represents the voltage applied to the probe tip and \(\varphi\) is the local surface potential. \(\epsilon\) is the capacitance gradient that depends on tip shape \(R\), tip–sample separation \(z\) (e.g., local topography), and the local dielectric properties of the sample \(4\pi\epsilon_0 f(\epsilon)\). The local dielectric constant \(\epsilon\) is dominated at elevated relative humidity by charge separation of mobile ions on the surface.\(^\text{10,13,17}\) Surface potential \(\varphi\) has contributions both from uncompensated fixed lattice charges and from integration of the electric field through the dipoles of a relaxed surface region. Surface ions displaced by partial hydration from their original position in the lattice to other fixed positions also provide a contribution.\(^\text{21}\)

An electric-force image is proportional to \(\Delta F(x, y)\) in the lateral plane, relative to the setpoint force established when the tip was engaged. Compared to the tip scan speed in \(x\)-\(y\), the mechanical response of the tip in \(z\) is instantaneous so that the electric-force image is in fidelity with the instantaneous force. When the tip is positioned over the substrate, the forces acting on it include an electrostatic contribution from \(\varphi\) of the substrate, a polarization contribution from the dielectric constant of the substrate, and a polarization contribution from the effective dielectric properties of mobile ions on the surface of the substrate. The corresponding properties of the nanostructures affect the forces acting on the tip when it is positioned there. The three forces respond to sample topography because of the dependence of force on distance.

**Methods**

**Nanostructure Growth.** The nanostructure films are grown on freshly cleaved MnCO\(_3\) substrates in aqueous solutions.\(^\text{2,4}\) The dried samples are imaged under humid air using contact- and electric-force techniques. Contact images, also collected for aqueous conditions, confirm that the dimensions, the shapes, and the overall appearance of the nanostructures are unaffected by the drying process. The detailed protocol for growing the nanostructures is provided in Jun et al.\(^\text{2}\) Briefly, an aqueous solution purged with oxygen gas at 298 K for 2 h is adjusted to pH 6.3 using nitric acid (HNO\(_3\)) (70%, EM Science) or NaOH (98.6%, J. T. Baker). Sodium nitrate, which when dissolved adsorbs negligibly to surfaces, is used to maintain the ionic strength of the solution at 10\(^{-2}\) M. The solution is flowed over a freshly cleaved (1014) surface of MnCO\(_3\) at 0.05 mL min\(^{-1}\) for approximately 2 h. Control experiments having all components and the morphology of the nanostructures are indistinguishable from the unmodified protocol.

**Electric-Force Imaging: Instrumentation.** The electric-force images are collected on a Digital Instruments Multimode atomic force microscope (AFM) having a Nanoscope IIIa controller and a signal access module (SAM; Model SBOB-1). Adaptation of this

Images collected with a dc tip bias are a convolution of topography, dielectric properties, and surface potential. Using an ac bias allows potential and dielectric contributions to be separated. The principle is that dielectric materials form a reactive circuit element that provides a frequency-doubled output to an ac input. Specifically, applying a tip bias voltage \( V = V_{dc} + V_{ac} \sin(\omega t) \) results in electric-force components \( F_1 \) and \( F_2 \) associated with the first- and second-harmonic frequencies, respectively. \( F_1 \) responds to the nonreactive circuit elements (i.e., surface potential). \( F_2 \) responds to the reactive circuit elements (i.e., polarizability). The use of topographic information obtained in contact-mode imaging can be used to approximately isolate the contributions of the surface potential and the dielectric properties to \( F_1 \) and \( F_2 \), respectively, from the topographic contribution to each case.

Physicochemical phenomena give rise to the electrical properties. In the case of a mineral surface in humid air, changes in \( F_2 \) are commonly ascribed to hydrated surface ions. The electrical properties of these ions are represented in the dielectric constant. Within tens of milliseconds, mobile surface ions reorganize to an induced condition imposed by the electric field emanating from the probe tip. The magnitude of this process depends on the amount of water sorbed to the mineral surface. Correspondingly, at high relative humidity, the strength of \( F_2 \) typically increases, and the contrast of the 2 images becomes dominated by the contribution of mobile ions. As a note, the electric forces associated with distinct surface ions greatly exceed those of water so that the measurements are sensitive to ions, rather than to water dipole, provided that sufficient concentrations of ions are present.

**Results and Discussion**

**Low RH: Excess Surface Potential Dominates dc Images.** At 16% RH, the electric-force images collected with a +2 V and −2 V tip bias have inverse contrast from one another (Figure 2). A negative tip bias results in a positive apparent height for the nanostructures whereas a positive tip bias leads to a negative apparent height. Therefore, the nanostructures appear as pits for the positive tip bias corresponding to a reduced attractive force of the tip over the nanostructures compared to over the substrate. The absolute magnitudes of the apparent heights with each tip bias are equal to one another at 16% RH and are somewhat greater than the topographic height (Figure 3). The presence of fixed charges, unable to respond to the tip bias through a polarization mechanism, can explain these observations thus implying that mobile ions are unimportant at low RH and that surface potential dominates the electric forces and hence the collected image.

The negative apparent heights (i.e., reduced attractive force) for a positive tip bias imply that the surface potential of the nanostructures is more positive than that of the substrate. Kelvin probe measurements separately performed by us² show that the surface potential of the nanostructures is 200 mV more positive than that of the substrate (i.e., \( \Psi_{\text{nanostructure}} - \Psi_{\text{substrate}} = 200 \) mV). Conversely, a negatively biased tip is attracted over the

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and for negative and positive tip bias (loop must retract the sample to restore the setpoint force. nanostructures compared to the substrate, and the increased force corresponds to a positive apparent height because the feedback loop must retract the sample to restore the setpoint force.

The above line of reasoning implies that the apparent heights for negative and positive tip bias (h and h+, respectively) should sum to zero when the electric forces on the tip arise solely from interactions with the nonpolarizable charges that make up surface potential. Figure 3c shows that (h− + h+) is approximately zero for RH < 33%. For low relative humidity, the electrostatic forces from fixed charges (i.e., the terms contributing to the surface potential) are therefore greater than the polarization forces from dielectric terms.

Medium RH: Mobile-Ion Component Develops. Increasing the relative humidity to 33% causes the apparent height of the nanostructures to become more negative for both positive and negative tip bias (Figure 3). The apparent heights decrease from +3.4 nm at 16% RH to +0.7 nm at 33% RH to −2.4 nm at 44% RH (Figure 3a) for negative tip bias. For positive tip bias, the heights drop from −3.5 nm at 16% RH to −4.2 nm at 33% RH to −5.8 nm at 44% RH (Figure 3b). Complementary measurements show that there is a small decrease in the excess surface potential of the nanostructures.5 Increasingly negative heights under both tip biases (i.e., attraction for both tip biases) imply the development of a polarizable component over the substrate. The convergence of positive and negative images for increasing RH is apparent in Figure 2 and corresponds to the trends seen in Figure 3. For a negative tip bias at 33% RH, little nanostructure−substrate contrast is observed in the −2 V image (Figure 2). This RH therefore corresponds to the compensation point of polarization and electrostatic force differences over the nanostructures compared to the substrate.

The mobile ions contributing to a polarization force result from the reactions of the MnCO3 substrate with the additional surface water present at higher relative humidity. For comparison, there is a sharp increase in the polarization force over calcite CaCO3 above 55% RH50 because of the completion of monolayer water sorption and the beginning of multilayer growth.10,23 A similar process appears to occur on rhodochrosite MnCO3 at 33% RH. We further propose that upon hydration additional mobile charges are available over the substrate more so than over the nanostructures. The trends in Figure 3a and 3b support this conclusion. The trends are consistent with increased water sorption and ion mobilization over the substrate relative to the nanostructures. Although the absolute attraction to both the nanostructure and the substrate must increase with increasing polarization forces at high RH, the relative increase over the nanostructures may be stronger or weaker compared to the substrate. Given that the substrate serves as the zero point at every RH (i.e., at the moment when the tip is engaged), weaker or stronger relative attractions over the nanostructures correspond to a trend of increasingly negative or positive heights, respectively, for increasing RH. The actual measurements show a negative trend indicating less relative polarization and hence weaker ion mobility on the nanostructures compared to the substrate for increasing RH.

Although we have inferred from the dc data trends that the polarization force is greater over the substrate than over the nanostructures for increasing RH, the 2ω images provide direct evidence to this effect. The 2ω images directly capture polarization forces and filter electrostatic forces as explained above. The 2ω polarization heights of the nanostructures are −4 nm compared to the +2 nm topographic height (Figure 4). The smaller polarization height implies that the polarizability of the nanostructures is less than that of the substrate.

High RH: Mobile Ions Dominate dc Images. Above 52% RH, the apparent heights become increasingly more negative. They decrease from −3.3 nm at 52% RH to −5.6 nm at 74% RH for negative tip bias (Figure 3a). For positive tip bias, they drop from −6.4 nm at 52% RH to −8.9 nm at 74% RH (Figure 3b). The slope in Figure 3c is constant for this RH range. These trends are consistent with a continued increase in mobile charge over the substrate and little or no change in fixed surface potential, in agreement with Na et al.5 The increased mobilization of surface ions is explained by multilayer water sorbed to the surface above 52% RH. The polarization force derived from the mobile surface ions renders negligible in comparison with the electrostatic force derived from the surface potential.

Nanostructure Edge Effects. Halos appear at the edges of the nanostructures when imaging with a negative dc bias at elevated RH (Figure 5b). The halos do not appear when imaging with a positive dc bias. In cross section, the halos are 1.5 nm ridges around the edges of the nanostructures (Figure 5d). Although halos consistently occur for multiple samples imaged with a negative dc bias at RH > 40%, their widths and heights vary, possibly because of sample variability, sample tilt, or less than optimal imaging conditions. For example, the halos present in the −2 V dc images in Figure 2 are less distinct than their counterparts in Figures 5b and 6a2.

A tip-induced gradient of net positive charge near the nanostructure edges, implying the nonequivalence of cations and anions there, can explain the localized increase in the polarization force and, thus, the appearance of polarization ridges for negative tip bias. In line with this explanation, the halos are absent in surface-potential images of the nanostructures.5 The halos then are attributed to mobile charges that are closely associated with the nanostructure edge. The implication is that there is a dynamic

Figure 4. (a) Contact, (b) 2ω images, and (c) height profiles of a and b for Mn oxide nanostructures on a MnCO3 substrate at 75% RH. The arrow in each image points to the same nanostructure, reflecting image drift (i.e., the nanostructure itself is not moving).
exchange of mass at the edges. In agreement with this suggestion, above 75% RH the nanostructures begin to dissolve in an edge-mediated mechanism (Figure 6).

**Conclusions**

Water-layer growth on mineral surfaces mobilizes surface ions and thereby alters the surface electrical properties. For MnCO₃, surface polarizability arises from mobile ions, which greatly increase the surface dielectric constant, particularly above 30% RH. In comparison, ions are not mobilized on the surfaces of the Mn oxide nanostructures, possibly because of less water sorption. For negative tip bias, a positive-to-negative reversal in the apparent heights of the nanostructures relative to the substrate occurs at 30% RH. This crossover may indicate the completion of a water monolayer and the beginning of multilayer coverage corresponding to a transition in the dominant electric force from electrostatic to polarization.

The series of changes apparent in the images at low, moderate, and high RH is consistent with mass transfer among the nanostructures and the substrate. The observations suggest that this process is driven by the reaction of water with the edges of the nanostructure. The dynamic aspects of the mass transfer provide a plausible pathway for the mobilization of coprecipitated toxic metals in the natural environment.

With increasing RH, shifts occur in the dominant contribution to the electric forces over mineral surfaces. The surface potential contribution is important at low RH, whereas the polarization of mobile ions becomes the major component for sufficiently high RH. Dominant mechanisms for low, medium, and high RH are schematically summarized in Figure 7 for a probe biased at -2 V dc. Electric-force images for increasing RH may provide a surrogate approach for the study of the evolution of the electrical double layer on a mineral surface. Reactive, bare surface charge is progressively satisfied by mobile, hydrated counter charge with increasing RH. Adsorption of metal ions, organic compo-
nents, or cells on soil particles could be studied by extending the approach outlined herein.

**Appendix**

This Appendix outlines the collection of 2ω electric-force images using a Digital Instruments Multimode AFM system that is equipped with a signal access module (SAM). A Pt-coated Si$_3$N$_4$ tip (Nanosensors, Inc.; nominal force constant of 0.19—0.40 N m$^{-1}$) is biased with an ac sinusoidal waveform of 2 V$_{pp}$ at 5 kHz. The waveform is applied to the tip by connecting the “ANA2” input port of the SAM to a function generator (Agilent Technologies Inc., Model 33120A, Palo Alto, CA). The mechanical deflection of the tip in response to the electric forces is recorded by the photodiode in the optical head, and the voltage from the photodiode is directed from the “In0” output port of the SAM to a lock-in amplifier (Stanford Research Systems, Model SR530). The 10 kHz output of the photodiode detector is transformed to its amplitude as a dc signal by the lock-in amplifier. The reference input for the amplifier is supplied by the “SYNC” signal from the function generator. The amplifier is typically set to a time constant of 1 ms and a sensitivity of 50 mV. The output of the amplifier is directed to the “In0” input port of the SAM. In this way, the Multimode software is adapted by running “contact mode” with the lock-in output as the feedback source. The setpoint for the feedback loop, which is set to a value greater than the free-air value, engages the tip by bringing it close to, yet not in contact with, the surface. As the tip nears the surface, the electric force increases, which causes the lock-in output voltage to increase. Images are typically collected with a tip speed of 0.6 μm s$^{-1}$ and integral and proportional gains of 0.05 and 0.1, respectively.

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