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Insights into the various mechanisms by which *Shewanella* spp. induce and inhibit steel corrosion

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Shewanella species are frequently selected as model strains to investigate microbially influenced steel corrosion. This selection is due to their relevance for corrosion, but also because of their easy cultivation in aerobic media. Unfortunately, these cultivation advantages do not lead to a straight-forward interpretation of their corrosion inducing or inhibiting mechanisms. The metabolic versatility of *Shewanellae* indeed enables a wide variety of corrosion mechanisms. This work reviews the metabolic capacities and the extracellular electron transfer mechanisms of *Shewanellae* and explains how these abilities lead to the various mechanisms by which *Shewanellae* induce and inhibit corrosion. It should be emphasized that the medium composition (presence of electron donor, acceptor, carbon source) strongly affects which mechanism is in play. Overall, this work concludes that *Shewanellae* model strains offer great opportunities to study corrosion, thanks in part due to genetic engineering options, but the full complexity of their corrosion processes should always be kept mind.

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INTRODUCTION

Corrosion causes enormous costs by damaging industrial metallic infrastructure[1]. In the presence of oxygen, steel corrosion is mainly a chemical (abiotic) process, resulting from a series of spontaneous reactions, leading to the oxidation of Fe(0) in steel with atmospheric oxygen to the typical rust colored Fe(III) (hydr)oxide corrosion products:

$$Fe(0) + {}^{1}/_{2}\,O_2 + H_2O \rightarrow Fe^{2+} + 2\,OH^- \quad (1)$$

$$2\,Fe^{2+} + {}^{1}/_{2}\,O_2 + H_2O \rightarrow 2Fe^{3+} + 2\,OH^- \quad (2)$$

$$Fe^{3+} + 3\,OH^- \rightarrow Fe(OH)_3 \quad (3)$$

In the absence of oxygen, chemical corrosion is rather due to the slow reaction of Fe(0) with protons in water leading to H_2 evolution:

$$Fe(0) + 2\,H^+ \rightarrow Fe^{2+} + H_2 \quad (4)$$

In anoxic conditions, mostly black colored corrosion products are formed, due to the precipitation of Fe(II) with sulfides.

The activity of microorganisms can induce and accelerate these corrosion reactions[2,3], i.e. a process called microbial (influenced or induced) corrosion (MIC). Many different types of microorganisms can be involved in MIC, which are often divided into different groups based on their metabolism and thus resulting corrosion mechanism. For instance, microorganisms causing corrosion are classified as sulfate reducing bacteria (SRBs), Fe(III) reducing bacteria (IRBs), nitrate reducing bacteria (NRBs), acid producing bacteria, methanogens, etc.[4,5]. However, neither quantification of these microbial groups using qPCR, nor microbial community analysis using next generation sequencing techniques, is sufficient to diagnose MIC[1,6]. This illustrates the need to better understand which microorganisms are involved in corrosion and how they exactly cause MIC in order to develop improved MIC diagnostic tools and ultimately enable prevention and mitigation of MIC.

One group of microorganisms that is regularly (but not always) found in corrosive microbial communities are *Shewanella* species (spp.) (Table 1). Interestingly, *Shewanellae* have been identified in various corrosion environments, ranging from aerobic communities[7] to anaerobic methanogenic and acetogenic enrichments[8,9] (Table 1). In addition, several *Shewanella* strains have been isolated from corrosion samples (Table 2). However, *Shewanellae* are not the most common corroders, as definitely not all corroding communities contain *Shewanella* spp.[2,10]. Nevertheless, *Shewanella* strains are very frequently used as model microorganisms in corrosion experiments (Table 3), likely not only because of their relevance for MIC, but also because of their easy cultivation in aerobic conditions and standard rich media.

Shewanella spp. are often considered as IRBs, since their key trademark is their ability to reduce Fe(III). Recently, *Shewanellae* have also been investigated for their possible direct electron uptake from steel[11,12]. Besides these traits, *Shewanella* spp. can use various electrons acceptors and donors, affecting corrosion in different ways. Here, our aim is to review how the metabolic versatility of *Shewanella* spp. leads to the various mechanisms by which these microbes cause or even inhibit corrosion. We will explain that the chemical conditions (medium composition) have a strong impact on the outcome of corrosion studies using *Shewanella* strains. Ultimately, our goal is to make scientists who study MIC using *Shewanella* model strains aware of the complexity of the corrosion processes caused by these microbes.

This review starts with an overview of the ecological and metabolic versatility of *Shewanella* spp., as well as their extracellular electron transfer (EET) mechanisms. Next, the various corrosion mechanisms of *Shewanellae* are discussed in depth based on the latest literature. Finally, this review concludes with an overview of the different challenges and opportunities arising from the use of *Shewanella* spp. for MIC studies.

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Table 1. Overview of studies that reported the abundance of *Shewanella* spp. in corrosive microbial communities.

Abundance *Shewanella* in corrosive microbial community	Source	Reference
40%	Methanogenic community growing on Fe(0) granules as sole electron donor and CO_2 as sole electron acceptor, enriched from coastal marine sediments	8
22-35%	Separators and storage tanks of shale gas facility	86
10%	Corroded seal rings off-shore facility	76
3.7%	316 L stainless steel coupons immersed in oxic seawater	7
0.6%	Acetogenic community growing on Fe(0) powder as sole electron donor and CO_2 as sole electron acceptor, enriched from corrosion crust from scrap bikes	9

Several more studies found evidence for the presence of *Shewanella* spp. in corrosion samples, but did not report their exact abundance. It should be noted that definitely not all corrosive microbial communities contain *Shewanellae*.

Table 2. Overview of *Shewanella* strains isolated from corrosion samples.

Species/strain	Source	Reference
S. putrefaciens	Oil field water, using aerobic plating	87
S. putrefaciens	Cooling water systems, using iron sulfite medium	61
S. oneidensis	Water sample from sour oil well	88
S. fodinae 4t3-1-2LB	Acetogenic enrichment growing on Fe(0) powder as sole electron donor and CO_2 as sole electron acceptor	9
S. chilikensis CCC -APB5	Corroded seal rings off-shore facility	76
S. putrefaciens IB6 *S. xiamenensis* IB13 *S. hafniensis* IB14 *S. oneidensis* IB15	Stainless steel coupons exposed to waste water	89

ECOLOGICAL AND METABOLIC DIVERSITY OF *SHEWANELLA* SPP.

Shewanella spp. are Gram-negative, facultative anaerobic bacteria, belonging to the order of the *Alteromonadales* and the class of the *Gammaproteobacteria*[13,14]. Currently, about 71 *Shewanella* spp. have been formally described, of which at least eight species have been related to MIC of steel, including *S. oneidensis*, *S. algae*, *S. putrefaciens*. *S. chilikensis*, *S. fodinae*, *S. loihica, S. xiamenensis* and *S. hafniensis* (Fig. 1). In addition, *S. algae* was reported to accelerate titanium alloy corrosion[15]. Most *Shewanella* spp. have been isolated from marine environments, but they are present in all sorts of ecological niches, ranging from freshwater habitats to animal intestines and contaminated environments[14,16]. Members of the *Shewanella* genus survive in a wide range of conditions, varying in nutrient availability, salinity, temperature and hydrostatic pressure[13,16].

Shewanella spp. are known for their extraordinary metabolic versatility[14,17], which is illustrated in Fig. 2. *Shewanellae* use many different electron acceptors, including oxygen, nitrate, fumarate, sulfite, thiosulfate and others[17]. In addition, *Shewanellae* are well studied for their use of solid-state or extracellular electron acceptors, including Fe(III) and Mn oxides and anodes, requiring special outward EET mechanisms, which are described below. *Shewanella* spp. are rather restricted in their use of electron donors, since they only use simple organic substrates like lactate, pyruvate, formate, few sugars, simple amino acids, peptides and nucleotides[14,17], with oxygen as electron acceptor. In anoxic conditions, their range of organic substrates is further restricted[18]. *Shewanella* spp. can also use H_2 as electron donor[19,20], while more recently it has been described that these microorganisms can use cathodes[21,22] and also Fe(0)[12,23,24] as electron donor. This requires specific inward EET mechanisms, which are discussed in detail below. *Shewanella* spp. can metabolize inorganic electron donors in combination with inorganic electron acceptors[19], but it should be noted that these microbes are obligate heterotrophs, meaning that they cannot fix CO_2 and need an organic compound as carbon source to be able to grow and build new biomass[17]. Finally, in the absence of electron acceptors, *Shewanella* spp. can perform fermentation reactions, such as the fermentation of pyruvate and formate leading to H_2 formation[25,26]. Neither of these reactions support growth, but they allow for energy generation for cell survival[27].

EXTRACELLULAR ELECTRON TRANSFER BY *SHEWANELLA* SPP.

Shewanella spp. are well known for their use of extracellular electron acceptors, such as Fe(III) and Mn oxides and by analogy also anodes[16,18] (Fig. 2). Their use of anodes as electron acceptor leads to interesting biotechnological applications, such as microbial fuel cells and biosensors, while the reduction of Fe(III) is an important aspect leading to MIC, as explained below. Using extracellular electron acceptors requires outward EET, i.e. the transport of electrons from the cytoplasma, over the inner and outer membrane, to an electron acceptor outside of the cell. *Shewanella oneidensis* MR1, the best studied *Shewanella* model strain, performs EET using the Mtr pathway, an electric conduit consisting of four multi-heme cytochromes, CymA, MtrA, MtrC, and OmcA, and a porin protein MtrB, which together span the periplasmic space[17,18] (Fig. 2). Other *Shewanellae* have EET pathways highly similar to the Mtr pathway of *S. oneidensis* MR1[17]. The cytochromes MtrC and OmcA of *S. oneidensis* MR1 are located on the outer surface of the cell and can directly transfer electrons to Fe(III) or an anode[28]. *S. oneidensis* MR1 even forms nanowires, consisting of outer membrane extensions, in order to extend it surface area and thus its direct EET possibilities[29]. Nevertheless, *S. oneidensis* MR1 mainly uses redox mediators to transfer its electrons to an extracellular electron acceptor[18,30]. A redox mediator or electron shuttle is an organic compound that

Table 3. Overview of studies that reported an increased or decreased corrosion rate by *Shewanella* spp. and the inferred corrosion mechanism.

Shewanella species/strain	Increase (+) or decrease (−) of corrosion rate	Analytical method	Steel type	Presence of O_2	Possible electron donors or acceptors	Inferred corrosion mechanism (Letter refers to Fig. 3)	Reference
S. oneidensis	−4 times	Weight loss	Mild steel coupons	Yes	Lactate, yeast extract, peptone	(a) Corrosion inhibition due to O_2 consumption (c) Corrosion inhibition due to O_2 scavenging by Fe(II)	46
S. oneidensis MR1	−1.5 times	Weight loss	Carbon steel coupons	Yes	Lactate	(a) Corrosion inhibition due to O_2 scavenging (c) Corrosion inhibition due to O_2 scavenging by Fe(II)	45
S. oneidensis MR1	+2 times	Weight loss	Biofilm covered plate in electric contact with uncovered plate	Yes	Lactate	Corrosion increase due to incomplete biofilm coverage	45
S. algae	+6.7 times	Max. pit depth	Stainless steel	Yes	peptone, Fe(III)citrate	Corrosion increase due to incomplete biofilm coverage	49
S. putrefaciens	+(n.d.)	Electrochemical	Carbon steel	No	Lactate, amino acids	(b) Corrosion increase due to Fe(III) reduction	52
S. putrefaciens	+1.5 times	Weight loss	Mild steel coupons	No	Fe(III)citrate, lactate	(b) Corrosion increase due to Fe(III) reduction	20
S. oneidensis MR1	+2-3 times	Electrochemical (5 days)	Carbon steel	No	Amino acids H_2 generation by electrode	(b) Corrosion increase due to Fe(III) reduction	58
S. oneidensis MR1	+1.3 times	Weight loss (5 months)	Carbon steel	No	Amino acids	(b) Corrosion increase due to Fe(III) reduction	59
S. algae	+(n.d.)	Electrochemical atomic force microscopy	Stainless steel	No	Fe(III)citrate, peptone, yeast extract	(b) Corrosion increase due to Fe(III) reduction	54
S. loihica	−(n.d.)	Chemical analysis precipitates	Iron plates	Yes	Fe(III)citrate, lactate	(d) corrosion inhibition due to formation of stable Fe(II) precipitates	57
S. putrefaciens	+4.2 times	Weight loss	Mild steel	No	Sulfite, lactate	(e) Corrosion increase due to H_2S formation	20
S. chilikensis CCC -APB5	+5.7 times	Average pit depth	Carbon steel	No	lactate, acetate, pyruvate, thiosulfate	(e) Corrosion increase due to H_2S formation	62
S. chilikensis CCC -APB5	+2.5 times	Weight loss	Carbon steel	No	lactate, acetate, pyruvate, nitrate	(f) Corrosion increase due to nitrite formation	62
S. oneidensis MR1	+6 times	Weight loss	Carbon steel	No	Nitrate, lactate	(f) Corrosion increase due to nitrite formation	24
S. oneidensis MR1	+11 times	Weight loss	Carbon steel	No	Nitrate, no lactate	(f) Corrosion increase due to nitrite formation + (g/h/i) EMIC	24
S. fodinae 4t3-1-2LB	+7 times	Measurement of succinate	Fe(0) powder	No	fumarate	(g) direct EET and/or (i) indirect H_2-mediated EET	9
S. oneidensis MR1	+4 times	Weight loss electrochemical	Carbon steel	No	Fumarate, little tryptone	(g) direct EET and (i) indirect H_2-mediated EET	12
S. oneidensis MR1	+2.5 times	Average pit depth	Stainless steel	Yes	Amino acids from LB medium	(g) direct EET	11

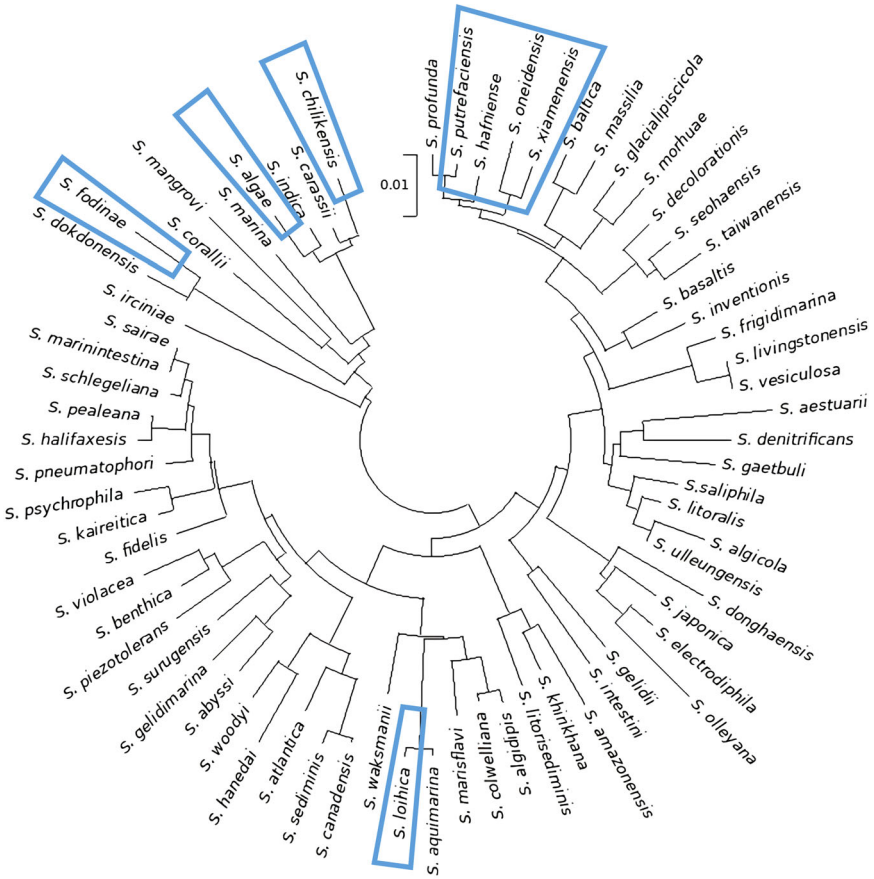

Fig. 1 Phylogenetic tree highlighthing known corrosive *Shewanella* spp. The tree shows all known 97 species of *Shewanella*. The highlighted species have previously been related to metal corrosion (Tables 2 and 3). The phylogenetic tree was designed using the UPGMA method and MEGA6 software[85], with 1000 bootstraps for branching, and the tree topology by 1000 re-samplings. The OTUs sequences were obtained in the NCBI Sequence Read Archive (SRA) database.

can be reversibly reduced and oxidized. *S. oneidensis* MR1 excretes flavins as redox mediators, which are reduced by the outer membrane cytochrome MtrC[28,31]. Once reduced, these mediators diffuse towards the extracellular electron acceptor, where they donate their electron and become oxidized again. This mediated EET mechanism is the most important outward EET strategy of *S. oneidensis* MR1, as was shown by medium exchange experiments[31,32] and the study of a mutant lacking flavin secretion[30]. This explains why *S. oneidensis* MR1 only form thin biofilms and remains largely planktonic[33], in contrast to for instance *Geobacter* spp., which mainly use direct EET and form thick electroactive biofilms[34]. Furthermore, this mediated EET mechanism explains why the transfer of electrons to extracellular electron acceptors can be accelerated by the addition of flavins[35].

Interestingly, *S. oneidensis* MR1 was also found to use cathodes as electron donor with fumarate as electron acceptor[21,36] (Fig. 2). Also with oxygen as electron acceptor, *S. oneidensis* MR1 consumed cathodic electrons, even though this did not support cell growth[22], likely because of the lack of an organic carbon source. Without the presence of an electron acceptor, *S. oneidensis* MR1 used cathodic electrons for the reduction of protons to generate H_2[37]. All these studies first grew a *S. oneidensis* MR1 biofilm on electrodes poised as an anode with lactate as electron donor, after which the electrodes were transferred to a different medium with an electron acceptor (ex. fumarate, O_2) and were poised as a cathode (more negative electrode potential). Cathodic electron uptake started immediately after the transfer of the electrode, without the need for altered gene expression or protein synthesis, suggesting that the electron uptake from a cathode by *S. oneidensis* MR1 occurs through direct inward EET by reversing the Mtr pathway[21,36]. This was further confirmed using gene deletion mutants lacking parts of the Mtr pathway[21,22]. The importance of redox mediators in cathodic electron uptake by *S. oneidensis* MR1 was not investigated in these studies, since planktonic cells and redox mediators were removed when transferring the electrode. Nevertheless, flavins secreted by *S. loihica* were already found to catalyze cathodic O_2 reduction[38]. Recently, soluble Fe(II) was also found to play a role as electron shuttle in the cathodic electron uptake by *S. oneidensis* MR1[39].

Besides a direct and mediated inward EET, an indirect EET mechanism with H_2 as intermediate also seems likely for *Shewanellae* using a cathode as electron donor. Electrodes poised as cathodes often have sufficiently negative potentials to enable electrochemical H_2 evolution by the cathode[40]. Moreover, several microorganisms have been found to catalyze cathodic H_2 evolution through the excretion of hydrogenase enzymes[41,42]. In addition, it was proposed that microorganisms consuming H_2 down to low H_2 partial pressures can thermodynamically stimulate the cathodic H_2 evolution reaction[40]. *Shewanella* spp. were already found to stimulate cathodic H_2 evolution[37] and consume H_2[19] likely down to low H_2 levels, since they have a low H_2 threshold (when using fumarate and nitrate as electron acceptors)[43]. Nevertheless, indirect EET with H_2 as intermediate has not yet been investigated for its role in cathodic electron uptake by *Shewanella* spp.

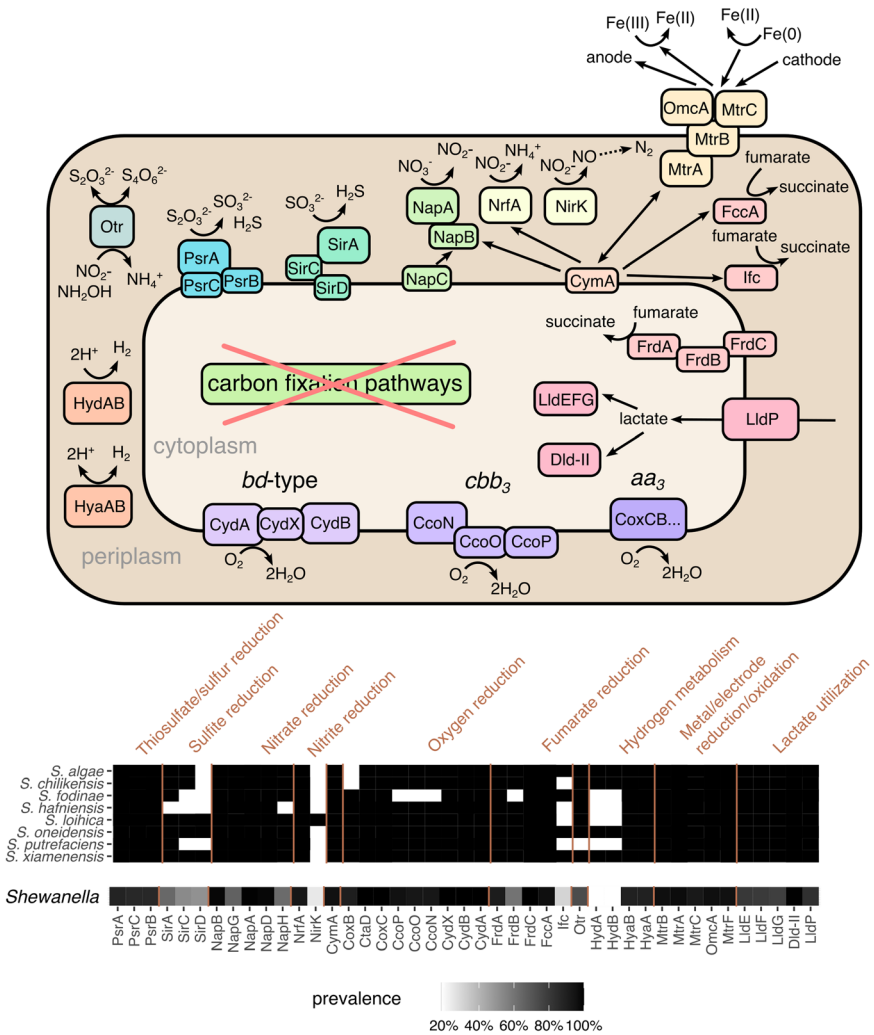

Fig. 2 Metabolic versatility of *Shewanella* spp. (top) Illustration of all the metabolic traits of *Shewanellae* relevant for microbial corrosion. (Bottom) Presence of genes encoding the indicated enzymes across reference genomes from the eight species of *Shewanella* linked to microbial corrosion, as well as overall prevalence across 97 named *Shewanella* species. Note that CymA has a central function in electron transfer to many different terminal electron acceptors, and that Otr has been shown to reduce nitrite, tetrathionate, and hydroxylamine. Details on the methods and additional information is available in Supplementary Information. The genome comparison shows that most of the metabolic traits relevant for microbial corrosion are common among *Shewanella* spp., including those which are not yet linked to microbial corrosion.

All these different inward EET mechanisms for cathodic electron uptake are of high relevance to understand MIC by *Shewanellae*, since they could explain how *Shewanella* spp. use Fe(0) as electron donor (Fig. 3), which is an extracellular electron donor analog to a cathode.

CORROSION MECHANISMS OF *SHEWANELLA* SPP.

The different mechanisms by which *Shewanella* spp. and other microorganisms cause steel corrosion can be divided in two main categories[44] (Fig. 3). The first set of MIC mechanisms is defined as chemical MIC (CMIC) and entails the microbial conversion of chemical components present in the aqueous solution in contact with the metal, or of those present in the passive layer of precipitates covering the steel surface. By altering the chemical composition of the solution or of the passive layer, microbes increase (or decrease) the corrosion rate. In case of *Shewanella* spp., CMIC is related to the conversion of O_2, Fe(III), thiosulfate, sulfite and nitrate, as described below. All these components are used by *Shewanellae* as electron acceptors and therefore CMIC by *Shewanellae* is usually studied with the addition of an electron donor, such as for instance lactate, amino acids or other rich medium components[20,45–48]. The second set of MIC mechanisms is electric MIC (EMIC), which is defined as the microbial conversion of Fe(0) in steel itself. Fe(0) acts as electron donor in EMIC, thus this process is studied with the addition of a suitable electron acceptor for *Shewanellae*, such as fumarate or nitrate[23,24]. Since Fe(0) is an extracellular electron donor, EMIC requires inward EET and the various EET mechanisms discussed above in relation to the use of a cathode as electron donor by *Shewanellae* are also of relevance for EMIC of steel[6].

CMIC

O_2 and Fe(III) reduction: corrosion inhibition and/or acceleration

Shewanellae are facultative aerobic bacteria, meaning that they use O_2 as preferred electron acceptor in oxic conditions (Fig. 2). Since oxygen causes strong chemical corrosion (Reaction (1)), microbial O_2 consumption could decrease and inhibit corrosion in

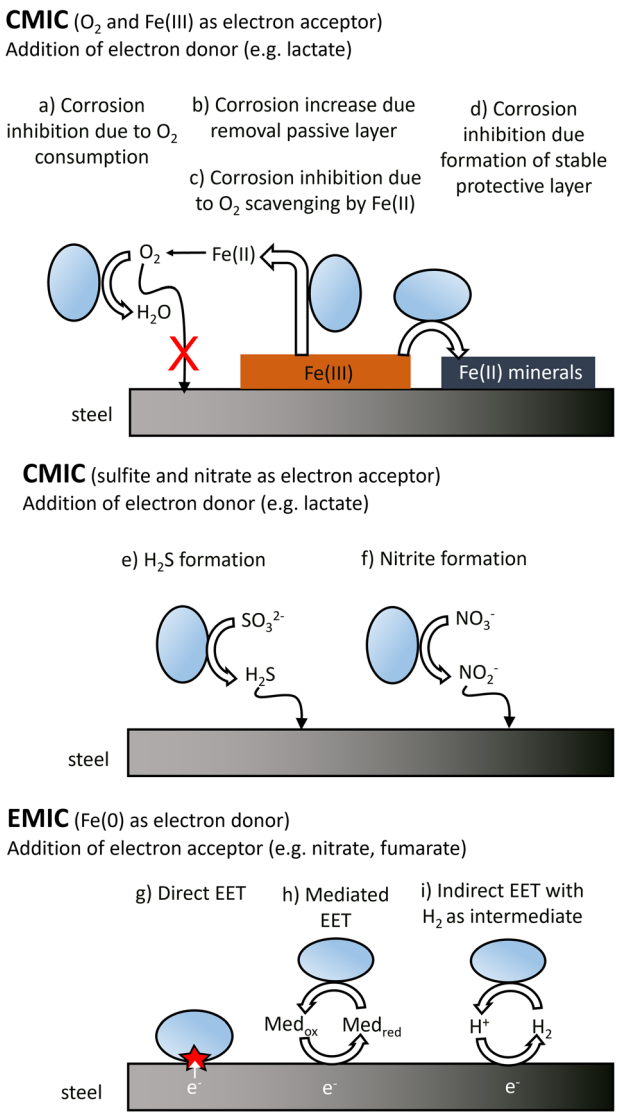

Fig. 3 Overview of the different corrosion mechanisms proposed for *Shewanella* spp. CMIC stands for chemical MIC and in the case of *Shewanella* spp. entails the conversion of electron acceptors (O_2, Fe(III), thiosulfate, sulfite and nitrate) present in the aqueous solution or in the passive layer on the steel surface. CMIC by *Shewanellae* is studied with the addition of an electron donor, e.g. lactate. In contrast, EMIC stands for electric MIC, which is defined as the use of Fe(0) in the steel itself as electron donor by *Shewanellae*. EMIC is studied by addition of an electron acceptor, e.g. fumarate or nitrate. (Top) CMIC mechanisms related to the use of O_2 and Fe(III) as electron acceptor. **a** Corrosion is inhibited by O_2 consumption, **b** Fe(III) reduction increases corrosion due to the removal of the passive layer; **c** but also inhibits corrosion due to scavenging of O_2 by dissolved Fe(II); **d** Fe(II) can also form stable precipitates and thereby rather protect steel from corrosion. (Middle) CMIC mechanisms related to the use of sulfite (**e**) and nitrate (**f**) as electron acceptor. (Bottom) EMIC mechanisms related to the use of Fe(0) as electron donor. EMIC can be related to a (**g**) direct EET; (**i**) a mediated EET; or (**h**) indirect EET with H_2 as intermediate.

aerobic conditions (Fig. 3a). Lower corrosion rates were indeed reported with *S. oneidensis* MR1 in comparison to uninoculated controls[46] (Table 3) and also *S. putrefaciens* was found to have a protective effect against pitting corrosion in oxic conditions[48]. In addition, Miller et al.[45] described that *S. oneidensis* inhibited corrosion of carbon steel, but only if it completely covered the metal (Table 3). In contrast, when a steel coupon free of biofilm was brought in electric contact with a coupon covered with *Shewanella*, increased corrosion rates were recorded[45] (Table 3). In addition, a biofilm deficient mutant was found to lead to lower corrosion protection[46], while increased pitting corrosion also resulted from incomplete biofilm coverage by *S. algae*[49] (Table 3). Heterogeneous biofilm coverage likely leads to increased corrosion due to the formation of oxygen concentration cells[50,51]. The biofilm free parts act as zones where oxygen reduction occurs (only the cathodic part of Reaction (1): $½\ O_2 + 2e^- + H_2O \rightarrow 2\ OH^-$), while the electrons come from anodic zones where the corrosive half reaction takes place ($Fe(0) \rightarrow Fe^{2+} + 2e^-$). These anodic zones are the biofilm covered spots, as O_2 is depleted under the biofilm due to O_2 consumption. Interestingly, without the addition of lactate, Miller et al.[45] found much less driving force for the acceleration of corrosion, likely because microbial O_2 consumption is limited without electron donor.

Oxic corrosion leads to the formation of Fe(III) (hydro)oxide corrosion products (Reaction (3)), which precipitate on the steel surface and form a passive layer, protecting the metal against further corrosion. Upon depletion of O_2, *Shewanella* spp. can switch to the use of Fe(III) as electron acceptor (Fig. 2). Microbial Fe(III) reduction can remove the passive layer, thereby increasing the metal's susceptibility for corrosion (Fig. 3b). It was indeed reported that *S. putrefaciens* accelerated corrosion by reducing Fe(III) in the passive film on carbon steel in anoxic conditions with the addition of lactate as electron donor[52] (Table 3). In contrast, Fe(III) reduction can also result in corrosion protection, since the resulting dissolved Fe(II) acts as O_2 scavenger (Fig. 3c). *S. oneidensis* was indeed found to lower the corrosion susceptibility of mild steel during Fe(III) reduction[53]. In addition, Dubiel et al.[46] reported that the *S. oneidensis* wild type led to stronger corrosion protection than a mutant deficient in Fe(III) reduction (menaquinone gene deleted). These contradicting findings on the role of microbial Fe(III) reduction on corrosion could possibly be explained by differences in flow regime[50]. Dissolved Fe(II) accumulates and scavenges incoming O_2 best in a static environment, while dissolved Fe(II) is depleted and fresh O_2 is continuously introduced under a high flow regime, stimulating corrosion.

In complete absence of O_2, Fe(III) reduction mostly causes an increased corrosion rate (Fig. 3b), as shown by Little et al.[52] (Table 3). Even on stainless steel, *Shewanellae* were found to degrade the passive layer by Fe(III) reduction[47,54,55]. Also with the addition of Fe(III) citrate to the medium (alternative Fe(III) source), *S. putrefaciens* increased the mass loss of mild steel[20] (Table 3). As discussed above, Fe(III) (hydr)oxide reduction requires outward EET, in which flavin mediators are known to play an important role. Riboflavin addition to the medium was therefore found to increase Fe(III) removal from the passive layer and increase pit depths[47].

With the presence of bicarbonate or phosphate in the medium, microbial Fe(III) reduction can lead to the formation of stable Fe(II) minerals (such as Fe(II) carbonates and phosphates), which rather form a protective layer[56] and can be applied for the stabilization and protection of corroded iron objects[57] (Fig. 3d) (Table 3).

In anoxic conditions, chemical corrosion results in the formation of H_2 (Reaction (4)) and *S. oneidensis* was indeed found to increase H_2 levels by corroding carbon steel coupons[58–60]. The generated H_2 can act as electron donor for the Fe(III) reduction by *Shewanellae*[19,20], even though this does not support cellular growth. Schutz et al. [58] reported that Fe(III) reduction in the presence of H_2 and without lactate in the medium (but small amounts of amino acids) increased the corrosion of carbon steel with a factor of 2-3 times over a time period of 5 days (Table 3). Over a time frame of 5 months, a corrosion increase of only 1.3 times was found (Table 3), while there was no increased corrosion when the amino acids were omitted from the medium[59]. This further demonstrates the importance of the medium composition

on the outcome of MIC studies, since long-term corrosion by *Shewanellae* is likely only feasible if the medium supports growth of these microorganisms. In addition, it should be noted that the effect of microbial Fe(III) reduction on the corrosion rate likely depends also on whether or not the experimental procedures established or removed a passive layer on the steel surface before the start of the experiment[47,59].

Sulfite, thiosulfate and nitrate reduction: corrosion increase

Besides oxygen and Fe(III), *Shewanella* spp. also use sulfite, thiosulfate and nitrate as electron acceptors, when the conditions are anoxic (Fig. 2). Microbial reduction of thiosulfate and sulfite leads to H_2S formation, which is a powerful corroding reactant inducing Reaction (4)[44] (Fig. 3e). McLeod et al.[61] demonstrated that their *Shewanella* isolates reduced sulfite to sulfide, while Dawood et al. [20] found that these isolates caused up to a four times increase of the mass loss of mild steel coupons with sulfite as electron acceptor and lactate as electron donor (Table 3). Also Salgar-Chaparro et al.[62] found that *S. chilikensis* caused strong pitting corrosion with the addition of thiosulfate as electron acceptor (Table 3).

In addition, *Shewanellae* can use nitrate as electron acceptor (Fig. 2). *S. oneidensis* MR1 performs dissimilatory nitrate reduction to ammonia with the transient formation of nitrite[63], while some other *Shewanellae* can denitrify nitrate to N_2[16]. Miller et al.[24] demonstrated that the accumulation of nitrite, resulting from nitrate reduction by *S. oneidensis* MR1 with lactate as electron donor, increased the mass loss of carbon steel coupons (Fig. 3f). Salgar-Chaparro et al.[62] reported that *S. chilikensis* caused uniform corrosion and strong mass loss of carbon steel with the addition of nitrate (Table 3) (while there was rather pitting corrosion with the addition of thiosulfate). Curiously, nitrate and nitrite are often used in oil and gas installations to prevent corrosion and souring by SRBs, offering energetically more favorable electron acceptors for the microbial community than sulfate[64,65]. Miller et al.[24] discussed that the nitrite concentration, as well as the heterogeneity of the biofilm coverage, could be determining for whether nitrite leads to a corrosion increase or decrease.

EMIC

Only recently, the possible role of EMIC in corrosion by *Shewanella* spp. has been investigated. As explained above, Fe(0) acts as extracellular electron donor during EMIC, thus EMIC can only be studied with the addition of an electron acceptor (e.g. nitrate and fumarate) and in absence of an organic electron donor. Miller et al. [24] found that *S. oneidensis* MR1 reduced nitrate to nitrite in the absence of lactate and concluded that Fe(0) oxidation must have supported nitrate reduction. They found an 11 times increase of the mass loss of carbon steel coupons after 10 days, while there was just a 6 times increase with the addition of lactate (Table 3), and discussed that besides nitrite accumulation (CMIC), EMIC must have contributed to this increase[24]. Some other studies also suggested EMIC for *Shewanellae* reducing nitrate, but did not exclude possible organic electron donors from their medium, nor included controls to assess the corrosive effect of nitrite accumulation[66,67]. With fumarate as electron acceptor, a 7-times corrosion increase of Fe(0) powder was found for *S. fodinae* 4t3-1-2LB strain[23] (Table 3). Also *S. oneidensis* MR1 was found to increase the weight loss from carbon steel, when fumarate was added as electron acceptor[12] (Table 3). Philips et al.[23] included several controls to evaluate if corrosion was induced by the medium or by the formed metabolites (malate, succinate, other metabolites were tested using cell-free spent medium), but none of these could explain the strongly increased corrosion. Consequently, only the use of Fe(0) as electron donor for the reduction of fumarate (EMIC) could explain the observed corrosion increase.

Similarly as discussed above for cathodes, the extracellular electron uptake from steel, causing EMIC, can be due to three different mechanisms (Fig. 3). First of all, EMIC could entail a direct inward EET (Fig. 3g) (recently also called electrobiocorrosion[2]). In case of *Shewanella* spp., such a direct EET could be enabled through the reversal of the Mtr pathway. Hernandez-Santana et al.[12] indeed found that a Mtr deletion mutant had a decreased corrosion rate in comparison to the wild type of *S. oneidensis* MR1, demonstrating the involvement of direct EET in EMIC. Nevertheless, the mutant still had a higher corrosion rate than in sterile conditions, thus direct EET was not the only mechanism involved in EMIC. Similarly, Li et al.[47] reported a lower current on an active steel surface (passive layer abraded) for the OmcA deletion mutant of *S. oneidensis* MR1. This study, however, included lactate in all treatment, besides fumarate as electron donor, since growth inhibition was observed without lactate[47]. A direct EET mechanism was also inferred from the reduced corrosion of stainless steel by an Mtr deletion mutant of *S. oneidensis* MR1 in aerobic conditions and in rich medium[11], but this study did not discuss whether the Mtr pathway could have been involved in Fe(III) reduction, while several previous studies (Table 3) have shown that with the addition of electron donors, corrosion can be accelerated by the reduction of Fe(III) from the passive layer (discussed in detail above). Moreover, also this study found that the deletion mutant had a higher corrosion rate than sterile conditions[11], suggesting that also other mechanisms were on play. Fortunately, the results of Hernandez-Santana et al.[12] were more conclusive that *Shewanella* can use direct EET to cause corrosion. Intriguingly, this result makes *Shewanellae* part of the very few microorganisms, including some *Geobacter* model strains[68,69], for which direct inward EET has been clearly proven to contribute to MIC.

A second option is that EMIC is related to mediated inward EET (Fig. 3h). Philips et al.[23] performed a medium exchange experiment and reported that corrosion by *S. fodinae* continued with the same rate after the medium exchange, indicating that mediated EET was not involved. Electrochemical measurements further confirmed that no redox mediators were excreted by their *S. fodinae* strain[23]. Nevertheless, flavin mediators were thought to play a role in EMIC by *S. oneidensis* MR1, since the addition of exogenous riboflavin increased the initial corrosion of pure iron[56] and the pitting depth and corrosion rate of stainless steel[47] (both studies with fumarate and lactate) .

As a third option, EMIC could involve an indirect inward EET mechanism through the use of H_2 as intermediate, since H_2 is generated by the anoxic corrosion reaction (Reaction (4)). Already in 1934, the scavenging of H_2 from a steel surface, was proposed as an important mechanism by which microorganisms cause corrosion, i.e. the cathodic depolarization theory[70]. Several studies observed that *Shewanella* spp. were able to consume the H_2 formed on iron or steel surfaces[20,61,66]. However, none of these studies clearly demonstrated that this microbial H_2 consumption caused a corrosion increase, since an organic electron donor (ex. lactate) was always added, meaning that other corrosion mechanisms (CMIC) could not be excluded. Moreover, the cathodic depolarization theory was thought to be disproven by the finding that some hydrogenotrophic microorganisms did not cause corrosion, while related strains isolated with Fe(0) as sole electron donor did induce severe corrosion[44,71,72]. This reasoning, however, did not incorporate that hydrogenotrophic microorganisms can differ strongly in their H_2 consumption characteristics[6,40,73,74]. Strains isolated with Fe(0) are likely well adapted to use low H_2 partial pressures (and have a high affinity for H_2). Moreover, microbes that can maintain a low H_2 partial pressure on the Fe(0) or steel surface, most likely also induce stronger corrosion[40]. Philips et al.[23] found that their corrosive *S. fodinae* strain maintained H_2 partial pressures below detection limit of a TCD detector. Also *S. oneidensis* created low H_2 levels during the corrosion of carbon steel[12]. This study also included a *S. oneidensis*

mutant incapable of H_2 consumption, which had a lower corrosion rate than the wild type, but which was still higher than the sterile control. Interestingly, together with their results on the Mtr mutant, Hernandez-Santana et al.[12] thus demonstrated that *Shewanella* uses both a direct inward EET and an indirect inward EET with H_2 as intermediate to accelerate corrosion through EMIC. It can be expected that the relative contribution of indirect EET through H_2 is dependent on the steel composition, since pure iron leads to rapid H_2 generation, while no H_2 was found on stainless steel[69].

CHALLENGES AND OPPORTUNTIES OF USING *SHEWANELLA* SPP. FOR MICROBIAL CORROSION STUDIES

Our discussion has shown that the metabolic versatility of *Shewanella* spp. (Fig. 2) leads to a wide variety of mechanisms by which these species cause or inhibit steel corrosion (Table 3, Fig. 3). *Shewanella* strains are often chosen to study microbial corrosion, because of their relevance for MIC (Tables 1 and 2), but likely also because of their straightforward cultivation in aerobic rich media. Corrosion scientists, however, should be aware that the simple cultivation of these microorganisms unfortunately does not come with simple interpretation of their corrosion mechanism. The complexity of the involved corrosion processes can indeed lead to confusing interpretations. For instance, Zhou et al.[11] described a direct inward EET mechanism (EMIC) for *S. oneidensis*, but did not discuss to which level Fe(III) reduction (outward EET), or the formation of O_2 concentration cells, could have been involved, while these processes were previously described for similar experimental conditions (rich medium, oxic conditions, stainless steel)[47,49]. Similarly, Chang et al.[55] studied the role of EET in corrosion by *S. algae*, but did not differentiate between outward EET involved in Fe(III) reduction and inward EET involved in EMIC.

Our discussion above explained that the corrosion mechanism resulting from the metabolic activity of *Shewanellae* strongly depends on the composition of the medium, similar as has been described for other microorganisms[1,75]. The main difference in the medium composition results from the addition of an electron donor to study CMIC, while an electron acceptor is added to study EMIC. Moreover, *Shewanellae* can only grow with the addition of an organic carbon source. Scientists should thus carefully design the composition of the medium, in order to come to sound conclusions on the corrosion mechanism. Many studies include a variety of different electron donors and acceptors in the medium[55,66,67,76], but can therefore not come to a conclusion on the involved corrosion mechanism. Nevertheless, even with well selected medium components, *Shewanella* spp. could use different corrosion mechanisms concurrently[12,24]. Differentiation between those mechanisms requires the inclusion of thoughtful experimental controls, such as sterile medium controls, controls with possible metabolites (e.g. nitrite, succinate, malate)[23,24] and spent medium controls[41]. It is also important to realize that growth media often contain redox mediators (part of the vitamin solutions and yeast extract) and other components affecting corrosion[1], while compounds such as amino acids and riboflavin can impact attachment by *Shewanella* spp.[48,77]. Growth media might thus not be representative for realistic corrosion environments[1]. In general, the relevance of all medium additions should be questioned, since concentrations of for instance lactate and fumarate are most likely rather low in the environment.

All the studies reviewed in this work used one *Shewanella* strain as a model organism to study MIC. Few studies already investigated the interactions of a *Shewanella* strain with another microbe during corrosion processes[53,67,78,79]. For instance, *S. oneidensis* was found to diminish the corrosion of carbon steel caused by *Desulfovibrio desulfuricans*[53], while *S. algae* was rather found to accelerate corrosion by *Desulfovibrio caledoniensis*[79]. Similarly, *S. oneidensis* increased corrosion of stainless steel by *Bacillus licheniformis*[67]. In real corrosion environments, however, diverse microbial communities are present, in which much more complex ecological interactions take place. In addition, local microenvironments and dynamic conditions likely add to the complexity of the corrosion process[3]. This means that it remains highly difficult to assess which corrosion mechanisms occur in relevant corrosion environments and thus to accurately diagnose MIC[1,2].

Despite these challenges, *Shewanella* spp. also offer interesting opportunities for the study of MIC. Thanks to their metabolic variability, *Shewanella* spp. offer the possibility to test the importance of the various corrosion mechanisms in a wide diversity of environmental conditions. In addition, their fairly easy genetic manipulation[80] offers opportunities to distinguish between the different mechanisms that can occur concurrently[12]. So far, only few corrosion studies have used *Shewanella* deletion mutants[11,12,46,47], in contrast to the high number of studies that have used mutants to investigate EET to Fe(III) and electrodes by *Shewanellae*[18,34]. Nevertheless, smartly selected mutants could aid in differentiating between the many different corrosion mechanisms of *Shewanellae* (Fig. 3). It should thereby kept into account that *Shewanellae* use the Mtr pathway both for inward and outward EET (direct EMIC vs. CMIC through Fe(III) reduction), as discussed above. Genes solely related to inward EET and not to outward EET have already been identified[81], offering interesting candidate genes to test deletion mutants differentiating between outward and inward EET. Furthermore, gene deletion mutants can bring detailed insights in the role of various other processes (e.g. attachment, biofilm formation, nanowires, flavin excretion) in steel corrosion or its inhibition by *Shewanellae*[82].

Interesting opportunities also lie ahead to create corrosion inhibiting conditions by applying a good understanding of the metabolism of *Shewanella* spp. As detailed above, *Shewanellae* often inhibit corrosion in oxic conditions due to their O_2 consumption (Table 3, Fig. 3a). In addition, Fe(III) reduction by *Shewanellae* can create dense Fe(II) phosphate and precipitations, protecting steel surface from further corrosion[56,57] (Fig. 3c). Alternatively, the addition of $CaCl_2$ to the medium, together with the formation of CO_2 from to the oxidation of organic electron donors, was shown to lead to biomineralization of $CaCO_3$ by *S. putrefaciens*[83], also offering corrosion inhibition. These corrosion protection methods still need to be tested in real environments and over the long term, but nevertheless offer interesting opportunities for future corrosion prevention strategies.

Finally, the corrosion processes induced by *Shewanellae* could also be of interest to create new materials. For instance, Jia et al.[84] used the corrosion and biomineralization processes by *S. oneidensis* to create surface modifications on nickel foam (i.e. common electrode material in water electrolysers), offering interesting possibilities to replace current chemical treatments, which are expensive, complicated and requiring toxic chemicals.

CONCLUSION

Shewanella spp. are highly interesting microbes to study microbial corrosion processes, since their metabolic versatility entails that they can induce and inhibit corrosion through various mechanisms. The composition of the growth medium (presence of electron acceptor, electron donor, carbon source) has a strong impact on which corrosion mechanisms are in play, but some corrosion mechanisms can also occur concurrently. Scientists should keep this complex interplay between different corrosion mechanisms in mind, when opting for *Shewanella* spp. as model strains for microbial corrosion experiments. Differentiation between the different corrosion mechanisms is possible by inclusion of well designed experimental controls. Moreover, *Shewanella* spp. offer the interesting opportunity to include

smartly selected deletion mutants, thanks to their fairly easy genetic manipulation.

DATA AVAILABILITY

Annotations of relevant functional genes in *Shewanellae* genomes used in Fig. 2 were deposited at Zenodo (https://doi.org/10.5281/zenodo.10122203).

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AUTHOR CONTRIBUTIONS

The concept of this work was developed by JP and LP. JP analyzed the existing literature and wrote a full draft. The phylogenetic tree (Fig. 1) was made by LP. IPGM made Fig. 2 and performed the related genome analysis. Figure 3 was made by JP. All authors revised the draft and approved the final submission.

COMPETING INTERESTS

All authors declare no competing interests.

ADDITIONAL INFORMATION

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