

Article

Reduction of Hg(II) by Fe(II)-Bearing Smectite Clay Minerals

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Abstract: Aluminosilicate clay minerals are often a major component of soils and sediments and many of these clays contain structural Fe (e.g., smectites and illites). Structural Fe(III) in smectite clays is redox active and can be reduced to Fe(II) by biotic and abiotic processes. Fe(II)-bearing minerals such as magnetite and green rust can reduce Hg(II) to Hg(0); however, the ability of other environmentally relevant Fe(II) phases, such as structural Fe(II) in smectite clays, to reduce Hg(II) is largely undetermined. We conducted experiments examining the potential for reduction of Hg(II) by smectite clay minerals containing 0–25 wt% Fe. Fe(III) in the clays (SYn-1 synthetic mica-montmorillonite, SWy-2 montmorillonite, NAu-1 and NAu-2 nontronite, and a nontronite from Cheney, Washington (CWN)) was reduced to Fe(II) using the citrate-bicarbonate-dithionite method. Experiments were initiated by adding 500 μM Hg(II) to reduced clay suspensions (4 g clay L^{-1}) buffered at pH 7.2 in 20 mM 3-morpholinopropane-1-sulfonic acid (MOPS). The potential for Hg(II) reduction in the presence of chloride (0–10 mM) and at pH 5–9 was examined in the presence of reduced NAu-1. Analysis of the samples by Hg L_{III} -edge X-ray absorption fine structure (XAFS) spectroscopy indicated little to no reduction of Hg(II) by SYn-1 (0% Fe), while reduction of Hg(II) to Hg(0) was observed in the presence of reduced SWy-2, NAu-1, NAu-2, and CWN (2.8–24.8% Fe). Hg(II) was reduced to Hg(0) by NAu-1 at all pH and chloride concentrations examined. These results suggest that Fe(II)-bearing smectite clays may contribute to Hg(II) reduction in suboxic/anoxic soils and sediments.

Keywords: montmorillonite; nontronite; elemental mercury; reduction

1. Introduction

Mercury (Hg) is present in the environment as a result of natural and anthropogenic processes including mineral weathering, volcanic emission, mining activity, fossil fuel burning, and industrial and consumer use [1,2]. As such, Hg is a common contaminant in many terrestrial and aquatic systems [3,4], and its bioaccumulation in organisms, including humans, is a major environmental concern [5–7]. Although Hg can exist as Hg(II), Hg(I), or Hg(0), Hg(I) is prone to disproportionation and is not commonly found under typical environmental conditions. Hg(II) is particularly soluble in water and can form highly toxic compounds like dimethylmercury as a result of microbial activity [8,9]. Metallic Hg(0) exists as a liquid at room temperature and is also quite toxic, but is considerably less soluble in water than Hg(II). However, due to its low vapor pressure, Hg(0) readily partitions into the atmosphere and is mobile on a global scale. Thus, the reduction of Hg(II) to Hg(0) in soils and sediments, facilitated by both abiotic and microbially-mediated processes, is a key component of the

cycling of Hg between atmospheric and aquatic/terrestrial reservoirs and the overall biogeochemical cycling of Hg [3,9–11].

Iron (Fe) is a highly abundant element in the lithosphere (~5% by mass) and Fe oxides (including formal Fe oxides, oxyhydroxides, and hydroxides such as ferrihydrite ($\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$), hematite ($\alpha\text{-Fe}_2\text{O}_3$), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), magnetite (Fe_3O_4), goethite ($\alpha\text{-FeOOH}$), lepidocrocite ($\gamma\text{-FeOOH}$)), and Fe-bearing clay minerals (smectites, illites, chlorites, etc.) are common constituents of soils and sediments. The biogeochemistry of Fe in most aquatic and terrestrial environments is driven largely by microbial activity, particularly in Fe-rich soils and sediments where Fe redox cycling by microorganisms is a significant component of C cycling and energy flux [12–16]. Microbial reduction of ferric iron (Fe(III)) can result in the formation of a broad range of Fe(II) species including soluble and adsorbed Fe(II) and mineral phases containing structural Fe(II) (e.g., magnetite, siderite (FeCO_3), vivianite [$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$], green rust, chukanovite [$\text{Fe}_2(\text{OH})_2\text{CO}_3$], and Fe(II)-bearing clays) [17–27]. Fe(II) is one of the most abundant reductants typically present in aquatic and terrestrial environments under suboxic and anoxic conditions [28–30], often providing substantial redox buffering capacity to these systems, and many Fe(II) species are effective reductants for a wide range of organic and inorganic contaminants, including nitroaromatics, chlorinated hydrocarbons, nitrate, heavy metals, and radionuclides [31–42]. In 2003, we reported the reduction of Hg(II) to Hg(0) by green rust [43], a layered redox-reactive Fe(II)-Fe(III) hydroxide with a pyroaurite-type structure. Since then, other Fe(II)-bearing minerals have been shown to reduce Hg(II) to Hg(0), including magnetite [44–47], siderite [48], and mackinawite (FeS) [49], as well as solution phase and adsorbed Fe(II) [50,51]. These results suggest that other Fe(II)-bearing minerals may be effective reductants for Hg(II).

Smectite clays (e.g., montmorillonite, beidellite, nontronite, saponite, and hectorite) are a group of 2:1 (an alumina octahedral sheet bound between two tetrahedral silicate sheets) hydrous aluminum phyllosilicate minerals found in many soils and sediments. Among clay minerals, the high surface area and cation exchange capacity of smectite clays makes them particularly good sorbents for metals including Hg^{2+} [52–57]. Although composed primarily of Si and Al, smectites typically contain Fe (ranging from <1 wt% up to ~30 wt% [58]) due to isomorphic substitution of Fe^{3+} for Si^{4+} in the tetrahedral layer and Fe^{3+} for Al^{3+} in the octahedral layer. As such, smectite clays can be an important component of the Fe pool in soils and sediments. Moreover, the structural Fe(III) in smectites is redox active and can be reduced to Fe(II) by biotic and abiotic processes [59–66]. Although structural Fe(II) in smectite clays has been shown to reduce contaminants including nitroaromatics, chlorinated hydrocarbons, chromate, and pertechnetate [67–74], the ability of clays to reduce Hg(II) is unknown, impeding evaluation of their contribution to the redox cycling of Hg in the environment.

In this study we used X-ray absorption fine structure (XAFS) spectroscopy to examine the potential for reduction of Hg(II) by structural Fe(II) in a suite of smectite clay minerals containing 0–25 wt% structural Fe.

2. Materials and Methods

2.1. Clay Minerals

SYn-1 (Barasym SSM-100, a synthetic mica-montmorillonite), SWy-2 (a Na-rich montmorillonite from Crook County, WY, USA), NAu-1 (a green-colored, Al-enriched nontronite from Uley Mine, South Australia) and NAu-2 (a brown colored, Al-poor nontronite containing tetrahedral Fe from Uley Mine, South Australia) were obtained from the Clay Minerals Society's Source Clays Repository. CWN, a nontronite from Cheney, Washington, USA was purchased from Ward's Natural Sciences Establishment, Inc. SYn-1 and SWy-2 were in powder form and were used as received. Chunks of NAu-1, NAu-2, and CWN were ground in a ball mill. The clays were Na saturated, dispersed, and the clay-sized fraction (<2 μm) isolated by sedimentation as described by O'Loughlin et al. [75] and maintained as an aqueous suspension. The Fe content of the clay-sized fraction was determined by HF

dissolution. A 25 mg dry mass sample of each clay was placed in a 50 mL polypropylene centrifuge tube followed by the addition of 6 mL of 1.8 M H₂SO₄ and 500 µL of 48 wt% HF. The open tubes were placed in a boiling water bath for 30 min. After cooling to ambient temperature, 5 mL of a 5 wt% H₃BO₃ solution was added to neutralize the HF prior to analysis of the Fe concentration by inductively coupled plasma-optical emission spectrometry. Based on this analysis, the clays had the following Fe content (wt%): Barasym (0%), SWy-2 montmorillonite (2.8%), NAu-1 (18.8%), NAu-2 (24.8%), and CWN (21.4%).

2.2. Preparation of Reduced Clays

The clays were reduced (Figure 1) using a modified version of the citrate-bicarbonate-dithionite (CBD) method as described by Ilgen et al. [76]. Briefly, citrate-bicarbonate (CB) buffer solution was prepared by combining 800 mL of 0.3 M sodium citrate with 100 mL of 1 M NaHCO₃. A volume of clay suspension corresponding to 500 mg dry mass was added to 50 mL of CB buffer and dispersed with mild sonication. The CB/clay suspensions were then transferred to a 240 mL serum bottle, an additional 100 mL of CB buffer was added to each, and the bottles were sparged with Ar to remove O₂ from the suspension and headspace. After sparging for 15 min, 267 mg of sodium dithionite was added, and the bottles were sealed with rubber septa and aluminum crimp caps and placed in a 70 °C water bath for 30 min with periodic mixing. The bottles were then placed in an anoxic glove box (Coy Laboratory Products, Grass Lake, Michigan, 3–5% H₂ in N₂ and Pd catalyst to maintain O₂ in the box <1 ppm) and the CBD-reduced clay suspensions were immediately transferred to 250 mL centrifuge bottles with O-ring closures. The reduced clays were recovered by centrifugation and washed (i.e., resuspension followed by centrifugation) with a series of anoxic solutions over a period of ~6 h as follows: 1 wash with 75 mL of 5 mM NaCl; 2 washes with 75 mL of 2 M NaCl adjusted to pH 4 with 1 M HCl; 1 wash with 75 mL of 5 mM NaCl; and 1 wash with 75 mL of 20 mM 3-morpholinopropane-1-sulfonic acid (MOPS) buffer (pH 7.2). After the final washing, the clays were resuspended in 20 mM pH 7.2 MOPS buffer. All work with the CBD-reduced clays was conducted under anoxic conditions.

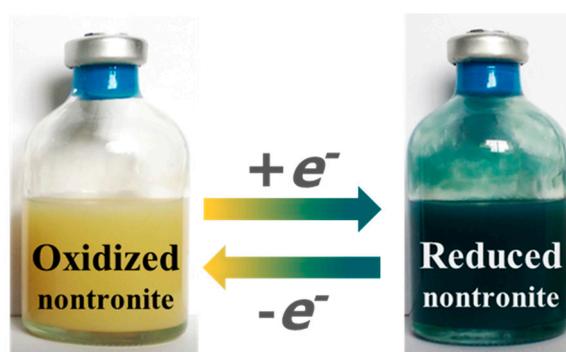


Figure 1. Oxidized and citrate-bicarbonate-dithionite (CBD)-reduced NAu-1 nontronite.

2.3. Experimental Setup

Experiments were initiated by spiking 10 mL of either native or CBD-reduced clay suspensions (4 g clay L⁻¹ in pH 7.2 MOPS buffer) in 15-mL polypropylene centrifuge tubes with 500 µL of 10 mM Hg(II) acetate. The tubes were placed on a rotating mixer (Rotamix RKVSD, Appropriate Technical Resources). After 24 h, samples were prepared for XAFS spectroscopy. The suspensions were centrifuged, and the solids were placed inside holes machined in 1.5 mm thick Plexiglass sample holders (slide-mount sample holders) that were then covered with Kapton film held in place with Kapton tape. All work was conducted under anoxic conditions and the samples for XAFS were transferred to the beamline nearby in gas-tight containers.

Using the procedure described above, the effects of pH were examined over the range of pH 5–9 with CBD-reduced NAu-1. Suspensions of NAu-1 were prepared in 20 mM

1,4-diethylpiperazine (DEPP, pH 5.14); 2-morpholinoethanesulfonic acid (MES, pH 6.08); MOPS (pH 7.10); 1,4-piperazinedipropanesulfonic acid (PIPPS, pH 8.09); or DEPP (pH 9.23) and spiked with 500 μL of 10 mM Hg(II). Similarly, the effects of chloride concentration were examined in suspensions of NAu-1 buffered at pH 7.2 in 20 mM MOPS containing either 0, 1, or 10 mM NaCl and spiked with 500 μL of 10 mM Hg(II).

2.4. Hg XAFS Analysis

Hg L_{III}-edge (12,284 eV) XAFS measurements were carried out at the MR-CAT/EnviroCAT insertion device beamline (Sector 10, Advanced Photon Source City State, Abbr (if USA), Country) [77]. X-ray absorption near edge spectra (XANES) and extended X-ray absorption fine structure (EXAFS) spectra were collected in fluorescence mode using gas-filled ionization chambers on samples prepared under anoxic conditions as described above in Section 2.3. Samples were transported in O₂-free containers to the beamline and spectra were collected at $-140\text{ }^{\circ}\text{C}$ within several hours of sample preparation using a Linkam® stage cooled by liquid N₂. The anoxic integrity of samples prepared and analyzed this way has been demonstrated in previous work [78]. Absolute energy calibration was established by setting the inflection point in the spectrum of Au foil to 11,919 eV. Relative energy calibration between samples was maintained by simultaneous in-line scanning a Hg/Sn amalgam sample [45]. Radiation-induced changes in the spectra were not observed at this temperature. Spectra were obtained from up to 10 fresh locations on each sample and averaged to produce the final spectrum.

Analysis of the spectra was based on comparisons to Hg standards. The standards spectra dataset included: hydrated Hg(II) and Hg(II) complexed to acetate in aqueous solution [45]; polycrystalline HgO from Sigma-Aldrich; 2 mM HgClO₄ sorbed to 4 g maghemite L⁻¹ at pH 6.0 [46]; Hg₂Cl₂ (calomel) powder obtained from Sigma-Aldrich; and Hg(0) produced by reduction with ferrous phases (magnetite, green rust) [43,46]. The polycrystalline Hg powders were mounted on the adhesive side of Kapton tape and their absorption spectra were measured in transmission. Solution samples were mounted in a 1.5 mm thick sample holder with Kapton film windows and the spectrum was measured in fluorescence. Adsorbed Hg standards were mounted as wet pastes in a 1.5 mm thick sample holder with Kapton windows and measured in fluorescence mode. Normalization and background removal of the data were done using the program AUTOBK [79].

3. Results and Discussion

3.1. Interaction of Hg(II) with Native and CBD-Reduced Smectites

The reaction of Hg(II) with the native clays is not expected to result in reduction of Hg(II), as a priori the solids have no reducing equivalents to be transferred to Hg (the clay purification process and the reactions with Hg(II) were carried out under ambient (i.e., oxic) conditions). Thus, the spectra measured from the native oxidized solids are expected to represent Hg(II) adsorbed onto the corresponding clays. Figure 2 compares the data to aqueous and solid Hg(II) standards. The edge position and shape of the clay samples is similar to the Hg(II) standards, showing a characteristic “knee” between 12,285 eV and 12,290 eV corresponding to the deep dip and the large second peak in the derivative spectra near 12,287 eV and 12,292 eV, respectively. Although there is speciation-dependent variation in their position and amplitude, these features in the XANES are present in all Hg(II) spectra and have been used for determining Hg(II) in prior work [45,46,48,49]. Therefore, Hg associates with the native clays as adsorbed Hg(II) and these spectra represent the speciation of solid-phase Hg(II) in the absence of redox processes.

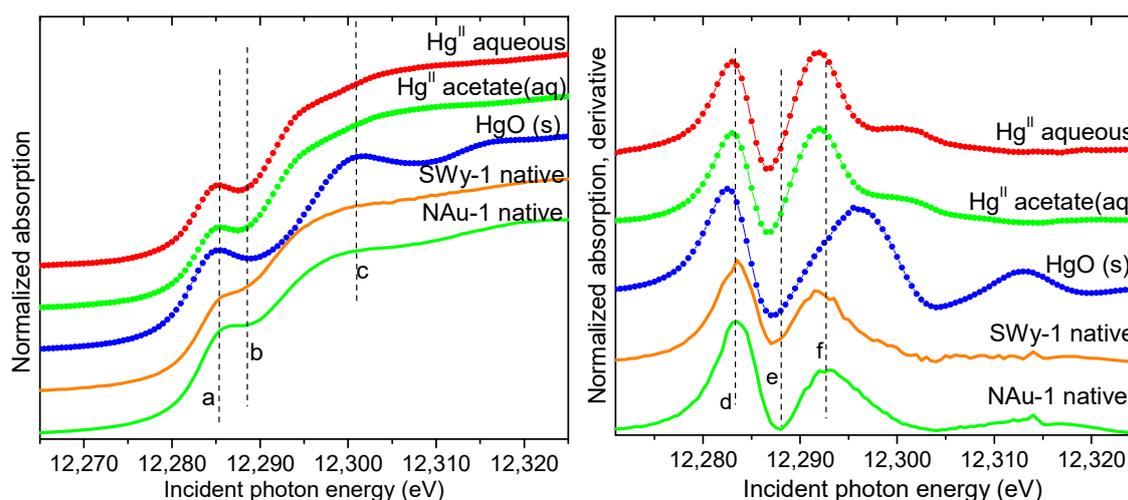


Figure 2. Hg L_{III}-edge XANES spectra (left) and derivative (right) obtained from the solid phase in the systems with native NAu-1 and SWy-2 clays. The spectra are compared to aqueous and solid Hg(II) standards (symbols), which exhibit a deep dip and the large second peak in the derivative spectra (features e and f). The vertical dashed lines (a–f) are a guide to the eye.

The Hg XANES spectra from the CBD-reduced clays reacted with Hg(II) are shown in Figure 3. Relative to the oxidized native clay systems discussed above only the spectrum from Hg(II) reacted with the CBD-reduced Barasym clay (0 wt% Fe) displays the XANES features corresponding to Hg(II); which indicates no reduction of Hg(II) by either Barasym or any potential reductants (e.g., unreacted dithionite) that might not have been removed during the washing procedure following CBD reduction. All other systems with reduced clays (i.e., those containing 2.8–24.8 wt% Fe) lack the “knee” and the features near 12,290 eV indicative of Hg(II). The Hg spectra from the reduced clay systems are identical to that of the Hg(0) standard. Therefore, in all systems with CBD-reduced clays containing Fe (SWy-2, NAu-1, NAu-2, and CWM), Hg(II) was reduced to elemental Hg(0) under the conditions of our study.

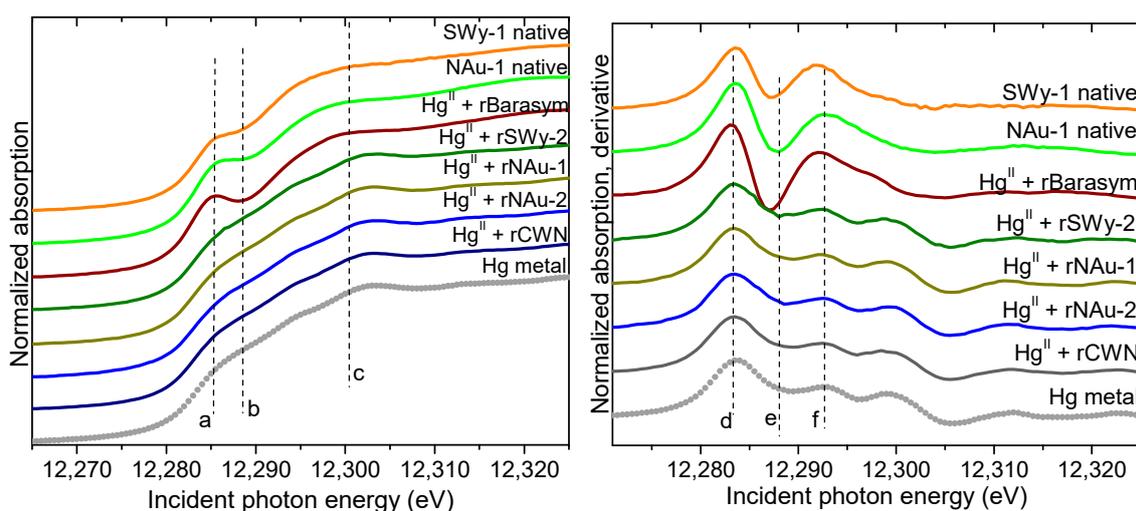


Figure 3. Hg L_{III}-edge XANES spectra (left) and derivative (right) obtained from the solids in systems with clays of different Fe content reduced by the CBD method. Spectra are compared to that of Hg(II) in the native (un-reduced) clays and to the Hg(0) standard (symbols). The vertical dashed lines (a–f) are a guide to the eye, delineating features corresponding to the different valence states of Hg.

3.2. Effect of pH on Hg(II) Reduction by CBD-Reduced NAu-1

The pH of natural systems can vary broadly, so we examined the potential for reduction of Hg(II) by CBD-reduced NAu-1 at pH values from 5–9, a range representative of the majority of aquatic and terrestrial environments. The XANES spectra from the CBD-reduced NAu-1 clay reacted with Hg(II) at pH 5, 6, 7, 8, and 9 are shown in Figure 4. Relative to the native NAu-1 clay system where Hg was associated with the solids as adsorbed Hg(II), the spectra of Hg in the reduced NAu-1 solids were identical to that of the Hg(0) standard. Therefore, the reduction of Hg(II) by Fe(II) in reduced NAu-1 clays was possible at all pH values between 5 and 9 under the conditions of our experiments and the resulting species was elemental Hg(0).

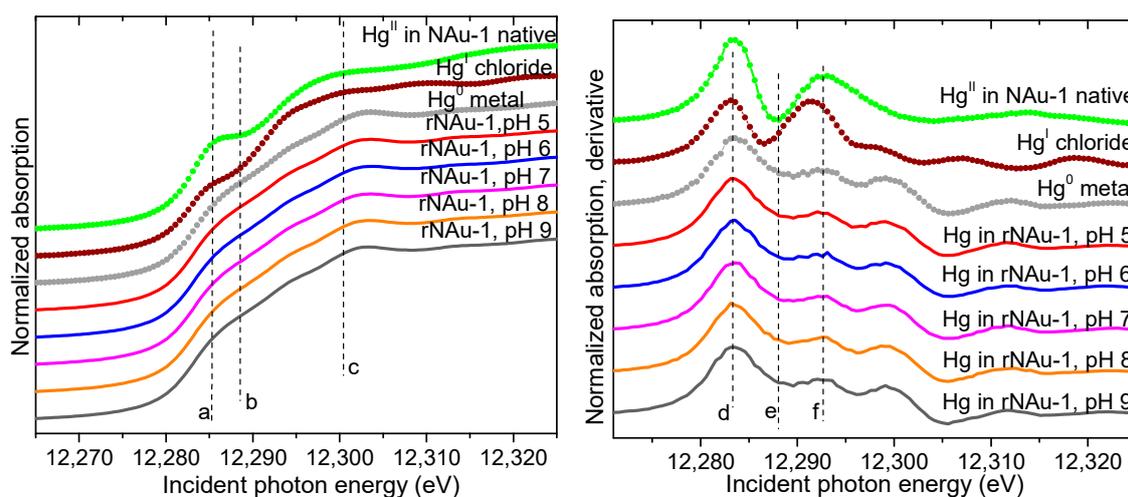


Figure 4. Hg L_{III}-edge XANES spectra (**left**) and derivative (**right**) from the solids in the rNAu-1 systems at pH 5–9 compared to standards (symbols). The vertical dashed lines (a–f) are a guide to the eye, delineating features corresponding to the different valence states of Hg.

3.3. Effect of Chloride Concentration on Hg(II) Reduction by CBD-Reduced NAu-1

Chloride (Cl[−]) is ubiquitous in aquatic and terrestrial environments and is known to form strong aqueous complexes with Hg(II) [80]. The formation of these complexes (e.g., HgCl⁺, HgCl₂, HgCl₃[−], and HgCl₄^{2−}) can influence the behavior of Hg(II), including inhibition of Hg(II) reduction [44,46,81–83] and sorption on clays, metal oxides, and natural sediments [53,84–87]. Previous work has shown that the presence of Cl[−] in a reducing Fe(II)/(III)-oxide system can prevent complete reduction of Hg(II) to Hg(0) and promote formation of metastable Hg(I) as calomel (Hg₂Cl₂) [46]. We tested for potential effects of Cl[−] on Hg(II) reduction by CBD-reduced NAu-1 clay at Cl[−] concentrations of 0, 1, and 10 mM; which covers the range of Cl[−] concentrations typical of freshwaters, near-surface groundwater, and soils. The XANES derivative spectra from these systems are compared to standards in Figure 5. The spectra lack the deep minimum near 12,287 eV and the second maximum near 12,292 eV that are characteristic of the Hg(II) and Hg(I) standards. Instead, the spectra at all Cl[−] concentrations are identical to the Hg(0) standard. Therefore, the presence of Cl[−] did not result in calomel formation and Hg(II) was reduced to elemental Hg(0) under the conditions of these experiments. However, given that Hg(I) species are generally metastable, it is important to note that the lack of detection of Hg(I) in the 1 and 10 mM Cl[−] systems does not preclude its formation and subsequent disappearance prior to the XAFS measurements of the solids made 24 h after exposure of Hg(II) to the CBD-reduced clay.

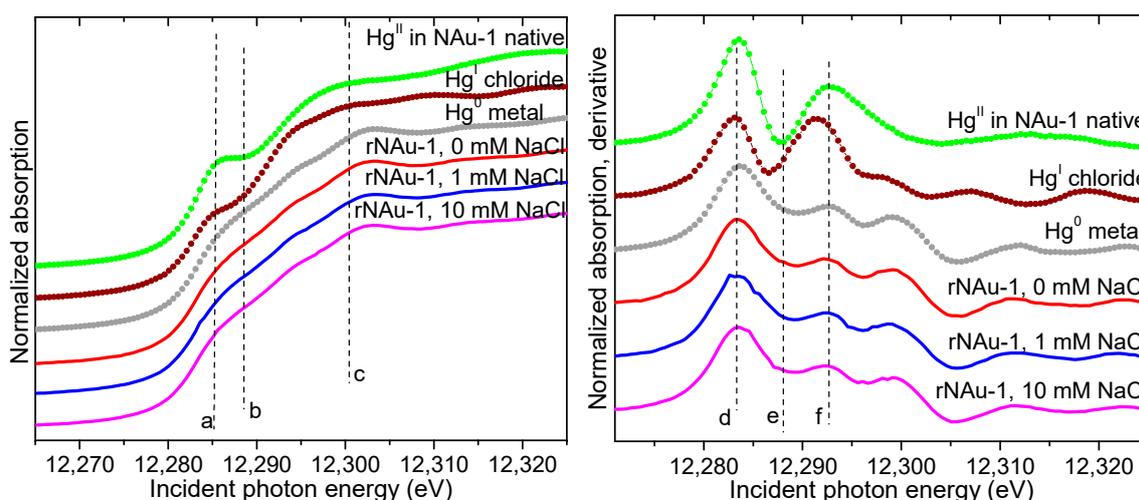


Figure 5. Hg L_{III}-edge XANES spectra (**left**) and derivative (**right**) from the solids in the rNAu-1 systems with increasing NaCl concentrations compared to standards (symbols). The vertical dashed lines (a–f) are a guide to the eye, delineating features corresponding to the different valences of Hg.

3.4. Environmental Relevance

Emission of Hg(0) from aquatic and terrestrial systems to the atmosphere is a major component of the global biogeochemical Hg cycle and reduction of Hg(II) to Hg(0) in soils and sediments is a fundamental part of this process [8–10]. However, the mechanisms of the reduction of Hg(II) to Hg(0) in soils and sediments are not fully understood [9]. Photochemical reduction of Hg(II) can occur in surface waters and at the soil surface [88–90] and the dark reduction of Hg(II) can occur via biotic and abiotic processes. Many microbes common to aquatic and terrestrial environments can enzymatically reduce Hg(II) to Hg(0), primarily as an inducible detoxification mechanism [91,92], although in some dissimilatory Fe(III)-reducing bacteria the ability to reduce Hg(II) is constitutive and involves the respiratory electron transport chain [93,94]. In addition, natural organic matter (NOM), including humic and fulvic acids, can reduce Hg(II) to Hg(0) [82,95–99]. Furthermore, the activity of Fe(III)-reducing microbes in soils and sediments generates Fe(II) species that can reduce Hg(II) to Hg(0) [43–46,48–51]—including structural Fe(II) in smectite clays as shown in this study—creating the possibility for coupled biotic–abiotic Hg(II) reduction pathways under Fe(III)-reducing conditions. Indeed, Peretyazhko et al. reported reduction of Hg(II) to Hg(0) by biogenic Fe(II) in a hydromorphic tropical soil [100]. Similarly, Debure et al. attributed reduction of Hg(II) to Hg(0) in anoxic subsurface sediments to the presence of magnetite and siderite [101], and Poulin et al., reported a correlation between aqueous Hg(0) concentrations and products of microbial Fe/Mn reduction in a riparian soil impacted by historic Hg contamination [102]. Given that Fe-bearing clays are common constituents of many soils and sediment and that structural Fe(II) in clays has been shown to reduce a broad range of organic and inorganic contaminants, it is reasonable to expect that they might contribute to Hg(II) reduction and subsequent Hg(0) emission in situ.

Our results showing the reduction of Hg(II) to Hg(0) by structural Fe(II) in smectite clay minerals increases the number of known Fe(II) species that can reduce Hg(II). However, fundamental aspects of this reaction need to be explored including: the reaction kinetics; the effects of Hg(II) complexation by NOM, minerals, and microbes; the presence of competing electron acceptors (e.g., molecular oxygen and nitrate); and the potential reactivity of structural Fe(II) in other phyllosilicate clay minerals (e.g., illites, vermiculites, etc.). Moreover, the reduction of Fe(II) in smectite clays in near-surface environments is likely to be due primarily to microbial activity, particularly by Fe(III)-reducing bacteria and archaea, and in laboratory studies the dynamics of Fe(II) speciation and clay mineralogy are often quite different during microbial reduction (or simulation of microbial reduction by the addition of Fe(II)) compared to strictly abiotic reduction (e.g., by dithionite as in this study) of structural

Fe(III) [62,63,65,103–107]. As such, additional studies focused on the dynamics of Hg(II) during microbial reduction of Fe(III)-bearing smectite clays are needed.

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