Arsenic Mobilization by the Dissimilatory Fe(III)-Reducing Bacterium Shewanella alga BrY

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The mobility of arsenic commonly increases as reducing conditions are established within sediments or flooded soils. Although the reduction of arsenic increases its solubility at circumneutral pH, hydrous ferric oxides (HFO) strongly sorb both As(V) (arsenate) and As(III) (arsenite), the two primary inorganic species. Thus, in the presence of excess HFO, reductive dissolution of iron may be the dominant mechanism by which As is released into solution.

In this paper, we report that the dissimilatory iron-reducing bacterium Shewanella alga strain BrY promoted As mobilization from a crystalline ferric arsenate as well as from sorption sites within whole sediments. S. alga cells released arsenate from the mineral scorodite (FeAsO₄·2H₂O) as a result of dissimilatory (i.e., respiratory) reduction of Fe(III) to Fe(II). Solid-phase analysis with SEM-EDS and XAFS (X-ray absorption fine structure) spectroscopy revealed that the valence states of Fe and As in the solid-phase product were identical to those in solution, i.e., Fe(II) and As(V). Additionally, As sorbed to sediments from Lake Cœur d’Alene, ID, a mining-impacted environment enriched in both Fe and As, was solubilized by the activity of S. alga BrY. In neither experiment was As(III) detected. We conclude that arsenic mobility can be enhanced by the activity of dissimilatory iron-reducing bacteria in the absence of arsenic reduction.

Introduction

Mining activity in the Silver Valley of northern Idaho has led to extensive contamination of Lake Cœur d’Alene (CDA) sediments with metals and trace elements such as Pb, Zn, Cd, Fe, Zn, and As (1, 2). Recent data indicate that maximum arsenic concentration is found near the sediment-water interface whereas maxima for less redox-active elements such as lead and zinc are located deeper within the sediment column (2, 3). This distribution is not predicted by the historical pattern of deposition and suggests that postdepositional mobilization of arsenic has occurred.

A number of studies suggest that arsenic can be mobilized in environments having steep redox gradients. Aggett and colleagues found that concentrations of As(V), As(III), and Fe(II) are elevated in surficial sediments and waters immediately overlying the sediment-water interface in Lake Ohakuri, New Zealand (4, 5). Although these observations were attributed to As diffusion and reduction consequent to Fe(III) reduction (4, 5), only microbially mediated arsenic reduction was demonstrated (5). Arsenic concentration also appears to be elevated in surficial sediments of the Amazon Shelf (6). Investigators working in this system determined that most As is associated with reactive metal oxides and hypothesized that microbial Fe(III) reduction was responsible for increased As solubilization (6). Finally, Seyler and Martin (7) observed that arsenic concentration in a permanently stratified lake peaks sharply at the oxygen chemocline, well above the sediment-water interface. In each of these examples, arsenic was found to accumulate near the anoxic-oxic boundary, suggesting that its mobility may be mediated in part by redox-sensitive sorption-dissolution reactions.

Reduction of As(V) to As(III) is one mechanism by which arsenic may be mobilized. Incubation of As-contaminated sediments from the Aberjona Watershed with exogenous ferric and ferrous arsenate minerals resulted in elevated concentrations of aqueous arsenic (8). Since the rate and extent of As solubilization from both ferric and ferrous arsenates were nearly identical, it was concluded that under these conditions dissimilatory iron-reducing bacteria (DIRB) did not influence arsenic solubility (8). Additionally, a respiratory As(V)-reducing bacterium isolated from this watershed, strain MIT-13, was capable of greater arsenic mobilization from synthetic minerals than were sediment consortia (8). Thus, arsenic-reducing bacteria may play a significant role in mobilizing As from iron-arsenate minerals via direct reduction of arsenate. Biological arsenic reduction has been detected in Lake CDA sediment microcosms (3), but the significance of this metabolism in situ is unknown.

The binding of As(V) by naturally occurring HFO is well established (6, 9). Recent data indicate that iron(III) oxides such as amorphous ferric hydroxide, ferrihydrite, and goethite sorb As(III) in addition to As(V) (10–13). Raven et al. (11) demonstrated that sorption of As(III) and As(V) onto ferrihydrite is highly pH- and concentration (As:Fe)-dependent. When [As] was low relative to [Fe] (0.267 mol of As (kg of Fe)⁻¹), As(V) was sorbed in slightly greater amounts than As(III) below pH 7.5, while the reverse was true above pH 7.5. The pH at which adsorption envelopes crossed decreased as relative [As] increased, until at a concentration of 13.3 mol of As (kg of Fe)⁻¹, more As(III) sorbed the ferrihydrite than As(V) over a range of pH 3–11. Clearly, the sorption properties of As(III) with respect to HFO must be taken into account in developing models to predict arsenic behavior in flooded soils and sediments.

When soils and sediments become reduced, pore water concentrations of both Fe(II) and arsenic have been observed to increase (14–18). Under these conditions, aqueous arsenic is predominantly in the +3 oxidation state, suggesting that reduction of As(V) to As(III) may be a prerequisite to As mobilization. It is equally possible, however, that the binding influence of iron(III) oxides on both As(V) and As(III) would influence the kinetics of arsenic mobilization. Thus, under reducing conditions, the mechanism of arsenic mobilization may also depend on Fe(III) reduction. In fact, on the basis of recent findings for As(III) sorption to iron hydroxides (10, 13), it seems highly likely that Fe(III) reduction is a necessary prerequisite.

The purpose of this study was to determine whether DIRB participate in arsenic mobilization, particularly as it pertains
to sediments of Lake CDA. We report evidence for arsenic mobilization from both synthetic and natural sediment materials in the absence of arsenic-reducing bacteria. Mobilization was mediated by DIRB, and the oxidation state of the arsenic remained unaltered.

Materials and Methods

Contaminated Sediment Source. Lake Coeur d’Alene is one of northern Idaho’s most popular recreation spots for water sports as well as hunting and fishing, and it serves as the water supply for at least six local communities (19). However, it has been contaminated by tailings and mine wastes from silver and lead mining activities along the North Fork of the CDA River near Kellogg, ID, now an EPA Superfund site (20). Several 50-cm cores were taken using a gravity corer (22) along a transect in Lake CDA near the CDA River delta at Harrison, ID (June 1997). Cores were retrieved in 2.5 in. PVC pipe, capped, and stored at 4 °C under a column of lake water. Upon returning to the laboratory, they were either preserved immediately in an anaerobic chamber (N2; CO2; H2; 75%; 15%; 10%) or stored at 4 °C under flowing N2 until processed.

Sediment redox conditions were inferred from depth profiles of reduced iron. HCl-soluble Fe(II) was determined by incubating 1 g of sediment with 10 mL of HCl (0.5 N) for >24 h and measuring the concentration of Fe(II) with ferrozine (23).

Total metal contaminants were determined by aqua regia digest followed by inductively coupled plasma (ICP) spectrophotometric analysis (ACME Analytical Labs, Vancouver, BC).

Microbial densities were estimated microscopically. Sediment materials were incubated in formaldehyde (4%) and disodium pyrophosphate (1 g L−1) for >24 h to dislodge cells from particulate material. Sediments were centrifuged at 500 rpm for 5 min, and total cell densities in the supernatants were estimated by staining with 4,6-diamidino-2-phenylindole (DAPI) and counting directly under epifluorescence (24).

As(V) and As(III) Determinations. Dissolved arsenic was speciated and quantified by modifying the method of Strickland and Parsons (25–27). As(V) (arsenate) concentrations were determined by acidifying 100–µL samples in 100 µL of HCl (24 mM). An aliquot of the acidified samples (100 µL) was then added to 900 µL of the reaction mix containing the following components per liter: 6 g of ammonium molybdate, 10.8 g of ascorbic acid, 0.136 g of potassium dihydrogen phosphate, and 67.3 mL of concentrated H2SO4. Each component was stored as a separate solution (25). Samples were heated in a water bath at 78 °C for 10 min and placed in ice for 5 min. The absorbance at 865 nm was compared to acidified arsenate standards.

As(III) (arsenite) concentrations were determined by oxidizing a second sample in 100 µL of KIO3 (5 mM) and HCl (48 mM) for 10 min and then assaying spectrophotometrically at 865 nm. The difference between oxidized and unoxidized samples represented the concentration of As(III). This method was used for arsenic concentrations ranging from 150 to 1000 µM (lower limit of detection ~50 µM). When lower concentrations of arsenic (15–100 µM) were quantified, the sample size was increased to 300 µL, and the entire acidified sample was added to 600 µL of reaction mix (lower limit of detection ~10 µM). Phosphate interferes with the assay by acting as an analogue of AsO4−3 and must be omitted or accounted for.

Media and Cultivation. Strict anaerobic techniques as described by Balch and Wolfe (28) were followed throughout the study. Incubations were performed in 20-mL pressure tubes sealed with butyl rubber stoppers and aluminum crimps. The media and buffers were boiled, cooled, and dispensed under flowing, deoxygenated N2 gas. All transfers were made using needles and syringes flushed with high-purity deoxygenated N2. Incubations were performed in 20 mM PIPES buffer (pH 7.0) amended with the following constituents per liter: 1.5 g of NH4Cl, 5 g of NaCl, 0.1 g of CaCl2, 0.1 g of KCl, and 10 mL of modified Wolfe’s vitamins and trace minerals (29, 30).

S. alga BrY is a facultatively anaerobic bacterium isolated from estuarine sediments in New Hampshire (31). Under anaerobic conditions S. alga BrY couples the oxidation of an electron donor to the reduction of Fe(III) to Fe(II). Cell suspensions of S. alga BrY were prepared by inoculating a single colony of cells grown on tryptic soy agar into 100 mL of tryptic soy broth in a 250-mL Erlenmeyer flask and incubating on a rotatory shaker at 30 °C, 125 rpm, 12–16 h. Cells were harvested by centrifugation (6000g, 20 min) under N2 gas, washed in the amended PIPES buffer, and resuspended in 10 mL of the same.

An anaerobic cell suspension (ca. 1010 cells mL−1 final concentration) of S. alga BrY was incubated in 10 mL of anaerobic PIPES buffer (pH 7.0) with 1 mM sodium arsenate as the sole electron acceptor and 10 mM lactate as the sole electron donor in order to determine whether S. alga BrY cells can enzymatically reduce As(V). Controls received no lactate.

Dissolution of Arsenic from Scorodite. Scorodite (FeAsO4·2H2O) was prepared as previously described (18). A S. alga BrY cell suspension (ca. 1010 cells mL−1) was incubated anaerobically in 10 mL of amended PIPES buffer with 10 mM (2.6 mg mL−1) scorodite and 10 mM lactate. Subsamples were centrifuged at 12000g for 10 min under a headspace of N2, and the supernatant was sampled for As(V), As(III), and Fe(II). Controls received either heat-killed cells or no cells. Heat-killed cells were prepared by incubating 5 mL of cell suspension in a water bath at 80 °C for 20 min.

Solid-Phase Analysis of Scorodite Reduction Products. Oxidation and structural states of solid-phase arsenic and iron were determined using X-ray absorption fine structure (XAFS) spectroscopy, which was performed on beamline 4-1 (an 8-pole wiggler) at the Stanford Synchrotron Radiation Laboratory (SSRL). The ring operated at 3 GeV with a current ranging from ~100 to ~50 mA. Energy selection was accomplished using a Si(220) monochromator with an unfocused beam. XANES spectra were recorded by fluorescent X-ray production using a wide-angle ionization chamber (32). A Ge filter was used with the ionization chamber to limit counting of scattered primary radiation. Incident and transmitted intensities were measured with in-line ionization chambers. XANES spectra were recorded over the energy range of ~200 to ~1000 eV about the K-edge of iron (7111 eV) and arsenic (11867 eV). Each scan was calibrated by placing arsenic or metallic iron between second and third in-line ionization chambers. Samples were mounted as thin films of the reacted solid to minimize self-absorption and sealed with a Kapton polyamide film to prevent oxidation or moisture loss while minimizing X-ray absorption. Thin films were created using a modified procedure of Marcus and Flood (33) to restrict the change in optical density to <0.1 in order to minimize self-absorption effects. Between three and six individual spectra were averaged for each sample.

The oxidation state of both arsenic and iron were determined by noting peak positions in first-derivative transforms of the spectra; oxidation states were quantified by noting integrated peak areas of Gaussian transforms of the spectra; oxidation states were quantified by noting integrated peak areas of Gaussian transforms of the spectra.
separated for identification/quantification. Local structural states of Fe and As were determined using the extended portion of the EXAFS (EXAFS) spectrum, using procedures described by Manning et al. (10). A detailed EXAFS analysis of model arsenic minerals, including scorodite, is presented in Foster et al. (34).

For scanning electron microscopy and energy dispersive spectroscopy, samples were dried under N2(g) and then mounted on a carbon stub. The materials were then carbon coated and analyzed on an Amray SEM operating at 20 keV. Infrared spectra of reacted solids in a matrix of KBr were recorded with a Perkin-Elmer Spectrum 2000 Fourier transform infrared spectrometer.

**Dissolution of Arsenic from Whole Sediments.** Surficial sediments of Lake CDA (upper 0–5 cm) were stirred in 1 vol of sodium arsenate (100 mM) in open air for 3 days to oxidize all Fe and to saturate all potential binding sites within the sediment with AsO43-. Saturated sediments were then equilibrated for 72 h in the anoxic amended PIPES buffer described above. Prior to inoculations, sediments were centrifuged at 6000g, 20 min, and resuspended in 1 vol of the same buffer. As(V)-saturated, sterile sediments (0.5 mL) were prepared by adding 0.5 mL of this suspension to 9.5 mL of anoxic amended PIPES buffer and then autoclaving (121 °C, 10 min). Incubations were initiated with the addition of 10 mM lactate (final concentration) and 0.5 mL of S. alga BrY cell suspension. Controls received either heat-killed cells or no cells. Incubations were sampled over time for As(V), As-(III), and Fe(II).

**Fe(III) Determination in Sediment Experiments.** Because hydroxylamine-reducible Fe(III) is thought to be well-correlated to microbially reducible Fe(III), its concentration was determined in the sediments artificially saturated with As(V) (see above) by the method described by Lovley and Phillips (35). Sediment slurry (0.5 mL) was added to 4.5 mL of HCl (0.5 N), and another 0.5-mL sample was reduced with hydroxylamine (0.25 M) in HCl (0.25 M) for 24 h. Fe(II) was quantified by the ferrozine assay, and the difference in Fe(II) concentrations between the two treatments was determined to be the concentration of hydroxylamine-reducible Fe(III).

**Results and Discussion**

**Sediment Characteristics.** The trace element enrichment of Lake CDA sediments by mine tailings has been thoroughly documented (1, 2, 19–21). Cores in this study were analyzed for Fe(II), total iron and trace element abundance, and total cell densities.

Environmental redox conditions are difficult to ascertain reproducibly. Fe(II) concentrations may be a useful alternative for estimating the redox status of environmental samples. The concentrations of HCl-soluble Fe(II) were approximately 23 mmol (kg of sediment)-1 (wt wt) at the sediment–water interface, increasing in the first 10–20 cm to approximately 47 mmol kg-1 (Figure 1). This pattern was consistently observed at all sample sites, indicating that Lake CDA sediments (CDA River delta site) are reduced beneath the sediment–water interface, increasing in the first 10 cm to approximately 20 cm to approximately 47 mmol kg-1. This pattern agrees with previously reported Lake CDA sediments (CDA River delta site) are reduced beneath the surficial material (top 10–15 cm). This pattern agrees with previously reported Lake CDA sediments (CDA River delta site) are reduced beneath the surficial material (top 10–15 cm). This pattern agrees with previously reported Lake CDA sediments (CDA River delta site) are reduced beneath the surficial material (top 10–15 cm). This pattern agrees with previously reported Lake CDA sediments (CDA River delta site) are reduced beneath the surficial material (top 10–15 cm).

**Evaluating the Potential for As(V) Reduction by S. alga BrY Cells.** The ability of DIRB to mobilize arsenic without altering its oxidation state has not been previously observed. To evaluate the mobility of arsenic under Fe(III)-reducing conditions, it was important to use an iron reducer that could not utilize As(V) as a terminal electron acceptor. Cell suspensions of S. alga BrY were therefore incubated anaerobically with sodium arsenate and lactate and monitored for the disappearance of As(V) in solution. Solution As(V) concentrations remained constant over 24 h (data not shown) with and without lactate, indicating that S. alga BrY was unable to enzymatically reduce arsenic.

**Fe(III) Reduction and Arsenic Dissolution from Scorodite.** A defined environment representative of soils and sediments was created with the Fe–As mineral scorodite (FeAsO4·2H2O; Ksp at 25 °C = 10-21.7 ± 0.5; see ref 36), a common, naturally occurring iron arsenate (18, 37). The synthetic scorodite used in this study had an FeAs ratio of 0.91, indicating surficial enhancement of As(V). To determine the capacity for DIRB to mobilize As from a sedimentary Fe–As mineral in the absence of arsenic reducers, S. alga BrY cells were incubated anaerobically in scorodite suspensions containing 10 mM lactate.

Initial concentrations of aqueous-phase As(V) were approximately 175 μM in both the treatment and the control groups, suggesting that during the time period required to set up the experiment (ca. 24 h) some As dissolution–desorption had occurred (Figure 2a). This result may be due to the high ionic strength (I = 0.117) of the amended buffer increasing the likelihood of anion exchange. However, As(V) in the heat-killed control group did not increase after
initiation of the experiment. This observation suggests that a steady-state in dissolution–desorption had been achieved. As(V) continued to dissolve in the presence of viable S. alga BrY cells throughout the duration of the experiment. No aqueous As(III) was detected (data not shown). As(V) concentrations in incubations containing 10 mM lactate and no cells did not change (data not shown).

In contrast to dissolved arsenate, initial aqueous Fe(II) concentrations in both the experimental and control groups were below the detection limit of the assay (i.e., below ~10 μM), indicating that no iron had been chemically reduced during the initial 24 h (Figure 2b). Soluble Fe(II) continued to increase in the viable-cell treatment for the duration of the study. In the heat-killed control, no Fe(II) was detected. Additionally, in a second control with no cells and 10 mM lactate, no Fe(II) was detected, indicating that abiotic electron transfer had not occurred (data not shown).

**Solid-Phase Analysis of the Scorodite Reduction Products.** Initial solid-phase constituents of scorodite (FeAsO₄·2H₂O) are exclusively in their oxidized states, As(V) and Fe(III). After reaction with S. alga, the solid phase is altered dramatically. Mint-green scorodite is transformed into a brilliant-green phase. The solids produced are dominated by arsenic and iron, with lesser amounts of chloride, as noted by SEM-EDS. After being inoculated with BrY, both cells and a new solid phase are deposited on the surface of scorodite (Figure 3). The newly deposited material occurs as elongated shards that radiate from isolated points on the scorodite surface. It is possible that these nucleation sites represent zones of BrY accumulation. The oxidation state of arsenic in the solid products remains unaltered in the pentavalent state. In contrast, both ferrous and ferric iron are abundant in the solid (Figure 4). The solid products are consistent with those of the solution phase in that the oxidation state of arsenic is not altered while that of Fe is reduced to the ferrous state.

The structural environment of both arsenic and iron are complex, due to a heterogeneous structural state. The radial fibers on scorodite have elemental ratios of 1 As to 1 Fe. Because the reacted solids have pronounced Fe(II) quantities, we presume that the materials are ferrous arsenates. Arsenic EXAFS spectra of the reacted materials are described by the local structural environment of As in scorodite (4 O at 1.68 Å; 4 Fe at 3.35 Å; 1 As at 4.19 Å; 2 As at 4.91 Å; from ref 38) coupled with prominent backscattering contribution from Fe at 3.10 Å (Figure 3, inset), characteristic of edge-sharing As and Fe polyhedra. The combined fit arising from the edge-sharing Fe and scorodite local structure (the final fit constructed with the following atomic coordinates: 4 O at 1.68 Å; 1.3 Fe at 3.10 Å; 3.4 Fe at 3.35 Å; 0.6 As at 4.19 Å) describes the experimental spectrum of the reaction product. Therefore, on the basis of the XAFS analysis and elemental ratios determined with SEM-EDS and the oxidation states of the products, it appears that the dominant solid-phase product is FeAsO₄·xH₂O. The ferrous arsenate solididentified here, FeHAsO₄·xH₂O, appears to be similar to other hydrous divalent metal arsenates such as yvonite, CuHAsO₄·2H₂O (39).

In addition to ferrous arsenate, green rust (hydrous ferrous, ferric hydroxide) was also noted by infrared spectroscopy. Symplesite (Fe₂(AsO₄)₃·8H₂O) is a possible solid-phase product (which is described by the local structure: 1 O at 1.60 Å; 1 O at 1.63 Å; 2 O at 1.70 Å; 2 Fe at 3.32 Å; 1 Fe at 3.34, 2 Fe at 3.36 Å; 1 As at 3.68 Å; see ref 40); this phase does not, however, appear to be a major reaction product on the basis of As:Fe molar ratios and the local structural environment of As determined with EXAFS spectroscopy.

Aqueous As(V) continued to increase beyond 1500 μM even after aqueous Fe(II) production subsided around 500 μM. In light of the fact that the theoretical Fe:As ratio in scorodite is 1:1 and the Fe:As ratio in the predominant reduction product was determined to also be around 1:1, the aqueous Fe:As ratio of 1:3 at first appears puzzling. Two factors contribute to this discrepancy. While the theoretical Fe:As ratio of scorodite is 1:1, the actual Fe:As ratio of the scorodite used in this study was in fact 0.91, indicative of As(V) sorption to the surface of the mineral. Therefore, as Fe(III) is reduced within the mineral, not only is coordinated As(V) released but As(V) bound to the surface is also released. This is supported by the observation that the aqueous Fe:As ratio decreases over time (see Figure 2a,b). It is also important to note that while the predominant reduction product was a ferrous arsenate with an Fe:As ratio of 1:1, this is not the only reduction product. Infrared spectra indicated the presence of green rust (a mixed-valence Fe(III)/Fe(II) hydroxide). The precipitation of green rust represents an additional sink for Fe(II), and accounts for the low aqueous Fe(II) concentrations relative to As(V).

**Fe(III) Reduction and Arsenic Dissolution from Whole Sediments of Lake CDA.** Whole sediments are considerably...
more complex than the synthetic mineral used in the previous experiments. To determine whether DIRB can mobilize arsenic through the reduction of iron in more complex natural materials, experiments were conducted with sediments from Lake CDA. *S. alga* BrY cells were incubated anaerobically in the presence of sterile, oxidized, surficial sediments that had been saturated with sodium arsenate. Hydroxylamine-reducible Fe(III) in the As-saturated sediment was 4.43 (±0.60 mmol kg\(^{-1}\)) (mean (SD), \(N = 3\)).

Initial As(V) concentrations were approximately 20 \(\mu\)M for both the viable-cell and heat-killed treatments (Figure 5a). Viable *S. alga* BrY cells solubilized approximately 80 \(\mu\)M As(V) over 40 h. Heat-killed controls released approximately 35 \(\mu\)M As(V) in the initial 8 h. This difference is statistically significant (\(p = 0.0008\)). Since the cell-free controls showed no change in soluble As(V) (data not shown), it is likely that whole cells or cellular constituents such as phosphates in the heat-killed controls were responsible for displacing sorbed As(V) from binding sites during the initial hours of the experiment. As(III) levels remained undetectable in all treatments throughout the duration of the experiment (data not shown).

Aqueous Fe(II) levels in the viable-cell treatment continued to increase over 40 h (Figure 5b), while in both controls (heat-killed S. alga BrY cells and no cells) no iron reduction was detected. It is thus clear that in the absence of direct enzymatic arsenic reduction, As(V) was mobilized from native Lake CDA sediments by the enzymatic reductive dissolution of Fe(III) by a dissimilatory iron-reducing bacterium.

In a previous study with the DIRB *Geobacter metallireducens* (8), no arsenic was mobilized from either ferric or ferrous arsenate minerals. However, the data presented here demonstrate that reductive dissolution of As-bearing Fe(III) minerals by the Fe(III)-reducing bacterium *S. alga* BrY mobilizes arsenate even in the absence of enzymatic As(V) reduction.

**Environmental Implications.** Sediments in Lake CDA are significantly enriched in iron, arsenic, and lead relative to sediments of a nearby unimpacted watershed (2). Unlike lead and other heavy metals, arsenic is concentrated in the upper 5–20 cm of these sediments (2, 3). This distribution is similar to patterns noted in other sedimentary environments (4–7). Arsenic-reducing bacteria may play a role in the process underlying these patterns. Additionally, sulfate-reducing bacteria (SRB) may influence arsenic mobility either by direct enzymatic arsenic reduction (41) or indirect arsenic reduction resulting from sulfidogenesis (41, 42). Depending on prevailing redox conditions, sulfidogenesis may lead either to soluble As(III) production or precipitation of insoluble arsenic sulfides (14). Our observations of steep redox gradients (Figure 1) and high Fe content in Lake CDA sediments (~10%, dry wt) led us to explore the possibility that bacterial iron reduction might also play an important role in As mobilization.
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arsenic in situ in Lake CDA as well as from native Lake CDA sediments having As(V) sorbed to various undefined binding sites. We have recently isolated three DIRB from As-contaminated Lake CDA sediments (44, 45), confirming that DIRB are part of the microbial community in this environment. Further research is needed to determine the extent to which such organisms are responsible for mobilizing arsenic in situ in Lake CDA as well as other As-rich environments.

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**Literature Cited**


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