



## 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  $0.13 \pm 0.03$  (1 $\sigma$ ) 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 ( $\alpha$ -NiS or millerite), polydymite ( $\text{Ni}_3\text{S}_4$ ), or godlevskite [ $(\text{Ni,Fe})_6\text{S}_8$ ] 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  $\text{Ni}^{2+}$  in Ni-bearing mackinawite is similar to that of  $\text{Fe}^{2+}$  in Ni-free mackinawite. EXAFS data fitting of Ni-bearing mackinawite with  $X_{\text{Ni}} = 0.42$  indicated a coordination number of  $4.04 \pm 0.30$  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:

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

where  $K_d$  is the distribution coefficient,  $K_e$  is the ratio of equilibrium constants for Ni-mackinawite and mackinawite ( $14.4 \pm 1.3$ ),  $W$  is an ion interaction parameter, and  $X_{\text{Ni}}$  is the mole fraction of end-member NiS in the solid solution. The experimentally determined value of  $W$  is  $17.74 \pm 1.15$  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 ( $\text{FeS}_2$ ) and Ni retention in the solid phase. When Ni-mackinawite was aged in the presence of dissolved oxygen, transformation to goethite ( $\text{FeOOH}$ ) and violarite ( $\text{FeNi}_2\text{S}_4$ ) was observed.

### 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 ( $\text{Fe}_3\text{S}_4$ ) together comprise the dominant components of solid-phase acid volatile sulfide (AVS) in sediments and aquifer solids 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

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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, 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:  $\text{Hg} \ll \text{Cu} < \text{Cd} \approx \text{Sn} \approx \text{Pb} < \text{Ni} < \text{Fe} < \text{Mn}$ . The large difference in solubility between HgS and FeS may favor capture of solid-phase sulfide by  $\text{Hg}^{2+}$  to form HgS (Jeong et al., 2007). Low pH ( $< 4$ ) promotes mackinawite dissolution,  $\text{H}_2\text{S}$  generation, and direct metal sulfide precipitation (Özverdi and Erdem, 2006). On the other hand, because MnS is more soluble than FeS,  $\text{Mn}^{2+}$  sorption at the mackinawite surface is favored (Arakaki and Morse, 1993). In addition, the initial  $[\text{Me}^{2+}]/[\text{FeS}]$  ratio plays an important role; for example, Jeong et al. (2007) found significant sorption of Hg(II) at  $[\text{Hg}^{2+}]/[\text{FeS}] < 0.05$  and precipitation of insoluble  $\beta$ -HgS at higher molar ratios.

Nickel uptake by mackinawite is of interest because the solubility contrast between FeS and NiS ( $\Delta \log K_{\text{sp}} \approx 6.2$ ) 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 ( $\text{Ni}_3\text{S}_4$ ; 2.23 Å; coordination number = 4; Wilkin and Rogers, 2010) indicating that structural substitution of Ni(II) into mackinawite may be possible. Nickel monosulfides,  $\alpha$ -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/ $\alpha$ -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  $\text{FeS}_4$  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  $\text{O}_2$ -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 set up 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 ( $\text{Na}_2\text{S}_4$ , 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  $\mu\text{m}$  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

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