Imaging the reduction of chromium(VI) on magnetite surfaces using *in situ* electrochemical AFM

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Keywords: Hexavalent chromium, magnetite, redox, atomic force microscopy

Abstract

Hexavalent chromium is a highly toxic and readily mobile metal contaminant introduced to the environment through a variety of industrial operations. In the presence of reductants, such as Fe(II), and catalytic mineral surfaces, such as iron oxides surfaces, Cr(VI) may be reduced to a less toxic and relatively insoluble form Cr(III). In this study, we investigate the interaction between Cr(VI) and the surface of the Fe(II)-bearing mineral magnetite, Fe(II)Fe(III)₂O₄, as an example catalyst, using electrochemical atomic force microscopy (EC-AFM). With this method, the redox potential is controlled by an electrode, and Cr deposition on the magnetite surface is imaged over time as a function of redox potential and pH of the solution. Quantitative analyses of volumetric growth and surface coverage reveal that more precipitation occurs over time at very negative (–500 mV at pH 3, –750 mV at pH 7, and –1000 mV at pH 11) and very positive (+1000 mV at pH 3 and +500 mV at pH 11) electrochemical potentials. Up to 70% of the surface is covered with precipitates at pH 7, while less coverage is observed at pH 11 (< 8%) and pH 3 (< 2%). Particle growth at pH 3 is predominantly lateral in nature with a tendency to form a higher number of smaller adsorbate particles. At pH 11, growth is primarily vertical (perpendicular to the surface), and smaller particles tend to aggregate into larger clusters on the surface with increasingly negative redox polarization. These

larger clusters (most likely subcrystalline Cr-(oxy)hydroxides) co-exist with rhombic, crystalline particles that likely have preferred crystallographic growth relationships with the magnetite substrate; the composition of this latter type of particle is most likely chromite, FeCr_2O_4 , based on the matching crystallography and stability under the Eh/pH conditions of this experiment.

Results from growth analyses were confirmed by batch experiments performed on the same samples used in the AFM, where changes in the Cr concentration in solution were monitored using inductively coupled plasma mass spectrometry (ICP-MS). Virtually all of the Cr was removed after 30 minutes at pH 7 (starting at $2\ \mu\text{M}$ Cr(VI)) at all potentials, $\sim 60\%$ at pH 3, and very little removal at pH 11. X-ray photoelectron spectroscopy (XPS) analyses of the magnetite surface at pH 3 suggest that only Cr(III) phases are present and that Cr and/or Fe-Cr oxide phases are more stable at very reducing conditions ($-750\ \text{mV}$), while Cr and/or Fe-Cr (oxy)hydroxide phases are present under more moderately-reducing conditions ($-250\ \text{mV}$). At pH 11, any Cr deposited is below the detection limit for XPS analysis ($< 1\%$ surface coverage); however, Fe(II)/Fe(III) ratios (~ 0.3) are lower than the expected ratio of magnetite, which indicates that some oxidation of the surface has occurred. This oxidized layer, possibly maghemite ($\gamma\text{-Fe}_2\text{O}_3$), hematite ($\alpha\text{-Fe}_2\text{O}_3$), or FeOOH , may inhibit the reduction of Cr(VI) on the surface.

1. Introduction

Chromium, like most transition metals, is redox-active and shows variable geochemical behavior with changes in oxidation state (typically III or VI). Under reducing conditions, Cr is present as Cr(III) and occurs naturally as the mineral ore chromite (FeCr_2O_4). Cr(III) may also precipitate as Cr_2O_3 (eskolaite) or as Cr(III)-hydroxides in aqueous environments at $\text{pH} > 3$. The oxidized form of chromium, Cr(VI), however, is highly carcinogenic and exists primarily as dissolved chromate ($\text{CrO}_4^{2-}(\text{aq})$), dichromate ($\text{Cr}_2\text{O}_7^{2-}(\text{aq})$), or as rare chromate solids (*e.g.*, crocoite, PbCrO_4). Cr(VI) persists in soils and natural waters indefinitely unless removed through leaching, uptake into the cells of plants and microorganisms, adsorption, or reduction and subsequent precipitation of Cr(III) phases (Bartlett, 1991). The World Health Organization proposes

a maximum allowable limit of $50 \mu\text{g L}^{-1}$ (about $1 \mu\text{M}$) total chromium in drinking water (WHO, 2011).

In the context of environmental contamination, Cr(VI) poses a significant hazard, while Cr(III) is relatively benign at low concentrations. Therefore, a detailed understanding of the redox transformations between Cr(VI) and Cr(III) has important implications for the chemical sequestration and remediation of chromium. Electron donors available to promote Cr reduction, *e.g.*, dissolved organic matter or $\text{Fe(II)}_{(\text{aq})}$, are relatively common; however, mineral surfaces are often needed to promote these redox reactions. Atoms at the surfaces of minerals may accept or donate electrons as active participants in the redox reactions, or the mineral surface may serve as a catalyst for the reaction by facilitating electron transfer via an electron shuttle through the surface. Furthermore, mineral surfaces may help lower the activation energy of the overall reaction by providing nucleation or adsorption sites for species in solution (Becker et al., 2001; Rosso and Becker, 2003; Tessis et al., 1999; Vorlicek and Helz, 2002). Minerals that are ubiquitous in aqueous environments, including sulfide minerals and Fe or Mn oxides/(oxy)hydroxides, play a critical role in surface-mediated reduction (Elsner et al., 2004; Hyland and Bancroft, 1990; Taylor et al., 2015). Macroscale kinetic experiments have demonstrated that these redox reactions are often catalyzed by the surfaces of sulfide and oxide minerals, yet the actual nanoscale reaction mechanisms are not understood (Gheju, 2011). Kinetic bottlenecks may include diffusion of chromate towards the mineral surface, dehydration of the chromate and reductant, outer- to inner-sphere surface complex transitions, and associated angular momentum changes due to electron-spin transfer (Renock and Becker, 2010). In order to clarify these atomic-scale processes, high-resolution microscopy and surface-sensitive analytical techniques are needed.

One way to observe the progress of a reduction/precipitation reaction is to study the formation of the reduction product as a function of solution chemistry and redox potential. In this study, atomic force microscopy (AFM) in combination with electrochemical methods (EC-AFM) has been developed and applied to image the reductive precipitation of Cr on a mineral surface. In our approach, the solution chemistry

(*i.e.*, pH, Cr concentration, type and concentration of background electrolyte) is constrained within an experimental cell (although slight modulations in the pH are inherent to the nature of redox reactions), and the redox potential is controlled by setting the voltage of a potentiostat for a given amount of time. This type of redox-dependent scanning probe microscopy, or electrochemical-SPM (EC-SPM) allows for *in situ* observations of reactions along a given Eh/pH path. Although homogenous reduction of Cr(VI) by Fe(II) in solution has been observed (Buerge and Hug, 1997; Flury et al., 2009), we focus on surface-mediated, heterogeneous reduction, because the experimental conditions can be controlled, and the reaction products can be observed with EC-AFM. EC-SPM has been used relatively rarely for geochemical applications, but this combined method has been a powerful tool in studying processes such as epitaxial mineral growth (Stack et al., 2004b), mineral dissolution morphology and kinetics (Etienne et al., 2004; Higgins and Hamers, 1995; Higgins and Hamers, 1996; Higgins et al., 1996), precipitation (Yuan et al., 2015), adsorption and thin film formation (Stack, 2008; Stack et al., 2004a), and electron transfer (Wigginton et al., 2009).

Here, EC-AFM is used to visualize the *in situ* adsorption/precipitation/reduction of Cr(VI) onto a magnetite (Fe_3O_4) surface. Magnetite is a mixed valence iron oxide mineral and is a major constituent of many different types of soil environments (Cornell and Schwertmann, 2006). Additionally, magnetite has been shown to facilitate the heterogeneous reduction of Cr(VI) to Cr(III) (Baig et al., 2014; Fendorf et al., 2000; Gheju, 2011; Jung et al., 2007; Kendelewicz et al., 1999; Kendelewicz et al., 2000; Peterson et al., 1996; Peterson et al., 1997). When Cr(VI) in solution is reduced to Cr(III), there is an associated change in angular momentum when its unpaired spins change from 0 to 3. Magnetite, which has both ferric (five unpaired spins) and ferrous (four unpaired spins) iron, can compensate for this change in angular momentum (each unpaired electron carries an angular momentum of $\hbar/2$). In order to precisely control the redox potential of the electrochemical cell, the electrode material/substrate of interest has to be adequately conductive to allow for the transfer of electrons from a voltage source to solution (or *vice versa*). Magnetite is a semiconducting mineral (with a band gap of 0.1 eV) and, therefore, well suited as a substrate to study surface-mediated redox reactions. In these experiments, a magnetite sample is loaded into an EC-AFM cell and

polarized at discrete redox potentials in the presence of a Cr(VI)-containing solution. Morphological changes in the magnetite surface and kinetic information are measured in terms of changes in the volume growth of Cr adsorbates/precipitates, the number of adsorbates/precipitates per unit area, or a combination thereof.

The goal is to observe, understand, and quantify Cr(VI) reduction and adsorption/precipitation onto magnetite at specific Eh and pH conditions. The Eh and pH are set by the applied electrochemical potential and the initial acid/base content in solution, respectively, and the progress of the reaction is monitored by imaging the magnetite surface over time. Redox equilibrium diagrams are useful for evaluating which species is predominant over a range of pH and Eh conditions and what process is being observed (Fig. 1); however, many redox reactions are very slow, and disequilibrium may occur when multiple redox couples are present. As a result of this, a reduction (or oxidation) process may be observed at a redox potential that is actually lower (higher) than expected from applying equilibrium conditions. In addition, it is possible that the dominant species predicted by the Nernst equation is less redox-active than other species or even redox-inactive. By measuring precipitation over time, we can compare the growth features that appear at the time scale of these experiments (*i.e.*, minutes to hours) with the species predicted at thermodynamic equilibrium. We can also observe the morphology of adsorbates or precipitates on the surface and see how it changes over time.

As a second, more methodological goal, the suitability of EC-AFM is evaluated to capture the kinetics of precipitation as a function of Eh/pH. This relatively new and underutilized approach is a way to specifically control Eh and pH and simultaneously look at growth and morphology changes *in situ* and in almost real time (depending on the time needed to acquire an image). This is a potentially powerful tool to study geochemically relevant redox processes. This morphologic information is complemented with surface-sensitive spectroscopy (XPS and AES) in order to determine the composition of Cr precipitates and analysis of the solution to measure the amount of Cr removed. This knowledge will help develop a mechanistic model for surface-mediated reductive precipitation of Cr.

2. Methods

2.1. Electrochemical AFM experiments

The magnetite samples used in this study are octahedral-dodecahedral crystals collected from Mineville, New York and the Itabira District, Minas Gerais, Brazil (Ward's Science, USA). Minor amounts of titanium and aluminum were measured with energy-dispersive x-ray spectroscopy (EDS). The crystals were cut using a water-saw parallel to triangular (111) growth faces. The chosen faces were largely free of inclusions. The large octahedral magnetite crystals from the Itabira District are associated with minor occurrences of high-grade hematite bodies in this iron-rich district, and impurities are generally minor. The samples were polished with silicon carbide paper (grit sizes 180, 400, 600, 800, 2400, and 4000) and 0.3 μm and 0.05 μm alumina powders in sequence. Samples were then sonicated for 10 minutes and rinsed with ethanol and acetone in order to remove any contaminants introduced through polishing. Samples were polished and rinsed immediately prior to EC-AFM experiments in order to expose a “fresh” surface and minimize oxidation of Fe(II) to Fe(III) on the surface. The exposed areas of the final samples were approximately 15 mm^2 to 18 mm^2 .

Our experimental setup consists of a three-electrode configuration in which magnetite serves as the working electrode, a platinum wire is the counter electrode, and a silver wire is the quasi-reference electrode (+250 mV vs. the standard hydrogen electrode, SHE). In this electrochemical cell (Appendix A Fig. A1. Bruker Corporation, Santa Barbara, California), the magnetite samples were affixed flat on an etched Teflon® disk using Torr Seal® low vapor pressure epoxy. The Teflon disk was then mounted to the base of the AFM fluid cell, and electrical contact was established with a spring through a small opening in the disk. The redox potential was controlled using a CHI 760D potentiostat, and EC-AFM experiments were performed using an in-house Dimension Icon atomic force microscope (Bruker). Electrolyte solutions were prepared using ultra-pure water (*i.e.*, Milli-Q® water, typically 18.2 $\text{M}\Omega\text{ cm}$ at 25 °C) and reagent-grade $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ and KCl. The pH was adjusted using 0.01 M HCl and 0.1 M NaOH. For all experiments, the initial pH of the electrolyte solutions was approximately 3, 7, or 11; these values were chosen in order to capture a broad range of possible pH conditions.

Previous studies have shown that magnetite can reduce Cr(VI) in solution at neutral pH, although less evidence exists at more extreme pH values (Peterson et al., 1996; Peterson et al., 1997). Due to the relatively small volume of the experimental cell (2 mL), the decision was made not to use a buffering agent in order to avoid possible complexation of Cr by the buffering agent in solution or competition for surface sites on the magnetite (Sibanda and Young, 1986; Sokołowska and Bal, 2005; Welch et al., 2002). Still, in order to consider the potential pH change, we estimate the upper limit of pH change as a function of hydronium consumption described in Eqns. 1a and 1b.

In the extreme case in which all the Cr in solution is reduced and none of the pH change is buffered by either the mineral surface or solution constituents, and by applying this estimate to the least pH buffered solution of pH 7, 10^{-5} M hydroxide ions would be produced (or an equal amount of hydronium consumed) in a 2 μM chromate solution. This would result in a maximum pH change of +2 units from pH 7 to 9. This effect would be negligible at pH 3 (3 to 3.004) or pH 11 (11 to 11.004). Geochemical modeling reveals that the phases expected to dominate at pH 7 are present over several pH units in either direction, and a change in pH from 7 to 9 would not greatly affect Cr speciation in this case, but would somewhat shift the equilibrium away from Cr_2O_3 towards dissolved chromate for oxidizing conditions (Fig. 1). Solutions were kept in opaque bottles and refrigerated at 4 °C to minimize the possibility of photochemical redox reactions (Kleber and Helz, 1992).

Contact mode and Peak Force Tapping (PFT) mode experiments were performed in fluid (1 μM $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ and 0.01 M KCl solution) using silicon nitride (DNP, nom. freq. 23 kHz, nom. spring constant 0.12 N/m) and silicon tips (ScanAsyst-Fluid+, nom. freq. 150 kHz, nom. spring constant 0.7 N/m). In PFT, developed by Bruker, the tip makes intermittent contact with the sample surface, but unlike regular tapping mode, the oscillation of the cantilever is kept at frequencies well below its resonance. This removes artifacts attributed to the dynamics of a resonating system. A linear scan rate of about 1.2 Hz was used with a resolution of 320 samples per line. For each experiment, the open

circuit potential, usually between 0 and -100 mV, was measured and allowed to stabilize for 400 seconds before beginning polarization of the magnetite electrode. Images were later cleaned and flattened using the NanoScope Analysis® software version 1.4 (Bruker Corp). After polarization, the experiment was stopped, and the Cr-electrolyte was removed from the cell and stored for subsequent ICP-MS analysis. The magnetite electrodes were then gently dried with compressed air, and immediately transferred into a controlled atmosphere Coy® vinyl glove box, where they continued to dry for at least 24 hours before XPS and AES analysis. The gas in the box was primarily N_2 (with 5% H), and O_2 levels are < 1 ppm (controlled using a desiccant with a palladium catalyst and an O_2 trap, see Taylor et al. (2015) for further details). All experiments were carried out at a temperature of 22 ± 2 °C. Both types of spectroscopic analyses were performed at the Electron Microbeam Analysis Laboratory at the University of Michigan.

A MATLAB script (release 2015a, the MathWorks, Inc., Natwick, Massachusetts, USA) was developed to quantify the precipitates observed on the AFM images. The script first estimates a background for each original grayscale image using a user-defined structural element. This structural element is chosen to distinguish and separate features in the image. The background is then subtracted from the original grayscale image. The intensity values of the corrected grayscale image are mapped to new values, such that 1% of these data are saturated at low and high intensities creating an increased contrast output image. The high-contrast image is then converted to a black and white image based on a threshold value specified by the user. This approach was preferred over standard threshold-finding strategies (*e.g.*, Otsu's method) because choosing a threshold allowed the visual selection of the closest-to-original result (Otsu, 1979). Objects can then be defined, measured, and counted from the binary or black and white representation of the original image. The binary image is a logical array with ones (1) where precipitates exist in the original image and zeros (0) where they do not. To obtain the precipitate heights only, this logical array is multiplied by the image height data exported from the AFM acquisition software. All heights not associated with precipitates are thus discarded. The sum of the heights that correspond to precipitates is finally multiplied by the appropriate area differential to estimate the volume of the precipitates. Importantly, defects on the magnetite surface or interference during the original image acquisition

influence the numbers obtained by this method, which should be taken as estimates instead of precise values. Overall trends and differences are likely to be more relevant in this model than absolute numbers.

2.2. X-ray photoelectron spectroscopy (XPS)

Characterization of the chemical oxidation states of Cr species on the magnetite surface was performed by measuring the peak chemical shifts of the electron binding energies (BE) using a Kratos Axis Ultra XPS with an Al K α x-ray radiation source (1486.6 eV). Before analyses, the samples were degassed overnight in a sample-transfer chamber under a vacuum pressure of $< 10^{-5}$ Torr. Analyses were then carried out at a pressure of $< 10^{-8}$ Torr. The x-ray emission current and anode voltage used during spectra acquisition were 8 mA and 14 keV, respectively. A charge neutralizer was used during spectra acquisition. Spectra were acquired using a hybrid lens and slot aperture (700 $\times$ 300 μ m). The analysis area was approximately 2 mm $\times$ 1 mm. For survey scans, a pass energy of 160 eV was used with a dwell time of 100 ms per 1 eV step (10 sweeps). Core scans were performed for the Cr 2p, Fe 2p, O 1s, and C 1s regions using a 20 eV pass energy and a dwell time of 400 ms per 0.1 eV step (20-50 sweeps). Spectra were analyzed using the Casa XPS software (version 2.3.16), and binding energies were calibrated to C 1s at 284.8 eV. The signal-to-noise ratio was increased by convolution using a 5-point quadratic polynomial.

2.3. Auger electron spectroscopy (AES)

Chemical analyses of the magnetite surfaces were also performed with AES. Measurements were taken using the Physical Electronics Auger Nanoprobe 680. The electron gun with a Schottky thermal field emitter was operated at a beam voltage of 10 keV and current of 10 nA. The electron energy analyzer is a full cylindrical mirror analyzer with a capture angle of $42 \pm 6^\circ$ for 360° around the analyzer axis. Samples were held under ultra-high vacuum (ca. $2.0 \cdot 10^{-9}$ Torr) for the duration of analysis. Although magnetite is a semiconducting mineral, some charge from the incident electron beam may accumulate on the surface and cause shifts in electron kinetic energy; therefore, all samples were fixed onto a tilted sample mount (30°) during analysis. Tilting the sample serves to scatter electrons from the incident beam away from the surface so that only a

relatively small number of electrons initiate the Auger process. Spectra were smoothed and differentiated using the MultiPak software package, version 9.6.0 (ULVAC-PHI 2014).

2.4. Inductively-coupled plasma mass spectroscopy (ICP-MS)

Aqueous Cr(VI) concentrations were measured from the diluted, acidified aliquots of electrolyte using an Agilent 7900 ICP-MS. The quantitative analysis method uses 100 sweeps per reading and the average of three to five replicates per measurement. Interferences were minimized by using a high He flow method in the collision-reaction chamber of the instrument. The analysis was controlled using a simple linear standard calibration curve with 6 points and Ga as internal standard. Internal standard variation was never above 15%. Analytical precision was better than 7% RSD based on check standards, laboratory reference material, and sample replicates.

3. Results and Discussion

3.1. Electrochemical AFM

3.1.1. Redox processes at pH 11

The magnetite surface was first imaged in the absence of an applied potential in order to survey the substrate before any induced sorption took place and to test if sorption occurred at the open circuit potential (OCP). With this step, a “background” image is obtained with which to compare growth features that appear on the surface as a function of time and potential (Fig. 2A). Scratches and grooves produced when polishing the magnetite surface serve as reference points during the experiment. The magnetite electrode was then polarized at specific electrochemical potentials (–250 mV, –750 mV, and +1000 mV), and the surface was imaged over a period of 20 to 35 minutes at each potential. In all experiments, unless otherwise stated, scanning was briefly paused between images in order to reset the potentiostat and resumed once the redox potential was set to ensure a stable potential during image acquisition. Images were then quantified and analyzed for changes in the number and size of adsorbates and/or precipitates (hereafter collectively referred as sorbates). While these values provide a quantitative measure of sorption over time, the level of uncertainty of the image analysis dictates that

the overall trends and relative differences between potentials (rather than the absolute values) be emphasized.

At -250 mV (vs. SHE), sorbates appear on the surface within the first 10 minutes of polarization. In general, these particles have a diamond-like or rhombic shape with dimensions of approximately $100\text{ nm} \times 100\text{ nm}$ and a range in height from 3-17 nm (average height 6.8 nm, Fig. 2B). The angle between the long axes of these rhombic adsorbates is slightly less than 90° (78° - 86°). In a replicate experiment (not shown), the scan angle was rotated by 45° in order to verify the rhombic particle shape was not an artifact of the AFM tip. Upon changing the scan angle, the pseudo-rhombohedral maintained their original orientation (with respect to stable surface features), which indicates that the observed shape reflects the morphology of the adsorbed particles. Some particles overlap with one another, which may indicate some epitaxial relationship between precipitates. No detectable particle growth was observed during the 35 minutes of polarization. There is also no apparent trend in particle distribution; the particles are distributed evenly on relatively flat regions of the magnetite surface.

After approximately 35 minutes of polarization at -250 mV, where only rhombic sorbates were observed, the Eh was set to -750 mV. At this potential, more rhombic features appear on the surface as well as a second class of larger, semi-spheroidal particles. These images are shown and described in further detail in Appendix B, Fig. B2. At this potential, the volume remains relatively constant around $6 \times 10^7\text{ nm}^3$.

In order to oxidize the sorbates deposited on the magnetite under reducing conditions, the magnetite was polarized at $+1000$ mV for 30 minutes. Equilibrium thermodynamics does not predict a persistent solid phase over such a wide range of Eh conditions. Therefore, the dissolution/desorption of both the larger semi-spheroidal features and the pseudo-rhombohedral were expected. Both types of particles, however, largely remain on the surface. Furthermore, growth of additional spheres was observed (Fig. 2C). The total sorbate volume is the greatest at the more positive potentials ($+250$ mV and $+500$ mV, Fig. 3). The number of particles counted on the surface decreases at $+250$ mV, which indicates that there are fewer, larger particles on the surface, although the percentage of surface coverage remains largely the same after 45

minutes of polarization (between 1 and 7%). It is possible that both the pseudo-rhombohedral and the (oblate) spheroids are stable, or at least metastable on the timescale of the experiments, over a range of Eh values, and/or the dissolution kinetics is too slow to observe over the time of the experiment.

In order to determine if growth is primarily due to an increase in sorbate height or due to lateral growth, sorbate volume and surface area are compared for the images acquired at -750 mV and $+500$ mV (Fig. 4). The volume increases at a higher rate than the rate of growth for the surface area (scaled for clarity), which indicates that growth is mainly vertical in nature. At -750 mV, the surface coverage remains constant over the duration of the experiment, so the entire volumetric increase may be attributed to vertical growth. The fact that it is more advantageous to grow on top of an existing sorbate indicates an increasing epitaxial mismatch for lateral growth; in other words, it is more energetically favorable to grow new layers on top, rather than making use of the additional bonding partners at a lateral step or kink site (Taylor et al., in rev.). At $+500$ mV, both the sorbate volume and area increase, which implies that the particles grow in the vertical and x - and y -directions (about 8% and 21% each, respectively). The square root of the surface area is also shown in order to compare equal dimensions; this length dimension remains unchanged at -750 mV, yet it increases at a gentle slope at $+500$ mV (21% increase). To summarize, growth at pH 11 at highly reducing conditions is primarily vertical, while highly oxidizing conditions result in both vertical and lateral sorbate growth. Sorbates that grow under oxidizing conditions are relatively large (~ 0.5 - 1 μm in diameter) and semi-spheroids compared with the rhombi that grow under more mildly reducing conditions. Under reducing conditions, the overall number of islands decreases slightly over time, which may be explained by diffusion and subsequent aggregation of particles on the surface complemented by fast vertical growth.

3.1.2. Redox processes at pH 7

As with pH 11, a series of AFM images was acquired as a function of time at the redox potentials 0 mV (open circuit potential), $+500$ mV, $+750$ mV, and -500 mV in a solution at a pH of 7. At the beginning of the experiment, deposition is observed on the magnetite surface (Fig. 2D). These conditions (redox- and pH-neutral) correspond to the

Eh-pH region where chromite is the dominant Cr phase; aqueous Cr(VI) undergoes reductive precipitation in the presence of the magnetite surface and accumulates on the surface as chromite. The texture of the growth features may be described as subhedral; well-defined edges develop on many of the particles and define a roughly rhombic shape. In some cases, two sides form a fan-shaped feature rather than a four-sided rhombohedron. Individual particles, or growth islands, are approximately 75-100 nm in length, yet these features tend to form larger aggregates. After increasing the potential to +500 mV, the general appearance of the surface remains largely unchanged, although results from image analyses indicate that there is a 9% drop in total particle volume in the first 10.5 minutes of polarization followed by a gradual increase from 4.4×10^6 to $4.6 \times 10^6 \text{ nm}^3$ over the next 10 minutes (Fig. 3).

At +750 mV, AFM images show significant rounding of the particles on the surface (Fig. 2E). The original rhombic shape of the precipitates is no longer observed, and the aggregates present at the open circuit potential have decomposed into broader and more gently sloping mounds on the surface. The percentage of the surface covered by growth features increases from approximately 37% at +500 mV to 55% at +750 mV; the volume, however, decreases by 23% after about 20 minutes of polarization. This trend may be explained by the dissolution of the particles on the surface. The cause of this “rounding” of particles is actually the creation of jagged edges through an increase in the number of kink sites. Kink sites are positions on the surface of a solid that have relatively few bonding partners and are consequently higher in energy. This higher energy state may exist during this experiment due to disequilibrium conditions caused by the rapid changing of the redox potential; however, from an equilibrium energetics point of view, the creation of more energetic kink sites must be compensated by a gain in energy. One possible candidate for this energy gain may be the oxidation and solvation of Cr: $\text{Cr(III)} \rightarrow \text{Cr(VI)O}_4^{2-}{}_{(\text{aq})}$. For example, Cr(III) sorbed onto the surface is oxidized, and the energy gained through the hydration of Cr(VI) balances out the energy deficit caused by the creation of more kink sites.

The final potential in this series of experiments was –500 mV. Polarization during 21 minutes at this potential resulted in an overall adsorbate volume increase of 9.4%. Most of this growth was observed on one side of the mound features produced at

+750 mV (Fig. 2F). These new growth features are primarily semi-spheroids approximately 30-50 nm in diameter. The percentage of surface coverage (~75%) is higher than that at the more positive potentials, yet does not increase over the duration of the experiment. These conditions plot within the Eh-pH region where FeCr_2O_4 is dominant (Fig. 1). These particles are smaller than those that first appear at the OCP. At –500 mV, more Cr(III), as well as Fe(II), is available to form solid compounds.

3.1.3. Redox processes at pH 3

Volume growth observed during the OCP and at +250 mV (up to 30 minutes) was minor in comparison to the growth seen at –500 mV and at +1000 mV (Fig. 3; Appendix C, Fig. C2). In this set of experiments, the potentiostat was set at –500 mV during the acquisition of an image (rather than between images), and the results show that deposition occurred almost immediately upon polarization (indicated by the white dashed line in Fig. 2H). In this case, image acquisition is initiated at the OCP, and the polarization is applied part way through the acquisition of the image. This change was made in order to capture growth at time steps shorter than the ~4.5 minutes per image. After this initial burst of growth, however, the total particle volume decreases before leveling out after 18 minutes. Larger, non-uniform semi-spheroidal particles are first observed on the surface, yet these larger features disappear after 13.5 minutes. Growth is relatively homogeneous over the entire scan area. Lateral vs. vertical growth analysis for images acquired at –500 mV shows a decrease in the average length and average height in relatively equal proportions (Appendix C, Fig. C2).

The positive potentials were also systematically explored at pH 3. The largest amount of volumetric increase occurs at +1000 mV. A representative EC-AFM image is shown in Fig. 2G. The adsorbates appearing for all positive potentials are all semi-spheroidal and relatively small (50-100 nm in diameter, ~25 nm in height). A lateral vs. vertical growth analysis reveals that highly oxidizing conditions (+1000 mV) and low pH values produces fast lateral growth with a significant increase in growth islands (Appendix C, Fig. C3).

Under reducing conditions (*i.e.*, more negative polarization potentials), $\text{Cr(VI)}_{\text{aq}}$ is heterogeneously reduced to the Cr(III) solids Cr_2O_3 or chromite, FeCr_2O_4 . These phases

are stable at pH values greater than 3.5. Indeed, sorption is observed at very reducing conditions for all three pH values (3, 7, and 11). In this case (*i.e.*, at pH 3), the initial disequilibrium caused by changing the electrochemical potential may allow for the precipitation of Cr-Fe oxides at pH conditions that are considered to be unstable for these phases. It is also possible that the pH increased slightly during the reduction reaction to allow for oxide precipitation (Eqn. 1a).

At both pH 3 and pH 11, adsorption/precipitation was highest at very low and very high potentials. At pH 7, maximum growth occurs at -500 mV, and dissolution is observed at $+750$ mV. While we can rationalize the presence of solid Cr(III) phases as either Cr(-Fe) oxides or Cr(-Fe) (oxy)hydroxides under reducing conditions, the precipitation at very positive potentials for pH 3 and 11 is counterintuitive. The Eh-pH model would predict aqueous HCrO_4^- or CrO_4^{2-} as the dominant Cr phases, yet results from batch chemistry experiments (to be discussed in Section 3.2) show a significant decrease in dissolved Cr at pH 3 (and not at pH 11). We cannot rule out the possibility of Cr(IV)O_2 , and another explanation is the precipitation of a ferric iron chromate, $\text{Fe(III)}_3(\text{CrO}_4)_2$. No solubility information was found for this compound; however, Ag_2CrO_4 and PbCrO_4 have very low solubilities ($K_{\text{sp}} \approx 10^{-12}$ and 10^{-13} , respectively). It is likely, therefore, that $\text{Fe}_3(\text{CrO}_4)_2$ is also highly insoluble. Although little thermodynamic/solubility information is available for $\text{Fe}_3(\text{CrO}_4)_2$, its low solubility may allow for precipitation with small amounts of Cr and Fe(III) in the system.

3.2. Batch chemistry analysis

Since the small area analyzed using EC-AFM may not be representative of Cr sorption over the entire working electrode surface, these observations were complemented by batch experiments. Changes in the concentration of Cr in solution were measured at 10-minute intervals over the course of several EC-AFM experiments. At each time interval, the experiment was stopped, and the entire volume of solution was removed and analyzed using ICP-MS. The magnetite electrode was then re-polished before the next experiment. Given the solubility behavior of Cr (*i.e.*, Cr(VI) compounds are often several orders of magnitude more soluble than Cr(III) compounds), we assume that any Cr removed from solution is Cr(III) that has precipitated or Cr(VI) that has

adsorbed onto the magnetite surface; the remaining Cr is present as an aqueous Cr(VI) oxyanion, such as $\text{CrO}_4^{2-}(\text{aq})$.

Results from pH 11 experiments indicate that very little Cr is removed from solution (Fig. 5). We would expect to see some Cr removal as either Cr_2O_3 or FeCr_2O_4 at the more negative potentials. As will be discussed in the next section, oxidation and subsequent passivation of the magnetite surface at pH 11 may explain the lack of Cr deposition. One point of concern for the analysis is the excursion above the initial Cr concentration of 2 μM at -1000 mV and -500 mV. The high error registered for these points likely arises from complications associated with the matrix pH adjustments required for measuring, which have an initial pH of 11. The small sample size of the EC cell prevented pH monitoring during and after the experiment. However, this variance does not invalidate the overall trend that relatively little Cr is removed from solution at pH 11.

At pH 7, nearly all of the Cr was removed from solution across all potentials (results not shown). This is consistent with the relatively high percentage of surface coverage measured from the AFM images. Although the total sorbate volume calculated at pH 7 is not as high as the volume calculated at pH 3, more of the surface is covered with sorbates. Extrapolating this observation over the entire electrode surface ($\sim 15 \text{ mm}^2$ vs. $1 \mu\text{m}^2$ for AFM images), it is feasible that all of the initial Cr(VI) in solution is reduced and precipitates as Cr(III) on the magnetite.

Overall trends of Cr reduction beyond the error of measurement can be distinguished, particularly for the experiments at pH 3. At pH 3, similar amounts of Cr removal from solution are observed at all potentials tested ($\sim 60\%$ after 30 minutes). Maximum removal occurred at $+1000$ mV, the most oxidizing potential ($\sim 65\%$), while the least Cr was removed at $+500$ mV ($\sim 59\%$). At $+500$ mV, approximately 50% of the Cr is removed, yet this rate of removal rapidly decreases and eventually levels out after 30 minutes of reaction. Cr removal at pH -500 mV, however, is nearly linear over the entire 30-minute period. EC-AFM experiments at this potential result in a rapid increase in initial growth followed by a decrease in the total particle volume before the volume levels out after ~ 15 -18 minutes of scanning. This surge in growth occurred on a time

scale shorter than the 10-minute interval used for the batch chemistry experiments, and therefore would not be captured by the ICP-MS data. Image analyses are still consistent with a linear decrease in the concentration of Cr in solution over time.

An attempt was made to measure the possible release of Fe into solution (as an indication of magnetite dissolution), but any Fe in solution was below the detection limit of the spectrometer, which is on the order of 1 ppb (10^{-9} M). White et al. (1994) report magnetite dissolution rates ranging from 0.3 to 13×10^{-14} mol·cm⁻²·s⁻¹ in pH 1-7 anoxic solutions, and these rates decrease with increasing pH. Using these rates to estimate the amount of Fe(II) released into solution over 30 minutes of polarization, Fe concentrations should be high enough to be detected by instrument (*i.e.*, 10^{-7} or 10^{-8} M). Dissolved O₂ present in the experimental solution may re-oxidize some of the Fe(II), so these estimates may be slightly high; however, the absence of measureable Fe in solution suggests that the sorbates present on the magnetite have a mixed Fe-Cr composition.

3.3. Spectroscopic analysis of the magnetite surface

3.3.1. X-ray photoelectron spectroscopy

XPS spectra were acquired in order to confirm Cr deposition through spatially-averaged spectroscopic evidence of Cr and to measure its oxidation state. This was done for a subset of the same magnetite samples that were previously used for EC-AFM experiments, polarized at -750 mV, -250 mV (pH 3 and pH 11), and +1250 mV (pH 11 only). For the samples prepared at pH 3, binding energies (BE) for Cr 2p_{3/2} peaks (calibrated to C 1s at 284.8 eV) are consistent with Cr(III) (main peak components range from 575.4-577.4 eV) (Jung et al., 2007). The chemical shift between Cr(III) and Cr(VI) is relatively large, approximately 2.5 eV for single peak-fitted spectra (Kendelewicz et al., 1999; Kendelewicz et al., 2000; Suzuki et al., 1997), no peaks were observed at this higher binding energy, typically around 579 eV. This indicates that Cr(VI) reduction on the magnetite surface is complete.

Multiplet splitting, not to be confused with spin-orbit splitting, can also occur when an atom has unpaired valence electrons, such as Cr(III) (with the electronic configuration: [Ar] 3p⁶ 3d³, *i.e.*, with three unpaired d electrons). Upon emission of a core-level electron, these unpaired valence electrons may couple with unpaired core

electrons to create a number of final energy states. This results in a multi-peak envelope rather than a sharp elemental line. In our initial fitting, we assume a single broad component to get a first approximation of the Cr 2p and O 1s peak positions (Fig. 6). In a more detailed fitting with at least two multiplet components for each peak, the Cr 2p binding energies for the magnetite polarized at the more reducing potential (−750 mV, pH 3) are slightly lower than those of the magnetite polarized at −250 mV. For clarity, the samples prepared at −750 mV and −250 mV will be referred to as sample A and sample B, respectively. For sample A (more reduced), positions of the main peak components are 575.4 and 576.8 eV, compared with 576.1 and 577.3 eV for sample B (less reduced). Additionally, the separation between $2p_{3/2}$ and $2p_{1/2}$ for sample A is more consistent with the peak separation reported for Cr_2O_3 and FeCr_2O_4 (9.45 eV reported by Ünveren et al. (2004) compared with 9.2 eV measured in this study). As predicted by geochemical modeling, we observe the formation of Cr and/or Fe-Cr oxide phases on the magnetite surface under very reducing conditions (−750 mV). The Cr 2p spectra for Cr_2O_3 and FeCr_2O_4 , however, are nearly identical (Biesinger et al., 2004; Biesinger et al., 2011; Jung et al., 2007), and due to the Fe 2p signal from the magnetite substrate, we were unable to distinguish between these two phases.

In comparison, the higher binding energies for chromium phases deposited on sample B (−250 mV) may be indicative of chromium (oxy)hydroxides $\text{Cr}(\text{OH})_3$, CrOOH , or perhaps an Fe-Cr solid solution, $(\text{Fe,Cr})(\text{OH})_3$. The binding energies for Cr(III) in $\text{Cr}(\text{OH})_3$ are typically 0.5-0.6 eV higher than those for chromium oxides, and this shift increases with increasing number of OH groups (Harvey and Linton, 1981; Kendelewicz et al., 2000; McCafferty et al., 1988). While this higher binding energy is still contained within the Cr $2p_{3/2}$ envelope for sample B, increased Cr-OH content may explain this shift towards the higher binding energy. Another way to evaluate the amount of hydroxylation is to compare O 1s peaks of experimental vs. unreacted magnetite (Fig. 7). The unreacted magnetite surface features an asymmetric O 1s peak with three main components. The largest component is attributed to lattice O atoms in the magnetite structure, while the other two components at lower binding energies are likely final state shake-ups (commonly observed in magnetite XPS spectra) and possible surface contamination (*e.g.*, carbonation, non-stoichiometric O atoms or even some partial

hydroxylation), respectively (Kendelewicz et al., 2000; Wandelt, 1982; Yamashita and Hayes, 2008). Two of the O 1s peak components for Cr₂O₃ and the polarized sample are very similar; however, there is an additional feature present in the reacted magnetite. This third component provides evidence of hydroxylation of the sample surface and the formation of Cr (and/or Cr-Fe) (oxy)hydroxide phases. At pH 6 and 8, Kendelewicz et al. (2000) report that this hydroxide layer contains little to no Fe. With the reduction of Cr(VI) to Cr(III), one would expect to see a corresponding increase in Fe(III) on the magnetite surface; however, both pH 3 spectra do not show a clear shift in Fe peaks or Fe(II)/Fe(III) ratios. This would imply that after 20 minutes of polarization, the surface is not yet saturated with reduced Cr precipitates, and some Fe(II) is still available to promote reduction.

XPS spectra from samples prepared at pH 11 show no peaks for Cr in the narrow scan, which indicates that any Cr deposited on the surface is below the detection limit of the instrument (~1% or greater, Fig. 6). It is interesting to note that the Fe(II)/Fe(III) ratio of the pH 11 samples is generally lower than the expected ratio in magnetite (avg. ratio = 0.33, rather than the stoichiometrically expected value of 0.50). Spectra from the +1250 and -250 mV samples also show Fe 2p satellite peaks that are not present in magnetite, but are attributed to ferric Fe present in minerals such as hematite or maghemite. According to Peterson et al. (1997), this oxidized overlayer may be the formation of maghemite, which passivates the magnetite surface from further Cr reduction. In that particular study, passivation was observed at more neutral pH values, but may explain why Cr is not seen on the surface of the pH 11 samples in our experiments.

In summary, Cr deposited on the magnetite surface at pH 3 is entirely reduced Cr(III). Under very reducing conditions (-750 mV), the Cr 2p peak positions and peak separation suggest that Cr oxides and/or Fe-Cr oxides (such as Cr₂O₃ or FeCr₂O₄) are present, while a shift towards a slightly higher binding energies and evidence of hydroxylation may denote Cr (oxy)hydroxide phases are more stable and deposited on the surface under less reducing conditions (-250 mV). At pH 11, no Cr is observed due to partial oxidation and possible passivation of the surface by, *e.g.*, maghemite, which would inhibit reduction or dramatically impede the kinetics of the reaction.

3.3.2. Auger electron spectroscopy

In an effort to identify the phases observed to grow under oxidizing conditions, AES spectra were collected from samples polarized at highly oxidizing conditions at pH 3 (+1000 mV), pH 7 (−500 mV), and pH 11 (+500 mV). While there is some indication that Cr₂O₃ is present at pH 3, +1000 mV, this evidence is not conclusive. See Appendix D for further detail.

4. Conclusions

In this study, electrochemical and atomic force microscopy methods are combined in order to image the deposition of Cr on the surface of magnetite at variable Eh and pH conditions. With this method, reactions that occur over the entire Eh-pH range can be observed *in situ* and complemented with further analysis of the surface and the solution. In this system, quantitative analysis of the AFM images reveals that more Cr precipitation occurs at very positive and very negative redox potentials at pH 3 and 11. At pH 7, maximum growth occurs at −500 mV, while the total sorbate volume decreases over time at +750 mV. At pH 3, the growth observed under oxidizing conditions is dominated by rapid lateral growth and the nucleation of new 2D growth islands, while growth at more reducing potentials (−500 mV) occurs as a rapid initial deposition of larger particles that decreased in both height and diameter over the 30 minutes of polarization. At pH 11, vertical growth was the primary growth mechanism at both reducing and oxidizing conditions.

Concurrent batch chemistry experiments (and subsequent ICP-MS analysis) show total Cr removal from solution at all potentials at pH 7, about 60% removal of Cr from solution at all potentials at pH 3, and little Cr removal at pH 11. These observations are supported by results from XPS analyses of the magnetite surface. At pH 3, Cr(III) and/or Cr(III)-Fe(III) oxide phases are present at the surface for samples prepared under highly reducing conditions (−750 mV). At more moderately reducing potentials (*e.g.*, −250 mV), XPS analysis suggests the presence of Cr(III)-O-OH phases deposited on the surface. All Cr present on the magnetite appears to have reduced from Cr(VI) to Cr(III), although more definitive phase identification may require x-ray techniques with a higher degree of spatial resolution, such as synchrotron-based x-ray absorption spectroscopy

(XAS). No Cr was detected on the surface at pH 11, although elevated Fe(II)/Fe(III) and Fe(III) satellite structures indicate that the magnetite surface at pH 11 is slightly oxidized, and this oxidized overlayer may inhibit Cr(VI) reduction. AES analysis, which is slightly more surface sensitive than XPS, supports the presence of some Cr on the surface at pH 11; however, interpretations drawn from these spectroscopic analyses suffered due to overlap between the O KLL peaks from the substrate and Cr LMM peaks. The deposition observed at positive potentials may be $\text{Fe}_3(\text{CrO}_4)_2$, yet more work is needed for confirmation. Angle-dependent XPS or high resolution XAS are possible techniques that would help determine Fe/Cr ratios as a function of depth.

Through the direct control of the oxidizing and reducing conditions as well as pH, EC-AFM in concert with chemical analysis of the solid and liquid, this method presents a new way to study the effects of Eh and pH on the reductive precipitation of Cr(VI). While Eh-pH diagrams may be a first indication of which phases dominate at certain conditions, we see significant sorption where the stability diagram does not predicted a solid phase. For this system, the extension of thermodynamic databases to include less crystalline Cr hydroxide phases would provide a better description of sorption processes at a wide range of Eh conditions. With further improvements, this relatively underutilized method may be a helpful tool to study the deposition and dissolution of redox-active metals on semi-conducting mineral surfaces in a broader geochemical context.

Acknowledgements

The authors are grateful for the support from the grant EAR1223976 from the National Science Foundation. We also thank Jerry Li at EMAL (U of M) for his assistance with AES analysis.

References

- Baig, S.A., Wang, Q., Wang, Z.X., Zhu, J., Lou, Z.M., Sheng, T.T., Xu, X.H., 2014. Hexavalent chromium removal from solutions: surface efficacy and characterizations of three iron containing minerals. *CLEAN*, 42(10): 1409-1414.
- Bartlett, R.J., 1991. Chromium cycling in soils and water: links, gaps, and methods. *Environ. Health Perspect.* 92: 17-24.
- Becker, U., Rosso, K.M., Hochella Jr, M.F., 2001. The proximity effect on semiconducting mineral surfaces: a new aspect of mineral surface reactivity and surface complexation theory? *Geochim. Cosmochim. Acta* 65(16): 2641-2649.
- Biesinger, M., Brown, C., Mycroft, J., Davidson, R., McIntyre, N., 2004. X-ray photoelectron spectroscopy studies of chromium compounds. *Surf. Interface Anal.* 36(12): 1550-1563.
- Biesinger, M.C., Payne, B.P., Grosvenor, A.P., Lau, L.W., Gerson, A.R., Smart, R.S.C., 2011. Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe, Co and Ni. *Appl. Surf. Sci.* 257(7): 2717-2730.
- Buerge, I.J., Hug, S.J., 1997. Kinetics and pH Dependence of Chromium(VI) Reduction by Iron(II). *Environ. Sci. Technol.* 31(5): 1426-1432.
- Cornell, R.M., Schwertmann, U., 2006. The iron oxides: structure, properties, reactions, occurrences and uses. John Wiley & Sons.
- De Yoreo, J.J., Vekilov, P.G., 2003. Principles of crystal nucleation and growth. *Reviews in mineralogy and geochemistry*, 54(1): 57-93.
- Elsner, M., Haderlein, S.B., Kellerhals, T., Luzi, S., Zwank, L., Angst, W., Schwarzenbach, R.P., 2004. Mechanisms and products of surface-mediated reductive dehalogenation of carbon tetrachloride by Fe(II) on goethite. *Environ. Sci. Technol.* 38(7): 2058-2066.
- Etienne, M., Schulte, A., Mann, S., Jordan, G., Dietzel, L.D., Schuhmann, W., 2004. Constant-distance mode scanning potentiometry. 1. Visualization of calcium carbonate dissolution in aqueous solution. *Anal. Chem.* 76(13): 3682-3688.
- Fendorf, S., Wielinga, B.W., Hansel, C.M., 2000. Chromium transformations in natural environments: The role of biological and abiological processes in chromium(VI) reduction. *Int. Geol. Rev.* 42(8): 691-701.
- Flury, B., Frommer, J., Eggenberger, U., Mäder, U., Nachtegaal, M., Kretzschmar, R., 2009. Assessment of long-term performance and chromate reduction mechanisms in a field scale permeable reactive barrier. *Environ. Sci. Technol.* 42(8): 691-701.
- Gheju, M., 2011. Hexavalent chromium reduction with zero-valent iron (ZVI) in aquatic systems. *Water Air Soil Poll.* 222(1-4): 103-148.
- Harvey, D.T., Linton, R.W., 1981. Chemical characterization of hydrous ferric oxides by X-ray photoelectron spectroscopy. *Anal. Chem.* 53(11): 1684-1688.
- Higgins, S.R., Hamers, R.J., 1995. Spatially-resolved electrochemistry of the lead sulfide (galena) (001) surface by electrochemical scanning tunneling microscopy. *Surf. Sci.* 324(2-3): 263-281.
- Higgins, S.R., Hamers, R.J., 1996. Chemical dissolution of the galena(001) surface observed using electrochemical scanning tunneling microscopy. *Geochim. Cosmochim. Acta.* 60(16): 3067-3073.

- Higgins, S.R., Hamers, R.J., Banfield, J.F., 1996. In-situ real-time imaging of the surface reactions of metal sulfide minerals with electrochemical STM. *Abstr. Pap. Am. Chem. Sci.* 211: 70-COLL.
- Hyland, M.M., Bancroft, G.M., 1990. Palladium sorption and reduction on sulphide mineral surfaces: An XPS and AES study. *Geochim. Cosmochim. Acta.* 54(1): 117-130.
- Jung, Y., Choi, J., Lee, W., 2007. Spectroscopic investigation of magnetite surface for the reduction of hexavalent chromium. *Chemosphere*, 68(10): 1968-1975.
- Kendelewicz, T., Liu, P., Doyle, C., Brown, G., Nelson, E., Chambers, S., 1999. X-ray absorption and photoemission study of the adsorption of aqueous Cr (VI) on single crystal hematite and magnetite surfaces. *Surf. Sci.* 424(2): 219-231.
- Kendelewicz, T., Liu, P., Doyle, C.S., Brown Jr, G.E., 2000. Spectroscopic study of the reaction of aqueous Cr(VI) with Fe₃O₄ (111) surfaces. *Surf. Sci.* 469(2-3): 144-163.
- Kleber, R., Helz, G., 1992. Indirect photoreduction of aqueous chromium (VI). *Environ. Sci. Technol.*, 28: 307-312.
- McCafferty, E., Bennett, M.K., Murday, J.S., 1988. An XPS study of passive film formation on iron in chromate solutions. *Corros. Sci.* 28(6): 559-576.
- Otsu, N., 1979. Threshold selection method from gray-level histograms. *Ieee Transactions on Systems Man and Cybernetics*, 9(1): 62-66.
- Peterson, M.L., Brown Jr, G.E., Parks, G.A., 1996. Direct XAFS evidence for heterogeneous redox reaction at the aqueous chromium/magnetite interface. *Colloids Surf. A.* 107: 77-88.
- Peterson, M.L., Brown Jr, G.E., Parks, G.A., Stein, C.L., 1997. Differential redox and sorption of Cr (III/VI) on natural silicate and oxide minerals: EXAFS and XANES results. *Geochim. Cosmochim. Acta.* 61(16): 3399-3412.
- Rai, D., Eary, L., Zachara, J., 1989. Environmental chemistry of chromium. *Sci. Total Environ.* 86(1): 15-23.
- Rai, D., Sass, B.M., Moore, D.A., 1987. Chromium (III) hydrolysis constants and solubility of chromium (III) hydroxide. *Inorg. Chem.* 26(3): 345-349.
- Renock, D., Becker, U., 2010. A first principles study of the oxidation energetics and kinetics of realgar. *Geochim. Cosmochim. Acta.* 74(15): 4266-4284.
- Riou, A., Bonnin, A., 1978. Structure cristalline de Fe₂(CrO₄)₃(H₂O)₃ alpha. *Acta Crystallographica B*, 24: 706-709.
- Rosso, K.M., Becker, U., 2003. Proximity effects on semiconducting mineral surfaces II:: Distance dependence of indirect interactions. *Geochim. Cosmochim. Acta.* 67(5): 941-953.
- Sibanda, H., Young, S., 1986. Competitive adsorption of humus acids and phosphate on goethite, gibbsite and two tropical soils. *J. Soil Sci.* 37(2): 197-204.
- Sokołowska, M., Bal, W., 2005. Cu(II) complexation by “non-coordinating” N-2-hydroxyethylpiperazine-N’ -2-ethanesulfonic acid (HEPES buffer). *J. Inorg. Biochem.* 99(8): 1653-1660.
- Stack, A.G., 2008. Applications of electrochemical scanning tunneling microscopy to adsorption and thin films in geochemical systems. *Abstr. Pap. Am. Chem. Sci.* 235.

- Stack, A.G., Eggleston, C.M., Engelhard, M.H., 2004a. Reaction of hydroquinone with hematite I. Study of adsorption by electrochemical-scanning tunneling microscopy and X-ray photoelectron spectroscopy. *J. Colloid Interface Sci.* 274(2): 433-441.
- Stack, A.G., Erni, R., Browning, N.D., Casey, W.H., 2004b. Pyromorphite growth on lead-sulfide surfaces. *Environ. Sci. Technol.* 38(21): 5529-5534.
- Suzuki, S., Oku, M., Waseda, Y., 1997. Changes in the Chemical State and Composition of the Clean Surface of K_2CrO_4 and $K_2Cr_2O_7$ due to Air Exposure and Argon Ion Bombardment. *Surf. Interface Anal.* 25(3): 161--166.
- Taylor, S.D., Marcano, M.C., Rosso, K.M., Becker, U., 2015. An experimental and ab initio study on the abiotic reduction of uranyl by ferrous iron. *Geochim. Cosmochim. Acta.* 156(0): 154-172.
- Taylor, S.D., Powell, B.A., Becker, U., in rev. Influence of the goethite (α -FeOOH) surface on the stability of distorted fcc PuO_2 and PuO_{2-x} phases. *Surf. Sci.*
- Tessis, A.C., Penteado-Fava, A., Pontes-Buarque, M., De Amorim, H.S., Bonapace, J.A., de Souza-Barros, F., Vieyra, A., 1999. Pyrite suspended in artificial sea water catalyzes hydrolysis of adsorbed ATP: enhancing effect of acetate. *Orig. Life Evol. Biosph.* 29(4): 361-374.
- Ünveren, E., Kemnitz, E., Hutton, S., Lippitz, A., Unger, W., 2004. Analysis of highly resolved x - ray photoelectron Cr 2p spectra obtained with a Cr_2O_3 powder sample prepared with adhesive tape. *Surf. Interface Anal.* 36(1): 92-95.
- Vorlicek, T.P., Helz, G.R., 2002. Catalysis by mineral surfaces: implications for Mo geochemistry in anoxic environments. *Geochim. Cosmochim. Acta.* 66(21): 3679-3692.
- Wandelt, K., 1982. Photoemission studies of adsorbed oxygen and oxide layers. *Surf. Sci. Rep.* 2(1): 1-121.
- Welch, K.D., Davis, T.Z., Aust, S.D., 2002. Iron autoxidation and free radical generation: Effects of buffers, ligands, and chelators. *Arch. Biochem. Biophys.* 397(2): 360-369.
- White, A.F., Peterson, M.L., Hochella Jr, M.F., 1994. Electrochemistry and dissolution kinetics of magnetite and ilmenite. *Geochim. Cosmochim. Acta.* 58(8): 1859-1875.
- WHO, 2011. Guidelines for drinking water quality, 4th ed. Geneva: World Health Organization.
- Wigginton, N.S., Rosso, K.M., Stack, A.G., Hochella, M.F., 2009. Long-range electron transfer across cytochrome-hematite (α -Fe $_2$ O $_3$) interfaces. *J. Phys. Chem. C*, 113(6): 2096-2103.
- Yamashita, T., Hayes, P., 2008. Analysis of XPS spectra of Fe $^{2+}$ and Fe $^{3+}$ ions in oxide materials. *Appl. Surf. Sci.* 254(8): 2441-2449.
- Yuan, K., Ilton, E.S., Antonio, M.R., Li, Z.R., Cook, P.J., Becker, U., 2015. Electrochemical and spectroscopic evidence on the one-electron reduction of U(VI) to U(V) on magnetite. *Environ. Sci. Technol.* 49(10): 6206-6213.

Appendix A

A.1. Schematic of electrochemical AFM cell

Figure A1 presents a diagram of the electrochemical AFM cell used in these experiments.

Appendix B

B.1. Detailed description of image analysis procedure:

The raw data from each AFM image is exported as a 3-dimensional height matrix that preserves the topography of the surface as a function of the x and y location of the scanned area. Using the MATLAB script described in the Methods section, a user-defined structural element is chosen in order to identify features of interest on the surface and estimate the background, or the part of the image considered to be the magnetite substrate. This structural element is typically a circular disk that distinguishes surface elements; increasing the size of this disk allows for larger elements on the surface to be selected (and *vice versa* for a smaller disk), and the remainder is characterized as the background. These features are confirmed through visual selection, and the background is subtracted from the original grayscale image. With the background-subtracted image, the contrast is increased so that the selected features on the surface are easier to identify. Figure B1 presents each of these steps in detail, beginning with the original grayscale image (A), the original image minus the background (B), and the enhanced contrast image (with background subtracted) (C). At this step, the enhanced contrast images are converted to a black and white image by another user-defined threshold (D). Based on this black and white image, a binary array is created that indicates where sorbates are present (white) and where they are not (black). The number and size (volume and area) of the sorbates are calculated by combining this binary array with the image height information from the raw AFM data. Each image, normalized by the number of samples per line, represents one data point for each of the volume, area, size, and number of sorbate plots (Fig. 3) Figure B1 also shows a 3D model of the derived background (E), which highlights some of the surface defects and polishing grooves, which may influence the absolute values for the sorbate size and shape calculated with this method. For this reason, it is recommended that overall trends be emphasized more than absolute numbers.

792	Appendix C
793	C.1. Extended description of redox processes at pH 11
794	

In this section, further description, explanation, and interpretation of EC-AFM images at pH 11 and pH 3 are provided. During negative polarization at pH 11, two types of growth features appear on the magnetite surface: pseudo-rhombohedral and larger, spheroidal particles. Some of the rhombic particles appear to grow on top of and slightly adjacent to one another, such as those outlined in the panels labeled 9 and 22 minutes in Fig. C1. This type of crystallographically directed growth may indicate epitaxial or parallel growth on the surface. Crystal intergrowths are about equal in size, and their offset is approximately one-half of the length of each feature (50-60 nm). Epitaxial relationships may limit the size of each rhombic sorbate, which would explain the occurrence of more sorbates at more negative potentials instead of continued growth of individual particles. The semi-spheroidal particles are significantly larger than the rhombic; their diameters range from 200-600 nm with a height on the order of 20 nm. Over time (and particularly after 30 minutes), these semi-spheroidal particles diffuse towards each other to form a central particle with smaller pseudo-spheres on the periphery.

The semi-spheroidal particles are significantly larger than the rhombic; their diameters range from 200-600 nm with a height on the order of 20 nm. Over time (and particularly after 30 minutes), these semi-spheroidal particles diffuse towards each other to form a central particle with smaller pseudo-spheres on the periphery. This growth is shown in the lower panels of Fig. C1. The pseudo-spherical sorbates appear to lack a crystallographic or structural relationship to the magnetite substrate, which suggests they are mostly amorphous unlike the pseudo-rhombohedral. Since there is less of an epitaxial relationship between the semi-spheroidal particles and the magnetite surface, which would result in a crystallographic mismatch at a given size, growth of the semi-spheroidal sorbates is uninhibited. In addition, the fact that the semi-spheroidal features are more prone to surface diffusion indicates that they have a smaller (*i.e.*, less negative) interface energy between the sphere-magnetite interface compared to the rhombohedron-magnetite interface. One candidate for such a phase is poorly crystalline chromium hydroxide (Rai et al., 1989; Rai et al., 1987).

C.2. Extended description of redox processes at pH 3

Figures C2 and C3 provide lateral vs. vertical growth analyses for polarization at -500 mV and $+1000$ mV. After an initial burst of growth at -500 mV, the total volume decreases, although the number of particles increases from ~ 70 to 180 (Fig. C2). The average particle length and average height decrease at approximately the same rate. Such a rapid precipitation event may be due to the disequilibrium cause by the initial polarization at very reducing conditions followed by a slow return to a quasi-steady state. At $+1000$ mV, there is an increase in volume of total adsorbate of $\sim 30\%$ within 30 minutes (Fig. C3). This increase in volume is solely due to an increase in surface coverage, *i.e.* lateral growth, as shown by the overlap of the scaled volume and scaled area in Fig. C3. Scaling the square root of the surface area shows that this length dimension slightly increases during the ~ 30 minutes of polarization and that the entire volume also increases for the experimental settings used. Such an increase in newly-formed adsorbates would normally be expected in a highly-supersaturated state that is, according to classical crystal growth theory, dominated by two-dimensional nucleation (De Yoreo and Vekilov, 2003).

Appendix D

D. 1. Auger electron spectroscopy

At pH 3, Cr Auger peaks were observed for features resembling the particles imaged in the AFM (Fig. D1). Cr has five Auger lines, although two of these have very low kinetic energies and are difficult to distinguish above the background. The most significant peaks occur at ~ 490 , 530 , and 560 eV, all of which are LMM transitions, yet we will focus on the 490 eV peak; the 530 eV line is almost entirely overwhelmed by the strong O KLL line, and the 560 eV peak is relatively weak in comparison. While it is common practice to differentiate AES spectra due to the broad shape of many Auger lines, here, we show the undifferentiated spectra in order to emphasize the contrast in shape for this set of peaks. The shapes of Auger peaks are potentially very sensitive to changes in chemistry and atomic arrangement of a given compound, especially if the Auger transition involves valence electrons. This particular energy range includes the Cr LMM peak at ~ 490 eV and the O KLL peak at ~ 510 eV, both of which involve two valence electrons for each transition. All three spectra closely resemble the spectrum for

magnetite, including two relatively strong energy loss lines on the lower kinetic energy side of the O KLL peak at 510 eV. The overlap of the O KLL peak with the Cr LMM peak at 490 mV complicates the identification and interpretation of Cr peaks; however, the Cr LMM peak from the first analysis spot is asymmetric and has a distinct shoulder on the lower kinetic energy side of the peak. The O KLL peak for spot 1 is also asymmetric with a similar shoulder feature. The O KLL peaks were manually aligned at 510 eV in order to emphasize peak shape and to correct for surface charging; this shift was less than 1.7 eV. The presence of these shoulders can either indicate the presence of multiple bond types (*e.g.*, the main O peak could be attributed to oxygen bonded to Fe or Cr, and the shoulder with a lower kinetic energy could be due to O bonded to H) or a different structural environment for that particular element. In an attempt to identify the chemical and oxidation state of Cr from the spectra collected from the magnetite surfaces, AES spectra were collected from three Cr reference compounds with Cr in three different oxidation states: Cr⁰ (Cr metal), Cr³⁺ (eskolaite, Cr₂O₃), and Cr⁶⁺ (crocoite, PbCrO₄, Fig. D2). Because Cr₂O₃ and PbCrO₄ are insulating minerals, the beam energy used to collect these spectra was 3 keV in order to reduce the amount of peak shift due to charging, which explains why the O KLL line is closer to 515 eV. Beam energy does not affect peak morphology. Assigning oxidation states with AES can be quite challenging due to a high background signature, the broad nature of Auger peaks, and the high potential for peak overlap from Auger transitions involving shallow atomic levels; however, we can say with some certainty that Cr⁰ is not likely present on this magnetite surface (pH 3, +1000 mV). The shape of the Cr LMM 490 eV peak for Cr⁰ is sharp and slightly shifted towards higher kinetic energies, which is not consistent with the Cr measured in the pH 3, +1000 mV sample. On the other hand, Cr₂O₃ provides an Auger line that is most similar to the Cr LMM peak for the first spot analysis: a strong peak close to 490 eV and a shoulder on the lower kinetic energy side. This comparison provides some evidence that the particle analyzed contains Cr(III) as in Cr₂O₃ or FeCr₂O₄. Spots 2 and 3 are identical to the magnetite reference spectrum.

At pH 7, AES spectra of the magnetite surface were taken after 30 minutes of polarization at -500 mV (SEM image of scan area and undifferentiated spectra shown in Fig. D3). In the SEM image, a precipitate is shown in white (labeled 'sorbate') on top of

the darker magnetite substrate. The sorbate material contains some amount of Ti (that was dissolved, as an impurity, out of the magnetite substrate), evident by the Ti LMM transition labeled in the AES spectrum. At 498 eV, the energy loss feature produced from the O KLL transition in the magnetite has a distinct shoulder on the higher kinetic energy side of the peak. This shoulder is possibly produced by the overlap with the Cr LMM peak at ~490 eV. The AES reference spectrum for chromite is also presented in Fig. D3; however, there is no clear indication that chromite contributes to the Cr shoulder feature.

AES spectra were also collected from the Cr-sorbed magnetite surface prepared at pH 11, +500 mV. The presence of semi-spheroidal particles deposited homogeneously on the surface distinguishes this sample from the pH 3 and pH 7 samples (Fig. D4). These particles are also present in AFM images acquired under similar oxidizing conditions. The AES spectrum for these particles does contain Cr LMM peaks around 490 eV (as a shoulder) and 530 eV (labeled with arrows in Fig. D5). Unfortunately, these peak positions as well as their morphology are similar to the peaks in both Cr₂O₃ and PbCrO₄ reference spectra, and the Cr oxidation state cannot be confidently identified. At pH 11, the magnetite surface is positively charged, and less adsorption of CrO₄²⁻ would occur. If all the Cr in solution is present as Cr(VI), it is conceivable that these particles are an Fe(III) chromate phase, *e.g.*, Fe₂(CrO₄)₃·3 H₂O (Riou and Bonnin, 1978).

Figure 1 caption: Eh-pH diagram of chromium at the experimental conditions (2 μM chromate solution). Modeled with Geochemists' Workbench LLNL thermodynamic database.

Figure 2 caption: Fig. 2. EC-AFM height and Peak Force Error (PFE) images. A-C: pH 11, D-F: pH 7, G-K: pH 3. A. Color bar: $\pm 18\text{ nm}$. Open circuit potential (OCP): height (A1), PFE (A2). B. Color bar: $\pm 18\text{ nm}$. Polarization -250 mV , 20 min: height (B1), PFE (B2). White outlines highlight rhombic growth features. C. Color bar: $\pm 50\text{ nm}$. Polarization $+1000\text{ mV}$, 13 min: height (C1), PFE (C2). White squares indicate new growth at this potential. D. Color bar: $\pm 50\text{ nm}$. OCP: height (D1), PFE (D2). E. Color bar: $\pm 50\text{ nm}$. Polarization $+750\text{ mV}$, 21 min: height (E1), PFE (E2). F. Color bar: $\pm 50\text{ nm}$. Polarization -500 mV , 28 min: height (F1), PFE (F2). G. Color bar: $\pm 40\text{ nm}$. Polarization $+1000\text{ mV}$, 13.5 min: height (G1), PFE (G2). (H-K) Color bar: $\pm 40\text{ nm}$. Polarization -500 mV , PFE, 4.5 min (H), 9 min (I), 13.5 min (J), 18 min (K). White dashed line in (H) shows where polarization began.

Fig. 3. Sorbate quantification from EC-AFM images at pH 3, 7, and 11. (A) Total sorbate volume. – 250 mV A and –250 mV B represent two different series of AFM images scanned over different areas of the surface. (B) Volume/sorbate area. (C) Percentage of surface coverage. (D) Number of sorbates plotted over time.

Figure 4 caption: A comparison of volumetric growth dimensions at pH 11, -750 (A) and +500 mV (B). The total volume and the total area covered by adsorbates (scaled for clarity) are plotted in dark blue and black, respectively. A more rapid increase in total volume versus area implies that growth on the surface is predominantly vertical at -750 mV. Growth at +500 mV is both lateral and vertical at approximately equal rates, given the 60% increase in total volume and 48% increase in area.

Figure 5 caption: Changes in total dissolved Cr concentration as a function of time and Eh at pH 3 and 11. Most of the Cr stays in solution at pH 11. However, at pH 3, Cr concentration decreases more at very high and very low potentials.

Figure 6 caption: XPS Cr 2p and O 1s spectra. Peak positions shown are the result of single peak fitting. The Cr 2p_{3/2} and 2p_{1/2} peaks are clearly visible in the spectra for samples prepared at pH 3; however, Cr 2p peaks do not appear in the pH 11 spectra. This implies that any Cr on the surface is below the detection limit of the instrument.

Figure 7 caption: Comparison of O 1s core spectra for unreacted magnetite, Cr_2O_3 , and the magnetite sample polarized for 20 minutes at -250 mV, pH 3.

Appendix I - Simplified schematics of a second generation electrochemical cell. Figure modified from Bruker.

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Figure A1 caption: Schematic of electrochemical AFM cell

Figure B1 caption: Detail of image analysis procedure for sorbate quantification. (A) Original grayscale image. (B) Original image minus script-generated background. (C) Enhanced contrast image. (D) Black and white binary image. (E) 3D background model.

Figure C1 caption: Particle growth during polarization of the magnetite electrode at -750 mV as a function of time. Each image (which is peak force error data) was scanned in sequence. New growth features are marked by the white rectangles.

Figure C2 caption: Lateral vs. vertical growth at pH 3, -500 mV. The total volume decrease after ca. 35 minutes of reaction likely due to rapid initial precipitation followed by the dissolution of larger particles, shown here by decreasing average particle length (green line).

Figure C3 caption: Lateral vs. vertical growth at pH 3, +1000mV. Growth at pH 3, +1000 mV is primarily lateral, illustrated by the overlapping of the total volume and total area curves.

Figure D1 caption: SEM image (A) and undifferentiated Auger spectra (B) collected from pH 3, +1000 mV magnetite surface. Three analysis spots are labeled in the SEM image, and their corresponding spectra are shown from 450 to 550 eV. The first spot measured was focused on a particle $\sim 1 \mu\text{m}$ in diameter, the second spot on a flat, white feature, and the third spot on the “background” magnetite. The spectrum for point 1 has asymmetric Cr LMM and O KLL lines, which could indicate that multiple Cr phases are present, including Cr_2O_3 .

Figure D2 caption: Overlay of Auger spectra between 450 and 550 eV for Cr in three oxidation states: Cr⁰ (Cr standard), Cr³⁺ (Cr₂O₃), and Cr⁶⁺ (PbCrO₄).

Figure D3 caption: SEM image (A) and AES spectra (B) of pH 7 surface. The white sorbate material labeled in the SEM image contains Ti as well as Cr. The Cr LMM peak at ~ 490 eV creates a shoulder on the higher kinetic energy side of the O KLL energy loss feature from the magnetite substrate (highlighted in the red circle). A chromite AES spectrum (scaled for clarity) is also shown. Spectra are shifted to the background O KLL peak to account for peak shifts due to charging.

Figure D4 caption: Secondary electron images of particles on the surface of magnetite deposited at pH 11, +500 mV, taken using the Auger Nanoprobe. (A) Low resolution. (B) High resolution.

Figure D5 caption: AES spectrum for pH 11, +500 mV. Arrows indicate the presence of Cr peaks at ca. 490 and 530 eV, although the Cr oxidation state cannot be identified from this spectrum. It is possible that under oxidizing conditions, $\text{Fe}_2(\text{CrO}_4)_3 \cdot 3(\text{H}_2\text{O})$ can precipitate on the surface.