

Phosphate Dissolution Caused by Bioreduction of Poorly Crystalline Al(III)/Fe(III) Hydroxide Coprecipitated Minerals

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Abstract

Under reducing conditions, phosphate dissolution has been attributed to the release of that associated with Fe(III)-oxide minerals, whereas, for Al(III)-oxide minerals, the dissolution of associated phosphate has been considered to be less susceptible. The objective of this research was to determine bioreduction of Fe(III) and dissolution of phosphate as affected by the proportion of Al(III) in Fe(III)/Al(III)-hydroxide coprecipitates (Al-FH). Aqueous suspensions of phosphated Al-FHs with 0 to 100% Al/(Al+Fe) molar ratios were microbially reduced using *Shewanella putrefaciens* CN32. During 4 d-reduction, 33 % of initial Fe(III) was reduced from pure Fe(III) hydroxide; however, the Fe(II) production from Al-FH with 50% Al coprecipitation was 64 % of initial Fe(III). The presence of Al did enhance the reducibility of Fe(III) in Al-FH systems by altering surface chemistry of Al-FH. Accompanying Fe bioreduction, phosphate dissolution occurred and varied with different Al contents in Al-FHs, indicating that redox-inactive Al(III) play a distinct role in controlling phosphate cycles by affecting reduction of poorly crystalline Fe(III) hydroxide.

Key Words

Phosphate, dissolution, Fe hydroxide, bioreduction, Al hydroxide, coprecipitation

Introduction

Phosphate is a major nutrient in soils and a pollutant in aquatic environments; its fate in soils and associated environments has been of interest to scientists concerned with plant nutrition and environmental protection (Sharpley *et al.* 2002). Soil with lower redox potentials may show enhanced phosphate dissolution, which has been implied to be related to the reductive dissolution of Fe-oxides (Patrick and Khalid 1974; Holford and Patrick 1981; Phillips 1998). The biogeochemical cycling of Fe in aquatic and terrestrial environments is often driven by and coupled with microbial processes. Poorly crystalline and crystalline Fe(III) (hydr)oxides can be utilized as electron acceptors by dissimilatory Fe-reducing bacteria (DIRB) (Lovley and Phillips 1986). In soils, most Fe (hydr)oxide are Al-substituted (Schwertmann and Taylor 1989) due to the ubiquity and abundance of Al in rocks and soils. Therefore, coprecipitated systems between Al and Fe (hydr)oxides are properly considered as a potential media affecting phosphate agrogeochemical cycles. The objective of this study was to determine the bioreducibility of Fe(III) hydroxide as affected by proportion of Al(III) in Fe(III)/Al(III)-hydroxide coprecipitates (Al-FH) and the following phosphate dissolution.

Material and Methods

Materials of Al-FH were synthesized by mixing solutions of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and hydrolyzing with 1.0 M KOH with Al/(Al+Fe) molar ratios of 0, 0.1, 0.2, 0.5, 0.75, and 1.0 (hereafter referred as 0-, 10-, 20-, 50-, 75-, and 100-Al-FH). Bioreduction of Al-FH with pre-sorbed PO_4 was conducted by inoculating dissimilatory Fe(III)-reducing bacteria, *Shewanella putrefaciens* CN 32. Concentrations of Al+Fe and pre-sorbed P were 50 mM and 1000 mmol/kg, respectively. Local structure transformation of bioreduced Al-FH was examined using X-ray absorption spectroscopy (XAS) at the National Synchrotron Light Source, Brookhaven National Laboratory in Upton, NY. The initial pH was 6.8, but drifted to between 8.6–8.8 during 4 d of incubation.

Results and Discussion

Fe(III) bioreduction.

No significant Fe(II) dissolution was observed during Al-FH bioreduction. Total Fe(II) production (0.5 M HCl extractable) during 4 d-incubation of various Al-FH is shown in Figure 1a. In general, Fe(III) reduction increased over time (except 100-Al-FH). With regard to various Al coprecipitations, the Fe(II) production decreased as Al proportion increased at the first day of incubation. At the end of incubation, however, Al-FH with 10% Al coprecipitation produced greatest Fe(III) reduction, and the Fe(II) concentration dropped as Al proportion increased from 10 to 75%. In order to evidence the effect of Al coprecipitation on Fe(III) reduction, Fe(II) production is converted to the percentage of initial Fe(III) addition and shown in Figure 1b.

The proportion of Fe(III) reduced tended to increase as Al coprecipitation increased from 0% to 50% at the first day. This trend was more pronounced after 4 d-incubation, wherein the proportion of Fe(III) reduced from 50-Al-FH (65 %) approximately doubled that from pure Fe hydroxide (33 %), suggesting that the coprecipitation of Al hydroxide may promote the long-term reducibility of Al-FHs. Al-FHs with 12 d-bioreduction were examined by extended X-ray absorption fine structure (EXAFS) spectroscopy to determine the related mechanisms. The second shell of all samples was ascribed to Fe-Fe paths with interatomic distance of 3.04 and 3.47 Å (Figure 2). The rising second-shell intensity of 0-Al-FH implied the increasing crystallinity of 0-Al-FH structure during bioreduction, whereas 75-Al-FH behaved in an opposite way. Inhibiting the crystallization of Fe (III) hydroxide by Al coprecipitates could enhance the reducibility of Al-FH in that it renders surfaces of Fe(III) hydroxides more accessible for electron transfers.

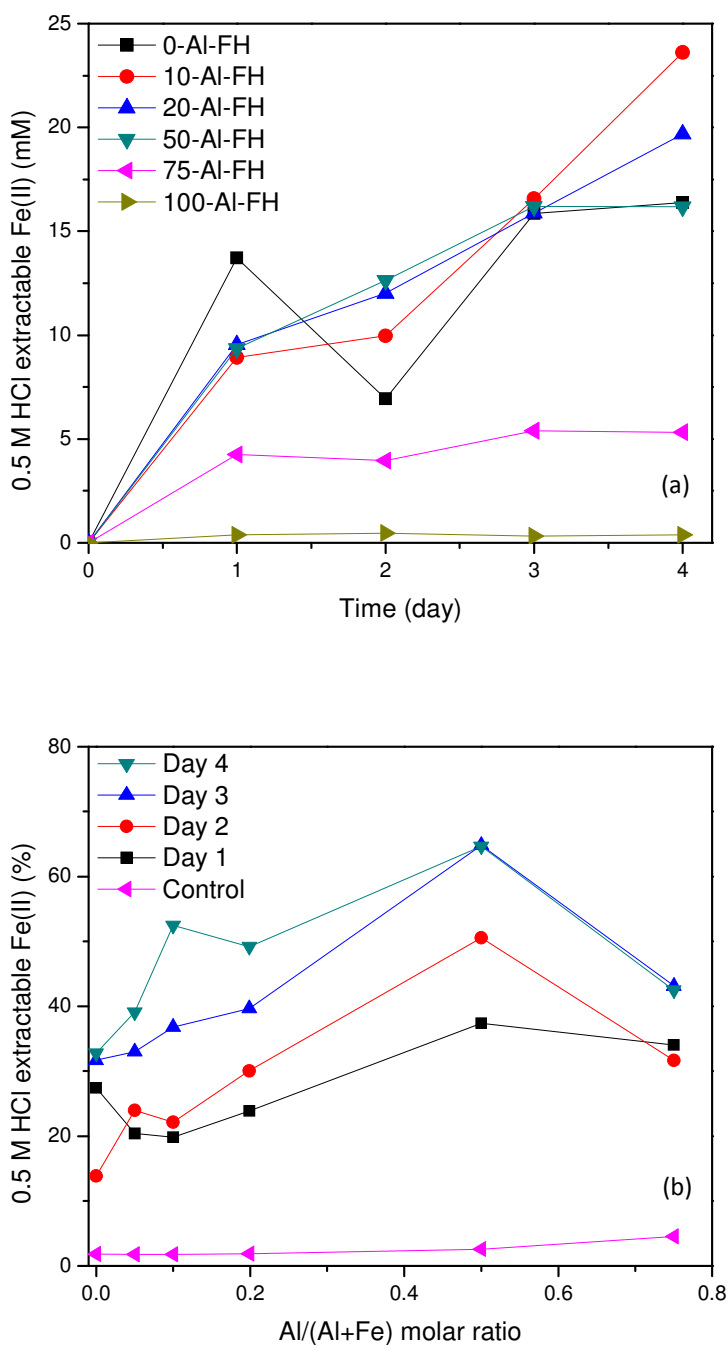


Figure 1. HCl-extractable Fe(II) produced during bioreduction of various Al-FHs represented as (a) concentration and (b) percentage of initial Fe(III) addition. Fe(II) production of uninoculated controls were collected at the fourth day.

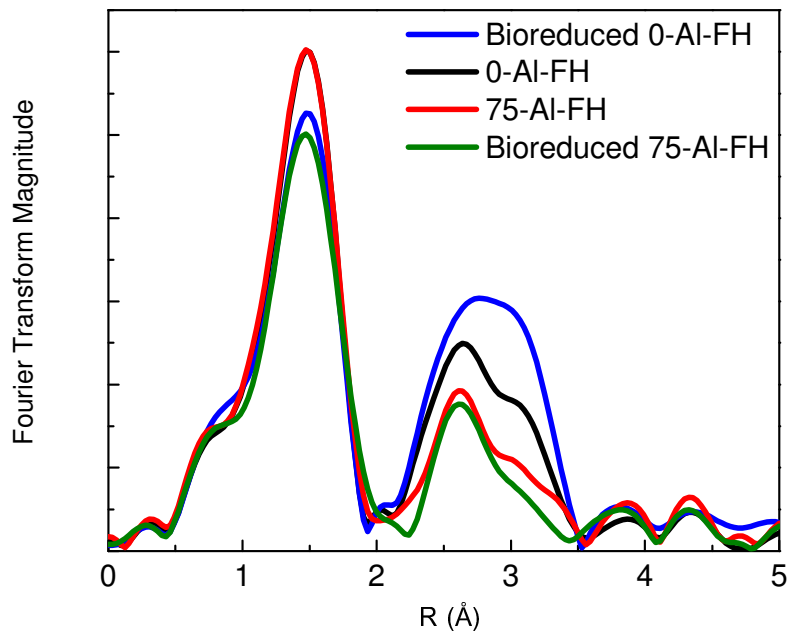


Figure 2. Fourier transformed Fe K-edge EXAFS spectra of 0-Al-FH and 75-Al-FH and that with 12 d-bioreduction (without phase correction).

Phosphate dissolution

Phosphate dissolution accompanied Fe(III) bioreduction of various Al-FHs is shown in Figure 3. In the absence of Al coprecipitation, dissolved phosphate increased by up to 5-fold over time, reaching 12.6 $\mu\text{mol/L}$ after 4 d-incubation. Two possibilities could account for phosphate dissolution: (1) reductive dissolution of phosphated Fe(III) sites, and/or (2) the increasing pH happened during Fe(III) reduction process (Figure 4).

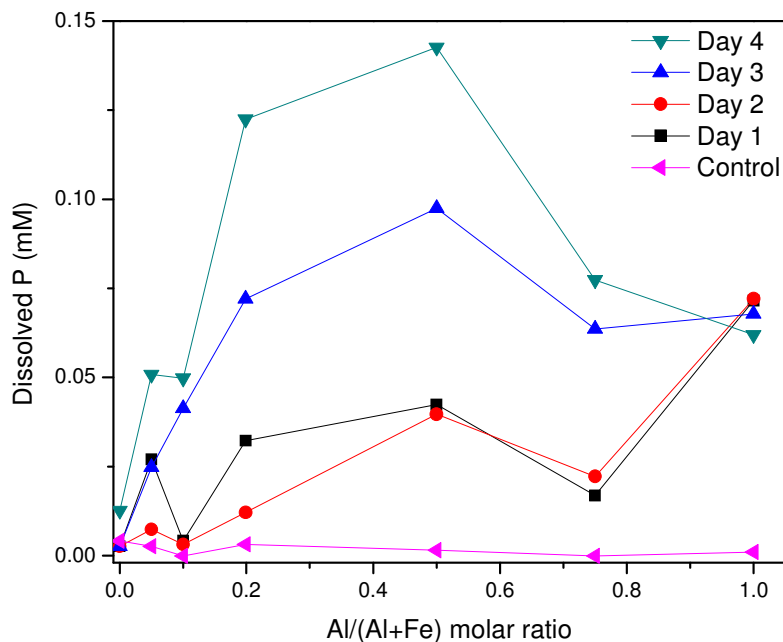


Figure 3. Dissolved phosphate occurred during bioreduction of various Al-FHs. Dissolved phosphate of uninoculated controls were collected at the fourth day.

Phosphate dissolution from various Al-FHs also increased over time generally, except that from pure Al hydroxide. In the suspension of 50-Al-FH, dissolved phosphate reached the greatest concentration during 4 d-incubation than that from other Al-FHs. Wherein, phosphate concentration stayed constant initially but

increased essentially at the last 2d-incubation, which rose from 97.5 $\mu\text{mol/L}$ at day 3 to 142.6 $\mu\text{mol/L}$ at day 4. Although phosphate concentration increased almost 50% in 24h, the pH values of these two samples were similar. Therefore, phosphate dissolution caused by the increasing pH might be considered as a minor effect. At the end of incubation, dissolved phosphate increased substantially as the proportion of Al in the coprecipitates increased from 0 to 50%, and then decreased as Al proportion was further increased to 75%. The behavior of phosphate dissolution mimicked the tendency of Fe(II) production represented as proportion of initial Fe(III) addition (Figure 1b), indicating surface chemistry of Al-FH may have decisive effects in reductive phosphate dissolution.

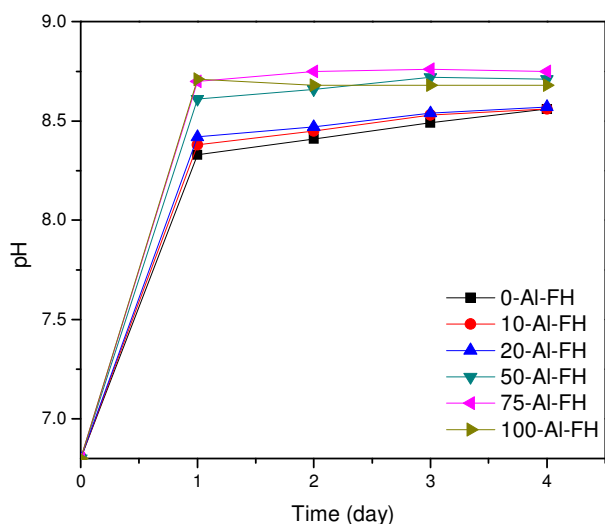


Figure 4. The pH values during four day-bioreduction of various Al-FHs. The pH values for uninoculated controls were collected at the fourth day and ranged from 6.91~6.99 among all Al-FHs (data not shown).

Conclusion

This research demonstrated that phosphate dissolution could be induced by microbial reduction of poorly crystalline Fe(III) hydroxide, and this Fe(III) bioreduction was enhanced with increasing Al(III) hydroxide coprecipitation. Bacterially mediated redox processes strongly influence Fe(III) reducibility, which may be controlled by surface chemical properties of Fe-bearing minerals. Studies in local structure transformation during bioreduction process are necessary. The ubiquity of Al(III) in soils has generated interest in determining its impact on biogeochemical destinies of iron and phosphate. Regardless of the redox-inactive nature, Al(III) could potentially affects Fe(III) reduction and phosphate dissolution in reductive aquatic and terrestrial environments.

Reference

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