Interfacial Forces are Modified by the Growth of Surface Nanostructures

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Interfacial forces formed by chemical reaction can modify the interfacial forces present in aqueous solution near a surface. This study uses force-volume microscopy to explore this phenomenon for the growth of manganese oxide nanostructures on rhodochrosite. The interfacial forces above the oxide nanostructures are dominated by electrostatic repulsion for probe–surface separations greater than ca. 2 nm but are overtaken by van der Waals attraction for shorter distances. Across the investigated pH range 5.0–9.7, the maximum repulsive force occurs 2.4 (±1.1) nm above the oxide nanostructures. The magnitude of the repulsive force decreases from pH 5.0 to 6.5, and then increases steadily up to pH 9.7. Specifically, \( f_{\text{max}}(pH) = 23(±4)[6.8(±2.1) - pH] \) for pH < 6.5 and \( f_{\text{max}}(pH) = 19(±2)[pH - 6.1(±1.0)] \) for pH > 6.5. This dependence indicates that oxide nanostructures have a point of zero charge in the pH range 6–7. In comparison to the nanostructures, the rhodochrosite substrate induces only small interfacial forces in the same pH range, suggesting a neutral or weakly charged surface. The quantitative mapping of interfacial forces, along with the associated influencing factors such as pH or growth of nanostructures, provides a basis for more sophisticated and accurate modeling of processes affecting contaminant immobilization and bacterial attachment on mineral surfaces under natural conditions.

1. Introduction

Rhodochrosite (MnCO₃) is an important component of anoxic sediments and soils (1–3). At the oxidative–anoxic interface, a rhodochrosite surface can be oxidized by dissolved oxygen and form oxide structures (MnOₓ) of a few nanometers high (4, 5). These nanostructures have surface potentials several hundred millivolts higher than rhodochrosite itself (6, 7). The patchwork of exposed rhodochrosite surface and oxide nanostructures results in a heterogeneous layout of surface potential, which suggests that differences in chemical composition and structure at the nanoscale can induce dramatic local variations in surface properties. These variations can further modify surface interactions with the surrounding environment. In aqueous solution, the interactions of a surface with ions, molecules, and cells are often manifested as the interfacial forces between them, thereby strongly influencing surface adsorption. The nanoscale heterogeneity of interfacial force is therefore an important regulator of contaminant immobilization and bacterial attachment (8, 9).

In this paper, we map out the interfacial-force heterogeneity of a reacted rhodochrosite surface having a layout of oxide nanostructures. With a miniature probe to represent an adsorbate, interfacial forces over reacted rhodochrosite are measured using force–volume microscopy (FVM). The interfacial forces above the oxide nanostructures are dominated by electrostatic repulsion from far away (ca. 30 nm) to as close as approximately 2 nm. For even smaller separations, the electrostatic repulsion is overtaken by van der Waals attraction. Therefore, at some intermediate distance \( z_{\text{max}} \), there is a maximum \( f_{\text{max}} \) in the interfacial repulsion. The competition between electrostatic repulsion \( f_e \) and van der Waals attraction \( f_{\text{vdw}} \) to the total interfacial force \( f_{\text{total}} \) is the basis of the Derjaguin–Landau–Verwey–Overbeek (DLVO) model widely used to understand surface adsorption on the molecular level (10, 11):

\[
f = f_e + f_{\text{vdw}}
\]

where \( f_e \) is positive and \( f_{\text{vdw}} \) is negative by convention. Measuring \( f \) at various surface–probe distances \( z \) allows the characterization of \( f_e(z) \) for \( z > z_{\text{max}} \) and \( f_{\text{vdw}}(z) \) for \( z < z_{\text{max}} \) from which surface properties including charge, potential, and Hamaker constant can be assessed. Specifically, by extracting the maximum value of \( f(z) \) at each \( x–y \) lateral position, the FVM technique quantifies the interfacial-force heterogeneity as \( f_{\text{max}}(x, y) \) and \( z_{\text{max}}(x, y) \), where \( x \) and \( y \) are the coordinates in the surface plane.

Force–volume microscopy investigates interfacial forces using a scanning probe microscope (SPM) operated in the force-curve mode (12). Like other SPM techniques, FVM surveys an area in a raster fashion and takes measurements at many sampling locations along the raster lines. However, different from most SPM techniques that take only one measurement (e.g., height or potential) at each sampling location and move the tip along continuously, FVM stepwise parks the tip 16 times during a one-line raster scan and records a force curve from 0 to 50 nm. In a two-dimensional raster scan, a set of 256 force curves is acquired. Force–volume microscopy has been applied to the studies of clean surfaces of various minerals, including mica (13, 14), silica (14–19), hematite (16), alumina (20, 21), fluorite (22), and calcite (22). FVM has also been applied for mapping organic (bio)molecules adsorbed on mica (23–26) as well as copper adsorbed on silica (27). To our knowledge, however, there is no previous report of the application of FVM to map the interfacial-force heterogeneity of environmentally relevant nanostructures, such as those described in this study, and the implications for contaminant immobilization and bacterial attachment.

2. Materials and Methods

2.1. Preparation of Aqueous Solution. Aqueous sodium nitrate was prepared from ACS grade salt (Strem Chemicals, Newburyport, MA) using fresh Millipore water (Barnstead International, Dubuque, IA, 18 MΩ cm). The solution pH was adjusted between 5.0 and 9.7 using reagent-grade HNO₃ or NaOH (see further in Supporting Information, Table S1). Aqueous sodium and nitrate ions were chosen for ionic-strength control and pH adjustment because they have low adsorption affinities with manganese-oxide and manganese-carbonate surfaces (28, 29). Once made, the solution was sealed in a syringe until use within a couple of hours.

2.2. Preparation of Oxide Nanostructures on Rhodochrosite. Single crystals of rhodochrosite were prepared as described previously (5, 6). A surface of (1014) orientation

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was cleaved with a razor blade to fabricate a sample of approximately 2-mm wide, 3-mm long, and 0.5-mm high. Oxide nanostructures were grown by reacting the freshly cleaved rhodochrosite with dissolved oxygen for 2 h at pH 6.3 and with an ionic strength of 100 mM NaNO₃ (6). After reaction, the sample was removed from the reactor without washing, air-dried, and fixed to a steel puck using melted dental wax. Drying prior to fixing was necessary to avoid water ebulition when in contact with hot wax. To remove residual NaNO₃, rinsing with pure water, which can form dissolution pits that complicate surface topography, was avoided. Instead, residual NaNO₃ was washed away by copious flushing inside the microscope fluid cell prior to measurement.

For imaging and FVM measurements, the rhodochrosite sample was sealed by pressing the fluid cell on the steel puck with an O-ring. The fluid cell was then filled with experimental solution supplied by a syringe. The fluid cell and the sample were flushed with copious solution (>100 cell volumes) before any measurement. Imaging and FVM measurements were carried out in the presence of 1 mM NaNO₃ solution, and the tip was fully immersed inside the sealed fluid cell.

2.3. Force—Volume Microscopy. Force—volume measurements were made with a Veeco multimode scanning probe microscope equipped with a NanoScope IIIa controller, a signal access module, a silicon nitride probe (model: NP-S), and a micro fluid cell (ca. 50 μL). The microscope piezo was calibrated using a standard grid (Veeco).

The principle of force measurement using scanning probe microscopy is documented in the literature (12), and FVM is a standard mode available in the Veeco software (version 4.43r8). Only a brief description is therefore provided herein, as follows. The probe starts ca. 50 nm above the surface and gradually descends in steps of less than 0.25 nm (Figure S1). The approach speed is less than 200 nm/s, ensuring both that the ionic atmosphere has sufficient time to equilibrate with the charged probe and that the hydrodynamic drag is negligible (30). At each step, the microscope records the vertical deflection of the probe cantilever by a laser beam shone on its back. The cantilever deflection d is proportional to the interfacial force f by the cantilever spring constant k, as follows:

\[ f = k \cdot d \]  

Moreover, the distance z between the tip and the surface can be calculated from d (cf. Figures S1 and S2). The basic information from FVM measurements is therefore a set of 256 f—z data pairs defining a force—distance curve at each sampling location. In this study, we reduce the force—distance curve to a single data pair \( f_{\text{max}} - z_{\text{max}} \) (i.e., the maximum observed repulsive force and the associated distance from the surface) for further analysis and interpretation.

2.4. Calibration of Cantilever Spring Constant. The spring constant \( k \) of the probe cantilever was calibrated based on the thermal-noise method in air (31–34). Thermal noise was extracted via the “Ino” port of the signal access module using a data acquisition card (National Instruments model PCI-6221 with a BNC2110 connector block) and NIDAQ Tools MX for Igor Pro (WaveMetrics, Portland, OR). The value of k was calculated from the power spectral density of the thermal noise (12). The calibration sensitivity \( s \) used in calculation was measured on hard silicon chips (SPI Supplies, West Chester, PA) (see further in Figure S1). The calibration temperature was monitored using a thermistor (Omega, Stamford, CT, model 44033, accuracy of 0.1 °C) placed next to the probe.

2.5. Microscope and Protocol. Measurements were conducted in two steps. In the first step, contact-mode microscopy was employed to locate a representative region of 1-μm² area that contained both oxide nanostructures and exposed rhodochrosite surface. In the next step, force—volume microscopy was performed over this region in a lateral matrix of 16 × 16 sampling locations, corresponding to 62.5 × 62.5 nm² per sampling point. The FVM measurements were performed after the experimental assembly had reached thermal equilibrium at 25 ±2°C (35), typically after ca. 30 min. One force—volume measurement required ca. 15 min.

Care was taken for reproducibility and comparability of the results. Specifically, a single probe was used for the entire set of experiments to ensure comparability among the results. Measurements were conducted for eight different pH values in random order, and the trends with respect to pH were independent of order. These control experiments helped to guard against possible changes of probe chemistry due to contamination from contact and force imaging as contributing to the interpretation of the observations.

3. Results

Figure 1 shows representative force—distance curves for measurements both over the grown oxide nanostructures (Figure 1a) and over the remaining exposed rhodochrosite substrate (Figure 1b). Over the oxide nanostructures, the interfacial force f is attractive for surface—probe separations smaller than 2 nm but then becomes repulsive for greater separations. We obtain values of \( f_{\text{max}}(\text{MnO}_3) = 72 \) pN at \( z_{\text{max}}(\text{MnO}_3) = 3.77 \) nm at pH 9.5, which can be compared to values of \( f_{\text{max}}(\text{MnCO}_3) = 0.05 \) pN and \( z_{\text{max}}(\text{MnCO}_3) = 0.68 \) nm.
over rhodochrosite. These results indicate that the nano-
structures exert appreciable interfacial forces on the SPM
probe whereas the interfacial forces between rhodochrosite
substrate and the probe are comparatively much weaker.

Figure 2 shows representative topography and FVM-based
images of the reacted rhodochrosite surface at pH 9.5. The
false-color topography of the background image is scaled
such that the 3.0-nm nanostructures are yellow and the 0.0-
nm baseline of exposed rhodochrosite is orange. Inset b-i,
for which nanostructure relief is in cyan and the substrate
is in pink, shows the topographical height $h$ of the region
selected for force measurements. Insets a-i and c-i show maps
of $f_{\text{max}}$ and $z_{\text{max}}$ at pH 9.5 obtained from individual force
distance curves for the 16 × 16 sampling locations in the
selected region (i.e., inset b-i). Inset a-i is color-scaled to
represent $f_{\text{max}}(\text{MnO}_x)$ in blue and $f_{\text{max}}(\text{MnCO}_3)$ in red, with
various shades of off-color white in between. Inset c-i uses
green and red to represent $z_{\text{max}}(\text{MnO}_x)$ and $z_{\text{max}}(\text{MnCO}_3)$,
respectively. Histograms of $f_{\text{max}}$, $h$, and $z_{\text{max}}$ for insets a,b,c-i are
provided to the right-hand side in insets a,b,c-ii. The
histograms show that $f_{\text{max}}(\text{MnO}_x) = 51.0(±30)$ pN, $z_{\text{max}}(\text{MnO}_x) = 3.1(±0.9)$ nm, and $h(\text{MnO}_x) = 2.9(±0.6)$ nm. Corresponding
values for the exposed substrate are $f_{\text{max}}(\text{MnCO}_3) = 2(±22)$
pN, $z_{\text{max}}(\text{MnCO}_3) = -0.3(±0.4)$ nm, and $h(\text{MnCO}_3) = 0$.

Topography images taken before and after the FVM mea-
urements have no detectable changes (not shown).

In Figure 2, the color boundaries within the coarse-scale
grids of $f_{\text{max}}(\text{MnO}_x)$ shown in inset a-i and of $z_{\text{max}}(\text{MnO}_x)$
shown in inset c-i match well the finer-scale topography
shown in inset b-i. This correspondence indicates that the
growth of these nanostructures induces changes in the
interfacial forces. Interestingly, a narrow streak of exposed
rhodochrosite between two pieces of nanostructures, as
marked by the arrow in inset b-i, is visible neither in inset
a-i nor in inset c-i. The explanation is that above the surface
the interfacial force at a sampling location is influenced not
only by the surface directly beneath it but also by surrounding
areas. The maximum interfacial force over the narrow streak
of rhodochrosite is strongly affected by the abutting
nanostructures.

Figure 3 shows the dependence of $f_{\text{max}}$, $h$, and $z_{\text{max}}$ on pH
over both the oxide nanostructures and the exposed rhodo-

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**FIGURE 2.** Topography is shown in image background. Inset panels show (a) the maximum interfacial repulsion $f_{\text{max}}$ at each point in the raster scan, (b) the corresponding topographic heights $h$, and (c) the distance of maximum interfacial repulsion to surface $z_{\text{max}}$. The conditions are as follows: reacted rhodochrosite surface in 1 mM NaNO$_3$ solution at pH 9.5. The background image shows the topography of a 4 × 4-µm$^2$ area, in which oxide nanostructures are depicted in yellow against the orange rhodochrosite floor. The center of the topography image (sampling area of 1 × 1 µm$^2$) was selected for the force measurements.
chrosite substrate. The solid lines in Figure 3a represent a piecewise linear regression of $f_{\text{max}}$(MnO$_x$) with pH (cf. Table S3):

$$f_{\text{max}}$(MnO$_x$) = \begin{cases} 23(\pm 4)[6.8(\pm 2.1) - \text{pH}] & \text{for pH} < 6.5; \\ 19(\pm 2)[\text{pH} - 6.1(\pm 1.0)] & \text{for pH} \geq 6.5. \end{cases}$$

Similar trends are observed with other reacted-rhodochrosite samples, although the magnitude of $f_{\text{max}}$ may be different from sample to sample due to the differences in probe geometry and growth conditions (cf. Figure S3). In comparison, linear regressions of $f_{\text{max}}$(MnCO$_3$), $\bar{h}$(MnO$_x$), $z_{\text{max}}$(MnO$_x$), and $z_{\text{max}}$(MnCO$_3$) with pH are statistically not significant (cf. Table S4, Supporting Information), indicating no detectable dependence on pH. For this reason, the average values of these quantities are shown in Figure 3. The horizontal dashed lines represent $f_{\text{max}}$(MnCO$_3$) = 1(±1) pN, $\bar{h}$(MnO$_x$) = 2.8(±0.6) nm, $z_{\text{max}}$(MnCO$_3$) = 0.04(±0.45) nm, and $z_{\text{max}}$(MnO$_x$) = 0.04(±0.45) nm.

4. Discussion

The observations of Figure 1 imply that the interfacial forces between reacted rhodochrosite and the silicon nitride probe are dominated by electrostatic repulsion and van der Waals attraction. Therefore, classical DLVO theory is sufficient to describe the interactions. Extended (X-) DLVO theory that considers additional forces such as acid–base, steric, and hydrodynamic forces is not necessary for the interpretation of the FVM measurements of this study (36). Because of the low ionic strength used in our experiments, only primary energy minima are apparent in Figure 1, and secondary energy minima often observed at higher ionic strength are absent (37, 38).

4.1. Electrostatic Repulsion. The presence of a strong electrostatic repulsive force over the oxide nanostructures in 1 mM NaNO$_3$ solution at pH 9.5 and the absence of it over the exposed substrate suggest that the nanostructures possess a high net charge. The charge difference between nanostructures and substrate cannot be attributed to surface roughness, which is comparable on both surfaces as shown by the similar peak widths in Figure 2b–ii. In comparison, the substrate is either overall neutral or has at most a small charge. The net charge giving rise to a repulsive force over the nanostructures can be deduced as negative because the silicon nitride probe is negatively charged at pH 9.5 (27, 39–41). A model of electrostatic repulsion, based on the Poisson–Boltzmann equation and the Debye–Hückel approximation, is as follows (12):

$$f_e = A \exp(-\kappa z) + B \exp(-2\kappa z) \text{ for } z > \kappa^{-1} \quad (4)$$

This model assumes that the tip of the probe has a cone geometry and that the nanostructures can be acceptably modeled as flat, infinite surfaces. The value of $\kappa$ in eq 4, which is $9.6 \text{ nm}^{-1}$ in 1 mM NaNO$_3$ solution at 25 $^\circ$C, is the reciprocal of the Debye length and characterizes the thickness of the electrical double layer (42).

Using the data in Figure 1a from $z = 9.6$ to 40 nm, we obtain the least-squares regression of force–distance relationship of electrostatic repulsion over the oxide nanostructure, as shown by the solid line curve in Figure 1a (cf. Table S2 for statistical analysis). The robustness of the regression for replicate measurements (cf. Figure S4) confirms that possible contamination from ions added by deposition of room dust or by substrate dissolution is not important. These ions, if present in an important quantity, would compress the electrical double layer, reduce the Debye length, and force discrepancies into the regression. This conclusion that the ionic strength is essentially dominated by NaNO$_3$ is also consistent with the dissolution rate of rhodochrosite, for which a contribution of less than 10 $\mu$M Mn$^{2+}$ and CO$_2^{2-}$ is expected from MnCO$_3$ dissolution in a 5-h experimental period (43).

The physical model of coefficients $A$ and $B$ in eq 4 depends on whether the nanostructures and the probe can be better approximated as constant charge-density or constant potential surfaces. A positive value of $B$ suggests that a constant charge-density surface is the better description (12). In this case, $A = 4\pi R \sigma_{\text{nano}} \epsilon / (\pi \kappa)$ and $B = 2\pi R \sigma_{\text{nano}} \epsilon / (\pi \kappa)$, where $R$ is the radius of tip curvature (10 nm), $\epsilon$ is vacuum permittivity, and $\kappa$ is the dielectric constant of water. The values of $A$ and $B$, which are equal at pH 9.5 to 44 (±11) pN and 155 (±42) pN, respectively, can be used to estimate surface charge density on the nanostructures $\sigma_{\text{nano}}$ as well as on the tip $\sigma_{\text{tip}}$. Specifically, $\sigma_{\text{nano}} = -0.0019 (±0.0005) \text{ C/m}^2$, corresponding to one negative elementary charge per 84 (±24) nm$^2$. For comparison, titration data at pH 9.5 and 1 mM ionic strength for the iron oxide goethite ($\alpha$-FeOOH, pH$_{\text{pzc}}$ 8.25) suggests 1 charge per 29 nm$^2$ (44). Regarding the silicon nitride tip, the measurements indicate that $\sigma_{\text{tip}} = -0.013 (±0.002) \text{ C/m}^2$, which lies at the lower end of the literature values ($-0.013$ to $-0.022 \text{ C/m}^2$) (27, 39–41).
The surface charge $\sigma_{\text{nano}}$ of the oxide nanostructures implies a potential difference $\psi_{\text{nano}}$ relative to the bulk aqueous solution. Namely, the Graham model appropriate for an infinite and flat surface (42) states that $\psi_{\text{nano}} = \sigma_{\text{nano}}/(\varepsilon_0 \varepsilon_r k_B T) = -26 (\pm 7) \text{mV}$ for pH 9.5 and 1 mM NaNO₃ solution. Modeling efforts solving the nonlinear Poisson–Boltzmann equation for the finite extent and shape of the nanostructures are beyond the scope of this paper (45, 46).

4.2. van der Waals Attraction. The electrostatic repulsion over the oxide nanostructures is overtaken by van der Waals attraction at one sampling point along the direction before moving to the next (12). Consequently, the probe quickly snaps to the surface. If we assume that an extrapolation of eq 4 to $x_{\text{max}} = 3.77 \text{nm}$ provides an approximate estimate of $f_{\text{vdw}}(\text{MnO}_x)$, we obtain by eq 1 that $f_{\text{vdw}}(\text{MnO}_x) = -28 \text{pN}$ (i.e., attractive). Moreover, the Hamaker constant, which is a coefficient in expressions of the van der Waals attractive force that expresses the electron fluidity in the material and the capacitance of tip–sample geometry (42), is approximated at pH 9.5 by $H_{\text{nano}} = -6f_{\text{vdw}}/x_{\text{max}}^2 = 2.4 \times 10^{-13} \text{J}$ between the tip and the nanostructures.

In comparison, the van der Waals attraction between the exposed rhodochrosite and the tip is barely discernible for the same range of surface–probe distances (Figure 1b), possibly because the rhodochrosite is an insulator whereas the manganese oxide nanostructures may be semiconductors. The difference may also arise in part from the presence of greater net surface charge on the oxide nanostructures, which produce stronger electrical fields than the exposed rhodochrosite and may therefore polarize the probe to a greater extent (42).

4.3. Point of Zero Charge of Oxide Nanostructures. The dependence of $f_{\text{vdw}}(\text{MnO}_x)$ on pH (Figure 3a) suggests that the surface of the oxide nanostructures and that of the silicon nitride probe have similar points of zero charge (pH$_{\text{pzc}}$), specifically around $6 \pm 1$. The changes on the nanostructures and the probe must both reverse from being negative to being positive at approximately similar pH because $f_{\text{vdw}}(\text{MnO}_x)$ is repulsive at both pH < 6.5 and pH > 6.5. Otherwise, an electrostatic attraction (i.e., $f_{\text{vdw}}(\text{MnO}_x) < 0$), which was not observed, would have been measured for pH values between pH$_{\text{pzc}}$(probe) and pH$_{\text{pzc}}$(MnO$_x$) because over this range the nanostructures and the probe would have been oppositely charged. The charge reversal around pH$_{\text{pzc}}$(MnO$_x$) on the oxide nanostructures can be explained by a proton–hydroxide charging mechanism similar to that of iron oxides (44):

$$\text{MnO}_x \text{H}^+ + e^- \leftrightarrow \text{MnO}_x^- + \text{H}^+ \quad (5)$$

$$\text{MnO}_x^- + \text{H}_2\text{O} + e^- \leftrightarrow \text{MnO}_x\text{OH}^- + \text{H}^+ \quad (6)$$

where $K_1$ and $K_2$ are equilibrium constants and pH$_{\text{pzc}}$(MnO$_x$) = ($pK_1 + pK_2$)/2.

We estimate with 95% confidence that pH$_{\text{pzc}}$(probe) and pH$_{\text{pzc}}$(MnO$_x$) lie between 5.9 (±2.1) to 7.2 (±1.0) based on twice the uncertainty of force measurements, as estimated using data for $z > 40 \text{ nm}$. The estimated pH$_{\text{pzc}}$ values overlap with pH$_{\text{pzc}}$(probe) between 4.5 and 7.2 reported in the literature (27, 39, 40, 47) as well as several bulk manganese oxides, such as pH$_{\text{pzc}}$(MnO$_2$) between 5.3 and 7.7 and pH$_{\text{pzc}}$(MnOOH) between 6.2 and 8.5 (46–50). The estimate of pH$_{\text{pzc}}$(MnO$_x$) differs significantly, however, from pH$_{\text{pzc}}$(MnO$_2$) > 10 and pH$_{\text{pzc}}$(MnO$_{1.88}$) < 2.4 (46–50). The proposed pH$_{\text{pzc}}$(MnO$_x$) of between 6 and 7 for the grown nanostructures, which may have properties different from bulk materials, is nonetheless reasonable compared to the values of at least some bulk manganese oxide materials.

The measurements show that the surface charge of exposed rhodochrosite is effectively indistinguishable from neutral across pH 5.0–9.5 in our experimental system. For comparison, regarding surface charge density, Van Cappellen et al. (51) interpreted the acid–base titration experiment of Charlet et al. (52) using a surface complexation model for the species >CO$_2$H$^+$ and >MnOH$^+$. Comparison of our measurements of surface charge to the model of Van Cappellen et al. (51) is complicated by differences in the regime of experimental conditions. For example, the ionic strengths used by Charlet et al. (52) were significantly greater than those used by us. Other differences included the addition of CO$_2$ (0.005–0.5 atm) and Mn$^{2+}$ (1–2.5 mM) by Charlet et al. (52), both of which alter surface charge. Nevertheless, using the equilibrium constants obtained by van Cappellen et al. (51) and the Graham equation (42) suitable for our low-potential condition, we estimate a surface charge for rhodochrosite of $\sigma_{\text{vdw}} = -0.00043 \text{C/m}^2$ at pH 9.5 and 1 mM ionic strength (cf. Figure S5). This value, which is an order of magnitude smaller than $\sigma_{\text{nano}}$, agrees qualitatively with our experimental observation that the surface charge of the rhodochrosite is much less than that of the oxide nanostructures.

4.4. Implications to Environmental Systems. The repulsive interfacial force induced by oxide nanostructures at distances greater than 2.4 (±1.1) nm creates an energy barrier for similarly charged adsorbates to approach the surface. By integrating the force–distance curve shown in Figure 1a from 3.77 to 30 nm, we estimate that the energy barrier is 6.2 $\times$ 10$^{-19}$ J at pH 9.5 for a colloidal particle or a bacterial cell to approach the surface, under the assumption that the SPM probe qualifies as an acceptable surrogate for them. If the adsorbate is a spherical colloidal particle and settles under gravity, the diameter of the colloidal particle must exceed 3.4 $\mu\text{m}$ to overcome this barrier with its inertia, according to Stokes’ law (53) (see Table S5). For a bacterial cell having swimming motility, a minimum speed of 17 mm/s is required to glide through the barrier under the assumption that its inertia equals its kinetic energy (see Table S5). For comparison, bacterial such as Vibrio cholerae and Pseudomonas aeruginosa, however, swim with a speed less than 0.1 mm/s (54) (see Table S5). These considerations, however, omit that some bacterial cells use flagella or pili to reach the surface, thereby having an alternative strategy to overcome the repulsive electrostatic barrier. From the other point of view, attraction also exists for charged species in solution having an opposite charge to the nanostructures (i.e., unlike the SPM probe). Furthermore, neither strong attraction nor repulsion is present over neutral regions of the surface, such as those representing remaining exposed rhodochrosite. The implication is that certain adsorbates are favorably directed to some parts of the surface rather than others. The net result is a mechanism for focusing adsorbates to certain parts of the surface and thereby templating a heterogeneous layout of them.

The interfacial-force heterogeneity demonstrated herein for oxide nanostructures grown on rhodochrosite is more generally applicable to other chemical systems. For example, Taboada-Serrano et al. (27) showed that the adsorption of copper cations also creates force heterogeneity on silica surfaces. For applications directed to the natural environment, accounting for surface heterogeneity is complex but important when processes such as contaminant immobilization or bacterial attachment are the focus.
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Supporting Information Available

Table S1: Chemistry of experimental solution. Table S2: Analysis of variance and parameter estimates for the regression to eq 4 in Figure 1a. Table S3: Piecewise linear regression of \( f_{\text{max}}(\text{MnO}_4^-) \) and pH in Figure 3a. Table S4: t-Tests on the linearity of \( f_{\text{max}}(\text{MnO}_4^-), h(\text{MnO}_4^-), z_{\text{max}}(\text{MnO}_4^-), \) and \( z_{\text{max}}(\text{MnO}_3^-) \) with pH. Table S5: Estimate of colloid particle size and cell speed to overcome the repulsion barrier over oxide nanostructures at pH 9.5. Figure S1: Experimental setup of force-curve measurement. Figure S2: Raw data of the force curves shown in Figure 1. Figure S3: Maximum interfacial force-curve measurement. Figure S2: Raw data of the force cell speed to overcome the repulsion barrier over oxide \( \text{CO}_3^2^- \) with pH. Table S5: Estimate of colloid particle size and pH. Figure S5: Estimation of rhodochrosite surface charge measured at various pH conditions. Figure S4: Replicates of Figure 1a. Figure S5: Estimation of rhodochrosite surface charge based on the surface complexation model. This information is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited


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