MINERALOGICAL AND GEOCHEMICAL CONSTRAINTS ON CHROMIUM
OXIDATION INDUCED BY BIRNESSITE

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Abstract

Manganese (Mn) oxides are highly redox active minerals that are pervasive in soils and sediments on the surface of the Earth. Mn oxides are the only minerals known to oxidize Cr(III) to Cr(VI) in both experimental and natural systems. Cr(VI), a mobile contaminant in groundwater, can promote carcinogenesis in humans. Cr(III), however, is a nonreactive trace metal essential for glucose uptake by mammals. Among all Mn oxide polymorphs, birnessite induces the fastest oxidation kinetics and the highest reactivity with Cr(III). However, the mechanism of electron transfer between dissolved Cr and Mn oxide particles, particularly with respect to birnessite, is poorly understood. Mitigation and remediation of Cr(VI) requires a quantitative knowledge of this mechanism.

Here we present a novel method for simultaneous measurement of the birnessite structure and the extent of Cr oxidation at different solution pH conditions. We collected time-resolved synchrotron X-ray diffraction (TR-XRD) and X-ray Absorption Near Edge Structure (XANES) patterns of triclinic Na-birnessite every 15 minutes while passing pH controlled 1.0 mM Cr(III) nitrate solutions through a capillary cell. In addition, we quantified Cr(VI) concentrations of the eluate solution every 150 minutes using spectrophotometry.

Consistent with Fendorf and Zasoski (1992), we observed an increased rate of Cr(VI) production with decreasing pH. We attribute the comparatively slow kinetics of Cr(III) oxidation at pH 5.0 and 4.0 to a transformation from triclinic to hexagonal birnessite. This solid-state transition reproducibly coincided with a ~10-fold decline in the oxidation of aqueous Cr(III). In the presence of triclinic birnessite, 25 mol% of the influent Cr(III) was oxidized to Cr(VI), dropping to 3 mol% after the transformation to hexagonal birnessite. Control experiments without Cr(III) revealed no evidence for birnessite transformation within the same
time range, and experiments with hexagonal birnessite as the starting material generated solutions with low concentrations (~3 mol%) of dissolved Cr(VI) from start to finish.

At pH 3.0 and 2.0, however, production of Cr(VI) was consistently higher than was observed at pH 5.0 and 4.0. Specifically, at pH 2, 80 mol% of the influent Cr(III) was oxidized to Cr(VI) for the duration of the experiment. In addition, we monitored the continuous elution of aqueous Mn(II) at pH 3.0 and 2.0, whereas we found little evidence for aqueous Mn(II) in solutions at pH 5.0 and 4.0. We detected no crystalline Cr (hydr)oxide precipitates during the reactions at any pH. XANES analysis showed evidence for both Cr (III) and Cr(VI) adsorbing onto the surface of birnessite at all pH concentrations.

We propose that Cr(III) is oxidized to Cr(VI) by an electron exchange that reduces Mn(III) in birnessite to Mn(II). At pH 3.5 and higher, the structure of birnessite consequently transforms to hexagonal birnessite. By this pathway, the birnessite crystal structure critically controls the oxidation of dissolved Cr(III) due to the accessibility of reactive Mn(III) in triclinic birnessite relative to hexagonal birnessite. Below pH 3.5, however, birnessite dissolution systematically exposes reactive sites that enable the continuous oxidation of Cr(III) to Cr(VI).
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Introduction

The heavy metal chromium (Cr) is the twenty-first most abundant element on the Earth’s crust, existing at an average concentration of 100 µg/g (Nriagu and Nieboer, 1988). Cr is most abundant in ultramafic rocks, and soils derived from such weathered rocks contain high amounts of Cr (Matzat and Shiraki, 1974). More than 30,000 tons of Cr waste are generated each year from a variety of industrial applications such as chrome plating, pigment production, and leather tanning (Shi et al., 1991). Among industrialized countries across the globe, Cr is the most common redox-active inorganic groundwater contaminant (Nriagu and Nieboer, 1988).

The two stable oxidation states of dissolved Cr, Cr(III) and Cr(VI), pose markedly different health hazards to humans (Shi et al., 1991). The relatively immobile Cr(III) is an essential nutrient for glucose metabolism in mammals, whereas labile Cr(VI) is a toxin that causes skin lesions, lung disease, and carcinogenesis (Sanz, 1989; Costa, 1997). The carcinogenicity of Cr(VI) arises through cellular uptake and reduction to the relatively insoluble Cr(III) by glutathione (GSH), ascorbic acid (AA), hydrogen peroxide (H₂O₂), NADPH, and certain enzymes such as GSH reductase (Cieślak-Golonka, 1996). The intracellular reduction of Cr(VI) to lower oxidation states [Cr(V) and Cr(IV)] causes DNA lesions (DNA base modification, protein cross links) and chromosomal mutations (Shi et al., 1991). In vitro studies have shown that chromium’s reactive intermediates induce DNA strands to break. In addition, free radicals generated from reduction have significant carcinogenic implications, causing direct cellular damage or producing H₂O₂ that can re-oxidize Cr(III) to Cr(VI) (Kortenkamp et al., 1989; De Flora et al., 1990).

Manganese (Mn) oxides are the only class of minerals known to oxidize Cr(III) to Cr(VI) (Bartlett and James, 1979; Eary and Rai, 1987). In addition to numerous laboratory experiments
that have documented the transformation of Cr(III) to Cr(VI) by Mn oxides (Eary and Rai, 1987; Fendorf and Zasoski, 1992; Manceau and Charlet, 1992; Weaver and Hochella, 2003; Landrot et al., 2012b), two field studies have shown that aqueous Cr can be oxidized by Mn oxides. Oze et al. (2007) report that birnessites mediate the oxidation of Cr(III) released to solution during the weathering of ultramafic and serpentinitic soils and sediments. In addition, Fandeur et al. (2009) report Cr(III) oxidation in the presence of Mn oxides in lateritic regolith.

In addition to environmental concerns, understanding the oxidation of Cr(III) may provide further insight into Precambrian atmospheric oxygenation. Fractionation of Cr following oxidation can serve as a proxy for atmospheric oxygenation (Frei et al., 2009). Cr isotope data from banded iron formations and mid-Proterozoic sediments containing ironstones from ~2.6-2.8 Ga and ~0.8 Ga indicate two periods of significant Cr isotope fractionation in the rock record, indicating a rise in the oxidation of Cr(III) to Cr(VI) (Frei et al., 2009; Planavsky et al., 2014). However, in order to understand fully how Cr isotopic data are related to the rise of atmospheric oxygen, the process of Cr(III) oxidation to Cr(VI) by Mn oxides must be better understood.

Over thirty varieties of manganese (Mn) oxides exist in various geological settings as nodules, desert varnishes, fine-grained concretions, and aggregates (Post, 1999). Many Mn oxides participate in redox and cation exchange reactions in soils (Negra et al., 2005; Lopano et al., 2007; Fleeger et al., 2013; Fischel et al., 2015). Their reactivity is due to their open tunnel or layered crystal structures, and by their fine grain sizes with concomitantly high surface areas. In addition, most Mn oxides have a low point of zero charge (PZC), and thus have a high capacity for adsorbing cations to the mineral surface in circumneutral fluids (Yu, 1997). Consequently, even trace amounts of Mn oxides can influence the chemistry of sediments and the coexisting aqueous system.
The birnessite group of Mn oxides occurs commonly in surficial, wet sediments and soils, and birnessites are among the most chemically active manganates (Post, 1999). For example, Weaver and Hochella (2003) observed that birnessite induces the fastest Cr oxidation kinetics among Mn oxides (namely hausmannite, manganite, romanechite, cryptomelane, lithiophorite, pyrolusite, and birnessite). Birnessite consists of octahedrally coordinated Mn oxide sheets with cations between the layers, and it occurs with two distinct structural symmetries: triclinic and hexagonal (Figure 1a).

Triclinic Na-birnessite has fully occupied octahedral sheets, with Mn predominantly in the tetravalent and trivalent oxidation states. X-ray photoelectron spectroscopy (XPS) analyses reveal fractions of 2 mol% Mn(II), 38 mol% Mn(III), and 68 mol% Mn(IV) in synthetic triclinic Na-birnessite (Ilton et al., 2016; Figure 1b). Molecular water groups coordinate Na\(^+\) cations within the interlayer (Post et al., 2002; Cygan et al., 2012).

In contrast, hexagonal birnessites have more Mn(II) and less Mn(III) in their structures (Silvester et al. 1997; Manceau et al. 2012). An XPS analysis of hexagonal H-birnessite yielded approximately 10 mol% Mn(II), 22 mol% Mn(III), and 68 mol% Mn(IV) (Ilton et al., 2016). Between 10 and 30 mol% of the octahedral sites in hexagonal birnessites may be vacant, with Mn(II), Ca(II), Zn(II), or other cations located in the interlayer above the vacancy sites (Silvester et al., 1997; Lanson et al., 2000; Fleeger et al., 2013). Mn(III) coordinated with 6 oxygen anions in the octahedral sheet of birnessite creates Jahn-Teller distortions along the a- and b- axes. Consequently, triclinic birnessite exhibits a lower symmetry than does hexagonal birnessite, which has a higher Mn(IV):Mn(III) ratio.

Although some researchers have argued that a disordered hexagonal birnessite, sometimes described as δ-MnO\(_2\), is the only variety that occurs naturally (Luther and Popp,
2002; Villalobos et al., 2003), several recent investigations have documented that both triclinic and hexagonal birnessite co-exist in natural settings (Tan et al., 2010; Shiraishi et al., 2016). Natural birnessites typically are poorly crystalline; however, they yield very broad X-ray diffraction peaks, so that an array of spectroscopic and diffraction approaches is required to determine the structural symmetry of the material (e.g., Bargar et al. 2009; Ling, 2016). Consequently, synthetic birnessites are used as analogs to their natural counterparts in order to correlate crystal structure with reactivity.

Previous work has demonstrated that the chemistry of the solid can impact the redox chemistry of Cr in solution. Using X-ray photoelectron spectroscopy (XPS), Banerjee and Nesbitt (1999) determined that Cr(III) adsorbs to the birnessite surface and undergoes a subsequent electron exchange with Mn(IV) and Mn(III). They infer that Mn(IV) primarily controls the oxidation of Cr(III), and that intermediate products of Cr(IV) and Cr(V) form before stabilizing into Cr(VI).

Although these and other researchers have argued that Mn(IV) is capable of oxidizing Cr(III) (e.g., Manceau and Charlet 1992; Banerjee and Nesbitt 1999; Kim et al. 2002; Negra et al. 2005), many studies provide convincing results that, relative to Mn(IV), Mn(III) is even more effective in driving the oxidation of Cr(III) (Weaver and Hochella 2003; Simanova and Peña 2015). In their study of the oxidation of Cr(III) by Mn oxides, Weaver and Hochella (2003) argue that Mn(III)-rich phases are particularly reactive oxidants when Mn(II) is also present, because the combination of reducible Mn(III) and highly soluble Mn(II) can promote Cr(III) oxidation when a fresh Mn(III)-rich surface is exposed during dissolution.

Since the oxidation of Cr(III) presumably is accompanied by the reduction of Mn(III), and possibly Mn(IV), the reaction between Cr(III) and birnessite must impact the crystal
chemistry of the birnessite as well. Time-resolved X-ray diffraction experiments by Fischer (2011) suggested a feedback between dissolved Cr(III) and birnessite, and this work established that dissolved Cr(III) induces a transformation from triclinic Na-birnessite to hexagonal H-birnessite over an order of magnitude more rapidly than did control solutions without dissolved Cr(III). Fischer’s (2011) study, however, did not explicitly monitor the production of aqueous Cr(VI) during this birnessite transition.

The pH of the solution also plays a significant role in Cr(III) oxidation mediated by Mn oxides. Fendorf and Zasoski (1992) analyzed the oxidation state of Cr in solution using UV-Vis spectrometry upon reaction with δ-MnO₂. They posit that the rate of Cr(III) oxidation increases at lower pH, and adsorption of the Cr species is favored at higher pH. While the results of Fendorf and Zasoski (1992) and Landrot et al. (2012b) clearly demonstrate higher rates of Cr(III) oxidation at pH 3.0 and 3.5 than at pH 4.0 and 5.0, the explanations for such a difference have been controversial. One model suggests that the differences in the surface charge of birnessite may explain this disparity. The PZC of δ-MnO₂ has been estimated to be approximately 2.7 to 2.8 (Morgan and Stumm, 1964; Fendorf and Zasoski, 1992). The surface of birnessite will become more negatively charged as pH increases beyond 3; thus, sorption of Cr(III) is expected to be increasingly favored at pH 3.0, 4.0, and 5.0. Indeed, Fendorf and Zasoski (1992) measured decreased total Cr concentrations in their reacted aqueous product at higher pH through ICP-optical emission spectroscopy (ICP-OES), indicating that more Cr had been taken up by the solid material with increasing pH.

Although the higher affinity for adsorption at higher pH would lead to increased loading of Cr(III) on the birnessite surface, the oxidation kinetics actually decreased at pH 4.0 and 5.0 (Fendorf and Zasoski, 1992). This paradox may be a consequence of inhibitory mechanisms that
limit the oxidation of Cr at pH greater than 3. Phase equilibria models support the idea that blocked surface sites at higher pH inhibit the oxidation of Cr(III) by birnessite. Cations in solution can create a competition with Cr(III) for active Mn(III) sites. Mn(II) and Cr(VI) liberated from the redox reaction can sorb onto the active sites and inhibit further oxidation of Cr(III) in solution (Amacher et al., 1982; Weaver and Hochella, 2003; Dai et al., 2009). Though some results suggest that Mn(II) and Cr(VI) do not act as competing metal sorbates on birnessite (Fendorf et al., 1992), Dai et al. (2009) note that the rate of Cr(III) oxidation increases to initial levels after removing adsorbed Mn(II) from the MnO₂ reactive surface by treating the sample with HCl.

The precipitation of Cr hydr(oxides) on the mineral surface can also act as a barrier to the oxidation of dissolved Cr(III). In a 1.0 mM solution at pH = 5.0, Cr precipitates as Cr(OH)₃(s) (Rai et al., 1987; Figure 2). If Cr(OH)₃(s) coats the surface of birnessite, then active sites are armored against further reaction (Fendorf and Zasoski, 1992; Chung, 1998). Further, X-ray diffraction measurements revealed chromium hydroxide or chromium hydroxide hydrate in birnessite-fluid mixtures when triclinic birnessite was reacted with pH 5.2 solutions containing 1 mM and 10 mM CrCl₃ for up to 3 hours (Fischer, 2011).

**Focus of the present work.** If Weaver and Hochella (2003) are correct in ascribing a greater reactivity to structural Mn(III) than to Mn(IV), then we can hypothesize that triclinic Na-birnessite will promote the oxidation of Cr(III) to Cr(VI) more effectively than will hexagonal H-birnessite. However, hexagonal H-birnessite, which has less Mn(III) in its octahedral sheet than does triclinic Na-birnessite, is the favored phase at acidic pH. For example, Mn(III)-rich triclinic Na-birnessite spontaneously transforms to Mn(III)-poor hexagonal H-birnessite at pH 3 within 6 hours. This behavior seems at odds with previous studies that convincingly demonstrate faster
Cr(III) oxidation at lower pH (Fendorf and Zasoski, 1992; Landrot et al., 2012b). Thus, the overall effect of pH on the redox interactions between Cr(III) and birnessite is difficult to explain due to competing effects involving: 1) the transformation of triclinic to hexagonal birnessite, which diminishes the fraction of Mn(III) sites and presumably limits Cr oxidation; 2) the variable charge of the birnessite surface above and below the PZC; and 3) the tendency of birnessite to dissolve when pH is lower than 3.

Few of the previous studies of this system have accounted for the differences in the oxidative potential of triclinic and hexagonal birnessite, and none have explored a correlation between the production of Cr(VI) and the transition from triclinic to hexagonal birnessite. Moreover, nearly all previous studies investigating the oxidation of Cr by Mn oxides have been conducted with batch reactions of powdered Mn oxides with dissolved Cr. Although batch experiments offer advantages in that they allow for continuous monitoring of aqueous chemistry (pH, dissolved cation concentrations, etc.) during mineral-fluid reactions, batch experiments can be limited with respect to measuring the time-dependence of reactions and of interrogating the state of the reacting solid.

In contrast, flow-through experiments provide a direct measurement of the reaction rate by continuous analysis of both the solid and liquid phases of the product (Heaney et al., 2008). In the present study, we employed a variety of in situ characterization techniques to monitor the structure of birnessite and the chemical properties of Cr simultaneously. For the first time, we have combined synchronous time-resolved X-ray diffraction (TRXRD), X-ray absorption spectroscopy (XAS), and wet-chemical analyses by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and UV-Vis spectrophotometry to characterize the interactions of dissolved Cr(III) and Cr(VI) with birnessite. TRXRD allows users to monitor real-time structural
changes for a powder of interest and quantify phase abundance as a dissolved species interacts with the solid (Heaney et al. 2008). XAS can accurately distinguish Cr(III) from Cr(VI) when adsorbed to birnessite (Landrot et al., 2012b). Wet chemical analyses of the eluate reveal the changing abundances of aqueous Cr(III) and Cr(VI).

We employed these techniques to analyze the redox reaction between synthetic triclinic birnessite and Cr(III) in solutions at starting pH values of 2.0, 3.0, 4.0 and 5.0. We did not use buffers in light of the work by Ling et al. (2015) demonstrating that commonly used buffers such as HEPES and MES will themselves induce a phase transformation from triclinic to hexagonal birnessite.
Methods

To monitor the structure of the birnessite and the oxidation state of Cr in real time, both flow-through and batch experiments were conducted. We performed batch runs to determine the proper chemical and temporal parameters for the flow-through experiments. In addition, the batch experiments allowed for ground-truthing of the flow-through experiments. Our flow-through experiments were designed to enable the simultaneous collection of X-ray diffraction, X-ray absorption, and wet chemical analysis with time-resolution ranging from 2 hours to 13 hours as dissolved Cr(III) interacted with birnessite powders. Our goal was to measure changes in the crystalline sample and in the fluid through techniques that did not require termination of the experiment or tampering with the samples. Table 1 outlines all of the experiments conducted in this investigation.

Birnessite synthesis

Synthesis of triclinic Na-birnessite was conducted following methods outlined in Lopano et al. (2007), based on the protocols from Golden et al. (1986). 200 mL of 0.5 M MnCl$_2$ was mixed with 250 mL of 5.5 M NaOH. The mixture was then aerated using a glass frit for five hours at a rate of 1.5 L/min. The precipitate was evenly distributed into 14 tubes and centrifuged at 1910 rpm for 5 minutes. The solution was decanted, and rinsed with deionized (DI) water five times. The rinsed product was then stored in ~350 mL DI water. Prior to usage, the solid was filtered using a 0.05 µm Whatman Nucleopore Track-Etched polycarbonate membrane filter, rinsed three times with 100 mL DI water, and air dried. Using X-ray diffraction (Rigaku II D/MAX RAPID microdiffractometer, Mo tube source $\lambda = 0.7093$ Å), the phase purity of triclinic Na-birnessite was confirmed with <1 wt% hausmannite.
Hexagonal H-birnessite was synthesized by reacting 100 mg of dried triclinic Na-birnessite with 250 mL of 0.001 M HCl for approximately 24 hours. The reacted solid material was then filtered using a 0.05 μm Whatman Nuclepore Track-Etched polycarbonate membrane filter, and rinsed three times with 100 mL DI water. The dried sample was then characterized using XRD.

**Preparation of Cr(III), Cr(VI) and colorimetric indicator solutions**

Cr(III) solutions were prepared by using 1.0 mM Cr(NO$_3$)$_3$·9H$_2$O (Acros Organics, 99% purity) and 10 mM NaNO$_3$ in 1L of 18.2 MΩ deionized water. The electrolyte NaNO$_3$ was used to maintain a constant ionic strength of the solutions. The pH of the solution was adjusted using 1 N NaOH or 1 N HNO$_3$. The pH 2.0 and 3.0 solutions were gray in color, whereas the pH 4.0 and 5.0 solutions were gray to light green. The pH and the concentration of the solutions were chosen outside the stability fields for Cr(OH)$_3$ to avert the formation of precipitates (Figure 3).

Cr(VI) solutions were prepared by diluting a standard solution of 0.1 N K$_2$Cr$_2$O$_7$ to contain 1.0 mM Cr(VI) in 1L of 18.2 MΩ deionized water. 10 mM NaNO$_3$ was added to the diluted mixture to control the ionic strength of the mixture. The pH of the solution was adjusted using 1 N NaOH or 1 N HNO$_3$.

An indicator solution to detect Cr(VI) in solution containing 1,5 diphenyl carbazide was produced for UV-Vis analysis, following a modified protocol developed by James and Bartlett (1979). In a beaker, 0.30 g 1,5 diphenylcarbazide was dissolved with 100 mL of 95% ethanol. Upon complete dissolution of the 1,5 diphenylcarbazide powder, 280 mL of deionized water and 120 mL of 15.2 N H$_3$PO$_4$ were slowly added to the mixture. The mixed solution was then transferred to a brown glass bottle, and stored at 5°C until usage. The diphenylcarbazide
indicator solution changes from clear to a magenta color when mixed with a solution that contains Cr(VI). Within low and high concentration limits, the intensity of the magenta color increases linearly with higher concentrations of Cr(VI) in solution.

**Batch Experiments for birnessite-induced oxidation of Cr(III)**

Batch experiments were conducted to determine the rates at which dissolved Cr(III) will undergo oxidation to Cr(VI) in the presence of synthetic Na-birnessite as a function of solution pH. Approximately 100 mg of triclinic Na-birnessite or hexagonal H-birnessite were placed in solutions containing 100 mL of 1.0 mM Cr(NO$_3$)$_3$·9H$_2$O and 10 mM NaNO$_3$ at selected pH concentrations of 2.0, 3.0, 4.0, and 5.0. The mixtures were agitated for 24 hours. Small aliquots (~3 mL) of the mixtures were taken out of the mixing bottles in one- to two-hour intervals throughout the experiment. The aliquots were then filtered through a 0.05 µm Whatman Nuclepore Track-Etched polycarbonate membrane filter, and then diluted 25 to 100-fold with deionized water. The 1,5 diphenylcarbazide indicator solution was then added to the diluted solution and analyzed for [Cr(VI)] using UV-Vis spectrophotometry (see spectrophotometry protocol below). Upon completion of the batch experiment, the reacted birnessite samples were separated from the reacted solution using a 0.05 µm Whatman Nuclepore Track-Etched polycarbonate membrane filter. The reacted birnessite was air-dried, and analyzed through powder X-ray diffraction (as described below).

**Conventional X-ray Diffraction**

For XRD analyses, approximately 5 mg of the dried, reacted birnessite powder were placed in a 0.05 mm Kapton tube and sealed with molding clay on both ends. The samples were
characterized with a conventional sealed Mo tube source ($\lambda = 0.7093$ Å) on a Rigaku II D/MAX-RAPID microdiffractometer (Materials Characterization Laboratory, Pennsylvania State University). During a 10-minute exposure time, samples were rotated 360° around the phi axis at 1° s$^{-1}$.

**Time-Resolved X-ray Diffraction Experiments**

Changes in the structure of the starting birnessite powders in response to fluid chemistry were monitored through time-resolved X-ray diffraction of the powder in conjunction with time-resolved spectrophotometry of the eluate. Flow-through analyses that explored the oxidation of Cr(III) were conducted with 1.0 mM Cr(NO$_3$)$_3$·9H$_2$O solutions at pH 2.0, 3.0, 4.0, and 5.0. For purposes of comparison, we also performed time-resolved X-ray diffraction experiments with Cr(VI) in the initial solution. These runs were conducted with a 0.5 mM K$_2$Cr$_2$O$_7$ solution at pH 4.0.

**Time-resolved analysis by lab bench chromatography.** To gauge chemistries and run times that would optimize our synchrotron X-ray diffraction experiments, we replicated the flow-through geometry by a lab bench chromatographic column in which ~1 mg of birnessite powder was packed between two cotton plugs within a 1.50 mm HDPE tube (Figure 2a). Cr(III) solutions containing 1.0 mM Cr(NO$_3$)$_3$·9H$_2$O were pumped through the birnessite powder using N$_2$ gas, and the reacted solutions were captured in a Nalgene bottle. From the Nalgene bottle, the eluate was driven using pressurized N$_2$ gas to a fraction collector (Gibson FC-205) that changed sampling tubes every 30 min. The eluate fractions were diluted 50 to 200-fold using DI water, mixed with the Cr(VI) indicator solution, and analyzed with by UV-Vis spectrophotometer (see below).
Time-resolved analysis by synchrotron X-ray diffraction. Once the rates of the Cr(VI) oxidation reactions were ascertained by our bench column experiments, we performed time-resolved X-ray diffraction analyses at the GeoSoilEnviroCARS (GSECARS) beamline 13-BM-C and 13-ID-E at the Advanced Photon Source, Argonne National Laboratory. The flow-through reaction cell was adapted from that described in Wall et al. (2011) with some modifications to minimize solution leakage. Solutions containing 1.0 mM Cr(NO$_3$)$_3$·9H$_2$O or 0.5 mM K$_2$Cr$_2$O$_7$ with 10 mM NaNO$_3$ were passed through a 0.7 mm quartz glass capillary (Charles Supper) containing weighed amounts (ranging from 15 to 40 mg) of synthetic triclinic or hexagonal birnessite.

Driven by forcing pressures of 1.0 to 6.0 psi N$_2$ gas, the Cr(III) or Cr(VI) solutions passed through the birnessite samples at a rate of 0.25 to 1 drop/min (~ 0.005 to 0.02 mL/min). The wavelength of the incident X-ray was refined using a LaB$_6$ standard, and the wavelengths used for our three data collection visits were 0.8257 Å, 0.8266 Å, and 0.8317 Å. X-ray diffraction patterns were collected for 8 s to 30 s during experiments that ranged from 2 to 14 hrs. The areas of the incident X-ray sources were 0.3 mm x 0.3 mm at 13-BM-C and 1 mm x 1.1 mm at 13-ID-E, and the beam was focused on a single slice of each rotating capillary throughout the duration of the flow-through experiments. During the diffraction collection, the sample rotated through a 30° phi angle to correct for preferred rotation. Full circle images were captured with a MAR165 CCD detector. The diffraction rings were integrated and recast as one-dimensional intensity versus 2Θ patterns using the software Dioptas (Prescher and Prakapenka, 2015), with a polarization factor of 0.999.

The reacted eluate solutions were collected in 15 mL HDPE bottles on a rotating autosampler. The autosampler, a 30-cm diameter polyethylene platform designed to hold the
HDPE bottles in place during motion, rotated in 15° intervals every 15 to 45 minutes depending on the total length of the experiment. Each bottle typically contained 0.1 to 0.6 mL of reacted solution depending on the drip rate of the solution and the duration of the experiment. The autosampler was driven by Newport RTM Stage, a program that can be operated outside of the hutch using EPICS open source software (http://www.aps.anl.gov/epics).

Figure 2b shows a photograph of the experimental setup for the time-resolved X-ray diffraction experiments at beamline 13-ID-E at the Advanced Photon Source in Argonne National Laboratory.

**Structure Refinements**

Rietveld structure refinements (Rietveld, 1969) of the TRXRD data were conducted using the EXPGUI (Toby, 2001) interface of the General Structure Analysis System (GSAS) software (Larson and Von Dreele, 1994). Initial parameters for triclinic Na-birnessite and hexagonal H-birnessite were obtained from Post et al. (2002) and Heaney et al. (2003), respectively. The starting parameters for these phases are compiled in Table 2. A diffraction pattern generated by a LaB₆ standard accounted for peak profile parameters that represented broadening from the instrument. Background intensities were fitted with a Chebyshev function using 11 terms. The peak profiles were modeled by a pseudo-Voigt profile function as parameterized by Thompson et al. (1987), with asymmetry correction by Finger et al. (1994), and micro-strain anisotropic broadening terms by Stephens (1999). Refinements were obtained by initially toggling the scale factor and determining the unit cell parameters. Then, the background parameters were adjusted, followed by varying the peak profile coefficients. Finally, the atom positions and atomic
occupancies were adjusted if necessary. The $\chi^2$ values for the refinements ranged from 2.301 to 4.382.

**Time-Resolved Chromium K-edge X-ray Absorption Near Edge Structure**

Chromium $K$-edge X-ray absorption near edge structure (XANES) spectra were collected at GSECARS beamline 13-ID-C at the Advanced Photon Source (APS), Argonne National Laboratory, Illinois. Fluorescence XANES spectra were collected using a 4-element Vortex detector (SII NanoTechnology) between 5888 and 6225 eV. The energy step width was set to 0.2 eV in the near edge region (5979-6014 eV).

The data were processed (background subtraction, normalization) using the ATHENA interface to the IFEFFIT software program (Newville, 2001; Ravel and Newville, 2005). The fraction of Cr that was present as Cr(VI) was quantified by linear combination fitting of the pre-edge feature at 5993 eV (Bianconi et al., 1985; Long et al., 1989; Strub et al., 2008). Cr(OH)$_3$ was used as a Cr(III) standard, and K$_2$Cr$_2$O$_7$ was used as a Cr(VI) standard. The margin of error in determining the ratio of Cr(VI):Cr(III) among the sorbed Cr species was +/- 5%.

**Wet Chemical Analyses for Mn, Cr, and Na**

Collected eluate samples from batch experiments and flow-through experiments were analyzed for total Mn, Cr, and Na. Solutions were analyzed using a Perkin-Elmer Optima 5300 UV Inductively Coupled Plasma Atomic Emission Spectrometer at the Materials Characterization Laboratory at The Pennsylvania State University. The detection limits for Mn, Cr, and Na are 0.005 μg/mL, 0.01 μg/mL, and 0.01 μg/mL, respectively. Analytical error varied between 1% to 5%.
Eluate solutions were measured for Cr(VI) concentrations within 12 hr by visible light spectrophotometry. Reacted solutions from batch experiments and lab bench chromatography flow-through experiments were analyzed using a Hach DR/4000 UV-Vis spectrophotometer at The Pennsylvania State University. The eluate collected during the synchrotron TR-XRD experiments were analyzed using a Cary 50-UV-Vis spectrophotometer at the Center for Nanoscale Materials, Argonne National Lab. Calibration of the spectrophotometers was conducted using 0.1 N K$_2$Cr$_2$O$_7$ (Alfa Aesar, 99%) standard solutions that were serially diluted four times with 18.2 MΩ deionized water. Due to the extremely low volumes of the collected eluate, each sample was diluted 10- to 1000-fold with 18.2 MΩ deionized water depending on the volume of the eluate and the initial [Cr(VI)]. A modified 1,5 diphenylcarbazide method from Bartlett and James (1979) was used. Approximately 1.0 mL of the diphenylcarbazide indicator solution was added to 10 mL of the diluted reacted eluate. After mixing, the solution was left to sit for at least 15 minutes to allow the color to develop. Concentrations of dissolved Cr(VI) were determined by measuring absorption at $\lambda = 540$ nm.
Results and Discussion

Effects of Solution pH on Birnessite-Induced Cr(VI) Production

The oxidation of Cr(III) by Mn oxides has been observed in numerous batch reactor experiments using both natural and synthetic samples (Bartlett and James, 1979; Eary and Rai, 1987; Manceau and Charlet, 1990; Fendorf and Zasoski, 1992; Weaver and Hochella, 2003). In the present study, we measured Cr(VI) production in the presence of birnessite in batch experiments, and we also collected time-resolved measurements of [Cr(VI)] in the eluate of a flow-through system. The oxidation behaviors that characterized the flow-through methodology were consistent with those reported from both our own and other researchers’ batch experiments.

In our batch experiments, ~100 mg of triclinic birnessite were mixed with 100 mL 1.0 mM Cr(NO$_3$)$_3$·9H$_2$O solutions at pH 2.0, 3.0, 4.0, and 5.0. We observed an initial increase in the oxidation of Cr(III) to Cr(VI) within 2 to 3 hours, after which the concentration of Cr(VI) reached a steady state (Fig. 4). In agreement with the observations of Fendorf et al. (1992), as pH decreased, the production of Cr(VI) increased. For the batch experiments at pH 2.0, approximately 90% of the initial Cr(III) in the solution oxidized, whereas only 20%, 15%, and 5% of the dissolved Cr(III) was oxidized in reactions at pH = 3.0, 4.0, and 5.0, respectively (Figure 4).

Our flow-through reaction experiments revealed the same sensitivity of Cr(III) oxidation to pH. Measurements of Cr(VI) in the eluate from our flow-through cells provided clear evidence for Cr(III) oxidation in the presence of synthetic Na-birnessite at pH 2.0, 3.0, 4.0, and 5.0 (Figures 5a, 6a, 7a, 8a). However, the time-resolution inherent in the flow-through methodology allowed us to monitor the temporal behavior of Cr(VI) production, and these experiments exposed a dramatic difference at higher pH (4 and 5) relative to lower pH (2 and 3).
When 1.0 \textit{mM} \text{Cr(III)} solutions reacted with triclinic birnessite at pH 4.0 and 5.0, the concentrations of \text{Cr(VI)} in the eluate were initially high and then rapidly dropped to sustained \text{Cr(VI)} production at a tenth of the initial values. Specifically, in both the pH 4.0 and 5.0 experiments, the initial generation of \text{Cr(VI)} was as high as 0.20 \textit{mM} during the first two hours of the reaction, and that intensity was followed by a decline to approximately 0.025 \textit{mM} \text{Cr(VI)}. (Figure 5a, 6a). The productivity of \text{Cr(VI)} at pH 5.0 was notably briefer than that at pH 4.0. While the concentration of \text{Cr(VI)} in the eluate had diminished to 0.05 \textit{mM} within ~1.5 hours at pH 5.0, the drop-off to a concentration of 0.05 \textit{mM} required ~2.2 hours at pH 4.0.

At pH 3.0 and 2.0, the production of \text{Cr(VI)} \textit{increased} rather than decreased with time. At pH 3.0, the concentration of \text{Cr(VI)} in the eluate increased from 0 to 0.25 \textit{mM} at the start of the reaction, transiently decreased to 0.15 \textit{mM}, and increased again to final concentrations of ~0.3 \textit{mM}, at 1.5 hours, similar to the final concentrations observed in batch experiments (Figure 4, 7a). The high generation of \text{Cr(VI)} at pH 2.0 was the most dramatic. When a 1.0 \textit{mM} \text{Cr(III)} solution at pH 2.0 was passed through triclinic birnessite, oxidation of \text{Cr(III)} to \text{Cr(VI)} increased over the first hour to an eluate concentration of ~0.9 \textit{mM} \text{Cr(VI)}, and that high productivity (ranging between 0.8 and 0.9 \textit{mM} \text{Cr(VI)} in the eluate) persisted as long as birnessite powder was present (Figure 8a, 8b). In one experiment in which a pH 2.0 solution containing 1.0 \textit{mM} \text{Cr(III)} flowed through triclinic Na-birnessite, ~0.9 \textit{mM} \text{Cr(VI)} was produced for 24 hours (Supplementary Information A).

\textbf{Transformation of Triclinic to Hexagonal Birnessite by dissolved \text{Cr(III)}}

According to the phase equilibria calculations of Rai et al. (1987), at pH 5.0, a 1.0 \textit{mM} \text{Cr(III)} solution will precipitate solid \text{Cr(OH)}$_3$ (Figure 3). Fendolf (1992) and Feng (2007)
propose that the deposition of Cr(OH)$_3$ will armor the birnessite surface at sufficiently high pH, inhibiting the oxidation of Cr(III). Although this reaction may explain the rapid drop in Cr(VI) production at pH 5.0 in our experiments, we note that our synchrotron X-ray diffraction did not detect crystalline Cr(OH)$_3$ in any of our runs. It is possible that the Cr(OH)$_3$ was either non-crystalline, or that it formed as a nanocrystalline coating that eluded detection by X-ray diffraction techniques.

An alternative explanation for the dependence of Cr(III) oxidation on pH takes birnessite structural transformations into consideration. In his Ph.D. dissertation, Fischer (2011) demonstrated that dissolved Cr(III) will induce a transition from triclinic Na-birnessite to hexagonal H-birnessite. He inferred that the oxidation of Cr(III) to Cr(VI) was accompanied by a reduction of Mn(III, IV) to Mn(II), leading to a symmetry change in the birnessite structure.

By coupling measurements of Cr(VI) production with crystallography, the present study provides strong support for this redox mechanism. Our X-ray diffraction patterns indicated a transformation from triclinic Na-birnessite to hexagonal H-birnessite during reaction with Cr(III) solutions at pH 2.0, 3.0, 4.0 and 5.0 (Figure 9, 10a, 11, 12a). We quantified the relative concentrations of triclinic and hexagonal birnessite at a given time in two ways. First, we monitored the integrated intensity of the (002) peak for triclinic birnessite as a function of time; this analysis yielded a measure of triclinic birnessite content and was independent of the nucleation and growth of hexagonal birnessite (Figures 5b, 6b, 7b, 8b). Second, the reaction of triclinic to hexagonal birnessite was quantified through whole-pattern structure refinement. Using Rietveld analysis, we measured the fractions of triclinic and hexagonal birnessite using two synthetic end-member birnessite varieties as standards. A comparison of these two approaches yielded a strong similarity between the two analytical methods (Figure 14).
expected, the disappearance of triclinic birnessite as measured by 002 peak integration preceded the transition to hexagonal birnessite as measured by Rietveld analysis, since the formation of hexagonal birnessite is associated with an activation energy.

If the oxidation of Cr(III) to Cr(VI) is promoted specifically by the availability of reactive sites in triclinic birnessite, then analyzing the disappearance of triclinic birnessite is more appropriate than is the ratio of triclinic to hexagonal birnessite. Figures 5b and 6b plot the abundance of triclinic birnessite during reaction with pH 5.0 and 4.0 solutions containing 1.0 mM Cr(III), respectively. As triclinic birnessite disappeared, oxidation of Cr(III) began to decline as Cr(VI) production tailed off to 0.025 mM, and hexagonal birnessite replaced triclinic birnessite. This correspondence was observed reproducibly over all experiments at these pH concentrations.

To confirm that triclinic rather than hexagonal birnessite is necessary to oxidize Cr(III), we passed a solution containing 1.0 mM Cr(III) at pH 4.0 through synthetic hexagonal H-birnessite. From the onset of the reaction, the concentration of Cr(VI) in the eluate remained at only 0.025 mM, very similar to the concentration of dissolved Cr(VI) produced once the triclinic birnessite had transformed to hexagonal birnessite in our previous runs (Figure 15). This control experiment with synthetic hexagonal birnessite as the reactant confirms the relative inability of hexagonal birnessite to oxidize Cr(III) above pH 3.

Ling et al. (2015) explored the relative stability of triclinic and hexagonal birnessite as a function of pH, and they conclude that hexagonal birnessite is favored below pH 8.2, and triclinic birnessite above. However, the rate of the transformation from triclinic to hexagonal birnessite is dramatically slower when pH exceeds ~3. We attempted to verify whether triclinic birnessite experienced a phase transition at pH 4.0 and 5.0 in the absence of dissolved Cr(III) under our experimental conditions. As shown in Figure 10b, there was no evidence of a phase
transition from triclinic to hexagonal birnessite when an acidified solution at pH 4.0 was passed through a sample for over 12 hours. Fischer (2011) reports identical results from reactions conducted at pH 4.4 and 5.2 for up to 3 hours. In contrast, at pH 4.0 and 5.0, triclinic birnessite completely transformed to hexagonal birnessite in less than 4 hours in the presence of Cr(III) in solution.

To determine whether Cr(VI), like Cr(III), can induce a transformation from triclinic Na-birnessite to hexagonal H-birnessite, we passed a solution at pH 4.0 containing 0.5 mM K$_2$Cr$_2$O$_7$ through a capillary containing triclinic Na-birnessite (Figure 11). No changes in the diffraction pattern were observed over 13 hours, indicating that Cr(VI) will not promote the transition.

Proposed Model for the Cr(III)-Induced Transition from Triclinic to Hexagonal Birnessite

Weaver and Hochella (2003) compare the ability of seven different Mn oxides to oxidize Cr(III), and they report birnessite to be the most effective. They attribute the high reactivity of birnessite to the open architecture of the phyllomanganate crystal structure and to the abundance of Mn(III) in these Mn(III, IV) oxides. Recent XPS analyses of Mn(II):Mn(III):Mn(IV) ratios in birnessite reveal that Mn(III) is present in a variety of natural and synthetic birnessite samples (Ilton et al. 2016), but triclinic birnessites are systematically more enriched in Mn(III) than are hexagonal birnessites. For example, Ilton et al. (2016) observe that Mn(III) represents 38 mol% of the total Mn in synthetic triclinic Na-birnessite compared with 22 mol% in synthetic hexagonal H-birnessite. Mn(IV) abundances are relatively similar between triclinic Na-birnessite and hexagonal H-birnessite (60 mol% and 68 mol% of total Mn, respectively).

Despite the higher oxidation potential of Mn(IV) relative to Mn(III) (Stone, 1983), Jahn-Teller distortions render trivalent Mn cations within the octahedral sheet of birnessite most
vulnerable to redox reactions (Weaver and Hochella 2003; Simanova and Peña 2015). Thus, we propose that the transformation from triclinic to hexagonal birnessite is mediated primarily by an electron exchange between Cr(III) and Mn(III) according to the following reaction:

\[
\text{Cr(III)}_{\text{aq}} + 3\text{Mn(III)}_{\text{Tri-Birn}} \rightarrow \text{Cr(VI)}_{\text{aq}} + 3\text{Mn(II)}_{\text{Hex-Birn}}
\]  \hspace{1cm} (1)

Since Mn(II) cations are too large to occupy sites within the octahedral sheet (Post 1999), this reaction shifts Mn cations from the phyllomanganate sheets into the interlayer region. That in turn creates vacancies co-existing with Mn(IV) cations within the sheets, with Mn(II) cations occupying positions above the vacancies within the interlayer. This transformation is consistent with our Rietveld refinements of the hexagonal birnessite reaction products. In hexagonal birnessite, the Mn occupancy in the octahedral sheets of hexagonal birnessite remained at ~80% through the reaction, while the Mn occupancy in the interlayer increased from ~9% to ~15% over time.

**Birnessite Transitions and Cr(VI) Production at pH 2 and 3**

At pH = 2.0 and 3.0, triclinic Na-birnessite transformed to hexagonal H-birnessite both with and without Cr(III) in solution in our experiments. Surprisingly, the phase transformation at pH 2.0 occurred more rapidly in the absence of dissolved Cr(III) (Figure 12b). In 1.0 mM Cr(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O solutions at pH 2.0, the transformation required 1.5 hours, whereas without dissolved Cr(III), the transition occurred in 0.5 hour (Figure 12a). We suggest that the phase transition from triclinic to hexagonal birnessite at pH 2.0 and 3.0 was driven by two processes: oxidation of Cr(III) coupled with disproportionation of Mn(III) by H\textsuperscript{+}. 
Many researchers have explored the transformation of triclinic to hexagonal birnessite in acidic solutions (e.g., Drits et al. 1997; Silvester et al. 1997; Lanson et al. 2000). The instability of dissolved Mn(III) in acid solutions relative to Mn(II) and Mn(IV) has been recognized for over a century (Grube and Huberick, 1923; Selim and Lingane, 1959), and Drits and co-workers extended these observations of Mn behavior to the solid state. Thus, Silvester et al. (1997) propose that when pH is 3 or lower, Mn(III) cations in birnessite disproportionate according to the following reaction:

$$2\text{Mn(III)}_{\text{Tri-Birn}} \rightarrow \text{Mn(II)}_{\text{Hex-Birn}} + \text{Mn(IV)}_{\text{Hex-Birn}}$$

such that the Mn(II) relocates from the octahedral sheet to the interlayer, creating vacancies. In the absence of other dissolved cations, the disproportionation reaction generates hexagonal H-birnessite, with only H\(^+\) (or H\(_3\)O\(^+\)) cations within the interlayer.

The mechanics of the disproportionation reaction in birnessite is still unknown, but it seems likely that H\(^+\) displaces Na\(^+\) within the interlayer and bonds to basal O anions in the octahedral sheet. Thus, if Cr(III) is present in the solution as disproportionation of Mn(III) to Mn(II) and Mn(IV) occurs, then H\(^+\) and Cr(III) must compete with each other for reactive surface sites. We propose that this competition reduces the rate at which triclinic Na-birnessite transforms to hexagonal H-birnessite in our experiments at pH 2.0.

Despite the studies of Fendorf et al. (1992) and others showing that the generation of Cr(VI) is greater at low pH (2 and 3) than at higher pH (4 and 5), Feng et al. (2006) argue using a thermodynamic model that Cr(III) oxidation is most favored at pH ~3.2. We note, however, that classical thermodynamics can be unreliable in predicting the behavior of these systems.
Birnessite is a metastable phase, and the relative Gibbs free energies of formation for the hexagonal and triclinic birnessites used in our experiments are not known.

We suggest that the heightened Cr(VI) production at pH 2 and 3 relative to pH 4 and 5 can be attributed to two factors: 1) changes in surface charge below the PZC; and 2) the effects of dissolution of birnessite at pH $\leq 3.5$ (Murray, 1974). Dissolution seems strongly to be tied to the production of Mn(II). Both the oxidation of Cr(III) (Reaction 1) and the disproportionation of Mn(III) at low pH (Reaction 2) generate Mn(II), which is stable as a hexa-aqua cation in solution. Our visual inspections of the birnessite powders during the flow-through experiments, particularly at pH 2.0, revealed that the samples were disappearing with continued reaction, suggesting a reduction of Mn(IV) and Mn(III) to Mn(II) followed by release from the interlayer of the crystal structure to the solution. More quantitatively, we detected Mn(II) in the reacted eluates using ICP-AES, and these analyses revealed a significantly larger concentration of Mn(II) in the reacted eluate at pH 2.0 than at pH 4.0 (Figure 17). Weaver and Hochella (2003) also report that at pH 4.4, the production of aqueous Mn(II) is extremely small when birnessite reacts with 0.1 $mM$ Cr(III). These results imply that the reduction of Mn(III,IV) to Mn(II) by aqueous Cr(III) at pH 4 to 5 leads to only a minor loss of Mn(II) from the crystal structure to the solution.

Furthermore, the positive charge of the surface below the PZC paradoxically may impart a greater redox reactivity to dissolved transition metal cations. If Cr(III) or Cr(VI) sorbs to the surface of birnessite without subsequent detachment, then the site of adsorption is no longer available to mediate redox reactions. Thus, when the surface is negatively charged, cation sorption may persist and inhibit Cr(III) oxidation. Consequently, it was important for us to
monitor the attachment of Cr(III) and Cr(VI) on the surfaces of hexagonal and triclinic birnessite as a function of pH.

**Sorption of Cr to the surface of the birnessite at pH 4 and 5**

Investigating the adsorption of metals on soil minerals such as birnessite can provide insights into the material’s efficacy for remediation of metals such as As(III), Cr(III), and Co(II) through uptake or oxidation (Bartlett and James, 1979; Murray and Dillard, 1979; Sun and Doner, 1998). Sorption of Cr onto the surfaces of Mn oxides has been widely discussed as the primary mechanism of the oxidation-reduction feedback between Cr and Mn oxides (Manceau and Charlet, 1992; Weaver and Hochella, 2003; Feng et al., 2006; Landrot et al., 2012a). Landrot et al. (2012b) used Quick X-Ray Absorption Fine Structure Spectroscopy in batch experiments to investigate Cr(III) oxidation in the presence of various synthetic MnO$_2$ samples. They observe an increase in the concentration of Cr(VI) adsorbed to the surface of the birnessite, indicating that sorbed Cr species on birnessite oxidize over time. In addition, they quantified the amount of Cr(VI) sorbed to the surfaces of Mn oxide samples and confirmed that oxidation of Cr(III) occurs more rapidly at lower pH. Sorption of both Cr(III) and Cr(VI) onto other types of minerals, such as iron oxides and silicates, has also been described (Peterson et al., 1997).

In the present study, we complemented *in situ* crystallographic analyses with time-resolved XANES, which allowed us to measure the ratio of Cr(III) to Cr(VI) within the sample window that was simultaneously interrogated by X-ray diffraction. In addition, we employed ICP-AES to measure total Cr concentrations in eluate fractions collected during flow-through experiments.
By comparing dissolved Cr concentrations in our starting solutions with the Cr concentrations in the eluate fractions collected every 30 to 60 min, it was possible to measure the amount of Cr taken up by birnessite. For example, when a 1.0 mM Cr(III) solution at pH 4.0 and pH 5.0 was passed through a triclinic Na-birnessite powder in separate experiments, 25% of the dissolved Cr sorbed to birnessite (Figure 18). Beyond 1 hr, ICP-AES analyses of the subsequent eluate collections indicated virtually no loss of Cr from solution.

Our XANES analyses provided additional evidence that Cr sorbed to the surface of the birnessite in our experiments at pH 4.0 and 5.0. In the absence of birnessite powder, a sample containing 1.0 mM Cr(III) and another containing 1.0 mM Cr(VI) in solution yielded no signal in our XANES spectra, indicating that aqueous Cr was not detected by the fluorescence spectrometer used for our XANES experiments. As seen in Figures 19 and 20, however, when 1.0 mM Cr(NO$_3$)$_3$·9H$_2$O solutions reacted with triclinic Na-birnessite at pH 5.0 and 4.0, an absorption edge at ~6010 eV increased in intensity for the first 3.4 hours and then plateaued. This $K$-edge peak in the Cr XANES spectrum reveals the total concentration of Cr (both Cr(III) and Cr(VI)) that is sorbed to the sample. The observed increase of the Cr $K$-edge signal indicates that greater amounts of Cr adsorbed to the surface of the birnessite with time, and the termination of growth of the $K$-edge suggests that Cr sorption persisted until the surface sites were saturated.

The absence of a Cr $K$-edge peak over the first 0.7 hours of the experiments at pH 5.0 and 4.0 suggests that no Cr sorbed to the surface of the birnessite within this sampling window (Figure 19, 20). We conclude that the length of the induction period was determined by the rate at which the reaction front progressed through the birnessite sample in these flow-through experiments, and the duration of this induction period correlated with the reaction of triclinic to hexagonal birnessite.
Furthermore, we measured the relative amounts of Cr(III) and Cr(VI) sorbed to the surface of the birnessite using XANES. All of the XANES spectra were normalized such that the intensities of the absorption edge at ~6010 eV were the same. That allowed us to evaluate the intensities of the pre-edge peaks at 5993 eV over the duration of the experiments (Figures 21, 22). When all of the dissolved Cr exists as Cr(VI), the pre-edge feature at 5993 eV has the same intensity as does the absorption edge at ~6010 eV (Bianconi et al., 1985). When all of the dissolved Cr occurs as Cr(III), the pre-edge structure is not discernible (Figure 21). Thus, when the absorption edge intensities at 6010 eV have been normalized, it is possible to quantify the ratio of Cr(VI) to Cr(III) by comparing the pre-edge intensities at 5993 eV.

Following the practice of previous researchers, we compared our spectra with those of Cr standards and then applied linear combination fitting to quantify the ratio of Cr(VI):Cr(III) sorbed to birnessite (Bianconi et al., 1985; Long et al., 1989; Strub et al., 2008; Landrot et al., 2012b). At pH 5.0 and 4.0, the fraction of Cr(VI) relative to Cr(III) on the surface of the triclinic birnessite increased over 3 hours from 0% to 20% and 25% Cr(VI), respectively, and thereafter the ratio stabilized (Figure 5c, 6c). The increase in the fraction of Cr(VI) was concurrent with the growth of the amount of total Cr adsorbed to the surface of the birnessite. The sorption of both Cr(III) and Cr(VI) occurred during and after the transition of triclinic birnessite to hexagonal birnessite (Figure 5b, 5c, 6c, 19, 20). The increases in the adsorption of total Cr and in the ratio of Cr(VI):Cr(III) ceased when all of the reactive sites presumably were occupied by adsorbed Cr species.

**Proposed Model for the sorption of Cr onto the surface of birnessite at pH 4 and 5**
Manceau and Charlet (1992) infer that dissolved Cr species diffuse toward vacancies in the octahedral sheets of birnessite, and then sorb above the vacant sites within the interlayer. Since the octahedral sites of the triclinic Na-birnessite were fully occupied at the onset of our experiments, the coupled redox reaction between Cr(III) and Mn(III) (Reaction 1 above) must not involve vacancies, at least initially. Rather, the exchange of electrons that produces Cr(VI) and Mn(II) creates octahedral vacancies and transforms triclinic to hexagonal birnessite. Consequently, we infer that our Cr K-edge XANES spectra were sensitive to Cr cations that had sorbed to the vacancies within the octahedral sheet of hexagonal birnessite following the transition (Figure 5b, 6b).

Previous EXAFS analyses have indicated that Cr(VI) sorbs onto birnessite as an outer-sphere complex, whereas Cr(III) sorbs onto the surface as an inner-sphere complex (Manceau and Charlet, 1992; Landrot et al., 2012a). In our experiments at pH 5.0 and 4.0, the sorption of Cr(III) and Cr(VI) to the surface of birnessite continuously increased until the transition from triclinic to hexagonal was complete. Thus, we conclude that when the pH is above the PZC, both Cr(III) and Cr(VI) can form inner-sphere complexes at the vacancy sites on the octahedral sheets and do not readily desorb. Rather, it seems more likely that Cr(III) bonded as an outer-sphere complex to the fully occupied octahedral sheet of triclinic birnessite during the initial stages of interaction, consistent with its rapid sorption and desorption following electron exchange with Mn(III).

**Sorption of Cr to the surface of birnessite at pH 2 and 3**

Prior researchers have reported evidence for sorption of Cr to the birnessite surface in highly acidic solutions (Eary and Rai, 1987; Johnson and Xyla, 1991). In our time-resolved
XANES experiments involving 1.0 mM Cr(III) solutions and triclinic Na-birnessite at pH 2.0 and 3.0, the Cr K-edge exhibited an increase in intensity for the first 1.4 and 1.8 hours, respectively, after which the intensities decreased (Figure 23, 24). These reductions in Cr K-edge intensities signaled a decrease in the relative amounts of Cr sorbed to the surface of birnessite, offering additional evidence that birnessite was dissolving at pH 2.0 and 3.0 as the surface sites with adsorbed Cr dissolved. However, the intensity of the Cr K-edge at pH 2.0 declined much more significantly than at pH 3.0. We speculate that a higher distribution of a positive surface charge of the birnessite at pH 2.0 caused Cr to readily desorb, and contribute to the decline in the intensity of the XANES absorption edge. A comparison of the relative sorption of Cr at pH 2.0 to 5.0 indicates a sharp loss of Cr signal only at pH 2.0 (Figure 27).

Normalized XANES spectra at pH 3.0 indicated that the fraction of Cr(VI) on the surface of the birnessite gradually increased to 25%, despite the decline in the total amount of sorbed Cr after 1.7 hours (Figures 23, 25). At pH 2.0, the pre-edge intensities relative to the absorption edge were much stronger than those at higher pH. Once the triclinic birnessite completely disappeared, the Cr(VI):Cr(III) ratios reached a maximum of 80% Cr(VI) (Figure 8c). This high ratio of Cr(VI):Cr(III) on the surface of the birnessite occurred in parallel with elevated measurements of Cr(VI) in solution (Figures 24, 26). With prolonged fluid flow, however, the Cr(VI):Cr(III) of the adsorbed species at pH 2.0 decreased, presumably due to the dissolution of the solid.

Our results provide strong evidence that the interactions between dissolved Cr and birnessite occurred at the surface of birnessite, and not within the interlayer regions. Specifically, the cessation of Cr(III) oxidation in the absence of dissolution at pH 5.0 and 4.0 – and the increase in oxidation of Cr(III) during the dissolution of birnessite at pH 3.0 and 2.0 --
are consistent with surface-mediated processes. Whereas alkali and alkaline earth cations readily exchange into the birnessite interlayer (Golden et al. 1986; Lopano et al. 2007, 2009), transition metal cations are better known to sorb to the octahedral sheets and to insert themselves within octahedral vacancies (Peacock and Sherman 2007; Sherman and Peacock 2010). Although Zn$^{2+}$, which is equally stable in tetrahedral and octahedral coordination environments, will locate within the birnessite interlayer to make highly crystalline chalcophanite (Post and Appleman, 1988), the emplacement of heavy metals into the birnessite interlayer more often is sterically challenged and leads to turbostratic disordering of the octahedral sheets (Ling 2016; Qin et al. 2017). We interpret the strong increase in Cr(III) oxidation during the dissolution of birnessite as evidence that the continual exfoliation of the octahedral sheets exposes unreacted Mn(III), until all of the birnessite has dissolved.

**Kinetics of the Phase Transformation**

The correlation between the oxidation of Cr(III) and the transformation from triclinic to hexagonal birnessite allows us to employ the kinetics of the phase transition as a proxy for the rate of Cr oxidation. Fischer (2011) reports that the rate at which the birnessite phase transition occurs in solutions with [Cr(III)] ranging from 1 to 50 $mM$ increases as pH decreases from 5.2 to 3.2, and he developed rate equations as a function of pH and [Cr(III)].

In the present study, the abundance of each phase was calculated using structure refinements of diffraction data (Figure 28a). The rate of the transformation of triclinic birnessite was determined using the differential method (Brantley et al., 2008). Once the rates of transformation were determined for each pH, the logs of the rates of transformation were plotted
to illustrate their dependence on pH (Figure 28b). After Fischer (2011), a rate law was derived that describes the reaction containing two reactants:

\[
\text{Rate} = k' [H^+]^x [\text{Cr(III)}]^y
\]  

(3)

where \([H^+]\) represents the pH of the solution and \([\text{Cr(III)}]\) represents the concentration of Cr in the reaction. Since the concentration of the Cr solution was kept constant, we can propose a pseudo-first rate (linear) reaction where triclinic Na-birnessite \(\rightarrow\) hexagonal H-birnessite:

\[
\text{Rate} = -\frac{d[\text{triclinic}]}{dt} = k [H+]^x
\]  

(4)

where \(k = k' [\text{Cr(III)}]^y\).

The \(k'\) constant in Equation 3 can be calculated from the \(y\)-intercept in Figure 9b as 0.39 min\(^{-1}\), and the slope of the line in Figure 9b is the reaction order, \(x\). Thus, the rate law, when converted to minutes, can be expressed as

\[
\text{Rate} = 0.39 \text{ min}^{-1} [H^+]^{0.43}
\]  

(5)

A comparison of our rate law with that of Fischer (2011) reveals that our reaction order is one order of magnitude higher. Thus, we observed a much stronger dependence of reaction rate on solution pH. This disparity can be attributed to several factors. First, experimental conditions differed in the reaction parameters of the two studies. Fischer (2011) used CrCl\(_3\) rather than Cr(NO\(_3\))\(_3\)·9H\(_2\)O as the source of Cr(III), and the run durations were longer in our experiments (up to 4 hours on Fischer (2011) and up to 12 hours in this study). Moreover, we note that this
A series of experiments in Fischer (2011) showed a greater degree of scatter ($R^2 = 0.651$) than did his other experiments, whereas our data were well fit as a pseudo-first order relation ($R^2 = 0.973$).

**Oxidation of Cr(III) by Natural Hexagonal Birnessite**

In order to compare the reactivity of synthetic birnessite with natural analogs, we explored the oxidation of Cr(III) at pH 4 in one flow-through experiment with a birnessite sample collected from Glasgow, PA. This natural sample is a by-product of a remediation system to remove dissolved Fe and Mn from acid mine wastes generated at an abandoned coal mine near Tyrone, PA, and the sample was likely biogenically precipitated on coconut coir in a metal remove unit installed by Eco-Islands, Inc. Ling (2016) has shown that the Glasgow sample is a variety of ranciéite, a hexagonal birnessite with Ca and Mg in the interlayer. Our flow-through experiments with this ranciéite yielded similar results to those obtained using synthetic hexagonal H-birnessite at pH 4.0 (Figure 9). Specifically, the ranciéite oxidized less than 5 mol% of the Cr(III) in the flow-through solution to Cr(VI). In addition, our XANES analyses revealed the sorption of Cr(III) onto the surface of the Glasgow birnessite, supporting the presence of vacancy sites in the octahedral sheet, further reinforcing its resemblance to synthetic hexagonal birnessite (Supplementary Information C). Additional experiments with natural samples are a logical extension of this research, but these preliminary results suggested that synthetic birnessite samples can serve as analogs for the oxidation of Cr in natural settings.
Conclusions

In this study, we demonstrated that oxidation of Cr(III) occurred in a flow-through reaction with both synthetic triclinic Na- and hexagonal H- birnessite. Through our X-ray diffraction and spectroscopic experiments, we monitored in situ the structure of the birnessite, the oxidation state of the Cr in solution, and the adsorption and oxidation state of the Cr species on the surface of the birnessite in a time-resolved manner. We showed that the structural state of birnessite strongly controls the oxidative potential of Cr; triclinic Na-birnessite exhibited much more robust oxidative capabilities than did hexagonal H-birnessite at pH 4 and 5. We attribute this heightened oxidation of Cr to the greater concentration of Mn(III) in the octahedral sheet in triclinic relative to hexagonal birnessite. We also confirmed the sorption of Cr(III) to surface sites of hexagonal H-birnessite through Cr K-edge XANES. Below pH 3, dissolution strongly enhanced the conversion of Cr(III) to Cr(VI) by exposing active oxidation sites in hexagonal H-birnessite. Our studies validated many previous observations regarding the behavior of Cr; however, this is the first study to demonstrate the central role that the mineralogical phase of birnessite plays in the oxidation of Cr. A natural sample of birnessite from Glasgow, PA, exhibited a similar oxidation behavior as its synthetic counterpart. Thus, characterizing the structural state of natural birnessite samples is essential in order to constrain the oxidation paths of Cr in near-surface waters.
References


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Appendix

Figures

Figure 1. a) Schematic diagram of triclinic birnessite and hexagonal birnessite (from Ling et al., 2015). b) XPS analyses displaying the fractions of Mn(IV), Mn(III), and Mn(II) for synthetic hexagonal and triclinic birnessite from fitting the Mn3p peak (from Ilton et al., 2016).
Figure 2a. The experimental set-up of a flow-through reactions conducted at Penn State University. A solution containing Cr(III) is passed through a HDPE tube containing synthetic birnessite packed between two cotton plugs. The reacted solution is collected using a fraction collector that changes to a new test tube in 30 minute intervals. The eluate is analyzed for Cr(VI) using a UV-Vis spectrophotometric method.
Figure 2b. The experimental set-up at beamline 13 IDE at the Advanced Photon Source. The Cr(III) solution is passed through the mounted capillary containing the birnessite sample. The synchrotron x-rays provide a source to conduct x-ray diffraction and x-ray absorption spectroscopy. The reacted solution is collected in collection vials that rest on a motorized stage.
Figure 3. A plot of log [Cr(III)] vs. pH, illustrating Cr speciation (modified from Rai et al., 1987) in the solutions used in this study. The Cr hydroxide species of previous studies are also plotted for comparison.
Figure 4. Measurements of Cr(VI) produced in batch experiments with a solution containing 1.0 mM Cr(NO$_3$)$_3$·9H$_2$O at various pH levels and synthetic triclinic Na-birnessite. Solutions were sampled periodically throughout the duration of the experiment, and analyzed using a UV-Vis spectrophotometer following a diphenylcarbazide method modified from Bartlett and James (1979).
Figure 5. Results of both the solid and aqueous phases from a time-resolved flow-through reaction with a solution containing 1.0 mM Cr(III)(NO$_3$)$_3$·9H$_2$O at pH = 5.0 with synthetic triclinic birnessite. Plots indicate a) measurements of Cr(VI) produced in the reacted eluate, b) abundance of triclinic birnessite through the integration the (002) peak of stacked X-ray diffraction patterns, and c) the amount of Cr(VI)$_{\text{sorbed}}$ relative to the total Cr$_{\text{sorbed}}$ on the surface of the birnessite calculated from normalized Cr $k$-edge XANES.
Figure 6. Results of both the solid and aqueous phases from a time-resolved flow-through reaction with a solution containing 1.0 \( mM \) Cr(III)(NO\(_3\))\(_3\)·9H\(_2\)O at pH = 4.0. with synthetic triclinic birnessite. Plots indicate a) measurements of Cr(VI) produced in the reacted eluate, b) abundance of triclinic birnessite through the integration the (002) peak of stacked X-ray diffraction patterns, and c) The amount of Cr(VI)\(_{\text{sorbed}}\) relative to the total Cr\(_{\text{sorbed}}\) on the surface of the birnessite calculated from normalized Cr \( k \)-edge XANES.
Figure 7. Results of both the solid and aqueous phases from a time-resolved flow-through reaction with a solution containing \(1.0 \text{ mM} \ \text{Cr(III)(NO}_3)_3\cdot9\text{H}_2\text{O} \) at pH = 3.0 with synthetic triclinic birnessite. Plots indicate a) measurements of Cr(VI) produced in the reacted eluate, b) abundance of triclinic birnessite through the integration of the (002) peak of stacked X-ray diffraction patterns, and c) The amount of Cr(VI)\text{ads} relative to the total Cr\text{ads} on the surface of the birnessite calculated from normalized Cr k-edge XANES.
Figure 8. Results of both the solid and aqueous phases from a time-resolved flow-through reaction with a solution containing 1.0 mM Cr(III)(NO₃)₃·9H₂O at pH = 2.0 with synthetic triclinic birnessite. Plots indicate a) measurements of Cr(VI) produced in the reacted eluate, b) abundance of triclinic birnessite through the integration the (002) peak of stacked X-ray diffraction patterns, and c) The amount of Cr(VI)$_{\text{adsorbed}}$ relative to the total Cr$_{\text{sorbed}}$ on the surface of the birnessite calculated from normalized Cr $k$-edge XANES.
Figure 9. Time-resolved X-ray diffraction patterns illustrating the structural symmetry of birnessite during reaction with a solution containing 1.0 mM Cr(III)(NO$_3$)$_3$·9H$_2$O at pH = 5.00. Each exposure lasted 8 seconds during which the capillary was rotated 30 degrees.
Figure 10. Time-resolved X-ray diffraction patterns illustrating the structural symmetry of birnessite during reaction with a solution containing a) 1.0 mM Cr(III)(NO$_3$)$_3$·9H$_2$O at pH = 4.00 and b) deionized water without Cr(III) at pH = 4.00. Each exposure lasted 8 seconds during which the capillary was rotated 30 degrees.
Figure 11. Time-resolved X-ray diffraction patterns illustrating the structural symmetry of birnessite during reaction with a solution containing 1.0 mM Cr(III)(NO$_3$)$_3$·9H$_2$O at pH = 3.00. Each exposure lasted 8 seconds during which the capillary was rotated 30 degrees.
Figure 12. Time-resolved X-ray diffraction patterns illustrating the structural symmetry of birnessite during reaction with a solution containing a) 1.0 mM Cr(III)(NO₃)₃·9H₂O at pH = 2.00 and b) deionized water without Cr(III) at pH = 2.00. Each exposure lasted 8 seconds during which the capillary was rotated 30 degrees.
Figure 13. Time-resolved X-ray diffraction patterns illustrating the structural symmetry of birnessite during reaction with a solution containing 0.5 mM $K_2Cr_2O_7$ at pH = 4.00. Each exposure lasted 8 seconds during which the capillary was rotated 30 degrees.
Figure 14. A comparison of the two independent methods to quantify the relative concentrations of triclinic and hexagonal birnessite from X-ray diffraction patterns. Integration of (002) peaks and Rietveld structure refinement results from a time-resolved flow-through reaction with 1.0 mM Cr(III) solution at pH 4.0 with synthetic triclinic Na-birnessite. Results yielded a strong similarity between the two methods.
Figure 15. Cr(VI) production in a flow-through reaction with various birnessite samples and 1.0 mM Cr(III)(NO$_3$)$_3$·9H$_2$O at pH = 4.0. Blue dots plot results from a reaction with synthetic triclinic Na-birnessite, black hollow dots represent results reacting with synthetic hexagonal H-birnessite, and orange squares represent results from a reaction with natural birnessite collected from an acid mine drainage in Glasgow, PA.
Figure 16. Cr(VI) production in a flow-through reaction with various birnessite samples and 1.0 mM Cr(III)(NO₃) 9H₂O at pH = 2.0. Blue dots plot results from a reaction with synthetic triclinic Na-birnessite, and black hollow dots represent results reacting with synthetic hexagonal H-birnessite.
Figure 17. Soluble Mn(II) collected in the eluate of the reacted solution over time. Higher amounts of Mn(II) were measured from the reacted pH 2.0 solution than from the reacted pH 4.0 solution.
Figure 18. Total Cr collected in the reacted eluate of a pH 5.0 and 4.0 where a solution containing 1.0 mM Cr(III) solution passing through triclinic Na-birnessite over time. Decrease in [total Cr] in the eluate indicates a loss of Cr in the solution. The lost Cr is interpreted to be adsorbed onto the surface of the birnessite.
Figure 19. Chromium k-edge XANES plot of synthetic Na-birnessite in a capillary undergoing reaction with 1.0 mM Cr(III) solution at pH = 6.0. Energy is plotted as $\chi \mu$ over an increasing amount of incident x-ray energy. The height of the edge feature that begins at 6000 eV indicates the relative total Cr signal absorbed by the fluorescence detector.
Figure 20. Chromium k-edge XANES plot of synthetic Na-birnessite in a capillary undergoing reaction with 1.0 mM Cr(III) solution at pH = 4.0. Energy is plotted as $\chi\mu$ over an increasing amount of incident x-ray energy. The height of the edge feature that begins at 6000 eV indicates the relative total Cr signal absorbed by the fluorescence detector.
Figure 21. Fluorescence Chromium k-edge XANES plot of synthetic triclinic Na-
binnessite in a capillary reacted with a solution containing 1.0 mM Cr(III)(NO$_3$)$_3$·9H$_2$O at 
pH = 2.0. Energy is plotted as normalized $\chi \mu$ over an increasing amount of incident the X-
ray energy. The height of the pre-edge feature that at 5993 eV indicates the relative 
amount Cr(VI) present in the adsorbed Cr species. XANES patterns of Cr(III) and Cr(VI) 
standards are also plotted to illustrate presence of the distinct pre-edge feature of Cr(VI).
Figure 22. Fluorescence Chromium k-edge XANES plot of synthetic Na-birnessite in a capillary reacted with a solution containing 1.0 mM Cr(III)(NO₃)₃·9H₂O at pH = 4.0. Energy is plotted as normalized $\chi\mu$ over an increasing amount of incident the X-ray energy. The height of the pre-edge feature that at 5993 eV indicates the relative amount Cr(VI) present in the adsorbed Cr species. XANES patterns of Cr(III) and Cr(VI) standards are also plotted to illustrate presence of the distinct pre-edge feature of Cr(VI).
Figure 23. Chromium k-edge XANES plot of synthetic Na-birnessite in a capillary undergoing reaction with 1.0 mM Cr(III) solution at pH = 3.0. Energy is plotted as $\chi_{\mu}$ over an increasing amount of incident the x-ray energy. The height of the edge feature that begins at 6000 eV indicates the relative total Cr signal absorbed by the fluorescence detector. Cr adsorption increased in the first 1.7 hours of the reaction, and proceeded to decrease in the subsequent hours of the experiment.
Figure 24. Chromium k-edge XANES plot of synthetic Na-birnessite in a capillary undergoing reaction with 1.0 mM Cr(III) solution at pH = 2.0. Energy is plotted as $\chi_\mu$ over an increasing amount of incident x-ray energy. The height of the edge feature that begins at 6000 eV indicates the relative total Cr signal absorbed by the fluorescence detector. Cr adsorption increased in the first 1.8 hours of the reaction, and proceeded to decrease in the subsequent hours of the experiment.
Figure 25. Fluorescence Chromium k-edge XANES plot of synthetic Na-birnessite in a capillary reacted with a solution containing 1.0 mM Cr(III)(NO₃)₃·9H₂O at pH = 3.0. Energy is plotted as normalized $\chi\mu$ over an increasing amount of incident the X-ray energy. The height of the pre-edge feature at 5993 eV indicates the relative amount Cr(VI) present in the adsorbed Cr species. XANES patterns of Cr(III) and Cr(VI) standards are also plotted to illustrate presence of the distinct pre-edge feature of Cr(VI).
Figure 26. Fluorescence Chromium k-edge XANES plot of synthetic Na-birnessite in a capillary reacted with a solution containing 1.0 mM Cr(III)(NO$_3$)$_3$·9H$_2$O at pH = 2.0. Energy is plotted as normalized $\chi\mu$ over an increasing amount of incident the X-ray energy. The height of the pre-edge feature that at 5993 eV indicates the relative amount Cr(VI) present in the adsorbed Cr species. XANES patterns of Cr(III) and Cr(VI) standards are also plotted to illustrate presence of the distinct pre-edge feature of Cr(VI).
Figure 27. A comparison of the Chromium k-edge XANES absorption edge peaks of synthetic Na-birnessite in a capillary undergoing reaction with 1.0 mM Cr(III) solution at pH = 2.0, 3.0, 4.0, and 5.0. Energy is plotted as $\chi \mu$ over an increasing amount of incident x-ray energy. The height of the edge feature at 6020 eV was measured to determine the relative absorption at each pH level.
Figure 27. a) Results from Rietveld modeling of the time-resolved X-ray diffraction data monitoring the phase change from triclinic to hexagonal birnessite. The abundance of triclinic birnessite is plotted as a function over time. The slopes of the plots define the rate of transformation over time. Reaction with lower pH solutions resulted in faster transformations from triclinic to hexagonal birnessite. b) The log of the rate of transformation of triclinic birnessite to hexagonal birnessite plotted as a function of pH. A linear correlation can be derived from the pH of the solution passed through the capillary and the rate of phase transition, indicating the two variables are connected with each other. The slope of this plot is the rate order of the pseudo-first order reaction, and the y-intercept of this plot can be used to derive the constant of the rate law, k.
### Tables

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<td>Synthetic triclinic Na</td>
<td>1.0</td>
<td>-</td>
<td>5.1</td>
</tr>
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<td>Flow-Through</td>
<td>XRD, XANES, UV-Vis</td>
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<td>Synthetic triclinic Na</td>
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<td>-</td>
<td>3.4</td>
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<tr>
<td>Flow-Through</td>
<td>XRD, XANES, UV-Vis</td>
<td>4.0</td>
<td>Synthetic triclinic Na</td>
<td>1.0</td>
<td>-</td>
<td>9.1</td>
</tr>
<tr>
<td>Flow-Through</td>
<td>XRD, XANES, UV-Vis</td>
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<td>Synthetic triclinic Na</td>
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<td>-</td>
<td>11.9</td>
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<td>Flow-Through</td>
<td>XRD, XANES, UV-Vis</td>
<td>2.0</td>
<td>Synthetic hexagonal H</td>
<td>1.0</td>
<td>-</td>
<td>5.4</td>
</tr>
<tr>
<td>Flow-Through</td>
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<td>4.0</td>
<td>Synthetic hexagonal H</td>
<td>1.0</td>
<td>-</td>
<td>4.2</td>
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<td>Flow-Through</td>
<td>XRD, XANES, UV-Vis</td>
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<td>Natural &quot;hexagonal&quot;</td>
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<td>Synthetic triclinic Na</td>
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<tr>
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<td>UV-Vis</td>
<td>4.0</td>
<td>Synthetic hexagonal H</td>
<td>1.0</td>
<td>-</td>
<td>24.0</td>
</tr>
<tr>
<td>Flow-Through</td>
<td>UV-Vis, ICP-AES</td>
<td>4.0</td>
<td>Synthetic triclinic Na</td>
<td>1.0</td>
<td>-</td>
<td>24.0</td>
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<tr>
<td>Flow-Through</td>
<td>UV-Vis, ICP-AES</td>
<td>2.0</td>
<td>Synthetic triclinic Na</td>
<td>1.0</td>
<td>-</td>
<td>24.0</td>
</tr>
<tr>
<td>Batch</td>
<td>UV-Vis</td>
<td>2.0</td>
<td>Synthetic triclinic Na</td>
<td>1.0</td>
<td>-</td>
<td>25.0</td>
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<tr>
<td>Batch</td>
<td>UV-Vis</td>
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<td>Synthetic triclinic Na</td>
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<tr>
<td>Batch</td>
<td>UV-Vis</td>
<td>4.0</td>
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<td>-</td>
<td>25.0</td>
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<tr>
<td>Batch</td>
<td>UV-Vis</td>
<td>5.0</td>
<td>Synthetic triclinic Na</td>
<td>1.0</td>
<td>-</td>
<td>24.0</td>
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Table 1. A list of all of the experiments conducted in this study. Replicate experiments are not represented in this table.
Table 2. Rietveld unit cell parameters, atomic positions, site occupancy factors, and isotropic displacement factor for synthetic triclinic and hexagonal birnessite. Parameters for triclinic and hexagonal birnessite were obtained from Heaney et al. (2003) and Post et al. (2002), respectively.

<table>
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<tr>
<th>Space Group: C-1</th>
<th>parameters</th>
<th>Atom Positions</th>
<th>Site occupancy factor</th>
<th>U&lt;sub&gt;iso&lt;/sub&gt;</th>
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<td>c = 7.34 Å</td>
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<td>y</td>
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<td>γ = 90.0°</td>
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<td>Mn</td>
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<td>O</td>
<td>0.45</td>
<td>0.18</td>
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<tr>
<td>O</td>
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<td>Na/H&lt;sub&gt;2&lt;/sub&gt;O (int.)</td>
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<td>0</td>
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<td>Number of Variables: 11</td>
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<td>R&lt;sub&gt;WP&lt;/sub&gt;: 0.0213</td>
<td>χ&lt;sup&gt;2&lt;/sup&gt;: 2.857</td>
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</tbody>
</table>

<table>
<thead>
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<th>Space Group: P-3</th>
<th>parameters</th>
<th>Atom Positions</th>
<th>Site occupancy factor</th>
<th>U&lt;sub&gt;iso&lt;/sub&gt;</th>
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<tbody>
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<td>a = 2.84 Å</td>
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<td>c = 7.25 Å</td>
<td>x</td>
<td>y</td>
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<tr>
<td>α = 90.0°</td>
<td>β = 90.0°</td>
<td>γ = 120.0°</td>
<td>Mn&lt;sub&gt;(oct)&lt;/sub&gt;</td>
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<tr>
<td>O&lt;sub&gt;(oct)&lt;/sub&gt;</td>
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<td>O&lt;sub&gt;(int)&lt;/sub&gt;</td>
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<tr>
<td>O&lt;sub&gt;(int)&lt;/sub&gt;</td>
<td>0.667</td>
<td>Mn&lt;sub&gt;(int)&lt;/sub&gt;</td>
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<td>0</td>
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<tr>
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<td>R(F&lt;sup&gt;2&lt;/sup&gt;): 0.0233</td>
<td>R&lt;sub&gt;WP&lt;/sub&gt;: 0.0248</td>
<td>χ&lt;sup&gt;2&lt;/sup&gt;: 2.367</td>
</tr>
</tbody>
</table>
Supplementary Information A: Cr(VI) production in a flow-through reaction with various birnessite samples and 1.0 mM Cr(NO$_3$)$_3$·9H$_2$O at pH = 2.0 for 25 hours. [Cr(VI)] of approximately 1.0 mM was sustained throughout the entire duration of the experiment.
Supplementary Information B. Time-resolved X-ray diffraction patterns illustrating the structural symmetry of natural birnessite collected from Glasgow, PA during reaction with 1.0 mM Cr(NO$_3$)$_3$·9H$_2$O at pH = 4.00. Each exposure lasted 8 seconds during which the capillary was rotated 30 degrees.
Supplementary Information C. Chromium k-edge XANES plot of natural birnessite from Glasgow, PA in a capillary undergoing reaction with 1.0 mM Cr(III) solution at pH = 4.0. Energy is plotted as $\chi\mu$ over an increasing amount of incident x-ray energy. The height of the edge feature that begins at 5993 eV indicates the relative total Cr signal absorbed by the fluorescence detector.
Supplementary Information D. Fluorescence Chromium k-edge XANES plot of synthetic hexagonal H-birnessite in a capillary reacted with a solution containing 1.0 mM Cr(NO$_3$)$_3$·9H$_2$O at pH = 4.0. Energy is plotted as normalized $\chi\mu$ over an increasing amount of incident the X-ray energy. The height of the pre-edge feature that at 5993 eV indicates the relative amount Cr(VI) present in the adsorbed Cr species.
Supplementary Information E. Time-resolved X-ray diffraction patterns illustrating the structural symmetry of synthetic hexagonal H-birnessite during reaction solution with 1.0 mM Cr(III)(NO$_3$)$_3$·9H$_2$O was rotated 30 degrees.
Supplementary Information F. Time-resolved X-ray diffraction patterns illustrating the structural symmetry of synthetic hexagonal H-birnessite during reaction solution with 1.0 mM Cr(NO$_3$)$_3$·9H$_2$O at pH = 2.00. Each exposure lasted 8 seconds during which the capillary was rotated 30 degrees.
Supplementary Information G. Fluorescence Chromium k-edge XANES plot of synthetic hexagonal H-birnessite in a capillary reacted with a soltuion containing 1.0 mM Cr(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O at pH = 4.0. Energy is plotted as normalized $\chi\mu$ over an increasing amount of incident the X-ray energy. The height of the pre-edge feature that at 5993 eV indicates the relative amount Cr(VI) present in the adsorbed Cr species.
Supplementary Information H. Chromium k-edge XANES plot of synthetic hexagonal H-birnessite in a capillary undergoing reaction with 1.0 mM Cr(III) solution at pH = 2.0. Energy is plotted as $\chi\mu$ over an increasing amount of incident the x-ray energy. The height of the edge feature that begins at 5993 eV indicates the relative total Cr signal absorbed by the fluorescence detector.
Supplementary Information I. Fluorescence Chromium k-edge XANES plot of synthetic hexagonal H-birnessite in a capillary reacted with a solution containing 1.0 mM Cr(III)(NO$_3$)$_3$·9H$_2$O at pH = 2.0. Energy is plotted as normalized $\chi \mu$ over an increasing amount of incident the X-ray energy. The height of the pre-edge feature that at 5993 eV indicates the relative amount Cr(VI) present in the adsorbed Cr species.