Hg(II) Reduction by Siderite (FeCO₃)

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ABSTRACT

In groundwater, chemical reactions of Hg(II) with mineral surfaces play an important role in determining the concentration of mercury that is mobile and bioavailable. In this study, we investigated Hg(II) reduction by the ferrous carbonate mineral, siderite (FeCO₃), to better understand reductive transformation of mercury in anoxic carbonate-bearing waters. Kinetic experiments and X-ray adsorption spectroscopy (XAS) were conducted to examine the rate and mechanism of Hg(II) reaction with siderite. Hg(II) was reacted with synthesized siderite mineral at various concentrations and the subsequently formed Hg(0) was measured to assess the extent

of mercury reduction by siderite. Our experimental data showed that Hg(II) reduction by siderite resulted in the loss of Hg when reacted with siderite mineral suspensions concurrent to formation of gaseous Hg(0). Hg(II) reduction occurred within minutes and reaction rates increased with increasing siderite surface area. XAS analysis confirmed that Hg(II) was reduced to Hg(0) and revealed that reduced mercury was sorbed to siderite surfaces suggesting that electron transfer reactions occur at siderite/water interface. The results of our study suggest that Hg(II) reduction by siderite is a kinetically favorable pathway for the mercury mobilization in ferruginous carbonate-bearing waters.

INTRODUCTION

Mercury (Hg) is a highly toxic element and its contamination of groundwater is a significant environmental problem (*Barringer et al.*, 2013; *Lamborg et al.*, 2013). In the United States, elevated mercury levels have been reported in many aquifer systems, including groundwater wells in Kentucky (*Davidson and Fisher*, 2005), New Jersey's Kirkwood-Cohansey aquifer (*Barringer et al.*, 1997; *Barringer et al.*, 2005; *Barringer and Szabo*, 2006; *Barringer et al.*, 2006), and Delaware's Long Neck Peninsula (*Koterba et al.*, 2006). Around the world, Hg contamination of groundwater has reported in the Kathmandu Valley of Central Nepal (*Khatriwada et al.*, 2002), and in coastal aquifer of Southern Tuscany, Italy (*Grassi and Netti.*, 2000; *Protano et al.*, 2000). Mercury mobilization in groundwater likely includes a variety of

sources and processes related to the chemical form of Hg as well as the physical-chemical properties of the aquifer matrix. Currently, the molecular mechanisms of mercury mobilization remain poorly understood.

In groundwater, mercury can exist as Hg(II) or elemental Hg [Hg(0)] and changes in chemical speciation can greatly influence Hg transport (*Lindberg et al.*, 2005; *Navarro-Flores et al.*, 2000; *Walvoord et al.*, 2008). Depending on its chemical speciation, the migration of Hg can either be retarded due to reactions with mineral surfaces or mobilized in the liquid phase by groundwater advection. Previous experimental studies have shown that the divalent dissolved form of mercury, Hg(II), sorbs onto oxide minerals and clays (*Brigatti et al.*, 2005; *Farrah and Pickering*, 1978; *Kim et al.*, 2004), involving inner-sphere complexes for goethite (*Barrow and Cox*, 1992) and ternary surface complexes for amorphous iron oxides and quartz (*Tiffreau et al.*, 1995). Hg(II) also binds strongly with organic ligands present in natural organic matter (NOM) (*Khwaja et al.*, 2005; *Qian et al.*, 2002; *Skyllberg and Drott*, 2010) including humic substances (*Khwaja et al.*, 2005; *Xia et al.*, 1998) and microorganisms (*Mishra et al.*, 2011). On the other hand, dissolved elemental mercury, Hg(0)(aq), adsorbs weakly on soil minerals and sediment constituents. In the saturated zone where gas circulation is limited, Hg(0) can be transported and mobilized by groundwater flow. Although Hg(0) has higher vapor pressure (729 Pa m³/mol) and lower aqueous solubility (60 µg/l) compared to Hg(II) (*Merck*, 2014), *Schöndorf et al.* (1999) suggested Hg(0) concentrations in groundwater can be well above the health-based drinking water ingestion standards of 2 µg/L based on thermodynamic calculations. Furthermore, field studies have shown the frequent occurrence of Hg(0) in groundwater suggesting *in situ* formation of Hg(0) in aquifers (*Bollen et al.*, 2008). The conversion of Hg(II) to Hg(0) can be an important process that contributes to mercury mobilization in groundwater (*Bone et al.*, 2014; *Gabriel and*

Williamson, 2004; Ganguli *et al.*, 2000). Depending on its chemical speciation, the migration of Hg can either be retarded due to reactions with mineral surfaces or mobilized in the liquid phase by groundwater advection. Previous experimental studies have shown that the divalent dissolved form of mercury, Hg(II), sorbs onto oxide minerals and clays (Brigatti *et al.*, 2005; Farrah and Pickering, 1978; Kim *et al.*, 2004), involving inner-sphere complexes for goethite (Barrow and Cox, 1992) and ternary surface complexes for amorphous iron oxides and quartz (Tiffreau *et al.*, 1995). Hg(II) also binds strongly with organic ligands present in natural organic matter (NOM) (Khawaja *et al.*, 2005; Qian *et al.*, 2002; Skyllberg and Drott, 2010) including humic substances (Khawaja *et al.*, 2005; Xia *et al.*, 1998) and microorganisms (Mishra *et al.*, 2011). On the other hand, dissolved elemental mercury, Hg(0)(aq), adsorbs weakly on soil minerals and sediment constituents. In the saturated zone where gas circulation is limited, Hg(0) can be transported and mobilized by groundwater flow. Although Hg(0) has higher vapor pressure (729 Pa m³/mol) and lower aqueous solubility (60 µg/l) compared to Hg(II) (Merck, 2014), Schöndorf *et al.* (1999) suggested Hg(0) concentrations in groundwater can be well above the health-based drinking water ingestion standards of 2 µg/L based on thermodynamic calculations. Furthermore, field studies have shown the frequent occurrence of Hg(0) in groundwater suggesting *in situ* formation of Hg(0) in aquifers (Bollen *et al.*, 2008). The conversion of Hg(II) to Hg(0) can be an important process that contributes to mercury mobilization in groundwater (Bone *et al.*, 2014; Gabriel and Williamson, 2004; Ganguli *et al.*, 2000).

Chemical reactions with mineral-associated ferrous iron are known to reduce Hg(II) to Hg(0) (Allard and Arsenie, 1991; Charlet *et al.*, 2002; Skyllberg *et al.*, 2006; Wiatrowski *et al.*, 2009). The reduction of Hg(II) has been shown to be mediated by electron transfer processes with Fe(II) adsorbed onto phyllosilicate surfaces (Charlet *et al.*, 2002), and by reactions with

95 mixed Fe(II)-Fe(III) minerals such as green rust (*O'Loughlin et al.*, 2003) and magnetite (*Mishra*
96 *et al.*, 2011; *Wiatrowski et al.*, 2009). Recently, Bone et al. (2014) also demonstrated that
97 mackinawite (FeS) reduces Hg(II) under sulfidic conditions. These previous studies suggest that
98 geochemical reactions with Fe(II) minerals is a major pathway for mercury reduction in
99 subsurface environments.

100 Anoxic carbonate-bearing groundwater are frequently supersaturated with respect to the
101 ferrous carbonate mineral siderite (FeCO_3) ($K_{\text{sp}} = 10^{-10.7}$), resulting in the authigenic formation of
102 siderite in ferruginous zones of shallow anoxic aquifers (*Jensen et al.*, 2002). Siderite
103 precipitation occurs when dissolved ferrous iron generated by iron-reducing bacteria react with
104 dissolved carbonate species (HCO_3^- and CO_3^{2-}) in groundwater. The mineralization of siderite in
105 aquifer matrix can strongly affect the redox transformation of toxic metals since siderite can
106 interact with groundwater constituents and reduce a wide range of polyvalent inorganic
107 contaminants including U(VI), chromate, and selenite (*Buerge and Hug*, 1999; *Ithurbide et al.*,
108 2009; *Scheinost and Charlet*, 2008). To date, the reactivity of ferrous carbonate minerals
109 towards Hg is poorly understood, and Hg(II) reduction by siderite has not been examined.

110 In this study, we aimed to determine if siderite can reduce Hg(II) in order to better
111 understand the fate of mercury in carbonate-bearing ferruginous groundwater systems. We
112 conducted laboratory experiments to investigate the interaction of Hg(II) with siderite under
113 anoxic conditions. The extent of Hg(II) reduction was quantified at different siderite
114 concentrations and the reacted siderite samples were analyzed using X-ray Absorption Near
115 Edge Structure (XANES) spectroscopy to examine the Hg oxidation state and chemical
116 speciation on the siderite surface. We found that Hg(II) reacted rapidly with siderite and that
117 Hg(0) was formed as a reaction product.

MATERIALS AND METHODS

Siderite preparation: All solutions were prepared with boiled, N₂-degassed MilliQ water. For the synthesis of siderite, a 0.8 M Na₂CO₃ solution was titrated dropwise to 100 mL of 400 mM Fe₂SO₄ in an anaerobic Coy chamber. After reaching a final volume of 200 mL, stirring of the solution was stopped, and the precipitate was allowed to settle. The supernatant was then removed, and the solids were washed with deoxygenated deionized MilliQ water 6-8 times until solution reached pH 7. The precipitate was transferred to serum bottles sealed with butyl-rubber stoppers and stored in the anaerobic chamber before experimentation to prevent any phase transformation. Subsamples of the precipitate were taken for powder X-ray diffraction (XRD) and surface area analyzes. Comparison of the XRD pattern with the one in International Centre for Diffraction Data on Powder Diffraction Standards database confirmed the formation of siderite. Surface area was determined with using BET N₂ isotherms by Particle Technology Labs (Illinois, USA) and reported as 126.1 m²/g.

Hg(II) loss experiments in ferrous carbonate solutions: Various concentrations of deoxygenated ferrous carbonate and bicarbonate iron solutions were reacted with 184.1 ± 0.4 nM of mercuric chloride in 30 mL serum bottle under strict anoxic conditions. Control experiments containing only MilliQ water or ferrous iron solution made from dissolving trace metal grade FeSO₄ to yield 180 or 360 μ M were also examined to understand the effects of carbonate and bicarbonate ions in solution on mercury reduction under strict anoxic conditions. Experiments were conducted in foil-wrapped sealed serum bottles to prevent photochemical reactions with

141 ambient light. At the end of 24 hour of reaction period, experimental reaction bottles were
142 sacrificed and mixed with 0.5% concentrated H_2SO_4 to stop the reaction. Samples were then
143 transferred to 20 mL I-CHEM glass vials, and serum bottles were washed with 50% HNO_3 to
144 remove any Hg sorbed onto the glassware.

145 Sulfuric acid digested samples were analyzed using cold vapor atomic absorbance spectroscopy
146 (CVAAS) to determine the loss of Hg from the aqueous phase. Following EPA method 245.1,
147 the samples were mixed with 2.5% HNO_3 , 15% KMnO_4 (5% solution), and 8% $\text{K}_2\text{S}_2\text{O}_8$ (5%
148 solution), capped and heated in a water bath at 95 °C for two hours. These samples were then
149 cooled to room temperature, and reacted with 12% $\text{NH}_2\text{OH}\cdot\text{HCl}$ and 12% NaCl . After diluting
150 with 2% HCl , the samples were analyzed by CVAAS using a Leeman Labs Hydra AA (Hudson,
151 NH). The detection limit of our instrument was 0.4 nM. All chemicals used to prepare solutions
152 and materials were analytical reagent grades and all pH adjustments were made with minimal
153 amount of HNO_3 or NaOH .

154
155 **Hg(II) loss experiments in siderite mineral solution:** Experiments were conducted to
156 determine the extent of Hg(II) loss in presence of mineral siderite suspension. Reactions were
157 performed under anoxic conditions in sealed serum bottles with 70 mL of MilliQ water
158 representing a control experiment or siderite mineral suspension resulting in available siderite
159 surface area of $12.36 \text{ m}^2 \text{ L}^{-1}$. 20 mL of mercuric chloride was spiked into the strict anoxic
160 experimental bottles to result in mercuric chloride concentration of 55 nM. At different time
161 intervals (e.g., 0.5 and 24 h), each independent experimental reaction bottles were sacrificed and
162 analyzed for total remaining mercury in aqueous phase. Samples were digested with sulfuric acid
163 and analyzed using cold vapor atomic absorbance spectroscopy (CVAAS) to determine the loss

of Hg. Experiments and analysis were performed in triplicate at room temperature and all pH adjustments were made with minimal amount of HNO₃ or NaOH.

Hg(II) and Hg(0) trapping experiments with siderite mineral solution: Extent of Hg(II) loss in presence of mineral siderite suspension and the subsequent production of volatile Hg(0) were measured during the Hg(II) reduction experiments. Reactions were performed under anoxic conditions in sealed serum bottles with 70 mL of MilliQ water representing a control experiment or siderite mineral suspension resulting in available siderite surface area of 12.36 m² L⁻¹. 20mL of mercuric chloride was spiked into the strict anoxic experimental bottles to result in mercuric chloride concentration of 55 nM. To monitor the Hg(II) transformation to Hg(0) during the 1 hour of reduction reaction period, the gaseous Hg(0) was continuously collected by purging the reaction vessel for 1 h with N₂ into midget bubblers (Ace Glass, Vineland NJ, Catalog 75320-20) containing Hg(0) trapping solution (0.6% potassium permanganate, 2.5% sulfuric acid, 2.5% nitric acid). Samples were collected from both the reaction vessel and the trapping solution, and the Hg was analyzed using the CVAAS using a Leeman Labs Hydra AA (Hudson, NH). Experiments and analysis were performed in triplicate at room temperature.

Hg(II) reduction kinetic experiments: Radioactive ²⁰³HgCl₂ was spiked as the Hg(II) source during the reduction kinetic experiments with siderite followed by the methods described previously (Yu *et al.*, 2012). The added ²⁰³Hg(II) (specific activity, 2.5 Ci g⁻¹; kindly provided by Christy C. Bridges, Mercer University, GA) in the siderite mineral solution was at ~2.2 µg L⁻¹ or 10 nM. Three different siderite concentrations were examined during the experiments (6.18, 12.36, and 24.72 m² L⁻¹) at pH 7.5 under strictly anoxic condition at room temperature. All

reactions were carried out in sealed serum bottles containing deoxygenated water at room temperature. Reaction bottles were gently shaken occasionally during the reaction periods. Aliquots (0.5 mL) were removed from the sealed serum bottles using a needle and syringe every minute for approximately 45 min. Blank sample containing no siderite suspension was monitored to ensure the quality control of the experiments. ^{203}Hg analysis in EcoLume Scintillation Cocktail (ICN Radiochemicals, Irvine, CA) was performed by liquid scintillation counting using a Beckman LS-6500 Counter (Beckman Instruments, Fullerton, CA). Counts per minute (CPM) were determined for 3 min using a wide channel with an appropriate standard and calibration. Initial CPM readings in mineral suspensions were indistinguishable from those from the water controls, indicating that quenching due to minerals in suspension did not interfere with the radioactivity signal. See Table 1 for summary of all experimental conditions and variables.

Hg XANES experiments: X-ray absorption spectroscopy (XAS) analysis was performed on sorption sample reacted between 0.2 g L^{-1} siderite suspension and 552 nM (or 554 ppm) of HgCl_2 under anoxic condition at pH 6.5. After 2 h of reaction, the reaction suspension was collected by centrifuging it at 10,000 rpm for 20 min. The pellets were shipped on ice in anoxic container to Argonne National Laboratory (Illinois, USA) overnight and analyzed at the Advanced Photon Source. Reference compounds included hydrated Hg^{2+} , $\text{HgCl}_2(\text{s})$, $\text{Hg}(0)$, Hg -acetate, CH_3Hg -acetate, and hydrated CH_3Hg^+ . Hydrated Hg^{2+} reference standard was prepared using a 5 mM (equivalent to 1000 ppm) stock solution of $\text{Hg}(\text{NO}_3)_2$ adjusting the pH to 2. All pH adjustments were made with HNO_3 or NaOH . Based on the previous studies showing that $\text{Hg}(\text{II})$ is reduced to $\text{Hg}(0)$ via reaction with magnetite under anaerobic conditions (*Mishra et al.*, 2011; *Wiatrowski et al.*, 2009), we obtained our $\text{Hg}(0)$ reference compound by reacting 100 mL of a

0.2 g L⁻¹ anoxic magnetite suspension with Hg (II) at a Fe (II):Hg(II) molar ratio of 10 to 1. The Hg–acetate reference standard was prepared by dissolving 40 mg of mercuric acetate powder in 4mL of Milli-Q water and 0.25 mL glacial acetic acid, and adjusted to pH 5. HgCl₂ were analyzed in solid form. Hydrated CH₃Hg⁺ ion was prepared by adjusting the solution of a 5mM (1000ppm) stock solution of CH₃HgCl to pH 3.

Hg L_{III}-edge XANES spectra were collected at station 13BMD, GeoSoilEnvironCARS, which is a bending magnet station with Si(111) crystals and a 13 element Germanium detector. Standard operating conditions were 7-GeV machine energy and had a current typically around 100 mA during these measurements. Higher order harmonics were rejected by detuning the monochromator 30%. Sample pellets were placed between Kapton tape and liquid standards were placed in SPEX SamplePrep X-Cell cups for analysis. Spectra were collected at ambient temperature and pressure. Energy calibration was performed using HgCl₂ and assigning the first edge inflection point as 12,284 eV. The pre-edge background of each averaged scan was subtracted, and the absorption coefficient was normalized to a unit-edge step. Spectra were analyzed using the SixPACK (*Webb*, 2005) interface to IFEFFIT (*Newville*, 2001). See Colombo et al. (*Colombo et al.*, 2013b) for full detailed experimental conditions and reference compounds preparation methods.

In addition to qualitative comparison of pre-edge features of XANES spectrum of our sample to the ones of reference compounds, we used the first derivative of the Hg L_{III}-edge XANES spectra for spectral comparisons and linear combination fittings. For the linear combination fitting analysis, sorption sample spectrum was first sequentially fit with one model compound to find the best 1-component fit. A second reference compound was then systematically added to determine the 2- or 3-component fit that best explained the remaining

variation until the residual values did not show any significant improvement in the fitting analysis. For each multi-component fit, a least squares fitting module was used to determine the fraction of all the model types in the sorption sample. Similar residual analysis has been conducted by others on Hg speciation on sorption samples and successfully identified the best fits based on the comparison of residual values (*Colombo et al.*, 2013a; b; *Kim et al.*, 2000).

RESULTS

Hg(II) loss in presence of ferrous carbonate solutions

The role of carbonate was investigated by reacting Hg(II) with dissolved ferrous iron and carbonate in deoxygenated water (Table 2). In the absence of carbonate, bicarbonate, and/or the subsequent mineral precipitates, negligible amounts of Hg(II) reduction by dissolved ferrous iron was detected. Approximately 3% Hg loss within 0.5 h and about 7% at 24 h of reaction was measured when mercury reacted with dissolved ferrous iron alone, which was similar to the Hg loss in the control experiment of which Hg(II) was dissolved in deoxygenated water. However, the addition of either carbonate or bicarbonate to supersaturated solutions with respect to siderite ($\Omega = 4.1$) resulted in rapid Hg(II) loss. In the experiment with ferrous iron and sodium carbonate, approximately 80% of the total Hg was lost from the solution within the first 0.5 h of the reaction. The reaction was nearly complete in the first 0.5 h, as increasing the reaction time to 24 h resulted in only a marginal increase in Hg loss. In the set of second experiments of which Hg(II) was reacted with ferrous iron and sodium bicarbonate, the rate of Hg(II) loss was slower, with 17 – 24% loss in 0.5 h and about 75% loss after 24 h. A visible precipitate had formed in all of the reaction vessels containing the bicarbonate or carbonate solution whereas no visible precipitates formed in any of the control experiments.

Hg(II) reaction with siderite mineral suspension

The reduction of Hg(II) by siderite was investigated by reacting 0.1 g/L of siderite with Hg(II) in deoxygenated water (Table 3). The results indicated that more than half of the total Hg was lost from the siderite suspension within 0.5 h of reaction. After 24 h of reaction, 70% of the total Hg was lost from the mineral suspension. The trend of Hg loss was consistent in triple replicates over the same time period. Negligible Hg loss was observed in the control experiments containing only deoxygenated water. These results indicate that presence of siderite mineral significantly affects dissolved aqueous Hg concentrations resulting in rapid loss of total Hg from the reaction suspension. Similar observations of mercury loss from aqueous phases involving mercury and ferrous containing minerals have been reported from previous studies implying that electron transfer process during mercury reductive transformation is coupled with iron oxidation (Charlet *et al.*, 2002; Inoue and Munemori, 1979). To further identify the Hg transformation mechanisms, following mercury trapping experiments were conducted.

Hg(II) transformation to Hg(0) in presence of siderite

A mercury trapping experiment was conducted to determine whether the loss of mercury in the siderite suspension results in the formation of volatile Hg gas (Fig. 1). After 1 h of reaction time, only 10.3 ± 1.2 % of the Hg remained in suspension with the siderite, and $89.7 \pm 2.2\%$ was recovered in a potassium permanganate trap solution. In the control experiment performed in deoxygenated water without siderite, $90.7 \pm 5.9\%$ of the Hg remained in the reaction vessel, and $9.3 \pm 4.0\%$ was recovered in the trap. These results confirm that gaseous Hg, likely Hg(0), is a product of Hg(II) reductive transformation reaction with siderite. We cannot rule out the

possibility that other oxidative state of Hg, such as Hg(I), may exist as an intermediate species during the reductive transformation. However, due to low solubility of Hg(I) in water at room temperature, it is unlikely that the dissolved monovalent mercury exist in aqueous phase. Possibility of sorption or retention of different types of mercury species within the siderite/water interface is investigated using spectroscopic approach to further enhance understanding of mercury reduction transformation mechanism (see XAS analysis section).

Kinetic reduction experiments

Data from kinetic reduction experiments indicate that rate of Hg(II) reduction increases with increasing siderite surface areas in the suspension from 6.18 to 24.72 m² L⁻¹ (Fig. 2). At a siderite concentration of 12.36 m² L⁻¹, 53% of the Hg(II) loss occurred over 35 min of reaction whereas 40% of the Hg(II) loss was observed for the experiment conducted using 6.18 m² L⁻¹ of siderite suspension. Inset of Fig. 2 shows a plot of the linearized form of the initial reaction data (i.e., the first 10 min of reaction). As the siderite surface site density is in large excess compared to the Hg(II) concentration in all three kinetic reduction experiments, the Hg(II) reduction kinetics can be described using a pseudo first-order kinetic model using the following equation:

$$\frac{d[Hg(II)]}{dt} = -k_{rxn} [Hg(II)]$$

where k_{rxn} is pseudo first-order rate constant, and [Hg(II)] is the concentration of total Hg(II) remaining in the system. Comparison between the experimental measurements and model fits indicates that the pseudo first-order kinetic model provides a good quantitative description of the Hg(II) reduction data over the first 10 min of the reaction. The experimental data deviate considerably from the theoretical model fit after this short period as the extent and rate of the Hg reduction was decreased after this initial reaction period. Hence, the reaction rate constants are

determined by fitting the reaction data into the pseudo first-order kinetic model only over 10 min of reaction period (Table 4). Reaction rates increase with increasing concentration of siderite within this 10 min of reaction period. We found reaction rates of $1.94 \times 10^{-2} \text{ s}^{-1}$ for experiments conducted with $6.18 \text{ m}^2 \text{ L}^{-1}$ of siderite, $2.58 \times 10^{-2} \text{ s}^{-1}$ for $12.36 \text{ m}^2 \text{ L}^{-1}$ siderite, and $2.77 \times 10^{-2} \text{ s}^{-1}$ for $24.72 \text{ m}^2 \text{ L}^{-1}$ siderite.

XAS Analysis of Reacted Hg(II)

Hg-reacted siderite samples were analyzed using XANES spectroscopy to investigate the oxidation state and speciation of residual Hg sorbed to the siderite surface. Figure 3A shows the Hg L_{III}-edge XANES spectra of the siderite sample and reference compounds. The reference compounds display unique spectral characteristics that are related to the Hg oxidation state. For example, a pronounced pre-edge feature is observed in the XANES spectra of Hg(II) and HgCl reference compounds but is absent in the Hg(0) standard. Comparison of Hg-reacted siderite spectrum to the spectra of the reference compounds indicates that the residual Hg sorbed to the siderite surface is most similar to the Hg(0) standard. In particular, the XANES spectrum of Hg sorbed to siderite does not exhibit the distinctive pre-edge peak. We note that our XANES spectrum of Hg sorbed to siderite is in sharp contrast to spectra from the previous work of Hg(II) sorbed to iron oxyhydroxides (Al-Abed *et al.*, 2008) which demonstrated a distinctive pre-edge feature indicative of Hg(II) oxidation state.

To gain further insights into the oxidation state of Hg in the siderite sample, we analyzed the first derivative of the XANES spectra (Figure 3B). The first derivative analysis of Hg L_{III}-edge XANES spectra are particularly sensitive to oxidation state and coordination environment of Hg (Aakesson *et al.*, 1994; Huggins *et al.*, 1998; Riddle *et al.*, 2002) as the first derivative of

the Hg L_{III}-edge XANES spectra exhibits unique two major peaks due to the transitions of the L_{III} electron from core level to unoccupied orbitals (Fig. 3B). Table 4 shows the first (E1) and second (E2) inflection points which correspond to two maximum points in the first derivative of the spectra for reference compounds and sorption sample. We found only the E1 peak for our sorption sample positioned at 12,285.2 eV while that of Hg(0) reference was found at 12,285.0 eV, while all other reference compounds showed unique two E1 and E2 peaks. This close resemblance of XANES spectrum of our sorption sample to that of the Hg(0) reference compound in terms of the spectral features of first derivative of the Hg L_{III}-edge and their peak positions suggest that the Hg(0) is sorbed on siderite surfaces.

A linear combination fitting analysis of the XANES spectra was performed to quantify the Hg species in the siderite sample (Table 5). We found that two-component linear combination fitting using the Hg(0) and HgCl₂(s) reference compounds resulted in the fit with the lowest residual values suggesting that Hg on siderite surfaces is composed of Hg species in its oxidation environment similar to about 70% of Hg(0) and 30% of Hg(II). Performing three-component fit did not significantly improve goodness of the fit based on the residual values supporting our conclusion of speciation. Our XANES data provide direct evidence that the reduced Hg is associated with siderite surfaces. Although, the results from XAS experiments do not provide specific information about the reductive transformation mechanism, the data indicate that both Hg(II) and Hg(0) are bound to the surface, indicating sorption reaction is involved in the reductive transformation process. Additional studies are required to identify the Hg(II) and Hg(0) surface species and to elucidate the electron transfer pathway.

DISCUSSION

347

348 The loss of mercury in supersaturated ferrous carbonate and bicarbonate solutions likely
349 involve reactions with a solid phase. Co-precipitation of Hg(II), Hg(I), and Hg(0) with iron-
350 carbonate mineral phases and surface sorption of reduced mercury species would have resulted
351 in removal of Hg from solution. Mercury incorporation in siderite would be analogous to Hg(II)
352 incorporation in Fe(III) hydroxides, which has been shown to occur over a wide range of pH
353 conditions (*Inoue and Munemori*, 1979). For example, a study identified a new polymorph of
354 Hg(I) containing mineral phase, namely clearcreekite, $\text{Hg}^{1+}_3(\text{CO}_3)(\text{OH}) \cdot 2\text{H}_2\text{O}$, in San Benito
355 County in California (*Roberts et al.*, 2001). Aurivilliusite is another recently identified mercury
356 containing mineral phase with mixed Hg(I) and Hg(II) bonded to oxygen atoms (*Roberts et al.*,
357 2004). Amirbahman et al. (2013) also suggested presence of Hg(I) as an important surface
358 catalyst for mercury reduction in presence of iron bearing minerals. They proposed second-order
359 kinetic mechanisms to explain their observed reduction rates. Even though we cannot
360 definitively conclude that the increased loss of Hg(II) from the aqueous phase in ferrous
361 carbonate or bicarbonate solution is due to the co-precipitation and/or surface sorption reactions
362 of different mercury species in our system with iron and/or carbonate species, it is likely that
363 such reactions of mercury with different ion species in aqueous phase and/or surface catalyzed
364 mercury reduction would account for the observed significant loss of Hg in solution. Although
365 we cannot distinguish co-precipitation from surface sorption reactions of different mercury
366 species, the structural location of Hg would affect the redox transformation and the fate of
367 reduced Hg(0). Surface-associated Hg(0) can desorb and volatilize into the gas phase, while
368 co-precipitated Hg would be retained in the solid-phase. Further detailed analysis and studies on

the solid precipitate phase in these experiments as well as Hg coordination analysis are needed to elucidate the distribution of mercury species in precipitated ferrous carbonate solids.

Our study indicated that mercury reduction by aqueous ferrous iron in the absence of a soil phase is kinetically slow. A recent study by Amirbahman et al. (2013) on kinetics of Hg(II) reduction by Fe(II) suggested that surface-catalysis by iron minerals and the surface chemistry of the mineral phases are important factors affecting the rate in mercury reductive pathways (Amirbahman et al., 2013). Pasakarnis et al. (Pasakarnis et al., 2013) also demonstrated that mercury reduction in presence of magnetite is significantly controlled by the aqueous concentrations of Fe(II) and chloride, suggesting that the mineral phase stoichiometry and its subsequent change due to alteration of ion concentrations in aqueous phase have significant impact on mercury reduction pathways. Interestingly, Amirbahman et al. (2013) reported homogeneous mercury reduction in presence of aqueous Fe(II) alone at different pH than the experiments in our study further indicating the mercury reductive mechanisms are sensitive to aqueous phases chemistry.

Our mercury reduction kinetic data suggest that two different domains of reaction mechanisms exist under the experimental conditions. The first ten minutes of reaction between Hg(II) and siderite mineral indicate that the reaction follows the pseudo-first order kinetics due to the excess reactive surface sites. The retarded reaction rates for all of the experimental conditions during the remaining reaction periods suggest that limiting factors other than the difference in the available surface sites control the overall reaction mechanism. The pseudo first-order reaction rates of Hg(II) reduction by siderite are similar to Hg(II) reactions with ferrous mineral suspensions reported in previous studies (Mishra et al., 2011; O'Loughlin et al., 2003; Wiatrowski et al., 2009). Consistent with other model systems, the pseudo first-order theoretical

prediction is applicable to the experimental data for the initial stage of the reaction where multiple reaction kinetic pathways persist depending on the experimental conditions (*Dzombak and Morel*, 1986; *Ho and McKay*, 1999; *O'Shannessy and Winzor*, 1996). For example, Singh et al. (*Singh et al.*, 1996) reported that the sorption of Hg(II) by kaolinite obeyed multiple first order kinetics depending on presence of different types of organic ligands. Because reactions between dissolved ions and solid surfaces involve both transport phenomena and chemical reactions, the overall kinetics can rarely be described by a single rate constant. In our experimental system, the deviation from pseudo first-order kinetics in the later time points suggest that more than one process is controlling the rates of reduction.

Based on our kinetic and spectroscopic experimental data, we propose that reductive transformation of Hg(II) to Hg(0) by siderite is a two-step process. The first step involves sorption of Hg(II) onto siderite surfaces and reduction to Hg(0), and the second reaction step involves desorption of Hg(0) into the gas phase. We suggest that the first step is faster than the second one, and that the rate-limiting process in the second step is controlled by Hg(0) diffusion from the mineral surface. In the first step, the Hg(II) ions are sorbed onto the siderite surface followed by rapid electron transfer to the surface complex. The reduced mercury is weakly bonded to the mineral and Hg(0) can partition from the surface into solution. As surface Hg(0) concentrations increase, molecular rearrangement, Hg–Hg interactions, and van der Waals forces at the mineral-water interface may hinder desorption thus affecting the reaction kinetics. When the reaction approaches equilibrium, the accumulation of Hg(0) in solution further slows down the diffusion of reduced mercury from the siderite surface. Our proposed pseudo-first order model fits the experimental data well for the initial sorption of Hg(II) and reduction to Hg(0), but additional work is required to quantify the kinetics of the second step, e.g., the diffusion and

volatilization of Hg(0). It should also be noted that the reaction constants increased only marginally with increasing surface areas of siderite compared to other systems such as the one with magnetite (Wiatrowski *et al.*, 2009). The weaker dependence of the surface areas in this study further indicates that surface area is not the limiting factor for mercury reduction reaction with siderite mineral phase under the experimental conditions.

Nonetheless, we cannot rule out the possibility of a second-order kinetic reaction mechanism. Pasakarnis *et al.* (2006) and Amirbahman *et al.* (2013) suggested that the rapid transformation of Hg(II) to Hg(0) on mineral surface is partly due to intermediately sorbed Hg(I) acting as a surface-catalyst. Peretyazhko *et al.* (2006) reported rapid transformation of Hg(II) to Hg(0) in tropical hydromorphic soils in the presence of ferrous iron and described the kinetic experimental data using a pseudo-first order rate law but suggested the possibility of more complex reaction mechanism for mercury reduction in presence of iron bearing mineral phases. As clearly demonstrated in previous studies and our work, Hg(II) reduction mechanism in presence of iron bearing mineral phases involves complex and complicated reaction pathways. Additional detailed analysis to identify intermediate species is required to fully understand the mercury reduction pathways.

The data presented herein demonstrate that siderite can rapidly reduce Hg(II) to Hg(0). We show that reaction of Hg(II) with siderite results in significant loss of Hg from mineral suspensions and the formation of gaseous Hg(0). These findings suggest that chemical reduction of Hg(II) can readily occur in carbonate-bearing groundwater, as siderite is common in ferrous iron mineral in aquifers. In contrast to soils, where Hg(II) is strongly bonded to organic matter (Khawaja *et al.*, 2005; Skyllberg *et al.*, 2006; Skyllberg and Drott, 2010), groundwater has relatively low concentrations of organic matter and thus mineral surface mediated reduction of

dissolved Hg(II) may be more facile. Hg redox transformation in aquifers containing siderite may help explain the mobilization of mercury in anoxic groundwater where Hg(II) can be reduced and undergo advection in its elemental form. In natural systems, the reduction of Hg(II) to Hg(0) is likely to be complex biogeochemical phenomena affected by the dynamic interplay between microbial and abiotic redox pathways in subsurface environments as well as its dependence on several environmental factors. Future studies should be aimed at the understanding how the rate and extent of the Hg(II) reduction reaction is influenced by groundwater and aquifer composition, including the presence of organic matter, chloride, dissolved sulfide, and competing heterogeneous reactive surfaces.

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Table 1. Description of Batch Hg(II) Reduction Experiments

Experiment Name	Reactants	Measured Products	pH
Hg(II) loss experiments in ferrous carbonate solutions ^a	Hg(II)/ Dissolved Fe ²⁺ (180 μM)	Hg(II)	6.9
	Hg(II)/ Dissolved Fe ²⁺ (360μM)	Hg(II)	6.9
	Hg(II)/ Dissolved Fe ²⁺ (180 μM) with Na ₂ CO ₃ (360 μM)	Hg(II)	6.3
	Hg(II)/ Dissolved Fe ²⁺ (360 μM) with Na ₂ CO ₃ (720 μM)	Hg(II)	6.3
	Hg(II)/ Dissolved Fe ²⁺ (180 μM) with NaHCO ₃ (30 mM)	Hg(II)	7.8
	Hg(II)/ Dissolved Fe ²⁺ (360 μM) with NaHCO ₃ (30 mM)	Hg(II)	7.8
Hg(II) loss experiments in siderite mineral solution ^b	Hg(II)/Siderite suspension (12.36 m ² L ⁻¹)	Hg(II)	7.5
Hg(II) and Hg(0) trapping experiments with siderite mineral solution ^b	Hg(II)/Siderite suspension (12.36 m ² L ⁻¹)	Hg(0)	7.5
Hg(II) reduction kinetic experiments ^c	Radioactive ²⁰³ HgCl ₂ / Siderite suspension (6.18, 12.36, 24.72 m ² L ⁻¹)	²⁰³ Hg	7.5

^a[Hg(II)]_{initial} = 184 nM
^b[Hg(II)]_{initial} = 55 nM
^c[Hg(II)]_{initial} = 10 nM

Table 2. Loss of Hg from deoxygenated ferrous carbonate solutions

	pH	% Hg loss from solution ^a
		24 h reaction period
Water	6.5	7.6
Dissolved Fe ²⁺ (180 µM)	6.9	7.38
Dissolved Fe ²⁺ (360 µM)	6.9	6.87
Fe ²⁺ (180 µM) + Na ₂ CO ₃ ^b	6.3	77.3
Fe ²⁺ (360 µM) + Na ₂ CO ₃ ^c	6.3	79.7
Fe ²⁺ (180 µM) + NaHCO ₃ ^d	7.8	74.6
Fe ²⁺ (360 µM) + NaHCO ₃ ^d	7.8	75.1

^a initial Hg(II) concentration is 184.1 ± 0.4 nM. Hg loss was determined by measuring the remaining Hg(II) concentration using vapor atomic absorbance spectroscopy in the reaction bottle after 24h reaction period.

^b [Na₂CO₃] = 360 µM

^c [Na₂CO₃] = 720 µM

^d [NaHCO₃] = 30 mM

Table 3. Loss of Hg from siderite suspension

	Surface area (m ² g ⁻¹)	Total Hg remaining after reaction in siderite suspension ^b [nM]			Percent Lost
		0 h	0.5 h	24 h	24 hr
Water		51.7 ± 1.4	56.2 ± 3.2	55.4 ± 1.5	1.4 %
Siderite ^a	12.36	57.6 ± 1.1	23.1 ± 5.3	17.3 ± 2.9	70.0 %

^a Minerals prepared at pH = 4 were suspended at a concentration of 0.1 g L⁻¹ in deoxygenated water and adjusted to pH = 7.5 before addition of Hg(II).

^b Values represent means of triplicate experiments; errors represent the standard deviation of the mean.

Table 4. Psuedo-first order reaction rate constants for Hg(II) reduction by siderite at varying mass of the solid substrate at constant pH of 7.5 ± 0.02 over 10 min of reaction period.

[FeCO ₃] (mg L ⁻¹)	[FeCO ₃] (m ² L ⁻¹)	Rate constant (s ⁻¹)	Goodness of Fit (r ²)
50	6.18	1.94×10^{-2}	0.938
100	12.36	2.58×10^{-2}	0.952
200	24.72	2.77×10^{-2}	0.956

Table 5. Hg L_{III}-edge first inflection points (E1), second inflection points (E2), and separations (ΔE) of the first derivative of XANES spectra in reference compounds and sorption sample; Linear combination fit results to the first derivative of XANES spectrum of the sorption sample

Hg L _{III} -edge first derivatives and the inflection points			
ID	E1 (eV)	E2 (eV)	ΔE (eV)
Hg(II)–Acetate	12285.2	12298.4	13.2
Hg ²⁺ (aq)	12284.6	12294.1	9.5
Methyl–Hg–acetate	12286.4	12294.9	8.5
Methyl–Hg	12286.1	12295.2	9.1
HgCl ₂	12285.5	12294.3	8.8
Hg(0)	12285.0	–	–
Sorption Sample	12285.2	–	–
Fraction of mercury species in sorption sample by linear combination fitting of the first derivative of Hg L _{III} -edge XANES spectrum			
Component	Fraction	Residual	
Hg(0)	1	0.0624	
HgCl ₂	1	0.2131	
Hg(0) / HgCl ₂	0.63 / 0.37	0.0534	
Hg(0) / Hg(II)–Acetate	0.88 / 0.12	0.0618	
Hg(0) / Hg ²⁺ (aq)	0.98 / 0.02	0.0732

Figure 1. Formation of gaseous Hg(0) during Hg(II) reaction with siderite. The reaction time was 1 hour. Grey bars represent mercury remaining in the reaction vessel, and white bars represent mercury in the trapping solution. Reactions were performed under anoxic conditions in sealed 100 mL serum bottles with 70 mL of water or mineral suspension ($12.36 \text{ m}^2 \text{ L}^{-1}$). Reactions were performed in triplicate, and error bars represent standard deviations.

Figure 2. Kinetics of Hg(II) reduction by siderite. Experiments were conducted in deoxygenated water using ²⁰³Hg as a tracer. Symbols indicate experimentally determined data of percent Hg(II) remaining in solution plotted as a function of time at different siderite concentration. Linearized kinetic data is plotted in the inset with lines indicating the pseudo first-order kinetic model fit over 10 min of initial reaction period. See Table 4 for model predicted rate constants for different experiments.

Figure 3. Hg L_{III}-edge XANES spectroscopic analysis of siderite sample of Hg(II) reacted with siderite and reference compounds. (A) XANES spectra of sorption sample and reference compounds; (B) First derivatives of the XANES spectra of sorption sample and reference compounds. Dashed lines are at 12,286.3 and 12,294.0 eV. See Table 5 for corresponding peak positions for spectra.

Appendix

A. Loss of Hg from deoxygenated ferrous carbonate solutions and mineral saturation index

Experimental Conditions	pH	% Hg loss from solution ^a	Saturation Index ^b for Siderite (FeCO ₃) _{2(s)}	Saturation Index ^b for Fe(OH) _{2(am)}
Water	6.5	7.6	–	–
Dissolved Fe ²⁺ (180 μM)	6.9	7.38	–	-3.498
Dissolved Fe ²⁺ (360 μM)	6.9	6.87	–	-3.498
Fe ²⁺ (180 μM) + Na ₂ CO ₃ ^c	6.3	77.3	4.212	-2.278
Fe ²⁺ (360 μM) + Na ₂ CO ₃ ^d	6.3	79.7	4.212	-2.509
Fe ²⁺ (180 μM) + NaHCO ₃ ^e	7.8	74.6	4.212	-8.016
Fe ²⁺ (360 μM) + NaHCO ₃ ^e	7.8	75.1	4.212	-8.016

^a initial Hg(II) concentration is 184.1 ± 0.4 nM. Hg loss was determined by measuring the remaining Hg(II) concentration using vapor atomic absorbance spectroscopy in the reaction bottle after 24h reaction period.

^b Saturation index calculated using Minteq software.

^c [Na₂CO₃] = 360 μM

^d [Na₂CO₃] = 720 μM

^e [NaHCO₃] = 30 mM

B. XRD Diffraction Pattern for Synthesized Siderite Minerals