Surface-Potential Heterogeneity of Reacted Calcite and Rhodochrosite

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Nanostructures can form on mineral surfaces through reactions with H₂O or O₂ in the natural environment. In this study, nanostructures on the (1014) surfaces of calcite and rhodochrosite are characterized by their surface potentials using Kelvin probe force microscopy. Water-induced nanostructures on calcite have a topographic height of 1.1 (±0.6) nm and an excess surface potential of 126 (±31) mV at 45% relative humidity. The corresponding values for oxygen-induced nanostructures on rhodochrosite at the same RH are 1.3 (±0.7) nm and 271 (±14) mV, respectively. For increasing relative humidity on calcite, the topographic height of the nanostructures increases while their excess surface potential remains unchanged. In comparison, on rhodochrosite the topographic height remains unchanged for increasing relative humidity but excess surface potential decreases. The nonzero excess surface potentials indicate that the nanostructures have compositions different from their parent substrates. The surface-potential heterogeneity associated with the distributed nanostructures has important implications for reactivity in both gaseous and aqueous environments. Taking into consideration such heterogeneities, which are not included in state-of-the-art models, should improve the accuracy of the predictions of contaminant fate and transport in natural environments.

1. Introduction

Carbonate minerals, such as calcite (CaCO₃) and rhodochrosite (MnCO₃), are important in the environment for many reasons. First, they are key sources and sinks of calcium and manganese and thus have a great impact on the cycles of these elements (1, 2). Second, when CaCO₃ or MnCO₃ dissolves or precipitates, carbonate ions are released or incorporated, respectively. Changes in carbonate concentration affect alkalinity, solution pH, and the carbon cycle (3). Third, through coprecipitation or sorption carbonate minerals can immobilize heavy-metal and organic contaminants of health and ecological concern, in turn altering water quality (4–6). Fourth, calcium carbonate present in aerosol particles can play a significant role in neutralizing atmospheric acidity (7). Finally, carbonate minerals can facilitate biochemical reactions (8) and promote biofilm growth (9).

These many interactions of carbonate minerals with the environment are regulated by several factors, one of which is the surface potential of the mineral. Surface potential is a composite quantity linked to the local lattice structure of the reconstructed surface, the adsorption of water layers, and the mobile surface ions formed by dissolution (10). In turn, surface potential can affect the adsorption of ions and charged colloidal particles and promote their reactions with the surface. Advanced adsorption models usually take surface potential into detailed consideration (11). The surface potential of a mineral changes when one or more of the underlying contributing quantities are altered. Under natural conditions, mineral surfaces often react with important environmental constituents such as water and oxygen. Some of these reactions can result in the formation of new structures, including nanostructures having topographic heights of a few nanometers, on the mineral surface. Such nanostructures occur on the (1014) surfaces of calcite and rhodochrosite (12–16). These nanostructures may have different surface potentials from their parent substrates, thereby creating electrostatic heterogeneity and possibly influencing mineral reactivity.

Surface-potential heterogeneity can be mapped by Kelvin probe force microscopy (KPFM) (17, 18). Although KPFM is most widely used to map the heterogeneity of contact potential for conductive materials, its application has been extended to insulating surfaces, such as mica (19), alkali halides (20–22), and oxides (21). To our knowledge, however, there are no previous reports of KPFM applied to carbonate mineral surfaces. In the study described herein, KPFM was utilized to study the surface potential of the nanostructures that form on the (1014) surfaces of calcite and rhodochrosite. The measurements were conducted from 15 to 80% relative humidity (RH) to evaluate the contribution to surface potential of ions dissolved in the adsorbed surface water.

2. Materials and Methods

2.1 Preparation of Nanostructures. Single-crystal calcite and rhodochrosite were obtained as described previously (14, 15). Surfaces of (1014) orientation were prepared by cleaving a piece several millimeters thick and a few centimeters wide from the mineral with a razor blade in air. Nanostructures were prepared on calcite by fixing a newly cleaved sample on a steel puck with silver paste (SPI Supplies) and placing it in an environmental chamber (described below) at 80% relative humidity for 3 h (14). Silver paste was also attached to a corner of the sample surface to provide connectivity to the steel puck. For the preparation of nanostructures on rhodochrosite, a newly cleaved sample was placed in a Teflon reactor, which was continuously fed by an oxygen-saturated sodium nitrate (NaNO₃) (10 mM) solution for 3 h (15). The pH of the solution was adjusted to 6.3 by sodium hydroxide (NaOH). After reaction, the sample was removed from the reactor, air-dried, and mounted.

2.2 Microscope and Protocol. Surfaces were examined using conventional contact- and tapping-mode atomic force microscopy (C-/TM-AFM) as well as noncontact Kelvin probe force microscopy under controlled relative humidity. The C-/TM-AFM and KPFM measurements were performed using a Vecco multimode scanning probe microscope equipped with a NanoScope IIIa controller, an extender, and a platinum-coated silicon tip (Nanosensors PPP-EFM) (23). C-/TM-AFM and KPFM are all standard modes of operation offered by the Veeco software and hardware. Images were collected for areas of 1–25 μm² with a resolution of 256 or 512 pixels per line. Surface potential was measured with a tip-sample separation of 5–20 nm. Post-measurement data processing followed standard operations, including plane-
fitting, flattening, generating three-dimensional false-color images, and performing roughness analyses using NanoScope 4.3S (Veeco) and Nanoscope IV controller (Veeco) in tapping mode AFM (http://www.nanotec.es), and Igor Pro 5 (WaveMetrics).

2.3 Kelvin Probe Force Microscopy. Contact- and tapping-mode imaging techniques are standard methods (24, 25); therefore, they are not described further herein. A brief description of Kelvin probe force microscopy (26–28) is provided, as follows. The experimental setup of KPFM is shown in the Supporting Information (Figure S1) along with an equivalent circuit. The surface potentials of the tip vertex and the sample surface beneath the tip are represented by $V_{\text{tip}}$ and $V_{\text{surface}}$, respectively. Because they are independent of other circuit elements, at least for the conditions of this study, $V_{\text{tip}}$ and $V_{\text{surface}}$ are represented as batteries. The separation of the tip vertex from the sample surface underneath forms a capacitor having a voltage $V_{\text{capacitor}}$ across it. Other voltage drops across the silver paste, between the tip and the bulk material, between the cantilever and the surface, and between the sample surface and the steel puck in the circuit are also modeled as a combined battery having a voltage drop $V_{\text{other}}$.

The principle of the KPFM measurement is that a variable, nulling voltage $V_{\text{null}}$ is applied in the circuit by feedback control so that $V_{\text{capacitor}}$ becomes zero at each sampling location in a raster scan. In this case, we have

$$V_{\text{null}} = V_{\text{surface}} + V_{\text{tip}} + V_{\text{other}}$$

The feedback loop of KPFM works as follows. When $V_{\text{capacitor}} \neq 0$, charges of opposite signs start to accumulate at the tip vertex and the sample surface, respectively. At the beginning of the accumulation when the tip vertex and the sample surface are only slightly charged, $V_{\text{capacitor}}$ is not significantly altered. The tip vertex is then attracted to the sample surface by an electrostatic force $F_{\text{electrostatic}} = 1/2 \varepsilon C/2 \Delta V$ where $\varepsilon C/2 \Delta V$ is the capacitance gradient in the vertical direction (18). This attraction deflects the cantilever toward the sample surface, which is detected by the optical head of the AFM. A feedback signal adjusts $V_{\text{null}}$ until the cantilever deflection is eliminated. To ensure that the charge accumulation is always at its initial stage between adjustments of $V_{\text{null}}$, the capacitor is periodically discharged by an AC modulation (26–28). To minimize the effect of surface-ion polarization on tip response, the AC modulation is applied at the resonance frequency of the cantilever (ca. 60 kHz), which is much greater than the frequency of surface-ion relaxation ($\approx 0.1$ kHz (10)).

To prevent the interference from the change of topographic height during a raster scan, KPFM maintains a constant tip–sample separation to keep the tip–sample capacitance approximately stable. To achieve this objective, KPFM utilizes a consecutive lift mode, which operates as follows. For each raster line, the Veeco Nanoscope software instructs the tip to conduct two consecutive scans: a tapping-mode AFM scan followed by a KPFM scan. The first scan obtains the topographic height $h$ and produces a topography image. Using the height information, the second scan adjusts the vertical position of the tip to hold a preset tip–sample separation, which is approximately 5–20 nm in our application.

With the above approach, the unprocessed KPFM image is a map of $V_{\text{null}}(x,y)$ for surface lateral coordinates $x$ and $y$. Under the assumption that $V_{\text{tip}}$ and $V_{\text{surface}}$ do not depend on position, $-V_{\text{null}}(x,y)$ equals $V_{\text{surface}}(x,y)$ with a constant offset. A practical matter, however, is that $V_{\text{other}}$ is not fully independent of lateral position because the capacitances between the cantilever and the sample and between the sample surface and the steel puck differ between raster lines due to the raster movement (29) (see Figure S2 in the Supporting Information). This difference, as well as any constant offset, is removed by post-measurement planefitting and flattening with respect to the substrate terrace. In this process, the nulling voltage measured on the substrate terrace $V_{\text{null}}$ which equals $-(V_{\text{tip}} + V_{\text{other}})$, is subtracted from $V_{\text{null}}(x,y)$ to yield an excess surface potential $V_{\text{null}}(x,y)$, according to the following equation:

$$V_{\text{null}}(x,y) = V_{\text{null}}(x,y) - V_{\text{null}}' = V_{\text{surface}} - V_{\text{null}}'$$

Therefore, on the substrate terrace where $V_{\text{surface}} = V_{\text{null}}'$, $V_{\text{null}} = 0$. Over the nanostructures where $V_{\text{surface}} = V_{\text{nano}}$, $V_{\text{null}}'$ represents the difference in voltage change to a common ground between the nanostructures and the substrate, i.e., the difference in their surface potentials. Similarly, over a step, the difference in surface potential between the substrate step and the substrate terrace is measured.

2.3 Humidity Control. For humidity control, the microscope was enclosed in an environmental chamber (10) that was flushed continuously with humid nitrogen. Prior to entering the chamber, a portion of the nitrogen gas was bubbled through a deionized water reservoir and then was combined with the rest of the dry nitrogen. Varying the relative amount of the nitrogen flow going through the water reservoir altered the relative humidity. Relative humidity was typically increased monotonically to prevent complications due to the hysteresis between water adsorption and desorption (30). Relative humidity was monitored by a capacitive specific-humidity sensor (Ohmic Instruments, HC-700, accuracy: ±2% RH) and a thermistor (Omega, 44033, accuracy: 0.1 °C) placed next to the sample.

3. Results

In the following sections, we present the topographic heights of the nanostructures (Section 3.1), the excess surface potentials of the nanostructures (Section 3.2), and the effects of relative humidity on the nanostructures (Section 3.3). The reaction-induced nanostructures on the surfaces of calcite and rhodochrosite can be readily recognized in the topography and potential images examined at 45% relative humidity, as shown in Figure 1. Highly ordered pyrolytic graphite with an excess surface potential independent of humidity is also included as a control against possible artifacts due to water adsorption on the AFM tip. The ability of KPFM to distinguish surface features according to their compositions is further illustrated in Figure 2 by a piece of MnCO₃ debris on rhodochrosite. Height and excess surface potential of the nanostructures are plotted for increasing relative humidity in Figure 3.

3.1 Heights of Nanostructures. In the topographic images of Figure 1, the nanostructures are highlighted in light blue against the pink substrates (images row 1). The nanostructures are similarly observable in the potential images (row 2). The elevations of the nanostructures from the substrate terraces are shown by the topography cross sections (row 3). The heights of the nanostructures compared to the substrate terrace is measured statistically by the difference in the central values of Gaussian fits to a histogram of the height $h$ (row 4). Two distinct peaks are found for each sample, representing the nanostructures and the substrate terrace, respectively. We measure $h$(nano, CaCO₃) = 1.1 (±0.6) nm on calcite and $h$(nano, MnCO₃) = 1.3 (±0.7) nm on rhodochrosite. One-sigma standard deviation, presented in parentheses and calculated as the root-mean-square of the peak standard deviations, represents the experimental and data-processing uncertainties as well as surface heterogeneities due to lattice substitution and impurity. These heights are consistent with previous observations made under similar conditions (14, 15).

Other features apparent in the topography images include steps on calcite and both steps and dissolution pits on
rhodochrosite (31). The steps, created during the cleavage of the minerals, serve as boundaries for nanostructure formation. Nanostructures seldom grow across adjacent steps (15). The dissolution pits on rhodochrosite form during its contact with the reactive solution. The height of a step is typically less than 1 nm whereas a dissolution pit can be as deep as a few nanometers. For the samples shown in Figure 2a and b, \( h(\text{step,CaCO}_3) = 0.1 \) (±0.3) nm on calcite and \( h(\text{step,MnCO}_3) = 0.7 \) (±0.4) nm on rhodochrosite (see Supporting Information). In comparison, the distance between two layers of metal cations of unrelaxed (1014) surfaces are 0.25 and 0.30 nm for calcite and rhodochrosite, respectively (32).

The nanostructures, steps, and dissolution pits aside, the (1014) surfaces are mainly flat terraces. The roughness is comparable to that of the atomically flat HOPG sample. Moreover, Figure 1c is consistent with an HOPG structure of multiple graphite sheets. Sheet edges are indicated by white arrows. The average height difference between sheets is estimated as \( h(\text{step,HOPG}) = 0.7 \) (±0.4) nm at 45% relative humidity. This height difference corresponds to approximately twice the thickness of a graphite monolayer.
The potential cross sections show that centers, indicating heterogeneity inside the nanostructures. These features from their parent substrates and can do so with greater contrast than compared to the topographic height measured by tapping-mode AFM. According to $h(nano, CaCO_3) = 1.1 \pm 0.6$ nm and $h(nano, MnCO_3) = 1.3 \pm 0.7$ nm, we have 96.6% confidence to differentiate the reacted surfaces using tapping-mode AFM. Using KPFM, the confidence limit improves to over 99.99% for $V_{null}(nano, CaCO_3) = +126 \pm 31$ mV on calcite and $V_{null}(nano, MnCO_3) = +271 \pm 14$ mV on rhodochrosite.

As an advantage of the technique, the excess surface potential measured by KPFM can distinguish the nanostructures from their substrates and can do so with greater contrast than compared to the topographic height measured by tapping-mode AFM. According to $h(nano, CaCO_3) = 1.1 \pm 0.6$ nm and $h(nano, MnCO_3) = 1.3 \pm 0.7$ nm, we have 96.6% confidence to differentiate the reacted surfaces using tapping-mode AFM. Using KPFM, the confidence limit improves to over 99.99% for $V_{null}(nano, CaCO_3) = +126 \pm 31$ mV on calcite and $V_{null}(nano, MnCO_3) = +271 \pm 14$ mV (See further details in Supporting Information.)

As a disadvantage of the technique, KPFM has lower lateral resolution than tapping-mode AFM. The lower lateral resolution is largely due to the increased tip—sample separation of KPFM (14), implying a correspondingly larger area of influence under the tip and thus a reduced lateral resolution. The reduced resolution can be seen by comparing the cross sections of topography and potential in Figure 1b. The transition from the nanostructure to the substrate occurs over a longer distance for potential than for topography. This longer transition can be used to estimate the lateral resolution as ca. 15 nm for qualitative distinctions in the rhodochrosite sample of Figure 1 (see further in Supporting Information) which is only slightly bigger than the 10-nm diameter of the tip vertex. To obtain a quantitative measure of the surface potential (i.e., the fully developed value), however, a nanostructure must have lateral extent greater than 200 nm.

In addition to the nanostructures, KPFM measurements also reveal steps on mineral substrates. In the potential images of Figure 2a and b, a step is shown in a color darker than the terraces. Statistical analysis reveals that the step has a lower surface potential with $V_{null}(step, CaCO_3) = -11 \pm 16$ mV and $V_{null}(step, MnCO_3) = -37 \pm 24$ mV. Similar potential drops at the edges of HOPG sheets are also observed. As shown in Figure 1c, the $V_{null}(edge, HOPG) = -7.9 \pm 4.1$ mV with $V_{null}(terrace, HOPG)$ being defined as zero. This result is in acceptable agreement with the difference of $-30$ mV measured by Sommerhalter et al. (33) for an HOPG sample prepared in ultrahigh vacuum.

Except for steps and nanostructures, other features on the substrate all have zero excess surface potential even when they have different topographic heights. These features include different terraces, dissolution pits, and substrate debris. Figure 2 shows that a piece of MnCO₃ debris generated during sample preparation has a height of over 14 nm. It is partially enclosed by a nanostructure. This debris, with a diameter of 90 nm surrounded by a 400-nm structure, is not distinguishable in the potential image (row 2), indicating it has the same surface potential as the rhodochrosite substrate. This image is conclusive that KPFM under our imaging conditions is not sensitive to physical height.

**3.2 Excess Surface Potentials of Nanostructures.** Like the topography images, the potential images acquired using Kelvin probe force microscopy distinguish the nanostructures from their parent substrates. In the potential images of Figure 1, the nanostructures are identified as yellow islands against a blue floor of the substrate terrace. The potential images would be entirely blue if not for the difference in surface potential between the nanostructures and the substrate terrace because KPFM does not detect differences in physical height (see below). Some nanostructures on calcite appear to have lower excess surface potentials near the centers, indicating heterogeneity inside the nanostructures. The potential cross sections show that $V_{null}$ of the nano-
be explained by the water content incorporated at higher relative humidity in the calcium carbonate nanostructures, as previously proposed (14). On rhodochrosite, however, \( h(nano,MnCO_3) \) remains constant within uncertainty. As an upper limit, the statistical analysis implies that, if there is an undetectable increase, this increase must be smaller than 0.3 nm (27%). These results are consistent with the proposed manganese oxide composition of the rhodochrosite nanostructures (15), for which water has not been suggested as part of the nanostructures.

Unlike height, potential \( V_{null}(nano, CaCO_3) \) on calcite remains virtually constant from 15 to 78% RH. The mean value is estimated as \(+120 (±13)\) mV. In comparison, \( V_{null}(nano, MnCO_3) \) decreases 30% from \(+302(±91)\) mV to \(+202(±85)\) mV (also see movie in the Supporting Information). We propose that the differing responses of \( V_{null}(nano) \) to increasing relative humidity on calcite compared to rhodochrosite arise from differences of surface solubility of these two minerals (see Discussion).

A possible artifact, that changes of \( V_{null}(nano) \) could be caused by the increase of water adsorption on the tip at higher relative humidities (19), can be ruled out, as follows. The possible interference was checked by measuring a control sample of highly ordered pyrolytic graphite. Because HOPG is highly hydrophobic, it adsorbs little water under the experimental conditions. Any interference from the water adsorbed on the tip would alter \( V_{null}(edge, HOPG) \). Instead, \( V_{null}(edge, HOPG) \) remains constant, with a mean value of \(-11 (±2)\) mV from 10 to 80% RH. The absence of changes in \( V_{null}(nano, CaCO_3) \) provides a similar negative control. There are also no changes of the height between HOPG sheets across the same RH range. We then conclude that the changes in surface potential observed for rhodochrosite are real.

Although the heights on CaCO\(_3\) and the excess surface potentials on MnCO\(_3\) vary with increasing relative humidity, the lateral shapes of the nanostructures do not perceptibly change during the nearly 4 h of experiments on each sample (about 0.5 to 1 h at each RH condition). This result is shown in the Supporting Information as a movie for the nanostructures on MnCO\(_3\) during increasing relative humidity.

### 4. Discussion

The surface-potential heterogeneity revealed by KPFM indicates that the nanostructures have either different chemical compositions or different polymorph structures compared to calcite and rhodochrosite. Otherwise, like the MnCO\(_3\) debris shown in Figure 2, the nanostructures would have zero excess surface potential, in contrast to the positive excess surface potentials observed (Figures 2 and 3). This conclusion from direct KPFM observations is consistent with previous inferences based on indirect observations that the heights of the nanostructures self-limit at 1–3 nm (12–15). As an aside, KPFM thus represents an important analytical technique with some chemical sensitivity to complement purely height-based measurements.

Kendall and Martin (14) studied the calcite nanostructures using contact-mode AFM and scanning polarization force microscopy (SPFM). They observed, similarly to our results, that the height of the nanostructures decreases for decreasing RH. Based on the dependence of nanostructure height on RH and the different polarizabilities of the nanostructures and the substrate, they proposed that the nanostructures are hydrated calcium carbonate, i.e., CaCO\(_3\) loosely bound with H\(_2\)O, in epitaxial association with the underlying calcite lattice. Hausner et al. (16) similarly proposed amorphous CaCO\(_3\) as the nanostructures that they observed at 75% and 95% RH, although the involvement of water was not mentioned. Kendall and Martin (14) also indirectly hypothesized, based on a reversal of the polarization force over the nanostructures at low RH, that the surface potential of the nanostructures was greater than that of the substrate. The results of this study directly confirm the accuracy of that hypothesis.

Duckworth and Martin (12) and Jun et al. (15) investigated the rhodochrosite nanostructures using contact-mode AFM and X-ray photoelectron spectroscopy. They proposed that these nanostructures are composed of a Mn\(^{3+}\) oxide or a mixture of Mn\(^{2+}\) and Mn\(^{3+}\) oxides. These proposed compositions are consistent with the requirement of dissolved oxygen for the formation of the nanostructures on rhodochrosite (12, 15). Our present measurements further show that the height of these nanostructures does not change with increasing relative humidity. This observation is consistent with an absence of water in these nanostructures.

Differences in chemical composition or crystallographic structure between the nanostructures and the substrates can lead to different solubilities, implying different concentrations of mobile ions. The ions dissolve into the water layers adsorbed on the surface in humid air, contributing to surface potential (10, 34, 35). The difference in solubilities between the nanostructures and the substrates is the primary mechanism that accounts for the dependence of \( V_{null}(nano) \) on relative humidity.

On calcite, a monolayer of water molecules adsorbs to the (1014) surface at 50% RH and there are up to four layers at 80% RH (30, 36, 37). Kendall and Martin (10) found that the voltage change on the calcite surface, with respect to the common ground, increases for increasing relative humidity from \(-440\) mV at 20% RH to \(-340\) mV at 80% RH. The negative values are consistent with the direction of the dipole moments.
expected for the (1014) surface, in which a layer of unsatisfied and negatively charged carbonate oxygen sits 0.85 Å above a layer of unsatisfied but positively charged calcium (32). The solubility of hydrated calcium carbonate nanostructures is expected by us to be similar to that of the calcite substrate. Hence, the effect of RH on water adsorption, ions release, and the resulting change of surface potential should be similar for both the nanostructures and the substrate terrace. Since the nanostructures have an excess surface potential of +120 (±13) mV, the estimated voltage change on the nanostructures, with respect to the common ground of the substrate, remains negative but of a smaller magnitude. These results are expected for nanostructures that are amorphous and involve water in their structure (14, 16), both of which reduce the dipole moment of a surface, the first by disorder and the second by screening.

For rhodochrosite, based on the solubility products of bulk materials (e.g., \(-\log K_{sp}(\text{MnCO}_3) = 51.4\) (38) and \(-\log K_{sp}(\text{Mn}_2\text{O}_3) = 10.6\) (39)), manganese oxide nanostructures have solubility at circumneutral pH many orders of magnitude smaller than the manganese carbonate substrate. The lower solubility in turn implies that there are fewer dissolved, mobile ions on the nanostructures than on the substrate. Correspondingly, the ion density increases considerably more on the substrate than on the nanostructures for thicker water layers at higher RH. As explained above for calcite, the release of ions decreases the magnitude of surface potential by screening charge and relaxing oriented dipoles. The magnitude of \(V_{\text{terrace}}\) of eq 2 therefore decreases for increasing RH while that of \(V_{\text{nano}}\) changes very little, if at all. As a result, \(V_{\text{null}}(\text{nano}, \text{MnCO}_3)\) becomes less positive, as observed, since \(V_{\text{null}} < V_{\text{nano}}\).

Although we have considered only the release of mobile ions, other factors can also influence surface potential. For example, the adsorbed water layers themselves were proposed to contribute to the decrease of surface potential on mica (a very insoluble material) with increasing relative humidity (19). Except for the calcite substrate, no water-adsorption data are available for the other three surfaces of interest, including the nanostructures on calcite, the nanostructures on rhodochrosite, and the substrate of rhodochrosite. Slight differences in reaction conditions during nanostructure formation can also introduce differences in excess surface potential from sample to sample (see an example of 385 (±17) mV in the Supporting Information), although \(V_{\text{null}}(\text{nano})\) is always positive.

Negative excess surface potentials at steps compared to terraces were previously observed by Verdaguer et al. (35) studying the sodium-chloride surface. To explain their observations, they proposed that preferred dissolution of chloride anions occurs at the steps. In this study, we also observed that the step edges of HOPG, which are composed solely of carbon, also have lower excess surface potentials. Sommerhalter et al. (33) contributed the reduction of excess surface potential to the localized dipole moment at the edges of graphite sheets. For our carbonate minerals, both mechanisms may have contributed to the negative excess surface potentials at steps.

5. Implications to Environmental Processes

The reactivity of calcite and rhodochrosite surfaces and by extension those of other carbonates can be complicated by the formation of nanostructures and the associated lateral surface-potential heterogeneity to an otherwise homogeneous surface. For instance, the positive potentials of the nanostructures, combined with the mobility of the surface ions, imply that anions such as \(\text{CO}_3^{2-}\) and \(\text{HCO}_3^-\) or metal–oxo complexes are attracted to the nanostructures. Consequently, given the increased concentrations and increased chemical potentials, reactions in the areas surrounding the nanostructures or on top of them may be more favorable and rapid than in terrace locations. State-of-the-art modeling efforts, however, have yet to include the uneven distribution of reactivity due to surface-potential heterogeneity (7).

The results of this study for humid air may be plausibly extrapolated to the aqueous phase because the water structures near the mineral surface are similar in both environments. For instance, on the (1014) surface of calcite, the first layer of water is situated with its oxygen on top of the metal cation at a distance of 2.1 (±0.2) Å in humid air (40) and 2.3 (±0.1) Å in aqueous solution (41). These similarities suggest that the surface-potential heterogeneity measured with the first layer of adsorbed water at ca. 50% RH (36, 37) in air may also represent the zeta-potential heterogeneity at the stern layer in aqueous solution. Along these lines, the measured results at 80% RH may represent conditions further away in the diffuse layer.

Surface-potential heterogeneity does not exclusively exist between mineral substrates and their nanostructures. Wherever compositional or structural heterogeneity exists, surface-potential heterogeneity can be consequently created. Surface-potential heterogeneity may be generated by the adsorption of precipitates, colloids, or microorganisms to a single mineral surface. The techniques demonstrated herein for mapping these heterogeneities will be useful in future studies aimed toward mechanistic descriptions that connect macroscopic mineral reactivity to microscopic surface structure.

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Supporting Information Available

Table S1: Confidence levels of KPFM and tapping-mode AFM.
Table S2: F-test results for data shown in Figure 3. Figure S1: Experimental setup of Kelvin probe force microscope and an equivalent circuit. Figure S2: Raw potential image with stripes between raster lines; Figure S3: Height and potential histograms of steps and terraces for calcite and rhodochrosite surfaces of Figure 1. Figure S4: Topography image, potential image, and cross sections of manganese oxide grains. Figure S5: Lateral Resolution of KPFM. Figure S6: Example of similar results for another reacted rhodochrosite surface 49% relative humidity. Movie: series of potential images of manganese oxide grains. Figure S4: Topography image, potential image, and cross sections of manganese oxide grains.

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