Iodate Reduction by *Shewanella oneidensis* Requires Genes Encoding an Extracellular Dimethylsulfoxide Reductase

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Microbial iodate (IO$_3^-$) reduction is a major component of the iodine biogeochemical reaction network in anaerobic marine basins and radioactive iodine-contaminated subsurface environments. Alternative iodine remediation technologies include microbial reduction of IO$_3^-$ to iodide (I$^-$) and microbial methylation of I$^-$ to volatile gases. The metal reduction pathway is required for anaerobic IO$_3^-$ respiration by the gammaproteobacterium *Shewanella oneidensis*. However, the terminal IO$_3^-$ reductase and additional enzymes involved in the *S. oneidensis* IO$_3^-$ electron transport chain have not yet been identified. In this study, gene deletion mutants deficient in four extracellular electron conduits (EECs; $\Delta$mtrA, $\Delta$mtrA-$\Delta$mtrDEF, $\Delta$mtrA-$\Delta$dmsEF, $\Delta$mtrA-$\Delta$SO4360) and DMSO reductase ($\Delta$dmsB) of *S. oneidensis* were constructed and examined for anaerobic IO$_3^-$ reduction activity with either 20 mM lactate or formate as an electron donor. IO$_3^-$ reduction rate experiments were conducted under anaerobic conditions in defined minimal medium amended with 250 $\mu$M IO$_3^-$ as anaerobic electron acceptor. Only the $\Delta$mtrA mutant displayed a severe deficiency in IO$_3^-$ reduction activity with lactate as the electron donor, which suggested that the EEC-associated decaheme cytochrome was required for lactate-dependent IO$_3^-$ reduction. The $\Delta$mtrA-$\Delta$dmsEF triple mutant displayed a severe deficiency in IO$_3^-$ reduction activity with formate as the electron donor, whereas $\Delta$mtrA-$\Delta$mtrDEF and $\Delta$mtrA-$\Delta$SO4360 retained moderate IO$_3^-$ reduction activity, which suggested that the EEC-associated dimethylsulfoxide (DMSO) reductase membrane-spanning protein DmsE, but not MtrA, was required for formate-dependent IO$_3^-$ reduction. Furthermore, gene deletion mutant $\Delta$dmsB (deficient in the extracellular terminal DMSO reductase protein DmsB) and wild-type cells grown with tungsten replacing molybdenum (a required co-factor for DmsA catalytic activity) in defined growth medium were unable to reduce IO$_3^-$ with either lactate or formate as the electron donor, which indicated that the DmsAB complex functions as an extracellular IO$_3^-$ terminal reductase for both electron donors. Results of this study provide complementary genetic and phenotypic evidence that the extracellular DMSO reductase complex DmsAB of *S. oneidensis* displays broad substrate specificity and reduces IO$_3^-$ as an alternate terminal electron acceptor.

Keywords: iodate reduction, radioactive iodine, bioremediation, DMSO reductase, *Shewanella oneidensis*, anaerobic respiration, formate metabolism, molybdopterin
INTRODUCTION

Iodine is commonly found in the environment in the forms of iodide (I$^{-}$, 1 oxidation state), iodate (IO$_3^{-}$, 5 oxidation state), and organic iodine compounds (Whitehead, 1984; Amachi, 2013; Kaplan et al., 2014; Fuge and Johnson, 2015). An unstable radioisotope of iodine, $^{129}$I, is a nuclear waste product produced during uranium and plutonium fission reactions and displays a long half-life of 16 million years (Timar et al., 2014). $^{129}$I is found in contaminated groundwater at the U.S. Department of Energy Savannah River and Hanford Superfund sites from a long history of nuclear weapons testing (Emerson et al., 1997; Farrenkopf et al., 1997; Wong et al., 2002; Chance et al., 2007; Bluhm et al., 2010; Amachi, 2013; Kaplan et al., 2014; Fuge and Johnson, 2015; Guido-Garcia et al., 2015). Microbial IO$_3^{-}$ reduction has also received recent attention as a component of alternative strategies for the remediation of waters and sediments contaminated with radioactive iodine inadvertently released to the environment (Amachi, 2013; Kaplan et al., 2014; Riley et al., 2016; Mok et al., 2018; Toporek et al., 2019). The presence of environmental $^{129}$I presents a significant risk of bioaccumulation in the human thyroid gland, as iodine is a biologically active element for humans and vertebrate animals as a constituent of the thyroid hormones, thyroxine, and triiodothyronine (Whitehead, 1984; Fuge and Johnson, 2015). Despite the human health concerns that surround the fate and transport of radioactive iodine in the environment, the molecular mechanism of microbial IO$_3^{-}$ reduction remains poorly understood in the iodine biogeochemical cycle (Amachi, 2013; Gong and Zhang, 2013; Kaplan et al., 2014; Fuge and Johnson, 2015; Yeager et al., 2017).

Several IO$_3^{-}$-reducing microorganisms have been reported, which include Shewanella putrefaciens, Shewanella oneidensis, Desulfovibrio desulfuricans, Pseudomonas sp. strain SCT, and Rhizobiales bacterium strain DYZ35 (Councell et al., 1997; Farrenkopf et al., 1997; Amachi et al., 2007; Mok et al., 2018; Toporek et al., 2019). In particular, the facultative anaerobe S. oneidensis reduces a wide range of terminal electron acceptors, which includes oxidized forms of iron, manganese, nitrogen, sulfur, uranium, plutonium, technetium, and iodine (Farrenkopf et al., 1997; Venkateswaran et al., 1999; Neu et al., 2005; Newsome et al., 2014; Mok et al., 2018; Toporek et al., 2019). S. oneidensis transfers electrons to a variety of extracellular electron acceptors, which include Mn(III) and Fe(III) and Mn(IV) oxides (Cooper et al., 2016; White et al., 2016). To transfer the electrons to external metal oxides, S. oneidensis employs a variety of novel respiratory strategies, which include (i) direct enzymatic reduction via decaheme c-type cytochromes associated with extracellular electron conduits (EECs) located on the surface or surface extensions of the S. oneidensis outer membrane (Myers and Myers, 1992; DiChristina et al., 2002; Gorby et al., 2006), (ii) extracellular electron transfer via endogenous or exogenous electron shuttling compounds (Taillefert et al., 2007; Fennessey et al., 2010; Jones et al., 2010), and (iii) non-reductive Fe(III) solubilization by organic ligands to produce more readily reducible soluble organic Fe(III) complexes (Hernandez et al., 2004; Marsili et al., 2008; Roden et al., 2010). The previous studies of other IO$_3^{-}$-reducing microorganisms indicated that nitrate (NO$_3^{-}$) reductase may catalyze the reduction of IO$_3^{-}$ as an alternative electron acceptor (Tsuno, and Sase, 1969; Wong and Hung, 2001; Lee et al., 2018). However, results from the later studies indicated that neither assimilatory nor dissimilatory NO$_3^{-}$ reductases are required for IO$_3^{-}$ reduction by S. oneidensis (Mok et al., 2018). Recently, a putative periplasmic molybdopterin-dependent iodate reductase (Idr) system composed of four proteins (IdrA, IdrB, IdrP1, and IdrP2) was identified in Pseudomonas sp. strain SCT. The catalytic subunits IdrA and IdrB displayed amino acid sequence homology with the catalytic and electron transfer subunits of respiratory arsenite oxidase (Aio), and IdrA represented a novel clade within the dimethylsulfoxide (DMSO) reductase family (Yamazaki et al., 2020). Another estuarine bacterium, Denitromonas sp. IR-12, was also recently reported to utilize a molybdenum (Mo)-dependent IrdA for dissimilatory IO$_3^{-}$ reduction (Reyes-Umana et al., 2022).

The IO$_3^{-}$ reduction pathway of S. oneidensis shares electron transport components with EEC systems that reduce alternate electron acceptors such as metals, NO$_3^{-}$, sulfur compounds, DMSO, and trimethylamine N-oxide (Myers and Myers, 1992; DiChristina et al., 2002; Hernandez et al., 2004; Gorby et al., 2006; Taillefert et al., 2007; Marsili et al., 2008; Fennessey et al., 2010; Jones et al., 2010; Roden et al., 2010; Cooper et al., 2016; White et al., 2016). The electron transport pathways of S. oneidensis consist of upstream dehydrogenases linked via the menaquinone pool and the inner membrane-tethered c-type cytochrome CymA to downstream terminal reductase complexes associated with the metal-reducing EEC (Marsili et al., 2008; Roden et al., 2010; Gong and Zhang, 2013). The metal-reducing EEC of S. oneidensis is comprised of outer membrane β-barrel protein MtrB (and essential cysteine residue C42) (Wee et al., 2014) and decaheme c-type cytochromes, MtrA and MtrC (Shi et al., 2006, 2012; Coursolle and Granlic, 2010; Richardson et al., 2012; Richter et al., 2012; Szeinbaum et al., 2014). MtrC is translocated to the outside face of the outer membrane through GspD, the outer membrane secretin of the type II protein secretion system (Cianciotto, 2005; Dale et al., 2006; White et al., 2016). Other proteins that are essential for electron transport to external metal oxides include the c-type cytochrome maturation permease CcmB (Dale et al., 2007) and the cAMP receptor protein CRP required for anaerobic respiratory gene expression by S. oneidensis (Saffarini et al., 2003). On the other hand, S. oneidensis EEC-associated DMSO reductase DmsAB is comprised of DmsA,
which requires the Mo-binding co-factor molybdopterin, and the ferredoxin subunit DmsB, which contains [4Fe-4S] clusters as co-factors (Figure 1; May et al., 1988; Gralnick et al., 2006).

The previous work suggests that outer membrane (type II) protein secretion and metal reduction genes encoding the outer membrane MtrAB module of the EEC MtrCAB are required for IO$_3^-$ reduction by S. oneidensis with lactate, but not formate, as the electron donor (Toporek et al., 2019). However, the metal-reducing c-type cytochrome MtrC associated with the EEC MtrAB was not required for IO$_3^-$ reduction by S. oneidensis with any electron donor tested. These findings indicate that the IO$_3^-$ electron transport pathway is modular, electron donor-dependent, and terminates with an as yet unidentified IO$_3^-$ reductase that associates with an outer membrane EEC to deliver electrons extracellularly to IO$_3^-$ (Toporek et al., 2019).

In addition to MtrCAB, the S. oneidensis genome harbors three additional gene clusters that encode the EECs MtrDEF, DmsEFAB, and SO4357-4360 (Bucking et al., 2010; Coursole and Gralnick, 2010). MtrCAB and DmsEFAB are required for anaerobic reduction of Fe(III) and DMSO, respectively (Bucking et al., 2010; Coursole and Gralnick, 2010; Schicklberger et al., 2013). Furthermore, several Mtr and Dms paralogs are functionally interchangeable (Coursole and Gralnick, 2010, 2012; Schicklberger et al., 2013). For example, MtrD and DmsE may functionally replace MtrA (Coursole and Gralnick, 2010), while MtrF and to a partial extent OmcA may functionally replace MtrC (Coursole and Gralnick, 2010). MtrDEF reduces Fe(III) citrate at approximately half the rate of MtrCAB in ΔMtr mutants (Coursole and Gralnick, 2012). While the expression of SO4359 and SO4360 alone was sufficient to complement an mtrB mutant under Fe(III) citrate-reducing conditions (Schicklberger et al., 2013). These findings led us to hypothesize that S. oneidensis reduces IO$_3^-$ with separate lactate (MtrAB)- and formate-dependent EEC paralogs that deliver electrons extracellularly to IO$_3^-$ (i.e., function as electron donor-dependent IO$_3^-$ terminal reductases).

The main objective of this study was to identify the IO$_3^-$ reductase of S. oneidensis. The experimental strategy consisted of the following steps: (i) construction of three EEC paralog mutants via the deletion of mtrDEF, dmsEF, and SO4360 in a ΔmtrA mutant host strain, and subsequent testing for IO$_3^-$ reduction activity; (ii) replacement of Mo with tungsten (W) in defined growth medium and tests for IO$_3^-$ reduction activity; and (iii) construction of DMSO reductase mutant ΔdmsB (deficient in DMSO reductase protein DmsB) and tests of ΔdmsB for IO$_3^-$ reduction activity with formate and lactate as the electron donor.

**MATERIALS AND METHODS**

**Growth and Cultivation Conditions**

*Shewanella oneidensis* strains were routinely cultured aerobically at 30°C in lysogeny broth (LB) (10 g/L$^{-1}$ of NaCl, 10 g/L$^{-1}$ of tryptone, and 5 g/L$^{-1}$ of yeast extract). IO$_3^-$ reduction rate experiments were conducted under anaerobic conditions in M1 minimal medium (Myers and Nealson, 1988; Supplementary Material) amended with 20 mM sodium formate or lactate as the electron donor and 250 µM IO$_3^-$ as the anaerobic electron acceptor. Anaerobic growth of MR-1 on iodate is minimal under the incubation conditions used in this study. The toxicity threshold of MR-1 to iodate concentrations was previously determined in defined medium under aerobic and anaerobic incubation conditions (Toporek et al., 2019). When required for selection, gentamicin (20 µg mL$^{-1}$) or chloramphenicol (25 µg mL$^{-1}$) was amended to the appropriate growth medium for the selection of deletion mutant or the maintenance of recombinant plasmid vector pBBR1MCS (Kovach et al., 1995).

**In-Frame Gene Deletion Mutagenesis**

The genes mtrDEF, dmsEF, SO4360, and dmsB were deleted in frame from the S. oneidensis genome by following the previously described procedures (Supplementary Table 1; Burns and DiChristina, 2009). A dmsA deletion mutant was attempted but it was unsuccessful. Regions corresponding to 750 bp upstream and downstream of mtrDEF, dmsEF, SO4360, and dmsB were PCR amplified with Q5 High-Fidelity DNA polymerase (New England BioLabs, Ipswich, MA, United States) [primers D1/D2 and D3/D4 (Supplementary Table 2)] and subsequently joined using overlap extension PCR [primers D1/D4 (Supplementary Table 2)]. To construct ΔmtrA-ΔmtrDEF, ΔmtrA-ΔdmsEF, and ΔmtrA-ΔSO4360 mutants, the resulting fragments of mtrDEF, dmsEF, and SO4360 were cloned into suicide vector pKO2.0 (which does not replicate in S. oneidensis) and mobilized into S. oneidensis ΔmtrA (Szeinbaum et al., 2014) via conjugation with *E. coli* donor strain β2155 λ. pir (Chung et al., 1989). In addition, the resulting fragment of dmsB was also cloned into suicide vector pKO2.0 and mobilized into wild-type S. oneidensis via conjugation with *E. coli* donor strain β2155 λ. pir (Chung et al., 1989) to construct mutant ΔdmsB. S. oneidensis strains with the integrated plasmid were selected on LB agar containing gentamicin (20 µg mL$^{-1}$). Single crossover integrations were verified using PCR with primers flanking the recombination region (TF/TR) and were resolved from the genomes by plating on LB agar lacking NaCl and containing sucrose [10% (wt/vol)]. The in-frame deletion strains (ΔmtrA-ΔmtrDEF, ΔmtrA-ΔdmsEF, ΔmtrA-ΔSO4360, and ΔdmsB) were verified by PCR with primers TF/TR (Supplementary Table 2). Genetic complementation analysis of the ΔdmsB strain was carried out by cloning the wild-type gene (after amplification from the S. oneidensis genome using primer set dB-F and dB-R; Supplementary Table 2) into broad-host-range cloning vector pBBR1MCS (Kovach et al., 1995) and conjugally transferring the recombinant vector into the respective mutant strains via biparental mating procedures (Chung et al., 1989).

**IO$_3^-$ and Dimethylsulfoxide Reduction Activity Assays**

Mutant strains were initially inoculated in the liquid LB growth medium and incubated at 30°C for 24 h. About 10 ml of subcultures at an initial optical density at 600 nm (OD$_{600}$) of 0.02 was incubated at 30°C for 24 h. Subcultures were centrifuged
at 4,000 rpm for 30 min, resuspended in 10 ml of M1 growth medium amended with 10 mM formate and incubated aerobically at room temperature for 8 h. The preconditioned cells were inoculated in the 30-ml serum bottles at an initial OD$_{600}$ of 0.1 in M1 growth medium amended with either 40 mM DMSO or 250 µM I$_3^–$ and 10 mM formate and incubated anaerobically via continuous sparging with 100% high-purity (hydrated) N$_2$ gas. Cultures were incubated at room temperature with gentle stirring under anaerobic conditions maintained by continuous sparging with high-purity hydrated N$_2$ gas. At preselected time points, OD$_{600}$ was measured and I$_3^–$ concentrations were determined using the I$_3^–$-triiodide formation method described below. Cells corresponding to OD = 0.1 contain 50 mg protein as measured by the Bradford assay (Bradford, 1976). DMSO reduction was monitored by measuring anaerobic growth at OD$_{600}$. For substitution of molybdenum Mo with tungsten W in anaerobic I$_3^–$ reduction activity assays, Mo was replaced with equal molar concentration of W in M1 medium, and I$_3^–$ reduction activity was compared to I$_3^–$-reduction activity in normal M1 medium containing Mo. For the cultivation of recombinant strains carrying pBBR1MCS or pBBR1MCS-dmsB, 25 µg ml$^{-1}$ chloramphenicol and 0.1 mM IPTG were amended to the medium to maintain the plasmid and induce cloned dmsB gene expression, respectively.

**RESULTS**

I$_3^–$ Reduction Activity of Extracellular Electron Conduit Mutant Strains

To test the hypothesis that *S. oneidensis* employs periplasmic and outer membrane proteins other than MtrAB to deliver electrons to I$_3^–$, three additional EEC gene mutant strains ($\Delta$mtrDEF, $\Delta$dmsEF, and $\Delta$SO4360) were constructed in a $\Delta$mtrA mutant host strain. A $\Delta$mtrA gene deletion background was selected since $\Delta$mtrA retained wild-type I$_3^–$ reduction activity with formate as electron donor (Toporek et al., 2019). Mtr proteins and their paralogs (e.g., DMS operon) are modular and can provide partial compensation for each other in the absence of a primary component (Coursolle and Gralnick, 2010). To avoid the possibility of MtrA compensating for the lack of DmsE, we constructed all dms mutants with a $\Delta$mtrA background. The I$_3^–$ reduction activities of the three additional EEC mutant strains ($\Delta$mtrA$\Delta$mtrDEF, $\Delta$mtrA$\Delta$dmsEF, and $\Delta$mtrA$\Delta$SO4360) were determined with either lactate or formate as the electron donor.

**Determination of I$_3^–$ Concentrations via I$_3^–$-Triiodide Formation With I$^–$ at Acidic pH**

The extent of I$_3^–$ reduction was determined using the I$_3^–$-triiodide method (Afkhami et al., 2001; Mok et al., 2018; Toporek et al., 2019). Culture samples were added to the 96-well 500-µl microtiter plates. Sodium citrate buffer (0.1 M; pH 3.3) and potassium iodide solution (75 mM) were added to each well to initiate triiodide formation (I$_3^–$ + 5$I^–$ + 6$\text{H}^+$ $\rightarrow$ 3$I_2$ + 3$\text{H}_2\text{O}$). Absorbance at 352 nm was measured with a UV spectrophotometer (Multiskan Go; Thermo Scientific) within the first 3 min of reaction time. I$_3^–$ concentrations were determined from a previously generated calibration curve.

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**FIGURE 1** | Mtr paralogs of extracellular electron conduits (EEC) system responsible for anaerobic respiration in *S. oneidensis*. PEC, periplasmic electron carrier; IOMP, integral outer membrane β-barrel protein; ETR, extracellular terminal reductase.
**TABLE 1** | IO$_3^-$ reduction activities of wild-type and EEC paralog mutant strains of *Shewanella oneidensis* with lactate and formate as electron donors.*

| Condition or strain | Electron donor: lactate | Electron donor: formate |
|---------------------|-------------------------|-------------------------|
|                     | IO$_3^-$ reduction rate$^b$ (nmol hr$^{-1}$ mg protein$^{-1}$)$^d$ | Extent of reaction$^c$ (% of IO$_3^-$ reduced to I$^-$$^d$) | IO$_3^-$ reduction rate$^b$ (nmol hr$^{-1}$ mg protein$^{-1}$)$^d$ | Extent of reaction$^c$ (% of IO$_3^-$ reduced to I$^-$$^d$) |
| Abiotic             | 0 ± 0 (0)                | 0 ± 0 (0)                | 0 ± 0 (0)                | 0 ± 0 (0)                |
| MR-1                | 412.7 ± 77.0 (100)       | 55.5 ± 0.2 (100)         | 379.8 ± 7.2 (100)        | 51.6 ± 3.9 (100)         |
| ΔmtrA               | 28.6 ± 14.1 (7)          | 4.1 ± 0.7 (7)            | 286.9 ± 36.8 (76)        | 35.9 ± 2.8 (70)          |
| ΔmtrAΔmtrDEF        | 157.2 ± 8.2 (38)         | 13.2 ± 1.0 (24)          | 219.3 ± 1.0 (58)         | 29.0 ± 1.1 (56)          |
| ΔmtrAΔdmsEF         | 70.2 ± 10.3 (17)         | 8.3 ± 1.1 (15)           | 90.2 ± 43.1 (24)         | 10.2 ± 2.6 (20)          |
| ΔmtrAΔSO4360        | 143.1 ± 38.0 (35)        | 15.7 ± 1.1 (28)          | 238.2 ± 45.5 (63)        | 31.5 ± 0.7 (61)          |

$^a$Values represent means of triplicate samples; error represents one standard deviation.

$^b$Reaction rate was calculated from the first 4-h anaerobic incubation. Cells corresponding to OD = 0.1 contain 50 mg protein.

$^c$Extent of reaction is reported as the percentage of IO$_3^-$ reduced to I$^-$ upon completion of the 24-h incubation period, after which further IO$_3^-$ reduction was minimal.

$^d$The values in parentheses are in comparison with the wild-type rates (percent) within each set of lactate or formate values.

**FIGURE 2** | IO$_3^-$ reduction activity of *Shewanella oneidensis* wild-type (MR-1) and ΔmtrA, ΔmtrAΔmtrDEF, ΔmtrAΔdmsEF, and ΔmtrAΔSO4360 mutants with IO$_3^-$ as the electron acceptor and lactate (A) or formate (B) as the electron donor and their IO$_3^-$ reduction rate. Values are means of triplicate samples from anaerobic incubations. Error bars represent one standard deviation.

All mutant strains cultured with lactate displayed severely impaired (between 0 and 50% of wild-type activity) IO$_3^-$ reduction activities when compared to wild-type rates (ΔmtrA, 7 and 7% of the wild-type rate and extent of reaction, respectively; ΔmtrAΔmtrDEF, 38 and 24% of the wild-type rate and extent of reaction, respectively; ΔmtrAΔdmsEF, 17 and 15% of the wild-type rate and extent of reaction, respectively; and ΔmtrAΔSO4360, 35 and 28% of the wild-type rate and extent of reaction, respectively; Table 1 and Figure 2). These results further confirm that EEC component MtrA is required for IO$_3^-$ reduction with lactate as the electron donor (Toporek et al., 2019; Figure 1).

The ΔmtrAΔmtrDEF and ΔmtrAΔSO4360 mutant strains provided with formate as the electron donor displayed moderately impaired (between 51 and 70% of wild-type activity) IO$_3^-$ reduction activities when compared to wild-type rates (58 and 63% of the wild-type rate and 56 and 61% of the wild-type extents of reaction, respectively; Table 1 and Figure 2). The ΔmtrA mutant displayed a similar profile (between 71 and 102% of wild-type activity) with the wild-type strain (76% of the wild-type rate and 70% of the wild-type extent of reaction, respectively; Table 1 and Figure 2), while the ΔmtrAΔdmsEF mutant strain was severely impaired in IO$_3^-$ reduction activity with formate as the electron donor (24% of the wild-type rate and 20% of the wild-type extent of reaction, respectively; Table 1 and Figure 2). These results indicate that EEC component DmsE, but not MtrA, and OMP component DmsF, but not MtrB, are required for IO$_3^-$ reduction with formate as the electron donor (Figure 1).

**Replacement of Mo With W in Defined Minimal Growth Medium and the Effect on IO$_3^-$ Reduction Activity of *Shewanella oneidensis***

The *S. oneidensis* DMSO reductase DmsAB is composed of the molybdopterin-binding subunit DmsA and the ferredoxin subunit DmsB, which contains Mo and [4Fe-4S] clusters as cofactors, respectively (Figure 1; Gralnick et al., 2006). To test the hypothesis that *S. oneidensis* employs DmsAB as the IO$_3^-$...
terminal reductase we attempted to generate a ΔdmsA deletion mutant, as DmsA is the active component of DMSO reductase, but were unsuccessful. A previous study reported the similar inability to produce a ΔdmsA deletion mutant, which indicates that the dmsA deletion may be lethal (Gralnick et al., 2006). Mo is the critical catalytic element of the molybdopterin-binding DMSO reductase family, which includes DMSO reductase, nitrate reductase, and formate dehydrogenase (May et al., 1988; Hanzelmann and Mayer, 1998; Hille, 2002; Waite and Trucesdale, 2003). W readily replaces Mo in molybdopterin-binding enzymes, yet equimolar Mo substitution with W results in loss of enzymatic activity of DMSO reductase family enzymes (May et al., 1988; Hanzelmann and Mayer, 1998; McEwan et al., 2002; Waite and Trucesdale, 2003). The substitution of Mo with W did not affect cell fitness (Supplementary Figure 1). Depleting the wild-type strain MR-1 of Mo caused catalytic inactivation of the DmsA subunit and effectively generated a mutant strain deficient in DmsA catalytic activity. After growth in W-containing defined minimal medium, wild-type S. oneidensis reduced IO$_3^-$ at severely impaired rates when incubated with either lactate or formate as the electron donor (62 and 42 nmol hr$^{-1}$ mg protein$^{-1}$, respectively), corresponding to only 17 and 11% of the rates measured after growth in Mo-containing defined minimal medium (lactate, 371 nmol hr$^{-1}$ mg protein$^{-1}$; formate, 366 nmol hr$^{-1}$ mg protein$^{-1}$, respectively) (Figure 3 and Table 2). These findings indicate that Mo is required for IO$_3^-$ reduction with either lactate or formate as electron donor, potentially as the critical element of the molybdopterin-binding co-factor of DMSO reductase.

**IO$_3^-$ Reduction Activity of ΔdmsB Mutant With Lactate or Formate as Electron Donor**

To test the hypothesis that S. oneidensis employs DmsAB as the IO$_3^-$ terminal reductase, we generated a ΔdmsB gene deletion mutant. In a previous study, mutant strain ΔdmsB was unable to grow anaerobically with DMSO as a terminal electron acceptor (Gralnick et al., 2006). Fumarate reduction was not impaired by ΔdmsB deletion, which indicates that overall fitness is unaffected (Gralnick et al., 2006). In this study, ΔdmsB was also unable to grow with DMSO as electron acceptor and formate as the electron donor, while a ΔdmsB transconjugant strain provided with a wild-type copy of dmsB (ΔdmsB + pBBR1MCS-dmsB) grew at wild-type rates with DMSO as electron acceptor (Supplementary Figure 2). ΔdmsB was also severely impaired in IO$_3^-$ reduction activity with lactate or formate as the electron donor (18 and 30% of the wild-type rate and 18 and 16% of the wild-type extents of reaction with lactate or formate, respectively; Figure 4 and Table 2), while the ΔdmsB + pBBR1MCS-dmsB transconjugant strain reduced IO$_3^-$ at wild-type rates and extents of reaction.

**TABLE 2** Effect of replacement of molybdenum (Mo) with tungsten (W) on IO$_3^-$ reduction activities of Shewanella oneidensis.

| Condition or strain | Electron donor: lactate | Electron donor: formate |
|---------------------|-------------------------|-------------------------|
|                     | IO$_3^-$ reduction rate$^b$ (nmol hr$^{-1}$ mg protein$^{-1}$)$^d$ | Extent of reaction$^c$ (% of IO$_3^-$ reduced to I$^-$)$^d$ | IO$_3^-$ reduction rate$^b$ (nmol hr$^{-1}$ mg protein$^{-1}$)$^d$ | Extent of reaction$^c$ (% of IO$_3^-$ reduced to I$^-$)$^d$ |
| Abiotic             | 0 ± 0 (0)                | 0 ± 0 (0)               | 0 ± 0 (0)                | 0 ± 0 (0)               |
| MR-1 with Mo        | 370.9 ± 92.4 (100)       | 50.8 ± 2.0 (100)        | 366.0 ± 11.9 (100)       | 58.2 ± 2.3 (100)        |
| MR-1 with W         | 62.0 ± 9.4 (17)          | 9.0 ± 4.2 (18)          | 42.0 ± 1.0 (11)          | 17.2 ± 3.6 (30)         |

$^a$Values represent means of triplicate samples; error represents one standard deviation.

$^b$Reaction rate was calculated from the first 4-h anaerobic incubation. Cells corresponding to OD = 0.1 contain 50 mg protein.

$^c$Extent of reaction is reported as the percentage of IO$_3^-$ reduced to I$^-$ upon completion of the 24-h incubation period, after which further IO$_3^-$ reduction was minimal.

$^d$The values in parentheses are in comparison with the presence of Mo (percent) within each set of lactate or formate values.

**Figure 3** | Effect of molybdenum (Mo) substitution with tungsten (W) on IO$_3^-$ reduction activity of Shewanella oneidensis with IO$_3^-$ as the electron acceptor and (A) lactate or (B) formate as the electron donor. Values are means of triplicate samples from anaerobic incubations. Error bars represent one standard deviation.
![Graph](image_url)

**FIGURE 4** | IO$_3^-$ reduction activity of Shewanella oneidensis wild-type (MR-1) and ΔdmsB, ΔdmsB + pBBR1MCS, ΔdmsB + pBBR1MCS, MR-1 + pBBR1MCS strains with IO$_3^-$ as the electron acceptor and (A) lactate or (B) formate as the electron donor and their IO$_3^-$ reduction rate. Values are means of triplicate samples from anaerobic incubations. Error bars represent one standard deviation.

**TABLE 3** | IO$_3^-$ reduction activities of wild-type and dmsB mutant strains of Shewanella oneidensis.$^a$

| Condition or strain | IO$_3^-$ reduction rate$^b$ (nmol hr$^{-1}$ mg protein$^{-1}$)$^d$ | Extent of reaction$^c$ (% of IO$_3^-$ reduced to I$^-$)$^d$ | IO$_3^-$ reduction rate$^b$ (nmol hr$^{-1}$ mg protein$^{-1}$)$^d$ | Extent of reaction$^c$ (% of IO$_3^-$ reduced to I$^-$)$^d$ |
|---------------------|--------------------------------------------------|-------------------------|--------------------------------------------------|-------------------------|
| Abiotic             | 0 ± 0 (0)                                         | 0 ± 0 (0)               | 0 ± 0 (0)                                         | 0 ± 0 (0)               |
| MR-1                | 412.7 ± 77.0 (100)                                | 55.5 ± 0.2 (100)        | 366.0 ± 11.9 (100)                                | 58.2 ± 5.7 (100)        |
| ΔdmsB               | 72.9 ± 18.9 (18)                                  | 10.0 ± 1.0 (18)         | 108.2 ± 13.2 (29.5)                               | 9.4 ± 1.4 (16.2)        |
| MR-1 + pBBR1MCS     | 395.3 ± 36.0 (96)                                 | 56.4 ± 2.7 (102)        | 294.3 ± 21.7 (80)                                 | 47.5 ± 4.4 (81.2)       |
| ΔdmsB + pBBR1MCS    | 11.3 ± 20.5 (3)                                  | 2.0 ± 1.1 (4)           | 84.0 ± 13.3 (22.7)                                | 15.0 ± 8.2 (25.8)       |
| ΔdmsB + pBBR1MCS-dmsB | 381.5 ± 9.2 (92)                                | 56.5 ± 0.2 (102)        | 311.3 ± 16.7 (85)                                 | 53.9 ± 3.2 (92.6)       |

$^a$Values represent means of triplicate samples; error represents one standard deviation.

$^b$Reaction rate was calculated from the first 4-h anaerobic incubation. Cells corresponding to OD = 0.1 contain 50 mg protein.

$^c$Extent of reaction is reported as the percentage of IO$_3^-$ reduced to I$^-$ upon completion of the 24-h incubation period, after which further IO$_3^-$ reduction was minimal.

$^d$The values in parentheses are in comparison with the wild-type rates (percent) within each set of lactate or formate values.

(92 and 85% of the wild-type rate and 102 and 93% of the wild-type extents of reaction with lactate or formate, respectively; **Figure 5** and **Table 3**). As expected, control MR-1 + pBBR1MCS (96 and 80% of the wild-type rate and 102 and 81% of the wild-type extents of reaction with lactate or formate, respectively; **Figure 5** and **Table 3**) reduced IO$_3^-$ at near-wild-type rates, and control ΔdmsB + pBBR1MCS (3 and 23% of the wild-type rate and 4 and 26% of the wild-type extents of reaction with lactate or formate, respectively; **Figure 5** and **Table 3**) was severely affected. These results further indicate that DmsAB displays broad substrate specificity and reduces IO$_3^-$ as an alternate terminal electron acceptor.

**DISCUSSION**

The *S. oneidensis* genome encodes four EECs, each composed of three major components: periplasmic electron carrier (PEC), outer membrane β-barrel protein (OMP), and extracellular terminal reductase (ETR) (**Figure 1**). *S. oneidensis* EECs are involved in the reduction of Fe(III), Mn(IV), Mn(III), flavins, and DMSO (Bucking et al., 2010; Coursolle and Gralnick, 2010; Szeinbaum et al., 2014). Several EEC components are interchangeable and can functionally replace the corresponding paralog proteins (Coursolle and Gralnick, 2010, 2012; Schicklberger et al., 2013). *S. oneidensis* PECs include the decaheme c-type cytochromes MtrA, MtrD, DmsE, and SO4360 (Buckling et al., 2010; Coursolle and Gralnick, 2010, Schicklberger et al., 2013). MtrA is the primary PEC of the *S. oneidensis* Fe(III), Mn(IV), Mn(III), and flavin reduction systems. The overexpression of MtrD restores wild-type Fe(III)-citrate reduction rates to an ΔmtrA mutant (Bucking et al., 2010; Coursolle and Gralnick, 2010; Schicklberger et al., 2013). DmsE is primarily devoted to DMSO reduction (Gralnick et al., 2006; Bucking et al., 2010), but partially restores Fe(III)-citrate reduction to mtrA Mutants (Bucking et al., 2010; Coursolle and Gralnick, 2010; Schicklberger et al., 2013). SO4360 displays high amino acid sequence homology to other *S. oneidensis* PECs, but has not yet been assigned a respiratory function (Bucking et al., 2010; Coursolle and Gralnick, 2010; Schicklberger et al., 2013). The four *S. oneidensis* ETRs are involved in Fe(III) or DMSO reduction and include the decaheme c-type cytochromes...
FIGURE 5 | Hypothetical working model of the lactate (MtrAB)- and formate (DmsEF)-dependent IO$_3^-$ reduction electron transport pathways in Shewanella oneidensis. In the IO$_3^-$ reduction pathways, electrons originating from lactate dehydrogenase or formate dehydrogenase located at the head end of the electron transport chain are transferred to the inner membrane-localized menaquinone pool and subsequently to CymA, which facilitates electron transfer across the periplasmic space to decaheme c-type cytochromes MtrA or DmsE, respectively. At this location in the electron transport chain, the IO$_3^-$ reduction pathways diverge to MtrAB (lactate as electron donor) or DmsEF (formate as electron donor) and terminate with DmsA and DmsB, both of which associate with MtrA (or DmsE) and β-barrel protein MtrB (or DmsF). DmsA and DmsB are both secreted extracellularly by the type II protein secretion system to form a ternary complex with the MtrAB (or DmsEF) EEC modules on the outside face of the outer membrane (Gralnick et al., 2006).

The MtrAB module of MtrCAB is required for IO$_3^-$ reduction by S. oneidensis with lactate (but not formate) as the electron donor (Toporek et al., 2019). Similar electron donor-dependent respiratory phenotypes of S. oneidensis were also previously reported with technetium [Tc(VII)] as the terminal electron acceptor (Payne and DiChristina, 2006). Based on these previous findings, we hypothesized that S. oneidensis employed an ETR other than MtrC to deliver electrons to IO$_3^-$.

In our previous report, a lactate (MtrAB)-dependent S. oneidensis IO$_3^-$ reduction system was proposed (Toporek et al., 2019). In this working model, electrons originating from lactate dehydrogenase were transported via the menaquinone pool, CymA, and MtrAB to the unknown terminal IO$_3^-$ reductase that was translocated to the outside face of the outer membrane via type II protein secretion, while IO$_3^-$ reduction with formate as the electron donor was MtrABC-independent (Toporek et al., 2019). In the expanded working model with formate as the electron donor, electrons
of Pseudomonas sp. strain SCT and Denitromonas sp. IR-12 homologs that display amino acid sequence homology to respiratory arsenite oxidase; however, both systems require molybdopterin coordinating Mo (Yamazaki et al., 2020; Reyes-Umana et al., 2022). Results of this study provide new insights into the molecular mechanism of microbial IO$_3^-$ reduction, yield details important to the biogeochemical cycling of iodine in marine systems, and provide information crucial to the development of alternative bioremediation technologies for the treatment of radioactive iodine-contaminated subsurface environments.

**DATA AVAILABILITY STATEMENT**

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

**AUTHOR CONTRIBUTIONS**

H-DS, YT, JM, and RM performed the experiments. H-DS, YT, and TD wrote the manuscript. All authors had given approval to the final version of the manuscript.

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**SUPPLEMENTARY MATERIAL**

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmicb.2022.852942/full#supplementary-material

Bluhm, K., Croot, P., Wuttig, K., and Lochte, K. (2010). Transformation of iodate to iodide in marine phytoplankton driven by cell senescence. *Aquat. Biol.* 7, 248–254. doi: 10.3389/fabio.2010.00238

Bucking, C., Popp, F., Kerzenmacher, S., and Gescher, J. (2010). Involvement and specificity of Shewanella oneidensis outermembrane cytochromes in the reduction of soluble and solid-phase terminal electron acceptors. *FEMS Microbiol. Lett.* 306, 144–151. doi: 10.1111/j.1574-6968.2010.01949.x

Burns, J. L., and DiChristina, T. J. (2009). Anaerobic respiration of elemental sulfur. *Appl. Environ. Microbiol.* 75, 5209–5217. doi: 10.1128/AEM.00888-09

**REFERENCES**

Afkhami, A., Madrakian, T., and Zarei, A. R. (2001). “Spectrophotometric determination of iodate, iodide and bromate mixtures based on their reaction with iodide.”. *Anal. Sci.* 17, 1199–1202. doi: 10.2116/analsci.17.1199

Amachi, S. (2013). Iodine geochemistry and microbes: bacterial volatilization, accumulation, oxidation, reduction, sorption and dehalogenation of iodine. *Chikyukagaku* 47, 209–219.

Amachi, S., Kawaguchi, N., Muramatsu, Y., Tsuchiya, S., Watanabe, Y., Shinozuka, H., et al. (2007). Dissimilatory iodate reduction by marine *Pseudomonas* sp. strain SCT. *Appl. Environ. Microbiol.* 73, 5725–5730. doi: 10.1128/AEM.00241-07

Bagwell, C., Zhong, L., Wells, J., Mitroshkov, A., and Qafoku, N. P. (2019). Microbial methylation of iodide in unconfined aquifer sediments at the Hanford Site. *USA. Front. Microbiol.* 10, 2460. doi: 10.3389/fmicb.2019.02460

Beliaev, A. S., and Saffarini, D. A. (1998). Shewanella putrefaciens mtrB encodes an outer membrane protein required for Fe(III) and Mn(IV) reduction. *J. Bacteriol.* 180, 6292–6297. doi: 10.1128/JB.180.23.6292-6297.1998

Bluhm, K., Croot, P., Wuttig, K., and Lochte, K. (2010). Transformation of iodate to iodide in marine phytoplankton driven by cell senescence. *Aquat. Biol.* 11, 1–15. doi: 10.3354/ab00284

Bluhm, K., Croot, P. L., Huhn, O., Rohardt, G., and Lochte, K. (2011). Distribution of iodide and iodate in the Atlantic sector of the Southern Ocean during austral summer. *Deep Sea Res. 58*, 2733–2748. doi: 10.1016/j.dsr2.2011.02.002

Bradford, M. (1976). A rapid and sensitive method for quantification of microgram quantities of protein utilizing principle of protein-dye binding. *Anal. Biochem.* 72, 248–254. doi: 10.1006/abio.1976.9999

Bucking, C., Popp, F., Kerzenmacher, S., and Gescher, J. (2010). Involvement and specificity of Shewanella oneidensis outermembrane cytochromes in the reduction of soluble and solid-phase terminal electron acceptors. *FEMS Microbiol. Lett.* 306, 144–151. doi: 10.1111/j.1574-6968.2010.01949.x

Burns, J. L., and DiChristina, T. J. (2009). Anaerobic respiration of elemental sulfur and thiosulfate by Shewanella oneidensis MR-1 requires psrA, a homolog of the phsA gene of *Salmonella enterica* serovar Typhimurium LT2. *Appl. Environ. Microbiol.* 75, 5209–5217. doi: 10.1128/AEM.00888-09

Frontiers in Microbiology | www.frontiersin.org 9

April 2022 | Volume 13 | Article 852942
Hernandez, M. E., Kappler, A., and Newman, D. K. (2004). Phenazines and other redox-active antibiotics promote microbial mineral reduction. *Appl. Environ. Microbiol.* 70, 921–928. doi: 10.1128/AEM.70.2.921-928.2004

Hille, R. (2002). Molybdenum and tungsten in biology. *Trends Biochem. Sci.* 27, 189–196. doi: 10.1016/S0968-0004(02)00054-9

Hou, X., Aldahan, A., Nielsen, S. P., Possnert, G., Nies, H., and Hedfors, J. (2007). Speciation of I-129 and I-127 in seawater and implications for sources and transport pathways in the North Sea. *Environ. Sci. Technol.* 41, 5993–5999. doi: 10.1021/es070575s

Hou, X. L., Povinec, P. P., Zhang, L. Y., Shi, K. L., Biddulph, D., Chang, C. C., et al. (2013). Iodine-129 in seawater offshore Fukushima: distribution, inorganic speciation, sources, and budget. *Environ. Sci. Technol.* 47, 3091–3098. doi: 10.1021/es304460K

Jones, M. E., Fennessey, C. M., DiChristina, T. J., and Taillefert, M. (2010). Shewanella oneidensis MR-1 mutants selected for their inability to produce soluble organic Fe(III) complexes are unable to respire Fe(III) as anaerobic electron acceptor. *Environ. Microbiol.* 12, 938–950. doi: 10.1111/j.1462-2920.2009.01237.x

Kaplan, D. I., Denham, M. E., Zhang, S., Yeager, C., Xu, C., Schwehr, K. A., et al. (2014). Radiodine biogeochemistry and prevalence in groundwater. *Crit. Rev. Environ. Sci. Technol.* 44, 2287–2335. doi: 10.1080/10603163.2013.828273

Kenyon, J. A., Buesseller, K. O., Casacuberta, N., Castillejo, M., Otsuka, S., Masque1, P., et al. (2020). Distribution and Evolution of Fukushima Dai-ichi derived 17C3S, 134S, and 129I in Surface Seawater off the Coast of Japan. *Environ. Sci. Technol.* 54, 15066–15075. doi: 10.1021/acs.est.0c05321

Kovach, M. E., Eiler, P. H., Hill, D. S., Robertson, G. T., Farris, M. A., Roop, R. M. I. L., et al. (1995). Four new derivatives of the broad-host-range cloning vector pBRRI1MC, carrying different antibiotic resistance cassettes. *Gene* 166, 175–176. doi: 10.1016/0378-1119(95)00584-1

Lee, B. D., Ellis, J. T., Dodwell, A., Eisenhauer, E. E. R., Saunders, D. L., and Lee, M. H. (2018). Iodate and nitrate transformation related by Agrobacterium/Rhizobium related strain DVZ35 isolated from contaminated Hanford groundwater. *J. Hazard. Mater.* 350, 19–26. doi: 10.1016/j.jhazmat.2018.02.006

Marsili, E., Baron, D. B., Shikhare, I. D., Coursolle, D., Gralnick, J. A., and Bond, D. R. (2008). Shewanella secretes flavins that mediate extracellular electron transfer. *Proc. Natl. Acad. Sci. U.S.A.* 105, 3968–3973. doi: 10.1073/pnas.070525105

May, H. D., Patel, P. S., and Ferry, J. G. (1988). Effect of molybdenum and tungsten on synthesis and composition of formate dehydrogenase in *Methanobacterium formicicum*. *J. Bacteriol.* 170, 3384–3389. doi: 10.1128/jb.170.6.3384-3389.1988

McEwan, A. G., Ridge, J. P., McDevitt, R. J. F., and Forest, K. T. (2012). Structural insights into the type II secretion nanomachine. *Curr. Opin. Struct. Biol.* 22, 208–216. doi: 10.1016/j.sbi.2012.02.005

Mok, J. K., Toporek, Y. J., Shin, H. D., Lee, B. D., Lee, M. H., and DiChristina, T. J. (2018). Iodate reduction by Shewanella oneidensis does not involve nitrate reductase. *Geomicrobiol. J.* 35, 570–579. doi: 10.1080/01490450.2018.1430189

Myers, C. R., and Myers, J. M. (2012). Localization of cytochromes to the outer membrane of an organically grown Shewanella putrefaciens MR-1. *J. Bacteriol.* 194, 3429–3438. doi: 10.1128/jb.00377-11

Myers, C. R., Haft, R. J. F., and Forest, K. T. (2012). Structural insights into the type II secretion nanomachine. *Curr. Opin. Struct. Biol.* 22, 208–216. doi: 10.1016/j.sbi.2012.02.005

Riou, J., Coates, J. D., and Ballantine, D. M. H. (2006). Distribution and Evolution of Fukushima Dai-ichi related strain DVZ35 isolated from contaminated Hanford groundwater. *J. Hazard. Mater.* 350, 19–26. doi: 10.1016/j.jhazmat.2018.02.006

Marsili, E., Baron, D. B., Shikhare, I. D., Coursolle, D., Gralnick, J. A., and Bond, D. R. (2008). Shewanella secretes flavins that mediate extracellular electron transfer. *Proc. Natl. Acad. Sci. U.S.A.* 105, 3968–3973. doi: 10.1073/pnas.070525105

May, H. D., Patel, P. S., and Ferry, J. G. (1988). Effect of molybdenum and tungsten on synthesis and composition of formate dehydrogenase in *Methanobacterium formicicum*. *J. Bacteriol.* 170, 3384–3389. doi: 10.1128/jb.170.6.3384-3389.1988

McEwan, A. G., Ridge, J. P., McDevitt, R. J. F., and Forest, K. T. (2012). Structural insights into the type II secretion nanomachine. *Curr. Opin. Struct. Biol.* 22, 208–216. doi: 10.1016/j.sbi.2012.02.005

Mok, J. K., Toporek, Y. J., Shin, H. D., Lee, B. D., Lee, M. H., and DiChristina, T. J. (2018). Iodate reduction by Shewanella oneidensis does not involve nitrate reductase. *Geomicrobiol. J.* 35, 570–579. doi: 10.1080/01490450.2018.1430189

Myers, C. R., and Myers, J. M. (2012). Localization of cytochromes to the outer membrane of an organically grown Shewanella putrefaciens MR-1. *J. Bacteriol.* 194, 3429–3438. doi: 10.1128/jb.00377-11

Myers, C. R., and Nealon, K. H. (1988). Bacterial manganese reduction and growth with manganese oxide as the sole electron acceptor. *Science* 240, 1319–1321. doi: 10.1126/science.240.4857.1319

Neu, M. P., Iopicini, G. A., and Boukhalfa, H. (2005). Plutonium speciation affected by environmental bacteria. *Radiochim. Acta* 93, 705–714. doi: 10.1007/jenradi. 2015.08.019

Newsome, L., Morris, K., and Lloyd, J. R. (2014). The biogeochemistry and bioremediation of uranium and other priority radionuclides. *Chem. Geol.* 363, 164–184. doi: 10.1016/j.chemgeo.2013.10.034

Payne, A. N., and DiChristina, T. J. (2006). A rapid mutant screening technique for detection of techenium [Te (VII)] reduction-deficient mutants of Shewanella oneidensis MR-1. *FEBS Microbiol. Lett.* 259, 282–287. doi: 10.1111/j.1432-2076.2006.02278.x

Reyes-Umana, V., Henning, Z., Lee, K., Barnum, T. P., and Coates, J. D. (2022). Genetic and phylogenic analysis of dissipatory iodate-reducing bacteria.
identifies potential niches across the world’s oceans. ISME J. 16, 38–49. doi: 10.1038/s41396-021-01034-5
Richardson, D. J., Butt, J. N., Fredrickson, J. K., Zachara, J. M., Shi, L., Edwards, M. J., et al. (2012). The ‘porincytochrome’ model for microbe-to-mineral electron transfer. Mol. Microbiol. 85, 201–212. doi: 10.1111/j.1365-2958.2012.08088.x
Richter, K., Schickelberger, M., and Gescher, J. (2012). Dissimilatory reduction of extracellular electron acceptors in anaerobic respiration. Appl. Environ. Microbiol. 78, 913–921. doi: 10.1128/AEM.06803-11
Riley, B. J., Vienna, J. D., Strachan, D. M., McCloy, J. S., and Jerden, Jr. (2016). Materials and processes for the effective capture and immobilization of radiiodine: a review. J. Nucl. Mater. 470, 307–326. doi: 10.1016/j.jnucmat.2015.11.038
Roden, E. E., Kappler, A., Bauer, I., Jiang, J., Paul, A., Stoesser, R., et al. (2010). Extracellular electron transfer through microbial reduction of solid-phase humic substances. Nature Geosci. 3, 417–421. doi: 10.1038/ngeo970v2019.134683
Saffarini, D. A., Schultz, R., and Beliaev, A. (2003). Involvement of cyclic AMP (CAMP) and cAMP receptor protein in anaerobic respiration of Shewanella oneidensis. J. Bacteriol. 185, 3668–3671. doi: 10.1128/JB.185.12.3668-3671.2003
Schickelberger, M., Sturm, G., and Gescher, J. (2013). Genomic plasticity enables a secondary electron transport pathway in Shewanella oneidensis. Appl. Environ. Microbiol. 79, 1150–1159. doi: 10.1128/AEM.05556-12
Shi, L., Chen, B. W., Wang, Z. M., Elias, D. A., Mayer, M. U., Gorby, Y. A., et al. (2006). Isolation of a high-affinity functional protein complex between OmcA and MtrC: two outer membrane decaheme c-type cytochromes of Shewanella oneidensis MR-1. J. Bacteriol. 188, 4705–4714. doi: 10.1128/JB.01966-05
Shi, L., Rosso, K. M., Zachara, J. M., and Fredrickson, J. K. (2012). Mtr extracellular electron-transfer pathways in Fe(III)-reducing or Fe(II)-oxidizing bacteria: a genomic perspective. Biochem. Soc. Trans. 40, 1261–1267. doi: 10.1042/BST20120098
Szeinbaum, N., Burns, J. L., and DiChristina, T. J. (2014). Electron transport and protein secretion pathways involved in Mn(III) reduction by Shewanella oneidensis. Environ. Microbiol. Rep. 6, 490–500. doi: 10.1111/1758-2229.12173
Taillefert, M., Beckler, J. S., Carey, E., Burns, J. L., Fennessey, C. M., and Szeinbaum, N., Burns, J. L., and DiChristina, T. J. (2014). Electron transport pathways in Fe(III)-reducing or Fe(II)-oxidizing bacteria: a genomic perspective. Biochem. Soc. Trans. 40, 1261–1267. doi: 10.1042/BST20120098
Timar, J., Elekes, Z., and Singh, B. (2014). Nuclear data sheets for A=129. Nucl. Data Sheets 121, 143–394. doi: 10.1016/j.nds.2014.09.002
Toporek, Y. J., Mok, J. K., Shin, H. D., Lee, B. D., Lee, M. H., and DiChristina, T. J. (2019). Metal reduction and protein secretion genes required for iodate reduction by Shewanella oneidensis. Appl. Environ. Microbiol. 85, e2115–e2118. doi: 10.1128/AEM.02115-18
Tsunoagi, S., and Sase, T. (1969). Formation of iodide-iodine in the ocean. Deep Sea Res. Part I 16, 489–496. doi: 10.1016/0011-7471(69)90037-0
Venkateswaran, K., Moser, D. P., Dollhopf, M. E., Lies, D. P., Saffarini, D. A., MacGregor, B. J., et al. (1999). Polyphasic taxonomy of the genus Shewanella and description of Shewanella oneidensis sp. nov. Int. J. Syst. Bacteriol. 49, 705–724. doi: 10.1099/00207713-49-2-705
Waite, T. J., and Truesdale, V. W. (2003). Iodate reduction by isochrysis galbana is relatively insensitive to de-activated of nitrate reductase activity. Marine Chem. 81, 137–148. doi: 10.1016/s0304-4203(03)00013-6
Wes, S. K., Burns, J. L., and DiChristina, T. J. (2014). Identification of a molecular signature unique to metal-reducing gammaproteobacteria. FEMS Microbiol. Lett. 350, 90–99. doi: 10.1111/1574-6968.12304
White, G. F., Edwards, M. J., Gomez-Perez, L., Richardson, D. J., Butt, J. N., and Clarke, T. A. (2016). Mechanisms of bacterial extracellular electron exchange. Adv. Microb. Physiol. 68, 87–138. doi: 10.1016/bams.2016.02.002
Whitehead, D. C. (1984). The distribution and transformations of iodine in the environment. Environ. Int. 10, 321–339. doi: 10.1016/0160-4120(84)90139-9
Wong, G. T. F., and Hung, C. C. (2001). Speciation of dissolved iodine: integrating nitrate uptake over time in the oceans. Cont. Shelf Res. 21, 113–128. doi: 10.1016/s0278-4343(00)00986-8
Wong, G. T. F., Piumsomboon, A. U., and Dunstan, W. M. (2002). The transformation of iodate to iodide in marine phytoplankton cultures. Mar. Ecol. Prog. Ser. 237, 27–39. doi: 10.3354/meps23707
Yamazaki, C., Kashiwa, S., Horiuchi, A., Kasahara, Y., Yamamura, S., and Amachi, S. A. (2020). Novel dimethylsulfoxide reductase family of molybdenum enzyme. Environ. Microbiol. 22, 2196–2212. doi: 10.1111/1462-2920.14988
Yeager, C. M., Amachi, S., Grandbois, R., Kaplan, D. I., Xu, C., Schwehr, K. A., et al. (2017). “Microbial transformation of iodine: from radioisotopes to iodine deficiency,” in Advances in Applied Microbiology, Vol. 101, eds S. Sariaslani and G. M. Gadd (Amsterdam: Elsevier Inc), 83–136. doi: 10.1016/bs.aamb.2017.07.002

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