Suppression of Acid Mine Drainage from Pyrite through the use of Adsorbed Phospholipid

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  - Department of Energy-BES-Geosciences
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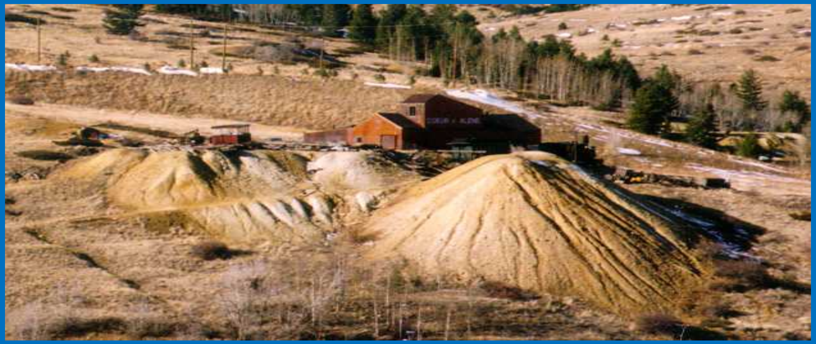
Acid Mine-Drainage due to Pyrite oxidation



Mine tailings

Groundwater Contamination

Goal: Develop a microscopic understanding of pyrite oxidation to be used to inhibit AMD

Pyrite and its oxidation

Oxygen

Water

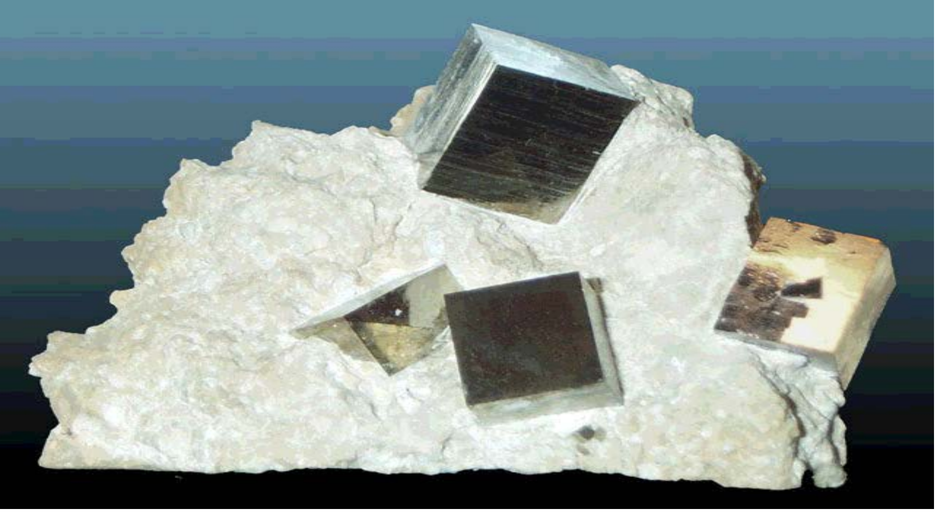
The challenge is to find a method that will inhibit the reactions between pyrite, water, and oxygen. Existing methods rely on creating a physical barrier to oxygen.

Composition of Typical Mining Waste

Elements	Fresh AMD (ppm)	Old AMD (ppm)
Sr	533.84 ± 10.24	78.28 ± 3.39
U	22.2 ± 7.7	19.27 ± 4.45
Rb	36.98 ± 3.75	< LOD
Th	12.95 ± 4.79	19.99 ± 3.98
Pb	10.07 ± 5.33	18.1 ± 4.68
Se	4.62 ± 2.93	10.76 ± 2.42
As	62.9 ± 6.9	10.26 ± 3.99
Zn	338.24 ± 20.65	< LOD
Cu	126.57 ± 20.21	56.56 ± 11.37
Ni	176.72 ± 40	< LOD
Fe	39306.26± 380.61	10681.81 ± 158.81
Mn	649.3 ± 78.4	< LOD
S	945061.56 ± 44137.18	866191.19 ± 37821.64
Ba	167.03 ± 29.5	< LOD

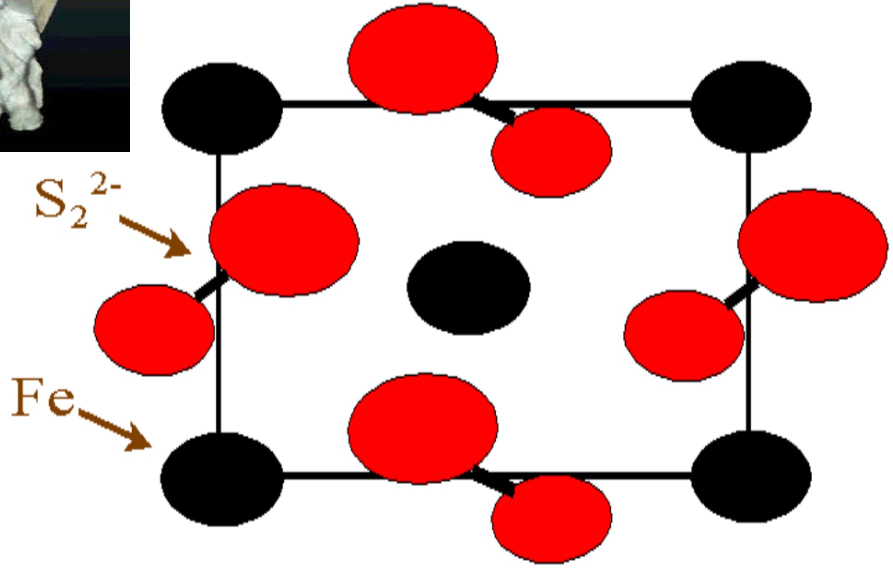
Magnitude of the Problem

- Pyrite (FeS_2), "fools gold", is the predominant sulfur containing solid in coal.
- Decomposition of pyrite is the main source of acid mine drainage i.e. contact of the pyrite with oxygen/water in the environment is the MAIN culprit.
- 10 million tons of pyrite waste are produced by coal mining states (i.e., Pennsylvania, Kentucky, Ohio, Illinois, Indiana, and Virginia)
- AMD affects thousands of miles of rivers and streams and over a hundred thousand acres of lakes and reservoirs in the US.
- Cost to the US mining industry is on the order of a million dollars a day.

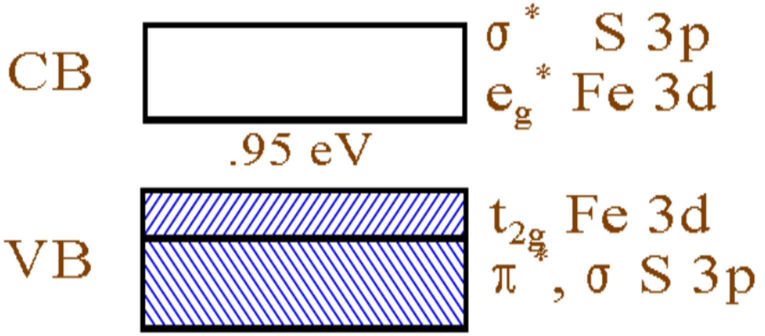


Pyrite

Geometric Structure



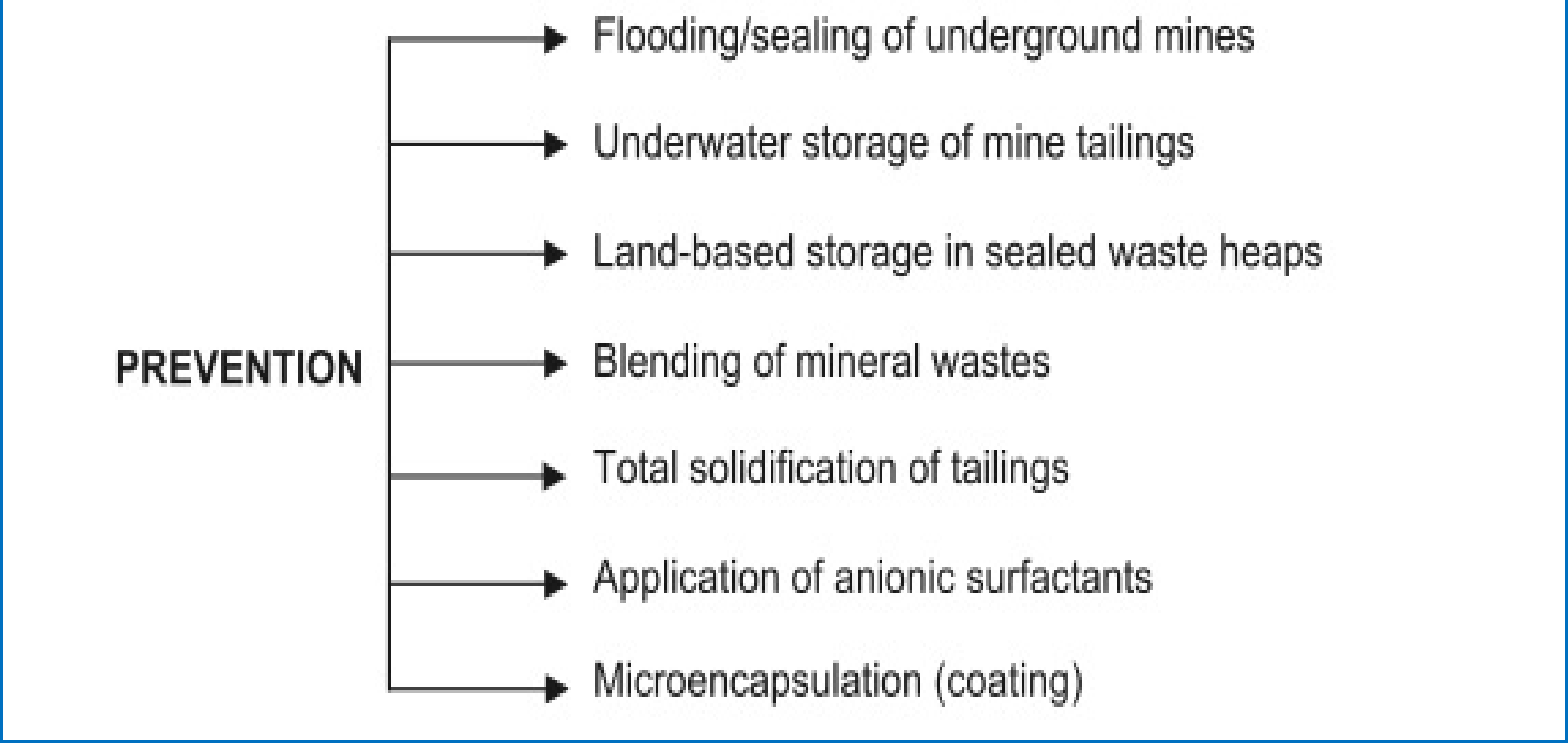
Electronic Structure



Composite Pyrite Oxidation Reactions

- $FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$
- $FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$
  - Many elementary reactions make up these reactions.
  - Understanding these steps will allow an intelligent modification of the surface for oxidation suppression?

Various AMD Remediation Methods

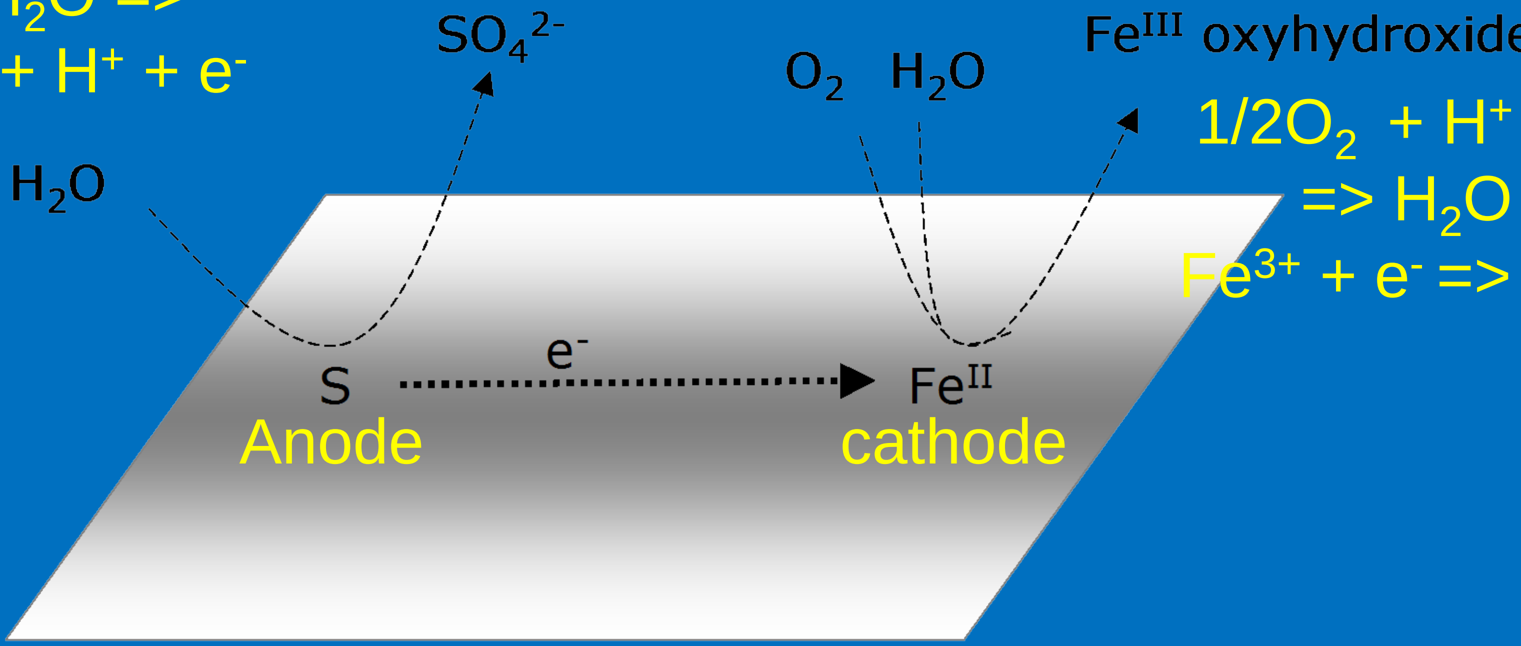


- "Prevention is better than cure" which is generally preferable, but this is not always pragmatic to minimize AMD generation

D.B. Johnson, K.B. Hallberg / *Science of the Total Environment* 338 (2005) 3–14

Summary of Experimental Observations

$>S + H_2O \Rightarrow$
$>S\text{-}OH + H^+ + e^-$



$1/2O_2 + H^+ + e^-$
$\Rightarrow H_2O$
$Fe^{3+} + e^- \Rightarrow Fe^{2+}$

Rimstidt, J. D.; Vaughan, D. J. Geochim. Cosmochim. Acta 2003, 67, 873-880.

i) Sulfate is dervied primarily from water-O in the aqueous environment.

ii) Whether Fe oxyhydroxide product forms on the surface or precipitates from solution cannot be discerned.

Influence of *Microbes*

- Direct mechanism: Involves enzymatic reactions taking place between the attached bacteria and mineral surface, with the microbe mediating both solubilization and iron oxidization directly at the mineral surface

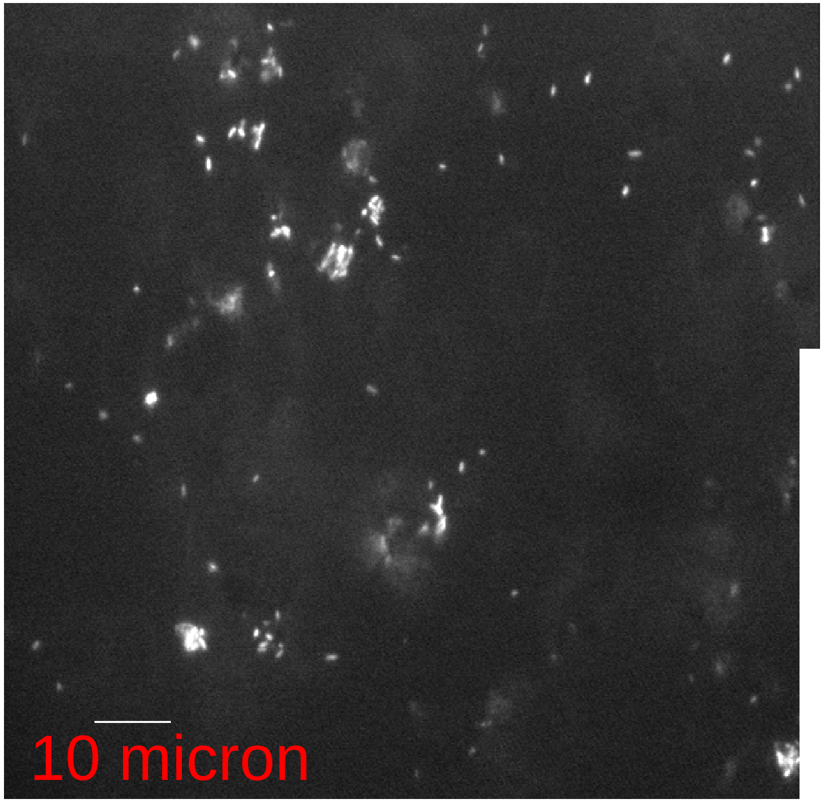
- Indirect mechanism: Mineral oxidizing agent is dissolved ferric iron $FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+$

  and the role of the microbe is to oxidize the ferrous iron product from the abiotic mineral oxidation to ferric iron

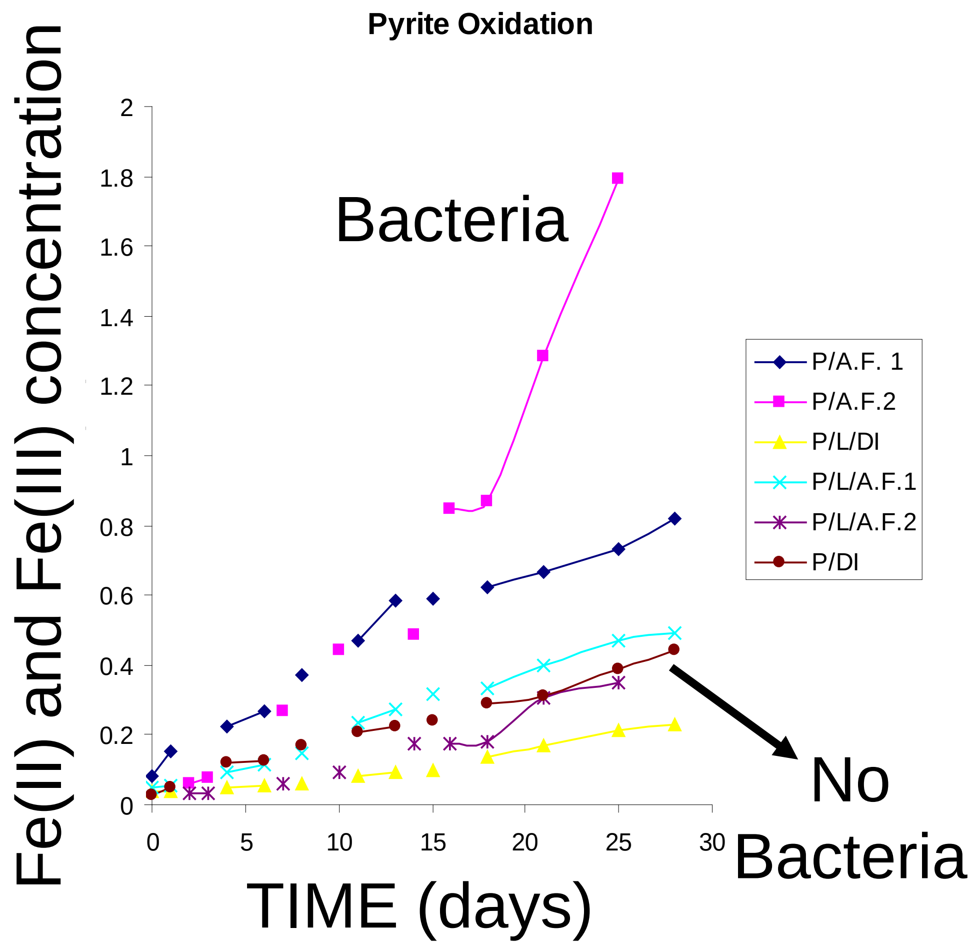
  $4\ Fe^{2+} + O_2 + 4\ H^+ \rightarrow 4\ Fe^{3+} + 2\ H_2O$

- When these two reactions are coupled, mineral oxidation proceeds with a net production of ferric iron, sulfate, and acidity

Biotic Contribution to Pyrite Oxidation is Significant



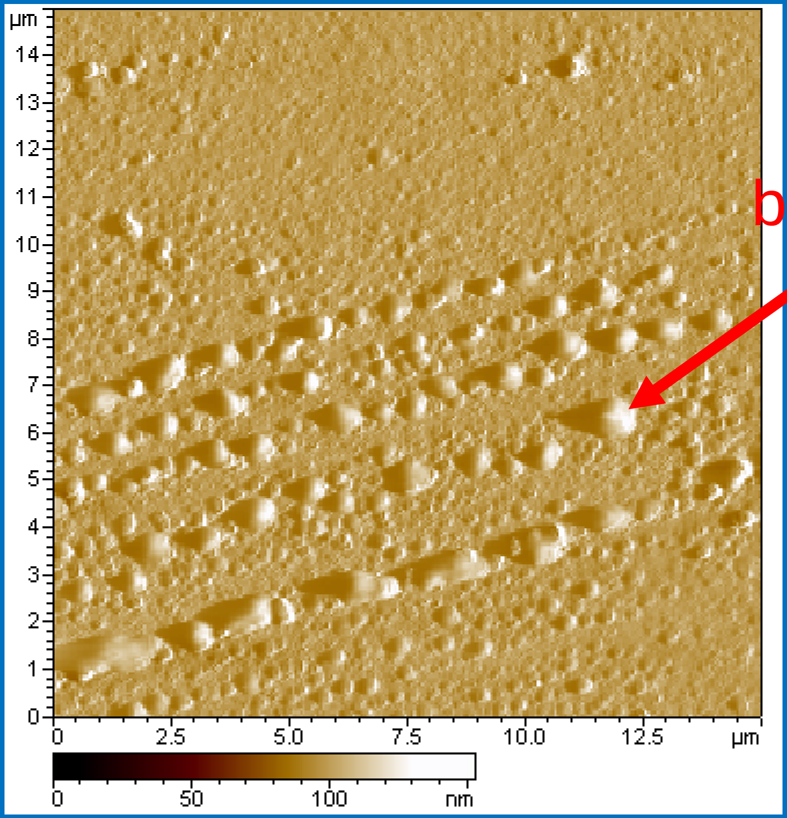
Acidithiobacillus Ferrooxidans

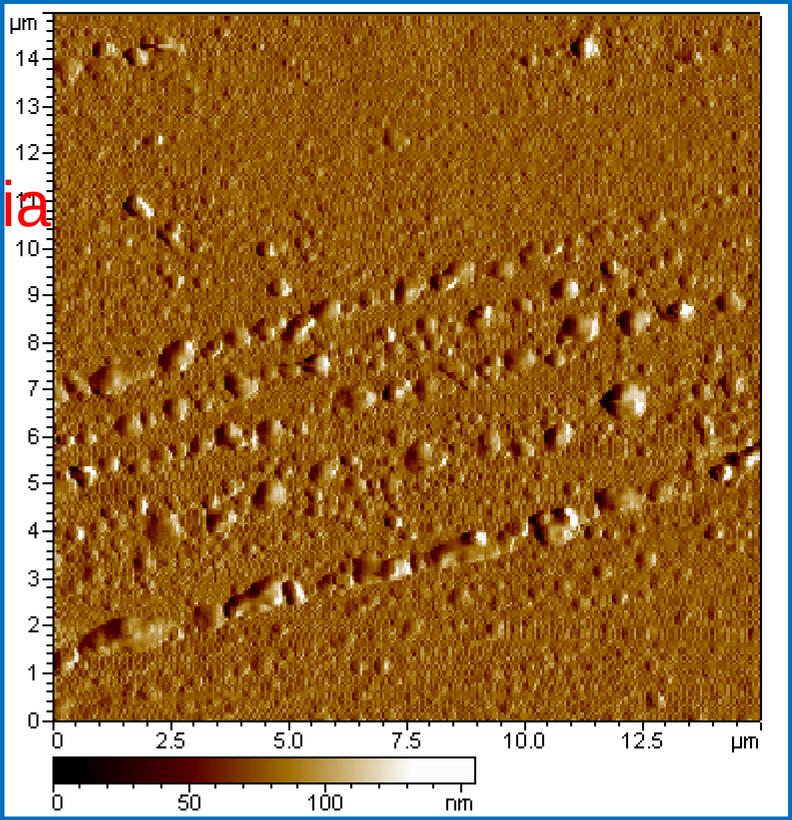


Bacteria drive the oxidation of Fe^{2+} to Fe^{3+}, a strong Oxidant of pyrite

$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$

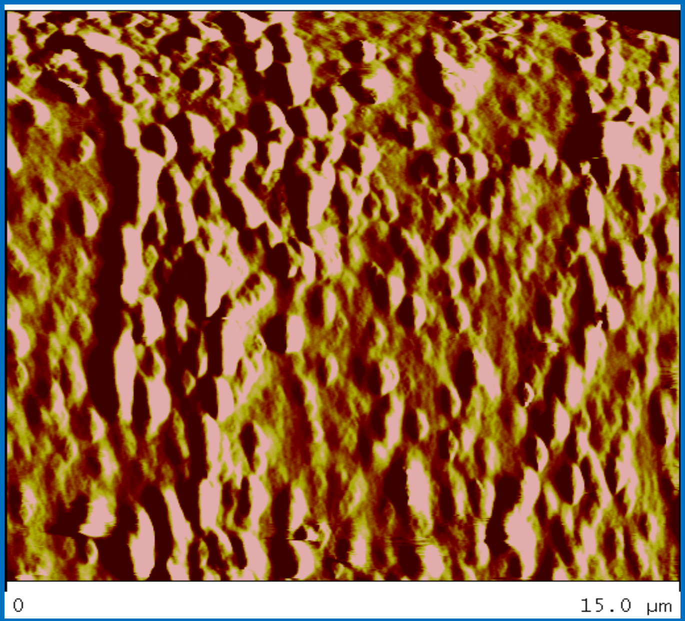
Initial adhesion of bacteria occurs at defect regions of Pyrite surface



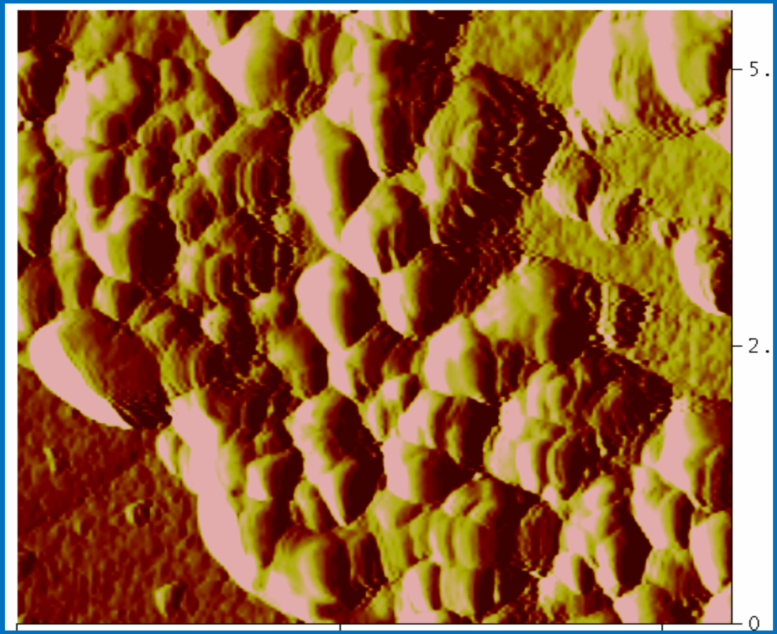


Pyrite after 10 day exposure to
Acidithiobacillus ferrooxidans

Microcolonies *Acidithiobacillus ferrooxidans* on pyrite

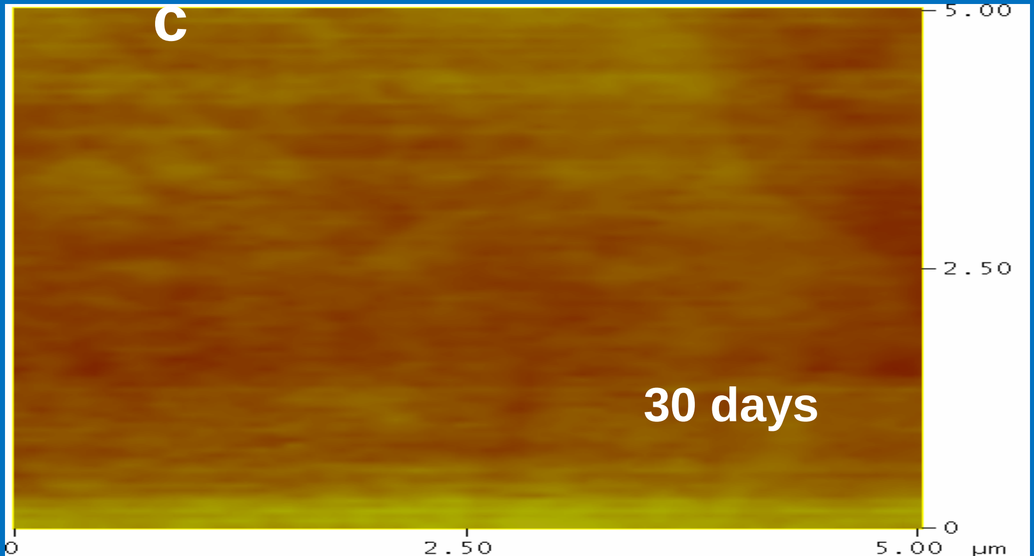


8 days

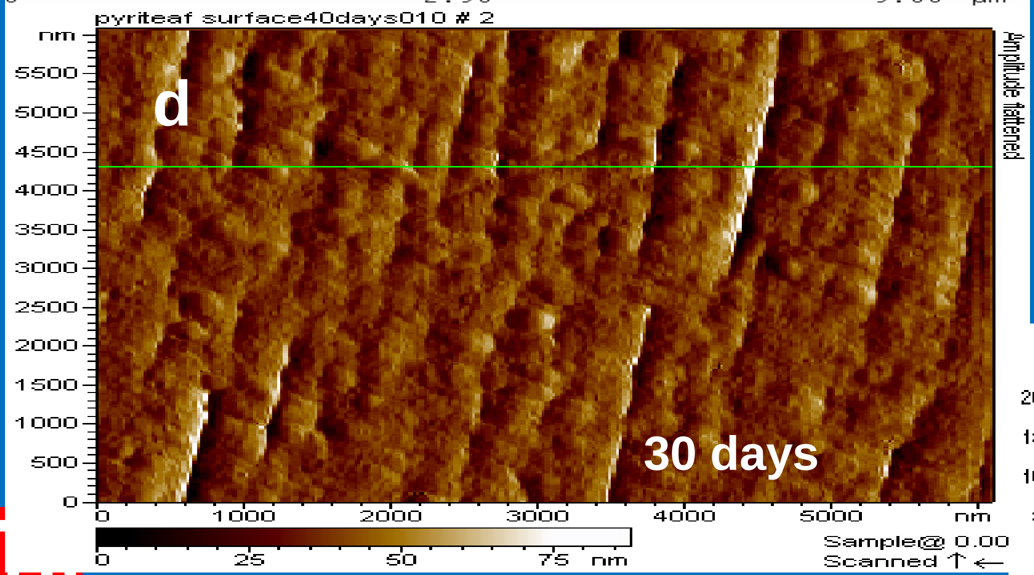


40 days

Effect of *Acidithiobacillus ferrooxidans* on pyrite Topography

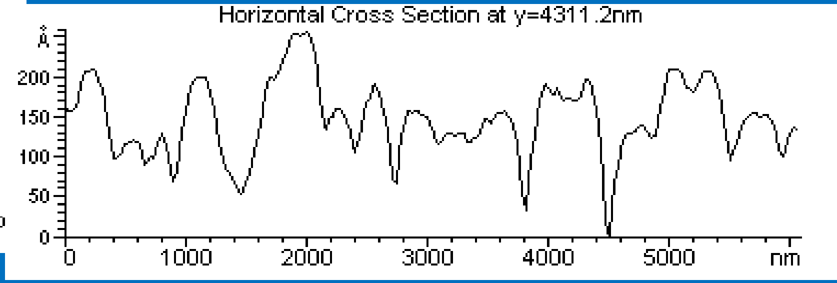


Bacteria absent



Bacteria present

and then removed



Addressing the Problem

- Need a barrier between pyrite and the environment i.e. the barrier should be WATER/AIR REPELLANT

- Barrier needs to bind strongly to those parts of pyrite that lead to AMD.

- Barrier should be applicable to pyrite/coal waste above the surface as well as subsurface in abandoned, and flooded mining sites.

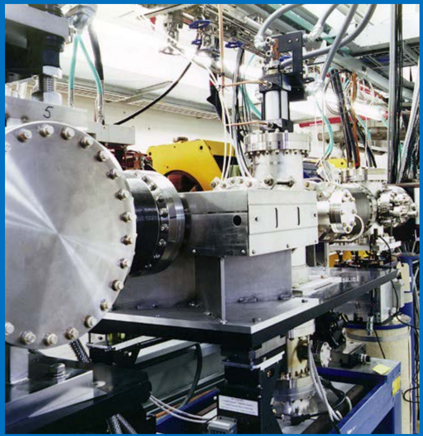
- Cost effectiveness and ease of application should be an important consideration.

Synchrotron based Techniques

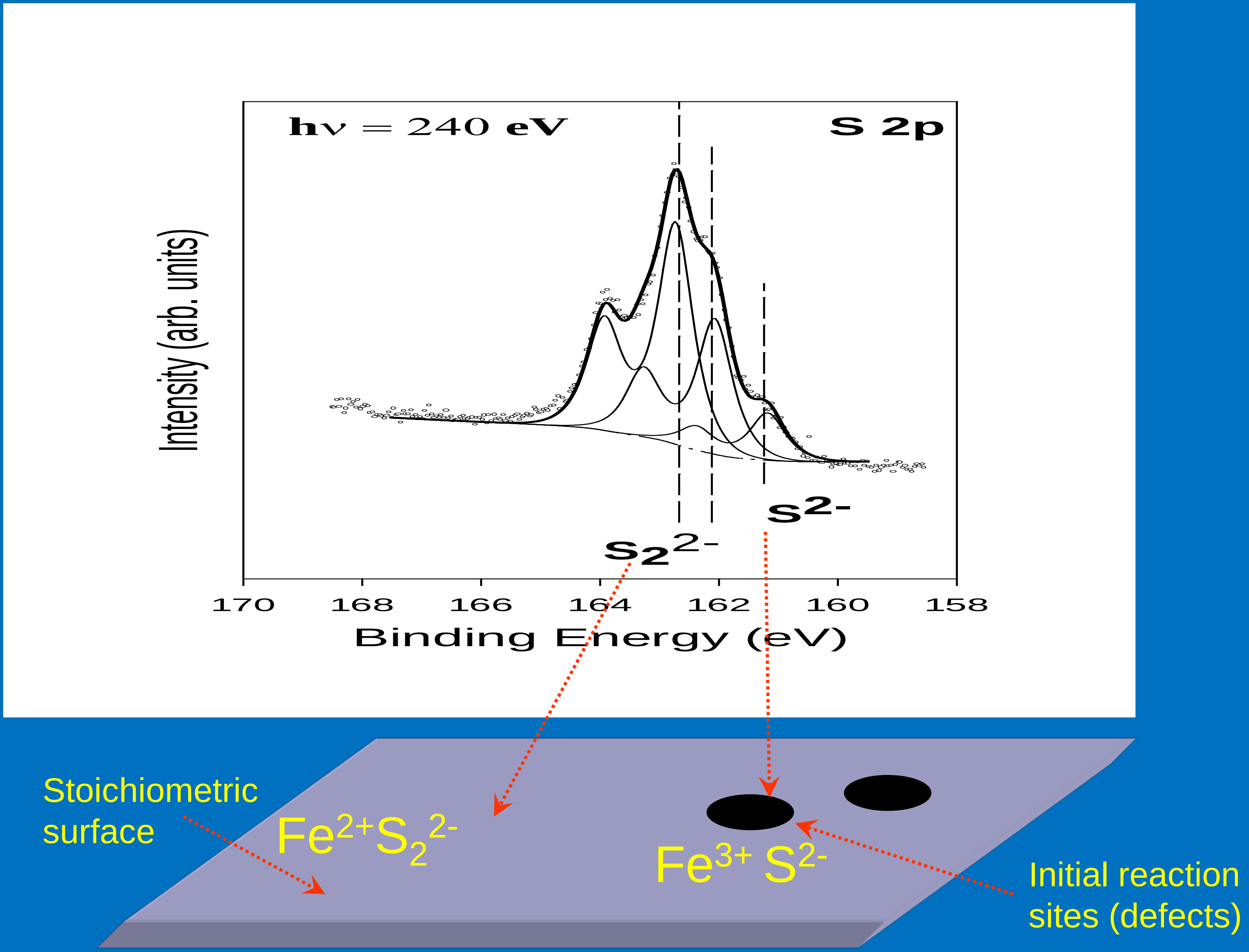
X-ray absorption fine structure

High-resolution Photoelectron spectrosocopy

National Synchrotron Light Source



Identification of Reactive sites on {100} FeS_2 using photoemission at the NSLS



Fundamental Surface Chemistry and Mechanism

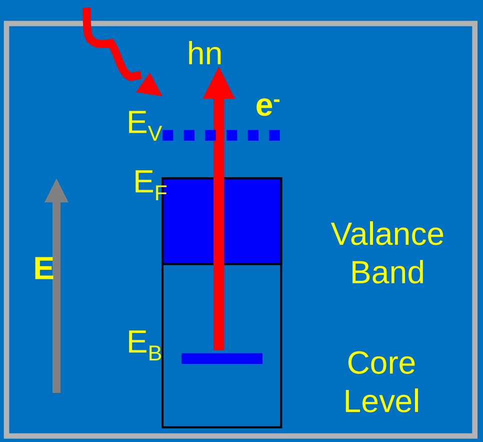
1. What are the surface species that form on pyrite

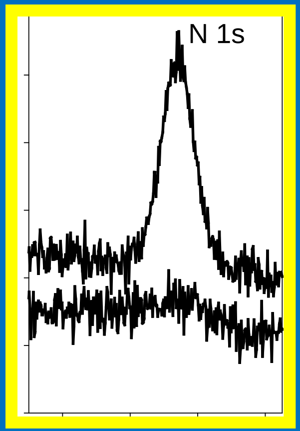
2. What are the active sites on pyrite?

3. Is the entire surface reactive?

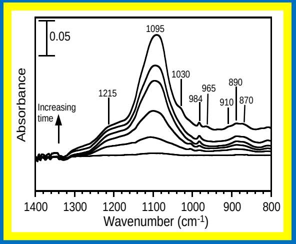
Some Techniques we use

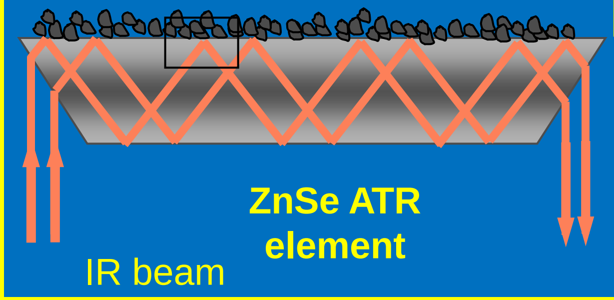
X-ray Photoelectron Spectroscopy

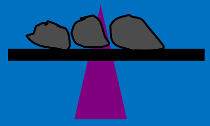




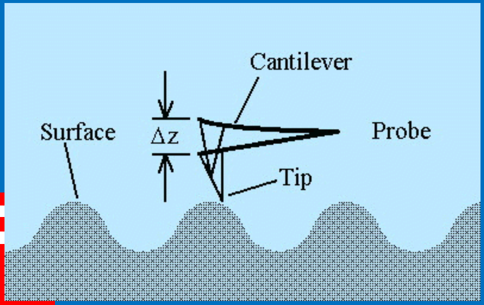
ATR FT- Infrared Spectroscopy

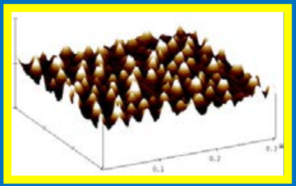




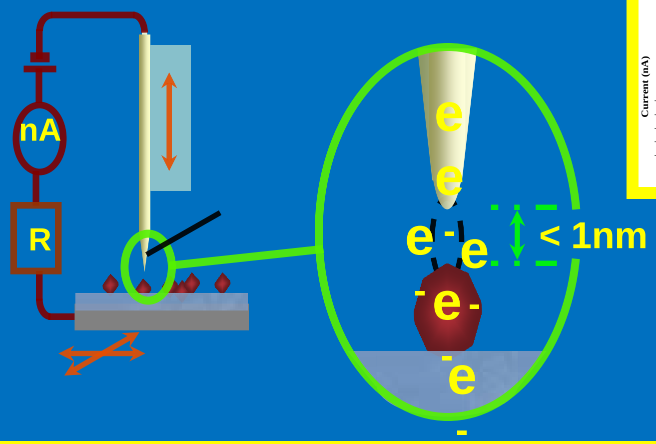


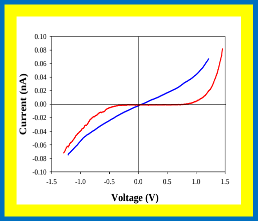
Atomic Force Microscopy





Scanning Tunneling Microscopy



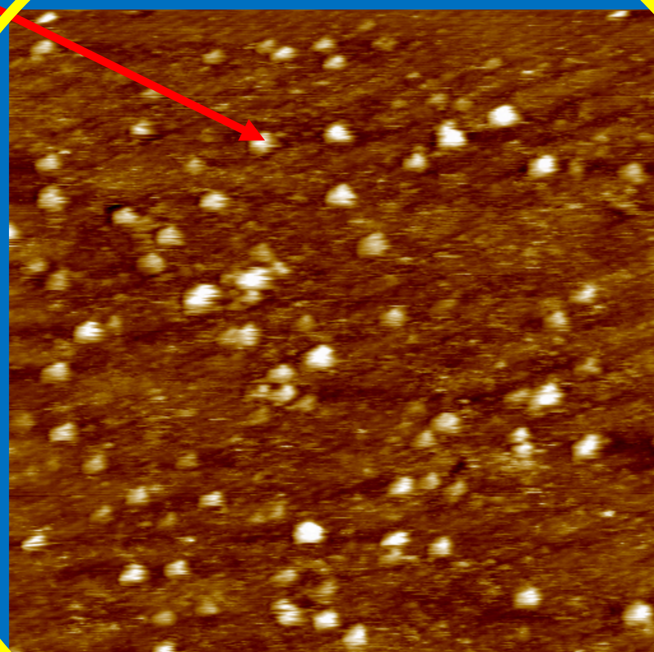


Atomic Force Microscope/ Scanning Tunneling Microscopy

STM of Pyrite surface after exposure to Oxidizing Environment

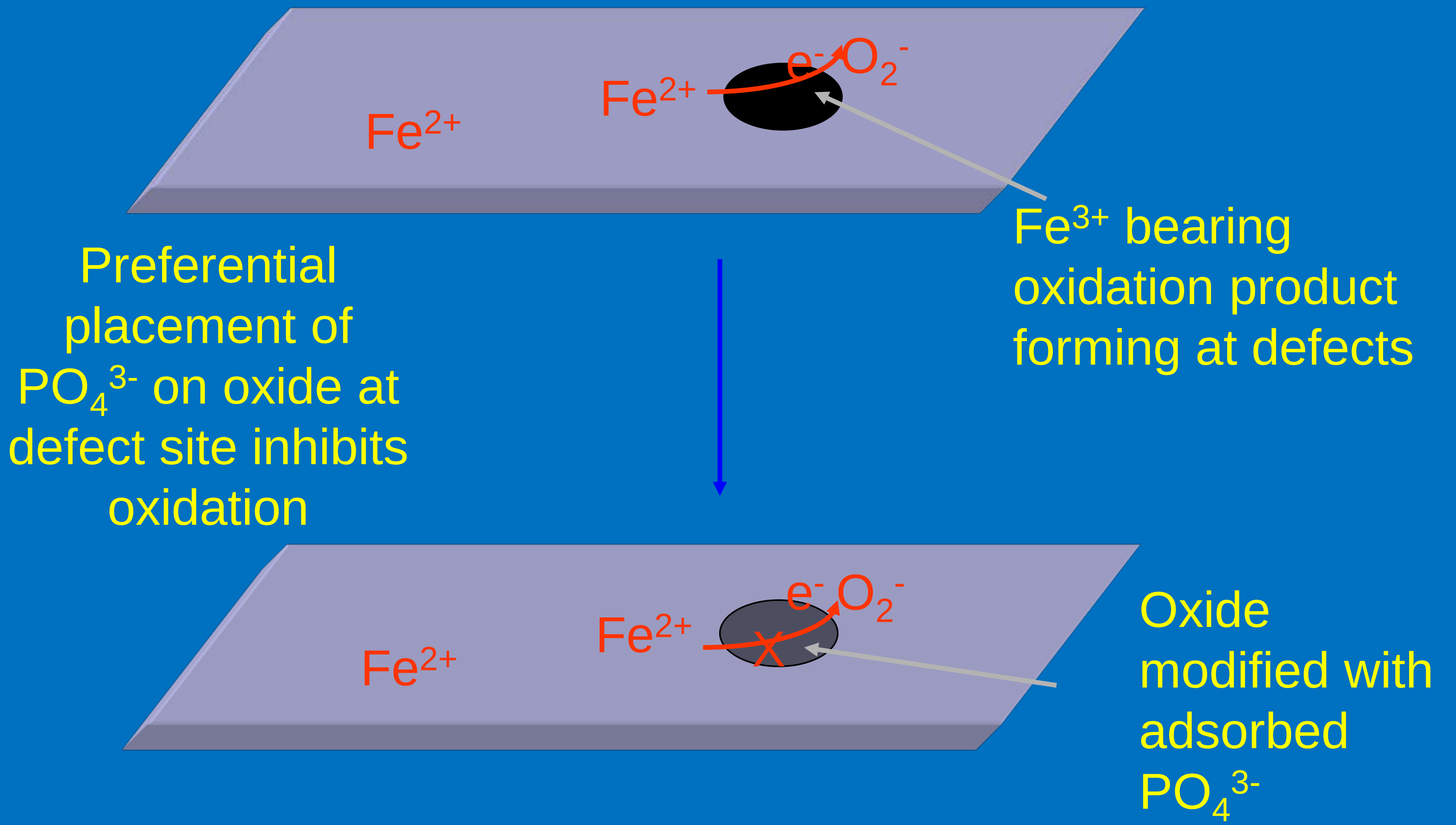
Microscopic View

Oxidation Product

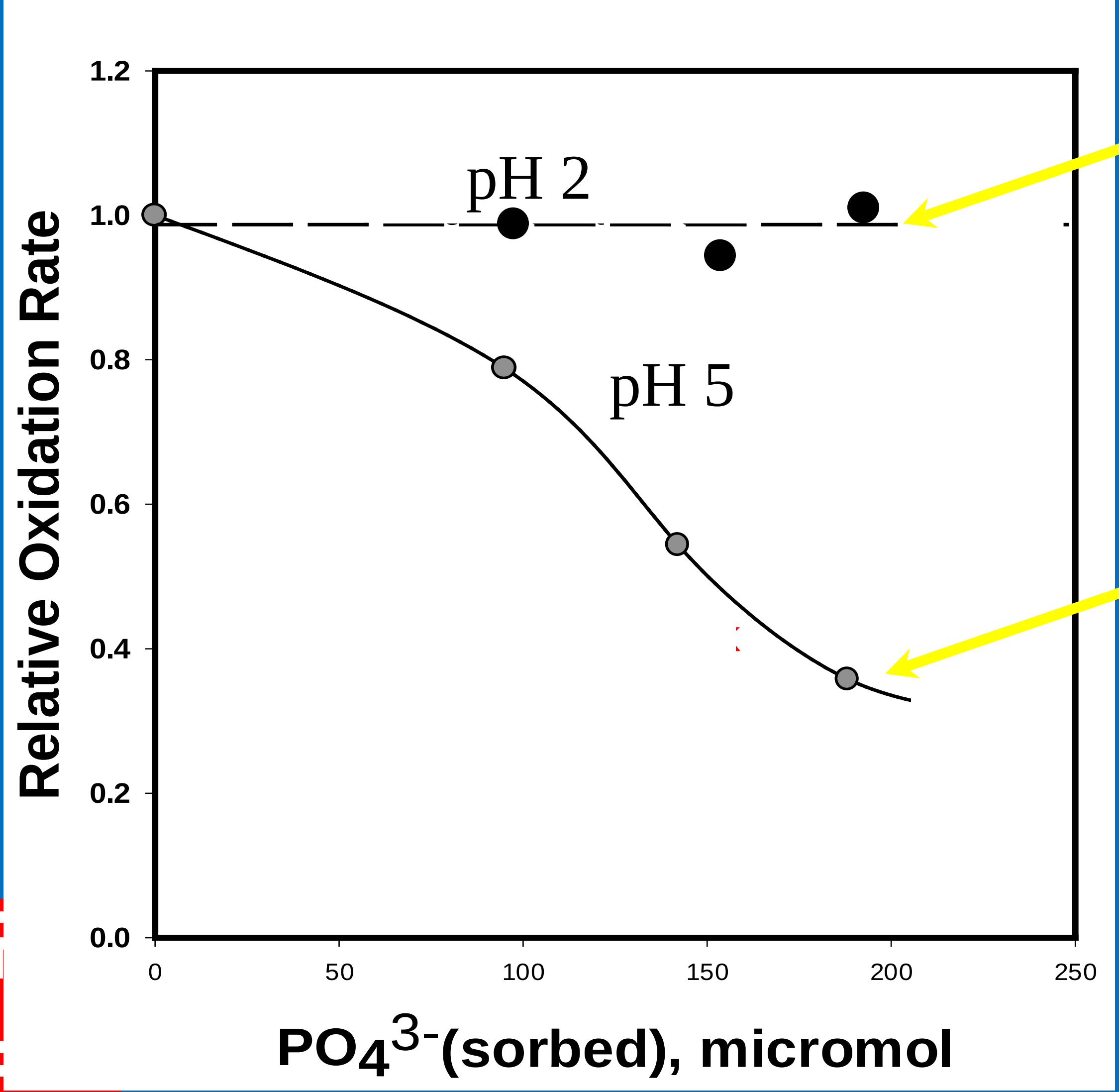


Hypothesis: Blocking
Initial oxidation product
Will suppress AMD

Impede oxidation by blocking fundamental step



Phosphate, PO_4^{3-}, Losses effectiveness at pH >3

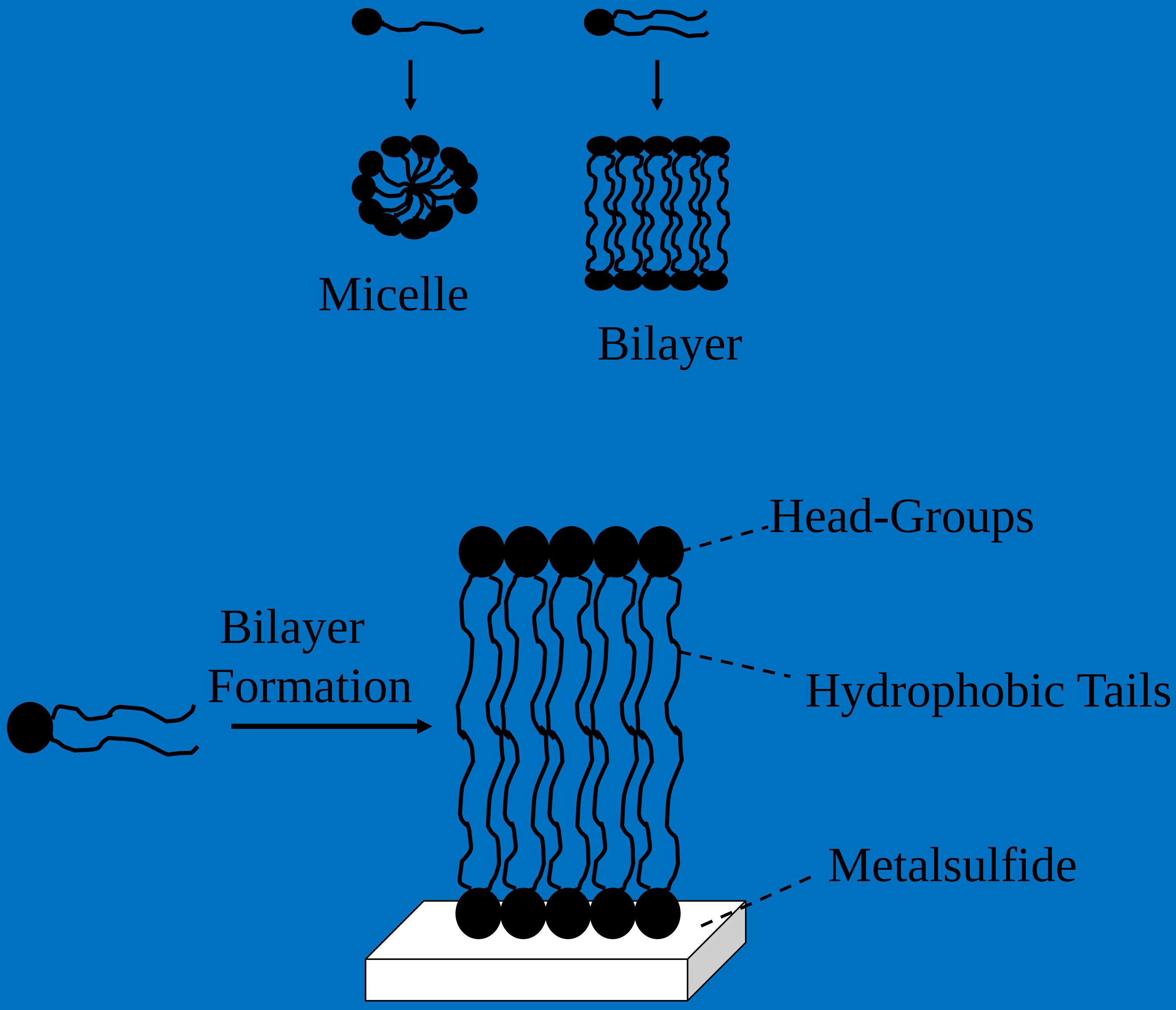


No effect of phosphate

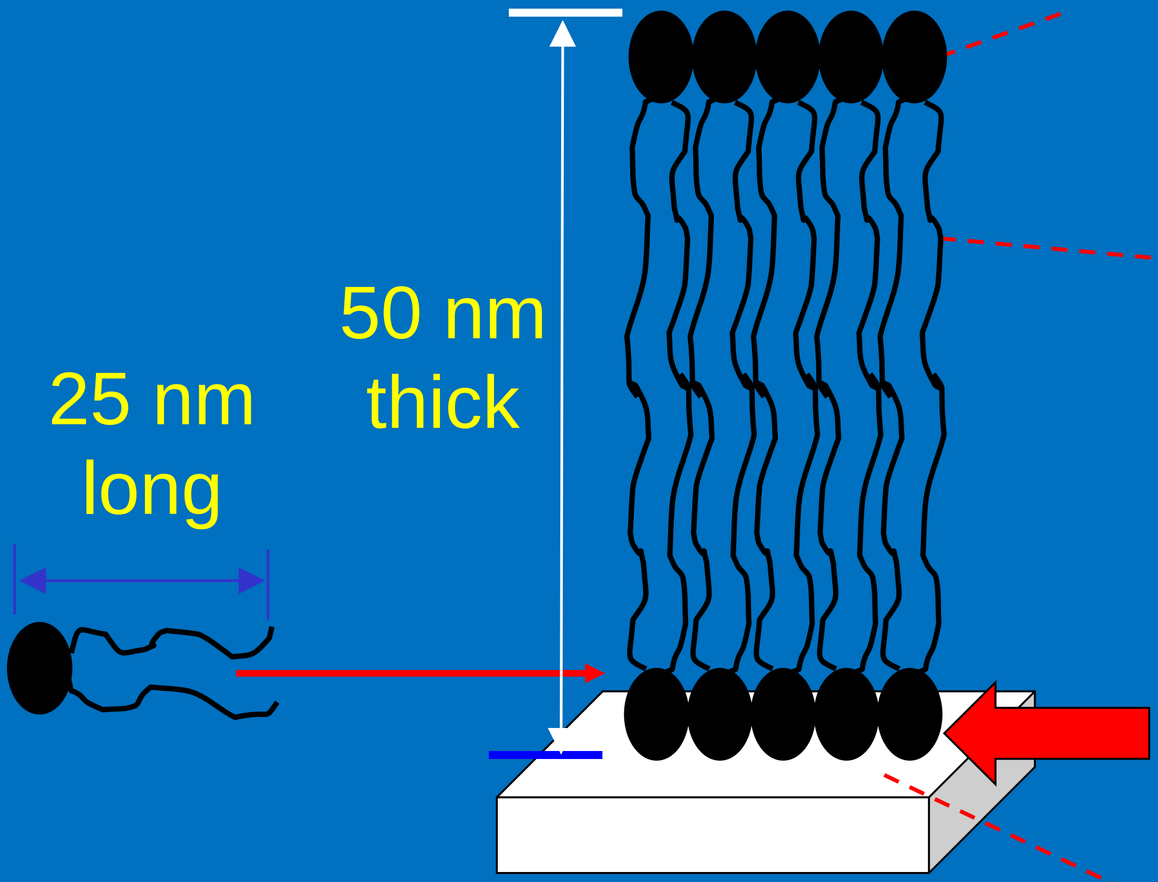
Phosphate-induced suppression

Where do we turn now? Need good protection at lower pH

- Hypothesis:
  - Lipid (two tail coatings)


Micelle
Bilayer
Bilayer
Formation
Head-Groups
Hydrophobic Tails
Metalsulfide

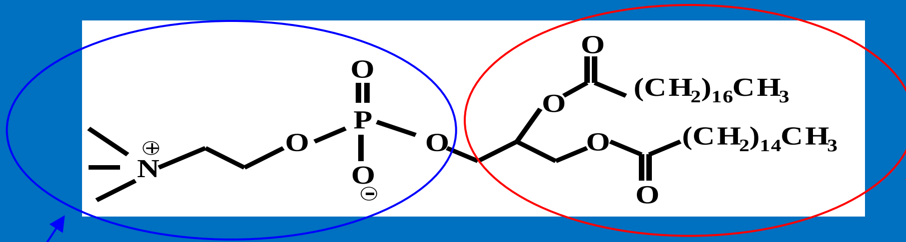
How Does it Work?



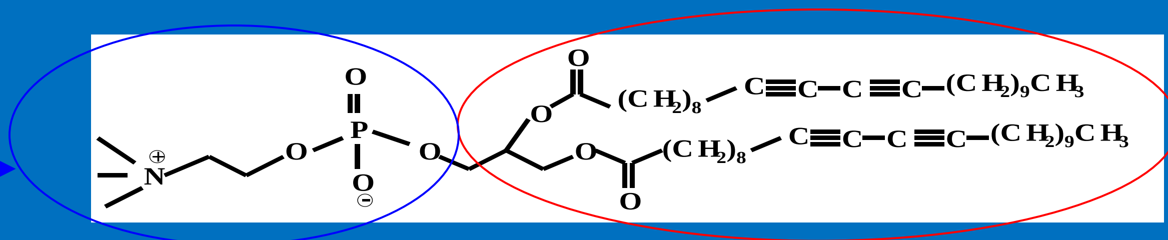
Example of lipids used to suppress pyrite oxidation

Head Group

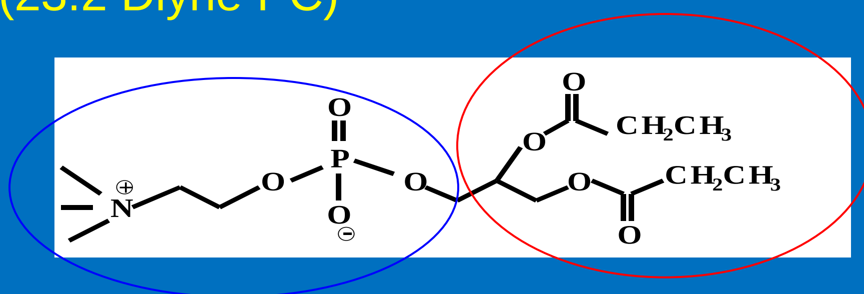
Tail



L-a-Phosphatidylcholine (egg PC)



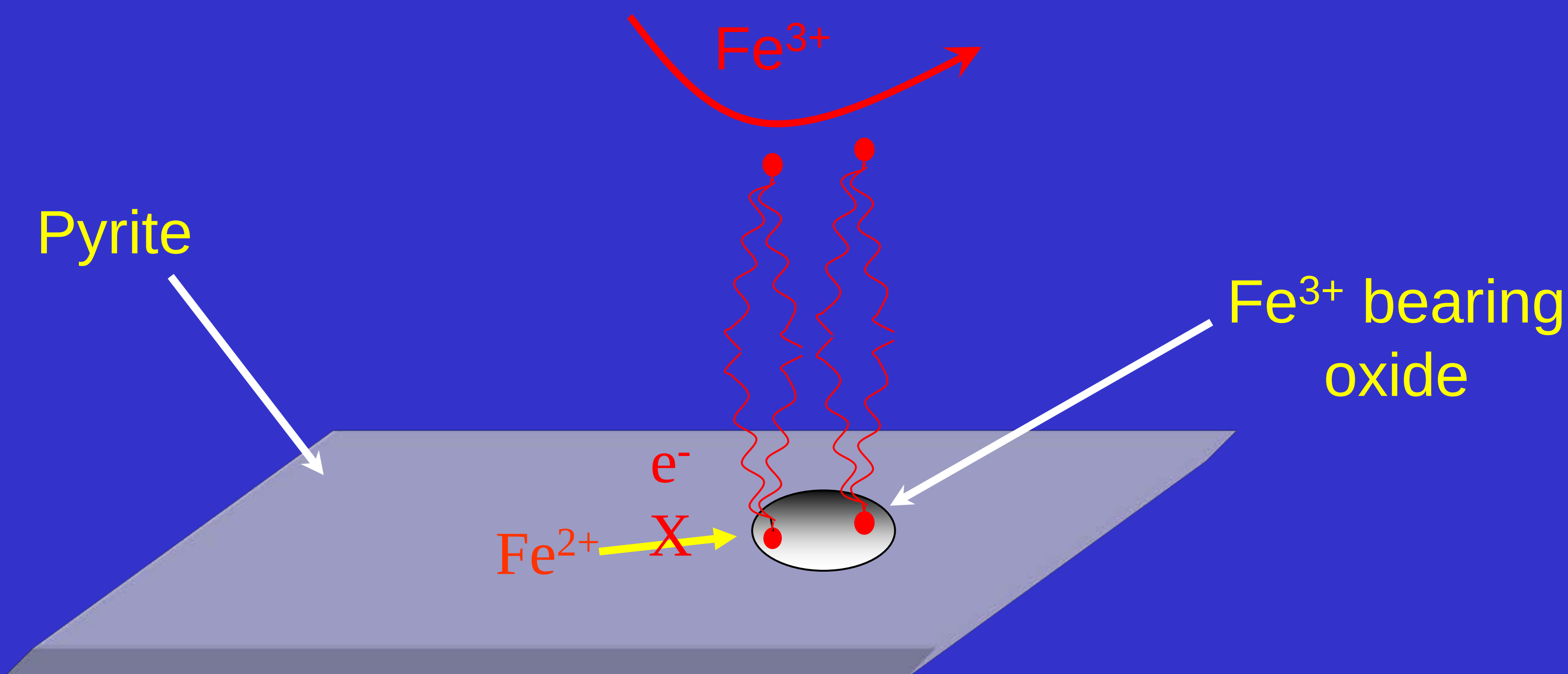
1,2-bis(10,12-tricosadiynoyl)-*sn*-Glycero-3-Phosphocholine (23:2 Diyne PC)



1,2-Dipropionoyl-*sn*-Glycero-3-Phosphocholine (3:0 PC lipid)

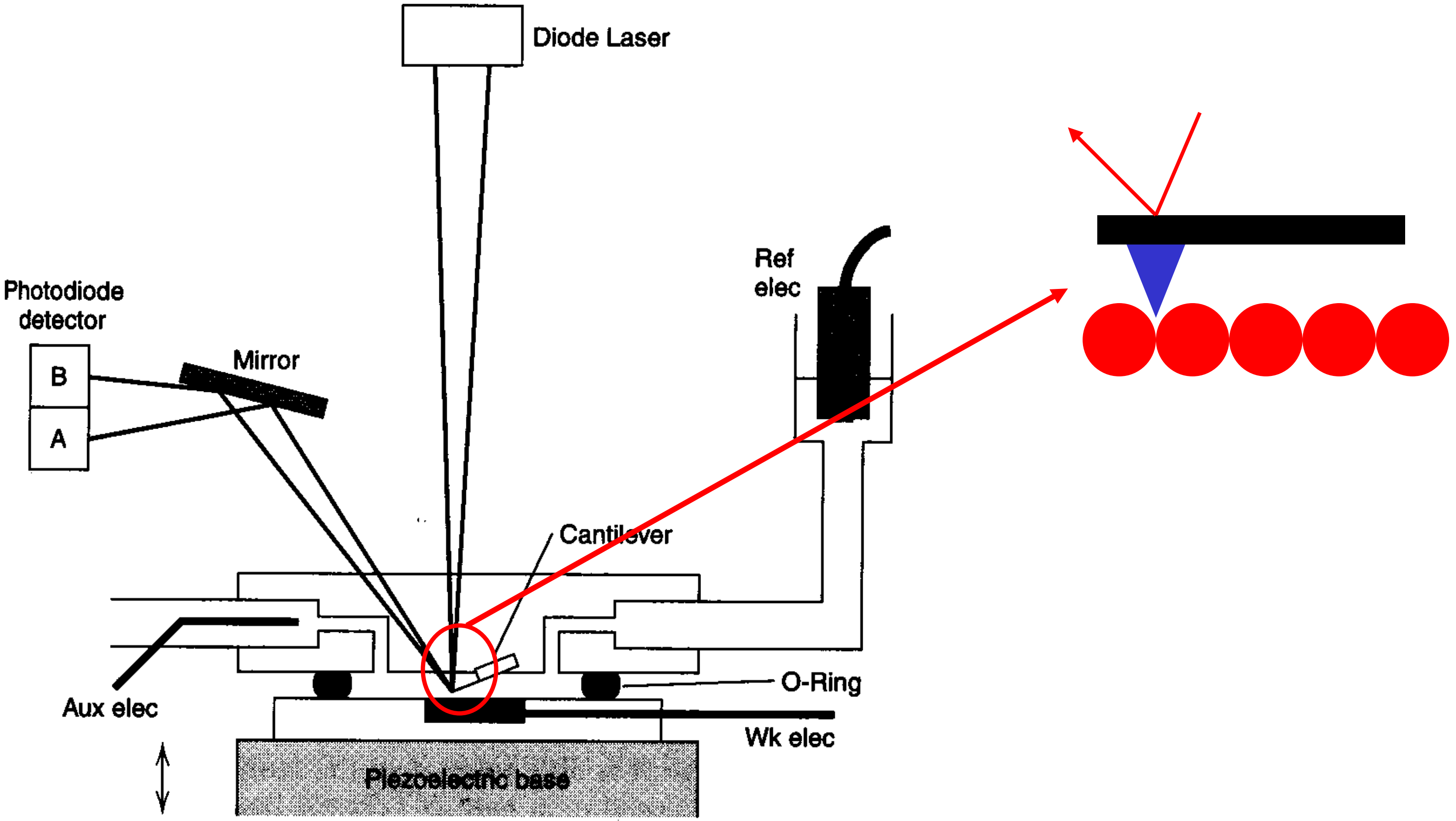
Acid Mine Drainage

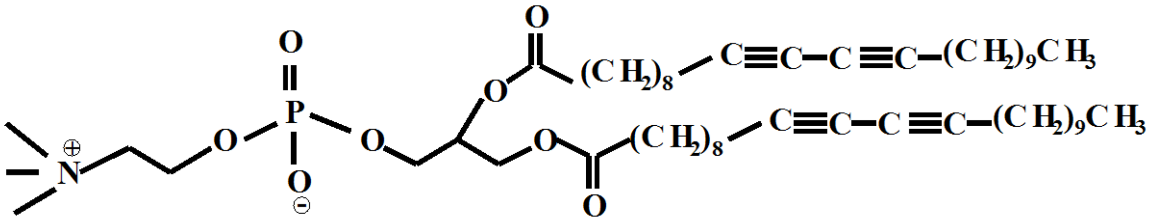
Suppress $Fe^{3+} + e^- \rightarrow Fe^{2+}$

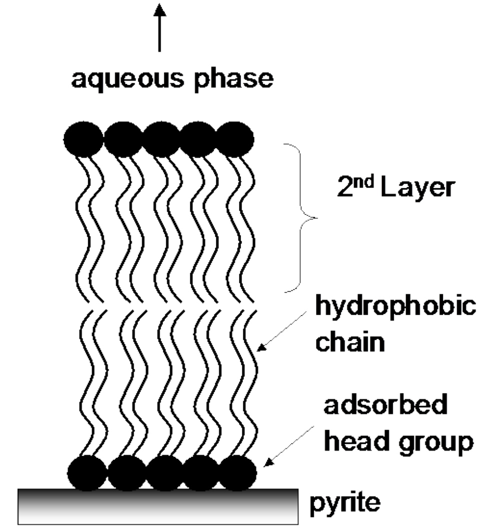


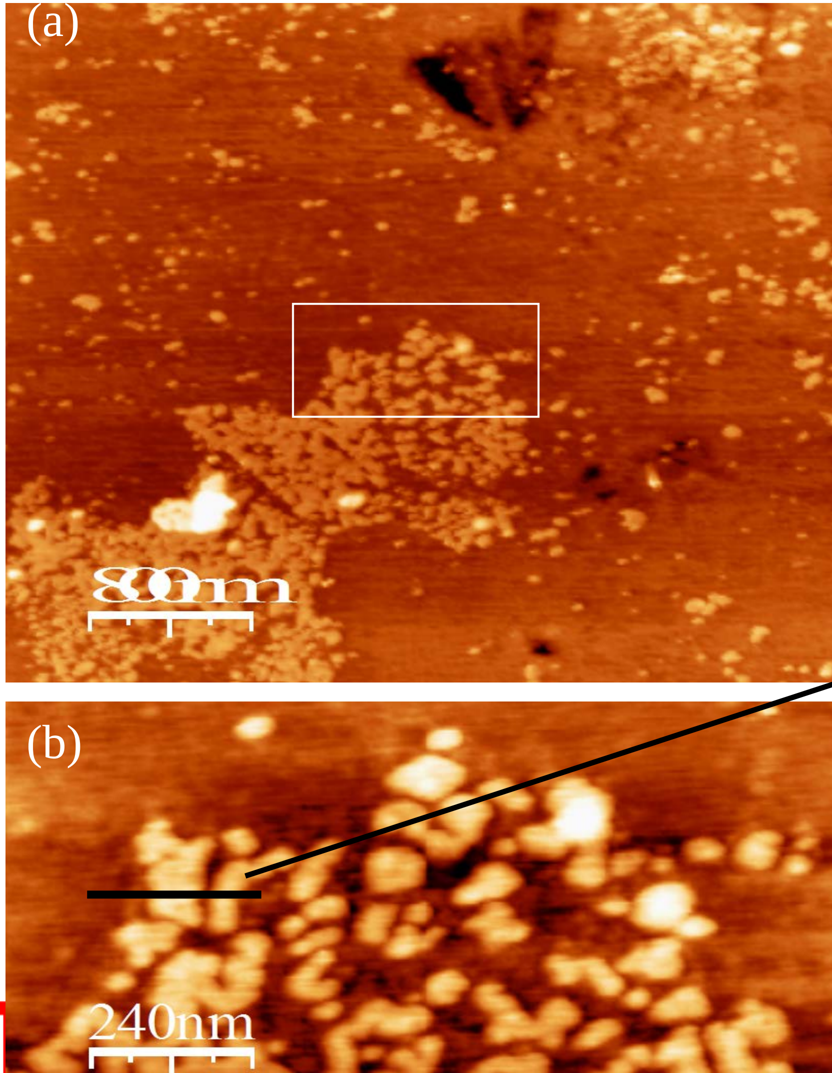
Atomic Force Microscope/
Scanning Tunneling Microscopy

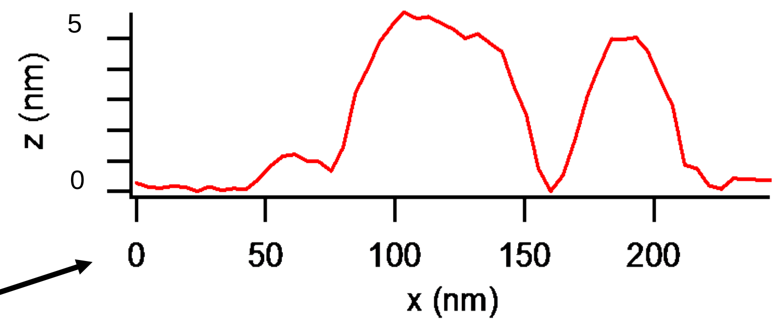
Atomic Force Microscopy





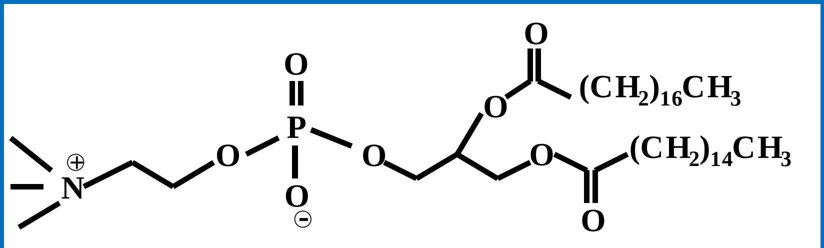






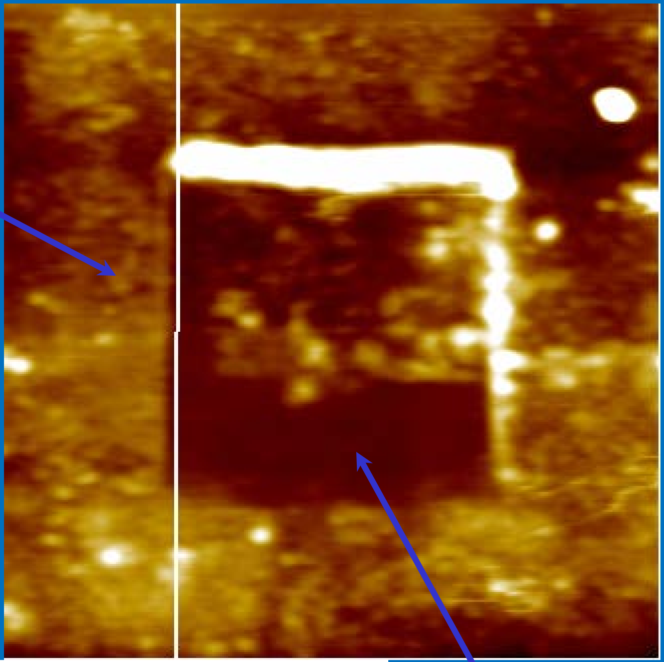
Zhang, X. V.; Kendall, T. A.; Hao, J.; Strongin, D. R.; Schoonen, M. A. A.; Martin, S. T., ES&T 2006, 40, (5), 1511-1515.

Lipid on pyrite

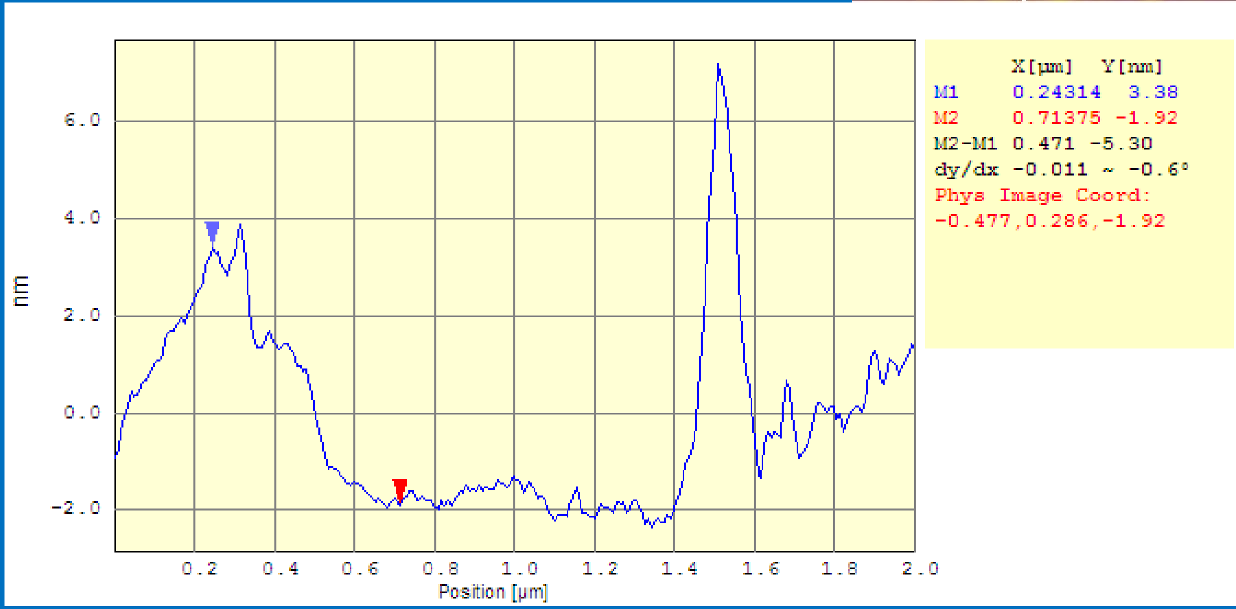


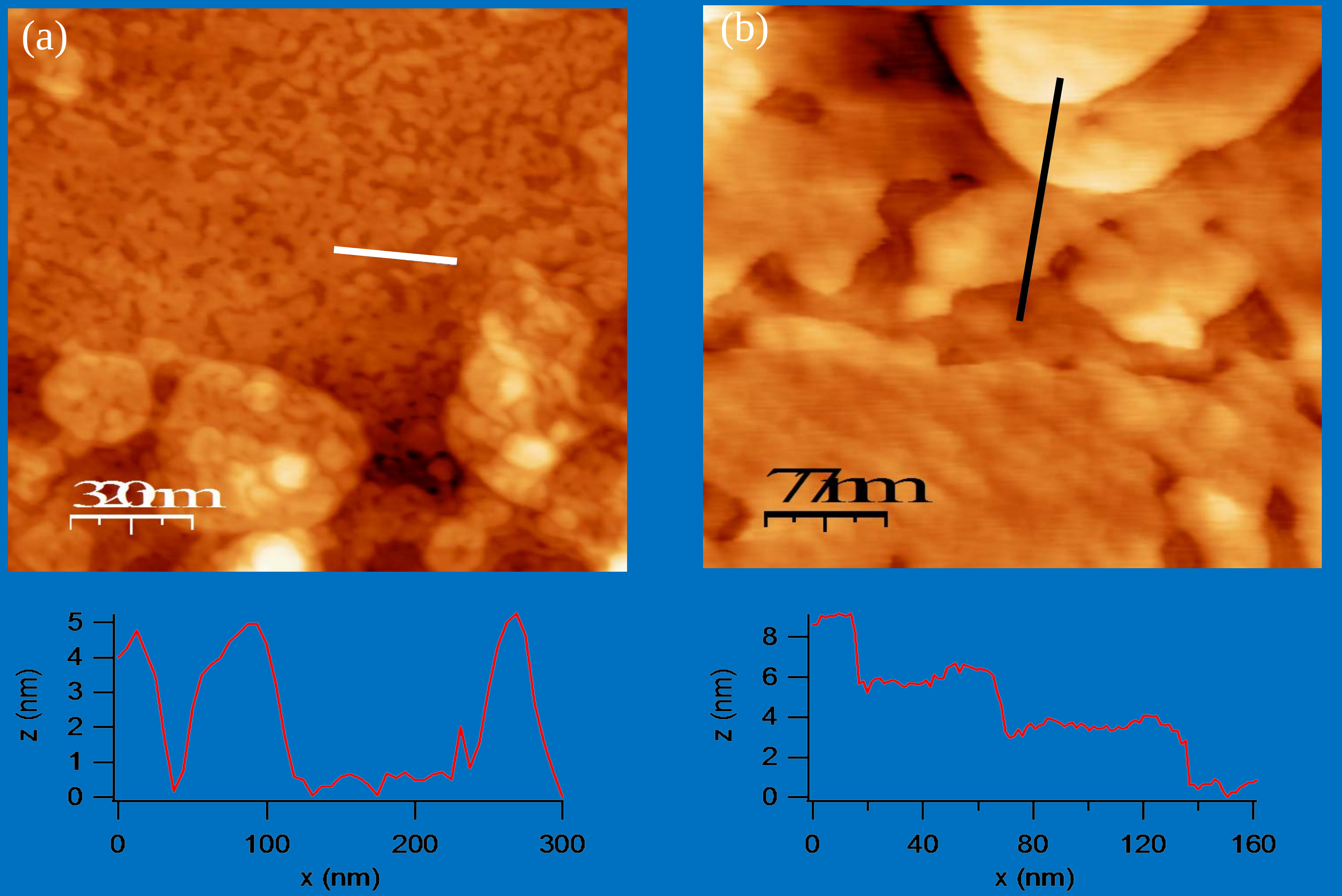
25 angstroms

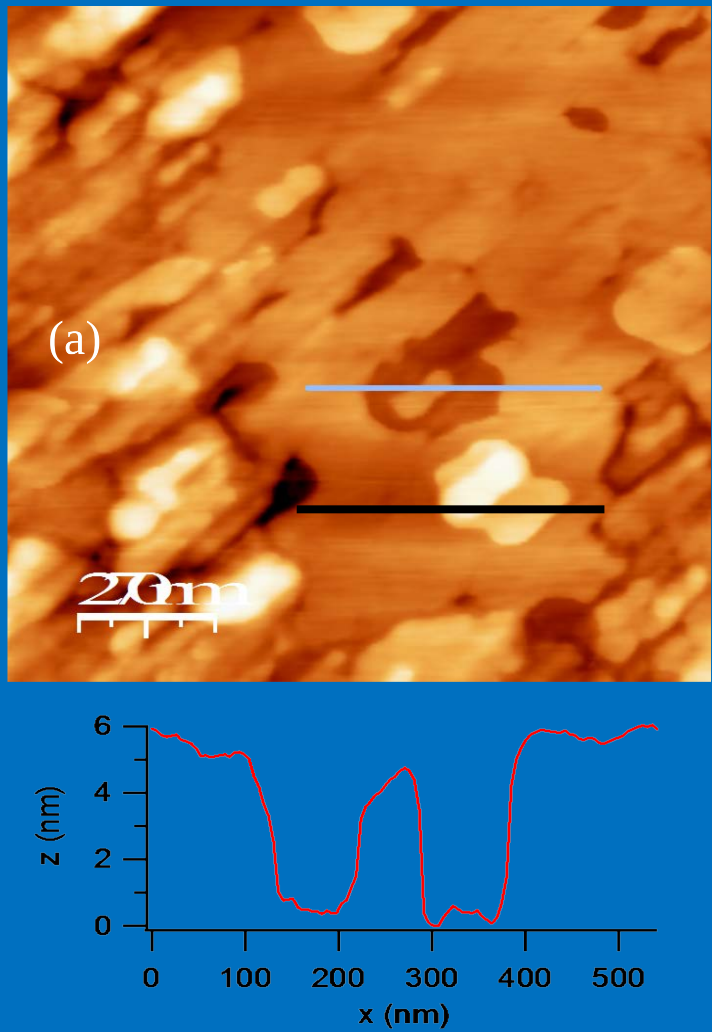
Bilayer = 25 x 2 = 50 angstroms

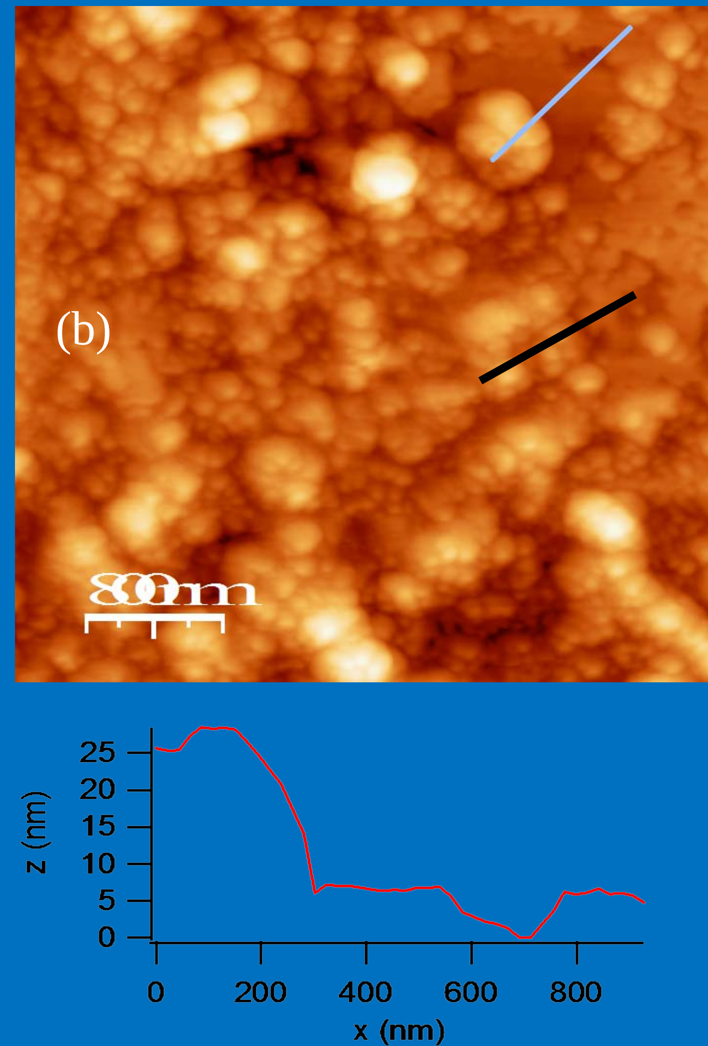


Pyrite surface




(a)
(b)
z (nm)
x (nm)
0
1
2
3
4
5
100
200
300
z (nm)
x (nm)
0
2
4
6
8
40
80
120
160


(a)
z (nm)
x (nm)
0
2
4
6
0
100
200
300
400
500


(b)
z (nm)
x (nm)
0
5
10
15
20
25
0
200
400
600
800

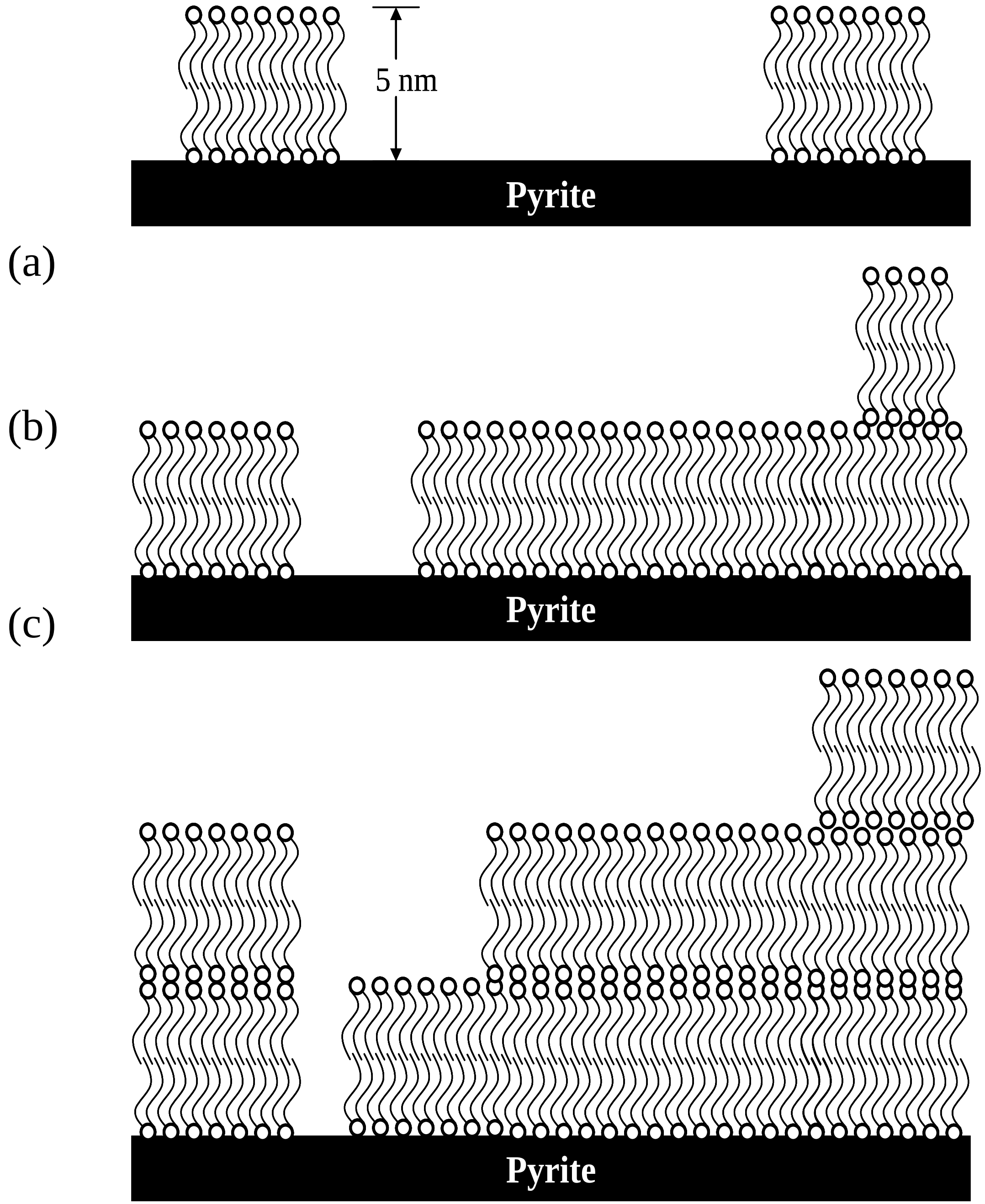
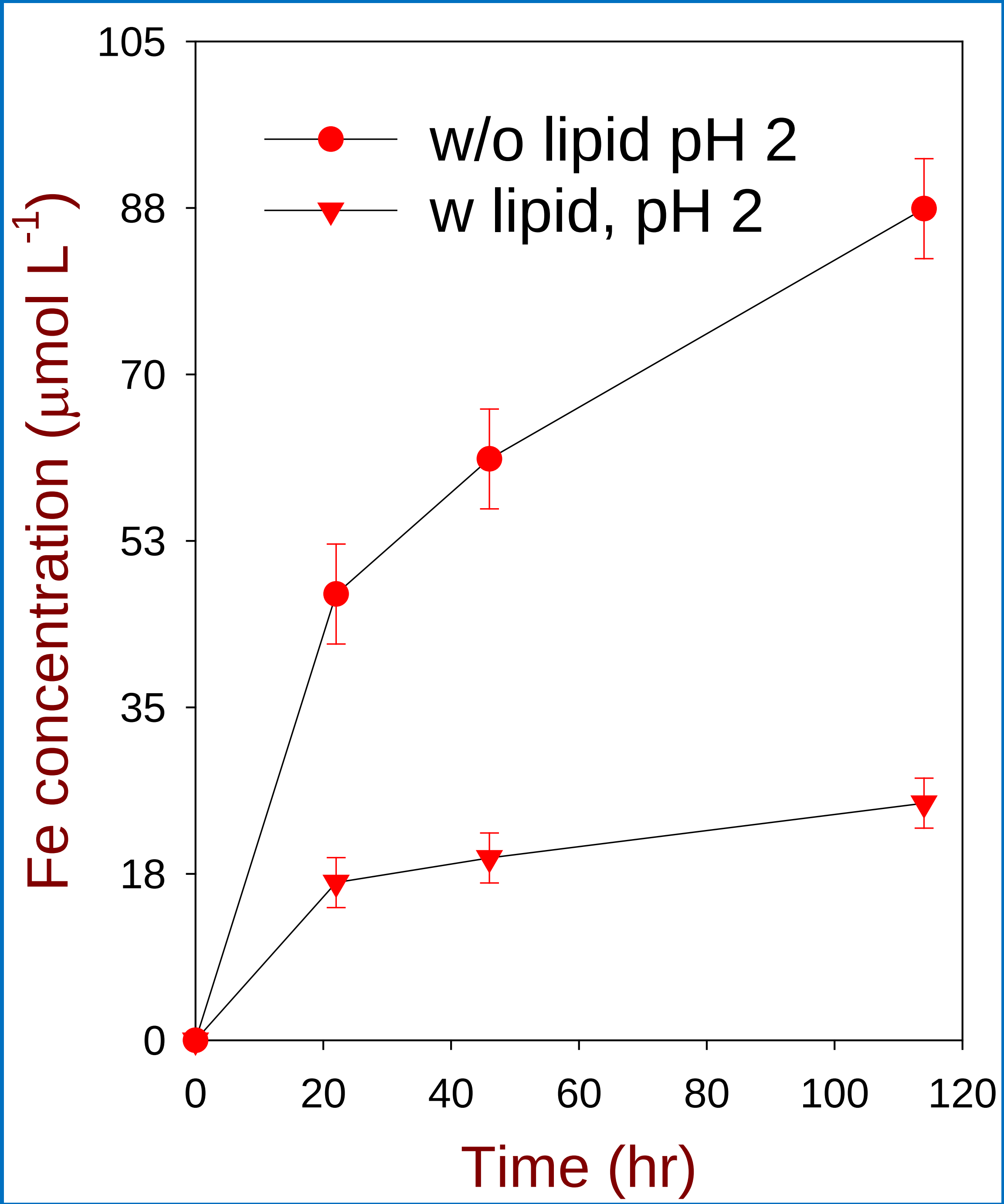


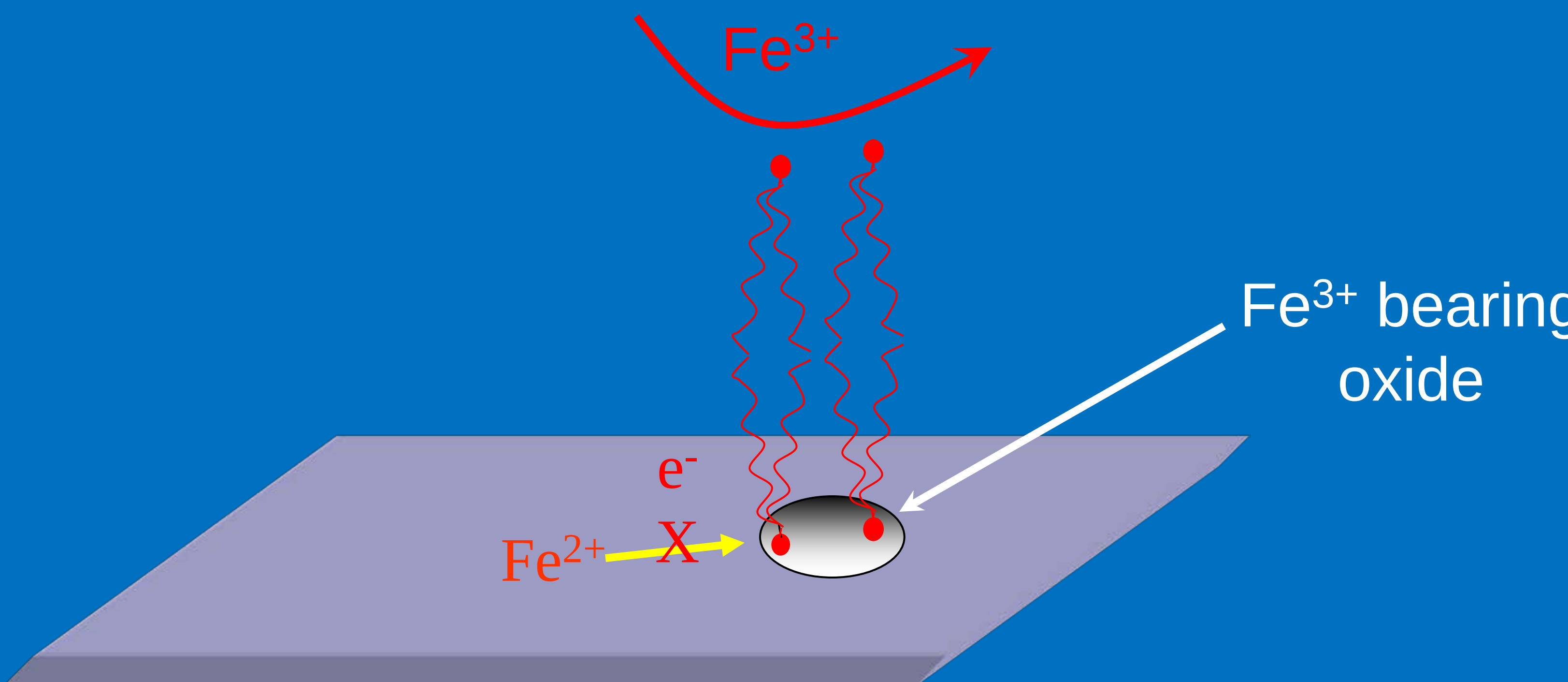
Figure 7

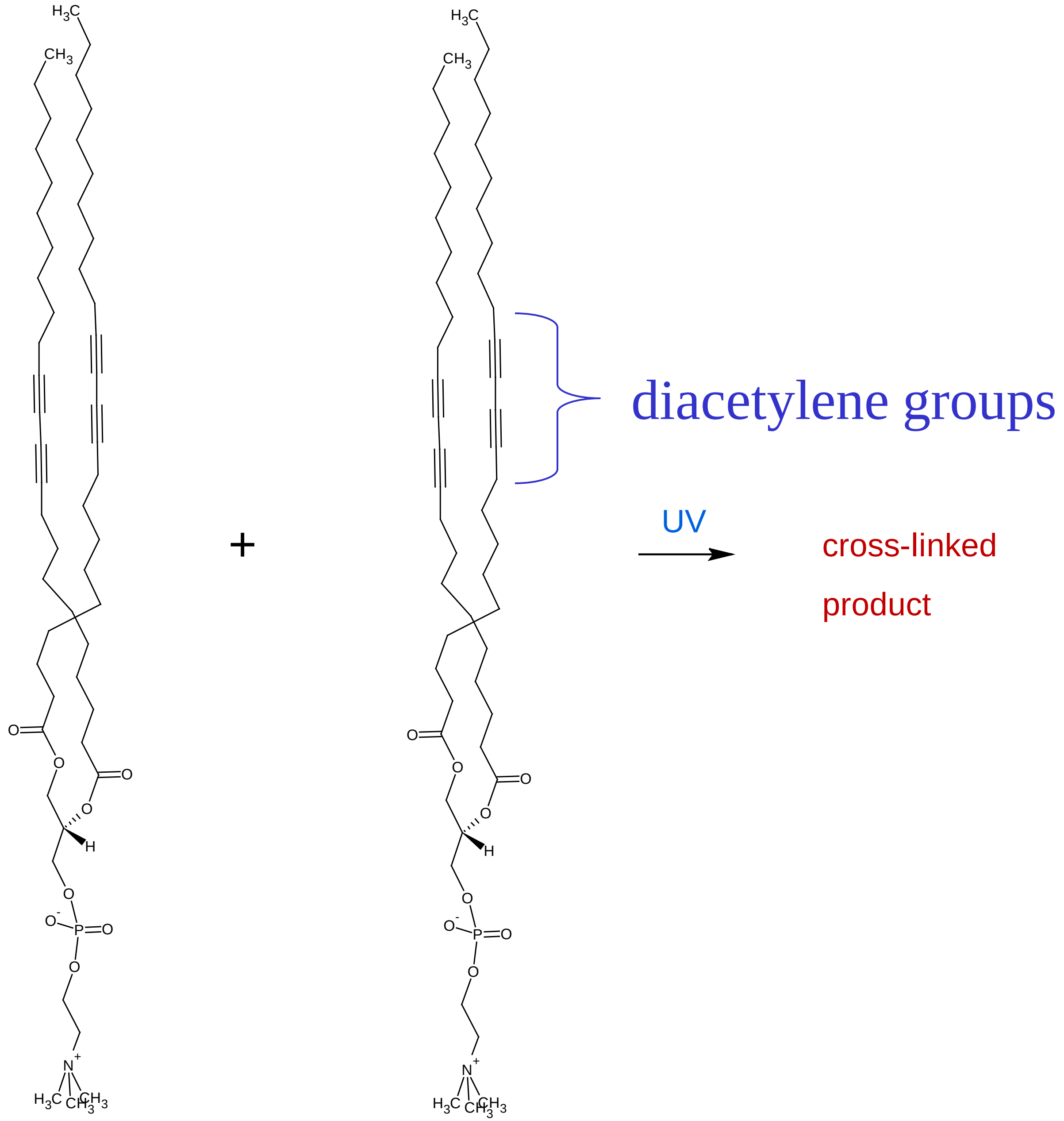
75 % suppression
Induced by
adsorption of
phospholipid



Acid Mine Drainage

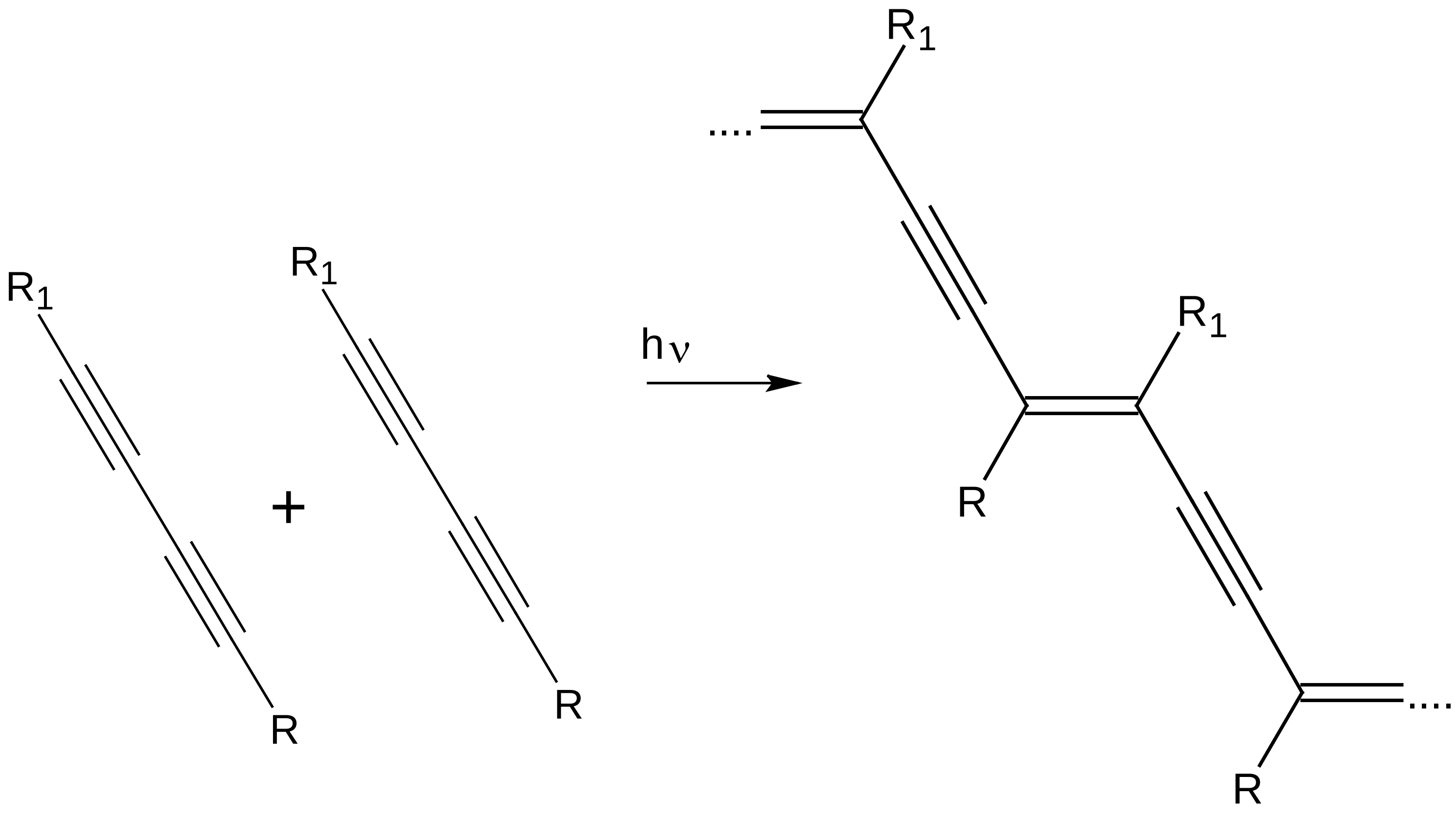
Suppress $Fe^{2+} \rightarrow Fe^{3+} + e^{-}$





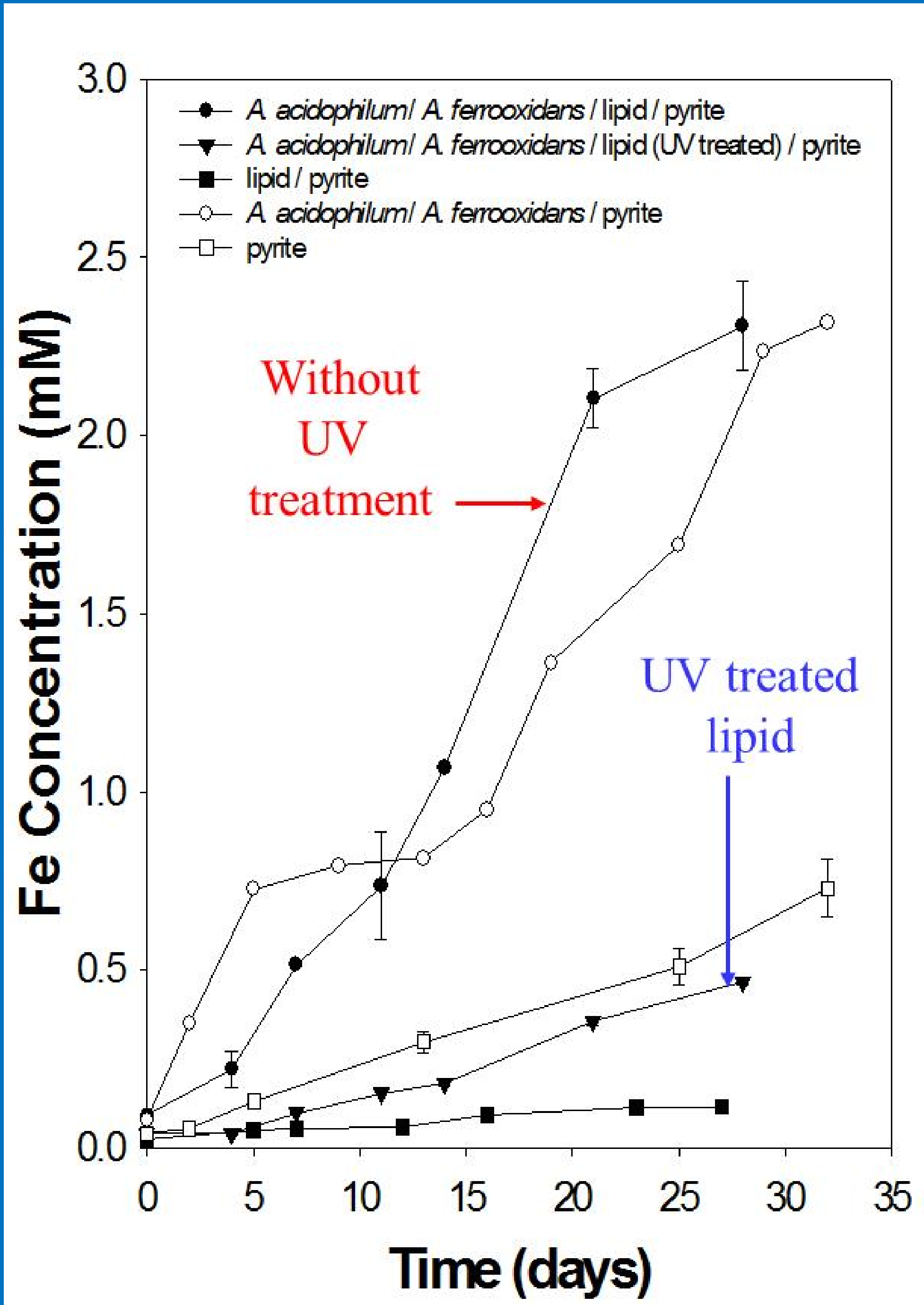
diacetylene groups
UV
cross-linked
product

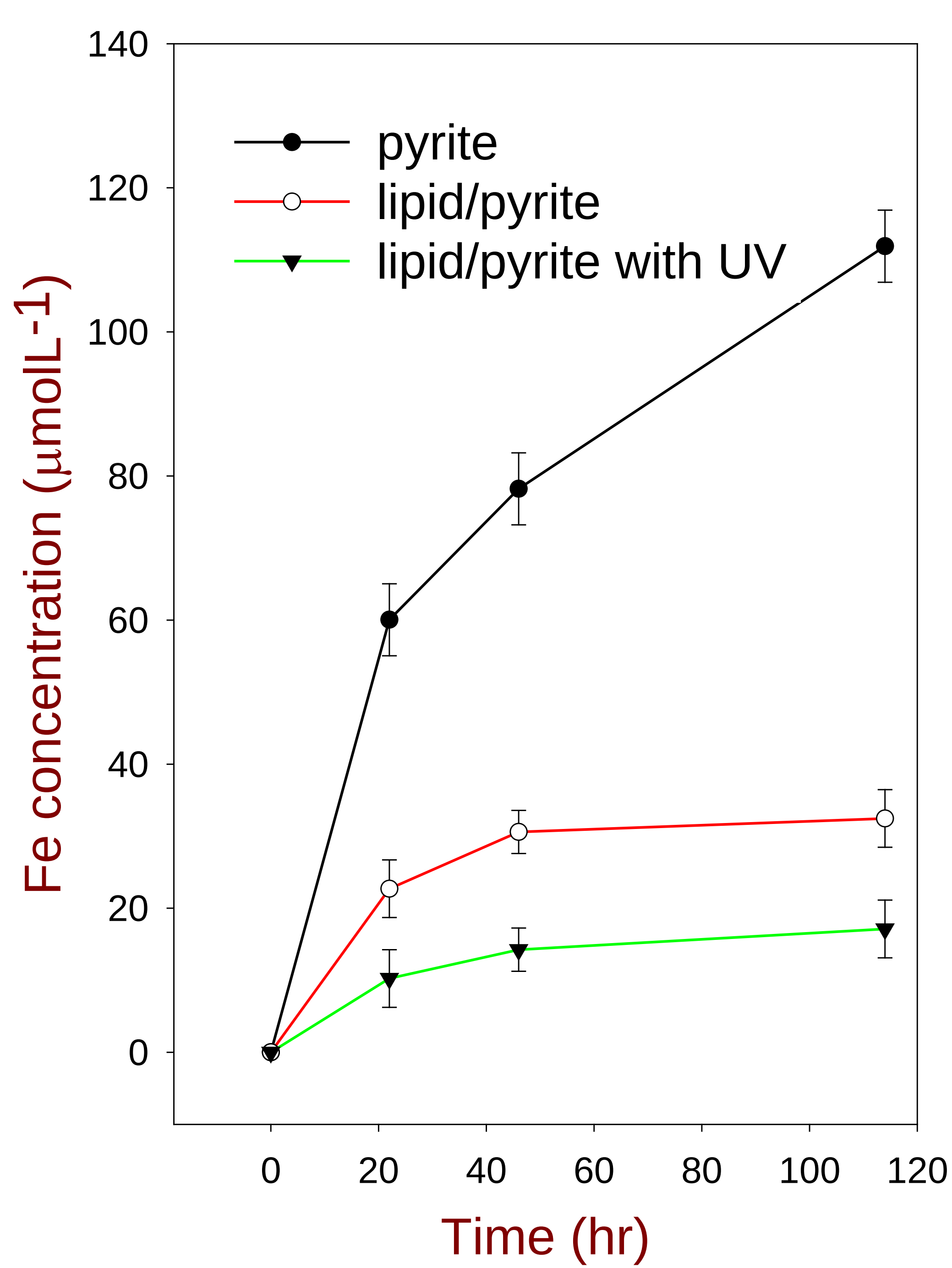
Cross-linking during UV light irradiation



The presence of Acidiphilium acidophilum (AA) disrupts lipid layer

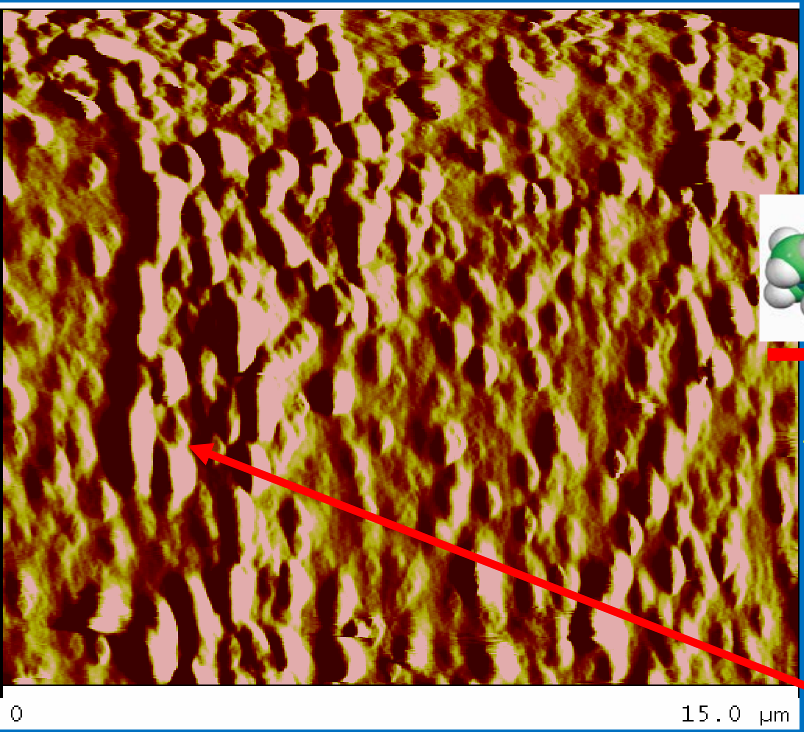
Cross-linking overcomes microbial Facilitated degradation of oxidation barrier

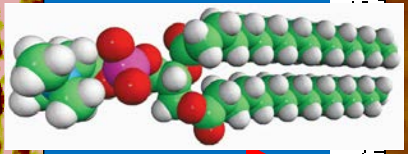


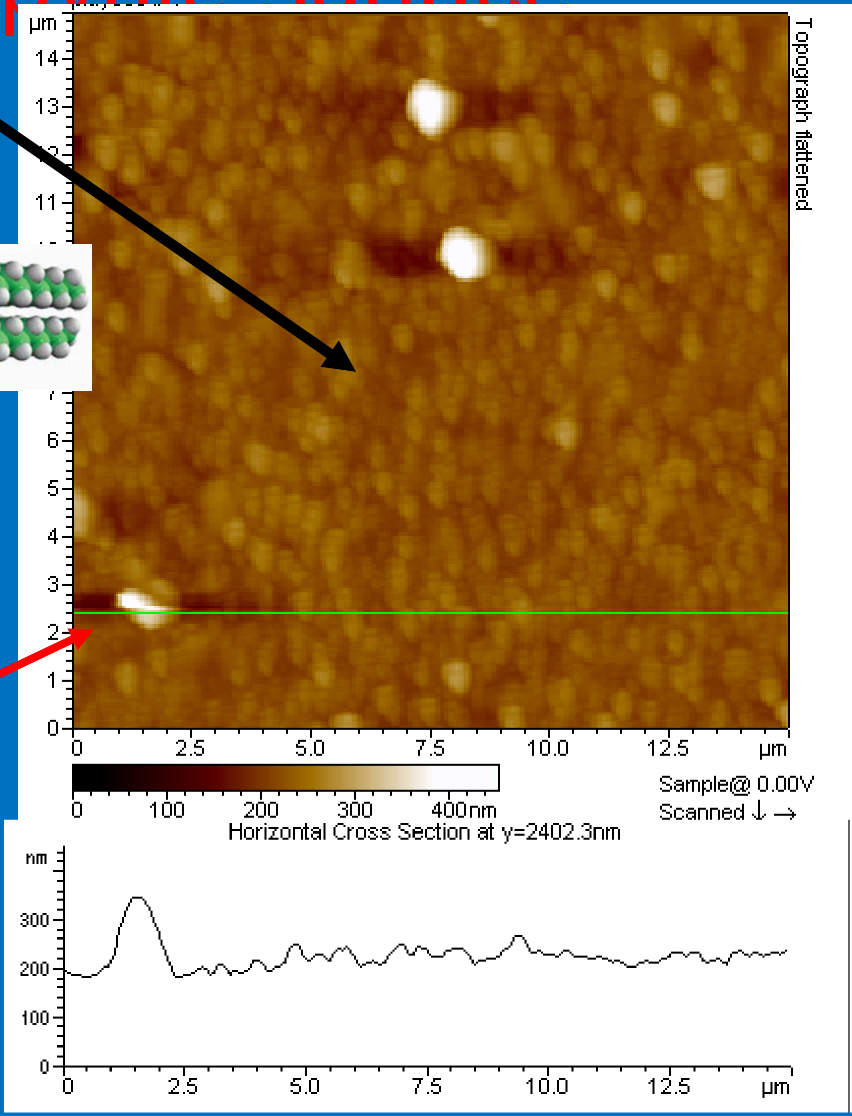


Fe concentration (μmolL-1)
Time (hr)
pyrite
lipid/pyrite
lipid/pyrite with UV
0
20
40
60
80
100
120
140

Can lipid perturbation and displace bacteria from the pyrite surface?





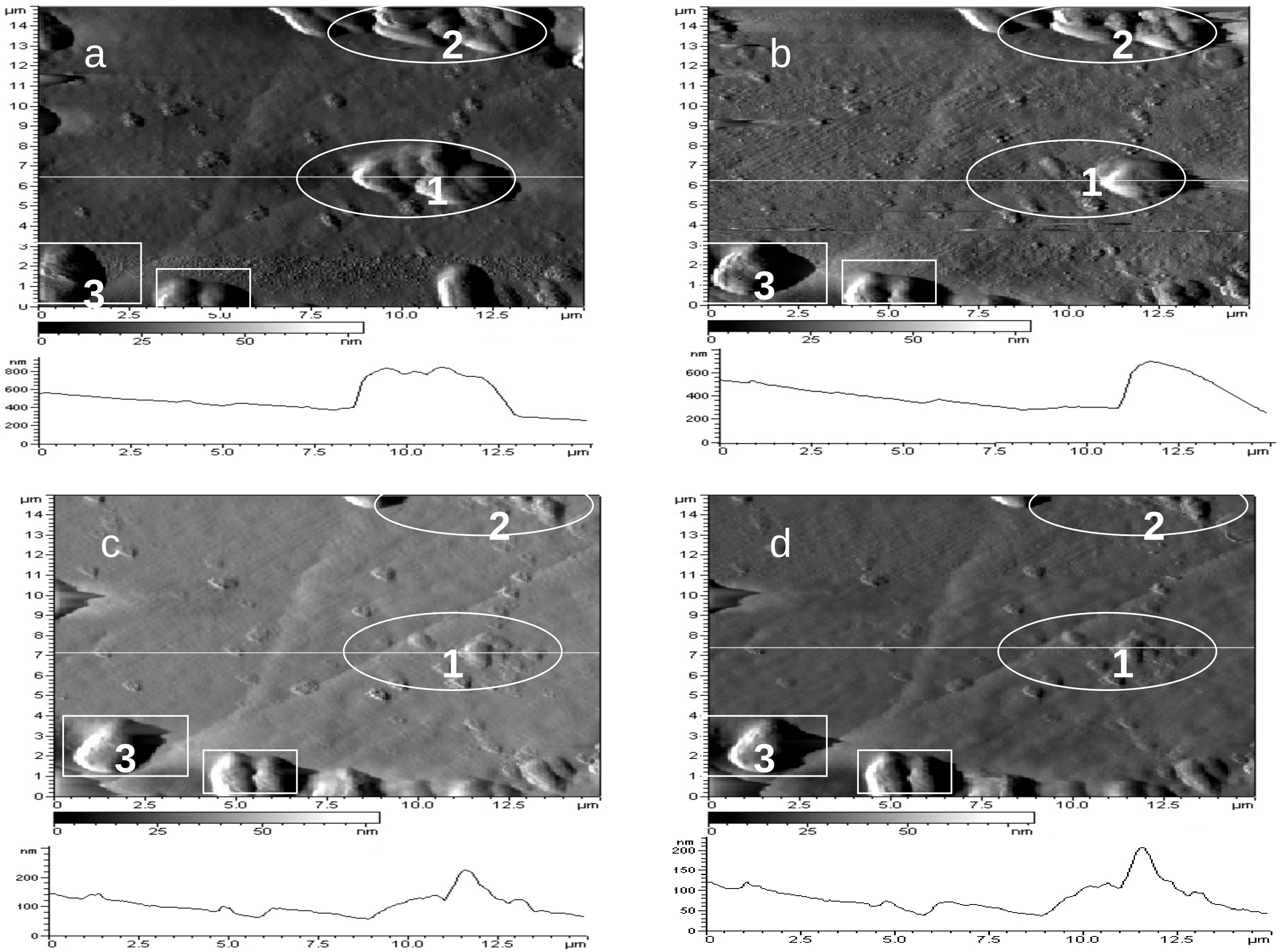


lipid

Addition of lipid

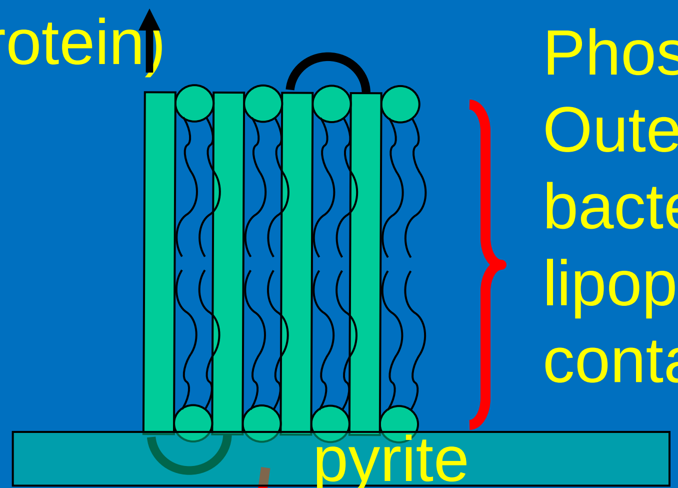
bacteria

Displacement of microbes by phospholipid

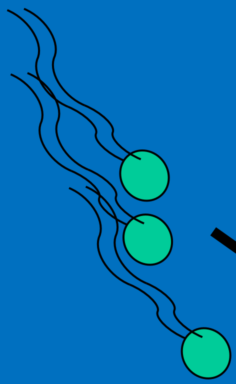


Displacement of bacteria by phospholipid

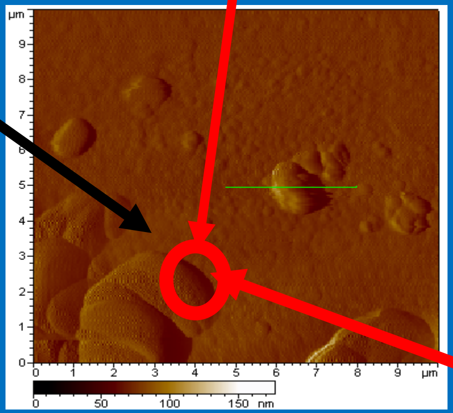
Cell wall peptidoglycan
(polysaccharides + protein)



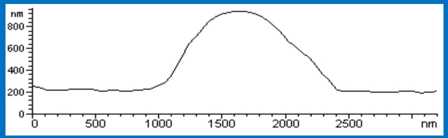
Phospholipid
Outer membrane of bacteria
lipopolysaccharide (LPS) containing



Free lipid
Introduced into solution



Bacteria/pyrite interface



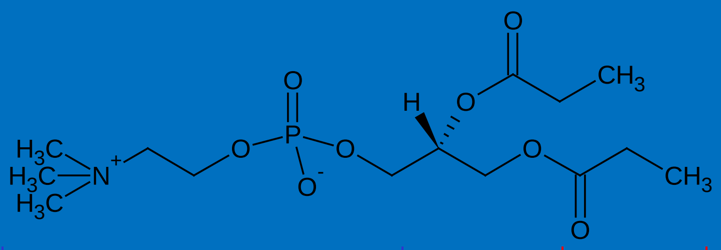
So Far

- Lipid shows binding via the phosphate group
- Lipid adsorption exhibits significant oxidation suppression even at fractional monolayer concentrations

Further question

- Is bilayer structure needed for efficient oxidation suppression?

Short vs. Long chain

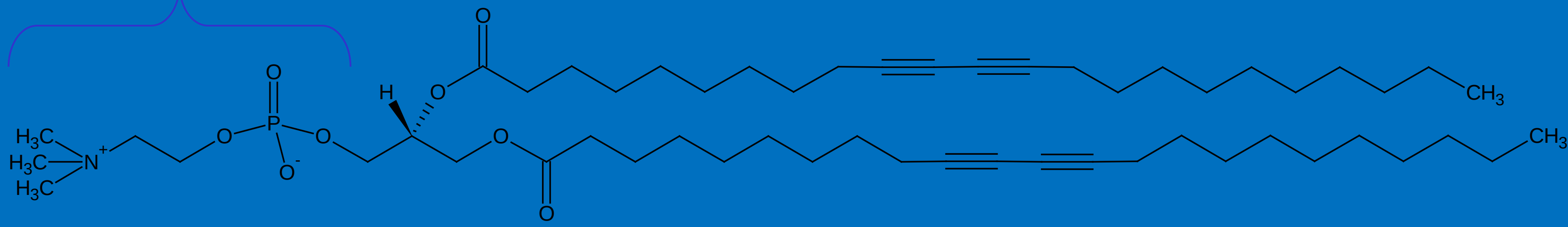


3:0 PC (no bilayer in solution)

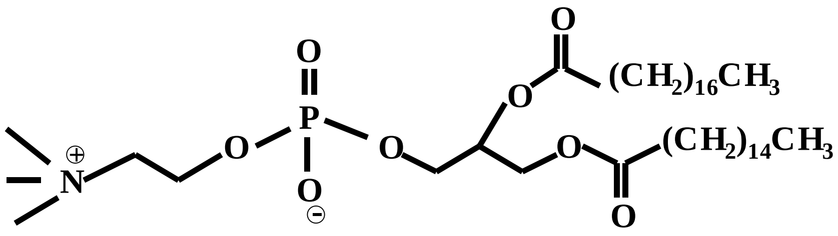
3 carbon

PC headgroup

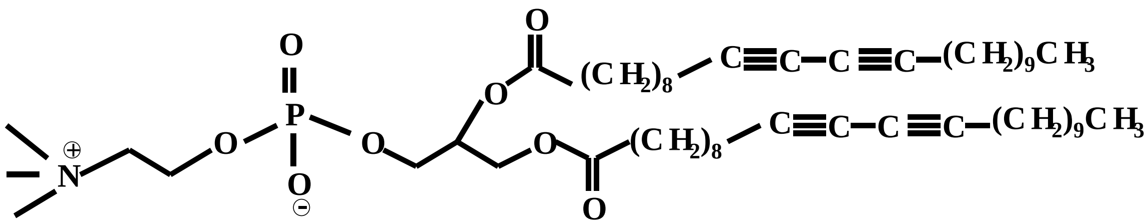
23 carbon



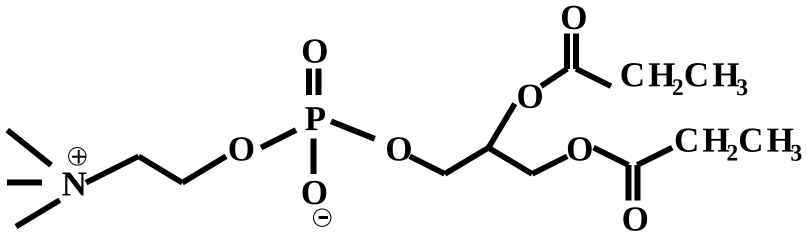
23:2 Diyne PC (bilayer in solution)



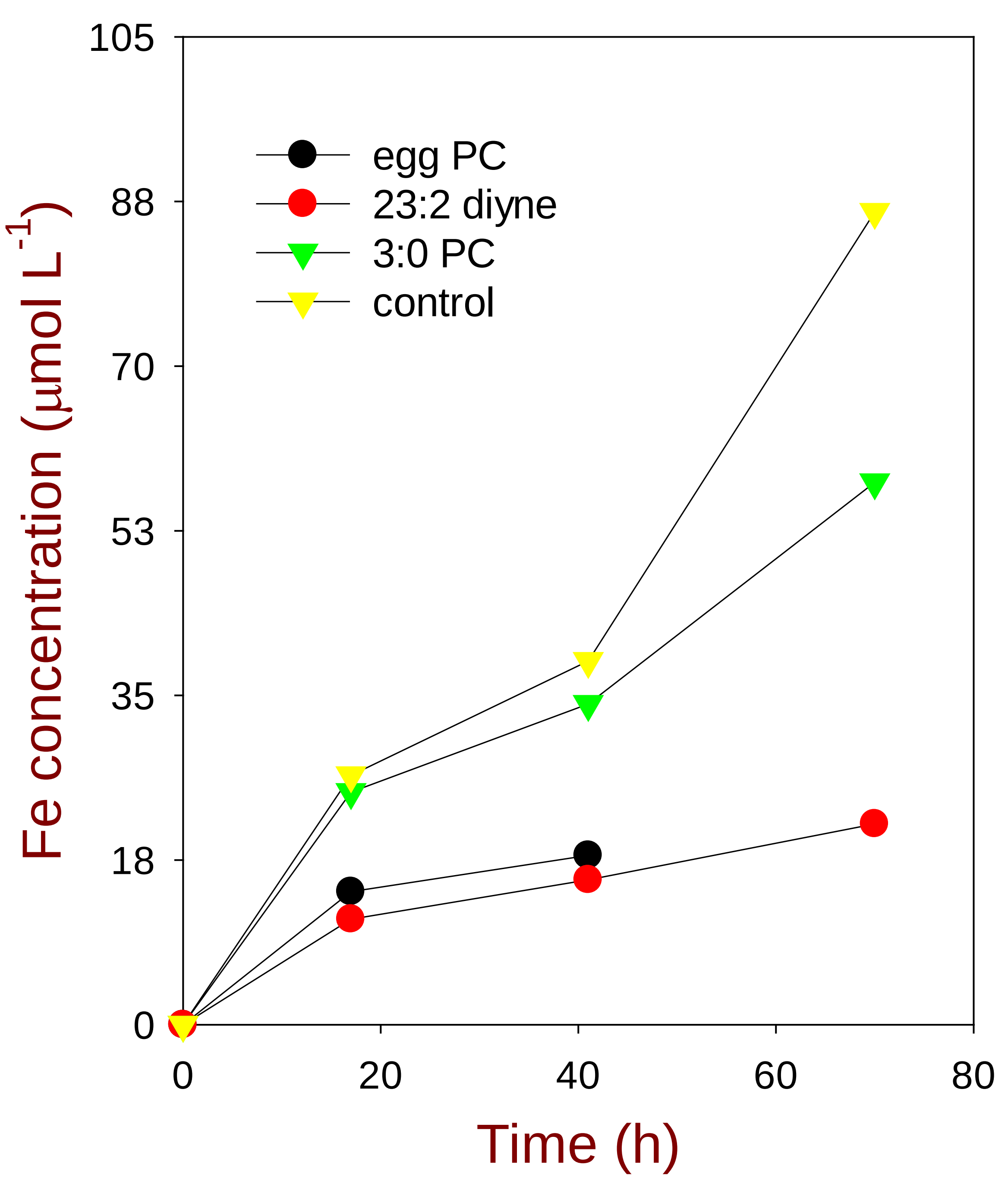
L-α-Phosphatidylcholine (egg PC)



1,2-bis(10,12-tricosadiynoyl)-*sn*-Glycero-3-Phosphocholine (23:2 Diyne PC)

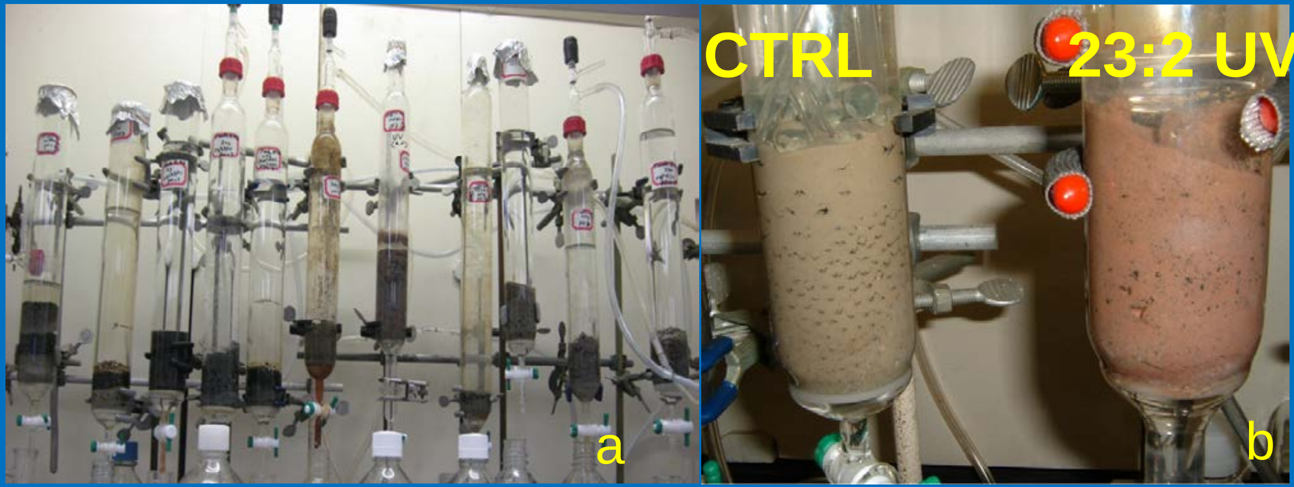


1,2-Dipropionoyl-*sn*-Glycero-3-Phosphocholine (3:0 PC lipid)



egg PC
23:2 diyne
3:0 PC
control
Fe concentration (μmol L-1)
105
88
70
53
35
18
0
0
20
40
60
80
Time (h)

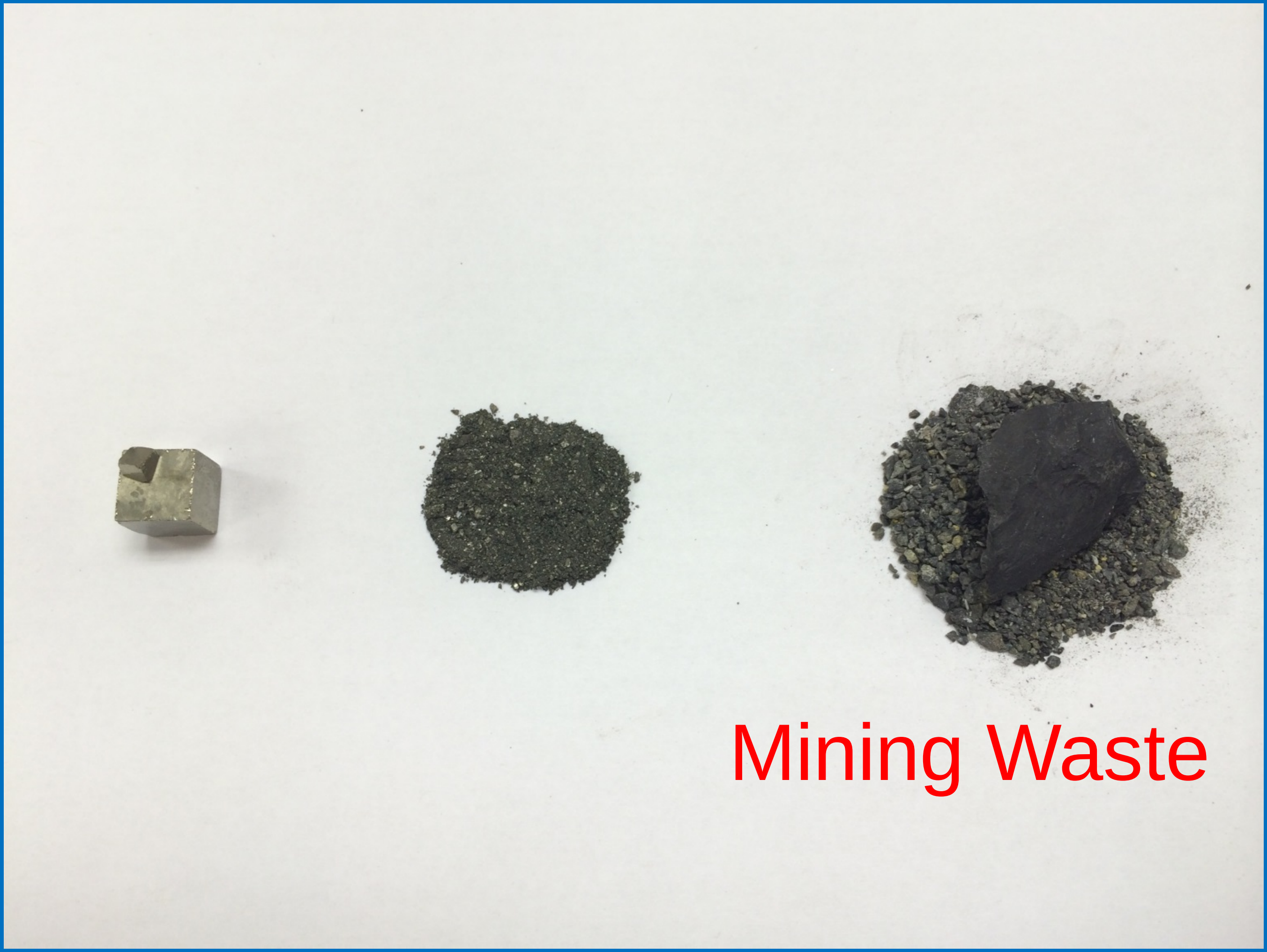
Column Experiments at Temple University



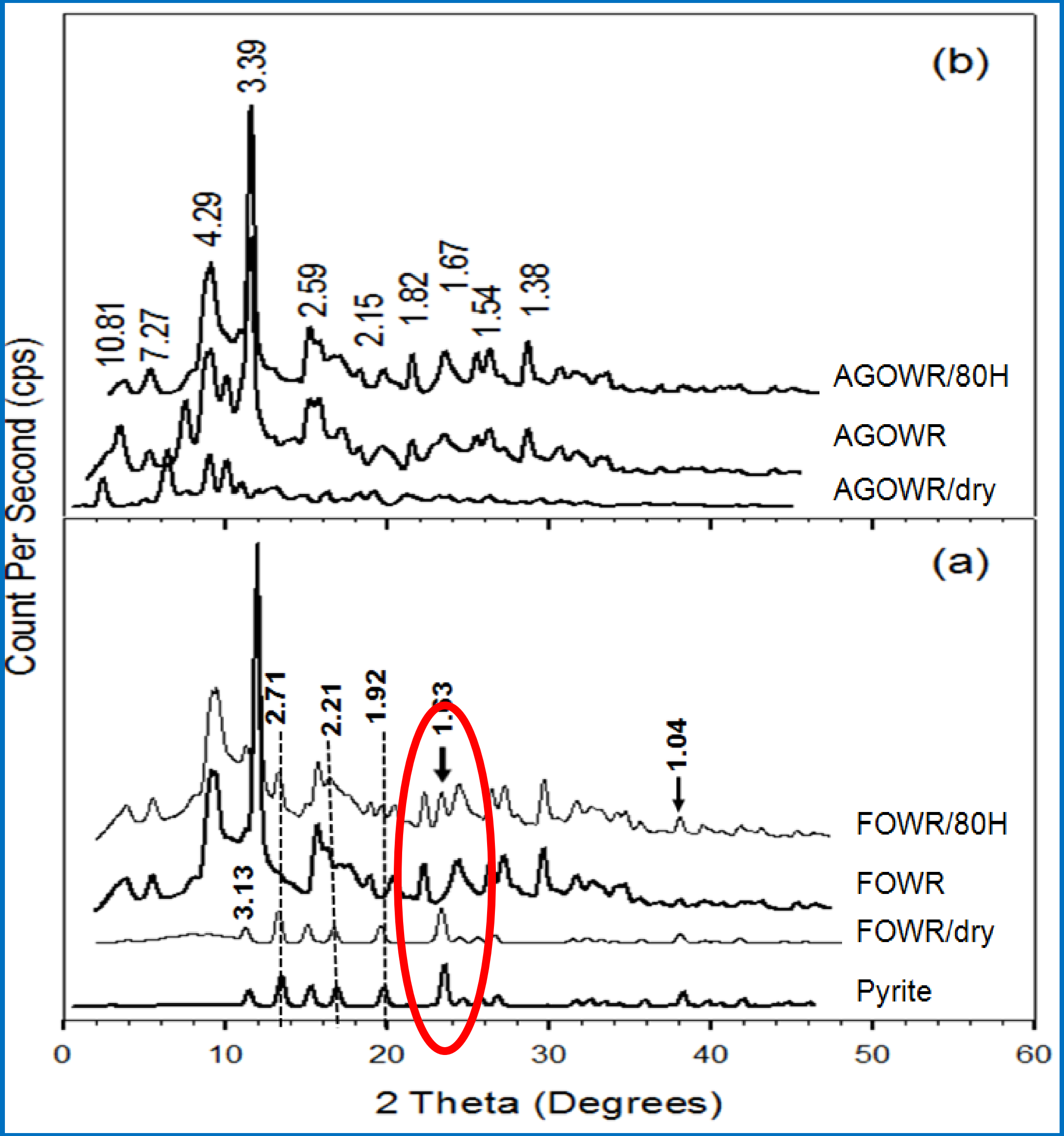
Images of mining waste. The one with the red tint Is coated with a lipid and then polymerized. The data shown in the following slides did not use a polymerizable lipid.

The representative data shown in the following slides were obtained by passing pH 7 water through the columns that contained mining waste.

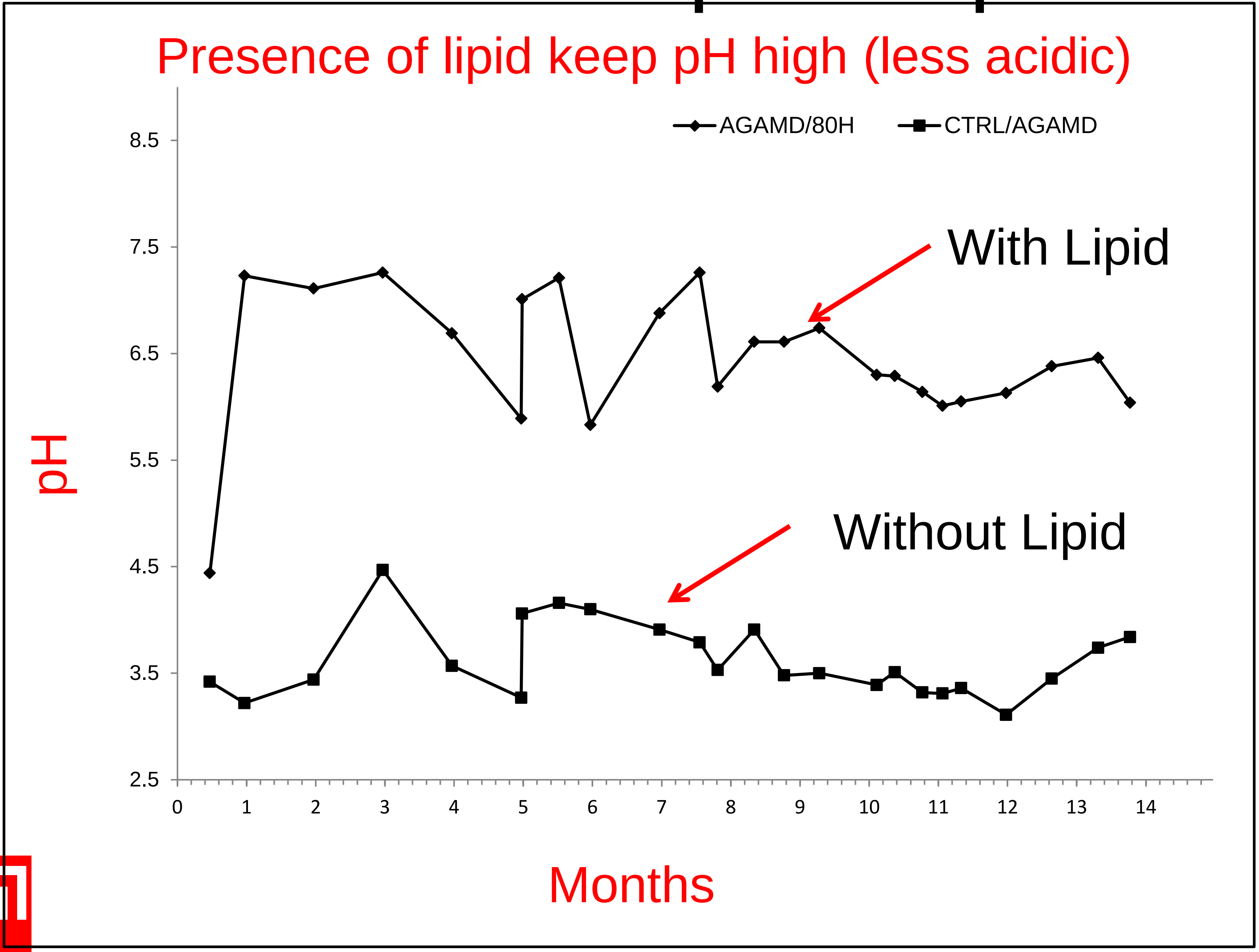
Column Experiment

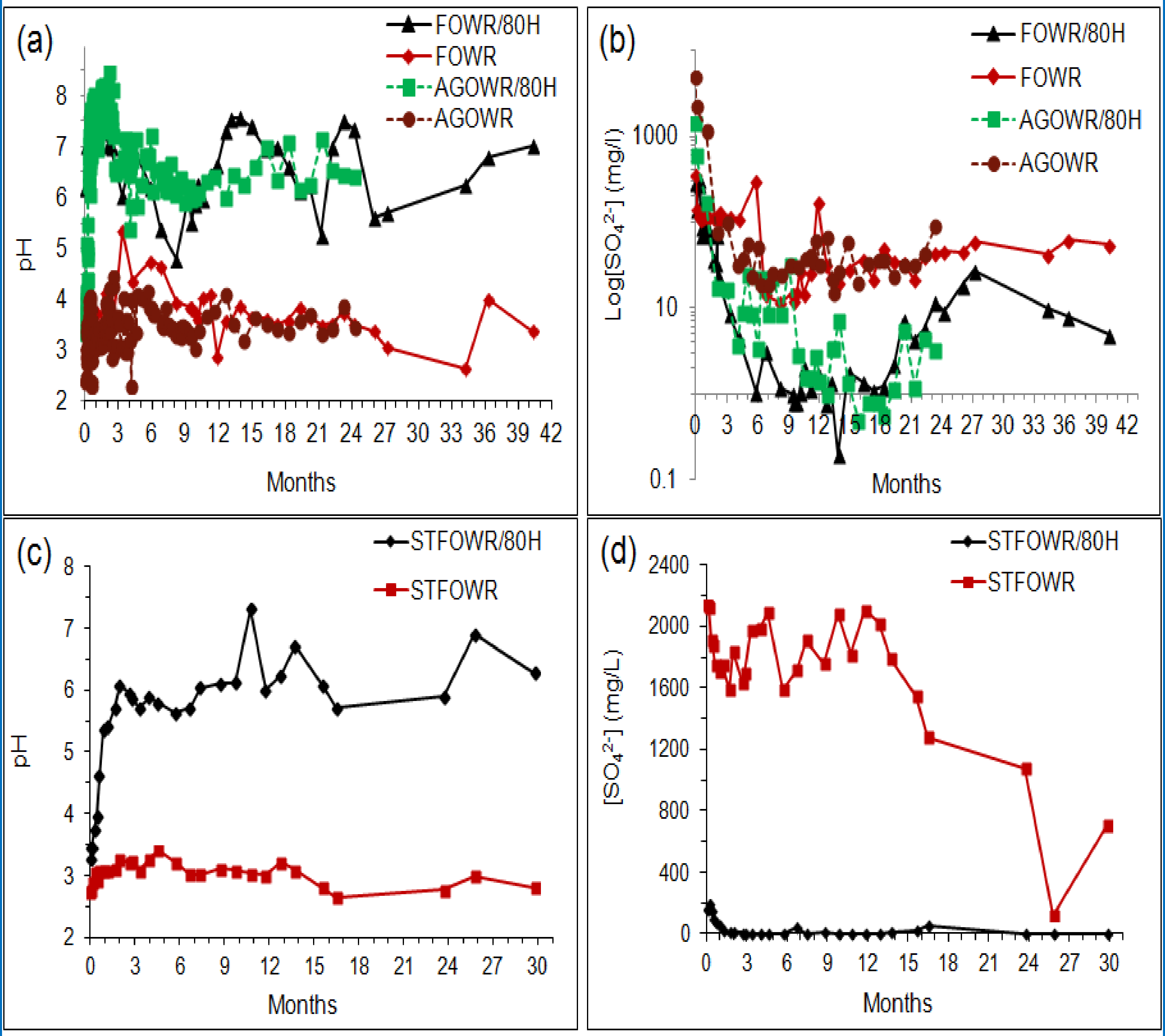


Pyrite is Stabilized by Lipid

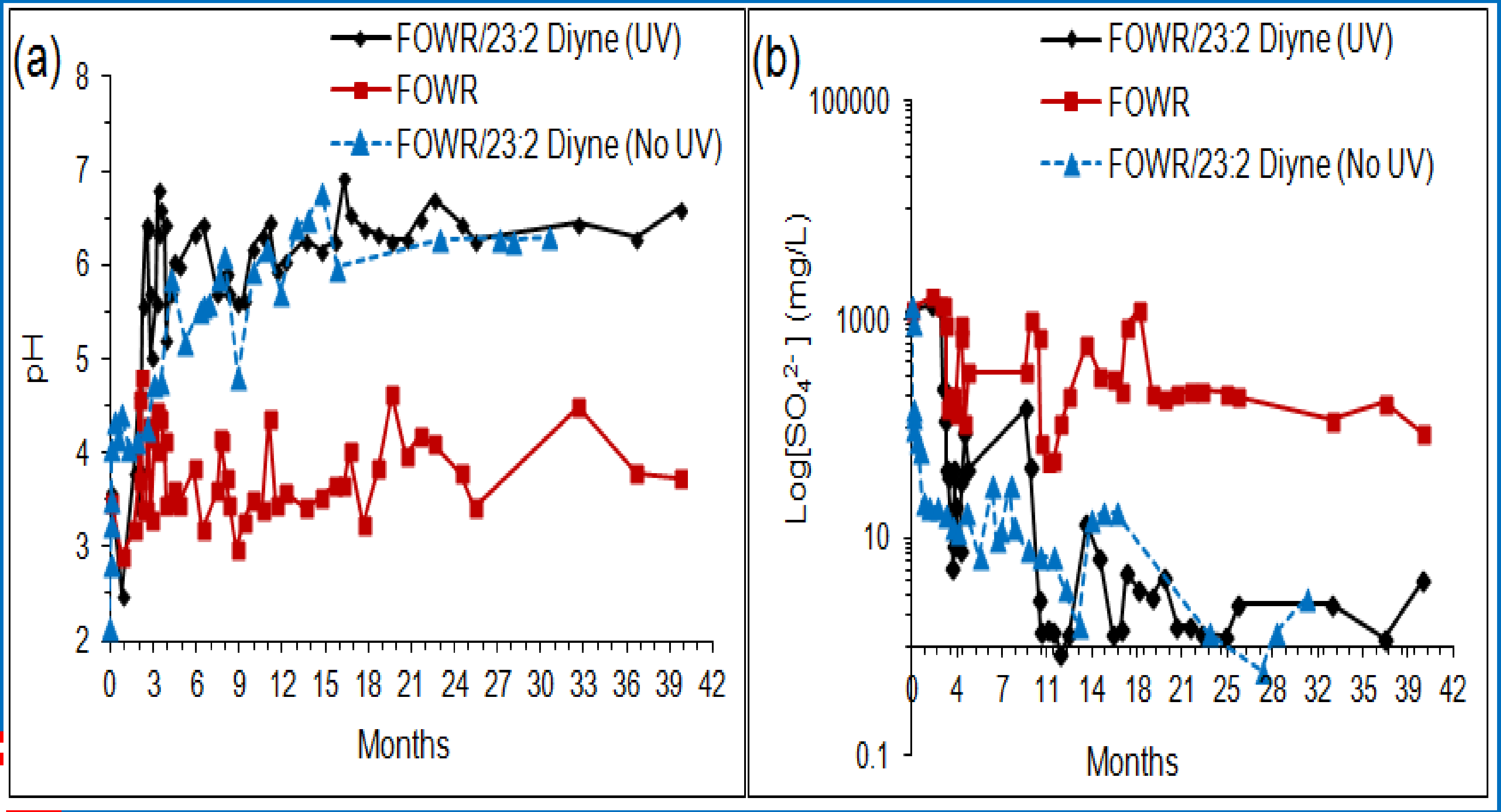


Effect of Lipid on pH





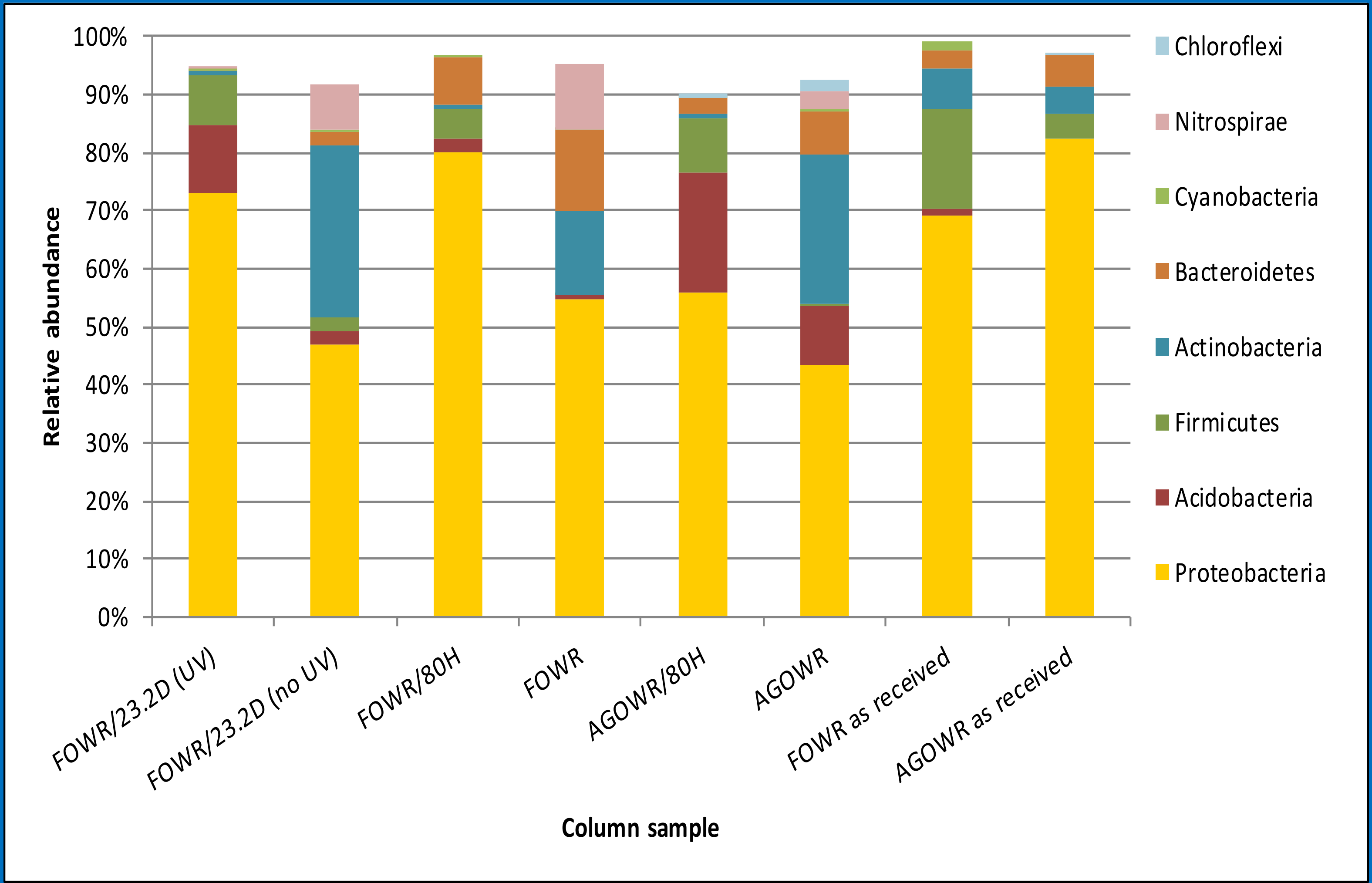
(a)
FOWR/80H
FOWR
AGOWR/80H
AGOWR
pH
Months
(b)
FOWR/80H
FOWR
AGOWR/80H
AGOWR
Log[SO4 2-] (mg/l)
Months
(c)
STFOWR/80H
STFOWR
pH
Months
(d)
STFOWR/80H
STFOWR
[SO4 2-] (mg/L)
Months


(a)
FOWR/23:2 Diyne (UV)
FOWR
FOWR/23:2 Diyne (No UV)
pH
8
7
6
5
4
3
2
0 3 6 9 12 15 18 21 24 27 30 33 36 39 42
Months
(b)
FOWR/23:2 Diyne (UV)
FOWR
FOWR/23:2 Diyne (No UV)
Log[SO4 2-] (mg/L)
100000
1000
10
0.1
0 4 7 11 14 18 21 25 28 32 35 39 42
Months

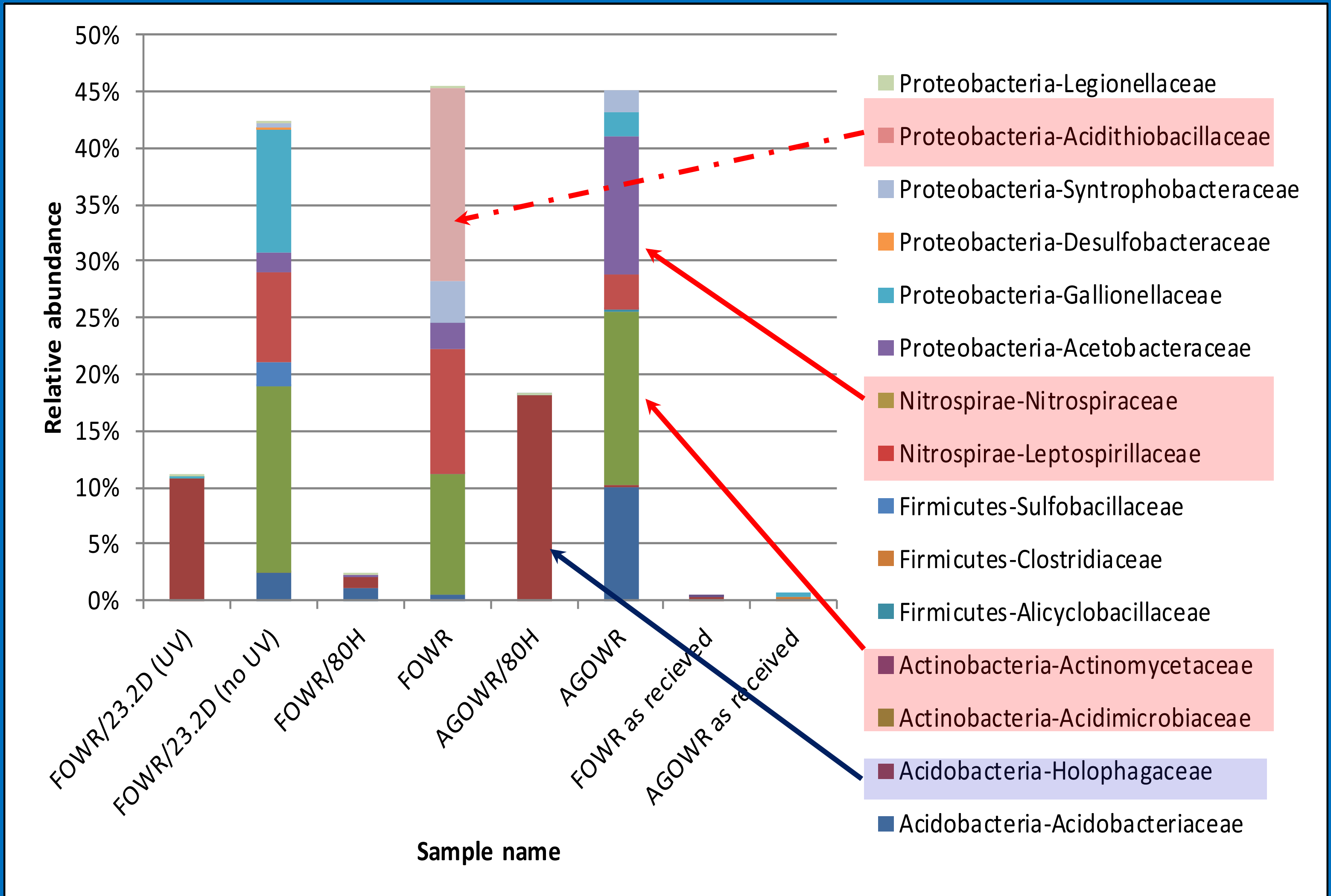
Metagenomic Studies

- 16S rDNA metagenomic pyrosequencing to determine the identity of the microbial communities.
- Autotrophic bacteria: make their own energy. In the context of AMD they are sulfur and iron oxidizing bacteria that drive the process
- Heterotrophic bacteria: Use organic compounds as a source of energy and carbon.

Abundance of major bacteria phyla detected in the column samples and dry samples. The phyla containing less than 1% of the total microbial species were not represented.



Abundance of AMD-specific bacteria families detected in the column samples and dry samples.



Summary of Metagenomic Studies

- A relatively higher proportion of Proteobacteria (mainly beta- and alpha-Proteobacteria) was observed in all lipid-treated mining samples, suggesting enrichment in heterotrophic species using lipids as carbon and energy source.

- A higher proportion of Actinobacteria and Nitrospira was observed in the control samples (lipid-free), suggesting that bacterial communities in non-treated samples were dominated by autotrophic bacteria using reduced iron and/or sulfur.

Summary

- A microscopic view of the surface led to hypotheses realated to suppressing AMD
- Reaction sites to blocked were identified on pyrite
- Phospholipids bind preferentially to reactive sites on pyrite
- Lipid bilayer form a robust hydrophobic coating that suppresses oxidation of the pyrite surface.
- Column tests show that the lipid bilayers suppress AMD in the laboratory environment for at least 3 years.
- Lipids alter the microbial communities associated with pyrite-containing Mining Waste.