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Release of Ni from birnessite during transformation of birnessite to todorokite:
Implications for Ni cycling in marine sediments

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ABSTRACT
The phyllomanganate birnessite is the main Mn-bearing phase in oxic marine sediments
where it exerts a primary control on the concentration of micronutrient trace metals in
seawater. However, during sediment diagenesis and under mild hydrothermal conditions
birnessite transforms into the tectomanganate todorokite. We have recently shown that the
transformation of birnessite to todorokite proceeds via a four-stage nucleation and growth
mechanism, beginning with todorokite nucleation, then crystal growth from solution to
form todorokite primary particles, followed by their self-assembly and oriented growth via
oriented attachment to form crystalline todorokite laths, culminating in traditional crystal
ripening (Atkins et al., 2014, GCA 144, 109-125). Here we determine the fate and
mobility of Ni sorbed by birnessite during this transformation process. Specifically, in our
recent work we predict that the presence of Ni within the phyllomanganate matrix will
disrupt the formation of todorokite primary particles. As such, contrary to current
understanding, we suggest that Ni sorbed by birnessite will slow the transformation of
birnessite to todorokite and/or be released to marine porewaters during sediment
diagenesis. Here we transform a synthetic, poorly crystalline, Ni-sorbed (∼1 wt% Ni)
hexagonal birnessite, analogous to marine birnessite, into todorokite under a mild reflux
procedure, developed to mimic marine diagenesis and mild hydrothermal conditions. We
characterize our birnessite and reflux products as a time series, including X-ray diffraction
(XRD), high-resolution transmission electron microscopy (HR-TEM) and extended X-ray
absorption fine structure (EXAFS) spectroscopy. In addition we determine Ni speciation
and mineral phase associations in a suite of natural marine ferromanganese precipitates,
containing intermixed phyllomanganate and todorokite. Our work shows for the first time
that Ni significantly slows the transformation of birnessite to todorokite and reduces the
crystallinity of the neo-formed todorokite phase, but does not alter the mechanism and
pathway of todorokite formation, compared to a Ni-free system. Furthermore, in systems
tending towards todorokite as the final diagenetic product, we see that up to 50 % of the
Ni originally sequestered by birnessite is released to solution during the transformation.
Our work indicates that the transformation of birnessite to todorokite in oxic marine
sediments likely provides a significant source of Ni to marine sedimentary porewaters and
potentially a hitherto unrecognized benthic flux of Ni to seawater.

KEYWORDS: vernadite, birnessite, buserite, todorokite, nickel, manganese oxide,
ferromanganese, transformation, oriented aggregation, seawater.
1. INTRODUCTION

The phyllomanganates birnessite and buserite, together with the tectomanganate todorokite, are the dominant Mn-bearing minerals in oxic marine sediments and ferromanganese deposits, where they are typically found as poorly crystalline and intermixed nanoparticulate phases (e.g., Goldberg, 1954; Burns and Burns, 1977; Usui and Terashima, 1997; Banerjee et al., 1999; Post, 1999). Birnessite and buserite in particular are highly reactive and through coupled sorption and redox reactions exert a strong control on the concentration, speciation and bioavailability of trace metals and micronutrients in seawater (e.g., Post, 1999). Indeed, the poorly crystalline phyllomanganates present in ferromanganese crusts and nodules are typically enriched in trace metals such as Ni, Cu and Zn by $\sim 10^6$ over their respective concentrations in seawater (e.g., Arrhenius, 1963; Koschinsky and Hein, 2003). Specifically with regard to Ni, ferromanganese oxides dispersed in pelagic sediments and precipitated as discrete crusts and nodules provide the only known sinks for Ni in the modern marine Ni cycle (Gall et al., 2013). These minerals typically contain between $\sim 0.2$-1 wt% Ni, exclusively sorbed to the Mn-rich fraction (e.g., Koschinsky and Halbach, 1995; Koschinsky and Hein, 2003; Peacock and Sherman, 2007a), as a result of a sorption equilibrium between Ni and poorly crystalline phyllomanganate that is predicted to provide a primary control on the concentration of Ni in the modern oceans (Peacock and Sherman, 2007b).

In oxic marine sediments however, the poorly crystalline phyllomanganates transform into todorokite during oxic diagenesis and under mild hydrothermal conditions. In the case of Ni, previous work shows that dissolved Ni is readily sequestered to birnessite via surface complexation above and below Mn octahedral vacancy sites present on the birnessite [001] surface (space group p63/mmc) (e.g., Manceau et al., 2007a,b; Peacock and Sherman, 2007a,b; Peacock, 2009; Peña et al., 2010). Subsequent to this initial sequestration, with aging and under pH conditions relevant to the marine environment, surface complexed Ni progressively migrates into the birnessite crystal lattice to become structurally incorporated (Peacock, 2009), and in natural marine ferromanganese precipitates Ni is found entirely incorporated into birnessite and buserite (Peacock and Sherman, 2007a). Despite our understanding of Ni sequestration by phyllomanganates, the mobility and fate of Ni and other micronutrients during the transformation of these phases into todorokite remains unclear. Our recent work on the mechanism of todorokite nucleation and growth suggests that, contrary to current understanding, trace metals like Ni might slow the transformation of birnessite to
todorokite and be released to marine sedimentary porewaters during this diagenetic
process, thus potentially providing a benthic flux of these micronutrients to seawater
(Atkins et al., 2014). A complete knowledge of the controls on Ni concentrations and
isotopic compositions in seawater is important for our understanding of the modern
marine Ni cycle (e.g., Cameron and Vance, 2014), and also for the interpretation of palaeo
Ni signals recorded in marine sedimentary archives (e.g., Cameron et al., 2009; Konhauser
et al., 2009).

In the natural environment Mn(III/IV) oxides are thought to form via the microbial
oxidation of Mn(II) (e.g., Brouwers, 2000; Francis et al., 2001; Bargar et al., 2000, 2005;
Villalobos et al., 2003; Tebo et al., 2005; Webb et al., 2005a, b; Saratovsky et al., 2006;
Spiro et al., 2010). However, although todorokite is often found intimately associated with
turbostratic phyllomanganate (termed vernadite) and both 7 Å (birnessite) and 10 Å
(buserite) semi-coherently stacked phyllomanganates (here all collectively termed poorly
crystalline phyllomanganates) in marine ferromanganese precipitates (e.g., Burns and
Burns, 1978a, b; Siegel and Turner, 1983; Usui and Terashima, 1997; Banerjee et al.,
1999; Bodei et al., 2007; Peacock and Moon, 2012), it is thought to only form during the
transformation of a phyllomanganate during oxic sediment diagenesis and under low
temperature hydrothermal conditions (e.g., Burns and Burns, 1978b). Indeed, observations from both natural ferromanganese samples and experiments largely support
this assertion. For example, todorokite is rarely found in hydrogenetic ferromanganese
crusts precipitated directly from ambient seawater, but is found to varying extents in
diagenetic ferromanganese nodules formed at the sediment-seawater interface with
influence from sediment porewaters, and is prevalent in hydrothermal ferromanganese
deposits formed in close proximity to hydrothermal fluids (e.g., Burns and Burns, 1977).
Moreover, all todorokite synthesis procedures to date involve the transformation of a
phyllomanganate via either a high temperature and pressure hydrothermal treatment (e.g.,
Giovanoli et al., 1975; Golden et al., 1987; Shen et al., 1993; Feng et al., 1995, 1998; Tian
et al., 1997; Vileno et al., 1998; Ching et al., 1999; Luo et al., 1999; Malinger et al., 2004;
Liu et al., 2005) or a more mild refluxing process at atmospheric pressure, designed to
better simulate todorokite formation in natural environments (e.g., Feng et al., 2004, 2010;
Cui et al., 2006, 2008, 2009; Atkins et al., 2014). To best replicate the morphological and
structural features of natural marine todorokite, these syntheses are typically performed in
a Mg-rich electrolyte (~1 M MgCl₂) where Mg is prevalent in marine sediment porewaters
and acts as a templating ion, expanding the precursor birnessite interlayers from ~7 Å to
~10 Å (e.g., Bodei et al., 2007), which closely matches the eventual tunnel dimensions of
the neo-forming todorokite (where ideal todorokite consists of triple chains of edge-
sharing MnO$_6$ octahedra that share corners to form 3D tunnels equating to ~10x10 Å
(Burns et al., 1985; Post and Bish, 1988; Post et al., 2003)). Attempts to synthesize
todorokite using Ca as a templating ion (likely more relevant to terrestrial todorokite)
typically result in an incomplete transformation (e.g., Golden et al., 1987) and may in part
explain the relative rarity of todorokite in terrestrial vs. marine settings (e.g., Chukrov
and Gorshkov, 1981; Dixon and Skinner, 1992; Manceau et al., 2007a,b). The necessity
for a high ionic strength is also demonstrated in the work to date, where relatively low
concentrations of MgCl$_2$ (~0.01 M) result in an intermediate birnessite with an interlayer
spacing that is somewhat larger (e.g., Cui et al., 2006) than that typically observed in
natural todorokite (e.g., Bodei et al., 2007).

Classically, the transformation of birnessite to todorokite is described as a
topotactic process, during which some of the morphological features and structural
elements of the precursor phyllomanganate are preserved in the neo-formed todorokite
(e.g., Bodei et al., 2007; Feng et al., 2010). Structural incorporation of heterovalent
cations, including Cu(II) and Ni(II), is thought to aid transformation (Burns and Burns,
1978a; Burns and Burns, 1979; Usui, 1979; Takematsu et al., 1984), as is the presence of
structural Mn(III) where, because of its Jahn-Teller distortion, Mn$^{3+}$-O-Mn$^{4+}$ bonds that
run parallel to the eventual [010] direction in todorokite (space group p2/m) should be
relatively weak and most susceptible to topotactic rearrangement (Bodei et al., 2007; Cui
et al., 2008; Zhao et al., 2015). However, the specific mechanistic details of the
transformation were largely unclear. Recently, we report a new nucleation and growth
model for the formation of todorokite in the marine environment (Atkins et al., 2014). The
initial nucleation and growth stages likely occur simultaneously and are initiated by a
thermally-induced kinking of the birnessite layers in nano-domains that act as nucleation
sites for the formation of todorokite primary particles, where a significant proportion of
structural Mn(III) and semi-coherent c-axis ordering are prerequisites for todorokite
formation (Atkins et al., 2014). Todorokite primary particles then grow along the
direction of tunnel growth ([010] crystallographic direction) via dissolution-
recrystallization and assemble spontaneously via oriented attachment (OA), attaching at
crystal faces perpendicular to the direction of tunnel growth ([100] crystallographic
direction), to form large laths of todorokite (Atkins et al., 2014). The process likely
culminates in a traditional ripening of the neo-formed todorokite crystals, commencing after the complete transformation of the birnessite precursor (Atkins et al., 2014).

While this new model explains many of the unique morphological and structural features observed in natural todorokites, it also raises important questions about the long-term sequestration of trace metals during phyllosilicate transformation and todorokite crystal growth. In addition to todorokite, there is now a diverse and rapidly growing catalogue of minerals known to grow via OA, including TiO$_2$, Cu and Fe (hydr)oxides, ZnS, cryptomelane-type Mn oxide and CaSO$_4$ (Penn and Banfield, 1998a,b; Penn and Banfield, 1999; Banfield et al., 2000; Gilbert et al., 2003; Huang et al., 2003; Waychunas et al., 2005; Portehault et al., 2007; Burrows et al., 2012; Van Driessche et al., 2012; Frandsen et al., 2014). Many of these minerals are ubiquitous in natural soils and sediments and play important roles in the biogeochemical cycling of trace metals, yet to date there have been few studies investigating the effects of OA type-growth on the retention of sorbed trace metal impurities. In our recent work, we propose that, contrary to traditional understanding, only structurally incorporated heterovalent cations with Jahn-Teller distortion, resulting in the relatively weak metal-O-Mn$^{4+}$ bonds necessary to facilitate phyllosilicate layer kinking, will promote the nucleation of todorokite and subsequent formation of todorokite primary particles (Atkins et al., 2014). We suggest that for Ni-sorbed phyllosilicates (where Ni(II) is not Jahn-Teller distorted) Ni(II) will slow the transformation of birnessite to todorokite, and be released to solution, in order that transformation can proceed. Indeed, it has been noted that natural todorokite typically contains significantly less Ni compared to the 10 Å phyllosilicate from which it crystallized (Siegel and Turner, 1983; Bodeï et al., 2007).

Considering the few studies to investigate the fate of sorbed trace metals during OA-type crystal growth, Kim et al. (2008) find that the progressive adsorption of Cu(II), Zn(II), As(V) and Hg(II) onto nanoparticulate goethite surfaces disrupts growth via OA, by essentially blocking attachment and aggregation interfaces. Similarly, Burrows et al. (2012) find that the growth rate of goethite nanorods via OA is inhibited due to the association of NO$_3^-$ with the aggregating crystal faces. These authors conclude that if nanoparticle growth by OA is to proceed, impurities at aggregation interfaces must either be structurally incorporated into the mineral structure or desorbed into solution. For poorly crystalline phyllosilicates however, because the octahedral layers are only a single Mn octahedron thick, impurities incorporated into the crystal structure are effectively still present at aggregation interfaces and so potentially still able to disrupt OA
(Atkins et al., 2014). These recent studies provide evidence to suggest that sorbed trace metal impurities might slow transformation and/or be desorbed into solution in mineral systems that grow via OA-type mechanisms.

In order to determine the effect of Ni on todorokite nucleation and growth, and investigate the mobility and fate of Ni sequestered by birnessite during its transformation into todorokite, we synthesize todorokite from a Ni-sorbed c-disordered hexagonal birnessite, via a mild reflux procedure. Our Ni-sorbed birnessite precursor is analogous to marine birnessite and displays sufficient ordering of the phyllomanganate layers along the c-axis to enable the identification of key spectral, structural and morphological features in the precursor c-disordered birnessite, 10 Å phyllomanganate intermediate and transformation products. The birnessite, 10 Å phyllomanganate and subsequent transformation products are extensively characterized including X-ray diffraction (XRD), and high-resolution transmission electron microscopy (HR-TEM), while the mobility and fate of Ni during the conversion is determined via HR-TEM energy dispersive spectroscopy (HR-TEM EDS), Ni K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy and inductively coupled plasma optical emission spectrometry (ICP-OES). In addition, we use μX-ray fluorescence (μXRF) and μEXAFS to determine the dominant Mn oxide mineralogy and Ni mineralogical phase associations in a suite of natural marine ferromanganese precipitates, namely a hydrogenetic crust, a diagenetic nodule and a hydrothermal-type deposit. With careful and combined analysis of our work we determine the effect of sorbed Ni on, and its mobility and fate during, the transformation of birnessite to todorokite, and use our findings to shed light on the cycling of Ni sequestered by birnessite in oxic marine sediments.

2. EXPERIMENTAL METHODS

2.1 Preparation of Ni-Sorbed Hexagonal Birnessite Precursor

Ni-sorbed c-disordered hexagonal birnessite with an interlayer spacing of ~7 Å and ~1 wt% Ni was synthesized following a modified method of Villalobos et al. (2003). Briefly, 320 mL of a 0.196 M KMnO₄ solution was added slowly to 360 mL of 0.51 M NaOH solution. Subsequently ~3.4 g of Ni(NO₃)₂ was added to 320 mL of a 0.366 M MnCl₂ solution and added slowly to the above mixture whilst stirring vigorously at room temperature. After 30 min 5x 1 mL suspension aliquots were taken in order to quantify the amount of mineral precipitated. The mineral suspension was then left to settle for ~4 hr,
after which the remaining supernatant was subsequently discarded and the wet mineral slurry centrifuged at 3200 g for 30 min. After centrifugation, the wet slurry was washed:
initially 4 times by mixing with 1 M NaCl, with the first 3 washes shaken for 45 min and the last wash adjusted to pH 8 and shaken overnight; then finally 10 times, 1x for 1 hr, 8x for 0.5 hr and 1x overnight, by mixing with Milli-Q water (MQ); with all suspensions centrifuged at 3200 g for 10 min. Approximately ¼ of the total resulting wet paste was sacrificed for ICP-OES, to determine the total concentration of Ni sequestered to the solid product, XRD, HR-TEM, BET surface area analysis and EXAFS spectroscopy. For ICP-OES, aliquots of the sacrificed wet paste were dissolved in 3 M HCl and analysed for Ni at the Trace Element Laboratory in the Department of Chemistry at the University of Hull, using an Optima 5300 DV. Sample standard deviation is calculated based on measurement of 3 separate aliquots. Our birnessite precursor contained ~1 wt% Ni (Table 1).

2.2 Transformation of Ni-Sorbed Hexagonal Birnessite to Todorokite

Our Ni-sorbed birnessite was transformed to todorokite following the method of Atkins et al. (2014), originally adapted from Feng et al. (2004, 2010). Briefly, the wet paste Ni-sorbed birnessite was suspended in ~4 L of 1 M MgCl₂ and stirred moderately for 18 hr at room temperature before centrifuging to a wet paste. This produced a Ni-sorbed 10 Å phyllovakite which was re-suspended in ~800 mL of 1 M MgCl₂ in a 1 L round bottom flask fitted with a glass condenser. The suspension was stirred continuously and heated to and kept at 100 °C using a combined heating mantle with magnetic stirrer. The suspension was then left to age under reflux for 4 wk, during which time suspension aliquots (~75 mL) were extracted at 3, 6, 12, 24, 48 and 72 hr, 5 days, and 1, 2 and 4 wk. Each aliquot was cooled in a water bath to room temperature before centrifuging at 3200 g for 10 min. Supernatant solutions were collected and the pH measured (calibrated to ±0.05 pH units with Whatman NBS grade buffers). Triplicate aliquots of each supernatant solution were filtered through 0.2 μm syringe filters and retained for Ni and Mn analysis via ICP-OES as above. All solid samples were washed extensively in 18.2 MΩ cm MQ water and oven dried at 30 °C, after which aliquots were subject to total digest for ICP-OES as above, XRD, HR-TEM, BET surface area analysis and EXAFS spectroscopy as below. It should be noted that Ni and Mn solution analysis, Ni total digest analysis and BET surface area were not measured at the 2 wk reflux time point.
2.3 Natural Ferromanganese Samples

A hydrogenetic crust (237KD; Pacific Ocean; location: 09°18’N, 146°03’W; water depth: 4830 m), diagenetic nodule (Nod-P-1; Pacific Ocean; location: 14°50’N, 124°28’W; water depth: 4300 m) and hydrothermal deposit (D17-1-IV; Lau Basin; location: 22°17.78’S, 176°38.89’W; water depth: 2063-1965 m) sample were supplied by J.R. Hein (United States Geological Survey). A small section (~ 20 mm in length and perpendicular to the growth layers, 15 mm wide and 5 mm deep) from the upper 0-60 mm of each bulk sample was cut using a wafering saw, and a small amount of material was extracted using a micro drill, ground to a fine powder and dissolved in 6 M HCl, and analysed for bulk Ni content by ICP-OES as above. Bulk Ni contents for the hydrogenetic, diagenetic and hydrothermal samples are ~0.4, 0.5 and 0.07 wt.% Ni, respectively. The sections were subsequently encased in high purity resin and self-supported ~30 μm thick polished sections were prepared for μXRF and μEXAFS (Peacock and Moon, 2012). Previously reported chemical analyses of the hydrogenetic, diagenetic and hydrothermal samples give bulk Mn:Fe ratios of 1.9, 5 and 114, respectively, which are within the ranges expected for ferromanganese precipitates assigned to these different genetic types (Rehkämper et al., 2002).

2.4 Characterization of Precursor, Intermediate and Reflux Products

Powder XRD patterns were collected using a Bruker D8 diffractometer, operating at 40kV/40mA and equipped with CuKα radiation (λ = 1.5418) and a LynxEye detector. Samples were analyzed over 2-90 °20 with a 0.009° step size and step count time of 7 sec. Data evaluation was undertaken using the DIFFRAC plus EVA software package. For the natural ferromanganese samples, distinctly Mn-rich regions of the samples (i.e., dark brown/black areas) were chosen to avoid obviously Fe-rich areas.

HR-TEM images were collected at the Leeds Electron Microscopy and Spectroscopy center in the Institute for Materials Research at the University of Leeds. Finely crushed powder samples were suspended in methanol and dispersed via sonication. Samples were then loaded onto individual holey carbon TEM grids and dried at room temperature. Imaging was performed at 200 kV on a Philips CM200 FEGTEM. EDS data was collected at several points of interest using the TEM. The wt% of Ni identified at each specific point of interest was measured using a standardless procedure where the errors associated with each wt% are given as the standard deviation of triplicate measurements, but the absolute limit of detection cannot be quantified. It is important to note that while
our EDS data can be used for relative comparison of Ni concentrations between measured points, it cannot be used as a quantitative measure of absolute Ni concentrations.

Specific surface area of all samples was measured using the BET-N$_2$ method using a Gemini V2365 system (Micromeritics Instrument Corp.). Samples were dried and degassed at room temperature for 24 hr. Reported BET values are ±5%.

2.5 X-ray Absorption and Fluorescence Spectroscopy

We collected Ni K-edge (8.333 keV) EXAFS spectra for our Ni-sorbed birnessite, 10 Å phyllomanganate and subsequent reflux products. Micro-focus $\mu$XRF elemental maps (for Mn, Fe and Ni) and $\mu$EXAFS (at the Ni and Mn-K edges (6.539 keV)) were also collected for the natural ferromanganese samples. Spectra were collected at Diamond Light Source (DLS) Ltd. on station B18 (synthetic samples) and I18 (natural samples). During data collection, storage ring energy was 3.0 GeV and the beam current was approximately 200 mA. Samples were presented to the X-ray beam as dry powders pressed into pellets (synthetic samples), or as ~30 µm thick self-supported thin sections (natural samples), held between Kapton tape. Data was acquired in fluorescence mode (Ni K-edge) or transmission mode (Mn K-edge). We saw no photo-redox or visible beam damage on the samples after 6 EXAFS scans to $k = 14$ Å$^{-1}$ but in order to minimize beam damage we recorded 4 spectra at a single x,y point before moving to a new point to record a further 4 spectra, collecting a total of 36 spectra (for Ni K-edge of the synthetic samples) or up to 9 spectra (9 for Ni K-edge and 4 for Mn K-edge of the natural samples). $\mu$XRF maps were collected at 8.4 keV with a pixel size of 10x10 µm and a count time of 1 sec per pixel. Maps were deadtime corrected and registered using custom beamline software. Maps were used to identify points of interest (POI) with positive Ni-Mn correlations, for collection of Ni and Mn $\mu$EXAFS. For $\mu$EXAFS the beam spot was ~2x3 µm. Energy calibration was achieved by assigning the first inflection point of Au (L3) foil to 11.919 keV.

EXAFS data reduction was performed using ATHENA (Ravel and Newville, 2005) and the Ni spectra were fit using DL_EXCURV (Tomic et al., 2005). Spectra were fit in $k$-space over 3 – 12 Å$^{-1}$, with no Fourier filtering, and the fitting included full multiple scattering as coded in EXCURV98 (Binsted, 1998). Multiple scattering calculations require specification of the full three dimensional structure of the Ni coordination environment (i.e., bond lengths and angles). This was done using hypothetical model clusters with either $C_1$ or $C_3$ symmetry, for various different Ni local
coordination geometries, including Ni adsorbed at Mn octahedral vacancies in the phyllomanganate layers (Peacock and Sherman, 2007b), Ni structurally incorporated into the phyllomanganate layers (Peacock and Sherman, 2007a,b) and Ni sorbed to todorokite (Fig. 1). Several reference compounds were used to help fit the EXAFS spectra, namely a synthetic Ni-sorbed c-disordered birnessite where Ni is surface adsorbed at the vacancies, a natural Ni-incorporated poorly crystalline phyllomanganate where Ni is structurally incorporated, and two Ni-sorbed todorokite samples prepared at 24 hr and 1 wk contact times (section 2.6). The reference spectra were fit by refinement of a single model cluster. Where appropriate, the sample spectra were fit by linear combination of different model clusters as coded in EXCURV98 (Binsted, 1998). Linear combination was performed over the $k$-range $3 – 12 \text{ Å}^{-1}$ with a linear combination of the $k^2$-weighted Chi($k$) for each cluster. In the linear combinations only EF and relative site occupancies were optimized. For all fits, the number of independent data points ($N_{\text{ind}}$) was determined using Stern’s rule (Stern, 1993) as $2\Delta k\Delta R/\pi + 1$ (Booth and Hu, 2009) where $\Delta k$ and $\Delta R$ are the range in $k$ and $R$-space actually fitted. The number of fitted parameters ($N_{\text{par}}$) was determined as the total number of parameters optimized during the various model refinements and was always less than $N_{\text{ind}}$.

We also performed linear combination fitting for some of the Mn spectra recorded for the natural ferromanganese samples in ATHENA. In these cases fitting was done with a linear combination of the Chi($k$) for the $\delta$MnO$_2$ and todorokite reference spectra, over the $k$-range $3 – 12 \text{ Å}^{-1}$, and without constraining the component sum to equal 1.

For the Ni spectra, fit in DL_EXCURV, the quality of the fits provided by the different model clusters was assessed using the EXAFS $R$-factor and the reduced Chi$^2$ function, which provides an absolute index of goodness of fit (and so can be used for comparing fit quality between fits where $N_{\text{par}}$ is not equivalent; all as coded in EXCURV98 (Binsted, 1996, 1998)). For the Mn spectra, fit in ATHENA, the errors reported are those typically applied to 2-component mixtures (e.g., Kim et al., 2000). The errors associated with the EXAFS modelling and linear combination fits are described in detail in the Supplementary Information (section S2.5).

2.6 Reference Compounds

A range of Ni-free synthetic Mn oxides were prepared as described in Atkins et al. (2014) and used as references during the above analyses, including triclinic Na-birnessite (Tc-Na-birnessite), crystalline hexagonal birnessite (Hx-birnessite), c-disordered
hexagonal birnessite, all with an interlayer spacing of ~7 Å, δMnO₂ and crystalline
todorokite. Mineral identity and purity was confirmed by XRD analysis of randomly
orientated powder samples.

The Ni-sorbed Mn oxides used as references during the EXAFS analysis included
a Ni-sorbed c-disordered birnessite, a Ni-incorporated natural poorly crystalline
phylلومanganate, and Ni-sorbed todorokite. Preparation of the Ni-sorbed birnessite and
todorokite reference samples is described in the Supplementary Information (section
S2.6). The natural phylломanganate is catalogued as hydrogenetic ferromanganese crust
sample 5DSR8 (Pacific Ocean; location: 04°09’S, 174°54’W; water depth: 1585 m) from
Chu (2004), and was sourced from the National Oceanography Centre, Southampton as a
dry powder with no further preparation performed.

3. RESULTS
3.1 Transformation of Ni Sorbed Hexagonal Birnessite to Todorokite
3.1.1 X-ray diffraction
XRD patterns for our Ni-sorbed birnessite, 10 Å phylломanganate and all
subsequent reflux products are shown in Figure 2. The diagnostic XRD features for our
birnessite, 10 Å phylломanganate and todorokite are discussed in Atkins et al. (2014) and
summarised here in the Supplementary Information (section S3.1.1).

Our birnessite shows 4 broad peaks at ~7.2 Å, ~3.6 Å, ~2.4 Å and ~1.4 Å,
respectively (for reference pattern see turbostratic birnessite, Drits et al., 1997). Following suspension in 1
M MgCl₂, the interlayer spacing is expanded from ~7 Å to ~10 Å as indicated by the
appearance of peaks at ~9.6 Å, ~4.8 Å and ~3.2 Å ([001], [002] and [003] basal
reflections, respectively) in our 10 Å phylломanganate (for reference pattern see busserite
JCPDS-32-1128). For both phases, the slight degree of asymmetry on the high angle side
of the ~2.4 Å peak indicates a lack of periodic ordering (Villalobos et al., 2006), however,
in agreement with our previous work, the basal reflections of our 10 Å phylломanganate
are more intense than those of the birnessite suggesting that the ion-exchange process
enhances the crystallinity and long range ordering of the layers (Atkins et al., 2014). For
both our birnessite and 10 Å phylломanganate, the d100/d110 peak intensity ratios are
close to √3 (at 2.42/1.41 and 2.40/1.41, respectively), and the 1.4 Å peak is symmetrical,
indicating that both phases have hexagonal layer symmetry with $a = b = 2.83$ Å (Drits et al., 1997).

Over the course of the reflux there is little evidence for the formation of todorokite (JCPDS-38-475) during the first 24 hr (Fig. 2). The four distinct changes in the XRD patterns, expected during the transformation of birnessite to todorokite (Atkins et al., 2014; section S3.1.1), only start to become visible by 48 hr reflux (Fig. 2). Firstly, by 48 hr reflux we observe broad characteristic todorokite peaks at ~2.2 Å, ~1.9 Å and ~1.7 Å, and a broad hump at ~1.5 Å, indicating that transformation of the 10 Å phyllomanganate to todorokite has begun (Feng et al., 2004; Atkins et al., 2014). As the reflux proceeds these peaks become sharper and more intense indicating the progressive formation of todorokite. Secondly, by 48 hr reflux the peak at ~2.4 Å has begun to split to reveal a shoulder at ~2.45 Å, which becomes more prominent with time. Thirdly, the peak at ~5 Å has begun to broaden, developing into a broad shoulder on the high-angle side at ~4.3 Å. Fourthly, the peak at ~1.4 Å has started to become progressively asymmetrical. These later three changes are those expected during the transformation of 10 Å phyllomanganate into todorokite (Feng et al., 2010; Atkins et al., 2014).

3.1.2 Transmission electron microscopy

HR-TEM images are shown in Figure 3 and highlight the gradual transformation of our 10 Å phyllomanganate into todorokite over the first 2 wk of reflux. Our 10 Å phyllomanganate has a rumpled plate-like morphology, where the edges of the layers measure ~5-7 nm wide (Fig. 3a, inset). Repetition of the [001] lattice planes indicates that the individual layers are reasonably well stacked over at least 3 nm. The measured interlayer of the 10 Å phyllomanganate is equal to ~0.82 nm (Fig. 3b), which although inconsistent with that measured via XRD (0.96 nm; Fig. 2), is consistent with the partial collapse of the layers under the high vacuum conditions of the TEM (e.g., Post and Veblen, 1990; Atkins et al., 2014). At 6 hr reflux the morphology is still dominated by the platy 10 Å phyllomanganate phase (Fig. 3c,d), however, small primary particles of todorokite elongated longitudinally along the direction of tunnel growth ([010]) and measuring ~6-10 nm wide across the direction of tunnel growth ([100]) are also visible within the sample matrix (Fig. 3c,d). These particles display poorly defined lattice fringes (Fig. 3c,d), and are therefore only poorly crystalline, consistent with the lack of todorokite XRD peaks in the first few hours of reflux (Fig. 2). At 24 hr reflux, the mineralogy is still dominated by the 10 Å phyllomanganate, however, the todorokite primary particles have
begun to form platy todorokite aggregates measuring ~200x200 nm (Fig. 3e), and in particular, large laths of todorokite measuring ~250 nm in length (along the direction of tunnel growth) and ~70 nm wide (across the direction of tunnel growth) (Fig. 3f). These laths are assembled from a number of smaller primary particle building blocks that vary in length but measure consistently between ~8-10 nm wide. With increasing reflux time, these secondary laths increase in size, particularly in the longitudinal direction, and after 1 wk we see large laths which dominate the overall morphology, measuring on average ~460 nm long and ~70 nm wide (Fig. 3g). By 1 wk reflux, we also see that individual laths are aligned with each other at 120° to form large aggregates of todorokite that exhibit a plate-like morphology (Fig. 3h). These large plates (>1000x500 nm), orientated in three distinct directions, are arranged into stacked layers along the [001] direction (Fig. 3h). By 2 wk reflux, the average size of the laths has increased further to ~700 nm long and ~150 nm wide, and the lattice fringes of the laths are notably more defined, indicating an increase in the crystallinity of the neo-formed todorokite with time (Fig. 3i,j); we are also unable to find any 10 Å phyllomanganate or phyllomanganate-like phase within the sample matrix, indicating that by this time point the 10 Å phyllomanganate has undergone essentially complete transformation into todorokite (multiple sub-samples of the solid extracted at this time point were scanned over extended areas, with images typified by Fig. 3i,j).

EDS data collected at 6 and 24 hr, and 1 and 2 wk reflux, for selected points (marked on Fig. 3, where point 1 and 2 are on the 10 Å phyllomanganate and todorokite matrix, respectively), is shown in Table 2 and provides a relative measure of Ni concentration and distribution in the 10 Å phyllomanganate and todorokite phases (section 2.4). From 6 hr to 1 wk reflux, despite the progressive formation of todorokite, the majority of the sequestered Ni in the measured sample points is associated with the 10 Å phyllomanganate and there is no detectable Ni associated with the todorokite primary particles or laths (Table 2). At 2 wk reflux, when there is no observable 10 Å phyllomanganate or phyllomanganate-like phase within the sample matrix, there is similarly no detectable Ni associated with todorokite (where several points on a number of different todorokite laths and plate-like aggregates were measured, all typified by the 2 wk EDS point, Fig. 3i, Table 2). Overall our EDS data can be interpreted to indicate that, of the solid-associated Ni, there is relatively more Ni associated with the transforming phyllomanganate compared to the neo-forming todorokite. EDS spectra are shown in Figure S1 (Supplementary Information).
3.1.3 Physiochemical characterisation

The absolute measurements of Ni wt% in our birnessite, 10 Å phyllomanganate and subsequent reflux products are shown in Table 1. Surface area, reaction solution Mn and Ni concentration, and pH are shown in Table 3 and/or Figure 4. The absolute concentration of Ni associated with the solid phase shows little variation from the birnessite to the 10 Å phyllomanganate, and subsequently up to and including the first 72 hr of reflux, with our birnessite containing 0.92±0.002 wt% Ni and our 72 hr sample containing 0.98±0.010 wt% Ni (Table 1). The concentration of Ni associated with the solid phase drops to 0.80±0.011 wt% Ni by 1 wk and the final todorokite product contains 0.54±0.003 wt% Ni by 4 wk reflux. Overall we observe a ~50 % reduction in the concentration of Ni sequestered to the solid product over the duration of the reflux.

Dissolved [Mn] in the reaction solution shows an initial spike from 0.003 mM by 3 hr, to 0.017 mM by 6 hr, remaining relatively constant up to and including 24 hr, and subsequently decreasing to 0.01 mM by 48 hr reflux (Fig. 4, Table 3). This initial spike is followed by a relatively gradual overall decrease towards the final time point, with [Mn] at 4 wk comparable to that measured at 3 hr reflux. Consistent with the decrease in solid-associated Ni during the course of the 4 wk reflux, dissolved [Ni] in the reaction solution increases from 0.004 mM by 3 hr to 0.093 mM by 4 wk reflux.

The surface area of the 10 Å phyllomanganate is 102.3 m²/g, which decreases to 84 m²/g by 3 hr, with little variation during the first 12 hr, then increases to 97 and 99 m²/g by 24 and 48 hr, respectively, with a second and more substantial drop to 37 m²/g by 1 wk reflux. Surface area then continues to decrease to 20 m²/g by the full 4 wk reflux. Overall we observe an ~80 % reduction in surface area over the duration of the 4 wk reflux (Fig. 4).

The pH of the cooled reaction solutions shows a slight increase from pH ~5.29 to 5.93 over the first 72 hr of reflux, then remains relatively stable until a more substantial drop occurs from pH ~5.81 at 1 wk to ~4.26 at 4 wk reflux (Table 3).

3.1.4 Ni K-edge X-ray absorption spectroscopy

3.1.4.1 Reference compounds

Ni K-edge EXAFS and Fourier transforms for the reference compounds are shown in Figure 5 and fits are summarized in Table 4. Visual inspection of the Ni-sorbed birnessite and Ni-incorporated natural phyllomanganate reference spectra indicate that the
Ni local coordination environment is very similar to that found previously for Ni adsorbed to hexagonal birnessite, where Ni is located at Mn octahedral vacancy sites present in the phyllomanganate layers (Peacock and Sherman, 2007a,b; Peacock, 2009; Peña et al., 2010), and Ni-rich marine ferromanganese precipitates were Ni is found entirely structurally incorporated into the phyllomanganate layers (Peacock and Sherman, 2007a,b; Peacock, 2009), respectively. In agreement with this previous work, the best fits to our Ni-sorbed and Ni-incorporated reference spectra are provided by optimization of the model clusters representing Ni adsorbed at vacancies and Ni incorporated into the phyllomanganate layers, respectively (Fig. 5, Table 4).

In contrast to Ni adsorbed on and incorporated into birnessite, there has been very little work to determine the crystal-chemical mechanism of Ni uptake by todorokite. Theoretically, trace metals could sorb to todorokite via outer-sphere surface complexation, where Ni might be located in the todorokite tunnels (e.g., Pakarinen et al., 2010), or via inner-sphere surface complexation, where Ni could adsorb to Mn(OH) sites present at the edges of the triple chains that form the todorokite framework, akin to Ni adsorption on triclinic birnessite in which there are no Mn octahedral vacancy sites (Peacock and Sherman, 2007b), and at high Ni loading on hexagonal birnessite when the vacancy sites are saturated (Maneeau et al., 2007a). Sorbed as an outer-sphere complex, the Ni-sorbed todorokite EXAFS spectrum would resemble that of Ni$^{2+}$(aq) where Ni is surrounded by 6 O at ~2.04±0.02 Å (e.g., Xu et al., 2007). Adsorbed at the Mn(OH) sites, the Ni-sorbed todorokite spectrum would likely reflect Ni adsorbed as either a tridentate corner-sharing complex, as per Ni adsorbed on triclinic birnessite with 2 Mn at ~3.05±0.05 Å (Peacock and Sherman, 2007b), a bidentate corner-sharing complex with 2 Mn at ~3.49±0.11 Å, as per Ni adsorbed on hexagonal birnessite (Maneeau et al., 2007a), or possibly a bidentate edge-sharing complex with 1 Mn at ~3.00±0.10 Å, as is reported for Cu(II) adsorbed on ferrihydrite (Scheinost et al., 2001; Moon and Peacock, 2012). To our knowledge, there are no EXAFS data for Ni structurally incorporated into todorokite, but Ni is expected to exclusively occupy the Mn sites at the edges of the triple chains (Post and Bish, 1988; Post et al., 2003; Bodei et al., 2007), which would yield an Ni coordination environment consisting of 6 O at ~2.04 Å, 4 edge-sharing Mn at ~2.87-2.91 Å and 4 corner-sharing Mn at ~3.48-3.50 Å (Bodei et al., 2007). Visual inspection of our todorokite sorption spectra at 24 hr and 1 wk contact time show the Ni local coordination environment is very similar in both spectra and most similar to Ni adsorbed on triclinic birnessite (Peacock and Sherman, 2007b). Accordingly our best fits to these spectra are provided by the cluster
representing Ni tridentate corner-sharing to Mn(OH) sites present at the edges of the
todorokite triple chains, and we find 6 O at 2.00-2.11 Å and 2 Mn at 2.98-3.10 Å. It
should be noted that the fits were improved (from reduced \( \text{Chi}^2 \sim 18 \) to \( \sim 15 \), Table 4) by
allowing a slight distortion of the Ni octahedron, evident as a very minor deviation of the
spherical coordinates of the surface binding O atoms from exact octahedral coordination
\((\text{O}_1, \text{O}_4 \text{ and } \text{O}_6 \), Table 4). The fits could not be improved by including any other Ni
coordination environments.

3.1.4.2. Experimental samples

Ni K-edge EXAFS and Fourier transforms for the experimental samples are shown
in Figure 6 and fits are summarized in Table 5. Spectra for our birnessite and 10
Å phyllomanganate are visually very similar to those in previous work where Ni is sorbed
in two distinct coordination environments, namely, adsorbed as a surface complex at
vacancies and also structurally incorporated into the phyllomanganate layers (Peacock and
Sherman, 2007b; Peacock, 2009). When Ni is present as a structurally incorporated
species in addition to a vacancy site adsorbed complex, the spectral shape of the
characteristic \( k \)-space features for Ni adsorbed at vacancies, at \( \sim 6 \) and 8 Å\(^{-1} \) (see the Ni-
sorbed birnessite reference spectrum (Fig. 5)), are modified towards the shape of these
features for Ni incorporated into the phyllomanganate layers (see the Ni-incorporated
natural phyllomanganate reference spectrum (Fig. 5)). Specifically, the feature at \( \sim 6 \) Å\(^{-1} \)
depens to produce a clear splitting of the \( \sim 5.5-7 \) Å\(^{-1} \) oscillation, while the feature at \( \sim 8 \) Å\(^{-1} \)
shoals resulting in a single peak for the \( \sim 7.5-9 \) Å\(^{-1} \) oscillation, both as a function of the
amount of structurally incorporated Ni (Peacock, 2009). The presence of Ni as both
surface adsorbed and structurally incorporated species is manifest in the Fourier transform
as two next-nearest Mn neighbour distances represented by peaks at \( \sim 3.5 \) and 2.9 Å,
respectively, whose relative amplitudes reflect the proportion of the total Ni occupying
vacancy sites vs. structurally incorporated positions (Peacock, 2009). Accordingly the
best fits to the birnessite and 10 Å phyllomanganate spectra are provided by a linear
combination of the Ni-sorbed birnessite and Ni-incorporated natural phyllomanganate
reference spectra (Fig. 6, Table 5). Specifically, we find that our birnessite contains
\( \sim 54 \pm 4 \) % Ni adsorbed at vacancy sites and \( \sim 46 \pm 4 \) % Ni structurally incorporated, while
our 10 Å phyllomanganate contains \( \sim 38 \pm 4 \) % Ni at vacancies and \( \sim 62 \pm 4 \) % Ni
incorporated. The increase in the proportion of structurally incorporated Ni from our
birnessite to 10 Å phyllomanganate is consistent with the observed increase in long range
order between our precursor and intermediate phases (Fig. 2). Partial dissolution-
recrystallization during Mg ion exchange is expected to favour structural incorporation of
surface adsorbed species (e.g., Bodei et al., 2007).

The reflux spectra are visually very similar to our birnessite and 10 Å
phyllomanganate, and remarkably similar to each other, up to and including 1 wk reflux
(Fig. 6). These observations indicate that the Ni local coordination environment in the
reflux samples is likely similar to that in the precursor and intermediate samples, and that
this environment does not significantly change throughout the reflux to 1 wk. In
particular, these reflux spectra do not resemble our reference spectra for Ni-sorbed
todorokite (Fig. 5). Neither is there any indication that a significant proportion of the Ni
has become structurally incorporated into the neo-forming toodorokite. In this latter
scenario, one would expect a change in the amplitude of the characteristic spectral features
resulting from edge- and corner-sharing Mn. Specifically, if a significant proportion of the
Ni originally associated with our 10 Å phyllomanganate was incorporated into the neo-
forming toodorokite then the amplitude of the spectral features at ~6 and 8 Å\(^{-1}\) in k-space,
which manifest as Ni-Mn distances at ~2.9 and 3.5 Å in R-space, should change somewhat
to reflect the fact that the local coordination environment of the Ni now includes 6 Mn at
~2.9 Å and 2 Mn at ~3.5 Å, as expected for Ni coprecipitated with a phyllomanganate, and
also 4 Mn at ~2.9 Å and 4 Mn at ~3.5 Å, as expected for Ni incorporated into toodorokite
(Bodei et al., 2007). While this change in the Ni local coordination environment would
not produce significant changes in the expected Ni-Mn interatomic distances, and the
absolute changes in the number of Mn next-nearest neighbours would be difficult to
resolve, the fact that the amplitude of these key spectral features, and in fact the entire
spectral signature, remains so remarkably consistent from 3 hr to 1 wk reflux is strong
indication that Ni remains sequestered by our 10 Å phyllomanganate as the reflux
proceeds, in agreement with our HR-TEM EDS (Table 2), and despite the fact that our
XRD (Fig. 2) and HR-TEM (Fig. 3) show a significant amount of neo-formed toodorokite
present in the sample matrix by 48 hr reflux. In agreement with these observations, the
best fits to the spectra for 3 hr to 1 wk reflux are provided by a linear combination of the
Ni-sorbed birnessite and Ni-incorporated natural phyllomanganate reference spectra, as
per our birnessite and 10 Å phyllomanganate samples (Fig. 6, Table 5). Specifically, we
find that of the total Ni sorbed, ~40 % is adsorbed at the vacancy sites with ~60 %
structurally incorporated, with no significant change in these proportions when comparing
the reflux samples to the 10 Å phyllomanganate sample, or each other.
Consistent with the absence of 10 Å phyllomanganate or a phyllomanganate-like phase in our HR-TEM images by 2 wk reflux, the 2 wk and 4 wk reflux spectra are visually very different to our birnessite, 10 Å phyllomanganate and the reflux spectra up to and including 1 wk (Fig. 6). Instead the 2 wk and 4 wk spectra are visually very similar to our reference spectra for Ni-sorbed todorokite where Ni is sorbed via tridentate corner-sharing surface complexes with 6 O at ~2.00-2.11 Å and 2 Mn at ~2.98-3.10 Å. (section 3.1.4.1; Table 4; Fig. 5). There is no obvious visual evidence for Ni-Mn edge- or corner-sharing distances at ~2.9 Å or ~3.5 Å indicative of Ni structurally incorporated into a phyllomanganate (~2.9 Å), adsorbed at vacancy sites on a phyllomanganate (~3.5 Å), or structurally incorporated into todorokite (~2.9 and 3.5 Å). Accordingly our best fits to these spectra are provided by refining the reference spectra for Ni-sorbed todorokite, resulting in refined parameters of 6 O at ~1.98-2.10 Å and 2 Mn at ~2.94-3.11 Å. The fits could not be improved by including any other Ni coordination environments. Because the Mn(OH) sites present at the edges of the todorokite triple chains and those at the edges of a phyllomanganate layer essentially provide the same local coordination environment for sorbed trace metals, the presence of Ni in tridentate corner-sharing configuration could indicate that Ni is newly associated with the neo-formed todorokite or in fact still associated with the 10 Å phyllomanganate, albeit via a different sorption mechanism compared to the previous reflux samples. However, the fact that we cannot identify any 10 Å phyllomanganate in our 2 wk samples (Fig. 3i,j) indicates that the solid-associated Ni at 2 wk and 4 wk reflux is most likely adsorbed to neo-formed todorokite.

3.2 Natural Ferromanganese Samples

3.2.1 Bulk X-ray diffraction

Bulk XRD patterns for our hydrogenetic, diagenetic and hydrothermal ferromanganese precipitates are shown in Figure 7. The Mn mineralogy of our hydrogenetic crust and diagenetic nodule is dominated by very poorly crystalline phyllomanganate, usually termed vernadite in natural samples (JCPDS-15-604) and δ-MnO₂ in synthetic analogues, with also a contribution from very poorly crystalline 10 Å phyllomanganate (buserite JCPDS-32-1128). The d100/d110 peak intensity ratios approximately equal \sqrt{3} indicating that the phyllomanganate layers have hexagonal symmetry with a = b = 2.83 Å (Drits et al., 1997). The presence of very poorly crystalline phyllomanganate phases in our hydrogenetic and diagenetic samples agrees with previous reports for these ferromanganese precipitate genetic types (e.g., Peacock and Sherman,
In particular, the presence of poorly crystalline 10 Å phyllosilicate in diagenetic ferromanganese precipitates is often reported in natural samples, where it is thought to have formed during mild dissolution-recrystallisation of poorly crystalline 7 Å phyllosilicate (e.g., Bodei et al., 2007). Our hydrothermal sample consists of mixed 7 and 10 Å phyllosilicate and todorokite phases, with characteristic todorokite peaks at ~2.2 Å [21-2] and ~1.7 Å [21-4], and a splitting of the ~2.4 Å peak region as expected when 10 Å phyllosilicate and todorokite are mixed (Atkins et al., 2014; section S3.1.1). The relatively high intensity of the basal reflections for 7 Å phyllosilicate (and to some extent for 10 Å phyllosilicate, noting that these peaks also result from todorokite) indicates that the phyllosilicate layers are significantly more ordered than in our hydrogenetic and diagenetic samples. The presence of todorokite in hydrothermal ferromanganese precipitates is often reported in natural samples, where it is thought to have formed during diagenesis and mild hydrothermal alteration of 10 Å phyllosilicate (e.g., Peacock and Moon, 2012). Further details on the XRD of our natural samples are presented in the Supplementary Information (section S3.2.1).

3.2.2 µXRF elemental mapping

Two-colour and tri-colour µXRF maps of the distribution of Fe (green), Mn (blue) and Ni (red) in our natural ferromanganese samples are shown in Figure 8, with scatter plots of the normalized fluorescence counts between Fe-Mn, Mn-Ni and Fe-Ni in Figure 9. The relatively pure green and blue colours of the Fe- and Mn-rich areas of the Fe-Mn maps indicate that Fe and Mn are strongly spatially segregated and anti-correlated in the scanned areas of all 3 samples (Fig. 8a,c,e; with Pearson correlations for the Fe-Mn plots at $r = -1.5$, -0.34 and 0.13 for the hydrogenetic, diagenetic and hydrothermal samples, respectively (Fig. 9a,d,g)). This Fe-Mn spatial distribution is observed at every probed spatial scale in natural ferromanganese precipitates (e.g., Manceau et al., 2004). On adding Ni (red) to both the hydrogenetic and diagenetic samples, the Mn-rich areas turn varying shades of magenta (blue + red), while the Fe-rich areas remain bright green (green + red = yellow) (Fig. 8b,d), indicating that the majority of the Ni is spatially associated and positively correlated with the Mn-rich fraction in the scanned areas (with $r$ Mn-Ni and Fe-Ni at 0.94 and -0.69 for the hydrogenetic sample (Fig. 9b,c) and 0.83 and -0.36 for the diagenetic sample (Fig. 9e,f), respectively). In contrast, on adding Ni (red) to the hydrothermal sample, there is little change in the colours of the Mn- or Fe-rich areas (Fig. 8f). Instead, small, intense red areas appear in the center left region of the map that show...
little spatial correlation with either the Mn- or Fe-rich fractions (with $r$ Mn-Ni and Fe-Ni at -0.28 and 0.17, respectively (Fig. 9h,i)), indicating that the majority of the Ni is predominantly concentrated in an unidentified mineral phase. The $\mu$XRF maps were used to select 4 physically discrete and chemically defined POI enriched in Mn and Ni (Fig. 8) that were subject to $\mu$EXAFS.

3.2.3 $\mu$EXAFS

Mn K-edge EXAFS of the Mn oxide reference compounds and $\mu$EXAFS of the natural ferromanganese samples are shown in Figure 10. In agreement with previous studies, our Mn oxide reference spectra show clear differences in $k$-space in the (6.5 – 9.5 Å$^{-1}$) indicator region (e.g., Webb et al., 2005a). For layered structures, the $k$-space peaks at ~6.7, 8 and 9.2 Å$^{-1}$ appear sharper and more intense with an increase in coherent stacking of the layers along the c-axis, i.e., from our $\delta$MnO$_2$ to Hx-birnessite (e.g., Webb et al., 2005a). For tunnel structures, these indicator features are less sharp and intense and significantly broader, with a notable increase in the background of the region between ~7.4-8.7 Å$^{-1}$, and the shoulder at ~5.5 Å$^{-1}$ also appears less pronounced, compared to layered structures (e.g., Webb et al., 2005a). These differences are evident when comparing our phyllomanganates ($\delta$MnO$_2$, Hx-birnessite and Tc-Na-birnessite) to our tectomanganate (high crystalline todorokite) reference spectra. In agreement with our XRD (Fig. 7), the spectra for the hydrogenetic and diagenetic samples are most similar to the reference spectrum for poorly crystalline phyllomanganate $\delta$MnO$_2$, while the spectral features at ~6.7, 8 and 9.2 Å$^{-1}$ for the hydrothermal sample recorded at two separate POI are less sharp and intense, and also broader, indicating the presence of todorokite. The hydrothermal sample also shows an elevated background between ~7.4-8.7 Å$^{-1}$ and a somewhat less pronounced shoulder at ~5.5 Å$^{-1}$, compared to the hydrogenetic and diagenetic samples. Given our bulk XRD shows that the phyllomanganate present in the hydrothermal sample is in fact more ordered than that found in our hydrogenetic and diagenetic samples, then the reduced intensity and sharpness, along with the broadening, of these indicator peaks is most likely due to the presence of todorokite rather than a very poorly crystalline phyllomanganate phase. Linear combination of the $\delta$MnO$_2$ and todorokite reference spectra indicate that the hydrothermal sample at POI1 and 2 contains ~70±10 % $\delta$MnO$_2$ and ~30±10 % todorokite.

Ni K-edge $\mu$EXAFS of the natural ferromanganese samples are shown in Figure 11 and the fits are summarised in Table 6. For our hydrothermal sample at POI2 the Ni
concentration was too low to generate a useable EXAFS spectrum. Spectra for our hydrogenetic and diagenetic samples, containing predominantly poorly crystalline phyllomanganate, and our hydrothermal sample, containing both phyllomanganate and todorokite, are visually most similar to our reference spectrum for Ni structurally incorporated into a natural phyllomanganate (Fig. 5). In particular, we observe a pronounced splitting of the spectral feature at ~6 Å⁻¹ and a single peak at ~8 Å⁻¹ as expected for Ni incorporated into the phyllomanganate layers (Manceau et al., 2007b; Peacock and Sherman, 2007a,b; Peacock, 2009). In all spectra, the splitting of the feature at ~6 Å⁻¹, and the amplitude of the corresponding peak in the Fourier transform at ~2.9 Å, is not as pronounced or as intense, respectively, as that observed in the Ni-incorporated natural phyllomanganate reference spectrum. In this sense the natural ferromanganese k-space spectra also resemble the experimental samples up to and including 1 wk reflux (Fig. 6), where we find Ni both structurally incorporated in, and surface adsorbed to, a phyllomanganate (section 3.1.4.2). However, in our natural ferromanganese spectra, we do not observe a significant peak in the Fourier transform at ~3.5 Å corresponding to Ni surface adsorbed at the vacancy sites. As for the Ni-incorporated natural phyllomanganate reference spectrum, the very minor peak at ~3.5 Å is fit by multiple scattering occurring in the near-coordination environment about the Ni atom (Peacock and Sherman, 2007a; Peacock, 2009). Accordingly, the best fits to the natural ferromanganese samples are provided by the cluster representing Ni incorporated into the layers of a phyllomanganate (Fig. 11, Table 6). Inclusion of Ni in any other local coordination environments did not improve the fits. Complete structural incorporation of Ni into the layers of natural marine phyllomanganates agrees with previous work for other Ni-rich hydrogenetic and diagenetic ferromanganese precipitates (Peacock and Sherman, 2007a). Importantly, in our hydrothermal sample containing both phyllomanganate and todorokite, despite the fact our µXRF indicates that the majority of the sequestered Ni is associated with an unidentified phase, we are still able to detect the spectral signature for a minority of Ni structurally incorporated into a phyllomanganate at POI1, and there is no evidence to indicate that Ni is adsorbed or incorporated by the co-located todorokite. This suggests that, in agreement with our experimental results up to an including 1 wk reflux, in sediments where both phyllomanganate and todorokite are present, the majority of the Mn-bearing solid-phase Ni is preferentially sequestered by the phyllomanganate phase.
4. DISCUSSION

4.1 Effect of Sorbed Ni on the Transformation of Birnessite to Todorokite

We transform a Ni-sorbed 10 Å phyllosilicate where, of the total Ni sorbed (~1 wt% Ni), ~60 % is structurally incorporated into the phyllosilicate lattice with the remaining ~40 % surface adsorbed at Mn octahedral vacancy sites present in the phyllosilicate layers (Table 5a). However, despite the presence of both structurally incorporated and surface adsorbed Ni, we find no evidence to suggest that this metal impurity has a significant effect on the overall growth mechanism of todorokite, previously established for our Ni-free system (Atkins et al., 2014). In contrast, we observe a significant reduction in the overall growth rate of todorokite, compared to our Ni-free system (Atkins et al., 2014). These effects are discussed below.

4.1.1 Growth mechanism

Our HR-TEM images clearly show the presence of todorokite primary particles (by 6 hr reflux; Fig. 3c,d) that are elongated along the direction of tunnel growth ([010]) by varying degrees, but are of consistent width across the direction of tunnel growth ([100]) over the entire duration of the reflux (from 6-10 nm wide after 6 hr (Fig. 3f) to ~8-10 nm wide after 2 wk reflux (Fig. 3j)). These primary particles are then crystallographically aligned and aggregated together across the direction of tunnel growth via the OA of the [100] crystal faces to form secondary todorokite laths (Fig. 3e,g,i). Both the length and width of these laths continues to increase with increasing reflux time (from ~250x70 nm by 24 hr, to ~450x100 nm by 1 wk and ~750x100 nm by 2 wk reflux; Fig. 3e,g,i, respectively). These laths also become increasingly more crystalline (with notably more defined lattice fringes at 2 wk reflux; Fig 3i,j), approximately commensurate with the complete transformation of the birnessite precursor (occurring at some point between 1 wk and 2 wk reflux where at 2 wk reflux we cannot observe any 10 Å phyllosilicate or phyllosilicate-like phase within the sample matrix; Fig 3i,j). These observations indicate that the formation of secondary todorokite laths can be directly attributed to the simultaneous growth from solution of primary todorokite crystallites along the [010] direction, and their OA across the [100] direction, occurring primarily during the first week of reflux, and that these laths undergo traditional crystal ripening, occurring over the following weeks of reflux when all the precursor birnessite has been consumed. The simultaneous occurrence of dissolution-recrystallisation and OA is expected in systems that undergo growth via OA, although one growth mechanism may dominate at any given
time point (e.g., Waychunas et al., 2005; Kim et al., 2008). This nucleation and growth
process is entirely consistent with the nucleation, primary particle growth, and crystal
ripening stages proposed for our Ni-free system (Atkins et al., 2014).

Surface area and reaction solution pH (Table 3) also follow similar trends over the
course of the transformation to those observed in our Ni-free system and likely reflect the
fact that todorokite growth simultaneously involves both growth from solution and OA
(Atkins et al., 2014). In this regard, the relatively abrupt decrease in surface area over the
first week followed by its more gradual decline over the following 3 wk of reflux (Table
3; Figure 4) likely reflects the increase in todorokite particle size resulting from OA,
followed by a decrease in particle size occurring during the crystal ripening stage. On the
other hand, the slight increase in pH over the first week of reflux (Table 3) likely reflects a
release of hydroxyls into solution during birnessite dissolution (as expected during the
dissolution of (hydr)oxides), and may also reflect the loss of surface area resulting from
OA (where particle growth via aggregation (OA) and the associated loss of surface area is
reported to cause a net dehydroxylation effect (e.g., Kim et al., 2008)). The more
significant decrease in pH over the following 3 wk of reflux (Table 3) is approximately
concomitant with the final crystal ripening growth stage (beginning at some point between
1 wk and 2 wk reflux). As explained in our previous work, we are unlikely to have
captured this final growth stage in our Ni-free system (that ran over 72 hr; Atkins et al.,
2014). While very few studies investigate (hydr)oxide phase transformation and
subsequent crystal ripening, Kim et al. (2008) suggest that nanoparticle surface structural
rearrangements during ripening may result in a decrease in solution pH. The pH decrease
in our Ni-sorbed system, and to some extent the lack of pH decrease in our Ni-free system,
are certainly consistent with a ripening-induced pH decrease as suggested in the literature.

In summary, all of the above observations are consistent with our previous work
and indicate that our four-stage model for birnessite to todorokite transformation (Atkins
et al., 2014) is applicable to both Ni-free and Ni-sorbed phyllomanganates.

4.1.2 Growth rate

Although the presence of both structurally incorporated and surface adsorbed Ni
does not alter the growth mechanism of todorokite, we do see that this metal impurity
significantly slows the growth rate and reduces the crystallinity of this neo-formed phase,
compared to todorokite formed in our Ni-free system (Atkins et al., 2014). In contrast to
the Ni-free system, where characteristic todorokite XRD peaks are evident by 3 hr and
todorokite primary particles are observed with HR-TEM by 6 hr reflux (Atkins et al., 2014), here the appearance of characteristic toodorokite XRD peaks is significantly delayed (only visible by 48 hr reflux (Fig. 2; where peaks may appear at any time point between the 24 and 48 hr scans)), and although primary particles are evident in the HR-TEM by 6 hr reflux, they comprise only a minor component of the overall sample matrix and are poorly crystalline (displaying only poorly defined lattice fringes (Fig. 3c,d)); both of which contribute to the early absence of toodorokite peaks in the XRD spectra. Overall, the XRD and HR-TEM data at equivalent time points throughout the Ni-free and Ni-sorbed reflux show that toodorokite formed in the Ni-sorbed system is only poorly crystalline (with significantly reduced intensity of the (001) and (002) reflections (XRD Fig. 2) and less well defined lattice fringes (HR-TEM Fig. 3c,d)). By 4 wk, despite the essentially complete transformation of our phyllomanganate to toodorokite and 2-3 wk of crystal ripening (Fig. 3), the crystallinity of the neo-formed toodorokite is still reduced (Fig. 2), compared to that formed by 72 hr reflux in the Ni-free system (Atkins et al., 2014).

In summary, it appears that the presence of ~1 wt% sorbed Ni has extended the timeframe required for the nucleation and growth of toodorokite (from ~72 hr in the Ni-free to ~1 wk in the Ni-sorbed system) and significantly reduced the crystallinity of the neo-formed toodorokite phase, even after an extended period of crystal ripening.

The reduction in toodorokite growth rate in the Ni-sorbed system can be understood in light of our four-stage nucleation and growth mechanism for its formation (Atkins et al., 2014). Specifically, during the initial nucleation stage, thermally-induced kinking of the phyllomanganate layers is facilitated by the Jahn-Teller distortion of structural Mn(III) present in the 10 Å phyllomanganate (Cui et al., 2008; Bodei et al., 2007; Atkins et al., 2014; Zhao et al., 2015), where moreover, the presence of sufficient structural Mn(III) is a prerequisite for toodorokite formation (Atkins et al., 2014). Given the importance of structural Jahn-Teller distorted cations, we predict in our previous work that structurally incorporated cation impurities without Jahn-Teller distortion, such as Ni, should slow the transformation of birnessite to toodorokite, by essentially slowing phyllomanganate layer kinking, thus slowing toodorokite nucleation and the subsequent formation of toodorokite primary particles (Atkins et al., 2014). Our results here, with ~0.6 wt% structurally incorporated Ni, confirm this prediction and can be attributed to a reduced rate of toodorokite primary particle formation.

We show for the first time that, contrary to traditional understanding, the presence of sorbed Ni, at concentrations equivalent to those found in natural marine
ferromanganese precipitates, does not aid the transformation of birnessite to todorokite and in fact significantly slows todorokite formation and reduces todorokite crystallinity. Our results suggest that other cation impurities without Jahn-Teller distortion that structurally incorporate into birnessite (e.g., Co(III) (Manseau et al., 1997); Fe(III) (Yin et al., 2013)) will have a similar effect on todorokite formation and crystallinity, compared to todorokite formed in a relatively impurity-free system.

4.2 Mobility and Fate of Ni During the Transformation of Birnessite to Todorokite

4.2.1. Ni mobility and fate in experimental Ni-sorbed system

We also postulate in our previous work that structurally incorporated metal impurities might be lost to solution in order to facilitate the transformation process (Atkins et al., 2014). It is now clear that during the transformation of Ni-sorbed birnessite to todorokite, over the course of a 4 wk reflux, ~50% of the initially sorbed Ni is released to solution (Table 1). Specifically, during the nucleation and growth stages, primarily occurring over first week of reflux, solid-associated Ni is sorbed to the phyllosmanganate phase via surface and structurally incorporated complexes (HR-TEM EDS Table 2 and Ni EXAFS Fig. 6), despite the progressive formation of todorokite (XRD Fig. 2 and HR-TEM Fig. 3), and there is at least a 20% release of Ni into solution (measured at 1 wk reflux; Table 1). During the final crystal ripening growth stage (beginning somewhere between 1 wk and 2 wk reflux), solid-associated Ni is sorbed to the todorokite as a surface adsorbed complex (observed at 2 wk reflux; Ni EXAFS Fig. 6), and, during the later stages of phyllosmanganate transformation (occurring between 1 wk and 2 wk reflux) and the subsequent todorokite crystal ripening (beginning within this timeframe when all birnessite has been transformed), there is a ~50% release of Ni into solution (Table 1). Ultimately we see that in systems tending towards todorokite as the final transformation product, solid-associated Ni decreases by ~50%.

It should be noted that our HR-TEM EDS data (Table 2), indicating that little if any Ni is associated with todorokite throughout the reflux, is not at odds with the fact we measure ~0.5 wt% Ni absolute Ni concentration in the todorokite product at 4 wk reflux (Table 1) because our EDS data cannot be interpreted as an absolute measurement of Ni associated with the phyllosmanganate or todorokite (section 2.4). Our EDS data can only be interpreted to indicate that the todorokite forming throughout the reflux and present at the final 4 wk time point contains relatively less Ni than the phyllosmanganate phase (section 3.1.2). In this sense the HR-TEM EDS data is consistent with a significant
decrease in solid-associated Ni as the reflux proceeds. It should also be noted that we do not attribute the observed Ni release to the pH-induced desorption of the Ni surface adsorbed onto our phyllomanganate and todorokite phases. While our experiments were performed at a pH below circumneutral, which decreased over the duration of the reflux (from a maximum pH of ~5.9 to a final pH of ~4.3; Table 3), our previous work shows that significant Ni desorption from a birnessite of comparable crystallinity requires pH < ~4 (Peacock and Sherman, 2007b). To our knowledge there is no published data on Ni (de)sorption from todorokite, but its point of zero charge is similar to that for birnessite (at pH ~3.5; e.g., Tan et al., 2008) and as such the pH-induced (de)sorption behaviour of Ni will likely be similar, particularly given the fact that the molecular mechanism of Ni adsorption to both birnessite and todorokite surfaces is also similar (involving tridentate inner-sphere surface complexes (section 3.1.4.2)).

4.2.2 Implications for Ni mobility and fate in marine sediments

Our experimental system is designed to broadly replicate the diagenesis of birnessite to todorokite in oxic marine sediments, using a reflux procedure that simulates todorokite formation in natural environments (e.g., Feng et al., 2004), with an electrolyte composition and concentration shown to best replicate the morphological and structural features of natural marine todorokite (e.g., Cui et al., 2006). On the other hand, the pH of our experimental system is lower than marine porewaters (circumneutral), yet work to date suggests that an increase in pH is unlikely to significantly alter the mechanism of todorokite nucleation and growth, or the fate of Ni during this process. In particular, while the todorokite primary particles likely possess reduced surface charge (todorokite pH$_{PZC}$ ~3.5) in our experimental system compared to marine porewaters (perhaps facilitating particle aggregation and thus OA-type growth; e.g., Banfield et al., 2000; Dale et al., 2015), net particle surface charge in both systems should be negative (e.g., Tan et al., 2008). As such, while the extent of OA might vary between our experiment and marine porewaters, OA-type growth is still likely to be an important growth mechanism for todorokite in marine sediments. Furthermore, the similarity in pH$_{PZC}$ between birnessite and todorokite indicates that the (de)sorption behaviour of these phases is likely broadly similar, with Ni strongly adsorbed after pH ~4.5, and significantly different pH-induced (de)sorption behaviour only occurring below pH ~4 (section 4.2.1). This indicates that Ni (de)sorption behaviour at the pH of marine porewaters will not be
901 significantly different to that occurring in our experiment, such that our experimental
902 system can be used as a broad proxy for Ni mobility and fate in oxic marine sediments.
903 Furthermore our analysis of natural marine ferromanganese deposits, as an
904 analogue for ferromanganese (hydr)oxides dispersed in marine sediments and precipitated
905 as discrete ferromanganese crusts and nodules, is consistent with our model mechanism
906 for the transformation of birnessite to todorokite, and the resulting mobility and fate of Ni
907 during this process. On the one hand, our experiments show that in Mn oxide precipitates
908 that contain both phyllomanganate and todorokite, Ni is preferentially sorbed by the
909 phyllomanganate phase, and as these precipitates become more todorokite rich, Ni is
910 released into solution, leaving the neo-formed todorokite product depleted in Ni compared
911 to the phyllomanganate precursor. Consistent with this, we find that in our natural
912 hydrothermal sample containing both phyllomanganate and todorokite, the Ni associated
913 with Mn oxides is indeed preferentially sorbed to the phyllomanganate phase, with no
914 evidence for its surface adsorption or structural incorporation by the co-located todorokite
915 (Fig. 8, 11). We also find that at the bulk scale our hydrothermal sample contains
916 significantly less Ni (~0.07 wt.%) than our phyllomanganate-rich hydrogenetic and
917 diagenetic samples (~0.4 and 0.5 wt.% Ni, respectively), while at the micro scale it is
918 commonly reported for other natural intermixed ferromanganese precipitates that neo-
919 formed todorokite typically contains substantially less Ni than its precursor 10 Å phyllomanganate (Siegel and Turner, 1983; Bodeï et al., 2007).
920 Overall our combined experimental and natural analyses are consistent with one
921 another and indicate that in marine sediments where birnessite near-completely transforms
922 to todorokite as the end product of diagenesis, at least half of the Ni originally sequestered
923 to birnessite will be released to marine sedimentary porewaters. Furthermore, our results
924 also show that the remaining solid-associated Ni will be adsorbed to neo-formed
925 todorokite via surface complexation, as opposed to structural incorporation, and will
926 therefore also be subject to remobilisation. Our work indicates that the marine diagenesis
927 of birnessite likely provides a significant source of Ni to sedimentary porewaters and thus
928 potentially a benthic flux of Ni to seawater.
930
931 **5. SUMMARY AND CONCLUSIONS**
932 We provide the first detailed understanding of the effect of sorbed Ni on the
933 transformation of birnessite to todorokite in the marine environment, and the mobility and
934 fate of this micronutrient during this diagenetic process. Specifically,
1. Sorbed Ni significantly slows the transformation of birnessite to todorokite and reduces the crystallinity of the neo-formed todorokite phase, but does not alter the mechanism and pathway of todorokite formation, compared to a Ni-free system. The inhibitory effect of sorbed Ni on todorokite formation can be attributed to a reduced rate of todorokite primary particle formation, where the presence of non-Jahn-Teller distorted Ni within the phyllosilicate matrix is unfavourable for phyllosilicate layer kinking thus inhibiting todorokite nucleation and the subsequent formation of primary particles. The fact that sorbed Ni slows the transformation process is contrary to current knowledge, where it is understood that Ni should aid the transformation of birnessite to todorokite.

2. Sorbed Ni is released to solution during the transformation of birnessite to todorokite.

3. In systems tending towards todorokite as the final product of diagenesis, at least 50% of the Ni originally sequestered by birnessite is released to solution, while the remaining solid-associated Ni is adsorbed to todorokite via surface complexation and is therefore also subject to remobilisation. Overall the marine diagenesis of birnessite likely provides a source of Ni to sedimentary porewaters and thus potentially provides a benthic flux of Ni to seawater.

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We thank Michael Ward (Leeds Electron Microscopy and Spectroscopy Centre) for assistance with TEM imaging. We thank Diamond Light Source for access to beamlines B18 (grants SP7326, SP8045) and I20 (SP7325) which contributed to the results presented here. We also thank Andrew Dent, Giannantonio Cibin, Stephen Parry (beamline B18), and Fred Mosselmans and Tina Geraki (beamline I18) for support at Diamond Light Source. We thank Bob Knight (University of Hull) for ICP-OES analysis. We are indebted to Jim Hein (United States Geological Survey) for the provision of natural ferromanganese precipitate samples, and thank Bob Jones and John Ford (National Oceanography Centre, Southampton) for preparation of micro thin-sections. A. L. Atkins was supported via a NERC studentship. We finally thank 3 anonymous reviewers and the Associate Editor for their careful and thoughtful comments to improve the manuscript.
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different average manganese oxidation states were synthesized, characterized, and transformed to todorokite at atmospheric pressure. 


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Van Driessche A. E. S., Benning L. G., Rodriguez-Blanco J. D., Ossorio M., Bots P.,


### Table 1: Absolute Ni concentrations for our birnessite precursor, 10 Å phyllomanganate intermediate and reflux products.

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt% Ni&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Birnessite</td>
<td>0.92±0.002</td>
</tr>
<tr>
<td>10Å phyllomanganate</td>
<td>1.03±0.005</td>
</tr>
<tr>
<td>3hr reflux</td>
<td>0.96±0.007</td>
</tr>
<tr>
<td>6hr reflux</td>
<td>1.07±0.010</td>
</tr>
<tr>
<td>12hr reflux</td>
<td>1.00±0.004</td>
</tr>
<tr>
<td>24hr reflux</td>
<td>1.04±0.003</td>
</tr>
<tr>
<td>48hr reflux</td>
<td>0.99±0.009</td>
</tr>
<tr>
<td>72hr reflux</td>
<td>0.98±0.010</td>
</tr>
<tr>
<td>1wk reflux</td>
<td>0.80±0.011</td>
</tr>
<tr>
<td>4wk reflux</td>
<td>0.54±0.003</td>
</tr>
</tbody>
</table>

<sup>a</sup>Error is standard deviation of 3 measurements made on separate solid aliquots.

### Table 2: HR-TEM EDS data for EDS spot measurements made on a selection of our reflux products. Positions of spot analyses are shown on Figure 3. Numbers in parentheses below the measured values are the errors given as the standard deviation of triplicate measurements for each spot.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu (wt%)</th>
<th>C (wt%)</th>
<th>Mn (wt%)</th>
<th>O (wt%)</th>
<th>Mg (wt%)</th>
<th>Ni (wt%)</th>
<th>Sum (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 hr EDS (1)</td>
<td>50.7 (0.7)</td>
<td>21.1 (0.8)</td>
<td>16.3 (0.4)</td>
<td>10.9 (0.6)</td>
<td>0.7 (0.1)</td>
<td>0.4 (0.1)</td>
<td>100.1</td>
</tr>
<tr>
<td>6 hr EDS (2)</td>
<td>51.9 (0.8)</td>
<td>25.9 (0.8)</td>
<td>12.5 (0.4)</td>
<td>8.9 (0.5)</td>
<td>0.7 (0.1)</td>
<td>0</td>
<td>99.9</td>
</tr>
<tr>
<td>24 hr EDS (1)</td>
<td>26.8 (0.4)</td>
<td>0</td>
<td>41.4 (0.5)</td>
<td>28.9 (0.6)</td>
<td>2.0 (0.1)</td>
<td>1.0 (0.1)</td>
<td>100.1</td>
</tr>
<tr>
<td>24 hr EDS (2)</td>
<td>22.3 (0.3)</td>
<td>0</td>
<td>35.5 (0.4)</td>
<td>39.5 (0.5)</td>
<td>2.6 (0.1)</td>
<td>0</td>
<td>99.9</td>
</tr>
<tr>
<td>1 wk EDS (1)</td>
<td>32.4 (0.5)</td>
<td>0</td>
<td>34.4 (0.5)</td>
<td>30.1 (0.7)</td>
<td>2.2 (0.2)</td>
<td>0.9 (0.1)</td>
<td>100</td>
</tr>
<tr>
<td>1 wk EDS (2)</td>
<td>37.0 (0.6)</td>
<td>4.6 (0.5)</td>
<td>31.5 (0.6)</td>
<td>25.3 (0.7)</td>
<td>1.7 (0.2)</td>
<td>0</td>
<td>100.1</td>
</tr>
<tr>
<td>2 wk EDS</td>
<td>31.8 (0.4)</td>
<td>14.0 (0.5)</td>
<td>28.4 (0.4)</td>
<td>24.2 (0.5)</td>
<td>1.7 (0.1)</td>
<td>0</td>
<td>100.1</td>
</tr>
</tbody>
</table>
**TABLE 3:** Specific surface area of the solid products, and Ni and Mn concentrations and pH of the reflux solutions for the 10 Å phyllo manganese intermediate (time 0) and subsequent reflux products.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Area $^a$ (m$^2$/g)</th>
<th>Ni$^b$ (mM)</th>
<th>Mn$^b$ (mM)</th>
<th>pH$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10Å phyllomanganate</td>
<td>102.3</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>3hr reflux</td>
<td>84</td>
<td>0.004 ± 8.1x10$^{-5}$</td>
<td>0.003 ± 3.8x10$^{-5}$</td>
<td>5.29</td>
</tr>
<tr>
<td>6hr reflux</td>
<td>88</td>
<td>0.006 ± 5.2x10$^{-4}$</td>
<td>0.017 ± 4.2x10$^{-4}$</td>
<td>5.47</td>
</tr>
<tr>
<td>12hr reflux</td>
<td>87</td>
<td>0.007 ± 8.1x10$^{-4}$</td>
<td>0.019 ± 6.5x10$^{-4}$</td>
<td>5.49</td>
</tr>
<tr>
<td>24hr reflux</td>
<td>97</td>
<td>0.010 ± 2.2x10$^{-4}$</td>
<td>0.018 ± 3.3x10$^{-4}$</td>
<td>5.56</td>
</tr>
<tr>
<td>48hr reflux</td>
<td>99</td>
<td>0.021 ± 3.9x10$^{-4}$</td>
<td>0.010 ± 3.2x10$^{-4}$</td>
<td>5.93</td>
</tr>
<tr>
<td>72hr reflux</td>
<td>95</td>
<td>0.030 ± 5.7x10$^{-4}$</td>
<td>0.008 ± 2.1x10$^{-4}$</td>
<td>5.95</td>
</tr>
<tr>
<td>5day reflux</td>
<td>84</td>
<td>0.042 ± 9.6x10$^{-4}$</td>
<td>0.009 ± 3.3x10$^{-4}$</td>
<td>5.82</td>
</tr>
<tr>
<td>1wk reflux</td>
<td>37</td>
<td>0.054 ± 1.1x10$^{-3}$</td>
<td>0.008 ± 1.9x10$^{-4}$</td>
<td>5.81</td>
</tr>
<tr>
<td>4wk reflux</td>
<td>20</td>
<td>0.093 ± 3.8x10$^{-4}$</td>
<td>0.002 ± 5.6x10$^{-3}$</td>
<td>4.26</td>
</tr>
</tbody>
</table>

$^a$All surface area measurements are ±5%. $^b$All reported errors are the standard deviation as determined from triplicate measurements. $^c$All pH measurements are ± 0.05 pH units.

**TABLE 4:** EXAFS fits for Ni sorbed and incorporated reference compounds, fit by refinement of a single model cluster.

<table>
<thead>
<tr>
<th>Shell</th>
<th>N</th>
<th>$R$ (Å)</th>
<th>$2\sigma^2$ $(\text{Å}^2)$</th>
<th>$\theta$</th>
<th>$\varphi$</th>
<th>EF</th>
<th>R (%)</th>
<th>Reduced Chi$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_0$</td>
<td>1.0</td>
<td>0.00</td>
<td>0.000</td>
<td>0</td>
<td>0</td>
<td>1.43</td>
<td>18.1</td>
<td>17.6</td>
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<tr>
<td>O$_1$</td>
<td>3.0</td>
<td>2.01</td>
<td>0.012</td>
<td>47</td>
<td>0</td>
<td></td>
<td></td>
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<tr>
<td>O$_2$</td>
<td>3.0</td>
<td>2.04</td>
<td>0.011</td>
<td>136</td>
<td>180</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn$_3$</td>
<td>3.0</td>
<td>2.88</td>
<td>0.012</td>
<td>90</td>
<td>270</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Mn$_4$</td>
<td>3.0</td>
<td>2.85</td>
<td>0.013</td>
<td>90</td>
<td>90</td>
<td></td>
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<tr>
<td>Mn$_5$</td>
<td>3.0</td>
<td>5.94</td>
<td>0.006</td>
<td>90</td>
<td>270</td>
<td></td>
<td></td>
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<tr>
<td>Mn$_6$</td>
<td>3.0</td>
<td>4.94</td>
<td>0.010</td>
<td>90</td>
<td>180</td>
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<tr>
<td>Mn$_7$</td>
<td>3.0</td>
<td>5.05</td>
<td>0.012</td>
<td>90</td>
<td>0</td>
<td></td>
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<tr>
<td>Mn$_8$</td>
<td>3.0</td>
<td>5.90</td>
<td>0.005</td>
<td>90</td>
<td>90</td>
<td></td>
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<tr>
<td>O$_9$</td>
<td>3.0</td>
<td>3.33</td>
<td>0.016</td>
<td>105</td>
<td>0</td>
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<tr>
<td>O$_{10}$</td>
<td>3.0</td>
<td>3.58</td>
<td>0.009</td>
<td>75</td>
<td>180</td>
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<tr>
<td>O$_{11}$</td>
<td>3.0</td>
<td>4.47</td>
<td>0.006</td>
<td>75</td>
<td>100</td>
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<tr>
<td>O$_{12}$</td>
<td>3.0</td>
<td>4.45</td>
<td>0.009</td>
<td>105</td>
<td>45</td>
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<tr>
<td>O$_{13}$</td>
<td>3.0</td>
<td>4.51</td>
<td>0.004</td>
<td>100</td>
<td>80</td>
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<tr>
<td>O$_{14}$</td>
<td>3.0</td>
<td>4.65</td>
<td>0.011</td>
<td>75</td>
<td>135</td>
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Ni-sorbed c-disordered birnessite 24 hr (Ni-birnessite′)

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>O1</th>
<th>O2</th>
<th>O3</th>
<th>Mn4</th>
<th>Mn5</th>
<th>O6</th>
<th>O7</th>
<th>Mn8</th>
<th>Mn9</th>
<th>Mn10</th>
<th>Mn11</th>
</tr>
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<tbody>
<tr>
<td>Ni0</td>
<td>1.0</td>
<td>0.00</td>
<td>0.000</td>
<td>0</td>
<td>0</td>
<td>3.45</td>
<td>13.9</td>
<td>10.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O1</td>
<td>3.0</td>
<td>2.08</td>
<td>0.011</td>
<td>60</td>
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Ni-sorbed todorokite 24 hr (Ni-todorokite_24hr)

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Ni-sorbed todorokite 1 wk (Ni-todorokite_1wk)

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* N is the number of atoms in a shell. R, θ and φ are the interatomic distance and spherical coordinates of the prototype atom in each shell with either C1 or \( \text{C}_3 \) symmetry. \( 2\sigma^2 \) is the Debye–Waller factor. EF is the correction to the Fermi energy value assigned in ATHENA. Values in italics were held constant during refinement.
TABLE 5: EXAFS fits for our birnessite precursor, 10 Å phyllosilicate intermediate and all reflux products.

a) Samples fit by linear combination of reference spectra.

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<th>Sample</th>
<th>EF</th>
<th>N Ni&lt;sup&gt;S&lt;/sup&gt;</th>
<th>N Ni&lt;sup&gt;V&lt;/sup&gt;</th>
<th>R (%)</th>
<th>Reduced Chi²</th>
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EF is the correction to the Fermi energy value assigned in ATHENA. $N_{Ni^S}$ is the number of Ni atoms (Ni site occupancy) for reference spectrum Ni-structurally incorporated natural birnessite (Ni-birnessite)<sup>S</sup>. $N_{Ni^V}$ is the number of Ni atoms (Ni site occupancy) for reference spectrum Ni-sorbed c-disordered birnessite (Ni-birnessite)<sup>V</sup>.
TABLE 5: EXAFS fits for our birnessite precursor, 10 Å phylلومanganate intermediate and all reflux products.

b) Samples fit by refinement of a single model cluster.

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2 wk reflux

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4 wk reflux

\( N \) is the number of atoms in a shell. \( R, \theta \) and \( \varphi \) are the interatomic distance and spherical coordinates of the prototype atom in each shell with either \( C_1 \) or \( C_3 \) symmetry. \( 2\sigma^2 \) is the Debye–Waller factor. \( \text{EF} \) is the correction to the Fermi energy value assigned in ATHENA. Values in italics were held constant during refinement.
### TABLE 6: EXAFS fits for natural ferromanganese samples, fit by refinement of a single model cluster.

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$N$ is the number of atoms in a shell. $R$, $\theta$ and $\phi$ are the interatomic distance and spherical coordinates of the prototype atom in each shell with either $C_1$ or $C_3$ symmetry. $2\sigma^2$ is the Debye–Waller factor. $EF$ is the correction to the Fermi energy value assigned in ATHENA. Values in italics were held constant during refinement.
FIGURE CAPTIONS

FIGURE 1: Molecular clusters used to model EXAFS spectra of (a) Ni surface adsorbed at Mn octahedral vacancy sites present in the layers of a hexagonal phylomanganate, (b) Ni structurally incorporated into the layers of a phylomanganate, and (c) Ni surface sorbed to todorokite as a tridentate corner-sharing complex.

FIGURE 2: X-ray diffraction patterns for our Ni-sorbed c-disordered birnessite precursor, Ni-sorbed 10 Å phylomanganate intermediate and subsequent reflux products. Characteristic X-ray diffraction peaks are labeled for our c-disordered birnessite (B), 10 Å phylomanganate intermediate (10Å P) and todorokite product (T) (based on Drits et al., 1997 for turbostratic birnessite, JCPDS-32-1128 for buserite and JCPDS-38-475 for todorokite, respectively). The * symbol indicates residual MgCl₂.

FIGURE 3: Transmission electron micrographs of: (a-b) Ni-sorbed 10 Å phylomanganate with image (a) highlighting the plate-like morphology and thick phylomanganate layer edges, and (b) highlighting the phylomanganate interlayer spacing. (c-d) Reflux product after 6 hr reflux, where (c) highlights the phylomanganate dominated mineralogy of the sample matrix and (d) highlights the formation of poorly crystalline todorokite primary particles, elongated along the [010] direction and relatively uniform in size (6-10 nm) across the [100] direction. (e-f) Reflux product after 24 hr reflux where (e) highlights the mixed birnessite/todorokite mineralogy and (f) highlights the formation of poorly crystalline plate-like todorokite, and the formation of large secondary todorokite laths, formed via the lateral aggregation of todorokite primary particle building blocks. (g-h) Reflux product after 1 wk reflux, indicating that the mineralogy is largely dominated by todorokite. (i-j) Reflux product after 2 wk reflux where the red lines in (i) highlight the lateral aggregation of primary todorokite particles and (j) highlights the relatively uniform widths of the individual todorokite primary particles. Circles in images (c), (e), (g) and (i) indicate the position of EDS analysis, where the circle is approximately equal to the size of the analyzed area. Approximate wt % of Ni at the selected EDS points is shown in Table 1.

FIGURE 4: Surface area of the solid reflux products and the concentrations of Ni and Mn in the reflux solution as a function of reflux time. The first surface area measurement is
the Ni-sorbed 10 Å phyllomanganate intermediate at 0 hr reflux; measurements of Ni and Mn in the reaction solution start at 3 hr reflux. For exact values and error measurements see Table 3 (errors for BET are ±5% of the measured value and for [Mn] and [Ni] are smaller than the data points).

FIGURE 5: Ni K-edge EXAFS and Fourier transforms of the EXAFS for the reference compounds. Ni-birnessite$^S$ is a Ni-incorporated natural poorly crystalline birnessite; Ni-birnessite$^V$ is a synthetic c-disordered birnessite at 24 hr contact time with Ni sorbed at the Mn octahedral vacancy sites, Ni-todorokite_24hr and Ni-todorokite_1wk are synthetic togorokite samples at 24 hr and 1 wk contact times, respectively. Solid lines are data, dotted lines are fits.

FIGURE 6: Ni K-edge EXAFS and Fourier transforms of the EXAFS for the experimental samples including Ni-sorbed c-disordered birnessite precursor, Ni-sorbed 10 Å phyllomanganate intermediate and subsequent reflux products at 3, 6, 24 and 48 hr, and 1, 2 and 4 wk. Solid lines are data, dotted lines are fits.

FIGURE 7: Bulk powder X-ray diffraction patterns for (a) the hydrogenetic ferromanganese crust collected from the Pacific Ocean (b) the diagenetic ferromanganese nodule from the Pacific Ocean and (c) the hydrothermal deposit, collected from the Lau Basin. X-ray diffraction peaks are labeled for phyllomanganate (P) (based on JCPDS-15-604 for vernadite, Drits et al., 1997 for turbostratic birnessite and JCPDS-32-1128 for buserite) and todogorkite (T) (based on JCPDS-38-475). □ denotes hydroxyapatite (Ca$_5$(PO$_4$)$_3$(OH)), ● denotes quartz (based on JCPDS 9-0432 and 46-1045, respectively).

FIGURE 8: µ-XRF elemental maps showing the distribution of Mn (blue), Fe (green) and Ni (red) in (a-b) the hydrogenetic ferromanganese crust sample, (c-d) the diagenetic ferromanganese nodule and (e-f) the hydrothermal ferromanganese deposit. Pixel size is 10x10 μm, and total map area for the hydrogenetic sample is 1700x1700 μm, and for the diagenetic and hydrothermal samples is 400x400 μm. Points of interest (POI) subject to µ-EXAFS analysis are shown (white boxes are not to scale).
FIGURE 9: Scatter plots displaying normalized fluorescence counts between Mn-Fe, Ni-Mn, and Ni-Fe, for (a-c) the hydrogenetic ferromanganese crust sample, (d-f) the diagenetic ferromanganese nodule and (g-i) the hydrothermal ferromanganese deposit.

FIGURE 10: Mn K-edge EXAFS for the selected POI in the natural samples. The hydrogenetic, diagenetic and hydrothermal samples are labeled as HG_FeMn, DG_FeMn and HT_FeMn, respectively. Dashed vertical lines indicate key k-space indicator regions at ~6.7, 8 and 9.2 Å^{-1}.

FIGURE 11: Ni K-edge EXAFS and Fourier transforms of the EXAFS for the natural hydrogenetic, diagenetic and hydrothermal samples, labeled as HG_FeMn, DG_FeMn and HT_FeMn, respectively. Solid lines are data, dotted lines are fits.
Atkins et al: Figure 1 (one column wide)

Figure 1

(a)

(b)

(c)
Figure 2 (two columns wide)

$\theta$ (Cu Kα radiation)

- Normalised Intensity
- 3.6Å [002] B
- 3.2Å [003] 10Å P/[003] T
- 9.6Å [001] 10Å P/[001] T
- 4.8Å [002] 10Å P
- 1.5Å [21<5] T
- 2.4Å [21<1]
- 1.4Å [110] B, 10Å P/[020] T
- 2.5Å [210] T

Birnessite precursor

10Å Phyllomanganate Intermediate

- 3hr reflux
- 6hr reflux
- 12hr reflux
- 24hr reflux
- 48hr reflux
- 72hr reflux
- 1 wk reflux

- 2.2Å [21<2] T
- 1.7Å [21<4] T
- 2.4Å [100] B, 10Å P
- 1.9Å [31<2] T
- 1.9Å [31<2] T
- 1.5Å [21<5] T
- 1.7Å [21<5] T
- 1.7Å [21<5] T
- 2.4Å [21<1] T
- 2.5Å [210] T
- 2.5Å [210] T
- 4.8Å [002] 10Å P/[003] T
- 9.6Å [001] 10Å P/[001] T
- 4.8Å [002] 10Å P
- 9.6Å [001] 10Å P/[001] T
Figure 3
Atkins et al: Figure 3 (two columns wide)
Figure 4

Atkins et al: Figure 4 (one column wide)
Atkins et al: Figure 5 (two columns wide)

Fourier transform $X(k)k^3$

- **Ni-todorokite**
  - _1wk_ (top)
  - _24hr_ (middle)
- **Ni-birnessite**
  - $V$ (second from top)
  - $S$ (bottom)

Wavenumbers (Å$^{-1}$)

Distance (Å)
Atkins et al: Figure 7 (one column wide)

Figure 7

Normalised Intensity

$\theta$ (Cu K-alpha radiation)

a) ~9.8 Å P
b) ~4.8 Å P
~2.4 Å P
~1.4 Å P

c) ~7.2 Å P
~3.5 Å P
~2.2 Å T
~1.7 Å T
Figure 10

Atkins et al: Figure 10 (two columns wide)

$X(k)k^2$

Wavenumbers (Å$^{-1}$)

Todorokite
Tc-Na-birnessite
Hx-birnessite
$\delta$MnO$_2$
HT_FeMn_POI2
HT_FeMn_POI1
DG_FeMn
HG_FeMn