

# Marine sulfate-reducing bacteria cause serious corrosion of iron under electroconductive biogenic mineral crust

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## Summary

Iron (Fe<sup>0</sup>) corrosion in anoxic environments (e.g. inside pipelines), a process entailing considerable economic costs, is largely influenced by microorganisms, in particular sulfate-reducing bacteria (SRB). The process is characterized by formation of black crusts and metal pitting. The mechanism is usually explained by the corrosiveness of formed H<sub>2</sub>S, and scavenging of 'cathodic' H<sub>2</sub> from chemical reaction of Fe<sup>0</sup> with H<sub>2</sub>O. Here we studied peculiar marine SRB that grew lithotrophically with metallic iron as the only electron donor. They degraded up to 72% of iron coupons (10 mm × 10 mm × 1 mm) within five months, which is a technologically highly relevant corrosion rate (0.7 mm Fe<sup>0</sup> year<sup>-1</sup>), while conventional H<sub>2</sub>-scavenging control strains were not corrosive. The black, hard mineral crust (FeS, FeCO<sub>3</sub>, Mg/CaCO<sub>3</sub>) deposited on the corroding metal exhibited electrical conductivity (50 S m<sup>-1</sup>). This was sufficient to explain the corrosion rate by electron flow from the metal (4Fe<sup>0</sup> → 4Fe<sup>2+</sup> + 8e<sup>-</sup>) through semiconductive sulfides to the crust-colonizing cells reducing sulfate (8e<sup>-</sup> + SO<sub>4</sub><sup>2-</sup> + 9H<sup>+</sup> → HS<sup>-</sup> + 4H<sub>2</sub>O). Hence, anaerobic microbial iron corrosion obviously bypasses H<sub>2</sub> rather than depends on it. SRB with such corrosive potential were revealed at naturally high numbers at a

coastal marine sediment site. Iron coupons buried there were corroded and covered by the characteristic mineral crust. It is speculated that anaerobic biocorrosion is due to the promiscuous use of an ecophysiologicaly relevant catabolic trait for uptake of external electrons from abiotic or biotic sources in sediments.

## Introduction

Iron, the fourth most abundant element in the earth's crust, is the principal redox-active metal in metabolic processes of essentially all living organisms. It is either involved in catalytic quantities as a component of a vast number of proteins, or in much higher, substrate quantities as the external electron donor or acceptor for specially adapted environmental microorganisms referred to as 'iron bacteria' (ferrotrophic bacteria, aerobic or anaerobic) or 'iron-respiring bacteria' respectively. In most biological functions, iron has the +II (ferrous) or +III (ferric) oxidation state. From a physiological point of view it appears astounding that also the native, metallic element (Fe<sup>0</sup>) can be involved in a biological process; this is anaerobic microbial corrosion. In technology, the process is often referred to as microbially influenced corrosion (MIC).

Iron is the technologically most widely employed metal, due to the abundance of its ores, straightforward melting and excellent mechanical properties. It is globally produced at a 25-fold higher extent (9.3 × 10<sup>8</sup> t year<sup>-1</sup>) than the second most widely employed metal, aluminum (US Geological Survey, 2011; data for 2009). Iron corrosion including MIC is thus of significant economic relevance. MIC affects industrial water-bearing systems such as oil and gas pipelines (Hamilton, 1985; Li *et al.*, 2000; Schwärmer *et al.*, 2008). It therefore causes, besides economic losses, also failures that are of environmental concern or even hazardous (Duncan *et al.*, 2009; Sherar *et al.*, 2011). A critical feature of MIC is that it is not as visible as the commonly known rusting of iron under air, but usually occurs as a 'hidden' process in the interior of iron pipes or on iron constructions buried in aqueous underground. There is much agreement that sulfate-reducing bacteria (SRB; more generally also sulfate-reducing microorganisms, SRM) are the main culprits of MIC (Hamilton, 1985;

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