Workshop on Alternative Fuels and Materials: Biocorrosion
NIST, Boulder CO, July 22 – 23, 2013

Corrosion of 1018 carbon steel in fuel/seawater incubations

Recep Avci[1]

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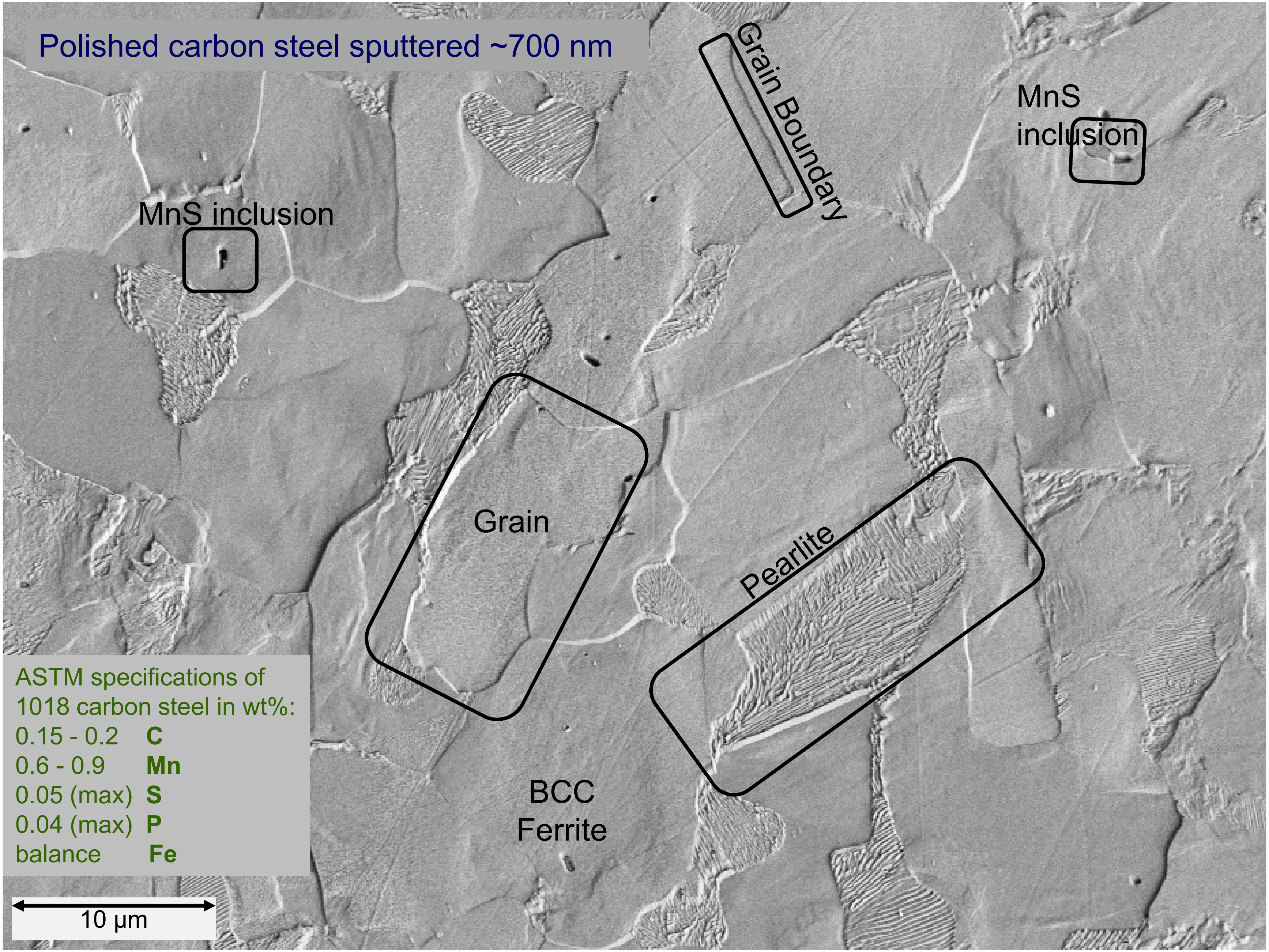
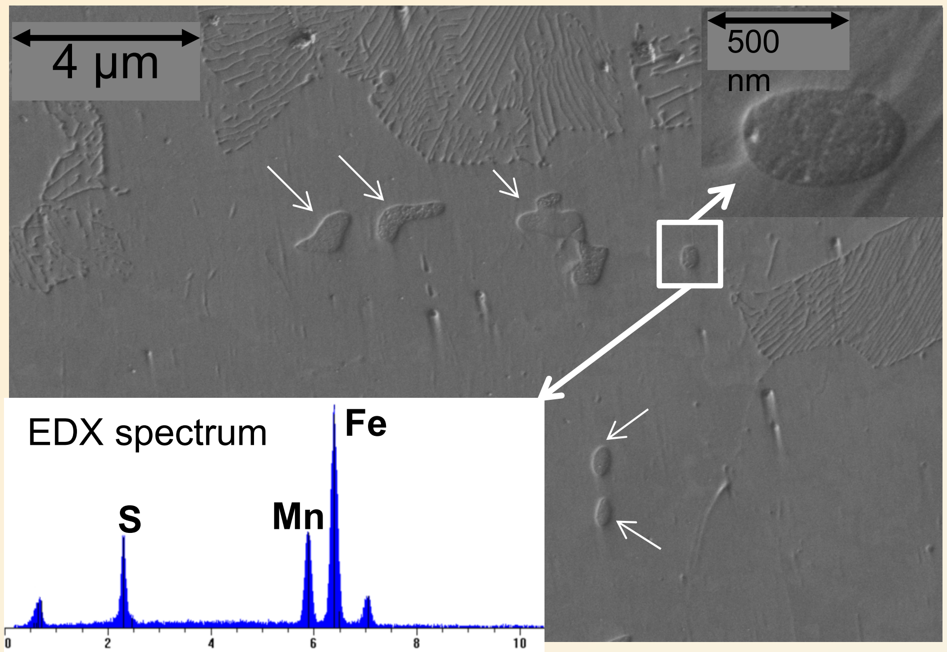
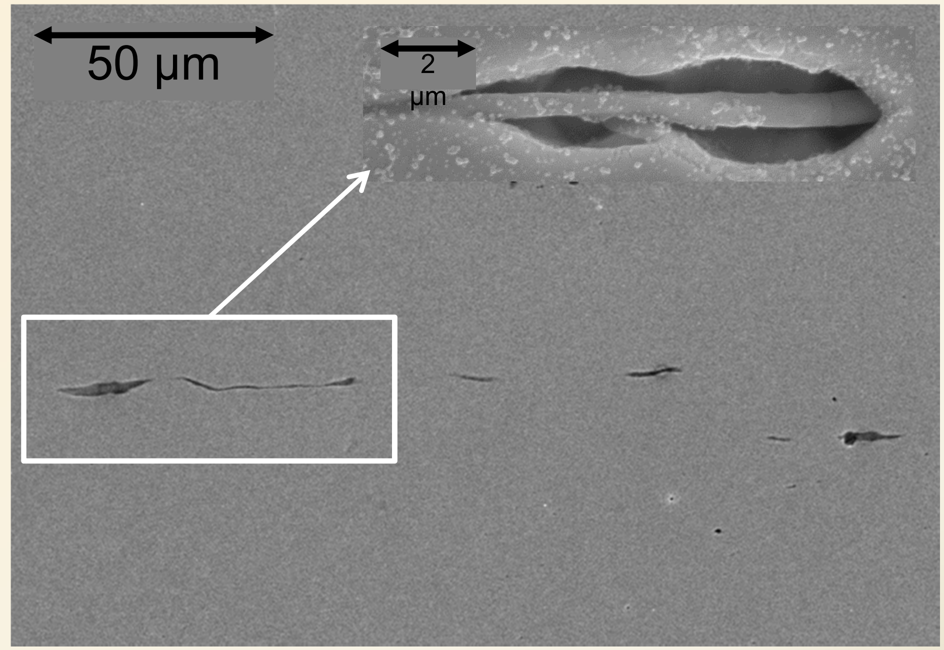

Polished carbon steel sputtered ~700 nm
Grain Boundary
MnS inclusion
MnS inclusion
Grain
Pearlite
BCC Ferrite
ASTM specifications of 1018 carbon steel in wt%:
0.15 - 0.2 C
0.6 - 0.9 Mn
0.05 (max) S
0.04 (max) P
balance Fe
10 μm

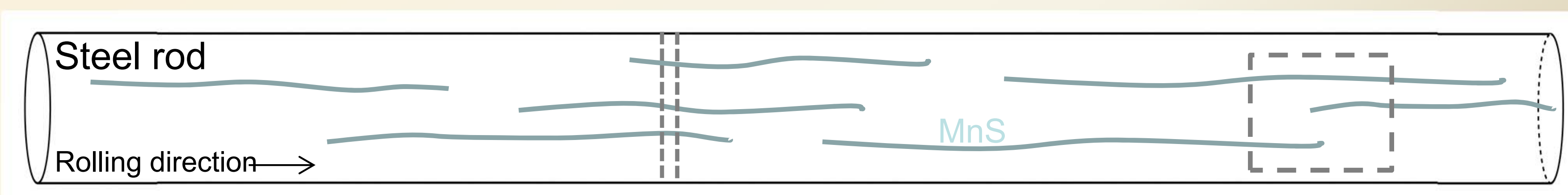
MnS inclusions are long micro-wires extending hundreds of microns along the rolling direction of the steel.





1. MnS inclusions imaged on clean steel coupon cut **perpendicular** to rolling axis of rod.

2. MnS inclusions imaged on clean steel coupon cut **parallel** to rolling axis of rod.



Pit statistics:

in 1018 Carbon steel:

pH ~ 7.4

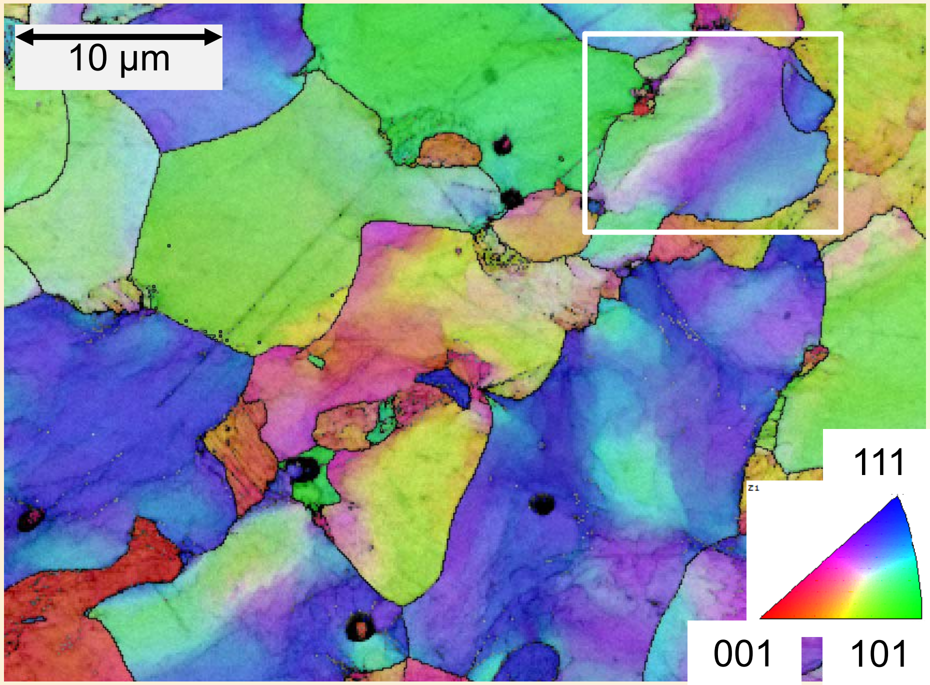
6000 inclusions per mm^2

When exposed to ALDC for 12 days:
1 out of ~3000 is susceptible to initial pitting attack

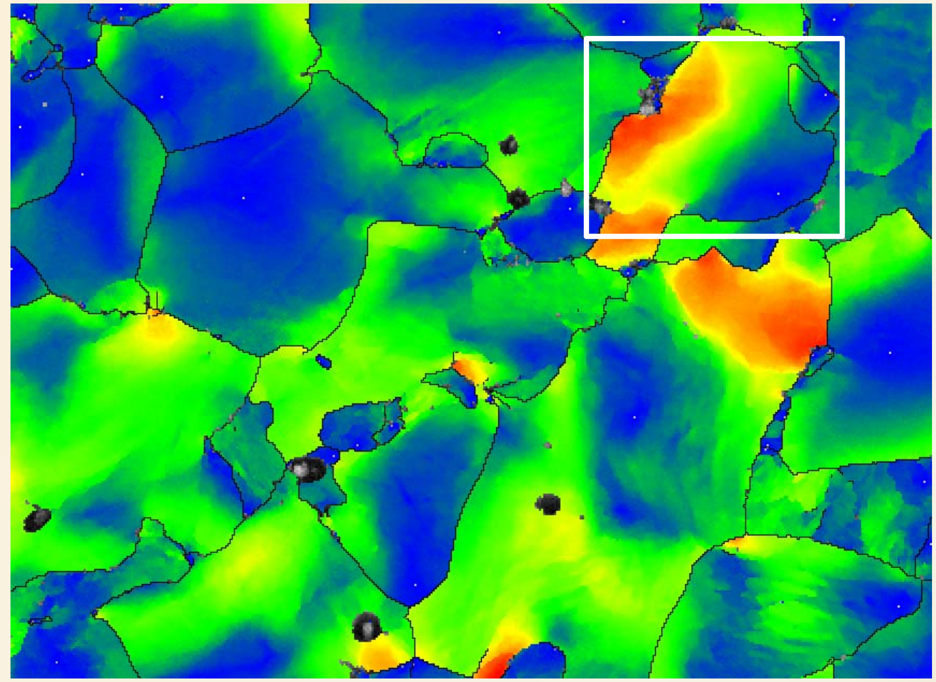
When exposed to abiotic sterile Widdel media for 2 weeks:
1 out of ~12,000 is susceptible to initial pitting attack

Ref. B.H. Davis, *Anaerobic pitting corrosion of carbon steel in marine sulfidogenic environment,* MSc Thesis: Physics Department, Montana State University, 2013

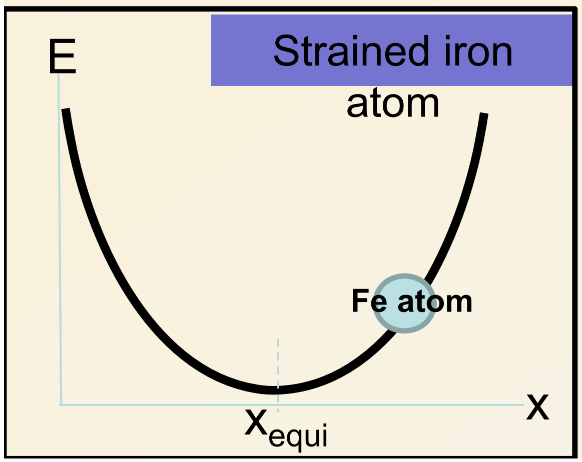
Derivative of orientation is **residual strain** in crystal lattice



1. EBSD map of lattice orientation.



2. EBSD map of residual strain over **same field of view**.



Strain varies within and among the different grains.

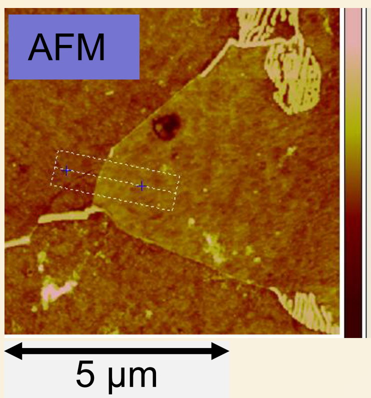
Legend:

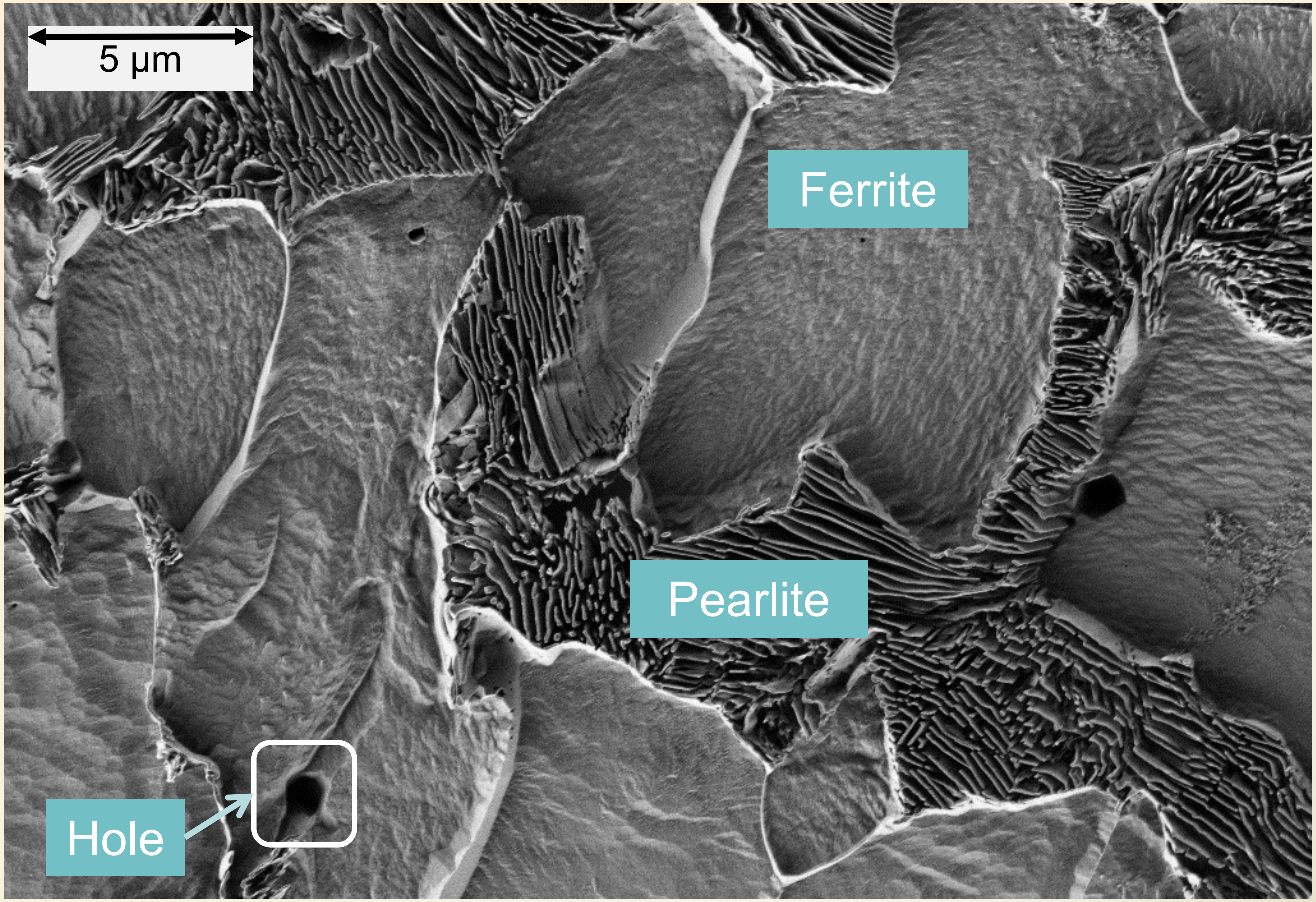
- No strain
- Highly strained
- Intermediate strain:

Differential corrosion on carbon steel grains

SRB:
Desulfoglaeba alkanexedens
(ALDC)

Low High
max - min 300 nm





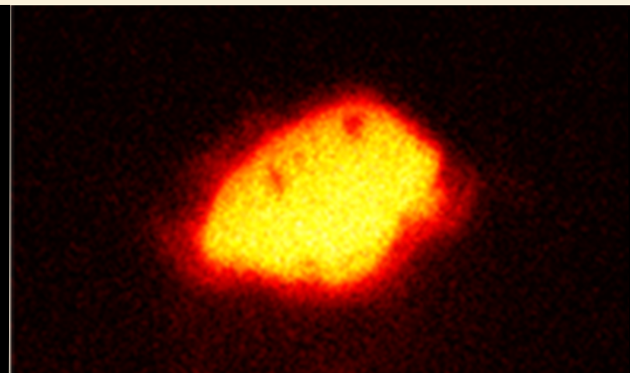
FEM image of polished carbon steel exposed to ALDC filtrate for 14 days, then stripped by chemical reagent to remove corrosion deposits.

Each grain corrodes at a slightly different rate. We hypothesize that high *corrosion rates* are correlated with *high residual strains*.

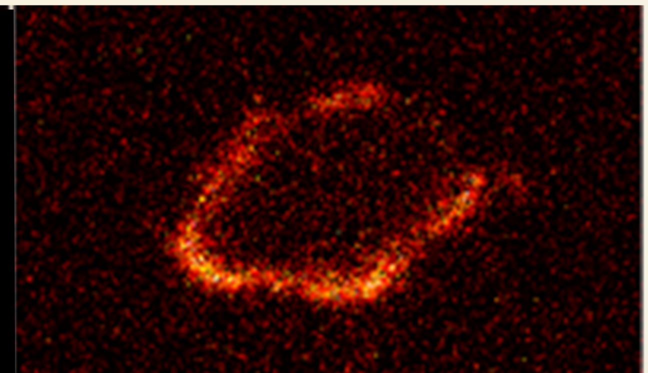
Pitting initiates around the inclusions

Auger maps (10 nm sputter)

SEM image



Sulfur map



Oxygen map

MnS after 11 days exposure in Widdel medium with $[H_2S] = 0.05$ mM, $[Cl^-] = 300$mM

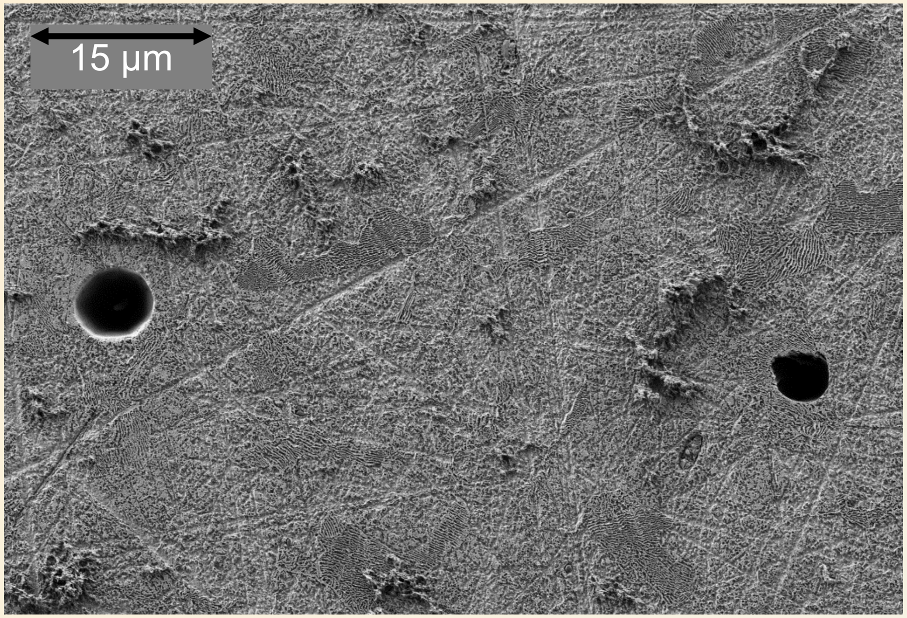
Strained dissolution of Fe

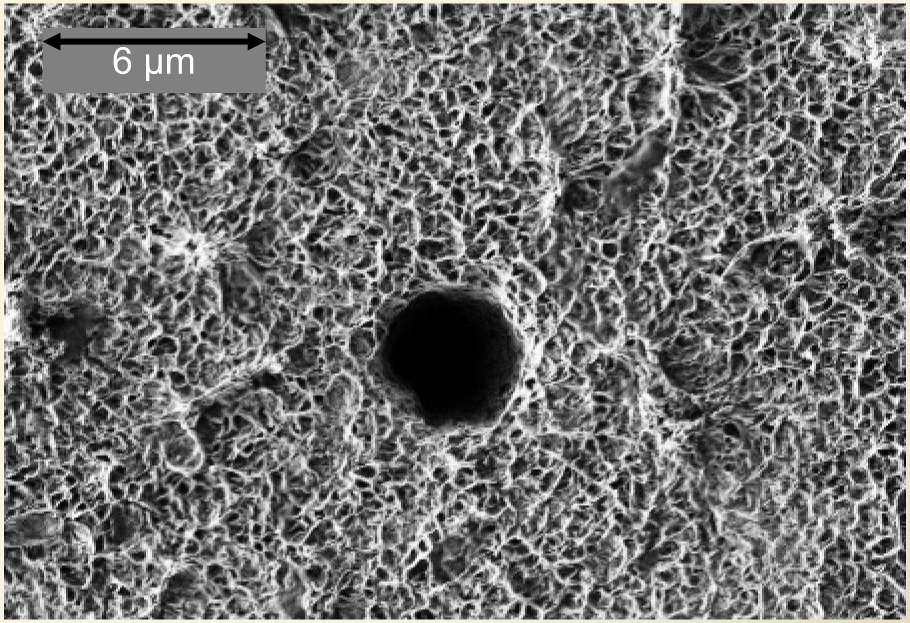
$$Fe^0 \rightarrow Fe^{2+} + 2\,e^-$$

Hydrolysis of Fe^{2+}

$$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2 + 2H^+$$

Pit development



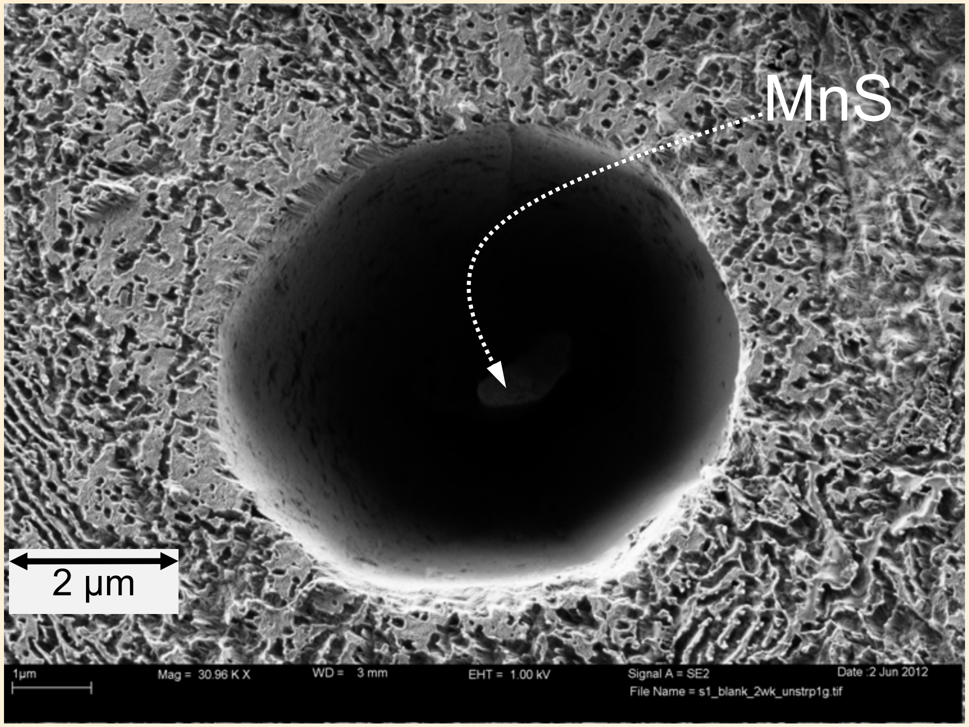


1. Pits (~5 µm diameter) on coupon surface exposed to **Widdel medium** for two weeks (**0.05** mM H_2S)

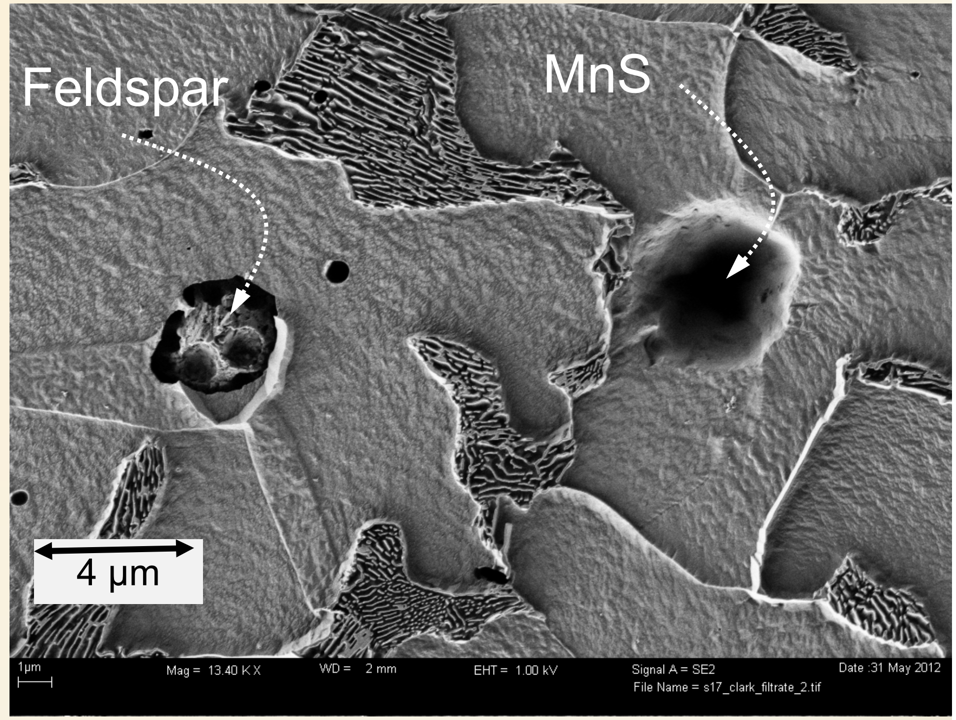
2. Pit on coupon surface corroded by **ALDC** for two weeks (~**16** mM H_2S). Note lack of thick biofilm.

ALDC is a slow growing organism that **does not form thick biofilm**.

Pit growth around MnS inclusions



Medium: Abiotic, *0.05 mM sulfide, 11 days*



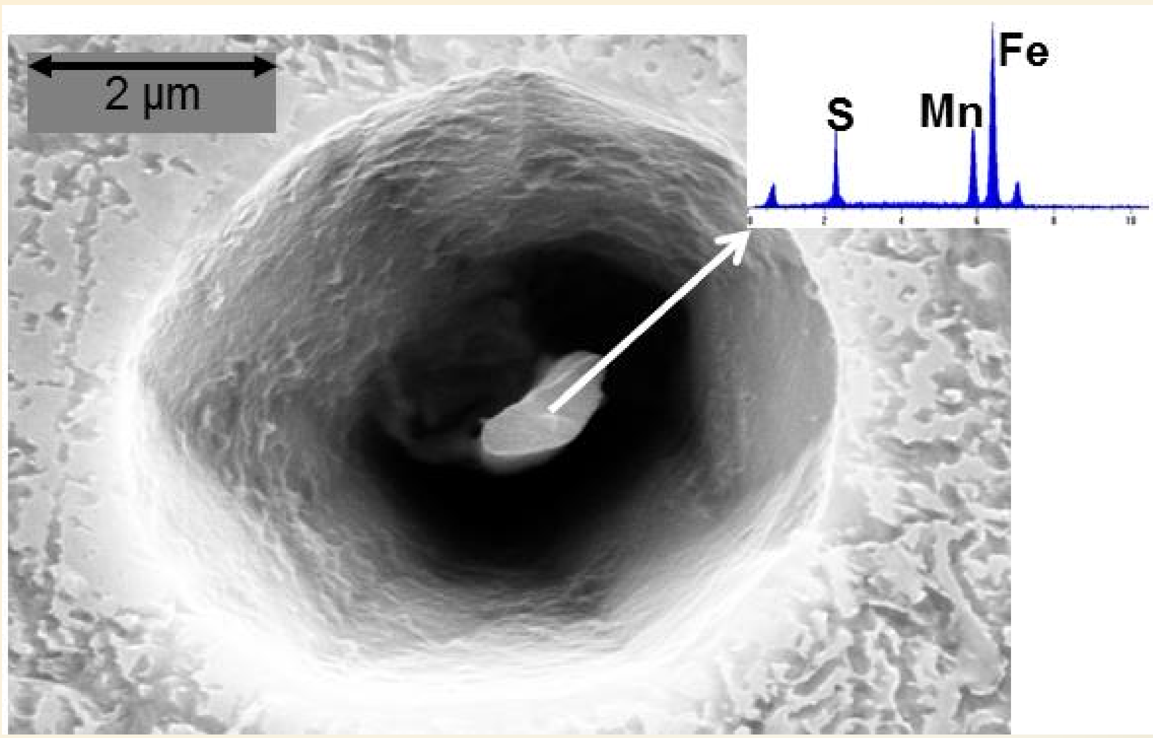
Medium: ALDC, 15 mM sulfide, 14 days
Corrosion products are stripped before analysis

- Pit initiation around MnS inclusions is due to local strain on the iron matrix due to stress exerted by the imperfections and impurities at these locations.
- Pit growth and development is due to the acidification of pits through the hydrolysis of Fe^{2+}
- At lower pH dissolution of MnS inclusions ($MnS + 2H^+ \rightarrow H_2S + Mn^{2+}$) increases the local H_2S abiotically, which promotes local corrosion along MnS micro-wires

Avci et al, **Corrosion Science**, 2013: Available online: http://dx.doi.org/10.1016/j.corsci.2013.06.049

Pitting corrosion

Large and deep pits generated around long MnS microwires after corrosion with or without SRB at pH 7



Large pit developed around MnS after 2 weeks exposure to Widdel medium (0.05 mM H_2S, 300 mM Cl^-)

<u>Hyrolysis of</u> Fe^{2+}

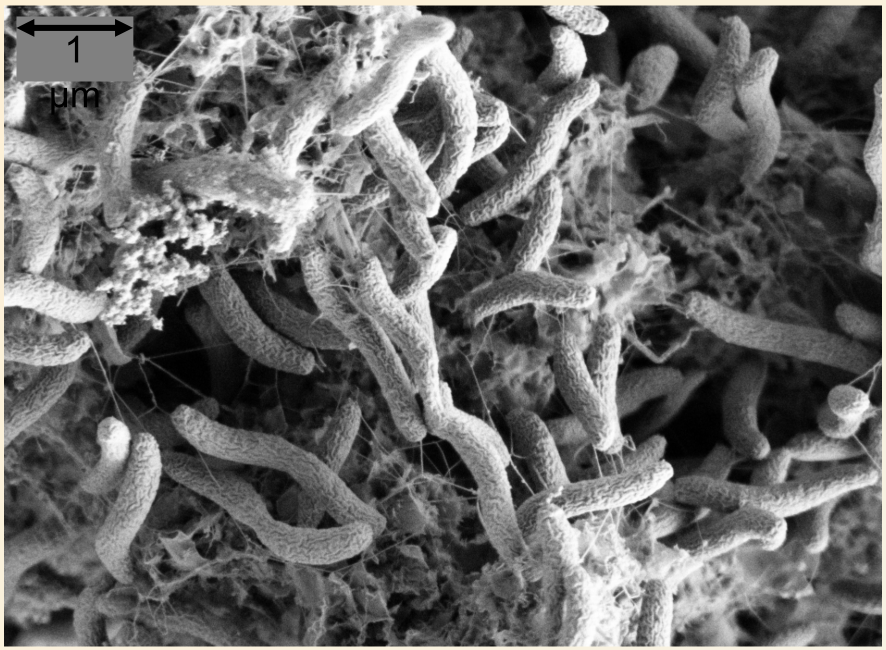
$$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2 + 2H^+$$

<u>Low pH: abiotic H_2S:</u>

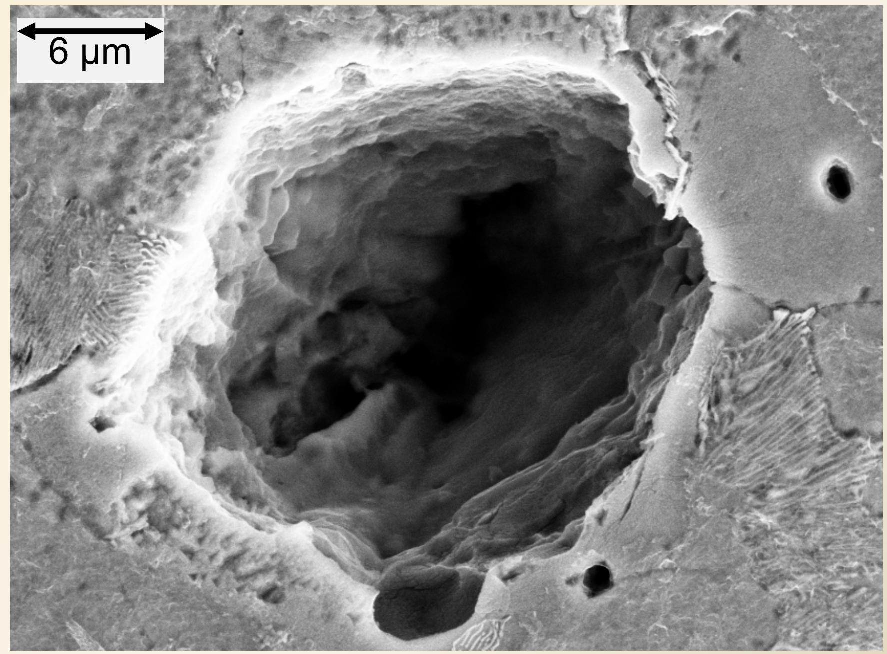
$$MnS + 2H^+ \rightarrow H_2S + Mn^{2+}$$

Severe pitting: Occlusion by biofilm

Pits on coupons corroded by *Desulfovibrio alaskensis* g20 much larger than those on ALDC & Widdel medium.

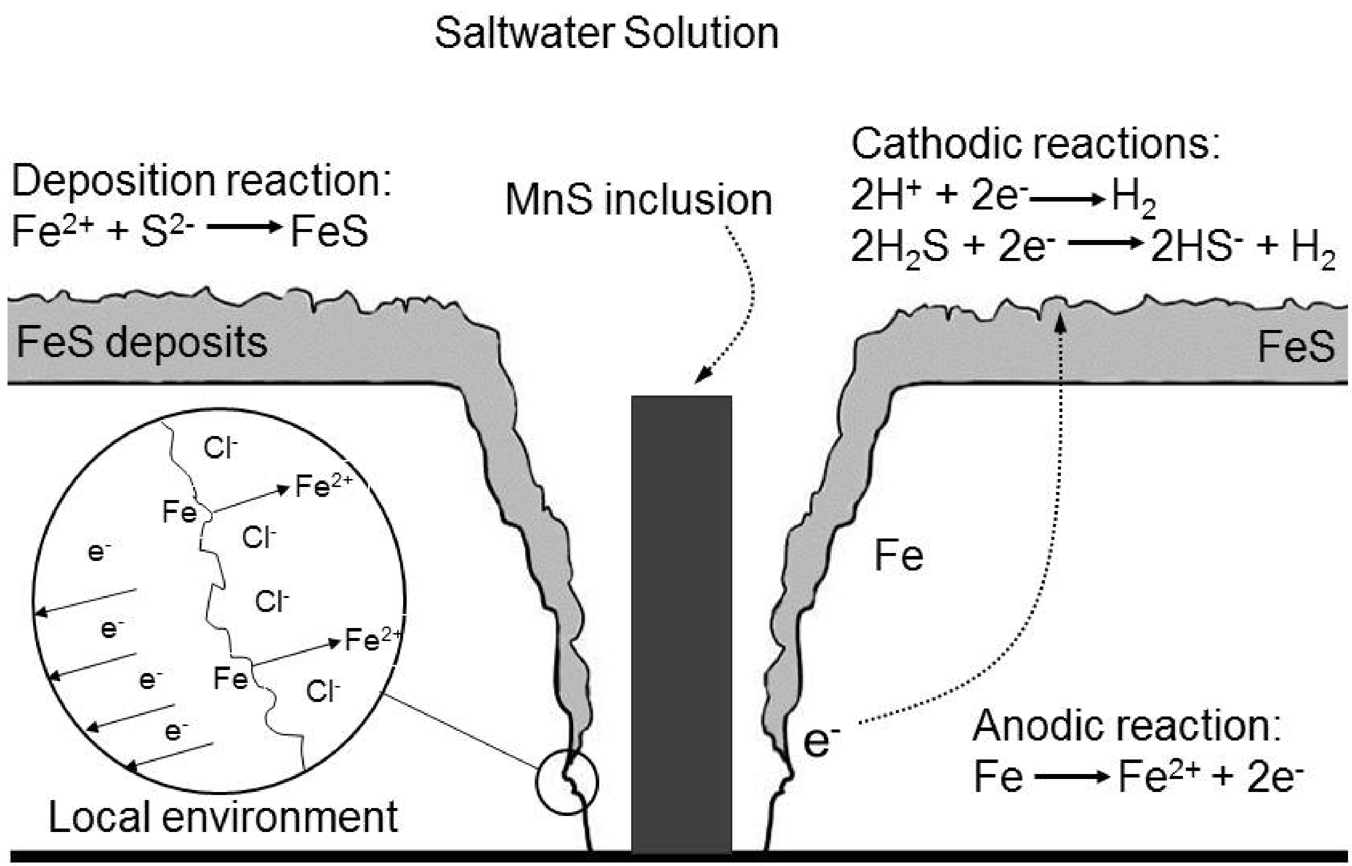


Thick *D. alaskensis* biofilm on steel after 2 days exposure in collaborator Matthew Fields' bioreactor.



Large pit formed underneath the thick *D. alaskensis* biofilm (~30 µm diameter).

D. alaskensis is a fast growing organism that **does form thick biofilm**.



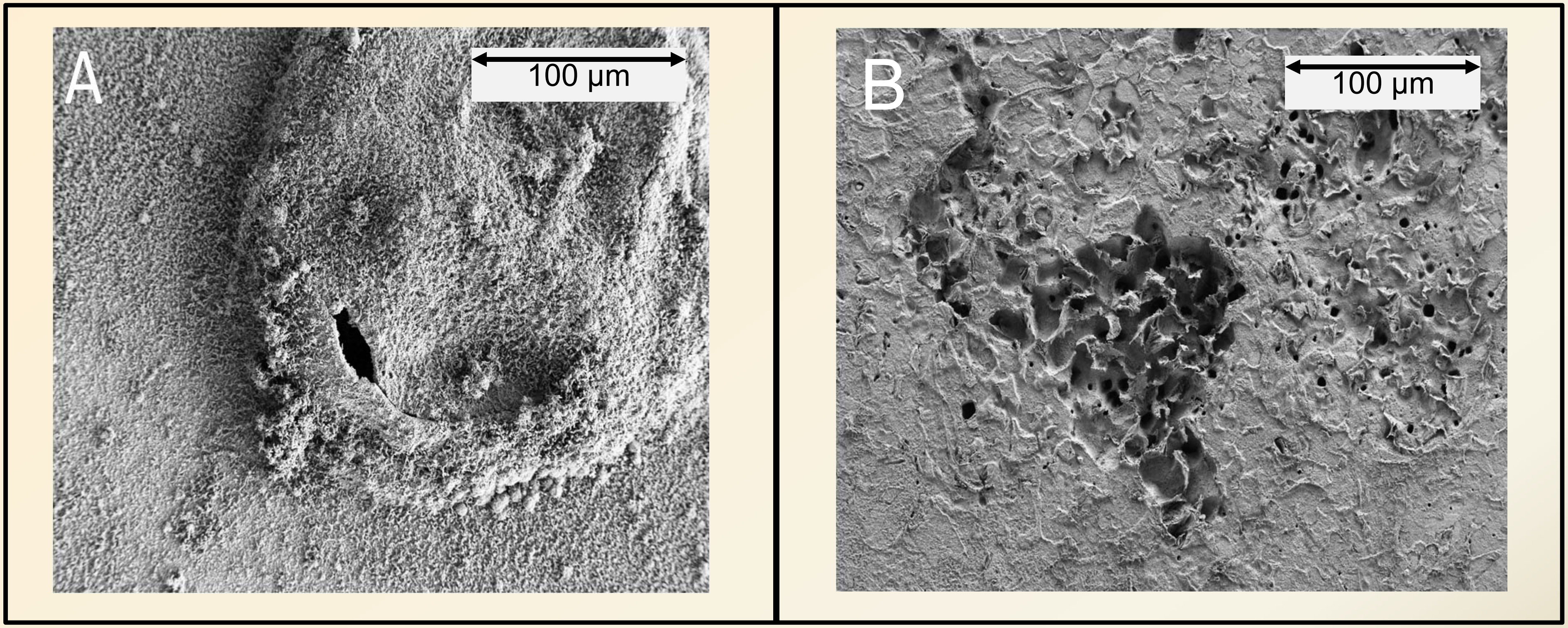
Hyrolysis of Fe^{2+} and Acidification

$$\mathbf{Fe^{2+} + 2\,H_2O \rightarrow Fe(OH)_2 + 2H^+}$$

Abiotic H_2S production around MnS:

$$\mathbf{MnS + 2H^+ \rightarrow H_2S + Mn^{2+}}$$

The presence of heavy biofilm accelerates pit initiation and growth



Steel coupons exposed *D. alaskensis* in Dr. Fields' bioreactor for 2 days (A) biofilm / corrosion deposit ; (B) view after biocorrosion deposits are removed exposing the high densities of pitting.

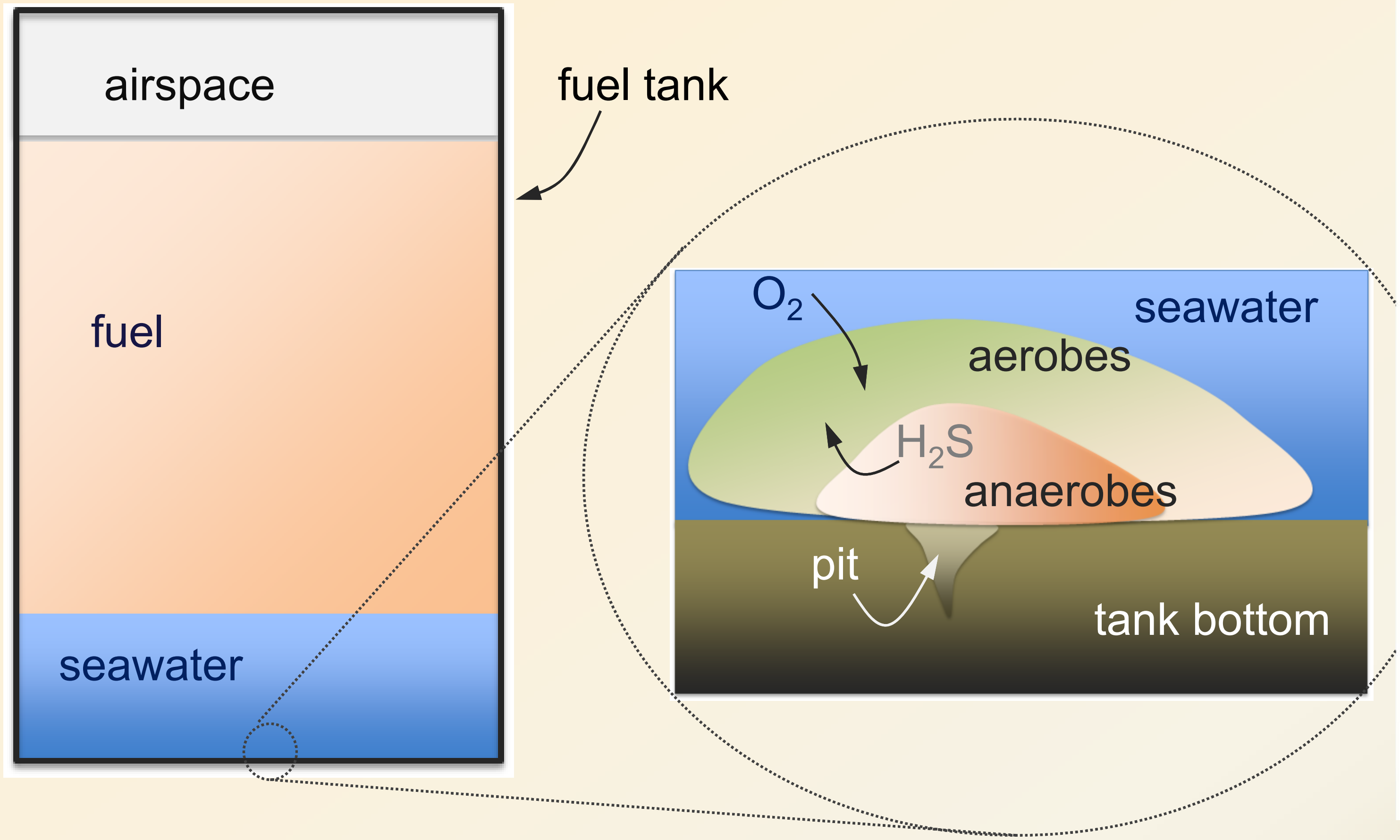
Occlusion by biofilm maintains acidic environment; creating auto- catalytic pitting mechanism.

Conclusions so far:

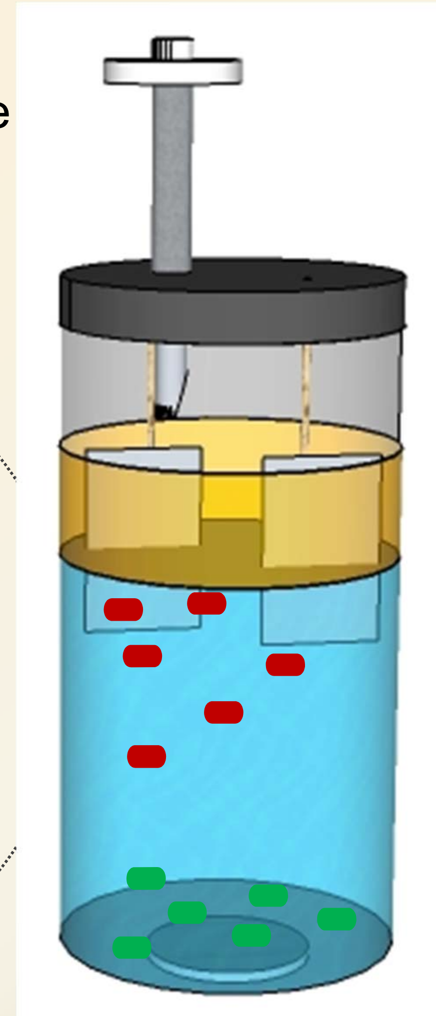
- We hypothesize r*esidual strain* can be correlated with *localized corrosion* on carbon steel .
- Each MnS (or other) inclusion, with its surroundings, has a unique material property, and the Fe matrix at the immediate surroundings of each inclusion suffers from residual strain due to metallurgical processing.
- The presence of biofilm accelerates pit growth because the biofilm creates a barrier between the pit and the outside of the biofilm, giving rise to acidic conditions which leads to dissolution of *all* (active and inactive) MnS inclusions, increasing pitting density and promoting pit growth.
- Metabolic products of SRB contribute to the corrosion directly by production of additional electron acceptors.
- Electron acceptors are spread over a large 3-D space (FeS is good electrical conductor) the anodic processes are limited to small areas on the clean Fe surface and pits. This causes large current densities inside pits, which advances pit growth.
- Under highly acidic conditions inside pits, MnS locally and abiotically produces corrosive H_2S via $MnS + 2H^+ \rightarrow H_2S + Mn^{2+}$, which accelerates the local corrosion process anaerobically and abiotically, causing pit growth and development along the MnS micro-wires. These then join pits to other pits, giving rise to macroscopic pitting.

A model reactor

Includes 3-electrode electrochemical probe



Real world



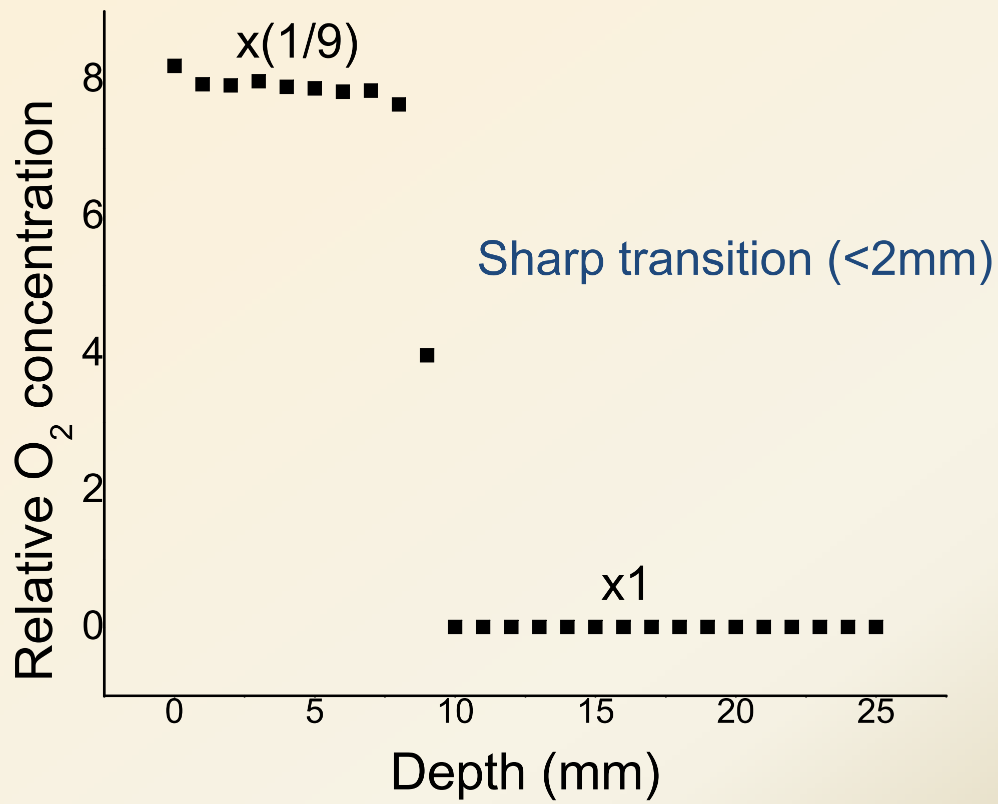
Model Reactor

Presence of thiosulfates cannot be ignored because when oxygen and sulfide react thiosulfates form: $2\ S^{2-} + 2\ O_2 + H_2O = S_2O_3^{2-} + 2\ OH^-$

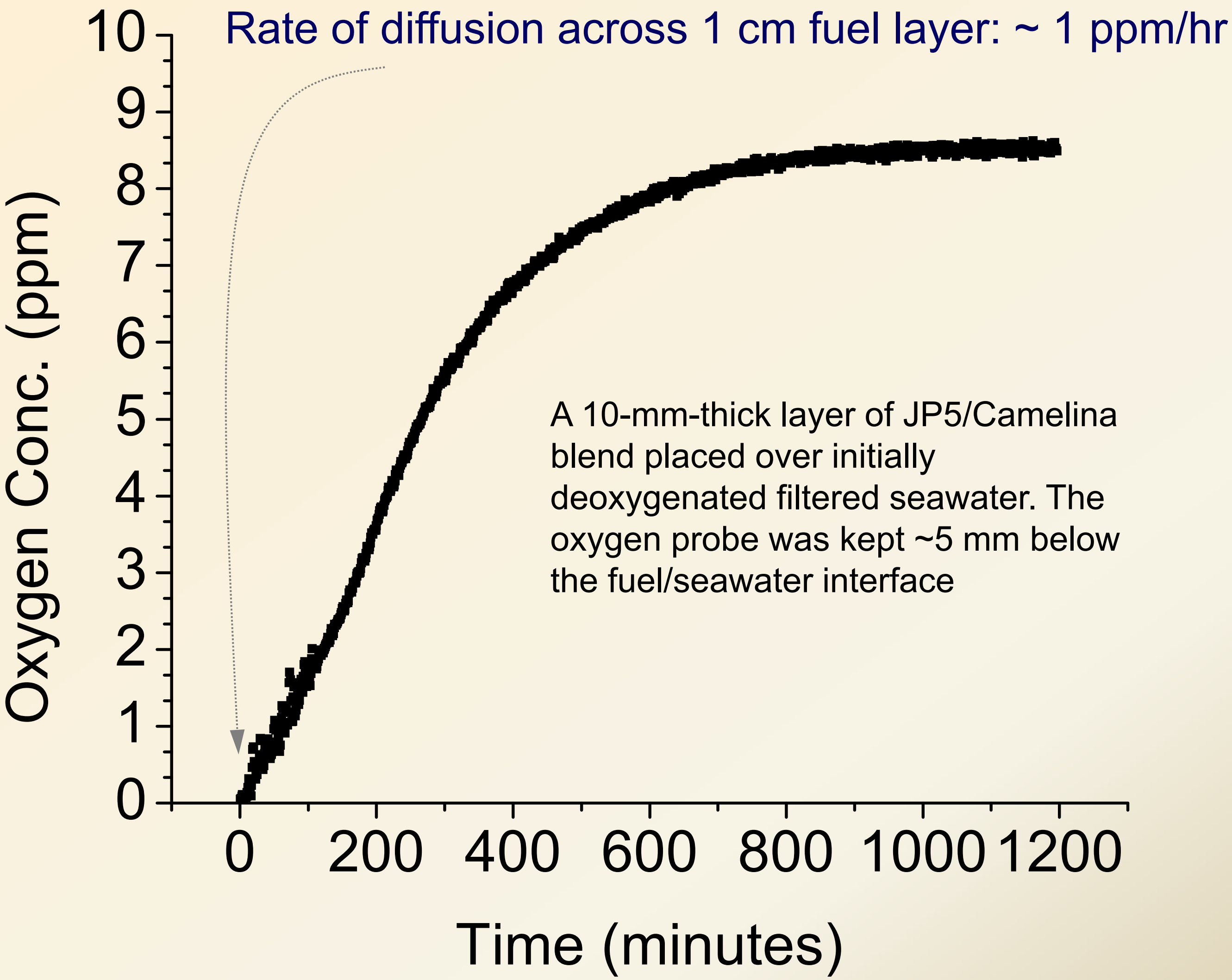
O_2 Transition across fuel/seawater interface in the presence of active aerobic bacteria

Inoculum: JP5 Camelina/*Marinobacter* (~4x10^5 cells per mL)
O_2 profile after 24 hrs of inoculation

(Pyruvate was *not* removed from medium before inoculation)

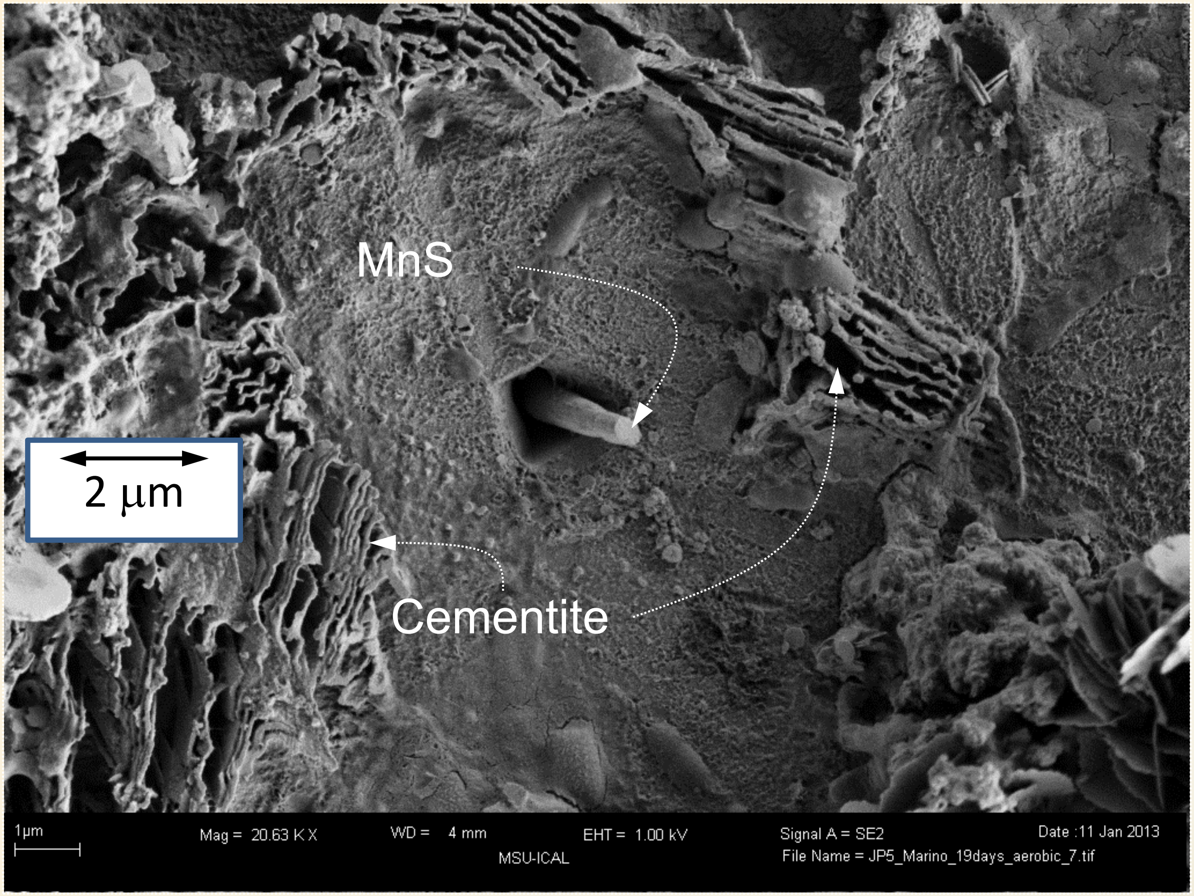


Diffusion of oxygen through fuel layer



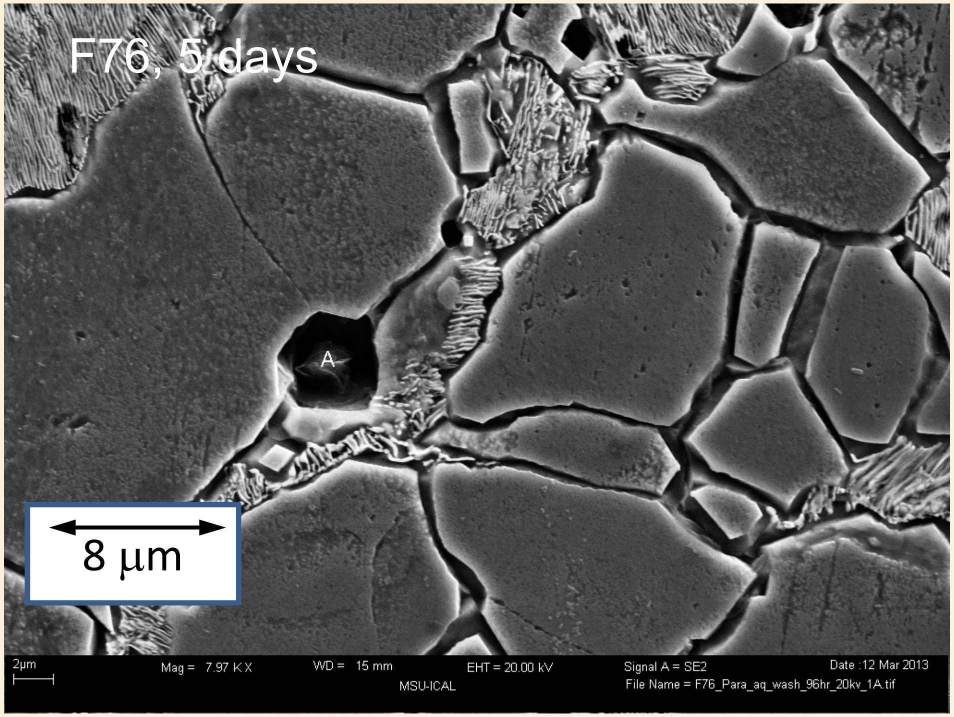
Corrosion in a JP5/seawater/*Marinobacter* environment

Inoculum: JP5/*Marinobacter.* Exposure: 19 days.

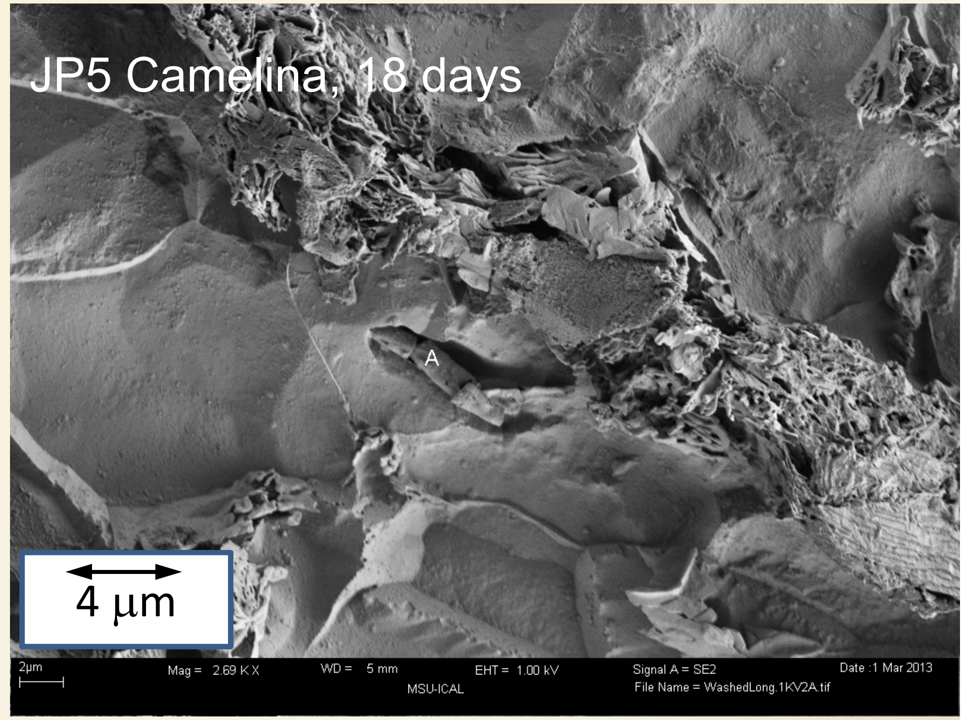


The corrosion is dominated by general erosion of the surface with no appreciable pitting

Corrosion in grains and grain boundaries in fuel/seawater environment



Corrosion in grain boundaries

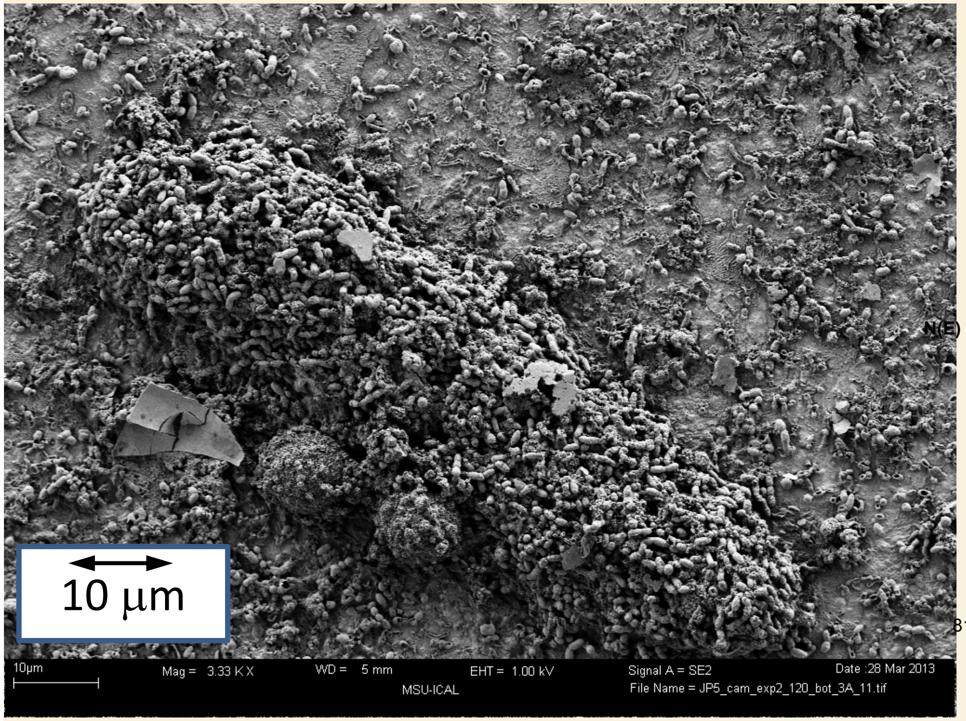


Differential corrosion of grains

F76: Grain boundary and pearlite attack. JP5 Camelina: Differential erosion of grains

Corrosion under JP5Camelina/KWSW bottom

Inoculum: *JP5Camelina/KWSW/Marinobacter/D. indonesiensis.* Exposure: 5 days.

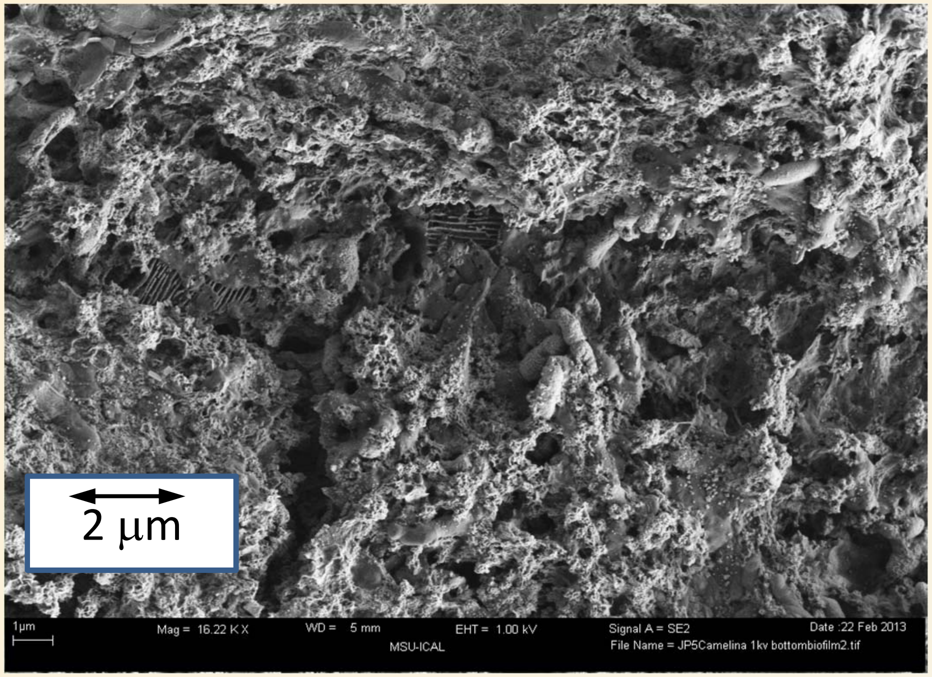


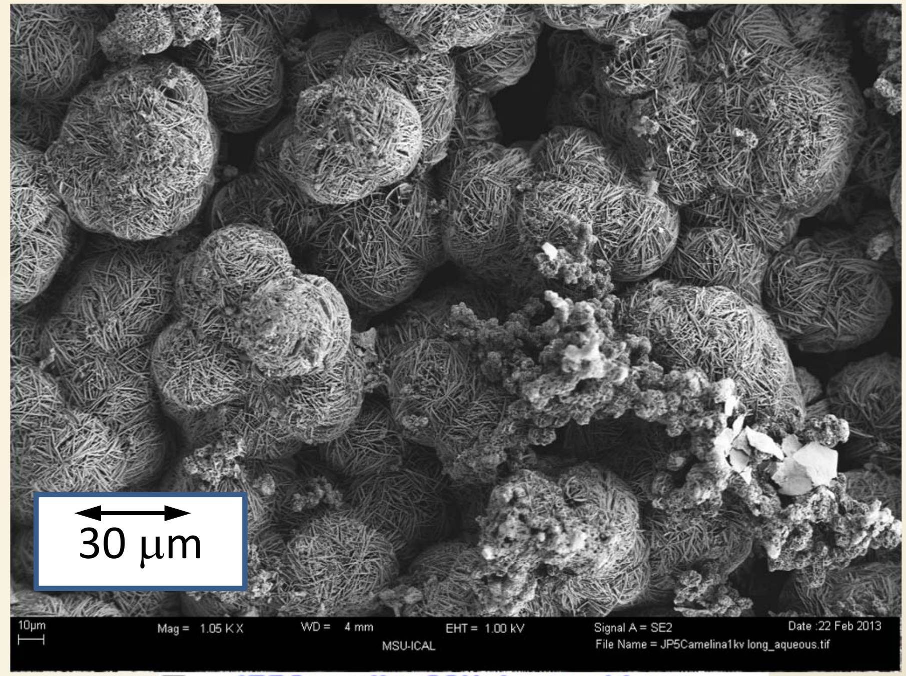
The coupon at the bottom was colonized by microorganisms, a mixture of *D. indonesiensis* and *Marinobacter (left)* . This gave rise to a highly complex corrosion process involving oxides and sulfides (XPS spectrum on the right).

Corrosion is dominated by oxides and sulfides

Complexity of corrosion in fuel/seawater environment

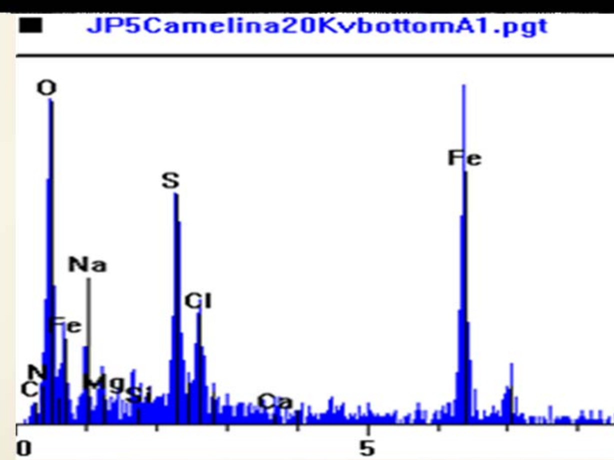
JP5Camelina/KWSW/*Marinobacter/D. indonesiensis: ~18 days*





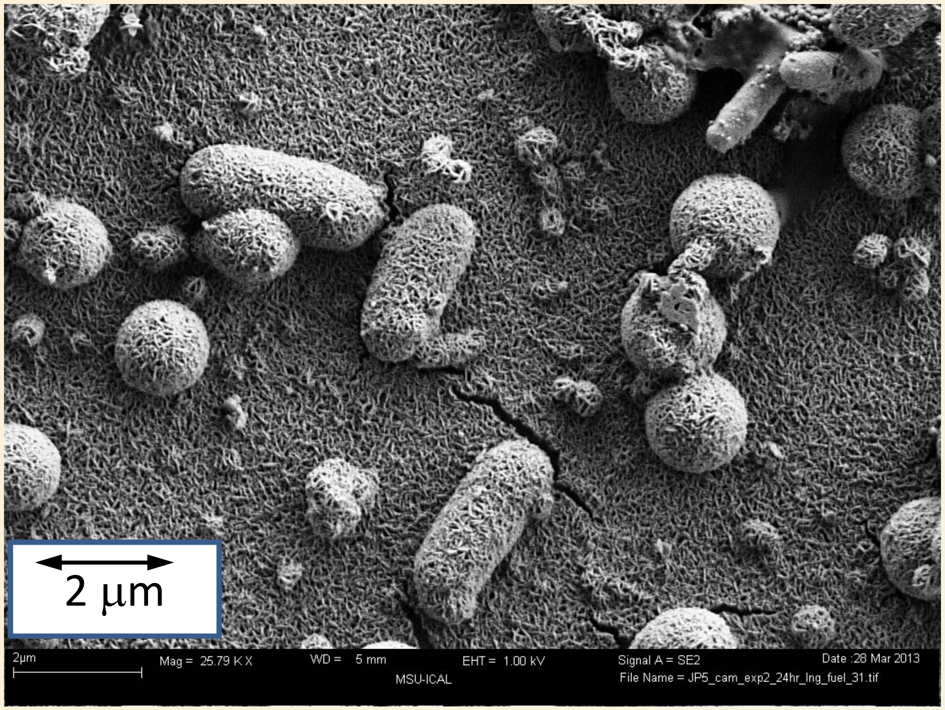
Two images from different regions of the coupon at the bottom.

Highly *heterogeneous* and *complex* mixtures of oxides and sulfides as suggested by the images (above) and the EDX spectra (right).

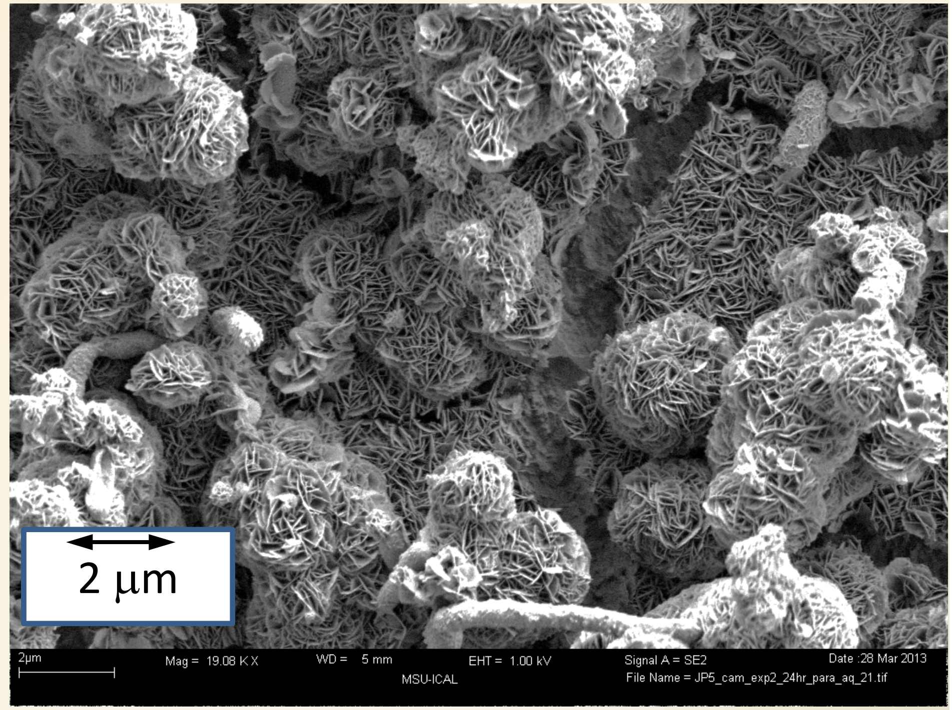


Do the bacteria colonize coupons in fuel?

Inoculum: JP5Camelina/KWSW/*Marinobacter*/*D. indonesiensis.* Exposure: 2 days.



Bacteria colonizing Fe surface in fuel!



View on the aqueous side.

Bacteria colonization on the fuel side accompanied by an oxide built up (left). Heavier biocorrosion on the aqueous side (right).

Conclusions of this section

- In the presence of active aerobic organisms, the oxygen concentration profile across a fuel/seawater interface shows a sharp transition within <2 mm.
- The diffusion rate of O_2 across a 1 cm layer of fuel is about 1 ppm/hr
- Corrosion in fuel/seawater environments is heterogeneous and complex, involving oxides and sulfide as well as intergranular and pitting corrosion.
- Removing the H_2S from the SRBs before inoculation ensures that all the sulfides observed were produced by the metabolic activities of the SRBs.

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Thank you for your time