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In-situ determination of the kinetics and mechanisms of nickel adsorption by nanocrystalline vernadite

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ABSTRACT

In-situ kinetics and mechanisms of Ni2⁺ uptake by synthetic vernadite were determined at pH 5.8 and I = 0.1 M NaCl using wet chemistry, atomic-resolution scanning transmission electron microscopy coupled with electron energy loss spectroscopy (STEM-EELS) and synchrotron high-energy X-ray scattering (HEXS) in both the Bragg-rod and pair distribution function formalisms. The structural formula of the initial solids was TCMn3⁺0.05Na⁺0.22(H2O)0.86H⁺0.06[TCNi2⁺0.86Mn3⁺0.04Vac0.1)O2], where species under brackets form the layer having “vac” layer vacancies, and where other species are present in the interlayer, with TC standing for “triple-corner-sharing” configuration. According to HEXS and STEM-EELS, adsorbed Ni2⁺ adopted mainly a TC configuration, and had a Debye-Waller factor about four times higher than layer Mn. Steady-state was reached after ~2.2 h of contact time, and the final structural formula of the solid was TCMn3⁺0.12TCNi2⁺0.05Na⁺0.12H2O0.36H⁺0.01[TCNi2⁺0.05Vac0.1)O2]. Atomic-scale imaging of the solids also evinced the presence of minor Ni adsorbed at the crystal edge. The retention coefficient R∞ = 10⁻⁵.76 ± 0.06 L kg⁻¹, computed from PDF data modelling and solution chemistry results, was in agreement with those available in the literature.

1. Introduction

Vernadite, a manganese (Mn) oxide, is ubiquitous in the environment, being found as nodules and coatings in soil and sediments or as rock varnishes in deserts and polar and temperate regions (Bargar et al., 2009; Burns and Burns, 1977; Chukhrov et al., 1985; Dorn, 1991; Dorn et al., 1992; Dorn and Oberlander, 1981; Exon et al., 2002; Fuller and Bargar, 2014; Glover, 1977; Manceau et al., 2003, 2004; Marcus et al., 2009; Palumbo et al., 2004; Paloumbo et al., 2001; Potter and Rossman, 1979). In surficial environments, vernadite precipitation by oxidation of aqueous Mn²⁺ in the presence of bacteria, fungi, and higher living forms (Grangeon et al., 2008; Lanson et al., 2008; Villalobos et al., 2006) is faster than abiotic oxidation catalysed by mineral surfaces by orders of magnitude (e.g., Hastings and Emerson, 1986; Tebo et al., 2004). Vernadite structure consists in the turbostratic stacking of layers made of (Mn⁴⁺O₆)₈ corner-sharing octahedra connected through their edges and separated from each other by hydrated interlayer cations (Giovanoli, 1980). These layers contain isomorphic substitutions of Mn⁴⁺ by cations of lower valences (e.g., Mn³⁺, Ni²⁺, Co²⁺) and/or layer vacancies (Grangeon et al., 2008; Lanson et al., 2008; Villalobos et al., 2006), which induce a layer charge deficit reported to reach values as high as 1.6 valence unit (v.u.) per layer octahedron (Lanson et al., 2008). The layer charge deficit created by substituted octahedron (1 or 2 v.u. for trivalent and divalent octahedral cations respectively) is mostly compensated for by adsorbed hydrated cations forming outer-sphere complexes (e.g. Na⁺, Ca²⁺), while the layer charge deficit created by vacant Mn site (4 v.u.) is most frequently compensated for by adsorbed cations forming inner-sphere complexes (e.g. Na⁺, Ca²⁺) and/or layer vacancies (Grangeon et al., 2008; Lanson et al., 2008; Villalobos et al., 2006), which induce a layer charge deficit reported to reach values as high as 1.6 valence unit (v.u.) per layer octahedron (Lanson et al., 2008).
elements and actinides is controlled, or at least influenced, by vernadite in certain soils, freshwater and marine sediments (Koschinsky and Halbach, 1995; Manceau et al., 2000, 2004, 2007a; Marcus et al., 2004; Peacock and Moon, 2012; Peacock and Sherman, 2007a; Takahashi et al., 2007). Amongst metals, Ni²⁺ is of special interest, because of its toxicity (Kasprzak et al., 2003; Wang and Wang, 2008; Weng et al., 2004) and of its wide use in industrial processes and manures for agriculture (Nicholson et al., 2003).

Upon contact with vernadite, Ni²⁺ can adopt three main configurations (inset in Fig. 1): adsorbed at the particle edge in a double corner-sharing configuration (DCNi), located above layer vacancies in a triple corner-sharing configuration (TCNi), or incorporated within the layer (ENi) (Grangeon et al., 2008; Manceau et al., 2007b; Peacock, 2009; Peacock and Sherman, 2007a, b; Peña et al., 2010). Ni is favoured when surface coverage (i.e., Ni/Mn ratio) is low, when the pH of the equilibrium solution is alkaline, and when contact time between solution and vernadite is long (Fig. 1).

In many environmental compartments, the interaction between Ni²⁺ in solution and vernadite takes place in open chemical system where contact time is limited. These include streams, rivers, or the critical zone in soils. The kinetics of Ni²⁺-vernadite interactions which influence the capacity of vernadite to uptake Ni²⁺ solution through the capillary, and to the other side to a waste container, using silicon tubing. A scheme of a similar set-up is available elsewhere (Marty et al., 2015). Flow rate was set to 20 mL h⁻¹. The input solution had a pH of 5.8 and contained 2 10⁻⁴ M NiCl₂ in a 0.1 M NaCl ionic background, as to remain in chemical conditions comparable to previously published data (Tonkin et al., 2004). Recording of data started as soon as the solution was allowed to flow. An acquisition step consisted in the successive recording of 20 frames (5 s collection time each) and lasted 5 min, because of the need to record detector's dark current. Each acquisition step was separated from the next one by a dwell time of 2 min. The 20 frames acquired at each step were averaged and integrated using the pyFAI package (Ashiotis et al., 2015). The same procedure was applied to the recording of the signal arising from a capillary containing only the aqueous solution. Data were transformed to X-ray pair distribution function (PDF) data using PdfGetX3 (Juhas et al., 2013), with the function formalisms made it possible to monitor sorption processes as a function of reaction time. These processes were further confirmed with atomic-resolution scanning transmission electron microscopy (STEM) coupled with energy electron-loss spectroscopy (EELS).

2. Materials and methods

2.1. Synthesis of the sample and chemical characterization

Synthetic vernadite (δ-MnO₂) was synthesized using the redox method (Villalobos et al., 2003). Briefly, a solution made of ~40 g KMnO₄ dissolved in ~1.3 L of deionized water was added to a solution made of 28 g NaOH dissolved in 1.4 L of deionized water. Then, a solution made of ~75 g MnCl₂·4H₂O was added, leading to the precipitation of synthetic vernadite which was separated from the solution by 10 series of centrifugation and Na saturation using a 1 M NaCl solution. The obtained Na-saturated synthetic vernadite was freeze-dried. An aliquot of the powder was used for the determination of the average Mn oxidation state (Mn AOS), using a potentiometric method (Grangeon et al., 2012).

2.2. High-energy X-ray scattering

High-energy X-ray scattering (HEXS) experiments were performed at station ID22 from the European Radiation Synchrotron Facility (ESRF, Grenoble, France), using energy of 69.9 keV and a Perkin Elmer XRD 1611CP3 flat detector. A polyimide capillary (diameter of 1.6 mm) was filled with synthetic vernadite, sealed on its two extremities using a frit-in-a-ferrule system (Idex Health & Science), and fixed in its measurement position. It was connected on one side to a peristaltic pump, used to flow the Ni²⁺ solution through the capillary, and to the other side to a waste container, using silicon tubing. A scheme of a similar set-up is available elsewhere (Marty et al., 2015).

Flow rate was set to 20 mL h⁻¹. The input solution had a pH of 5.8 and contained 2 10⁻⁴ M NiCl₂ in a 0.1 M NaCl ionic background, as to remain in chemical conditions comparable to previously published data (Tonkin et al., 2004). Recording of data started as soon as the solution was allowed to flow. An acquisition step consisted in the successive recording of 20 frames (5 s collection time each) and lasted 5 min, because of the need to record detector's dark current. Each acquisition step was separated from the next one by a dwell time of 2 min. The 20 frames acquired at each step were averaged and integrated using the pyFAI package (Ashiotis et al., 2015). The same procedure was applied to the recording of the signal arising from a capillary containing only the aqueous solution. Data were transformed to X-ray pair distribution function (PDF) data using PdfGetX3 (Juhas et al., 2013), with the contribution from the capillary and the aqueous solution being removed at this step. PDF data modelling was performed using PDFGui (Farrow et al., 2007). Turbostratification influences the PDF by attenuating the correlations resulting from pairs of atoms located on distinct layers as compared to those originating from atoms located on the same layer (Grangeon et al., 2015; Manceau et al., 2013). To circumvent this problem, the r interval of the simulation was restrained to the 1.2–7.2 Å range, i.e. to distances smaller than the layer-to-layer distance, using the model from Manceau and coworkers (Manceau et al., 2013). The atomic coordinates of ⁶⁹Ni and its coordination sphere were constrained from the qualitative analysis of PDF data (see below). During the modelling of the first PDF (collected on the sample before it was
contacted with Ni²⁺, the refined parameters were b (throughout the manuscript, data will be discussed in the frame of an orthogonal layer symmetry system – see below), the scale factor, the crystallite size (termed spdiometer in PDFGui), and the atomic correlated motion factor (Δ2 in PDFGui), as well as the occupancies of interlayer Na⁺ and $^{35}$C³Mn, the z-coordinates of interlayer Na⁺ and H₂O and thermal agitation factors. For these latter, two different set of values were refined: one for layer Mn, and one for the interlayer species (Na⁺ and H₂O). u₁₁ was equal to u₂₂ in each of the two sets. Thermal agitation factor of layer O was set to two times that of layer Mn to conform with previous studies (Villalobos et al., 2006), and that of TC species was set to four times that of Na⁺, as suggested by STEM observation (see below). Because of the observed hexagonal layer symmetry (see below), a and b were linked, so that $a = \sqrt{3} \times b$ ($\gamma = 90^\circ$). The occupancy of interlayer H₂O was set to three times that of Na⁺ (Post and Veblen, 1990). The number of layer vacancies was set to one minus the sum of the occupancy of $^{35}$C³Mn plus one fourth that of Na⁺. For all other PDF, collected during contact with Ni²⁺, the occupancy of $^{35}$C³Mn was set equal to that obtained on the first sample, because it was previously shown that the occupancy of $^{35}$C³Mn remains constant regardless of $^{1}$Ni²⁺ loading when equilibrium pH is acidic (Grangeon et al., 2008).

Similarly, all atomic agitation factors were set equal to those obtained on the first sample, with those of $^{35}$C³Ni and $^{35}$C³Mn being set equal. The number of layer vacancies was constrained to be equal to one minus the sum of the occupancies of $^{35}$C³Mn plus half that of $^{35}$C³Ni plus one fourth that of Na⁺. Thus, refinements were performed with only five free parameters. In all simulations, correlations between parameters remained below the threshold value (0.8) hard-coded in PDFGui. Note that as the set up imposed the use of relatively long (~5 cm) polyimide capillaries, a slight bending of this capillary could not be ruled out that would have influenced sample-to-detector distance and consequently refined lattice parameters.

Differential PDF were calculated after normalization of all PDF data to the correlation at 2.86 Å, which is related to the shortest 3Mn-Mn pair. A direct normalization by the incident photon flux failed, the overall intensity of the data changing with time due to a variable density of sample exposed to the beam, certainly because of compaction induced by the solution flow, or because of aggregation of particles.

Structure models obtained from PDF data modelling served as a basis for the calculation of XRD patterns using a modified version of the Calcipow program (Plancon, 2002), which is based on a matrix formalism capable of reproducing the effect of turbostratisim (Drits et al., 2007) and which was previously applied to the study of phyllosilicates, layered double hydroxides, and phyllomanganates having various quantity of structural defects (Gates et al., 2002; Grangeon et al., 2016; Hadi et al., 2014; Manceau et al., 1997; Villalobos et al., 2006). The sole free parameters during this refinement were the size of the crystallites in the ab plane, the background, constrained to be similar to the one used to model the structure of other synthetic vernadite (Manceau et al., 2013), and microstrains which were modelled following this previous study, with the $\delta$ parameter varying between 0.2 and 0.4. In these calculations, the isotropic temperature factors (B-factors) were set to 0.5 Å² for layer Mn, 1 Å² for layer O and 2 Å² for all other species.

2.3. Scanning transmission electron microscopy and electron energy loss spectroscopy

STEM and EELS analysis were carried out using a Cs-corrected Nion Ultra-STEM 200 operated at 100 kV. To increase the stability under the beam and to limit aggregation phenomena, samples were first embedded in epoxy resin and left 48 h in the dark for polymerization. The samples were then cut in slices of thickness ~50 nm and deposited on a lacey carbon film loaded on copper grids. Images were acquired in high-angular annular dark-field (HAADF mode) and were simulated using QSTEM software (Koch, 2002).

The EELS spectromicroscopy maps were obtained by collecting EELS spectra with spatial steps of 40 nm, acquisition times of 1 ms, energy ranges from 400 eV to 1000 eV and probe currents of 60 pA. In order to detect weak signal, the final EELS detector was an Electron Multiplying CCD that allows single electron sensitivity at 8 MHz read out speed.

3. Results and discussion

3.1. Qualitative study of XRD and PDF data

All XRD patterns collected as a function of time were typical for nanocrystalline turbostratic Mn oxide (Drits et al., 2007; Villalobos et al., 2006), all diffraction maxima being broad and some asymmetric with the intensity increasing sharply on the low $q$ side and decreasing slowly on the high $q$ side (Fig. 2). Crystallites were mainly built of isolated nanosheets, because no maxima could be observed at $q \leq 2.1 \text{Å}^{-1}$ (equivalent to a d-spacing of 3 Å). Indeed, if the crystallites were built of more than ~1.5 layers on average, a 001 reflection would be expressed at $\sim 0.5 \text{Å}^{-1} \leq q \leq \sim 0.9 \text{Å}^{-1}$ (Grangeon et al., 2014; Lanson et al., 2008), as vernadite layer-to-layer distance usually varies between 7 Å and 10 Å.

The band at ~4.4 nm⁻¹ is indicative of the layer symmetry (Drits et al., 2007; Webb et al., 2005): it is almost symmetrical when layer symmetry is hexagonal, or split in two maxima when layer symmetry is orthogonal. It was symmetrical for our sample, and layer symmetry was thus hexagonal. Bands were indexed however with an orthogonal system ($\gamma = 90^\circ$, $a = \sqrt{3} \times b$) for consistency with previous studies (e.g. Drits et al., 2007; Villalobos et al., 2006). In this frame of reference, the maxima at 2.59 Å⁻¹ (2.43 Å), 4.45 Å⁻¹ (1.41 Å) and 5.13 Å⁻¹ (1.22 Å) correspond to the 11,20, 31,02 and 22,40 bands, whose analysis is sufficient to determine the mean structure of vernadite, including the abundance of layer vacancies and TC species (Manceau et al., 2013).

The main changes observable in the patterns as a function of time – and thus of contact time with Ni²⁺ – lied in the high-q side of the 11,20 band where diffracted intensity systematically decreased (arrow in Fig. 2), leading to the appearance and strengthening of a hump at
and its O coordination sphere and by TCNi and the closest EMn atoms (TCNi-EMn distance — Fig. 4). Using this latter distance and the \( r \) value of the shortest EMn-EMn pair (\( \sim 2.87 \text{ Å} \) — Fig. 3a) as \( b \), the \( z \)-coordinate of the Ni atom \( z(\text{Ni}) \) above the plane formed by layer Mn atoms was 2.05 Å (Fig. 4a). Using geometrical constraints imposed by the hexagonal layer symmetry, the position of the second, third, fourth and fifth TCNi-EMn correlations (TCNi-EMn\(_x\) pairs, where \( x = 2,3,4,5 \)) could be predicted according to \( \sqrt{(z(\text{Ni}))^2 + y^2} \) Å where \( y = \sqrt{3 \times b, 2 \times b, \sqrt{7} \times b \text{ and } 3 \times b} \) (Fig. 4b), yielding respectively 5.37 Å, 6.09 Å, 7.85 Å, 8.84 Å. The second, third, fourth and fifth correlations were indeed observed at 5.36 Å, 6.11 Å, 7.82 Å and 8.83 Å.

Finally, a weak correlation was observed at \( \sim 3.0 \) Å, on the low-\( r \)-side of the shortest EMn-EMn correlation. Its evolution was mirrored by a negative correlation at \( \sim 2.8 \) Å, on the low-\( r \)-side of the same EMn-EMn correlation. Consistent with XRD observations that lattice parameters increased with TCNi loading (Fig. 2), this behaviour resulted from a continuous shift of the first EMn-EMn correlation towards high \( r \) values with time (inset in Fig. 3a). Similar but weaker evolution was observed for the EMn-O correlation at 4.45 Å, where a negative correlation at 4.31 Å and a positive one at 4.52 Å increased in intensity with time. At higher \( q \), such evolution was not observed, suggesting that the layer deformations induced by TCNi only affected the local order. This assumption of local disorder is reinforced by the fact that the d-PDF at \( q > 10 \) Å is dominated by TCNi-EMn correlations, demonstrating the presence of long-range order (Supplementary data Fig. S1).

### 3.2. Quantitative analysis of PDF data

To quantify TCNi as a function of time, the PDF were fitted using Manceau’s model (Grangeon et al., 2015; Manceau et al., 2013; Supplementary Fig. S1 and Fig. 5). \( z(\text{Ni}) \) was evaluated from the TCNi-EMn\(_x\) distance to limit the effect of local disorder. Consistently with qualitative observations (Figs. 2 and 3), TCNi increased with time, up to 0.12 ± 0.02 per layer octahedron. The sorption mechanism underwent two regimes: up to \( \sim 5400 \) s of contact time, the abundance of TCNi sharply increased from 0 to \( \sim 0.10 \) per layer octahedron. Then, increase was much weaker, plateauing at \( \sim 0.12 \) ± 0.02 TCNi per layer.

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**Fig. 3.** (a): All PDF data collected during the experiment. Indexation is made for the first pattern, which corresponds to the sample before its interaction with Ni\(^{2+}\). Inset shows the evolution of the position of the EMn-EMn correlation as a function of time. (b): d-PDF data, relative to the first pattern, which corresponds to the sample before its interaction with Ni\(^{2+}\). Inset shows the evolution of the position of the EMn-EMn correlation as a function of time.

**Fig. 4.** Schematic representation of a TCNi atom (red dot) and its coordination sphere (red polyhedron) above a layer built of Mn atoms (black dots) in octahedral coordination (grey polyhedra). (a): View parallel to the layer plane (ab plane). (b): View perpendicular to the ab plane. Circles materialize the first TCNi-Mn shells. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
The grey lines at the bottom are the residual fits, sorted from top to bottom. Simulation results for all PDF are available in the Supplementary Table S1. (b) Evolution of $^{65}$Ni as a function of time (colour as in Fig. 2c). (c) Experimental data in the $q$ space (black solid line), collected at $t = 0$ s and at $t = 11340$ s and comparison to patterns calculated using models obtained from PDF modelling (red solid line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The increase in lattice parameters evinced from the qualitative examination of both XRD and PDF data could not be quantified: although $b$ steadily increased from 2.8535 ± 0.0021 Å to 2.8586 ± 0.0018 Å, this evolution remained mostly within uncertainties (see Supplementary Fig. S1). The equivalent isotropic B-factor of layer Mn was 0.3 Å$^2$, close to the value of 0.5 Å$^2$ previously proposed (Lanson et al., 2008; Villalobos et al., 2006).

To further ensure that the 1.2–7.2 Å range used for refinement was sufficient to accurately describe the layer structure at the crystallite scale, some models obtained from PDF modelling were used to calculate XRD patterns which were compared to experimental data (Fig. 5c). Given that no structure parameter was refined but the crystallite size in the ab plane, which was found to be 6 nm, the agreement between calculation and experiment was satisfying. In particular, the modulation of the high-q side of the 11.20 band could be reproduced.

Using the Mn AOS of 3.9 obtained using potentiometric titration and results from PDF data modelling, the structural formula of the initial sample was determined to be $^{55}$Cr$_{2.65}$Na$_{0.23}$(H$_2$O)$_{0.69}$H$^+$0.06[(Mn$^{4+}$$_{0.66}$Mn$^{3+}$$_{0.04}$Vac$_{0.04}$)$_2$O$_3$], where species under brackets form the layer having "vac" layer vacancies, and where other species are present in the interlayer (H$^+$ is adjusted to ensure charge compensation). The chemical formula of the sample obtained at the end of the experiment was deduced from the results of PDF modelling, assuming that the increase in the number of vacancies was due to the expulsion of layer Mn$^{3+}$, yielding $^{55}$Cr$_{0.12}$Cr$_{0.88}$Mn$^{3+}$$_{0.09}$Na$^{+}$_{0.12}$(H$_2$O)$_{0.36}$H$^+$0.01[3(Mn$^{4+}$$_{0.87}$Vac$_{0.13}$)$_2$O$_3$]. Mn AOS could not be measured because of a too low amount of sample in the capillary. It was assumed that the increase in the number of layer vacancies was due to the expulsion of layer Mn$^{3+}$ because vacancies increased by 0.03 per layer octahedron as compared to the initial sample, close to the number of Mn$^{3+}$ in the initial sample (0.04). This possible expulsion of Mn$^{3+}$ by $^{55}$Cr, which however remains speculative because of experimental and modelling uncertainties, is analogous to that evidenced for $^{55}$Zn (Grangeon et al., 2012), and is coherent with the finding that sorption of $^{55}$Cr is accompanied by a decrease in $^{55}$Mn$^{3+}$ (Grangeon et al. 2008).

### 3.3. Direct imaging of Ni$^{2+}$ sorption sites at vernadite surface

From the present data analysis, Ni$^{2+}$ would mainly form $^{55}$CrNi. However, identifying a minor amount of $^{55}$Ni in a vernadite sample containing mainly $^{55}$CrNi is practically impossible using diffraction methods, owing to the similarities of their local environments (Grangeon et al., 2008). In order to overcome this limitation, STEM-EELS analysis was employed (Fig. 6).

The systematic bending of the layers prevented crystals from being exactly perpendicular to the beam, and thus hampered the acquisition of atomic-resolution HAADF images of a whole crystal, explaining why, in Fig. 6, only part of the image has atomic-resolution. In this part where a slight distortion was visible, due to the strong bending near the surface and to sample drift, two types of atoms were distinguished on the basis of their relative brightness (inset of Fig. 6a).

The EELS analyses showed the presence of three absorption edges at ~530 eV, ~640 eV and ~855 eV. The first one was assigned to the O K edge, while the second one clearly evinced the intense white line doublet from the Mn L$_{2,3}$ edge. The last one corresponded to the Ni L$_{2,3}$ edge and was only observed in areas that contained bright atoms (Fig. 6c), suggesting that bright atoms were Ni, whereas darker atoms were Mn. The STEM-HAADF images are often described as Z-contrast images with typically HAADF intensity considered to be proportional to Z$^{1.6}$. Such description cannot explain the difference of contrast observed in Fig. 6a, b for Mn (Z = 25) and Ni (Z = 28) atoms. Thermal diffuse scattering also plays a role in the HAADF intensity contrast and the origin of the stronger contrast of Ni with respect to Mn was thought to possibly result from a larger thermal agitation of $^{55}$Ni with respect to $^{55}$Mn. To test this hypothesis, STEM-HAADF calculations were performed using a model consisting of a vernadite layer with three vacancies, one being capped by...
Images were calculated with a Debye-Waller coefficient of TCNi equivalent to the one of EMn or four times larger, i.e. 0.5 Å² or 2 Å² (Fig. 7b, c). The Ni atoms became brighter only for an agitation factor of 2 Å². Furthermore, the intensity profile calculated for the largest agitation factors was in fair agreement with the experimental intensity (Fig. 7d), thus providing direct evidence for the higher thermal agitation factor of TC species as compared to that of EMn. Both STEM-EELS and STEM-HAADF confirmed the TC configuration of sorbed Ni.

Fig. 6a, b illustrates that Ni distribution within δ-MnO₂ structure was not ordered. Some regions contained Ni atoms which were only surrounded by Mn atoms over relatively long distances (~1 nm), whereas other regions were enriched in Ni. This, associated with the absence of TCNi-TCNi correlation in the PDF, suggested that the ordered vacancies distribution previously observed on other samples (Manceau et al., 2013) is not systematic. Finally, a minor presence of DCNi was detected (top left of Fig. 6a). It was recently proposed that the abundance of DCNi depends on sample Mn AOS: when Mn AOS decreases from 3.95 ± 0.05 down to 3.65 ± 0.05, the proportion of Ni at the edges of the crystals increases from 10-20% to about 80% (Simonova et al., 2015). Consistently, we could show that DCNi was a minor species when Mn AOS was 3.9.

Fig. 7. (a): Structure model used for the calculation of a STEM-HAADF image. As in Fig. 4, black spheres and grey octahedra respectively materialize layer Mn atoms and their coordination sphere, while red spheres and red octahedra materialize TCNi and its coordination sphere. (b): Calculated image assuming that Mn and Ni Debye-Waller factors are both equal to 0.5 Å². (c): Calculated image assuming that Mn and Ni Debye-Waller factors respectively are 0.5 Å² and 2 Å². DW stands for “Debye-Waller factor”. (d): Grey profiles of scaled experimental data (black solid line; same as in Fig. 6) and of calculations shown in (b) (red solid line) and in (c) (green dotted line). For these two latter, the profile was drawn along the line with arrows in (a). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
and steady-state was reached after ~8000 s (~2 h and 20 min) of
time, with the limitation that adsorption sites can only be interpreted in
the present study. Consequently, our characterization method appears
to 3.96 (Gray and Malati, 1979; Gray et al., 1978) vs. 3.9 in
the literature data obtained in similar conditions (Fig. 7; I = 0.1–0.5 vs.
I = 0.1 in the present study; pH values between 3.6 and 7 vs. 5.8 in
the present study; mean Mn oxidation degree in the range 3.83 (Kanungo et al., 2004) to 3.96 (Gray and Malati, 1979; Gray et al., 1978) vs. 3.9 in
the present study). Consequently, our characterization method appears
as a promising option to complement wet chemistry experiments.
Indeed, the time-resolved PDF provides a direct insight in the structure
of the solid, and allows determining the crystallographic sorption sites,
without the main limitation that it cannot probe trace amounts of adsorbed
species. Contrastingly, aqueous chemistry experiments make possible to
probe very small changes in solution composition and thus to quantify
adsorption processes over a wide range of aqueous metal concentra-
tions, with the limitation that adsorption sites can only be interpreted in
terms of sites density and affinity, without any possibility to attribute
them to crystallographic sites.

According to literature data, R₀ values depend weakly on pH
(Fig. 8); at I = 0.1, R₀ increases by ~0.4 log unit when pH increases
from 3.6 to 7. This is consistent with our reactivity model in which an
increased compensation by $H^+$ of the charge associated with the O
atoms forming a layer vacancy leads to a decrease in Ni²⁺ affinity for the
surface, since $H^+$ can compete with TCNi (Peacock and Sherman, 2007b).
A decrease in the mean manganese oxidation degree of the sample from 3.96 to 3.83, and thus an increase of the structural Mn⁴⁺
to Mn³⁺ ratio, leads to a slight increase of R₀ value. This is also
consistent with our model: TCNi may adsorb above vacancies by replacing TCNi⁴⁺ and adsorption of TCNi is possibly accompanied by the release in solution of $^{8}$Mn³⁺, thus generating new vacancies available for TCNi. Consequently, a higher abundance of $^{8}$Mn³⁺ and (or) TCNi⁴⁺ would improve vernadite adsorption reactivity towards Ni²⁺.

In the presence of pH conditions that are relevant to many environmental systems such as soils, Ni²⁺ adsorbed mainly as TCNi, and steady-state was reached after ~8000 s (~2 h and 20 min) of
interaction. Such kinetic rate is, at least, one order of magnitude faster
than those observed for adsorption at the surface of other soil minerals
(pyrophyllite, talc, gibbsite, and silica - Scheckel and Sparks, 2001).
This high adsorption kinetics rate, together with the high affinity
of vernadite surface for Ni²⁺ and other trace metals explains why
vernadite has been early described as a “scavenger” of trace metals
(Goldberg, 1954).

Notes
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Appendix A. Supplementary data

The d-PDF data and assignment of TCNi-Mn correlations (Supplementary Fig. S1) up to r = 25 Å and a list of parameters refined in all PDF data simulation procedures (Supplementary Table S1). Supplementary data associated with this article can be found in the online version, at doi:http://dx.doi.org/10.1016/j.chemgeo.2017.03.035.

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