THE EFFECTS OF BIOGEOCHEMICAL MODIFICATION OF Fe-RICH SMECTITE ON THE FATE OF Pb

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Abstract—Fe-rich smectite is ubiquitous in soil environments and closely linked to the fate and mobility of hazardous trace metals and particularly to the variations in the biogeochemical redox reactions of structural Fe that determine the sorption and desorption properties of clay minerals. The biotic/abiotic redox reactions of a Fe-rich smectite, nontronite (NAu-1), were performed at various reaction times using the Fe-reducing bacterium *Shewanella oneidensis* MR-1 at 30ºC and Na-dithionite ($Na_2S_2O_4$), respectively. The extent of biotic Fe-reduction of NAu-1 after 30 days of incubation reached up to 10.7% of total Fe and the range of abiotic Fe-reduction varied from 4.9−46.6% at reaction times of 5 min, 30 min, 1 h, and 4 h. The biotically and abiotically Fe-reduced NAu-1 samples were spiked with Pb concentrations of 0.07, 0.2, 0.5, and 1.0 mg/kg and incubated under aerobic or anaerobic conditions for 24 h.

The amounts of Pb in the supernatants were analyzed using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) and Multi-collector (MC)-ICP-MS. The amounts of Pb removed from the supernatants were negatively related to the extent of Fe(III) reduction in the abiotically Fe-reduced NAu-1 samples. In contrast, less Pb (~15%) was removed from the biotically Fe-reduced NAu-1 samples with a similar extent of Fe(III) reduction. Changes in the isotopic $^{208/204}$Pb ratio indicated that the lighter ^{204}Pb isotope was preferentially adsorbed to the NAu-1 samples with less Fe reduction and indicated that variations in the net layer charge affected isotopic fractionation. Significant differences in the $^{208/204}$Pb ratios for NAu-1 samples that were biotically Fe-reduced under anaerobic conditions were measured and indicate that the reversibility of the structural/chemical modifications that occur under redox conditions can affect Pb removal and, thus, isotope fractionation. These results collectively infer that the biogeochemical properties of clay minerals should be considered in order to understand the fate of trace metals in natural environments.

Key Words—Abiotic Reduction, Fe-reducing Microbe, Nontronite, Pb Isotopic Composition, Pb Removal.

INTRODUCTION

Clay minerals play a significant role in the adsorption of non-degradable heavy metals and the immobilization of hazardous trace metals in natural environments. Smectites have been widely used as efficient adsorbents to remove heavy metals from aqueous solutions (Plus *et al.*, 1991; Gupta and Bhattacharyya, 2008; Jiang *et al.*, 2010) because of the high surface area, high cation exchange capacity, and the feasibility for surface modification (Bhattacharrya and Gupta, 2006; Tanabe, 2012) to enhance the sorption capability. Smectite has been suggested as an effective adsorbent (Tsunashima *et al.*, 1981; McKinley *et al.*, 1995) for long-term treatment because of the importance of remediating U-contaminated sites (Tsunashima *et al.*, 1981; Chisholm-Brause *et al.*, 2001). Moreover, sorption studies on hydrous iron oxides (Gadde and Laitinen, 1974; Swallow *et al.*, 1980) and iron oxyhydroxides (Benjamin and Leckie, 1981; Lu *et al.*, 2011) have been continuously examined to optimize the sorption capacity in aqueous solutions at various pH levels, heavy metal concentrations, and ionic strengths. Recently, microbes have been reported to be capable of reducing clay mineral structural elements, such as Fe, which can modify the surface properties and grain sizes of Fe-rich smectites (Kim *et al.*, 2005; Jaisi *et al.*, 2007, 2008). These clay mineral modifications and biogeochemical redox reactions with heavy metals have been applied to immobilization experiments (Komlos *et al.*, 2008; Jaisi *et al.*, 2009; Bishop *et al.*, 2014; Singh *et al.*, 2017) because heavy metal mobility is redox sensitive. For example, the immobilization of the highly radioactive element technetium (Tc) was controlled by the redox reaction of nontronite with the Fe-reducing bacterium *Shewanella putrefaciems* CN32 (Jaisi *et al.*, 2009). Re-oxidation of Fe was coupled with Tc(VII) reduction to the immobilized Tc(IV) form, microbial Fe(III) reduction promoted clay aggregation with Tc, and re-oxidation of Fe was prevented so long-term immobilization of Tc was maintained.

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Lead (Pb) is a major pollutant from anthropogenic sources (Cheng and Hu, 2010). A limited number of studies have focused on Pb sorption and desorption behavior under various biogeochemical conditions. Moreover, the stable isotope ratios of Pb ($^{208/204}$Pb, $^{207/204}$Pb, $^{206/204}$Pb, $^{208/206}$Pb, and $^{207/206}$Pb) are frequently used as a 'fingerprint' to trace pollutant sources in natural environments (Rosman *et al.*, 1994; Kersten *et al.*, 1997; Mackenzie and Pulford, 2002; Cheng and Hu, 2010). Understanding the biogeochemical reactions of Pb with clay minerals during sediment transport could allow a more accurate determination of pollutant sources and soil provenance.

The purpose of the present study was to investigate the correlation between biogeochemical/structural modifications of clay minerals induced by biotic and abiotic Fe-reduction on the sorption and desorption behavior of Pb, using a range of Pb concentrations and isotopes under both aerobic and anaerobic conditions and a battery of methods, including X-ray diffraction (XRD) and a 1,10-phenanthroline Fe assay to characterize the structural and chemical modifications of Fe-reduced clay mineral (NAu-1) samples and Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Multi-collector (MC)-ICP-MS, and $^{208/204}$Pb isotopic ratios.

MATERIALS AND METHODS

Biotic/abiotic reduction of NAu-1

A bulk sample of nontronite, NAu-1, was purchased from the Source Clays Repository of The Clay Minerals Society. The <0.2 μm fraction was separated from a water column according to Stokes' Law, centrifuged to sediment the clay, and freeze-dried. The designation "NAu-1" will, henceforth, refer to the <0.2 μm fraction of NAu-1. The initial cell concentration of the facultative Fe reducer *Shewanella oneidensis* MR-1 was 3×10^8 CFU/mL and was inoculated into the M1 medium (Myers and Nealson, 1988) using 4 g/L NAu-1 as electron acceptor under anaerobic conditions. After 30 days incubation, the Fe-reduced NAu-1 samples were washed 3 times using deoxygenated distilled water to remove the microbes and the M1 medium.

The Na-dithionite ($Na_2S_2O_4$) treatment with a citrate-bicarbonate (CB) buffer (Stucki *et al.*, 1984) was used to abiotically reduce the Fe in NAu-1. Samples (5 g) of freeze dried NAu-1 were dispersed in 2 L of CB buffer (trisodium citrate, $Na_3C_6H_5O_7{\cdot}2H_2O$) and sodium bicarbonate ($NaHCO_3$) and equilibrated overnight. The clay/buffer solutions were heated to 70ºC in a water bath and 12 g of Na-dithionite was added. The reaction was stopped at various times (5 min, 30 min, 1 h, and 4 h) to control the extent of Fe(III) reduction by cooling the samples in an ice-bath. After treatment, the supernatants were removed using centrifugation and the samples were washed 3 times with deoxygenated 5 mM NaCl solution.

The extent of Fe(III) reduction for each Fe-reduced NAu-1 sample was measured using a 1,10-phenanthro-line assay (Stucki, 1981). Briefly, total Fe was extracted from 5-mg reduced NAu samples using a HF/H_2SO_4 extraction method. A 10% 1,10-phenanthroline-ethanol solution was added during the extraction to form an Fe-1,10-phenanthroline complex, which turns orange when it binds with Fe(II). Beer's law was used to calculate the Fe(II) concentrations using the absorbance of the Fe(II)-1,10-phenanthroline complex at 510 nm. The total Fe concentrations were calculated using the same procedure with 1,10-phenanthroline after complete reduction of Fe(III) to Fe(II) using hydroxylamine hydrochloride. Then, the extent of Fe(III) reduction was expressed as the %Fe(II) of total Fe (*i.e.* ($100 \times$ Fe(II)/total Fe)).

Pb-spiked reaction

Pb was spiked into the abiotically/biotically Fe-reduced NAu-1 samples under various experimental conditions, such as for different extents of Fe(III) reduction in the NAu-1 samples under both aerobic and anaerobic conditions. The Pb stock solution was made using Standard Reference Material 981 Common Lead Isotopic Standard (NIST SRM981) in order to trace isotope fractionation during the Pb-spiked reaction. Nitric acid (2M) was used to dissolve the Pb-wire (~60 mg) to prepare the Pb stock solution and then the exact concentration (1262 mg/kg) was measured using ICP-MS. The Pb stock solution was diluted with 10-mM MOPS (3-morpholinopropane-1-sulfonic acid) solution to several concentrations (21, 60, 150, and 300 mg Pb/kg).

Samples (600 mg) of NAu-1 were dispersed in 299 mL of 10 mM MOPS solution and then 1 mL of the Pb stock solution was added to prepare the final target concentrations of 0.07, 0.2, 0.5, and 1.0 mg Pb/kg. The reaction was stopped at 12 time intervals (0 min, 10 min, 20 min, 0.5 h, 1 h, 1.5 h, 2 h, 4 h, 7 h, 12 h, 18 h, and 24 h) by freezing the sample. The supernatants were prepared using a 0.2-μm PES (polyethersulfone) syringe filter (Merck Millipore Ltd., Tullagreen, Carrigtwohill, Ireland) before freezing. The separated pellets were analyzed using X-ray diffraction (XRD) and a 1,10-phenanthroline assay to confirm any mineralogical and biogeochemical changes in the NAu-1 samples (samples were prepared in an anaerobic chamber, but were exposed to the atmosphere at the moment of analysis). The XRD analysis was performed on air-dried, oriented mount samples using a Rigaku MiniFlex(II) automated diffractometer (Rigaku, Japan) using Cu-Kα radiation. The XRD patterns were recorded using 0.02º2θ steps from 2 to 14º2θ at a 1.5º2θ/min scan speed.

Inductively Coupled Plasma Mass Spectrometer (ICP-MS) and Multi-collector (MC)-ICP-MS analysis

Lead concentrations and Pb isotopic ratios ($^{208/204}$Pb, $^{207/204}$Pb, $^{206/204}$Pb, $^{208/206}$Pb, and $^{207/206}$Pb) in the supernatants were measured using ICP-MS (Elan DRC-e, PerkinElmer SCIEX, Concord, Ontario, Canada) and MC-ICP-MS (Nu plasma II, Nu Instruments, Wrexham,

UK). The $^{208/204}$Pb isotopic ratio was adopted because it showed a distinct fractionation. Column purification of samples was used prior to Pb analysis to increase the accuracy of the MC-ICP-MS analyses. Lead was separated from the matrix using an anion exchange column extraction as described by Choi *et al.* (2013). Briefly, ~2 mL of Biorad® MP-1M resin (the stationary phase for the separation) was packed into a Teflon® column using 4 mL of distilled water and then cleaned using 6 N HCl, 0.5 N HNO₃, and a 8 N HF/2 N HCl mixture. Before each sample was loaded into a MP-1M resin column, 6 mL of 7 N HCl with 0.001% H₂O₂ was loaded to condition the column. Then, 2 mL of a sample that had been dried and re-dissolved in the HCl and H₂O₂ mixture was loaded into the column. A 6-mL aliquot of the 7 N HCl and 0.001% H₂O₂ mixture was eluted through the column again to collect the Pb in the matrix solution. The collected solutions were dried and re-dissolved in 1 N HCl solution for the second extraction. The second column extraction was performed using fresh MP-1M resin packed into a Teflon® column that had been conditioned using 1 N HCl solution. The sample matrix was eluted from the column in the first step using 4 mL of 1 N HCl solution and then the separated Pb was eluted using 8 mL of 0.1 M HCl solution. The solution that contained the Pb collected at the final column purification step was dried and re-dissolved in 1% HNO₃ to determine the Pb concentrations and isotope ratios using an Elan DRC-e ICP-MS and a Nu Plasma II MC-ICP-MS at the National Institute of Environmental Research.

RESULTS

Biotic/abiotic reduction and re-oxidation of NAu-1

The extent of abiotic Fe(III) reduction in NAu-1 samples increased up to 46.6% after a 4 h reaction while biotic reduction was up to 10.7% after a 30-day incubation (Table 1). Both biotically and abiotically Fe-reduced NAu-1 samples were spiked with Pb under aerobic conditions and reoxidation of Fe occurred and the range in Fe(III) reduction was 1.1−6.4% within 24 h. Reoxidation of Fe (5.7−6.3%) was also measured under anaerobic conditions. The XRD patterns of the abiotically (sample #2, 11.5%; sample #4, 46.6%) and biotically (sample #5, 10.7%) Fe-reduced NAu-1 samples that were spiked with 1.0 mg/kg of Pb under aerobic (a) and anaerobic (an) conditions for 24 h were compared to samples without added Pb (Figure 1). Regardless of whether or not the sample was spiked with Pb, the abiotically Fe-reduced NAu-1 sample had a 14.7 Å d_{001} spacing (sample #2) typical of the nontonite structure (Figure 1a). The sample with greater Fe(III) reduction (sample #4) had a ~13.2 Å peak (Figure 1b). In contrast, a biotically Fe-reduced NAu-1 sample (sample #5) without added Pb had a lower basal spacing (d_{001} = 12.8 Å), but the basal spacing expanded (d_{001} = 14.2 Å) after Pb was added under both aerobic and anaerobic conditions (Figure 1c).

Pb concentrations in the supernatants

The Pb sorption capacities (mg/kg) of abiotically and biotically Fe-reduced NAu-1 samples for a range of initial Pb concentrations (0.07, 0.2, 0.5, and 1.0 mg/kg) were plotted against reaction time (min) for samples
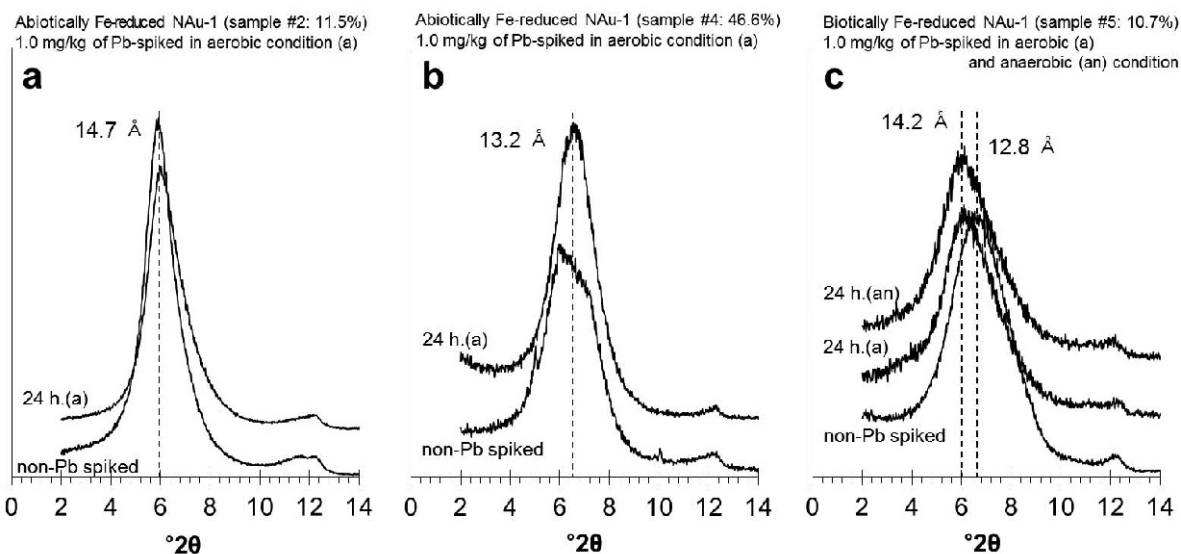

Figure 1. X-ray diffraction patterns for abiotically (sample #2: 11.5%, sample #4: 46.6%) and biotically (sample #5: 10.7%) Fe-reduced NAu-1 samples that were spiked with 1.0 mg/kg Pb under aerobic (a) and anaerobic (an) conditions after 24 h reaction and are compared to a NAu-1 sample without added Pb. The numbers in parentheses are the %Fe reduction values for the NAu-1 samples.

with Fe(III) reduction (samples #1−5) that ranged from 4.9 to 46.6% under both aerobic and anaerobic conditions (Figure 2). The amounts of Pb removed (100% of an initial 1.0 mg/kg Pb concentration was removed in 1440 min) from the supernatants were calculated to compare the Pb sorption behavior for each experimental condition. Under aerobic conditions, abiotically Fe reduced NAu-1 samples removed a range of Pb amounts (79.1% from sample #1, 98.0% from sample #2, 96.2% from sample #3, and 72.4% from sample #4) that depended on the extent of Fe(III) reduction (Figures 2a−2d). For a biotically Fe reduced NAu-1

sample with 10.7 % Fe(III) reduction (sample #5), 83.5% of Pb was removed under aerobic conditions (Figure 2e), but 99.5% of Pb was removed under anaerobic conditions (Figure 2f). An abrupt decrease in the supernatant Pb concentration (0.077 mg/kg to 0.006 mg/kg) was measured under anaerobic conditions (Figure 2f).

Pb isotopic composition

The isotopic $^{208/204}$Pb ratios for a total concentration of 0.5 mg/kg Pb added to abiotically reduced NAu-1 (samples #1 and #3) samples under aerobic conditions (Figure 3a) and a biotically reduced NAu-1 (sample #5)
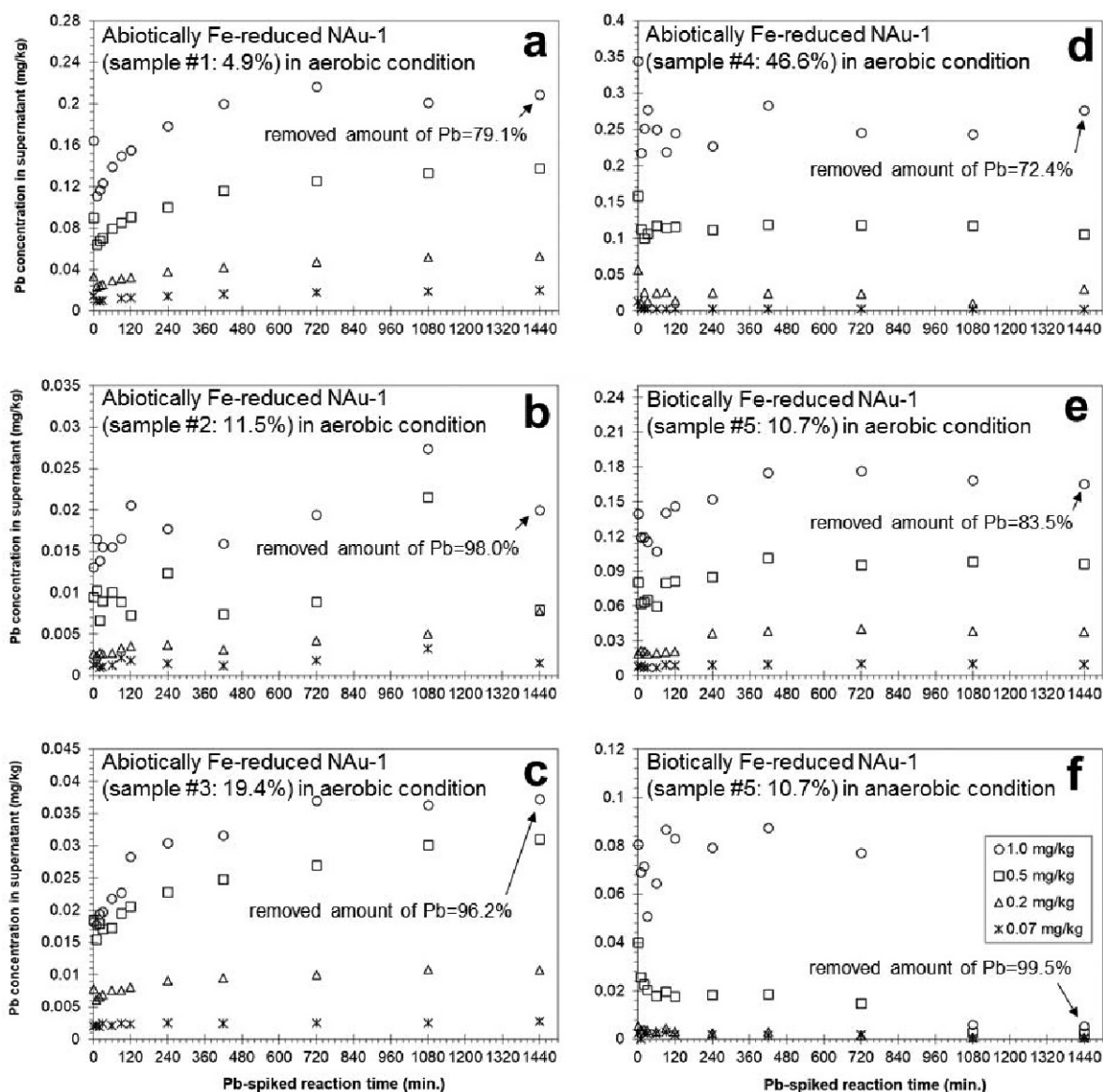

Figure 2. The Pb concentrations in supernatants for abiotically (sample #1, 4.9%; sample #2, 11.5%; sample #3, 19.4%; and sample #4, 46.6%) and biotically (sample #5, 10.7%) reduced NAu-1 samples under aerobic (a − e) and anaerobic (f) conditions for a range of Pb concentrations (0.07, 0.2, 0.5, and 1.0 mg/kg) at various reaction times. The amounts of Pb (%) removed were calculated using the Pb concentrations in the supernatants measured after 1440 min reaction (100% of an initial 1.0 mg/kg Pb concentration removed after 1440 min reaction). The numbers in parentheses are the %Fe reduction values for the NAu-1 samples.
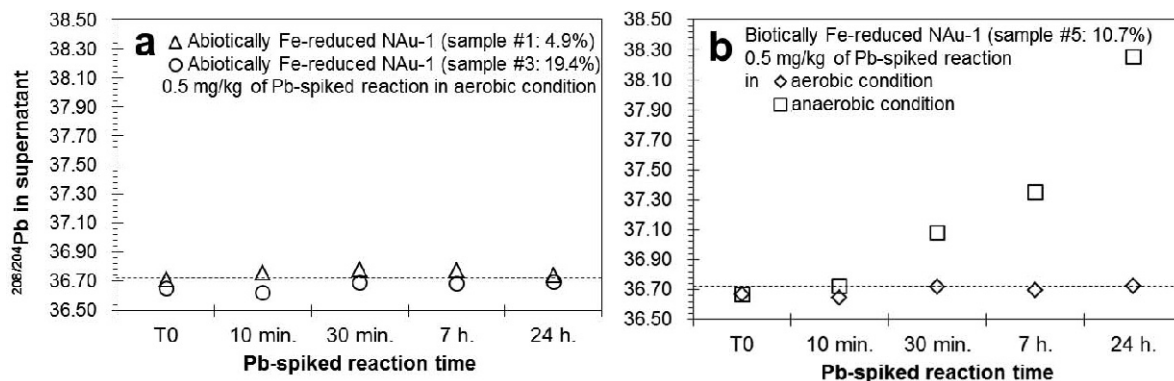
Figure 3. The $^{208/204}$Pb isotopic ratios for (spiked with 0.5 mg/kg Pb) abiotic NAu-1 (sample #1 and sample #3) samples under aerobic conditions (a) and a biotic NAu-1 (sample #5) sample under both aerobic and anaerobic conditions (b). The numbers in parentheses are the %Fe reduction values for the NAu-1 samples. The $^{208/204}$Pb isotopic ratio for the standard Pb used to spike the sample is indicated by the dashed line.

sample under both aerobic and anaerobic conditions (Figure 3b) were compared to the isotopic ratio of standard Pb (dashed line). The Pb isotopic compositions were measured in the supernatants and a higher $^{208/204}$Pb ratio indicates that the lighter ^{204}Pb isotope was preferentially adsorbed. Somewhat higher $^{208/204}$Pb ratios were measured for an abiotically reduced NAu-1 (4.9% Fe(III) reduction, sample #1) sample in comparison to sample #3 which underwent 19.4% Fe(III) reduction (Figure 3a). The biotically reduced NAu-1 (sample #5) sample had a significant increase in the $^{208/204}$Pb isotopic ratio after 30 min reaction under anaerobic conditions in comparison to aerobic conditions (Figure 3b).

DISCUSSION

The biogeochemical and structural modification of Fe-reduced NAu-1 samples may control Pb sorption behavior and induce isotopic fractionation. Changes in the amounts of Pb in the supernatants were likely associated with Pb adsorption to NAu-1 and/or precipitation, but no new Pb mineral phase was detected in the present study. For the abiotically Fe-reduced NAu-1 samples, Pb was removed (79.1−98.0%) as the extent of Fe(III) reduction was increased (Figures 2a−2c), although Pb had a small tendency for removal between 11.5 and 19.4% Fe(III) reduction. This observation is not surprising because the net negative charge of the NAu-1 structure after Fe(III) reduction was greater and caused a stronger tendency to adsorb cations. However, an abrupt decrease in the amount of Pb (72.4%) removed was measured in the sample (sample #4) that underwent the highest abiotic Fe(III) reduction (Figure 2d). The structural modification (layer collapse) of NAu-1 by 46.6% abiotic Fe-reduction shown by the 13.2 Å d_{001} peak (Figure 1b) may indicate heterogeneity in the structure of NAu-1 and, thus, modify sorption behavior. Less Pb (83.5%) was removed by a biotically Fe-

reduced NAu-1 (sample #5) sample in comparison to an abiotically Fe-reduced NAu-1 (98.0%) sample with a similar amount of Fe(III) reduction (11.5 and 10.7%, respectively) under aerobic conditions (Figures 2b, 2e). In previous studies, secondary-phase Fe-mineral precipitation has been reported for the biotic Fe-reduction of smectite (Dong *et al.*, 2009; Kim *et al.*, 2004; Koo *et al.*, 2014; Zhang *et al.*, 2007). In contrast, other studies observed no such secondary-phase Fe-mineral precipitation during either biotic or abiotic reduction (Komadel *et al.*, 1995; Lee *et al.*, 2006; Ribeiro *et al.*, 2009; Pentrakova *et al.*, 2013). The reason for these conflicting observations has yet to be identified but, in the present study, no secondary-phase Fe-mineral was observed. This indicates that either no Fe was liberated or possibly some amount of Fe(II) was liberated during biotic Fe reduction and became adsorbed to the NAu-1 samples (Neumann *et al.*, 2013). If the latter case occurred, the competition between liberated Fe and Pb for the limited sorption sites of Fe-reduced NAu-1 samples would largely determine the sorption behavior of Pb. For divalent cations in a multi-metal ion system (Pb, Cd, Ni, and Cu), less Pb adsorption was observed in kaolinite in comparison to a single-metal ion system (Jiang *et al.*, 2010). The sorption sites of biotically Fe-reduced NAu-1 samples may be occupied by liberated Fe(II), which can inhibit the adsorption of Pb to a biotically reduced NAu-1 (sample #5) sample.

No significant change occurred in the Pb isotopic composition for biotically Fe-reduced NAu-1 samples under aerobic conditions, while the removal of the lighter ^{204}Pb isotope continuously increased under anaerobic conditions (Figure 3b). This isotope fractionation is likely associated with irreversible biogeochemical modifications of NAu-1 as shown by the differences in the amounts of residual Fe(II) after the Pb-spiking reaction (1.1 and 5.7% in 24 h, Table 1). Furthermore, the abrupt decrease in the amounts of Pb in the supernatants after 18 h of reaction (Figure 2f) strongly

Table 1. Summary of the extent of abiotic/biotic Fe(III)-reduction in nontronite (NAu-1) at various reduction times and Pb reaction times for Pb-spiked samples under aerobic/anaerobic conditions.

			Extent of Fe(III) reduction of NAu-1 $((100 \times Fe(II)/Fe_{tot}),$ %)				
	— Abiotic/Biotic Fe-reduction of NAu-1 —			After reaction with Pb			
No.	Reduction time	Extent of Fe(III) reduction (% Fe(II))	Aerobic conditions, % Fe(II)		Anaerobic conditions, %Fe(II)		
			30 min	24 h	30 min	7 h	24 h
1	5 min	4.9	1.2	1.2			
2	30 min	11.5	1.9	1.5	9.1	6.7	6.3
3	Abiotic 1 h	19.4	2.9	1.7			
4	4 h	46.6	13.2	6.4			
5	Biotic 30 d	10.7	1.9	1.1	7.7	6.4	5.7

suggests that biogeochemical modification of biologically reduced NAu-1 under anaerobic conditions changed the sorption behavior; however, the specific mechanism was not identified in the present study.

The isotopic Pb composition of supernatants in abiotically Fe-reduced NAu-1 samples under aerobic conditions followed the Pb sorption behavior with the extent of Fe(III) reduction until the structural modification began (Figure 1). The NAu-1 sample with 4.9% Fe(III) reduction (sample #1) showed a slightly higher [208/204]Pb ratio in the supernatant in comparison to the NAu-1 sample with 19.4% Fe(III) reduction (sample #3). This indicates that NAu-1 samples with a greater net negative charge and a stronger Coulombic force selectively adsorbed the heavier [208]Pb isotope.

CONCLUSIONS

The Pb-spiking experiments using an Fe-rich smectite (NAu-1 nontronite) with biogeochemical properties modified by abiotic and biotic Fe-reduction indicate that Pb adsorption is closely linked to NAu-1 layer collapse followed by structural Fe(III) reduction. Particularly, irreversible structural modification and the amount of residual Fe(II) in biotically reduced NAu-1 samples significantly determined Pb sorption behavior and resulted in isotopic fractionation.

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