Opposing Effects of Humidity on Rhodochrosite Surface Oxidation
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ABSTRACT: Rhodochrosite (MnCO₃) is a model mineral representing carbonate aerosol particles containing redox-active elements that can influence particle surface reconstruction in humid air, thereby affecting the heterogeneous transformation of important atmospheric constituents such as nitric oxides, sulfur dioxides, and organic acids. Using in situ atomic force microscopy, we show that the surface reconstruction of rhodochrosite in humid oxygen leads to the formation and growth of oxide nanostructures. The oxidative reconstruction consists of two consecutive processes with distinctive time scales, including a long waiting period corresponding to slow nucleation and a rapid expansion phase corresponding to fast growth. By varying the relative humidity from 55 to 78%, we further show that increasing humidity has opposing effects on the two processes, accelerating nucleation from 2.8(±0.2) × 10⁻³ to 3.0(±0.2) × 10⁻² μm² h⁻¹ but decelerating growth from 7.5(±0.3) × 10⁻⁶ to 3.1(±0.1) × 10⁻⁵ μm² h⁻¹. Through quantitative analysis, we propose that nanostructure nucleation is controlled by rhodochrosite surface dissolution, similar to the dissolution—precipitation mechanism proposed for carbonate mineral surface reconstruction in aqueous solution. To explain nanostructure growth in humid oxygen, a new Cabrera—Mott mechanism involving electron tunneling and solid-state diffusion is proposed.

1. INTRODUCTION
Water vapor in the form of humidity is widely recognized as an important driver of mineral surface reconstruction in the atmosphere.¹ In humid air, water vapor condenses on mineral surfaces, creating a continuous layer of liquidlike water above a critical relative humidity (RH).² RH, a commonly used parameter for characterizing water vapor activity, is defined as the ratio of the partial pressure of water vapor to its saturated pressure at the same temperature (p/p₀). Although under ambient conditions the layer of condensed water is less than a few nanometers thick (nominal diameter of a water molecule: 0.34 nm),³ it is surprisingly reactive with underlying carbonate minerals, a major component of aerosol dusts produced by winds blown over arid regions.⁴,⁵ Observations made with atomic force microscopy (AFM) and related techniques show that water condensed on calcite (CaCO₃) can release mobile ions from the mineral surface through dissolution.⁶ Extended exposure of calcite to humid air produces nanometer-thick surface islands, presumably through the precipitation of mobile ions, of hydrated calcite⁵ or vaterite.⁵ Further extension of exposure time leads to the growth of islands into continuous films.⁹—¹² AFM force measurements show that surface islands and films dominate the underlying carbonates in van der Waals and electrostatic interactions.¹³—¹⁵ Given the generally recognized importance of carbonate mineral dusts in the atmosphere, these humidity-induced nanostructures can control the overall surface reactions between dust particles and atmospheric constituents such as nitric oxides,¹⁶—²⁴ sulfur dioxides,¹⁷,²⁴—²⁷ and organic acids.²⁸—³³

Manganese (Mn), an important redox-active trace metal element in aerosol dusts, has been associated with calcite as a lattice impurity, which is often incorporated into calcite by substituting calcium.³⁴ A model structure of manganese carbonate is rhodochrosite (MnCO₃), which has the same rhombohedral structure as calcite.³⁵ Water is known to condense on the (10̅14) surface of rhodochrosite in humid air, causing surface dissolution.⁷,¹³,³⁶ Different from calcite, however, the Mn²⁺ ions released from the dissolution of rhodochrosite can be oxidized by molecular oxygen in humid air to form surface oxide nanostructures.³⁷,³⁸ The morphology, kinetics, and formation mechanism of Mn-containing nanostructures have not been investigated. A detailed understanding of these physicochemical parameters is crucial to assessing the influence of redox-active impurities such as manganese on atmospheric reactions involving aerosol dust particles.

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2. EXPERIMENTAL SECTION

Natural rhodochrosite specimens were obtained from the Harvard Mineralogical Museum of Natural History. Pink translucent crystals with rhombohedral shapes were selected by visual inspection. Prior to each set of oxidation experiments, a fresh rhodochrosite surface was prepared by cleaving a crystal along the (101̅4) plane of perfect cleavage. The cleaved crystal was then attached to a steel puck using warmed dental modeling wax (Cavex, Holland), with the fresh surface facing up.

The in situ investigation of nanostructure formation was performed using a custom-built AFM system consisting of a Veeco Multimode III microscope and an enclosing environmental chamber. The chamber was supplied with humid O₂ and equipped with temperature and humidity sensors. The humidity in the chamber was controlled by altering the humidity of the supply gas, which was regulated by changing the fraction of dry gas passing through a piece of water-saturated NaCl tubing. The humidity control system was managed by a custom-written Igor (WaveMetrics, Lake Oswego, OR) routine using a proportional-integral-differential algorithm. Data acquisition and command delivery were executed using a PCI card (M6251, National Instruments, Austin, TX) and mass flow controllers (M100B, MKS Instruments, Andover, MA).

The formation of oxide films on a freshly cleaved rhodochrosite surface is monitored by periodically taking AFM images at a constant RH. Monitoring is performed using tapping mode over 100 μm randomly selected areas. The experimental temperature was stabilized around 25 °C, which was used to correct the reading of the humidity sensor in real time by the Igor routine.

3. RESULTS

Experiments performed to investigate rhodochrosite oxidation begin with cleaving a centimeter-sized rhodochrosite crystal with a razor blade. As shown in Figure 1a, the surface of a freshly cleaved rhodochrosite (101̅4) face consists of flat terraces separated by 0.26-nm-high atomic steps. The steps extend in either the [481] or [441] direction, forming long and narrow terrace lanes. The steps are not perfectly straight but smoothly curved, presumably reflecting the imperfect alignment of the razor blade with the (101̅4) plane during cutting. The two steps confining a terrace lane extend in parallel until they eventually join each other, forming a terminal point (arrows in Figure 1a).

The exposure of rhodochrosite to humid O₂ induces the formation of thin films, sometimes with unclosed holes, on the (101̅4) terraces, as shown by the AFM topography image in Figure 1b. Statistical analysis of a film inside a terrace lane (white box) reveals a topographical histogram that can be characterized by two Gaussian fits, as depicted in Figure 1c. The fit associated with lower topographical heights is attributed to the terrace whereas the fit with greater heights is attributed to the film. The difference in the two Gaussian means gives a film thickness of h = 1.0(±0.4) nm at 55% RH. As a control, when O₂ was replaced by high-purity N₂, no film was found within the same monitoring period.

Nanostructures formed on rhodochrosite by reacting with molecular oxygen have been previously identified as manganese oxides containing either Mn(III) or a mixture of Mn(II) and Mn(III). The chemical and structural differences between the MnCO₃ substrate and overlying oxide film MnOₓ (1 < x < 2) are evident in the AFM phase image of Figure 1d, which shows only two phases with merged step boundaries separating the same phase. The phase contrast is generated by differences between MnCO₃ and MnOₓ in the surface-potential-dominated electrostatic interaction with the AFM tip.

After more than 2 weeks of monitoring at 55% RH (monitoring frequency: at least once every 20 h), several nanometer-thick films are suddenly observed, as shown in Figure 2a, without any observation of scattered growth islands prior to the formation or during the growth of the films.

![Figure 1](image1.png)

**Figure 1.** Formation of oxide films on rhodochrosite in humid air. (a) Freshly cleaved rhodochrosite surface (arrows: terminal points of terrace lanes). (b–d) Rhodochrosite exposed to O₂ at 55% relative humidity at around 25 °C: (b) atomic force microscopy (AFM) topography image, (c) histogram of the topographical height of the boxed area in b, and (d) AFM phase image. Size of a, b, and d: 10 μm × 10 μm.

![Figure 2](image2.png)

**Figure 2.** Kinetics of oxide film growth. (a, b) Films at t = 2040 and 2100 min. (c) Advance of the growth front with time. Image size: (a) 6.5 μm × 6.5 μm; (b) 9 μm × 9 μm. Film thickness: h = 1.0(±0.4) nm, as estimated from Figure 1c.
Besides the growth and extension of already-formed films, the formation of new films (e.g., Film 5 in Figure 2b) was also observed during continuous AFM measurements in parentheses) and thus has faster formation of oxide nucleation is likely not in frequency does not promote nucleation, suggesting that greater than 55%, the apparent formation of individual growth islands. This is observed during continuous AFM monitoring, without the formation of new islands into which shows scattered islands and subsequent growth of the nanostructures on calcite have comparable rates.9 of island formation on the rhodochrosite surface under our advancement of the it advances rapidly with a rugged front (Movie S1). The fronts, (e.g., Film 4 in Figure 2a,b). fronts, (where \( k_n = 1/t_n \)). At 55% RH, \( t_n = 356(\pm 20) \) h (longest time period elapsed between measurements in parentheses) and \( k_n = 2.8(\pm 0.2) \times 10^{-3} \) h\(^{-1}\). The formation of oxide films is not observed at RH below 55% with 2 weeks of monitoring. Variation of the AFM monitoring frequency does not promote nucleation, suggesting that nucleation is likely not influenced by AFM scanning. For RH greater than 55%, film formation is observed at shorter \( t_n \) and thus has faster \( k_n \).

When oxide films are observed, most of them have already filled the width of the terrace lanes that they occupy (e.g., Films 1–4 in Figure 2a,b). The few still at the width-filling stage show that nucleation occurs at terrace steps (e.g., Film 5 in Figure 2b), consistent with previous observations of nanostructure nucleation on calcite9–12 and presumably initiated at a kink site along the steps.9 Once a film fills the width of the terrace lane, it advances rapidly with a rugged front (Movie S1). The advancement of the film eventually fills the entire terrace lane (e.g., Film 4 in Figure 2a,b).

The kinetics of film growth can be quantified by normalizing the advancement area \( A \) over the average length of growth fronts, \( (w_1 + w_2)/2 \), as shown by the inset of Figure 2c: \[ L = 2hA/(w_1 + w_2) \] where \( h \) is the film thickness. \( L \) estimated for different films shows a linear correlation with the growth time, \( t = t_n \)

\[ L = k_g(t - t_n) \] (1)

where \( k_g \) is the growth rate and can be estimated from the slope of linearity. The conservation of \( k_g \) among films suggests that film growth is an autocatalyzed reaction, a well-known phenomenon for Mn\(^{2+}\) oxidation in solution.40 The possibility that the movement of the AFM tip induces film growth is ruled out by varying the intervals between image scans and changing the scan direction (i.e., top down or bottom up). No tip influence is observed in our experiments, consistent with similar AFM measurements made with nanostructures grown on calcite.10

The three parameters used to characterizing rhodochrosite surface oxidation, namely, film thickness \( h \), nucleation rate \( k_n \) and growth rate \( k_g \) are obtained under four different RH conditions, as shown in Figure 3. All three parameters show systematic correlations with RH, suggesting that rhodochrosite surface oxidation by molecular oxygen is regulated by humidity. As RH increases from 55 to 78%, \( h \) and \( k_n \) increase whereas \( k_g \) decreases, indicating opposing effects of humidity on nucleation and growth.

4. DISCUSSION

According to the experimental observations described above, we propose that the surface reconstruction of rhodochrosite in humid oxygen consists of two consecutive steps with distinctive time scales. As illustrated in Figure 4, the two steps are (a) nucleation initiated by the surface dissolution of MnCO\(_3\), followed by the oxidation of released Mn\(^{2+}\), and (b) the growth of Mn oxide films through autocatalytic oxidation regulated by oxygen dissolution in condensed water and the solid-state diffusion of Mn\(^{2+}\). Details of the two-step mechanism, along
with the quantitative account of the relationships of $h$, $k_\alpha$, and $k_\beta$ with RH are described as follows.

The dependence of $h$ on RH (Figure 3a) is similar to the dependence of condensed water thickness $\tau$ on RH.\(^3,4\) According to water condensation on calcite (Figure S1a),\(^3\) $\tau = 2.7(p/p_0)^{n}$ in nanometers (see below for the estimation of $a$), following the Freundlich isotherm\(^41\) with limiting conditions of $\tau = 0$ at $p/p_0 = 0$ and $\tau = 2.7$ nm at $p/p_0 = 1$. In comparison, $h$ is approximately 1 nm higher than $\tau$ (Figure S1b) but lower than the self-limiting thickness of 2.3–2.5 nm suggested for MnO\(_x\) films in aqueous solutions.\(^38\) The correlation of $h$ and $\tau$ (Figure S1b) suggests that the nucleation of oxide nanostructures begins with MnCO\(_3\) dissolving in water condensed on rhodochrosite from the vapor phase, which generates Mn\(^{2+}\).\(^42,43\)

Dissolved Mn\(^{2+}\) on the rhodochrosite surface is then oxidized by molecular oxygen dissolved in the condensed water layer. Although the homogeneous oxidation of Mn\(^{2+}\) by O\(_2\) is slow, the presence of a surface such as rhodochrosite can greatly accelerate the reaction.\(^44\) The presence of a stabilizing surface presumably improves the rate of ligand exchange with oxygen, leading to the inner-sphere oxidation of manganese.\(^45\) In addition, the surface can also stabilize oxidation product MnO\(_x\) by providing anions and water for coordination.

The oxidation of surface Mn\(^{2+}\) can provide a sufficient number of MnO\(_x\) monomers for film nucleation. Using the solubility of bulk rhodochrosite in the aqueous solution ($pK_p = -4.4$),\(^46\) we estimate that the surface density of Mn\(^{2+}\) is 1.9 × 10\(^{15}\) ions m\(^{-2}\) by assuming [Mn\(^{2+}\)] = [CO\(_3^{2-}\)]. This is obviously an underestimate because CO\(_3^{2-}\) should have a much lower solubility of bulk rhodochrosite in the aqueous solution (p\(_K_p\) = 1.97). The value of $P_1$ in humid O\(_2\) is comparable to those in the aqueous solution equilibrated with 1 atm of O\(_2\).\(^50,51\) The decrease in $k_\beta$ with increasing RH, however, suggests that film growth is not a surface-controlled reaction, which would have led to a constant $k_\beta$ across the experimental RH range. Instead, we propose that film growth in humid O\(_2\) is controlled by the diffusion of oxygen through the water layer condensed on rhodochrosite. According to Fick's law, the flux of diffusion is $J = -D(dC/dr) \approx DP/(H\tau)$, where $D$ is the diffusion coefficient, $P = 1$ atm is the oxygen pressure, and $H = 769$ atm L mol\(^{-1}\) is Henry's constant for oxygen dissolution at 25 °C. Taking into consideration condensed water thickness $\tau$ and oxide film thickness $h$, the growth rate is thus expected to be

$$k_\beta = Joh = \frac{DPoh}{H\tau}$$

(3)

where $v = 10^{-5}$ m\(^3\) mol\(^{-1}\) is the molar volume of 2/3(Mn\(_3\)O\(_4\)). With $\tau = 2.7(p/p_0)^{n}$, the least-squares regression of eq 3 to data presented in Figure 3c gives $D = 1.2(\pm 0.3) \times 10^{-11}$ m\(^2\) s\(^{-1}\) and $a = 6.0(\pm 0.4) (R^2 = 0.95)$. The value of $D$ is smaller than not only the gas-phase diffusivity of 2 × 10\(^{-5}\) m\(^2\) s\(^{-1}\) for O\(_2\) but also its aqueous-phase diffusivity of 2 × 10\(^{-7}\) m\(^2\) s\(^{-1}\) suggesting that the condensed water on rhodochrosite acts like a solid phase. This is consistent with the proposal that the first layer of condensed water on a mineral surface is icesike.\(^2,3,5,4\)

In addition to the diffusion-limited supply of oxygen, the supply of manganese is also limited for rhodochrosite in contact with humid gas. When rhodochrosite is placed in an aqueous solution, the solution serves as a reservoir of Mn\(^{2+}\) ions. Manganese consumed by oxidation can be replenished by dissolution from the surface areas that are not covered by nanostructures.\(^38\) With the solution serving as a conduit channeling Mn\(^{2+}\) from dissolution sites to growth sites, Mn\(^{2+}\) can grow into the terminal ends of terrace lanes without a discernible reduction in growth rate or film thickness (e.g., Films 1 and 4 in Figure 2). This calls into question the supply of Mn\(^{2+}\) by dissolution and lateral diffusion, which would suggest the deceleration of growth, thinning of films, and
formation and deepening of dissolution pits as growth approaches terminal ends.

So what is the mass-transfer pathway for manganese to supply film growth? We propose that the diffusion of manganese follows a Cabrera–Mott mechanism that is widely used to describe metal oxidation.56 This mechanism consists of several steps. First, electrons tunnel through the first layer of the semiconducting film, which is formed by the catalytic oxidation of surface Mn²⁺ at the edge of a nucleus.57 Second, manganese follows a Cabrera–Mott diffusion whereas the rapid growth is limited by MnCO₃ dissolution whereas the rapid growth is limited by metal oxidation.56 This mechanism consists of a long waiting period before the presence of nucleation of oxide nanostructures, followed by a rapid advance of growth fronts. The formation of oxide nanostructures on rhodochrosite follows a dissolution mechanism involving electron tunneling and solid-state diffusion. The complex mechanism revealed here suggests that the presence of redox-active elements in aerosol dust particles can greatly complicate the transformation of these particles in a humid atmosphere.

5. SUMMARY

We have quantified the kinetics of nanostructure formation on a rhodochrosite surface in humid oxygen using in situ AFM. The formation of oxide nanostructures on rhodochrosite consists of a long waiting period before the presence of nanostructures, followed by a rapid advance of growth fronts. We interpret the long wait as slow oxide nucleation and the rapid advance as fast growth. By varying the relative humidity and the amount of condensed water on the rhodochrosite surface, we find that the slow nucleation is controlled by MnCO₃ dissolusion whereas the rapid growth is limited by oxygen diffusion. We propose that the nucleation of oxide nanostructures follows a dissolution–precipitation mechanism similar to that in aqueous solution. The growth of oxide films, however, conforms to a Cabrera–Mott mechanism involving electron tunneling and solid-state diffusion. The complex mechanism revealed here suggests that the presence of redox-active elements in aerosol dust particles can greatly complicate the transformation of these particles in a humid atmosphere.

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ASSOCIATED CONTENT

* Supporting Information
 Figure S1: The thickness of water condensed on calcite in humid air and its correlation with the thickness of the oxide film formed on rhodochrosite. Movie S1: Advancement of oxide films with time. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
 The authors declare no competing financial interest.

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