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# Precipitation of Arsenic Trisulfide by *Desulfotomaculum auripigmentum*

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**A newly discovered bacterium, *Desulfotomaculum auripigmentum*, precipitates arsenic trisulfide ($As_2S_3$). Precipitation of $As_2S_3$ by this organism results from its reduction of As(V) to As(III) and S(VI) to S(−II). At the As(III) concentration range of interest (0.1 to 1 mM), the stability of $As_2S_3$ is highly sensitive to pH and [S(−II)]. Thus, the relative rates at which *D. auripigmentum* reduces As(V) and S(VI) are critical to its formation of $As_2S_3$. Other As(V)- or S(VI)-reducing bacteria are unable to precipitate $As_2S_3$ either due to their inability to reduce both As(V) and S(VI) or because they reduce S(VI) too rapidly. Electron microscopy of thin sections showed that the precipitate forms both intra- and extracellularly. Microbial $As_2S_3$ formation nucleates precipitation of the mineral in the bulk milieu, whereas heat-killed cells alone do not serve as templates for its formation. Precipitation of $As_2S_3$ by *D. auripigmentum* suggests that $As_2S_3$ formation may be important in the biogeochemical cycle of arsenic.**

Over the past two decades, appreciation for the role of microbes in the precipitation of minerals and the redox transformation of many elements has grown (5, 17, 18, 22, 29). Bacteria are now believed to be involved in the deposition of magnetite in marine sediments (28), the formation of placer gold (30), and the precipitation of dolomite at low temperatures (29), to name but a few examples. Our understanding of the tremendous metabolic diversity of the microbial world has expanded in recent years with the discoveries that microbes can use a variety of elements, including Fe(III), Mn(IV), Se(VI), U(VI), and As(V) as terminal electron acceptors in anaerobic respiration (2, 16, 17, 22). In this report, we present an example of the convergence of these two microbial processes, biomineralization and dissimilatory metal reduction, in the case of As(V) reduction and precipitation of arsenic trisulfide ($As_2S_3$).

$As_2S_3$, a bright yellow solid, was once used as a golden pigment for dye and paint but today finds primary application in the semiconductor industry (11, 14). The formation of $As_2S_3$ in nature as the mineral orpiment has previously been observed only in extreme environments, such as geothermal reservoir fluids and hot springs, and has been assumed to be abiotic (7). We now provide evidence that a newly discovered As(V)-reducing bacterium, *Desulfotomaculum auripigmentum* (23), precipitates $As_2S_3$ both intra- and extracellularly. Microbial precipitation of $As_2S_3$ is the first example of the biomineralization of a toxic compound that is intimately tied to bacterial metabolism, which, in this case, involves the respiration of As(V) and S(VI) (23). Until now, dissimilatory reduction of As(V) to As(III) has been thought to increase the element's mobility (2, 16). The precipitation of $As_2S_3$ by *D. auripigmentum*, however, suggests that this is not necessarily the case.

## MATERIALS AND METHODS

**Medium.** *D. auripigmentum* pure and enrichment cultures were grown in freshwater minimal medium, supplemented with 10 to 20 mM sodium lactate, either 1 to 10 mM sodium sulfate or 1 mM cysteine, and 1 to 10 mM sodium arsenate. The medium was buffered at a pH of 6.8 with bicarbonate and reduced with $PdCl_2$ plus $H_2$ (300 μg/ml). Salts supplied per liter of medium were 0.14 g of $KH_2PO_4$, 0.25 g of $NH_4Cl$, 0.50 g of KCl, 0.15 g of $CaCl_2 \cdot 2H_2O$, 1.0 g of NaCl, and 0.62 g of $MgCl_2 \cdot 6H_2O$. The medium contained per liter 0.05 mg of *p*-aminobenzoic acid, 0.02 mg of biotin, 0.05 mg of nicotinic acid, 0.05 mg of calcium pantothenate, 0.05 mg of thiamine HCl, 0.1 mg of pyridoxine HCl ($B_6$), and 0.001 mg of cyanocobalamin ($B_{12}$); trace metals supplied per liter were 0.001 ml of concentrated HCl, 0.1 mg of $MnCl_2 \cdot 4H_2O$, 0.12 mg of $CoCl_2 \cdot 6H_2O$, 0.07 mg of $ZnCl_2$, 0.06 mg of $H_3BO_3$, 0.025 mg of $NiCl_2 \cdot 6H_2O$, 0.015 mg of $CuCl_2 \cdot 2H_2O$, 0.025 mg of $Na_2MoO_4 \cdot 2H_2O$, and 1.5 mg of $FeCl_2 \cdot 4H_2O$. All chemicals were purchased from Sigma Chemical Co. The isolation of *D. auripigmentum* is described elsewhere (23).

**Analyses.** Total arsenic [oxidized to As(V)], As(V), and background phosphate were measured by the molybdenum blue spectrophotometric assay (12); As(III) was determined by measurement of the difference between the oxidized and untreated samples. Sulfide was determined by the methylene blue method (10). Cells were 4′,6-diamidino-2-phenylindole stained and counted on a Zeiss Axioskop.

**Comparisons to other bacteria.** Experiments comparing *D. auripigmentum* to *Desulfobulbus propionicus* (31) (gift of Cindy Gilmour of The Academy of Natural Sciences) and strain MIT-13 (2) (gift of Dianne Ahmann of Duke University) were carried out in the medium described above, amended with 10 mM lactate, 14 mM sulfate, and 1 mM arsenate. Reduction of As(V) and S(VI) was observed over a 2-week period, as was cell growth. *D. propionicus* was tested separately for growth on 1, 5, and 10 mM arsenate with 10 mM lactate as the carbon and electron source, and S(VI) was excluded from this medium.

**SEM.** Scanning electron microscopy (SEM) samples were prepared by filtration onto a 0.2-μm-pore-diameter filter, followed by fixation in 2% (vol/vol) glutaraldehyde for 1 h, two 15-min rinses in Na-cacodylate (pH 6.8), and 10-min dehydrations in an ethanol series: 50, 70, 85, 95, and 100%. Samples were critical point dried with a Tousimis Samdri model PVT3 drier, sputter-coated with 20 nm of Au-Pd with a Technics Hummer II, and imaged with an Amray model 1000A operating at 30 kV under standard conditions.

**TEM and EDS.** Thin sections of *D. auripigmentum* were prepared after the cells were fixed in 2% glutaraldehyde in 50 mM HEPES (*N*-2-hydroxyethylpiperazine-*N*′-2-ethanesulfonic acid) buffer (pH 6.8) for 1 h, followed by three rinses in HEPES buffer for 5 min each. Dehydration in ethanol followed: 20, 50, 70, 85, and 90% for 10 min each, and 100% ethanol three times for 10 min each. Samples were embedded in LR White (Ted Pella Co.). After 24 h at 55 to 60°C, samples were cut on a Leica Ultracut S microtome to a 60-nm thickness. Confirmation of mineral identity in thin sections was performed by transmission electron microscopy (TEM) with a Philips C20 transmission electron microscope operating at 80 kV and equipped with an EDAX 9600 series analyzer for energy-dispersive X-ray spectroscopy (EDS). EDS was conducted with a counting time of 200 s, live time.

**STEM and EDS.** Whole-cell and thin-section specimens were mounted on carbon films supported on 200-mesh nickel electron microscopy grids (Ladd Research Industries). The relative arsenic and sulfur concentrations were determined from the average of six individual spectra acquired from thin sections of a microbial sample and compared to preparations of synthetic $As_2S_3$ (Aldrich) by using a Link Analytical EDS system for scanning transmission electron microscopy (STEM) on a VG-HB603 scanning transmission electron microscope. The area analyzed for each spectrum was about 2 $nm^2$. By measuring spectra from

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areas of known but different thicknesses, it was determined that a self-absorption correction was not required. The counting time was 240 s, live time.

## RESULTS

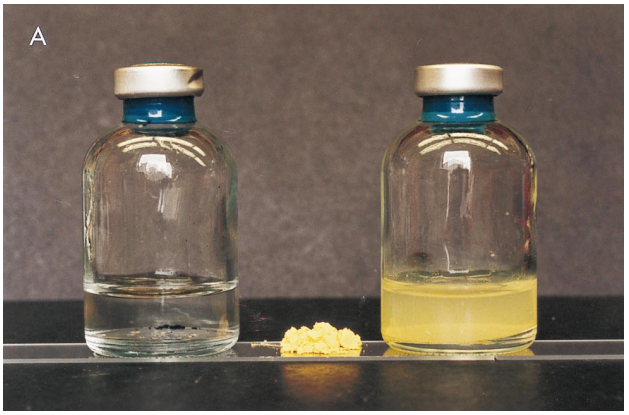
**Microbial precipitation.** Samples from the enrichment culture were inoculated into minimal medium supplemented with 10 mM lactate, 1 mM arsenate [As(V)] and 1 mM cysteine. After 1 week, a bright yellow precipitate was observed to form overnight (Fig. 1A). The isolate *D. auripigmentum* (Fig. 1B) also precipitated the bright yellow substance after a week's growth when 1 mM sulfate [S(VI)] was substituted for cysteine (Fig. 1C). Cells grown on solid medium amended with As(V) and S(VI) formed bright yellow colonies, typically less than 1 mm in diameter. After several days, the agar near the colonies began to turn yellow.

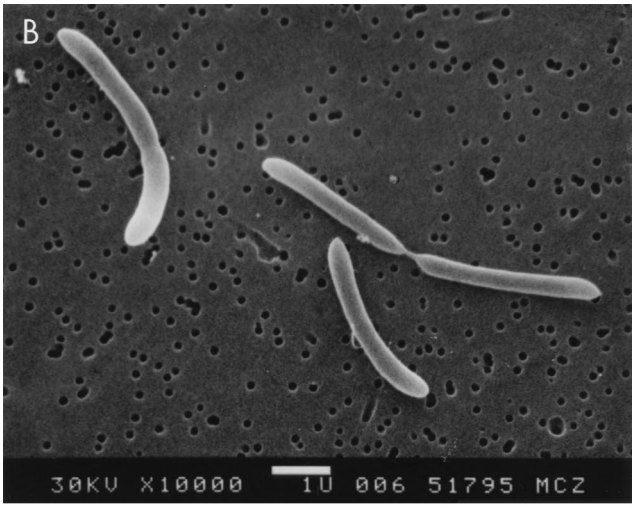
**Identification of precipitate.** The identity of the yellow precipitate was established by EDS in conjunction with electron microscopy. Preliminary EDS analysis of the small particles in Fig. 1C showed the precipitate to be inorganic, composed of As and S (data not shown). Finer mineral analysis with a scanning transmission electron microscope revealed the relative arsenic and sulfur compositions of a freshly precipitated sample to be 60.3% ± 0.6% As and 39.7% ± 0.6% S by weight (Fig. 2A). These proportions were found to be statistically indistinguishable from those of a synthetic $As_2S_3$ sample (60.9% As and 39.1% S).

X-ray maps of a single cell of *D. auripigmentum* illustrated that the arsenic and sulfur profiles corresponded to the regions of highest density and when analyzed for percent composition gave the expected ratio for $As_2S_3$ (Fig. 2B). Electron diffraction patterns gathered from particles near the poles of this cell indicated that the precipitate was amorphous. While $As_2S_3$ was clearly predominant in all samples analyzed regardless of age, small alteration products were observed to form over time. High-resolution mineral analysis (nanometer scale) showed spicular structures containing a slightly higher As/S ratio (possibly corresponding to amorphous AsS) to be present in samples that had aged for several weeks (data not shown). These structures clearly contrasted with the monodisperse spherical $As_2S_3$ particles.

**Redox transformations underlying $As_2S_3$ precipitation.** The importance of microbial As(V) reduction in the precipitation of $As_2S_3$ was first demonstrated in an experiment with an enrichment culture. In this experiment, As(V) reduction and $As_2S_3$ precipitation only occurred in the presence of bacteria and not in abiotic controls, and after 12 days, the bacteria had removed 40 to 50% of the dissolved arsenic in the system (Fig. 3A). Seeding of the medium with heat-killed cells also failed to nucleate precipitation.

In cultures of *D. auripigmentum* which were amended with As(V) and S(VI) in place of cysteine, the precipitation of $As_2S_3$ implied that this organism reduced arsenic and sulfur from As(V) to As(III) and S(VI) to S(−II). To verify and quantify these redox transformations, *D. auripigmentum* was grown on 10 mM pyruvate in the presence of 1 mM As(V) and 1 mM S(VI). Rapid As(V) reduction and concomitant accumulation of As(III) in the medium were observed (Fig. 3B). As the level of As(III) rose, trace quantities of S(−II) also appeared (Fig. 3C). Visible precipitation occurred on day 6, when nearly all of the As(V) had been reduced; at that point, As(III) and S(−II) began to be removed from solution (Fig. 3B and C). The pH measured at the beginning and end of the experiment remained constant at 6.8. The coincident reduction of As(V) and S(VI) by *D. auripigmentum* allows $As_2S_3$ to precipitate. Neither As(V) nor S(VI) is reduced in the absence of this



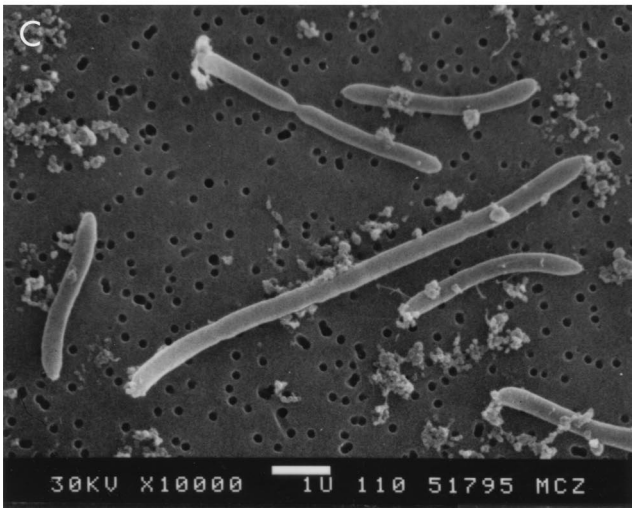




FIG. 1. Cultures before and after the precipitation of $As_2S_3$. (A) The bottle on the left shows the enrichment a few days after inoculation, and that on the right shows the enrichment after 2 weeks. A synthetic sample of $As_2S_3$ (Aldrich) lies between the two bottles. Pure cultures of *D. auripigmentum* look the same. (B) Scanning electron micrograph of *D. auripigmentum* on day 4. (C) Scanning electron micrograph of *D. auripigmentum* with particles of $As_2S_3$ on day 8. The bars represent 1 μm.

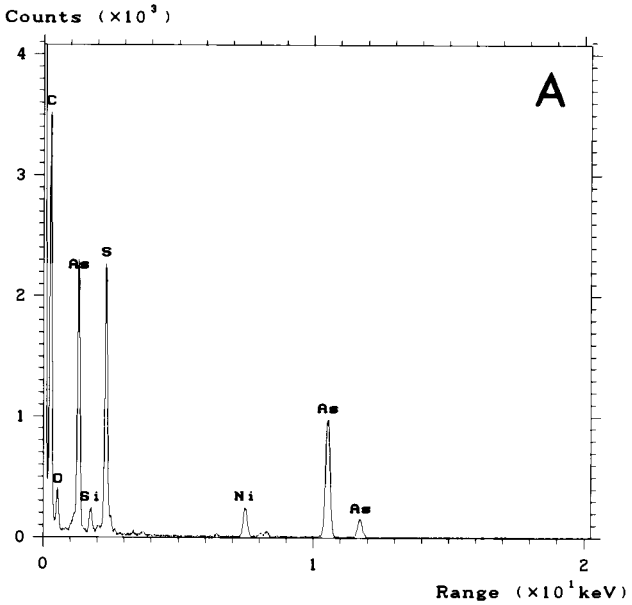
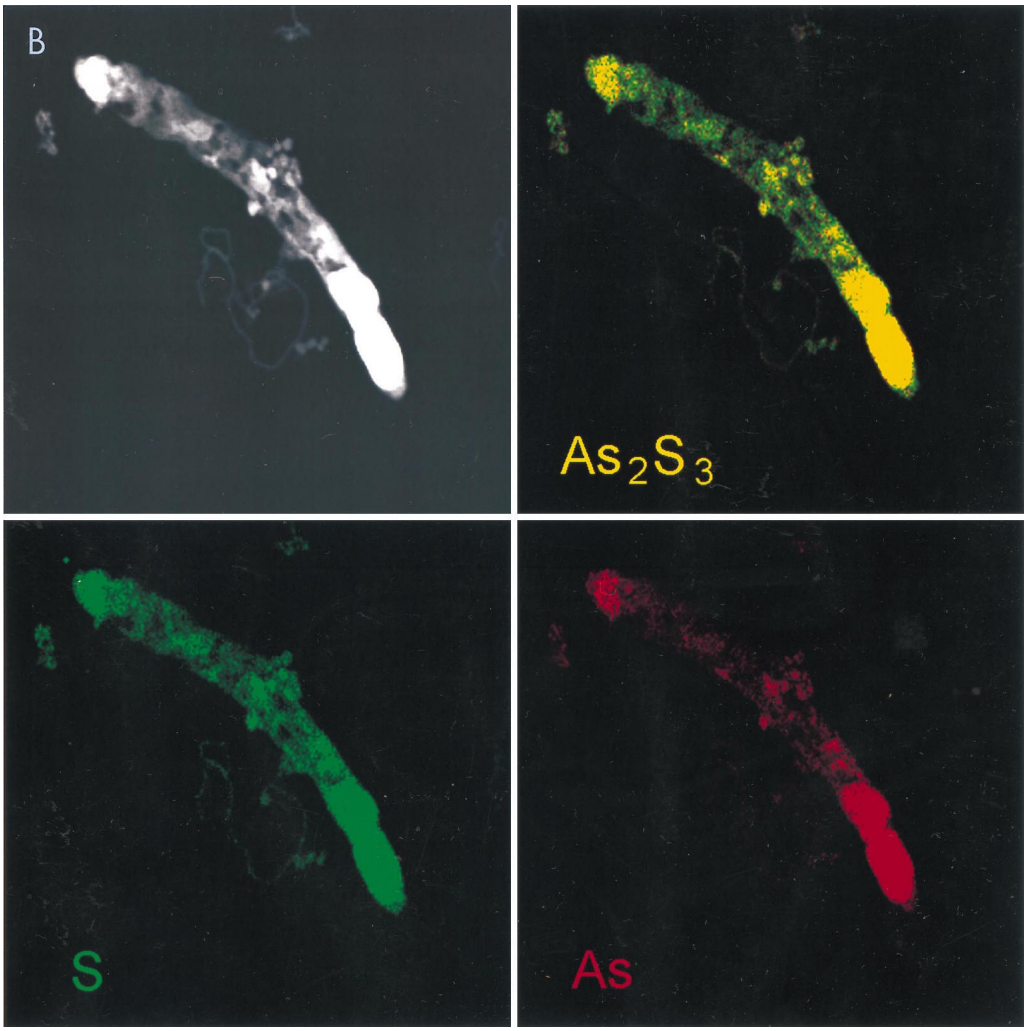



FIG. 2. Mineral analysis. (A) Representative EDS X-ray emission spectrum collected from electron-dense particles in a microbial thin section. Identical spectra were collected from particles of synthetic $As_2S_3$. The Si, O, and Ni peaks are due to background from the supporting grid. (B) The upper left quadrant is a dark-field image of a whole-cell mount of *D. auripigmentum*. Moving clockwise, the other quadrants show X-ray maps of $As_2S_3$, arsenic, and sulfur, respectively. The $As_2S_3$ map is an overlay of the arsenic and sulfur profiles. Magnification, ×20,000. The length of the bacterium is approximately 3 μm. Maps were acquired on a VG-HB603 STEM.



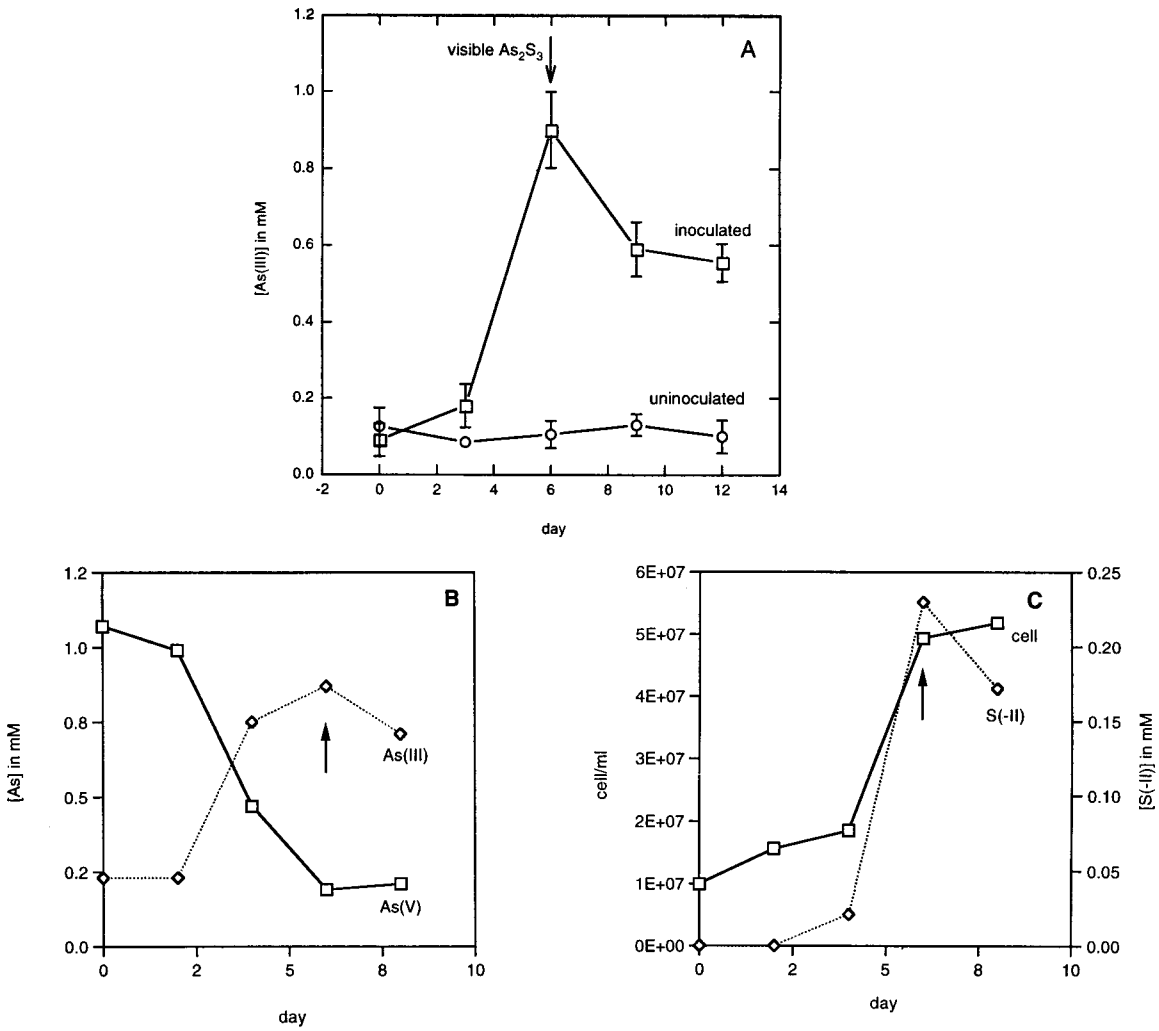



FIG. 3. Redox transformations of As(V) and S(VI). (A) As(V) is reduced to As(III) only in the presence of bacteria, and the precipitation of $As_2S_3$ removes 40 to 50% of the total arsenic. Error bars represent the range of duplicate cultures. The experiment was performed with an enrichment culture of cells growing on 10 mM lactate, 1 mM As(V), and 1 mM cysteine. Arrows are drawn where yellow precipitates of $As_2S_3$ were first observed. (B and C) Reduction of As(V) to As(III) (B) and S(VI) to S(−II) (C) by *D. auripigmentum* growing on 10 mM pyruvate, 1 mM As(V), and 1 mM S(VI).

organism. Precipitation does not occur when As(V) and S(−II) are added to the medium in its absence.

**Comparisons with other bacteria.** To test whether the metabolism underlying $As_2S_3$ precipitation was unique, we compared *D. auripigmentum* to MIT-13 [an As(V) reducer] and to *D. propionicus* [a S(VI) reducer]. All bacteria were supplied with 1 mM As(V), 14 mM S(VI), and 20 mM lactate. The MIT-13 inoculum came from an As(V)-reducing culture [10 mM As(V), no S(VI)], whereas the *D. propionicus* and *D. auripigmentum* inocula came from S(VI)-reducing cultures [10 mM S(VI), no As(V)]. While all three organisms reduced As(V) to As(III) over time, MIT-13 did not reduce S(VI) over the course of the experiment, whereas *D. propionicus* grew vigorously on S(VI) [2.5 mM S(II) appeared in the medium over 5 days; cells increased by an order of magnitude] and *D. auripigmentum* began to reduce S(VI) after As(V) reduction was essentially complete (data not shown). $As_2S_3$ precipitation occurred only in the *D. auripigmentum* cultures when As(III) concentrations had reached approximately 1 mM and S(−II) concentrations were still low (0.01 to 0.1 mM) (a+, Fig. 4). When S(−II) rose to 1 mM and above in the *D. auripigmentum* cultures, the precipitate dissolved (a−, Fig. 4). $As_2S_3$ formed in neither the MIT-13 cultures (m−, Fig. 4) nor the *D. propionicus* cultures (p−, Fig. 4). *D. propionicus* could not use As(V) as a terminal electron acceptor, since it failed to either grow on or reduce As(V) when As(V) was provided as the sole oxidant (data not shown). While *D. auripigmentum* was the only one of the three organisms to precipitate $As_2S_3$ in these experiments, microbial precipitation of $As_2S_3$ is not unique to this bacterium per se, but rather, it is a function of the ability of an organism to reduce both As(V) and S(VI) to appropriate concentrations of As(III) and S(−II). These experiments suggested that S(−II) concentrations between 0.1 and 1 mM were necessary to observe $As_2S_3$ precipitation.

**Abiotic $As_2S_3$ precipitation.** To better understand the chemical constraints on $As_2S_3$ precipitation implied by our comparative microbial experiments, we constructed a dominance diagram for $As_2S_3$ in equilibrium with various aqueous As(III) species (Fig. 4). The following reactions were considered:

$$1/2\ As_2S_{3\ (am)} + 3\ H_2O \Leftrightarrow H_3AsO_3 + 3/2\ H_2S \quad \log K = -11.9 \quad (7)$$

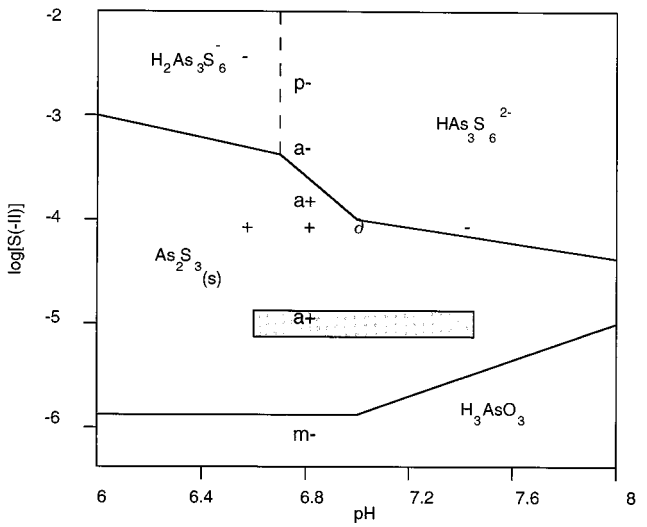



FIG. 4. Dominance diagram for $As_2S_3$ precipitation in equilibrium with various As(III) species. Total [S(−II)] assumes the species [$H_2S$], [$HS^-$], and [$S^{2-}$]. +, precipitation observed abiotically; −, precipitation not observed abiotically; ∂, precipitation kinetically slow abiotically (the shaded area indicates precipitation was expected but not observed abiotically); a+, precipitation observed for *D. auripigmentum*; a−, precipitation not observed for *D. auripigmentum*; p−, precipitation not observed for *D. propionicus*; m−, precipitation not observed for strain MIT-13.

$$3/2\ As_2S_{3\ (am)} + 3/2\ H_2S \Leftrightarrow H_2As_3S_6^- + H^+ \quad \log K = -5.0 \quad (7)$$
$$H_2As_3S_6^- \Leftrightarrow HAs_3S_6^{2-} + H^+ \quad \log K = -6.56 \quad (27)$$
$$H_3AsO_3 \Leftrightarrow H_2AsO^{3-} + H^+ \quad \log K = -9.29 \quad (24)$$
$$H_2S \Leftrightarrow HS^- + H^+ \quad \log K = -7.02 \quad (21)$$

The diagram predicts that the solubility of $As_2S_3$ should increase with pH and with high concentrations of S(−II): the greater the As(III) concentration, the broader the stability region of $As_2S_3$ with respect to pH and [S(−II)]. The diagram indicates that the stability of $As_2S_3$ is very sensitive to pH and [S(−II)] over the concentration range relevant to our experiments {pH between 6.5 and 7.0, [S(−II)] between 0.1 and 1.0 mM, [As(III)] = 1 mM}.

To test whether $As_2S_3$ could precipitate abiotically at the concentrations predicted by our diagram, we varied [S(−II)] and pH with [As(III)] constant at a concentration of 1 mM in the same medium used in our microbial experiments. We observed the expected pH and [S(−II)] effects: when S(−II) was fixed at 0.1 mM {log [S(−II)] = −4}, precipitation occurred at pH ≤7.0 (+, Fig. 4) but did not occur at high pH (7.4 [−, Fig. 4]); when pH was fixed at 6.6, precipitation occurred below 1 mM S(−II) {log [S(−II)] = −3}, but did not occur at high S(−II) {log [S(−II)] = −2.5} (−, Fig. 4). We did not observe $As_2S_3$ precipitation when S(−II) was supplied at 10 μM {log [S(−II)] = −5}, even though this concentration is predicted to fall within the stability region of $As_2S_3$ over a broad pH range when [As(III)] = 1 mM (shaded area, Fig. 4), and *D. auripigmentum* cultures precipitated $As_2S_3$ at these levels (a+, Fig. 4). The addition of heat-killed cells from clean medium (i.e., lacking precipitates) did not nucleate $As_2S_3$ formation in these samples. Abiotic precipitation at the $As_2S_3$ stability boundary {pH 7.0, [S(−II)] = 0.1 mM, [As(III)] = 1 mM} was kinetically slow: it took several hours before a precipitate became visible (∂, Fig. 4); at low pH, however, the bottles turned yellow within seconds. For the most part, visible $As_2S_3$ precipitation readily occurred abiotically within the expected region of the stability diagram provided As(III) and S(−II) concentrations were high enough to form visible particles (e.g., above 10 μM).

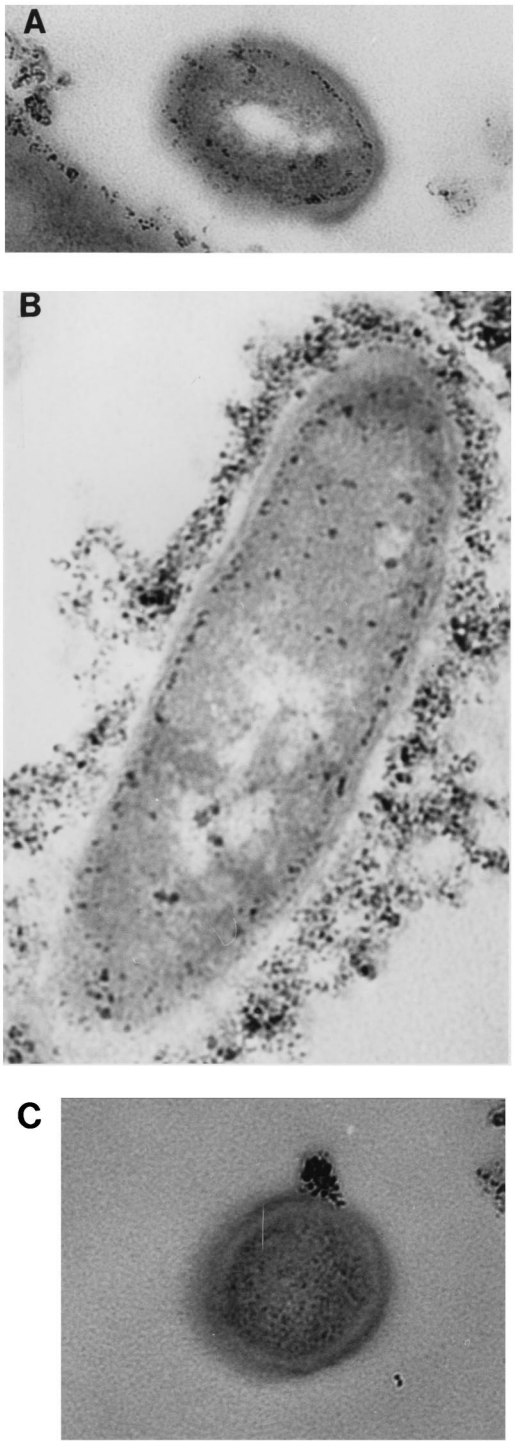



FIG. 5. Transmission electron micrographs of intracellular $As_2S_3$ precipitation (A), intracellular and extracellular $As_2S_3$ precipitation (B), and $As_2S_3$ particles associated with a membrane (C). Bar, 0.5 μm.

**Intracellular and extracellular precipitation.** To investigate whether the precipitation of $As_2S_3$ was solely an indirect effect of microbial production of As(III) and S(−II) in the external milieu, we prepared thin sections of *D. auripigmentum* a week

after the $As_2S_3$ precipitate first appeared in the medium. Electron micrographs showed small monodisperse particles of $As_2S_3$ (50 nm) concentrated intracellularly in the vicinity of the cytoplasmic membrane (Fig. 5A and B). Extracellular precipitates were observed surrounding the bacteria in great abundance, apparently coating the gram-positive cell wall (Fig. 5B). In one section, a cluster of $As_2S_3$ particles could be seen attached to the surface of a cell, seemingly surrounded by a membrane (Fig. 5C). Microbial precipitation of $As_2S_3$ appeared to be something more than a simple extracellular chemical reaction.

## DISCUSSION

Precipitation of $As_2S_3$ is not biomineralization in the strict sense of the word. Unlike the magnetosomes of the magnetotactic bacteria (9), $As_2S_3$ precipitates are not "boundary organized" but "biologically induced" (as defined by H. A. Lowenstam [18]) and form readily under the appropriate chemical conditions. Abiotic experiments demonstrate that the stability of $As_2S_3$ is highly sensitive to small changes in pH and S[−II], and microbial experiments confirm this sensitivity by showing that $As_2S_3$ precipitation by a given organism depends on the rate and extent to which it can reduce As(V) and S(VI). *D. auripigmentum* reduces the majority of As(V) to As(III) before reducing a significant fraction of S(VI) to S(−II) (23). Because of this, there is an interval when [S(−II)] is high enough to promote visible precipitation, yet low enough that $As_2S_3$ does not redissolve. In contrast, MIT-13 does not precipitate $As_2S_3$ because it cannot reduce S(VI). Even *D. propionicus*, which rapidly reduces S(VI) and As(V) [the latter most likely for detoxification purposes, since *D. propionicus* cannot respire As(V)] does not precipitate $As_2S_3$ because the high concentrations of S(−II) it produces cause the aqueous species $HAs_3S_6^{2-}$ to form rather than $As_2S_3$. The formation of $HAs_3S_6^{2-}$ also explains why $As_2S_3$ precipitates dissolve in the *D. auripigmentum* cultures when [S(−II)] approaches 1 mM. In both our microbial and abiotic precipitation experiments, the tendency for the delayed appearance and/or dissolution of the precipitates at the limits of the domain of stability of the solid is likely due to slow kinetics of formation and dissolution under these conditions.

Despite the ability of $As_2S_3$ to form in the bulk medium as a result of a biologically induced chemical reaction, significant amounts have also been observed inside the cell. This raises the question of the relationship between the intracellular and extracellular precipitates. Interestingly, when *D. auripigmentum* is grown on solid medium, its colonies turn bright yellow several days before a yellowish tint appears in the surrounding agar. The sharp yellow definition of the colonies suggests that precipitates that are closely tied to the cell form first and that additional precipitation in the bulk medium follows as the concentrations of As(III) and S(−II) rise because of diffusion or transport beyond the cell. Confirming this, the electron micrographs show that the particles associated with the membrane and cell wall are uniformly small (50 to 100 nm in diameter) and that the particles in the bulk medium are significantly larger. This suggests that cell-associated particles may nucleate additional precipitation in the outside milieu. The finding that precipitation occurs in the presence of metabolically active bacteria at concentrations where none is visible in abiotic experiments despite solution supersaturation reinforces this idea. It is well known that bacteria are capable of creating microenvironments which favor mineralization despite apparently unfavorable conditions in the bulk environment (5). In the case of $As_2S_3$ precipitation, reduction may take place independently on both sides of the cell membrane, or dead bacteria may release $As_2S_3$, which then adheres to the outside of living cells. Alternatively, an export mechanism is possible whereby membrane-bound particles could be transported from the membrane through the cell wall to the outside, as suggested by one of the electron micrographs (Fig. 5C). Such a mechanism has been observed in a gram-negative bacterium containing localized peptidoglycan hydrolases (13).

In any case, the intracellular and extracellular $As_2S_3$ precipitates are more than a mere consequence of an abiotic reaction due to incidental microbial production of As(III) and S(−II). On the contrary, $As_2S_3$ precipitation is linked to important metabolic processes. Dead $As_2S_3$-free cells (grown in medium which does not allow the formation of precipitates and then heat killed) do not appear to nucleate precipitation. First and foremost, precipitation is a direct product of respiratory growth on As(V) and S(VI) (23). Localization of the intracellular precipitates to the inside of the cytoplasmic membrane may not be a coincidence, because this is where we would expect As(V) and S(VI) reduction to be coupled to the respiratory chain. Second, precipitation may also serve as a detoxification mechanism for As(III). Precedent exists for bacterial precipitation of toxic metals such as cadmium (3), nickel (8), and selenite (19) both intra- and extracellularly. The high levels of As(III) which accumulate in the medium prior to the formation of $As_2S_3$ [suggesting cellular export of As(III)] seem to argue against precipitation as a primary mechanism for As(III) detoxification, although in support of this hypothesis, we have observed bacterial growth on 1 and 5 mM As(V) to be better in the presence of S(VI) than without. Perhaps the simplest argument for microbial precipitation of $As_2S_3$ is based on thermodynamics: the free energy to be gained from As(V) reduction would increase by maintaining a low level of As(III) in solution.

Microbial precipitation of $As_2S_3$ may have important consequences for arsenic cycling. Over the past two decades, evidence has been mounting that points to a missing sink for As(III) in various aquatic and sedimentary environments (1, 20). In areas such as the Upper Mystic Lake in Woburn, Mass., from which *D. auripigmentum* originates, interannual variability in the concentration and speciation of arsenic in the hypolimnion has been observed, with the redox state of arsenic often in apparent disequilibrium with those of iron and sulfur (4, 15, 26). The ability of microorganisms to influence such cycles through reduction (2, 16) and precipitation (25) of FeAsS has been documented. More recently, Dowdle et al. (6) suggested that $As_2S_3$ formation could possibly account for arsenic imbalances in As(V)-reducing sediments. This explanation was thought to be paradoxical, however, given that As(V) reduction inhibited S(VI) reduction in these sediments. The presence of organisms such as *D. auripigmentum*, which can reduce both As(V) and S(VI) and precipitate $As_2S_3$, would resolve this paradox. In environments with low Fe(II), $As_2S_3$ rather than FeAsS may be the dominant sink for As(III) (1). Depending on the ability of As(V)-respiring organisms present in a given environment to precipitate $As_2S_3$, the effect of microbial arsenate reduction should lead in some instances to the dissolution and enhanced mobility of arsenic and, in others, to its removal by precipitation.

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