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Uptake of nickel by synthetic mackinawite

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Abstract

The uptake of aqueous Ni(II) by synthetic mackinawite (FeS) was examined in anaerobic batch experiments at near-neutral pH (5.2 to 8.4). Initial molar ratios of Ni(II) to FeS ranged from 0.008 to 0.83 and maximum Ni concentrations in mackinawite, expressed as the cation mol fraction, were as high as $X_{\text{Ni}} = 0.56$ ($\text{Fe}_{1-x}\text{Ni}_x\text{S}$; $0 \leq x \leq 1$). Greater than 99% Ni removal from solution occurred when Ni loading remained below 0.13 ± 0.03 (1 σ) mol Ni per mol FeS due to sorption of Ni at the mackinawite surface. Characterization of experimental solids using X-ray diffraction and Raman spectroscopy showed patterns characteristic of nanocrystalline mackinawite; no evidence of nickel monosulfide (α -NiS or millerite), polydymite (Ni_3S_4), or godlevskite $[(\text{Ni},\text{Fe})_9\text{S}_8]$ formation was indicated regardless of the amount of Ni loading. Slight expansion of the c -axis correlated with increasing Ni content in synthetic mackinawite, from $c = 5.07 \pm 0.01$ Å at $X_{\text{Ni}} = 0.02$ to $c = 5.10 \pm 0.01$ Å at $X_{\text{Ni}} = 0.38$.

Ni K -edge extended X-ray absorption fine structure (EXAFS) spectra of synthetic Ni-bearing mackinawite are similar in phase and amplitude to the Fe K -edge EXAFS spectrum of Ni-free mackinawite, indicating that the molecular environment of Ni^{2+} in Ni-bearing mackinawite is similar to that of Fe^{2+} in Ni-free mackinawite. EXAFS data fitting of Ni-bearing mackinawite with $X_{\text{Ni}} = 0.42$ indicated a coordination number of 4.04 ± 0.30 and an average Ni_S bond distance of 2.28 Å, in good agreement with the Fe_S bond distance of 2.26 Å in mackinawite, tetrahedral Fe coordination, and slight lattice expansion along the c -axis. At lower Ni loadings ($X_{\text{Ni}} = 0.05$ –0.11), EXAFS analysis showed a decrease in Ni_S coordination towards CN = 3, which reflects the influence of sorbed Ni. Continued Ni uptake, past the maximum amount of sorption, was accompanied by proportional molar release of Fe to solution. Interstitial occupancy of Ni within the mackinawite interlayer may be transitional to structural substitution of Fe.

The Ni-mackinawite solid-solution is described by a one-site binary mixing model:

$$\ln K_d = \ln K_e - (W/RT)(1 - 2X_{\text{Ni}})$$

where K_d is the distribution coefficient, K_e is the ratio of equilibrium constants for Ni-mackinawite and mackinawite (14.4 ± 1.3), W is an ion interaction parameter, and X_{Ni} is the mole fraction of end-member NiS in the solid solution. The experimentally determined value of W is 17.74 ± 1.15 kJ/mol and indicates significant non-ideality of the solid solution.

Transformation processes were evaluated by aging Ni-mackinawite with polysulfides and solutions saturated with air. Reaction of Ni-mackinawite with polysulfides led to the formation of pyrite

(FeS₂) and Ni retention in the solid phase. When Ni-mackinawite was aged in the presence of dissolved oxygen, transformation to goethite (FeOOH) and violarite (FeNi₂S₄) was observed.

Keywords

Nickel; FeS; Mackinawite; Iron sulfide; Groundwater; Adsorption; Solid solution

1. Introduction

Sulfidic groundwaters and sediment pore waters are often saturated with disordered-FeS or mackinawite (FeS) indicating that these solids may be responsible for controlling concentrations of ferrous iron and sulfide in reducing aquatic environments (e.g., Berner, 1964, Davison, 1991). Disordered-FeS, mackinawite, and greigite (Fe₃S₄) together comprise the dominant components of solid-phase acid volatile sulfide (AVS) in sediments and aquifersolids and are possible precursors to the formation of pyrite (e.g., Berner, 1964, Schoonen and Barnes, 1991a, Rickard and Morse, 2005, Hunger and Benning, 2007). All of these iron sulfides, especially mackinawite, have capacity to remove bivalent metals from solution, such as lead, cadmium, nickel, manganese, copper, tin, and mercury (Jean and Bancroft, 1986, Morse and Arakaki, 1993, Arakaki and Morse, 1993, Parkmann et al., 1999, Coles et al., 2000, Jeong et al., 2007, Liu et al., 2008, Zavašnik et al., 2014, Dulnee and Scheinost, 2015). Consequently, iron sulfides are important sinks for trace metals in anoxic environments and may be advantageous for use in environmental applications to treat metal-contaminated water (Saunders et al., 2005).

Structural and surface properties of synthetic nanocrystalline mackinawite have been extensively examined (Mullet et al., 2002, Wolthers et al., 2003, Wolthers et al., 2005, Ohfuji and Rickard, 2006, Bourdoiseau et al., 2008, Jeong et al., 2008, Csákberényi-Malasics et al., 2012); these studies provide a foundation for understanding metal-mackinawite interactions. Possible mechanisms of metal uptake at the mackinawite surface are sorption, precipitation of a discrete metal sulfide via sulfide capture, and/or displacement of iron and formation of metal-substituted FeS (e.g., Framson and Leckie, 1978). Factors that may dictate specific metal uptake mechanisms are mineral solubility, pH, ionic radius, and coordination of the metal of interest relative to Fe in FeS. For the metals listed above, solubility products of monosulfides from least to most soluble follow the order: Hg << Cu < Cd ≈ Sn ≈ Pb < Ni < Fe < Mn. The large difference in solubility between HgS and FeS may favor capture of solid-phase sulfide by Hg²⁺ to form HgS (Jeong et al., 2007). Low pH (< 4) promotes mackinawite dissolution, H₂S generation, and direct metal sulfide precipitation (Özverdi and Erdem, 2006). On the other hand, because MnS is more soluble than FeS, Mn²⁺ sorption at the mackinawite surface is favored (Arakaki and Morse, 1993). In addition, the initial [Me²⁺]/[FeS] ratio plays an important role; for example, Jeong et al. (2007) found significant sorption of Hg(II) at [Hg²⁺]/[FeS] < 0.05 and precipitation of insoluble β-HgS at higher molar ratios.

Nickel uptake by mackinawite is of interest because the solubility contrast between FeS and NiS (xlog *K*_{sp} ≈ 6.2) is comparatively narrow relative to other bivalent metals and because

the average Fe_S bond distance (2.26 Å in mackinawite; coordination number = 4; Lennie et al., 1995) is comparable to the average Ni_S bond distance in polydymite (Ni₃S₄; 2.23 Å; coordination number = 4; Wilkin and Rogers, 2010) indicating that structural substitution of Ni(II) into mackinawite may be possible. Nickel monosulfides, α-NiS and millerite, have 6-fold and 5-fold Ni_S coordination, respectively, with average Ni_S bond distances that increase with coordination number (2.32 Å and 2.38 Å; Pauling, 1978). Based on differences in crystal chemistry, millerite/α-NiS and mackinawite are not expected to be miscible at low temperature, which complicates thermodynamic analysis of solid-solution formation and limits predictive capabilities of Ni transport and fate in reducing systems.

Nickel contamination in groundwater is usually linked to mining, smelting, metal plating, or metal recycling facilities, but is also related to natural sources such as the oxidation of trace metal-containing pyrite (Larsen and Postma, 1997, Noël et al., 2015, Houben et al., 2017). The earliest studies of mackinawite obtained from natural deposits around metal sulfide ores documented Ni enrichment in this mineral (e.g., Kouvo et al., 1963, Vaughan, 1969, Clark, 1970), with Ni concentrations up to about 20 wt% (Blain, 1978). Noël et al. (2015) reported on the vertical and lateral distribution of Ni in mangrove sediments accumulated downstream from weathered ultramafic deposits from New Caledonia using microscopy and Ni *K*-edge extended X-ray absorption fine structure (EXAFS) spectroscopy. In deeper anoxic sediments Ni was found associated with framboidal pyrite or disordered aggregates of submicron-sized pyrite crystals. In this case, it is unclear whether the Ni-pyrite association is related to transformation of Ni-enriched iron monosulfide precursors or to independent pyritization processes and sorption of mobilized Ni on pyrite surfaces (Noël et al., 2015). Thus, there remains uncertainty about the range and importance of possible Ni mobilization and attenuation processes in reducing groundwater and porewater systems.

Recently, Kwon et al. (2015) carried out calculations using density functional theory (DFT) to examine metal (Ni, Co, Cu) incorporation mechanisms involving mackinawite. Their modeling examined metal uptake at three structurally distinct sites: lattice substitution of iron, and intercalation between FeS₄ tetrahedral sheets in the mackinawite structure, either at tetrahedral or square-pyramidal interstitial sites. Proposals that metals could substitute for Fe or occupy interstitial sites in the mackinawite structure are based on X-ray Diffraction (XRD) and micro-hardness data (Clark, 1970, Vaughan, 1970) that provide a basis for theoretical analysis. The DFT modeling predicts structural change in FeS, such as expansion of lattice parameters and unit-cell volume, when a metal ion is substituted for Fe or intercalated into the FeS interlayer, and therefore serves as a point of comparison to experimental data which are currently sparse in the Ni-Fe-S system, with the exception of the study by Morse and Arakaki (1993). The objective of this study is to develop a better understanding of nickel retention by mackinawite using batch experimental techniques and characterization studies using XRD, Raman spectroscopy, scanning electron microscopy, and X-ray absorption spectroscopy.

2. Materials and methods

2.1. Batch studies

Batch experiments were conducted in an anaerobic chamber (Coy Laboratory Products) with an atmospheric composition of ~ 3% hydrogen in nitrogen; Pt catalyst plates were used to remove oxygen to below 1 ppm. All solutions were prepared from deionized water (Millipore Synergy UV) purged with ultra-high-purity nitrogen for > 30 min before use. Mackinawite was synthesized by mixing equivalent volumes of equimolar ferrous solution, from $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (Sigma-Aldrich, Reagent ACS), with sulfide solution from $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (Fisher, Certified ACS). Experiments were conducted in 43 mL amber glass vials fitted with gas-tight septa and screw top caps. After the precipitates settled (24 h), the supernatant was removed and replaced with fresh deoxygenated water; this process was repeated to remove excess sulfide and/or iron and to decrease concentrations of ammonia, sodium, and sulfate to < 0.01 M. Freeze-drying was avoided to keep the solids hydrated, dispersed, and free from potential oxidation. During the final addition of deionized water, aliquots of O_2 -free Ni solutions (from $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$; J.T. Baker, Reagent) were added to the vials. Solid/solution ratios ranged from 0.55 to 2.2 g FeS/L and Ni additions ranged from 0.5 to 45 mg. The molar ratio of Ni(II) to FeS in the batch experiments was 0.008 to 0.83. The Ni plus mackinawite suspensions were allowed to age for 48 h at room temperature (22–24 °C) prior to sampling. About 70% of these batch experiments were run in duplicate to verify trends and control experiments were set up to evaluate the potential for Ni sorption on the container walls and FeS behavior in Ni-free systems.

Three other types of aging experiments were conducted to test time-related behavior and the impact of potential geochemical perturbations and mineral transformation processes on Ni attenuation. Kinetic experiments were set up by fixing: the solid/solution ratio at 1.1 g/L, the initial Ni loading at 0.19 or 0.52 mol Ni per mol FeS, and tracking solution composition over about 55 h. In addition, mineral transformation experiments were setup by oxidizing Ni-loaded FeS in air-saturated solutions over a period of 28 d and by aging Ni-loaded FeS in the presence of polysulfides (Na_2S_4 , technical grade, Alfa Aesar) to evaluate Ni behavior during the pyritization process (Luther, 1991).

2.2. Solution analyses

At the end of the nickel uptake experiments, the supernatant was syringe-filtered using 33-mm 0.2 μm nylon filters. Filtered solutions were acidified with nitric acid (Optima) to pH < 2. Concentrations of dissolved Ni and Fe in the acid-preserved solutions were measured using inductively coupled plasma - optical emission spectrometry (ICP-OES, Perkin Elmer Optima 8300DV; analysis based on EPA Method 200.7). In cases where lower limits of detection were required for Ni (< 0.05 mg/L), magnetic sector mass spectrometry using medium resolution mode ($R = 4000$; HR-ICP-MS; Thermo Scientific Element XR; analysis based on EPA Method 200.8) was used for a quantitation level of 1 $\mu\text{g/L}$. Quality control samples for ICP-OES and HR-ICP-MS measurements included laboratory duplicates, laboratory blanks, matrix spikes, serial dilutions, interference check samples, calibration check standards, and second-source quality control samples. The final pH was measured on a portion of the unfiltered supernatant using an Orion semi-micro pH electrode calibrated

with NIST-traceable pH 4.01 and 7.00 buffer solutions. Dissolved sulfide concentrations in FeS suspensions prior to Ni addition were checked using the methylene blue colorimetric method on a Hach DR2700 spectrometer; concentrations were below the limit of quantification (< 0.01 mg S/L). Thus, even at the lowest levels of Ni-loading, initial molar $[\text{Ni(II)}]/[\text{S(-II)aq}]$ ratios were > 30 so reactions between Ni(II) and dissolved sulfide were negligible with respect to Ni removal.

The aqueous activities of Ni^{2+} and Fe^{2+} were calculated using the Geochemist's Workbench software package (v. 10, Aqueous Solutions LLC) and the thermo.com.V8.R6 +.dat database (Bethke, 1996). Ion activity products (IAPs) for Ni(OH)_2 and Fe(OH)_2 were calculated according to mass-action expressions. Activity coefficients were determined using the B-dot version of the Debye-Hückel equation. The aqueous species considered in the calculations included Ni^{2+} , NiOH^+ , Ni(OH)_2^0 , Ni(OH)_3^- , and NiSO_4^0 for the partitioning of dissolved Ni and Fe^{2+} , FeOH^+ , Fe(OH)_2^0 , Fe(OH)_3^- , and FeSO_4^0 for the partitioning of dissolved Fe. Ionic strengths of the modeled solutions ranged from 0.003 to 0.05.

2.3. Solid-phase analyses

Ni-bearing mackinawite samples for solid-phase characterization tests were prepared at a solid/solution ratio of 4 g/L, Ni additions of 1.7 to 48 mg, and by aging for 3 d prior to filtration. The solids were vacuum filtered (Nuclepore 47-mm polycarbonate, $1\ \mu\text{m}$), rinsed with methanol, dried, and ground to a fine powder in an anaerobic chamber. The solid powders were then poured into 1.8 mL cryogenic screw-top tubes (Nunc) for storage inside of an anaerobic glove box. Selected solids were characterized using XRD, scanning electron microscopy (SEM), Raman spectroscopy, and Ni and Fe *K*-edge X-ray absorption spectroscopy (EXAFS) typically within one week from the time of filtration.

XRD analyses were conducted using a Rigaku Miniflex II diffractometer housed inside of an anaerobic glovebox using Mn-filtered $\text{FeK}\alpha$ radiation ($\lambda = 0.1937$ nm). Diffraction data were collected from 5° to 90° 2θ with 0.01° 2θ step increments at a scan rate of 6 s per step. Each sample was scanned 3 times and the patterns were summed. NIST 640b standard reference material (silicon powder) was periodically scanned as a quality control check of d -spacing accuracy and the full-width at half-maximum of the Si(111) peak was used to evaluate the instrumental broadening effect for crystallite size determinations. Data collected from the XRD scans were imported into the Jade (Materials Data, Inc.) software package for analysis and matched to the Powder Diffraction File Data Base (PDF, International Centre for Diffraction Data).

Micro-Raman spectroscopy was carried out using a Bruker Senterra Raman spectrometer equipped with an Olympus microscope and a Peltier-cooled charge coupled detector. Raman spectra were excited by using a 532 nm He-Ne laser at a nominal resolution of $< 2\ \text{cm}^{-1}$. Sample powders were pressed onto aluminum stubs. The microscope was used to focus onto the sample with a $50\times$ MPlan objective lens ($\text{NA} = 0.75$). The instrument was operated with 5 s detector exposure time and up to 100 spectra accumulations in the range between 200 and $4000\ \text{cm}^{-1}$; incident laser energy was set at 10 mW. The instrument calibration was checked using a silicon wafer at a Raman shift of $520.5\ \text{cm}^{-1}$. Samples were inspected after

analysis using reflected-light microscopy and no visible sample damage from laser exposure was detected.

Particle morphology and composition was studied using SEM (JEOL JSM 6360 microscope) coupled with energy dispersive X-ray spectroscopy (EDX, Oxford Instruments INCA Xact spectrometer). An accelerating voltage of 20 keV was used and images were obtained with secondary and backscattered electron detectors. Samples analyzed by SEM were vortexed in methanol, dropped onto clean carbon planchets (Ted Pella, Inc.), dried in a vacuum desiccator, and coated with gold; samples were in contact with air for < 1–2 min prior to being coated and placed inside the high-vacuum chamber of the instrument. The X-ray spectrometer calibration was checked using a polished cobalt metal standard (Co $K\alpha$, 6.925 keV) prior to obtaining energy dispersive spectra.

2.4. Extended X-ray absorption fine structure (EXAFS) data collection

Solid phase Ni and Fe K -edge EXAFS measurements were made on the bending magnet located at MR-CAT Sector 10 (beamline 10-BM; Kropf et al., 2010) at the Advanced Photon Source (Argonne National Laboratory). At this beamline, a Si(111) double-crystal monochromator and a 50-mm-long second crystal provide a working energy range of 4.0 to 32 keV. The harmonic content of the incident X-ray beam was removed using the second crystal which has Bragg parallel and normal motions allowing for 50% detuning. The incident X-ray intensity was monitored through use of a nitrogen-helium gas-filled ionization chamber (20 cm path length), which resulted in 10% absorption of the X-rays (Ni-edge: $N_2 = 67\%$, He = 33%; Fe-edge: $N_2 = 44\%$, He = 56%). The fluorescent X-ray signal was monitored using a 4-element Vortex energy dispersive detector. The transmission signal was monitored through use of a nitrogen-argon gas-filled ionization chamber (20 cm path length), which resulted in 70% absorption of transmitted X-rays (Ni-edge: $N_2 = 70\%$, Ar = 30%; Fe-edge: $N_2 = 83\%$, Ar = 17%). The size of the X-ray beam at the sample was approximately 300 μm vertical by 630 μm horizontal. Energy resolution at the Ni K -edge (8333 eV) and Fe K -edge (7112 eV) was about 0.4 eV. Sample pellets were pressed between layers of Kapton tape within an anaerobic glovebox and transported to the beamline in N_2 -gas filled bags.

2.5. EXAFS data analysis

Multiple scans (2 to 11) of five experimental samples were collected and each scan was energy-corrected using appropriate metal reference foils. The raw data were background corrected, summed, and step-height normalized using the Athena software package (Ravel and Newville, 2005). EXAFS spectra were imported into Artemis (Ravel and Newville, 2005) and fitted to theoretical models constructed using Atoms (Ravel, 2001), FEFF6 (Rehr et al., 1991), and reference Ni₂S structures for α -NiS (Trahan et al., 1970), millerite (Rajamani and Prewitt, 1974), and polydymite (Lundqvist, 1947). The Fourier transform range was 3–9 Å and the fitting range was 1–3 Å (R -space). The EXAFS data were modeled with one sulfur shell. EXAFS fitting models were parameterized by coordination number (CN), a change in the Ni₂S distance (ΔR), a σ^2 value (Debye-Waller factor) for the Ni₂S signal, an amplitude reduction term (S_0^2), and one energy shift value (E_0). Experimental EXAFS data were modeled with fixed E_0 (2.760 eV), S_0^2 (1) and σ^2 (0.006 Å²) values

obtained for a co-refinement of model NiS compounds using the reference structures. The values of CN and R were allowed to vary during the fitting. All fits used a chi(k) weighting factor of 2. The goodness-of-fit between experimental data and model fits was assessed using the R Factor as follows:

$$R\text{ Factor} = \frac{\sum (k^2 \chi_{\text{exp}}(k) - k^2 \chi_{\text{calc}}(k))^2}{\sum (k^2 \chi_{\text{exp}}(k))^2} \quad (1)$$

which is automatically provided for each fit by the Artemis software.

3. Results

3.1. X-ray diffraction and Raman spectroscopy

Solids showed XRD patterns characteristic of nanocrystalline mackinawite after reaction with Ni^{2+} ions (Fig. 1). The diffraction patterns indicated no evidence of nickel monosulfide ($\alpha\text{-NiS}$ or millerite), polydymite (Ni_3S_4), or godlevskite [$(\text{Ni},\text{Fe})_9\text{S}_8$] formation, regardless of the amount of Ni loading. Also, diffraction data showed that mackinawite did not transform to greigite or pyrite, evidence the systems remained anaerobic during the Ni uptake experiments. At the highest Ni level in mackinawite (Fig. 1), the final precipitate also contained minor amounts of hydrous iron oxide (PDF 013-0092), which formed after concentrations of iron entered solution at neutral pH via displacement by Ni in the solid phase. The XRD data indicate that poorly crystalline mackinawite was the dominant product of short term aging in the Ni-FeS system.

Unit cell parameters were calculated from the diffraction data and are summarized in Table 1 along with literature data for synthetic mackinawite (Lennie et al., 1995, Wolthers et al., 2003, Jeong et al., 2008). Mackinawite prepared in this study showed constant unit cell dimensions along the *a*-axis, with $a = 3.67 \pm 0.01 \text{ \AA}$ (Table 1). This value is comparable in well-crystallized mackinawite (Lennie et al., 1995) and synthetic mackinawite aged for 3 days (Jeong et al., 2008). Expansion of the *c*-axis correlated with increasing Ni content in synthetic mackinawite, from $c = 5.07 \pm 0.01 \text{ \AA}$ at $X_{\text{Ni}} = 0.02$ ($\sim 1 \text{ wt\% Ni}$) to $c = 5.10 \pm 0.01 \text{ \AA}$ at $X_{\text{Ni}} = 0.38$ ($\sim 25 \text{ wt\% Ni}$; Table 1). Expansion along the *c*-axis implies larger distances between tetrahedral sheets and could be the result of Ni uptake between S₂S₂ layers in the mackinawite structure or lattice expansion from Fe replacement by Ni (see Kwon et al., 2015). Vaughan (1970) originally proposed that the mackinawite structure accommodates metals in tetrahedral coordination with sulfur between the S₂S₂ sheets parallel to (001). Synthetic mackinawite typically shows elongated lattice spacing compared to well-crystallized mackinawite (e.g., Wolthers et al., 2003, Ohfuji and Rickard, 2006, Jeong et al., 2008, Csákberényi-Malasics et al., 2012), possibly related to aging time, water uptake, and/or general conditions of crystallization. Thus, other factors could control the apparent *c*-axis expansion observed in this study; however, the Ni-containing samples shown in Table 1 were similarly precipitated, aged, and processed with the exception of the amount of Ni added.

The mean crystallite size was estimated using the Scherrer equation (Cullity, 1978):

$$L = K \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

where L is the mean crystallite diameter, λ is the X-ray wavelength in nanometers, β is the peak width of the diffraction peak at half maximum height in radians (corrected for instrumental broadening), K is a shape-related constant, normally taken as 0.9, and θ is the angular position of the diffraction peak. The Scherrer equation was applied to the (001), (101), and (111) peaks. The mean crystallite diameter determined was 4.3 ± 0.4 nm with no apparent correlation with Ni content, except at the highest Ni content where peak broadening indicated a smaller average particle size (3.4 ± 0.4 nm). This size range of primary crystallites in synthetic mackinawite is consistent with the findings of Wolthers et al. (2003), Ohfuji and Rickard (2006), and Jeong et al. (2008).

Micro-Raman spectra for nickelian mackinawite prepared in this study showed peaks at 212 cm^{-1} and 273 cm^{-1} (bandwidths of 20 and 28 cm^{-1} , respectively); the spectra show no apparent changes with increasing Ni content, in agreement with XRD analysis (Fig. 2). A broader, less intense peak was also indicated at 385 cm^{-1} (Fig. 2). These spectral features are characteristic of mackinawite prepared by mixing solutions of ferrous and sulfide salts and from the corrosion of steel coupons by sulfide ions (Bourdoiseau et al., 2008, El Mendili et al., 2014). For example, Bourdoiseau et al. (2008) reported two peaks for nanocrystalline mackinawite at 208 ± 1 and 282 ± 1 cm^{-1} . El Mendili et al. (2014) showed peaks at 210 cm^{-1} and 285 cm^{-1} ; 1 month of aging also resulted in low-intensity peaks at 376 cm^{-1} and 395 cm^{-1} . The Raman bands are attributed to the symmetric stretching mode of mackinawite and to a lattice mode (El Mendili et al., 2014). We observed no features in the Raman spectral data indicating the presence of other Ni sulfides (Bishop et al., 1998) or oxidative transformation of mackinawite to greigite and/or pyrite; these mineral transformations result in more complex Raman spectra (e.g., Bourdoiseau et al., 2011).

3.2. Electron microscopy and energy dispersive X-ray spectroscopy

Anaerobically dried particles of nickelian mackinawite were imaged using SEM (Fig. 3). Particle shapes and sizes are typical for synthetic mackinawite reported in previous studies (e.g., Coles et al., 2000, Liu et al., 2008, Csákberényi-Malasics et al., 2012). The micrographs show largely featureless, highly aggregated clumps of very fine-grained particles; the aggregated nature and shapes of the particles are likely a consequence of particle drying and sample processing (Arakaki and Morse, 1993, Jeong et al., 2008). Micro-scale X-ray emission data showed evenly distributed Ni concentrations near the mackinawite surfaces (Fig. 3), evidence that Ni uptake was not caused by precipitation of a separate Ni phase, consistent with the XRD and Raman analysis. In addition to S, Fe, and Ni, X-ray analysis showed minor amounts of Na and O, which were possibly from sorbed or entrapped Na^+ and SO_4^{2-} originally present in the experimental solutions.

3.3. Batch studies

3.3.1. Surface sorption—Previous experimental studies used periods of 24–48 h for evaluating metal retention by mackinawite (Parkmann et al., 1999, Coles et al., 2000, Jeong

et al., 2007, Liu et al., 2008, Dulnee and Scheinost, 2015); a 24 h reaction time appears to be more prevalently adopted in these studies. Time trends of Ni concentration in solution for systems with 1.1 g FeS/L and molar ratios of $[\text{Ni(II)}]/[\text{FeS}]$ equal to 0.19 and 0.52 showed an initial period (< 1 h) of rapid Ni removal from solution followed by a period from about 1 to 55 h with slower Ni uptake (Fig. 4). At the lower Ni loading, 48 h appears to be sufficient to achieve steady-state conditions, although Ni uptake by mackinawite is predicted to occur past 48 h at the higher level of Ni loading.

At the initial molar $[\text{Ni(II)}]/[\text{FeS}]$ ratio of 0.19, 70% of the Ni spike was removed during the first period of uptake (Fig. 4). At the higher loading level, 32% of the Ni was removed within the first hour of reaction. In both experiments, the first Ni uptake stage removed approximately 0.1 mmol of Ni from solution, or 1.5 to 1.8 mmol Ni/g FeS. This solid-phase concentration corresponds to the estimated density of sulfhydryl functional sites on the FeS surface ($[\equiv \text{SH}]_T = 1.45$ mmol/g, Jeong et al., 2008; $[\equiv \text{SH}]_T = 1.2$ mmol/g, Wolthers et al., 2005), suggesting that Ni(II) sorption at the FeS surface accounts for the initial rapid removal of Ni from solution. Coles et al. (2000) estimated that the amount of adsorbed Pb and Cd at the mackinawite surface was 0.91 and 2.03 mmol/g, respectively, also in general agreement with the expected concentration of sulfhydryl functional sites. From linear regression analysis, the rate of Ni uptake during the second, slower period of Ni removal was 0.005 mmol Ni/L·h ($R^2 = 0.93$) and 0.030 mmol Ni/L·h ($R^2 = 0.98$) at the low and high Ni loading condition, respectively. Thus, the rate of the slower removal process is dependent on Ni concentration in solution. The estimated rate of the initial rapid sorption process was 2.6 ± 0.3 mmol Ni/L·h; the resolution of data points is inadequate to determine if there is a rate-dependence on Ni concentration during this step. The second, slower process of Ni uptake indicated on Fig. 4 is inferred to represent a combination of Ni uptake between S₂S layers of the mackinawite structure and diffusion-controlled lattice penetration and structural substitution.

The uptake of Ni by mackinawite is plotted on Fig. 5A against the amount of Ni added for systems in which the density of FeS was 0.55, 1.02, and 2.25 g/L (Table A.1, Table A.2, Table A.3). The batch experimental conditions in Fig. 5A represent initial molar $[\text{Ni(II)}]/[\text{FeS}]$ values from 0.008 to 0.83 (Table 2). Greater than 99% Ni removal was achieved when Ni loading remained at levels < 1.4 mmol/g, corresponding to sorption of Ni at the mackinawite surface. The amount of Ni sorption was estimated to range from 1.0 to 1.6 mmol/g in this series of batch experiments (Table 2) in good agreement with time-resolved assessment shown in Fig. 4. At conditions where sorption was the dominant inferred Ni removal mechanism, solution concentrations of Ni were between 5 and 20 $\mu\text{mol/L}$. With increasing loading, Ni removal became less efficient. Removal trends deviated from the 1:1 Ni addition versus Ni removal line (Fig. 5A) and Ni concentrations reached levels as high as ~ 3.6 mmol/L. Maximum Ni concentrations in mackinawite ranged between $X_{\text{Ni}} = 0.30$ and $X_{\text{Ni}} = 0.56$ and showed an apparent increase with the solution density of FeS (Table 2). Removal efficiency at the highest Ni loadings ranged from 37 to 81%.

The pH measured at the conclusion of the batch experiments ranged from 8.4 to 5.2; in all cases the pH decreased with increasing initial $[\text{Ni(II)}]/[\text{FeS}]$ due to addition of slightly acidic Ni-SO₄ solutions (Table A.1, Table A.2, Table A.3). Within any series at constant

mackinawite solution density, the pH shift was typically < 1.5 pH units. The rate of mackinawite dissolution over this near-neutral pH range is expected to be slow relative to the observed rates of Ni removal (Pankow and Morgan, 1979) so the processes governing Ni removal are unlikely related to mineral dissolution. Solution pH controls the modeled aqueous speciation of Ni and Fe and is important in directing possible secondary precipitation and sorption processes. Across all of the batch tests, the saturation index of $\text{Ni}(\text{OH})_2$ ranged from -1.4 to -8.7 , typically with the most negative values in any series at the low pH/high Ni loading condition. These saturation indices indicate that nickel hydroxide was moderately to highly under-saturated and Ni removal via precipitation of $\text{Ni}(\text{OH})_2$ was not predicted in the batch experiments (Table 2).

3.3.2. Fe release—Once sorption sites at the mackinawite surface were filled, continued Ni uptake was accompanied by the equimolar release of Fe to solution (Fig. 5B). The inset of Fig. 5b shows paired Fe and Ni solution concentration data for the high density batch experiment (2.25 g/L; Table A.1). In this experiment, dissolved iron remained below the level of detection at Ni loading values below about 0.1 mmol. At higher levels of Ni loading, the concentration of Fe in solution correlated with the amount of Ni removed ($R^2 = 0.98$) and no secondary Fe precipitation was indicated. Solution concentrations of Fe versus Ni removed by the solid phase, for all of the batch tests, are combined on Fig. 5B. Concentration data were filtered as follows: i) Ni and Fe trends at and below the level of adsorption (1.4 mmol/g) were removed; ii) the level of Ni removal was corrected by subtracting the estimated amount of Ni sorption; and, iii) experimental pH values encompass the range between 5.2 and 7.0 where dissolution of mackinawite and sorption of $\text{Fe}(\text{II})$ onto the mackinawite surface are minimal (e.g., Jeong et al., 2007). Container blank tests and blank test results with FeS and no Ni added showed Fe concentrations below 20 $\mu\text{mol/L}$, which are negligible compared to the Fe concentration range shown on Fig. 5B (580 to 12,800 $\mu\text{mol/L}$). The trend shown on Fig. 5B indicates that non-sorption related Ni removal by mackinawite is associated with structural release of Fe. Previous studies have shown that Pb, Cd, and Hg removal by mackinawite is also associated with the release of structural Fe into solution (Coles et al., 2000, Jeong et al., 2007, Liu et al., 2008). The saturation index of $\text{Fe}(\text{OH})_2$ ranged from -0.84 to -4.9 , with the saturation index increasing with increasing Fe release, indicating that Fe removal via the precipitation $\text{Fe}(\text{OH})_2$ was not occurring in the batch experiments (Table 2). However, a batch test conducted at high Ni loading for XRD analysis, in one case, showed the presence of hydrous iron hydroxide at neutral pH after 3 d of aging (Fig. 1); thus, closed-system experiments that allow the concentration of displaced Fe to build up to high levels have potential to precipitate Fe.

3.4. EXAFS analysis

Ni K-edge EXAFS spectra of synthetic Ni-bearing mackinawite are similar in phase and amplitude to the Fe K-edge EXAFS spectrum of Ni-free mackinawite (Fig. 6A). The similarity in the K-edge EXAFS features indicate that the molecular environment of Ni^{2+} in Ni-bearing mackinawite is similar to that of Fe^{2+} in Ni-free mackinawite. Also, the extended X-ray absorption near edge (XANES) spectral regions for Fe and Ni in mackinawite are virtually identical (Fig. 6A). Ni K-edge EXAFS spectra of Ni-bearing mackinawite are distinct from the spectra of model Ni sulfides, millerite and $\alpha\text{-NiS}$ (Fig. A.

1), and attempts at EXAFS data fitting using NiS paths derived from these minerals yielded poor results. Improved theoretical phase-shift and amplitude functions were obtained using the crystal structure of the thiospinel polydymite (Lundqvist, 1947).

Results of EXAFS data fitting for synthetic Ni-bearing mackinawite are provided in Table 3 and the experimental k^2 -weighted EXAFS spectra (uncorrected for phase shift) and their Fourier transforms are shown in Fig. 6B. First-shell theoretical fits derived from crystal structure data are plotted with the experimental data. Fitting results for synthetic mackinawite with composition $\text{Fe}_{0.58}\text{Ni}_{0.42}\text{S}$ indicate a coordination number of 4.04 ± 0.30 and a Ni_S bond distance of 2.28 ± 0.01 Å, in close agreement with the 4-fold Fe coordination and Fe_S bond distance of 2.26 Å in Ni-free mackinawite (Lennie et al., 1995). No evidence is present indicating Ni_O bonding in the first shell. Our analysis of Ni in mackinawite is similar to the Ni_S shell in polydymite (Ni_3S_4), which exhibits tetrahedral coordination, but with a slightly shorter average bond distance of 2.23 Å. At lower Ni loadings, EXAFS analysis showed an overall decrease in the Ni_S coordination environment, towards CN = 3, which is considered to reflect the influence of sorbed Ni with a consistent Ni_S bond distance of 2.27 to 2.29 Å (Table 3). The CN is lower than 4 expected when Ni substitutes for Fe in the mackinawite structure or when Ni is present in an interstitial tetrahedral site. Based on fits of the EXAFS spectra, the Ni_S (first neighbor) distance (~ 2.28 Å) for synthetic Ni-bearing mackinawite is slightly longer than the expected Fe_S bond distance (2.26 Å). The result is close to the resolution of the technique but there is a suggestion of local expansion of the first coordination sphere around the substituting Ni^{2+} ion, consistent with the measured expansion along the c -axis with increasing Ni content in mackinawite (Table 1).

The amplitude reduction term (S_0^2) was set to 1. The Debye-Waller term (σ^2) and energy offset (E^0) parameters were fixed based on co-refinement of known Ni sulfide crystallographic models.

3.5. Transformation of Ni-bearing mackinawite

Potential mineral transformation processes were evaluated by aging Ni-mackinawite with polysulfides and dissolved oxygen. Reaction of Ni-mackinawite with polysulfides at pH = 6 led to the formation of pyrite and Ni retention in the solid phase (Fig. A.2). Although Ni incorporation into pyrite has not been previously evaluated in experimental studies, Ni is a common trace metal found contained within pyrite at levels up to about 0.6 wt% (e.g., Abraitis et al., 2004, Diehl et al., 2012, Houben et al., 2017). When Ni-mackinawite was aged for 28 d in the presence of dissolved oxygen, transformation to goethite (FeOOH) and violarite (FeNi_2S_4) occurred (Fig. A.2). Violarite has been found associated with weathering and oxidation of primary nickel sulfide ore minerals [pentlandite, $(\text{Fe},\text{Ni})_9\text{S}_8$] in supergene enrichment zones (Watmuff, 1974, Thornber, 1975). The violarite formation process involves oxidation of Ni(II) and Fe(II). Tenailleau et al. (2006) showed that the transformation of pentlandite to violarite was complete after 3 d at 120 °C and partial transformation was observed after 33 d at 80 °C. In this study, no FeS was observed in the X-ray diffraction data after 28 d (Fig. A.2). Ni was retained in the solid phase after the transformation studies.

4. Discussion

4.1. Mechanisms of Ni uptake by mackinawite

Several important points of comparison can be made between the experimental observations of this study and previous studies of Hg, Pb, and Cd uptake by mackinawite. Following the surface speciation model for mackinawite proposed by Wolthers et al. (2005), non-competitive Ni sorption reactions can be described by:

and

Proton release indicated in Eq. (4) is consistent with the overall decrease in pH that was observed with increased Ni loading in the batch experiments (Table A.1, Table A.2, Table A.3). The estimated capacity for surface adsorption of Ni by mackinawite from our batch studies was 1.4 ± 0.3 mmol/g ($n = 5$); thus, sorption is expected to be the dominant Ni uptake mechanism at molar $[\text{Ni(II)}]/[\text{FeS}]$ ratios below 0.13 ± 0.03 . This value was determined from the break in slope on time trends of Ni uptake (Fig. 4) and by evaluating the point where Fe appears in solution and Ni for Fe exchange begins (Fig. 5B). Rapid and efficient metal uptake at low loading levels are consistent features in previous studies of Hg, Pb, and Cd removal by mackinawite (Jeong et al., 2007, Coles et al., 2000). It is noted that uncertainty remains about the point of zero charge (PZC) and pH-dependent surface properties of mackinawite and other iron sulfides. Acid-base titrations have revealed a PZC at about pH 3 (e.g., Widler and Seward, 2002, Dekkers and Schoonen, 1994) and pH ~ 7.5 (Wolthers et al., 2005). These differences in the PZC may reflect contrasting mineral synthesis procedures (e.g., freeze drying vs. non-freeze drying), acid-base measurement conditions, and/or redox control during titration. Additional work is needed to examine whether Ni sorbed at the mackinawite surface can be released via surface competition reactions or by Ni(II)-complexing ligands.

Jeong et al. (2007) convincingly showed that at $[\text{Hg(II)}]/[\text{FeS}] > 0.05$, sorption sites at the mackinawite surface become saturated with Hg and the dominant Hg removal mechanism transitions to metacinnabar (β -HgS) precipitation. The large difference in solubility between β -HgS and FeS ($-\log K_{\text{sp}} = 35.1$) and the significant contrast in Hg-S and Fe-S bond distances ($2.53 \text{ \AA}$ vs. $2.26 \text{ \AA}$) would appear to be critical factors controlling the fate of Hg (Table 4). Coles et al. (2000) did not provide X-ray diffraction data for mackinawite after reaction with Pb and Cd; however, large differences in the solubilities of PbS, CdS, and FeS and differing Me-S bond distances suggest that replacement of FeS by PbS and CdS may have occurred (Table 4). Indeed, experimental and theoretical work in Framson and Leckie (1978) suggest that Cd adsorption and greenockite (CdS) precipitation result from reaction between Cd^{2+} ions and FeS. In this study, a separate Ni-S or Ni-Fe-S phase was not

identified at Ni loadings past the point of saturation on the mackinawite surface. As noted previously, the smaller $\log K_{sp}$ between FeS and either α -NiS or β -NiS (6.2 vs. 6.7; Table 4) and a more accommodating Ni-S bond distance and coordination environment help to explain this observation.

Quantum mechanical calculations conducted by Kwon et al. (2015) predict nearly constant a and b lattice parameters with progressive Ni substitution for Fe in mackinawite; the c parameter shows an initial increase to a composition of about $\text{Fe}_{0.94}\text{Ni}_{0.06}\text{S}$ and then a gradual decrease with increasing Ni substitution to $\text{Fe}_{0.75}\text{Ni}_{0.25}\text{S}$. In general, the unit cell is largely constant as Ni substitutes for Fe in mackinawite (Kwon et al., 2015). In contrast, significant expansion of the c parameter is predicted for intercalation, with modest increases in the c parameter with increasing Ni in the tetrahedral interstitial site (I-td) and larger increases with Ni occupying the square-pyramidal site (I-sp). For the composition: $\text{Fe}_{0.75}\text{Ni}_{0.25}\text{S}$, Kwon et al. (2015) predict c/a values of 1.32, 1.39, and 1.46 for substitution and Ni occupancy in the I-td and I-sp sites, respectively. Comparison of these theoretical predictions with experimental data in Table 1 shows reasonable correlation with Ni uptake in I-td; slight expansion of the c lattice parameter and increases in c/a correspond to increases in the Ni content of synthetic mackinawite. In addition, Ni K -edge EXAFS results showed Ni in 4-fold coordination, in agreement with the I-td site but not the 5-fold I-sp. site. However, Ni uptake in the interstitial layer does not explain the equimolar release of structural Fe that coincides with Ni incorporation into mackinawite; this experimental observation points to structural substitution following the exchange reaction:

It is proposed that uptake of Ni into mackinawite involves the I-td site, structural incorporation, and Fe release. Ni enters the mackinawite structure via interstitial spaces between FeS_4 tetrahedral sheets and subsequently invades the mackinawite structure and readily displaces Fe which is released into solution. In this proposed mechanism, interstitial occupancy of Ni may be a transition state that precedes structural substitution of Fe. Kwon et al. (2015) predict that structural substitution is favored over I-td for Ni, Co, and Cu. Furthermore, as metal loading increases, the stability of substituted metal is enhanced while the stability of I-td diminishes; thus, thermodynamic favorability of Ni-S over Fe-S bonding forces rapid accumulation of Ni within mackinawite and displacement of structural Fe. Our experimental data suggest that FeS structures involving Ni substitution and intercalation both play a role in the overall mechanism of Ni uptake by mackinawite.

4.2. Solid solution model

There is no evidence that FeS and α -NiS (or millerite) are miscible at room temperature; differences in crystal structures, bond distances, and solubility products suggest that a solid solution between these end members does not exist (Table 4). However, a distorted Ni-replaced mackinawite phase is theoretically possible. In this study, X_{Ni} values in mackinawite as high as 0.56 were produced. Furthermore, the solubility contrast between mackinawite and a hypothetical Ni-mackinawite may be $< 10^{6.2}$, i.e., the ratio of the

mackinawite and α -NiS solubility products, and the similar ionic radii of Fe^{2+} and Ni^{2+} may support solid-phase mixing (Table 4).

An overall equilibrium reaction describing the formation of a solid solution composed of mackinawite and Ni-mackinawite end members can be represented in the traditional way:

The equilibrium constant, K_e , for the metal exchange reaction (Eq. (6)) may be expressed as:

$$K_e = \frac{[\text{Fe}^{2+}]}{[\text{Ni}^{2+}]} \frac{\gamma_{\text{Fe}^{2+}}}{\gamma_{\text{Ni}^{2+}}} \frac{X_{\text{Ni}}}{1 - X_{\text{Ni}}} \cdot \frac{\lambda_{\text{Ni}}}{\lambda_{1 - \text{Ni}}} = K_d \cdot K_\lambda \quad (7)$$

where $[\text{Fe}^{2+}]$ and $[\text{Ni}^{2+}]$ are the molalities of Fe and Ni ions in aqueous solution, $\gamma_{\text{Fe}^{2+}}$ and $\gamma_{\text{Ni}^{2+}}$ are the aqueous activity coefficients of Fe^{2+} and Ni^{2+} , X_{Ni} and $1 - X_{\text{Ni}}$ are the solid phase mole fractions of Ni and Fe, and the λ terms are rational activity coefficients of NiS and FeS components in the solid phase. The equilibrium expression Eq. (7) is separated into an experimentally accessible quantity, K_d , and a term that requires an empirical activity model (K_λ). The activity coefficients of components in a symmetric regular solution are given by (Anderson and Crerar, 1993):

$$\ln_{\lambda\text{Ni}} \frac{(1 - X_{\text{Ni}})^2 W}{RT} \quad (8)$$

and

$$\ln_{\lambda 1 - \text{Ni}} \frac{(X_{\text{Ni}})^2 W}{RT} \quad (9)$$

where W is an ion interaction parameter. Combining terms and rearranging Eq. (7) leads to:

$$\ln K_d = \ln K_e - \ln K_\lambda = \ln K_e - \frac{WR}{T} (1 - 2X_{\text{Ni}}) \quad (10)$$

Values of K_d were calculated after correcting for sorption, i.e., removing the amount of sorbed Ni from the solid-phase concentration, so that only structurally incorporated Ni was factored into the calculation of K_d . Values ranged from about 0.02 to 4.82 and showed dependence on Ni concentration in the solid phase (Table A.4). Data from batch experiments dominated by structural substitution are shown in Fig. 5A within the shaded ovals. Linear regression analysis of these data following Eq. (10) gave $K_e = 14.4 \pm 1.3$ and $W = 17.74$

± 1.15 kJ/mol ($R^2 = 0.95$; Fig. 7). K_e represents the solubility ratio of end-member components of the solid solution ($\log K_{sp} = 1.16$):

$$K_e = \frac{K_{mackinawite}}{K_{Ni-mackinawite}} = \frac{10^{3.50}}{10^{2.34}} = 10^{1.16} \quad (11)$$

Lower solubility of the NiS component ($\log K_{sp} = 2.34$) provides the thermodynamic control of Ni for Fe substitution in mackinawite. The experimentally determined value of W is large and positive indicating significant non-ideality of the solid solution which is expected based on the size mismatch of the Ni^{2+} and Fe^{2+} ions. The positive sign of W means that the solution is less stable compared to a hypothetical ideal solution.

The batch experiments used to extract the thermodynamic data were based on 48 h reaction times. Results shown in Fig. 4 indicate that steady state conditions were likely achieved after 48 h at low Ni loadings, but possibly not at higher loadings. Also, data points on Fig. 5A that represent the transition between surface sorption and structural substitution do not fall along the linear trend shown in Fig. 7. This region could be controlled by intercalation of Ni and not structural substitution as described by Eq. (10). The solid-solution model was derived from compositions ranging from 3 to 43 mol% Ni (corrected for sorption) which is appropriate for practical applications; however, additional data collection at higher solid-phase concentrations, although challenging, would help determine whether a more complex asymmetrical solid-solution model is required. Finally, the average value of K_d from our experiments approached 1 and may be related to rates of reaction. As reaction rates increase, experimental observations in carbonate systems, for example, suggest that distribution coefficients decrease towards unity (e.g., Lorens, 1981, Morse and Bender, 1990, Arakaki and Morse, 1993). This finding applies to heterogeneous systems in which crystal growth plays a role in controlling aqueous and solid-phase concentrations of metals. In the systems studied here, the solid-phase sulfide concentration was fixed and precluded new crystal growth and potential growth-related controls on K_d .

4.3. Sorption model

Morse and Arakaki (1993) estimated the partition coefficient for Ni uptake by mackinawite to be 280 ± 181 at 25 °C. These previous experiments were conducted at low overall Ni loading (< 0.5 mmol/g; $X_{Ni} < 0.05$) and were likely influenced mainly by sorption and not metal exchange behavior. The batch sorption data from experimental conditions, where Ni sorption was dominant ($X_{Ni} < 0.13$), were fit to a Langmuir adsorption isotherm:

$$X_{ni} = \frac{q_m \cdot b \cdot C_{Ni}}{(1 + b \cdot C_{Ni})} \quad (12)$$

where q_m is the maximum Ni removed by sorption (0.13 mol/mol), b is a Langmuir fitting term, and C_{Ni} is the concentration of Ni in solution (mmol/L). This equation is plotted in Fig. A.3 and provides an empirical fit of the Ni uptake data at low to saturated surface

loadings. The amount of sorbed Ni at the mackinawite surface determined in this study is comparable to the experimental fit from Morse and Arakaki (1993) that was derived from experiments conducted at low Ni concentrations in solution (< 0.05 mmol/L) and low surface loadings.

5. Conclusions

The results demonstrate that nanocrystalline FeS has high capacity to remove Ni^{2+} ions from solution. In some cases, Ni content of experimental products exceeded the maximum levels (~ 20 wt%) measured in nickeliferous mackinawite from natural deposits (Vaughan, 1969, Clark, 1970, Sarkar, 1971, Blain, 1978). The uptake of Ni by mackinawite was characterized by multiple processes which proceeded towards equilibrium on different time scales. These findings are consistent with previous studies of bivalent metal uptake by mackinawite (Framson and Leckie, 1978, Morse and Arakaki, 1993, Arakaki and Morse, 1993, Parkmann et al., 1999, Coles et al., 2000, Jeong et al., 2007, Liu et al., 2008, Zavašnik et al., 2014, Dulnee and Scheinost, 2015) and reinforce the significant interest FeS has received in environmental studies.

The solid-solution model provides a quantitative framework for predicting Ni concentrations in equilibrium with mackinawite based upon the solution $a_{\text{Fe}^{2+}}/a_{\text{Ni}^{2+}}$ and solid-phase concentration of Ni. An interesting implication of the model is that Ni^{2+} concentrations are expected to decrease at constant Fe^{2+} as solid-phase Ni partitioning increases. This outcome stems from the positive sign of the ion interaction parameter. The opposite would be true if the solid solution exhibited a negative molar enthalpy upon mixing. Based on crystal chemistry data we speculate that related solid-solution models could be developed for mackinawite and Co(II), Zn(II), and possibly Cu(II).

The formation of mackinawite as an authigenic precipitate in subsurface installations of granular iron and/or organic carbon (permeable reactive barriers) for treating contaminated groundwater is well documented (e.g., Phillips et al., 2000, Furukawa et al., 2002, Beaulieu and Ramirez, 2013). Long-term studies have shown that sulfate reducing processes are sustainable in these remediation systems for decadal time scales (Wilkin et al., 2014) and accumulation of mackinawite within the reactive medium provides additional pathways for treatment of inorganic and organic contaminants via sorption, reduction, and/or degradation processes. Our results show that metal incorporation into the mackinawite lattice is also possible and serves as a competitive process to direct nickel sulfide formation in systems where FeS formation is dominant, either due to the presence of natural iron or to addition of reactive iron to the subsurface (Shen and Wilson, 2007). Related groundwater remediation technologies that manipulate redox conditions in the subsurface through injection of reactants such as soluble organic carbon (e.g., lactate, vegetable oil), sodium dithionate, and sodium sulfide are likely to produce secondary iron sulfides that are expected to play an important role in contaminant transformation and attenuation (He et al., 2015).

Applications of monitored natural attenuation (MNA) and engineered groundwater remedies, such as permeable reactive barriers, for inorganic contaminants include assessments of treatment capacity and potential contaminant re-mobilization. Following

geochemical manipulation of groundwater via reagent delivery, conditions are expected to change over time; thus, potential shifts in pH, redox, and concentrations of ligand-forming species are factored into evaluations of mineral transformation and secondary contaminant mobilization. Upward shift in the oxidation-reduction potential is especially concerning for in-situ reduction technologies. In this study, addition of zero-valent sulfur in the form of polysulfide resulted in the transformation of Ni-bearing FeS to Ni-bearing FeS₂. It is possible that stabilization of mackinawite by Ni incorporation (Kwon et al., 2015) affects the rate of pyrite formation. However, Ni incorporation into mackinawite and subsequent transformation to pyrite/marcasite is a possible mechanism to stabilize Ni in aquifer solids in systems where dissolved oxygen and nitrates remain low (Larsen and Postma, 1997, Houben et al., 2017), and this transformation process could be responsible for forming Ni-bearing pyrite (Morse and Luther, 1999, Abraitis et al., 2004). Concentric textural and compositional banding in bravoite [(Fe,Ni,Co)S₂; e.g., Ramdohr, 1980] suggests that Ni incorporation into pyrite, in some cases, may be related to growth from solution (Schoonen and Barnes, 1991b) rather than via the transformation of a FeS precursor. Growth-related Ni incorporation into pyrite may be more prevalent in hydrothermal systems (e.g., Lorand et al., 2015) or during secondary episodes of pyrite formation in sediments (Diehl et al., 2012). Aging Ni-bearing mackinawite in air-saturated water resulted in transformation to goethite and violarite with Ni maintained in the solid phase. Oxidation of sulfides is typically considered to be a source of metals to aquatic systems. Results presented here indicate that where reactive iron is available, Ni concentrations may be controlled at low levels during oxidation of mineral sulfides and may limit mobility of Ni as discussed in recent studies of sediment diagenesis (Dublet et al., 2014, Hinkle and Catalano, 2015, Robbins et al., 2015).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

X-ray diffraction patterns of Ni-bearing mackinawite formed at room temperature (22–24 °C; 48 h aging time); variable Ni-loading and pH. Powder diffraction files for mackinawite (00–015-0037) and iron oxidehydrate (00–013-0092; $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$) are shown for reference. The patterns indicate formation of mackinawite for $\text{Fe}_{1-x}\text{Ni}_x\text{S}$ with 0.02 x 0.38. Trace amounts of greigite (G) are indicated in the product of the experiment at $x = 0.23$.

Figure 2. Raman spectra of Ni-bearing mackinawite after 48 h of aging. Reference bands for α-NiS and β-NiS are from Bishop et al. (1998) and the RRUFF Project database (R080122; Lafuente et al., 2015), respectively.

Figure 3. SEM and energy dispersive X-ray spectroscopy analysis of a synthetic Ni-bearing mackinawite grain. The rectangular region marked in the upper left secondary electron micrograph was X-ray mapped (0.1 µm grid) and shows homogeneous elemental distribution of Fe and Ni (lower two panels).

Figure 4.

Batch experimental results showing time-dependent concentrations of Ni in systems containing 1.1 g FeS/L and initial Ni loading of 0.28 mmol (red circles) and 0.10 mmol (green triangles). The gray rectangles highlight the first hour of reaction where Ni sorption at the mackinawite surface was most important in controlling Ni concentrations in solution. Following Ni sorption ($t > 1$ h), Ni removal from solution continued, but at a slower rate. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Figure 5.

A) Retention of Ni by mackinawite at variable solution densities (0.55, 1.02, and 2.25 g FeS/L); > 99% Ni removal was achieved at loadings below 0.13 mol Ni per mol FeS. At the highest Ni loadings, removal efficiency ranged from 37% to 81%. The shaded ovals represent regions where structural substitution dominates Ni uptake over surface sorption and intercalation. B) Stoichiometric exchange of Fe for Ni. Inset figure shows the Fe-release trends for the high density experiments (2.25 g/L). Filled and open square symbols represent

data from the primary and replicate experiments, respectively. In these experiments, Ni removal with no apparent Fe release was observed at Ni loading < 0.1 mmol.

Figure 6.

A) Comparison of Fe (lower) and Ni (upper) K-edge EXAFS spectra of Ni-free and Ni-bearing mackinawite. Right panel shows extended XANES regions relative to the respective absorption edge energy (Fe = 7112 eV; Ni = 8333 eV). Similar structures of the Fe and Ni EXAFS spectra indicate that Fe and Ni occupy similar bonding environments in mackinawite. B) k^2 -weighted EXAFS and Fourier transforms uncorrected for phase shift for $\text{Fe}_{1-x}\text{Ni}_x\text{S}$ with X_{Ni} ranging from 0.05 to 0.42. Experimental data and fits are shown with black lines and red lines, respectively. EXAFS fit results are provided in Table 3. (For

interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Figure 7.

Linear regression analysis of $\ln K_d$ versus Ni content in mackinawite assuming a regular solid solution model.

Table 1.

X-ray diffraction data for crystalline mackinawite and synthetic Ni-free and Ni-bearing mackinawite. Ni concentrations in mackinawite are given in wt% and as $\text{Fe}_{1-x}\text{Ni}_x\text{S}$.

	Crystalline FeS		Synthetic FeS		Synthetic FeS plus Ni (this study)							
	$d(\text{\AA})^a$	$d(\text{\AA})^b$	$d(\text{\AA})^c$	$d(\text{\AA})^d$	$d(\text{\AA})$	$d(\text{\AA})$	$d(\text{\AA})$	$d(\text{\AA})$	$d(\text{\AA})$	$d(\text{\AA})$	$d(\text{\AA})$	$d(\text{\AA})$
hkl												
001	5.033	6.60	5.48	5.20	5.27	5.27	5.29	5.31	5.27	5.27	5.29	5.29
101	2.967	3.33	3.36	2.99	2.99	2.99	3.00	3.01	2.99	2.99	2.97	2.97
110	2.598	2.84	2.58	2.62	2.59	2.59	2.58	--	2.61	--	--	--
111	2.308	2.42	2.30	2.32	2.31	2.31	2.31	2.31	2.31	2.31	2.31	2.31
200	1.837	2.00	1.95	1.85	1.84	1.83	1.83	1.84	1.84	1.84	1.83	1.83
211	1.562	1.63	1.57	1.58	1.57	1.56	1.57	--	1.57	--	1.57	1.57
a -axis, $\text{\AA}$	3.67	4.02	3.65	3.67	3.67	3.67	3.67	3.66	3.67	3.67	3.67	3.67
c -axis, $\text{\AA}$	5.03	6.60	5.48	5.20	5.07	5.08	5.09	5.09	5.09	5.09	5.10	5.10
c/a	1.37	1.64	1.50	1.42	1.38	1.38	1.39	1.39	1.39	1.39	1.39	1.39
Ni, wt%	--	--	--	--	1	5	5	10	15	25	25	25
XNi	--	--	--	--	0.02	0.08	0.08	0.15	0.23	0.38	0.38	0.38

^aCrystalline mackinawite (Lennie et al., 1995).

^bSynthetic mackinawite, freeze-dried (MkA), aged <0.5 h (Wolthers et al., 2003).

^cSynthetic mackinawite, freeze-dried (MkB), aged <0.5 h (Wolthers et al., 2003).

^dSynthetic mackinawite, freeze-dried, aged 3 d (Jeong et al., 2008).

Table 2.

Summary of batch experimental conditions and results. Additional experimental data are provided in Table A.1, Table A.2, Table A.3.

FeS density (g/L)	[Ni(II)]/[FeS], initial (min – max)	pH range	Sorbed Ni (mmol/g)	Max Ni uptake (mmol/g)	Max Ni mol fraction, X _{Ni}	Ni(OH) ₂ saturation index (range)	Fe(OH) ₂ saturation index (range)
0.55	0.07 – 0.83	6.5 – 8.1	1.6	3.5	0.31	–2.6 to –1.4	–4.2 to –2.7
1.02	0.009 – 0.75	5.9 – 7.1	1.2	5.2	0.44	–3.8 to –8.7	–5.7 to –2.4
2.25	0.008 – 0.70	5.2 – 8.4	1.0	6.4	0.56	–5.6 to –1.6	–0.8 to –4.9

Saturation index = $\log \Omega = \log (\text{ion activity product}/K_{\text{sp}})$.

Table 3.

Ni K-edge EXAFS fit parameter results for synthetic Ni-bearing mackinawite.

Ni mol fraction, X_{Ni}	Path	CN	R , Å	σ^2 , Å ²	E^0 , eV	R factor
0.05	Ni-S	3.35±0.14	2.27±0.01	0.006	2.76	0.009
0.11	Ni-S	3.31±0.30	2.29±0.01	0.006	2.76	0.014
0.20	Ni-S	3.74±0.30	2.27±0.01	0.006	2.76	0.032
0.42	Ni-S	4.04±0.30	2.28±0.01	0.006	2.76	0.028

Table 4.

Crystal chemistry and solubility data for selected metal sulfides.

Metal sulfide	S–Me CN	S–Me Bond distance, Å	log K_{sp0}	log K_{sp} (FeS–MeS)
α -MnS alabandite	6:1	2.61	6.6	–3.1
FeS mackinawite	4:1	2.26	3.5 ^a	0
β -CoS jaipurite ^b	–	–	–2.3	5.8
NiS α -NiS	6:1	2.38	–2.7	6.2
Millerite β -NiS	5:1	av. 2.32 2.26–2.37	–3.2	6.7
ZnS sphalerite	4:1	2.35	–4.5	8.0
PbS galena	6:1	2.97	–7.9	11.4
SnS herzenbergite	5:1	2.62–3.29	–8.6	12.1
β -CdS greenockite	4:1	2.53	–8.9	12.4
CuS covellite	3:1–4:1	2.19–2.31	–15.8	19.3
β -HgS metacinnabar	4:1	2.53	–31.6	35.1

Crystal chemistry data (CN and bond distances) are from Makovicky (2006) and Vaughan and Craig (1978).

^aThe solubility product, log $K_{sp} = 3.5$, for the reaction $\text{FeS} + 2\text{H}^+ \rightleftharpoons \text{Fe}^{2+} + \text{H}_2\text{S}(\text{aq})$ is from Rickard (2006). All other log K_{sp0} values are from the thermo.com.V8.R6+.dat database, except thermodynamic data for β -NiS and β -CoS are from Vaughan and Craig (1978) and solubility data for α -NiS are from Wilkin and Rogers (2010).

^bJaipurite has generally been discredited as a natural species (Clark, 1974).