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Bacteria-materials interactions and Fe isotope fractionation - discriminating MIC from electrochemical corrosion

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In geological systems, bacterial interactions with iron are known to fractionate Fe-isotopes; e.g. experimental work involving dissimilatory bacterial reduction of Fe^{3+} to Fe^{2+} by *Shewanella alga* produces fractionation of Fe-isotopes by up to 1.3 ‰ ($\delta^{56/54}$Fe) $(1, 2)$. A similar fractionation factor of ∼1.5 ± 0.2 ‰, in terms of $\delta^{56/54}$Fe, was found for bacterial oxidation of Fe^{2+} to Fe^{3+} (3). However, no data currently exist on the magnitude of fractionation for industrial materials over relevant time scales, or whether different bacterial assemblages or mechanisms of corrosion exhibit different Fe isotope fractionations. Metal corrosion is estimated to cost $276 billion (∼ 3.1% of GDP) annually in the USA alone and is responsible for 15-30% of corrosion-related pipeline failures (4). Such corrosion is microbially induced and/or electrochemical in origin. Currently, there is no simple diagnostic test for identifying the role of MIC versus ECC and therefore biocides tend to be used indiscriminately, often where they may not be required. The use of biocides to control MIC is a major cost and presents an increasing environmental liability.

Here we compare the ratios of the three most abundant Fe isotopes ^{54}Fe, ^{56}Fe and ^{57}Fe ($\delta^{56/54}$Fe and $\delta^{57/54}$Fe) of microbially induced corrosion (MIC) and electrochemical corrosion (ECC) products with those of uncorroded cast iron starting materials. A major unknown was whether sufficient fractionation could be identified over the short time periods, relevant to industrial applications, and whether abiotic fractionation of Fe-isotopes would mask any signature associated with MIC.

In this study we provide a novel approach to distinguish MIC from ECC, by determining the iron isotope composition of corrosion-affected materials, offering a means to better target the use of biocides and providing a new tool in performance testing of Fe-based installations and materials. In laboratory experiments, MIC products of Fe in the presence of a pure strain of *Thiomonas* sp. WJ68 exhibit a major shift in Fe isotope ratios ($\delta^{56/54}$Fe and $\delta^{57/54}$Fe, by 1.26 and 1.95 per mil, respectively) compared to ECC products formed under identical but sterile conditions. The methodology has applications in a broad range of industrial environments, particularly in the petrochemicals sector.

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