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**EXTRACELLULAR IRON-SULFUR PRECIPITATES FROM GROWTH OF
*Desulfovibrio desulfuricans***

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ABSTRACT

We have examined extracellular iron-bearing precipitates resulting from the growth of *Desulfovibrio desulfuricans* in a basal medium with lactate as the carbon source and ferrous sulfate. Black precipitates were obtained when *D. desulfuricans* was grown with an excess of FeSO_4 . When *D. desulfuricans* was grown under conditions with low amounts of FeSO_4 , brown precipitates were obtained. The precipitates were characterized by iron K-edge XAFS (X-ray absorption fine structure), ^{57}Fe Mössbauer-effect spectroscopy, and powder X-ray diffraction. Both were noncrystalline and nonmagnetic (at room temperature) solids containing high-spin Fe(III). The spectroscopic data for the black precipitates indicate the formation of an iron-sulfur phase with 6 nearest S neighbors about Fe at an average distance of 2.24(1) Å, whereas the brown precipitates are an iron-oxygen-sulfur phase with 6 nearest O neighbors about Fe at an average distance of 1.95(1) Å.

INTRODUCTION

Sulfate reducing bacteria (SRB) in subsurface oil reservoirs can cause significant production problems, especially in formations that have been subjected to advanced recovery operations such as seawater flooding. In secondary petroleum production activities, waterflooding is the most successful and extensively used technique to recover oil from a field in which the natural pressure of the reservoir is no longer sufficient to force the oil out of the pores of the rock.^{1,2} Although waterflooding operations are of economic benefit—in terms of increased crude oil production—flooding oftentimes indirectly leads to an increase in the hydrogen sulfide, H_2S , content of the reservoir fluids, a condition known as souring.³ Oil fields with initially low indigenous levels of H_2S have been shown to produce increasing amounts of H_2S as waterflooding operations expand.⁴ This is due to, in part, the presence of SRB in the subsurface reservoir.⁵⁻⁷

Regardless of their origin and exact genera, sulfate reducers are potent generators of H_2S . The anaerobic, nutrient rich geothermal environments of waterflooded oil reservoirs are excellent habitats for the growth of SRB.^{8,9} The diversity and distribution of SRB species varies from reservoir-to-reservoir with the subsurface physical conditions, e.g., nutrient concentration, salinity, temperature, pressure, porosity, permeability, pH.^{8,10} The metabolism of SRB involves the eight-electron reduction of sulfate, $[\text{SO}_4]^{2-}$. One of the final products of the dissimilatory reduction of sulfate is H_2S . In sulfate-rich environments, the reduction proceeds without accumulation of intermediates, e.g., S(V), S(IV), S(II), S(0), S(I-). Depending upon the aquifer pH, the dissolved H_2S is in equilibrium with the SH^- or S^{2-} anions.¹¹

In addition to the undesirable effects of souring and the threat to human health, H_2S poses problems with corrosion. Microbial influenced corrosion (MIC) occurs when SRB/ H_2S attack the iron and its alloys found in the subsurface tubing, valves, rods, and other components of the well, to produce iron sulfides.¹²⁻¹⁷ Failures of ferrous metal oil-field equipment that occur as a result of MIC are of significant engineering concern and a cause of economic loss in the secondary production of petroleum. Moreover, the subsurface production of H_2S by SRB leads to yet another problem—fouling—wherein ultrafine solids clog the pores in the formation and reduce reservoir permeability.^{2,18} Colonies of sulfate reducers give rise to ultrafine extracellular precipitates.¹⁹ The solids precipitation can be severe if the reservoir contains iron, which is ultimately found as ferrous ion, Fe(II), in the anoxic downhole conditions. Regardless of the source of H_2S , reservoir souring in combination with the presence of iron can lead to the formation of a variety of ultrafine iron sulfur, Fe-S, precipitates. This happens when H_2S , SH^- , and S^{2-} react with dissolved Fe(II) in the

field aquifer and oil as well as with solid, iron-bearing reservoir minerals.⁴ These reactions produce black Fe-S precipitates.²⁰ The precipitation of extracellular Fe-S fines throughout the reservoir can block the movement of fluids.² Because the rate at which oil can be extracted depends upon the porosity and permeability of the rock, any blockage or plugging may lead to the premature decline in production of a field with a large amount of oil still in place.

Iron-bearing solids are generally ubiquitous in oil reservoirs as naturally occurring minerals such as sulfides, disulfides, carbonates, clays and clay minerals.²⁰ Depending upon the subsurface microbiological and geochemical environments, the formation of Fe-S precipitates in souring reservoirs can be understood in terms of either biotic or abiotic processes.⁴ The former involves microbiologically-influenced reactions of sulfide with dissolved and solid iron.²¹⁻²⁶ Of interest here is the extracellular MIC and biotically-mediated Fe-S production processes mentioned above, wherein H₂S reacts with iron in the extracellular environment to form fine black precipitates. This is to be contrasted with intracellular biologically-mediated mineralization of Fe-S compounds in magnetotactic bacteria.²⁷⁻³⁰ Abiotic processes involve reactions of sulfide produced by any number of inorganic souring mechanisms with iron in the subsurface environment. The suggestion has been made that the ferruginous sulfides produced by biotic microbial mediation and abiotic chemical processes may be distinctly different from one another and from the ferruginous sulfides present in the geochemical environment itself.^{16, 30, 31} Verification of this suggestion would have significant technical and economic impact on upstream petroleum production operations.

Although extracellular Fe-S precipitates obtained from the growth of SRB have been studied for some time,²¹⁻²⁴ the exact phase relationships are incompletely known and issues of contemporary interest.^{25, 26, 32} A fundamental understanding of the subsurface chemistry of iron and sulfur, in general, and the formation of biotic Fe-S precipitates, in particular, can provide insights about fouling in souring oil reservoirs. In addition to implications in petroleum production operations, biotically-mediated Fe-S precipitates are receiving attention as adsorbants.³³ We have isolated and characterized precipitates that formed in the presence of SRB by reaction of H₂S with ferrous ions in the extracellular environment. The noncrystalline Fe-bearing precipitates obtained from anaerobic growth of *Desulfovibrio desulfuricans* were examined by use of Fe K-edge XAFS (X-ray absorption fine structure), ⁵⁷Fe Mössbauer-effect spectroscopy, and powder X-ray diffraction.

EXPERIMENTS

Desulfovibrio desulfuricans (ATCC 29577) was grown anaerobically in unfiltered ATCC culture medium 207 with added resazurin, an E_h indicator. FeSO₄ was added in concentrations varying from 0.04 mg/mL to 1.0 mg/mL. Studies were also done with a medium of similar composition in which 2 g/L MgSO₄ was used in place of 2 g/L MgCl₂. Anaerobiosis was achieved and verified using a modification of benchtop techniques.³⁴ All manipulations took place under a sterile stream of N₂ gas using needles and syringes to inoculate anaerobic media in serum vials sealed with butyl rubber stoppers. Before incubation, the atmosphere in the vials was replaced by a sterile stream of N₂-CO₂ gas. All cultures were grown at 30°C. The precipitates were worked up under strictly anaerobic conditions under a N₂/CO₂ atmosphere in a Hydrovoid Air Control inert atmosphere box, equipped with gloves. After isolation by filtration, each sample was sealed in place on the filter paper, between layers of Kapton[®] tape. Zero-field, natural abundance ⁵⁷Fe Mössbauer spectra were acquired on the solid samples at 295, 77, and 5 K in a LHe exchange-gas cryostat as described elsewhere.²⁰ The Mössbauer spectra were recorded in the standard transmission geometry with a ⁵⁷Co/Rh source and a Kr/CH₄ detector. Velocity calibration over the range 0 ± 11 mm/s was checked by use of a natural iron foil (25 μm thick). All isomer shifts were quoted with respect to natural iron at room temperature. The instrumental linewidth was found to be 0.28 mm/s for iron foil. The data were folded and fit using the program WMOSS.³⁵ The isomer shift (δ, mm/s), quadrupole splitting (ΔE_Q, mm/s), linewidths (FWHM, Γ, mm/s) and internal magnetic field (H_{int}, kG) were obtained from the fits. Powder X-ray diffraction data were collected with a Scintag diffractometer using Cu Kα radiation. Iron K-edge transmission XANES (X-ray absorption near edge structure) and EXAFS (extended X-ray absorption fine structure) were collected at the APS using the BESSRC beam line 12-BM-B, equipped with a Si<111> monochromator. The energy

was calibrated with the inflection point in the first differential XANES of Fe (4 μm thick), which is at 7112 eV in accordance with previous work.³⁶ The XAFS was analyzed by conventional methods, as described elsewhere,^{37, 38} using EXAFSPAK³⁹ and FEFF7.02.⁴⁰

RESULTS AND DISCUSSION

Black precipitates associated with the growth of *D. desulfuricans* in media containing both MgSO_4 and FeSO_4 were isolated. In experiments with FeSO_4 as the sole sulfate source, there appeared to be a threshold level of FeSO_4 necessary for formation of black precipitates. With FeSO_4 concentrations of 0.2 mg/mL and higher, black precipitates were formed with bacterial growth. These black precipitates were extremely air-sensitive, rapidly converting to rust colored solids after short exposure. With FeSO_4 concentrations below 0.2 mg/mL, brown precipitates formed with bacterial growth. Powder X-ray diffraction data of both precipitates were essentially featureless, providing no evidence of crystallinity. Neither type of precipitate was attracted to a small permanent magnet.

The Fe K-edge XANES of the black precipitates is shown in Fig. 1. It is consistent with the presence of an iron-sulfur coordination environment, as found in Fe-S minerals such as pyrite, greigite, and pyrrhotite.^{37, 38, 41} The Fe XANES of pyrrhotite, containing high-spin Fe(II) in octahedral coordination with S, is shown in Fig. 1 as the dashed line. The absorption edge for the black precipitates is at a higher energy than that for pyrrhotite. This suggests the presence of Fe(III) in the black precipitates. The Fe K-edge XANES of the brown precipitates is also shown in Fig. 1. It is consistent with the presence of an Fe(III)-oxygen coordination environment, as found in Fe-O minerals such as hematite, goethite, ferrihydrite, jarosite, etc.⁴²⁻⁴⁴ Because iron XANES of sulfide minerals can be a misleading diagnostic indicator of Fe valence,⁴⁵ we exploited ⁵⁷Fe Mössbauer spectroscopy to provide insights about the iron valence and magnetism in the black as well as brown precipitates.

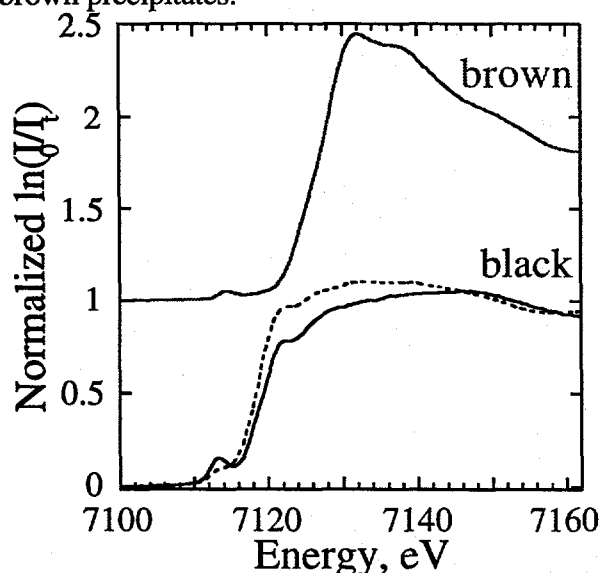
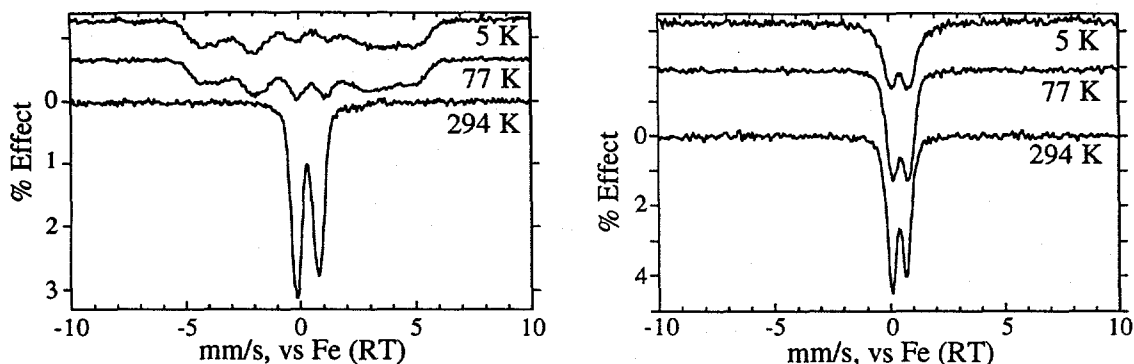


Figure 1. Fe K-edge XANES for brown (top) and black (bottom) precipitates—solid lines—obtained from growth of *D. desulfuricans*. The XANES for pyrrhotite, Fe_{1-x}S , is shown as the dashed line (bottom).

The variable-temperature Mössbauer spectra of the black solids are shown in Fig. 2. At room temperature, the spectrum is an asymmetric doublet that is adequately modeled with two overlapping quadrupole split doublets ($\delta_1 = 0.32$, $\Delta E_{Q1} = 0.76$, $\Gamma_1 = 0.39$ mm/s; $\delta_2 = 0.35$, $\Delta E_{Q2} = 1.21$, $\Gamma_2 = 0.35$ mm/s). The isomer shifts, δ , are typical of high-spin Fe(III) with octahedral coordination of S.⁴⁶ At 77 K, magnetic splitting is apparent by the decreased intensity of the doublet, which splits into a broad sextet that is typical of a broad distribution of hyperfine fields at iron. At 5 K, the magnetic ordering is complete to reveal another broad spectrum, which is not particularly well modeled with a sum of 2-3 overlapping sextets. Still, the magnetic splitting with H_{int} of approximately 225-265 kG is consistent with the presence of an Fe-S phase. For example, the Fe_{1-x}S (pyrrhotite, mackinawite) and $\text{Fe}_{3-x}\text{S}_4$ (greigite, smythite) minerals containing Fe(II) and mixed Fe(II)-Fe(III) ions, respectively, as well as amorphous Fe_2S_3 with Fe(III) exhibit similar

hyperfine fields of ca. 200-300 kG.⁴⁷ At 77 K and above, the Mössbauer spectrum of amorphous Fe₂S₃ is an asymmetric doublet, and at 4.2 K, the spectrum is a complex combination of broad, overlapping sextets,⁴⁸ much like that observed here. Likewise, the 4.2 K Mössbauer spectrum of an amorphous Fe(III) sulfide as a 500-iron atom cluster reveals a mean magnetic hyperfine field of 260 kG⁴⁵ that is consistent with the ordering observed for the black precipitates in Fig. 2 at 5 K. However, the Mössbauer spectrum of the black precipitates does not exactly correspond to any one of the known binary iron sulfides. This suggests the possibility that the black Fe-S precipitates from *D. desulfuricans* contain two or more different Fe-S species, each with two or more different iron sites.



Figures 2 (left) and 3 (right). Variable-temperature, zero-field ⁵⁷Fe Mössbauer spectra for the black and brown precipitates, respectively.

The brown precipitates isolated from cultures grown with low levels of FeSO₄ were also studied by Mössbauer spectroscopy. The spectra are shown in Fig. 3. At room temperature, the Mössbauer spectrum of these solids is an asymmetric doublet that is adequately modeled with two overlapping quadrupole split doublets ($\delta_1 = 0.39$, $\Delta E_{Q1} = 0.49$, $\Gamma_1 = 0.38$ mm/s; $\delta_2 = 0.41$, $\Delta E_{Q2} = 0.84$, $\Gamma_2 = 0.35$ mm/s). The isomer shift values are consistent with the presence of high-spin Fe(III) with octahedral coordination of O.⁴⁹ At 77 and 5 K, there is no evidence for magnetic splitting in the spectra. Rather, at 5 K, the symmetric doublet spectrum is satisfactorily modeled with one quadrupole split doublet ($\delta = 0.49$, $\Delta E_Q = 0.67$, $\Gamma = 0.57$ mm/s). The Mössbauer data of Figs. 2 and 3 indicate that the brown precipitates produced by the bacteria grown with low levels of FeSO₄ are distinctly different from the black precipitates produced by the bacteria grown with high levels of FeSO₄. Furthermore, the brown precipitates are different from the intentionally oxidized black precipitates.

Insights about the Fe coordination in the precipitates from *D. desulfuricans* were obtained from the Fe K-edge EXAFS. The primary data and their corresponding Fourier transforms (FTs) are shown as solid lines in Fig. 4. Each FT reveals one intense peak. It is due to the nearest S neighbors about Fe in the black precipitates and the nearest O neighbors about Fe in the brown precipitates. Both FTs reveal a weak, second peak that is attributable to the next nearest neighboring atoms, which were identified as S from best Z fits with O, S, and Fe atoms. The lack of any structurally significant features beyond about 3 Å in the FT data is consistent with the lack of crystallinity of the precipitates as determined by X-ray diffraction. The dashed lines in Fig. 4 illustrate the fits to the primary data. The agreement with the primary data indicates that the two-shell curve fitting models adequately describe the data. For the black precipitates, curve fitting revealed 6(1) S atoms at an average distance of 2.24(1) Å and 3(1) S atoms at an average distance of 2.84(2) Å. For the brown precipitates, there were 6(1) O atoms at an average distance of 1.95(1) Å and 4(1) S atoms at an average distance of 3.20(3) Å. The average Fe(III)-S₆ distance for the black precipitates is 0.015 Å shorter than that (2.39 Å) for pyrrhotite with Fe(II)-S₆ coordination, consistent with the 0.014 Å decrease in the ionic radius of Fe(III), for high-spin CN=VI.⁵⁰ The presence of a distant Fe...S interaction in the brown precipitates suggests the presence of an Fe-O-S phase.

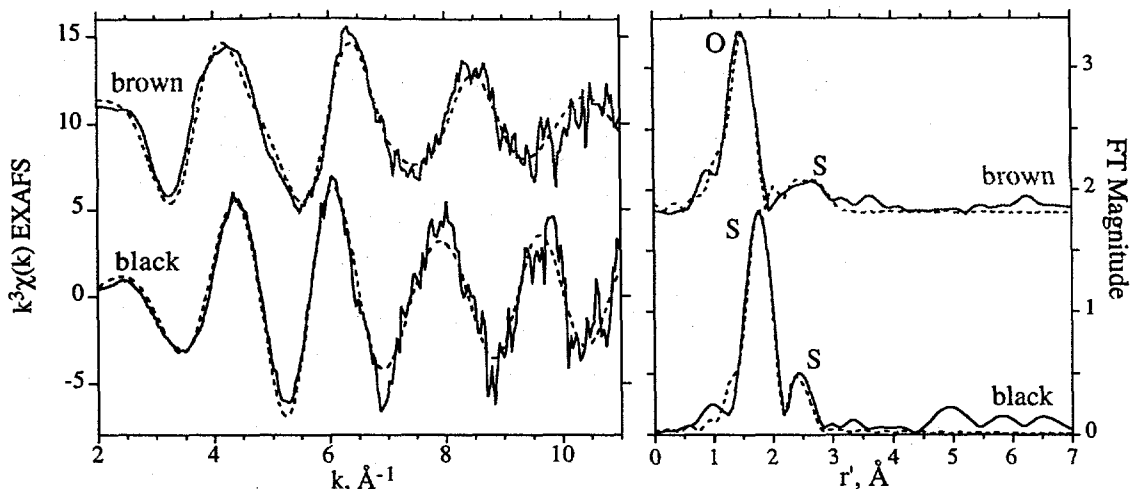


Figure 4. The Fe K-edge $k^3\chi(k)$ transmission EXAFS (left) and the corresponding FT data (right), not corrected for phase shift, for the brown (top curves) and black (bottom curves) precipitates.

Other researchers have previously described differences in precipitates associated with *D. desulfuricans* based on the amount of available ferrous ion. For example, Booth et al.^{12, 13} and King et al.^{14, 15} noticed that differences in the corrosive properties of H_2S produced from the metabolism of sulfate reducing bacteria depended on the amount of iron available to precipitate the sulfide. They speculated that when there was insufficient iron to precipitate all of the sulfide produced by the bacteria, the sulfide would form a protective film on metals, preventing corrosion.

CONCLUSIONS

Because of their element-specific, atomic scale perspective of matter, neither Fe XAFS nor Fe Mössbauer can be readily employed to identify bulk phases in the black and brown precipitates obtained from the growth of *D. desulfuricans*. X-ray diffraction is also of little help here because the precipitates showed no evidence of crystallinity. Still, the combined results indicate that the amorphous, nonmagnetic black precipitates produced by *D. desulfuricans* are consistent with the formation of an iron-sulfur phase containing high-spin Fe(III) in octahedral coordination, whereas the brown precipitates are consistent with an iron-oxygen-sulfur phase containing high-spin Fe(III) with octahedral coordination of O.

The presence of ferric ion, Fe(III), in both precipitates is surprising. The oxidation of $Fe(II)SO_4$ in the culture medium is not due to the presence of O_2 during the growth or work-up procedures. Because motile cells were confirmed in the spent media, the possibility of O_2 contamination is excluded—*D. desulfuricans* require rigorously anaerobic conditions for growth. Although the source of the oxidant is not known, we suspect that components of the culture medium may be involved. This suggestion is supported by our observation that Np(V) is reduced to Np(IV) in filtered ATCC culture medium 207 without resazurin, both with and without *D. desulfuricans*.⁵¹ In this regard, the Np(V)/Np(IV) and Fe(III)/Fe(II) redox couples have similar formal potentials.⁵¹ The conditions under which our black and brown *D. desulfuricans*-mediated laboratory precipitates were formed are clearly different from those in anoxic subsurface oil reservoirs, where the reducing environment maintains the presence of Fe(II).

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