# Preservation of organic compounds in circumneutral iron deposits

Niki Parenteau, Linda Jahnke, Sherry Cady, Tom Bristow, Sandra Siljeström, Sanjoy Som, David Des Marais, Jack Farmer

# Overview

1. Iron deposits on Mars
    a) Acidic
    b) Circumneutral
        - Partial Fe(II) oxidation, redox cycling
2. Circumneutral iron deposits on Earth
    a) Microbial populations
    b) Production and preservation of lipids
    c) GC-MS, ToF-SIMS
    d) Taphonomy
        - Factors that control early diagenesis
3. Implications for microbial biosignatures on Mars

# Acidic iron deposits on Mars


- Opportunity - Meridiani Planum (Grotzinger et al., 2005; McLennan et al., 2005)
- Oxidation of upwelling circumneutral Fe(II) groundwater from a basaltic aquifer (Hurowitz et al., 2010; Andrews-Hanna et al., 2007)

$$Fe(II)_{(aq)} + H_2O + h\nu = Fe(III)_{(aq)} + OH^- + 0.5\ H_2 \quad (1)$$

$$Fe(II)_{(aq)} + 0.25\ O_{2(aq)} + H^+ = Fe(III)_{(aq)} + 0.5 H_2O \quad (2)$$

$$0.5\ H_2O + h\nu = 0.25\ O_2 + H^+ + e^- \quad (2a)$$

$$H_2O + e^- = OH^- + 0.5\ H_2 \quad (2b)$$

$$Fe(III)_{(aq)} + 0.125\ SO_4^{2-} + 1.75\ H_2O = FeO(OH)_{0.75}(SO_4)_{0.125} + 2.75\ H^+ \quad (3)$$

# Circumneutral settings on Mars


- Curiosity (Grotzinger et al., 2014; Vaniman et al. 2014; Bristow et al., 2015; Treiman et al., 2015)
- Smaller degree of Fe(II) oxidation = less acidity
  - o Oxidation of Fe(II) in olivine to Fe(III) in magnetite and perhaps smectites
    - a) Circumneutral pH and low salinity

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**The origin and implications of clay minerals from Yellowknife Bay, Gale crater, Mars†**

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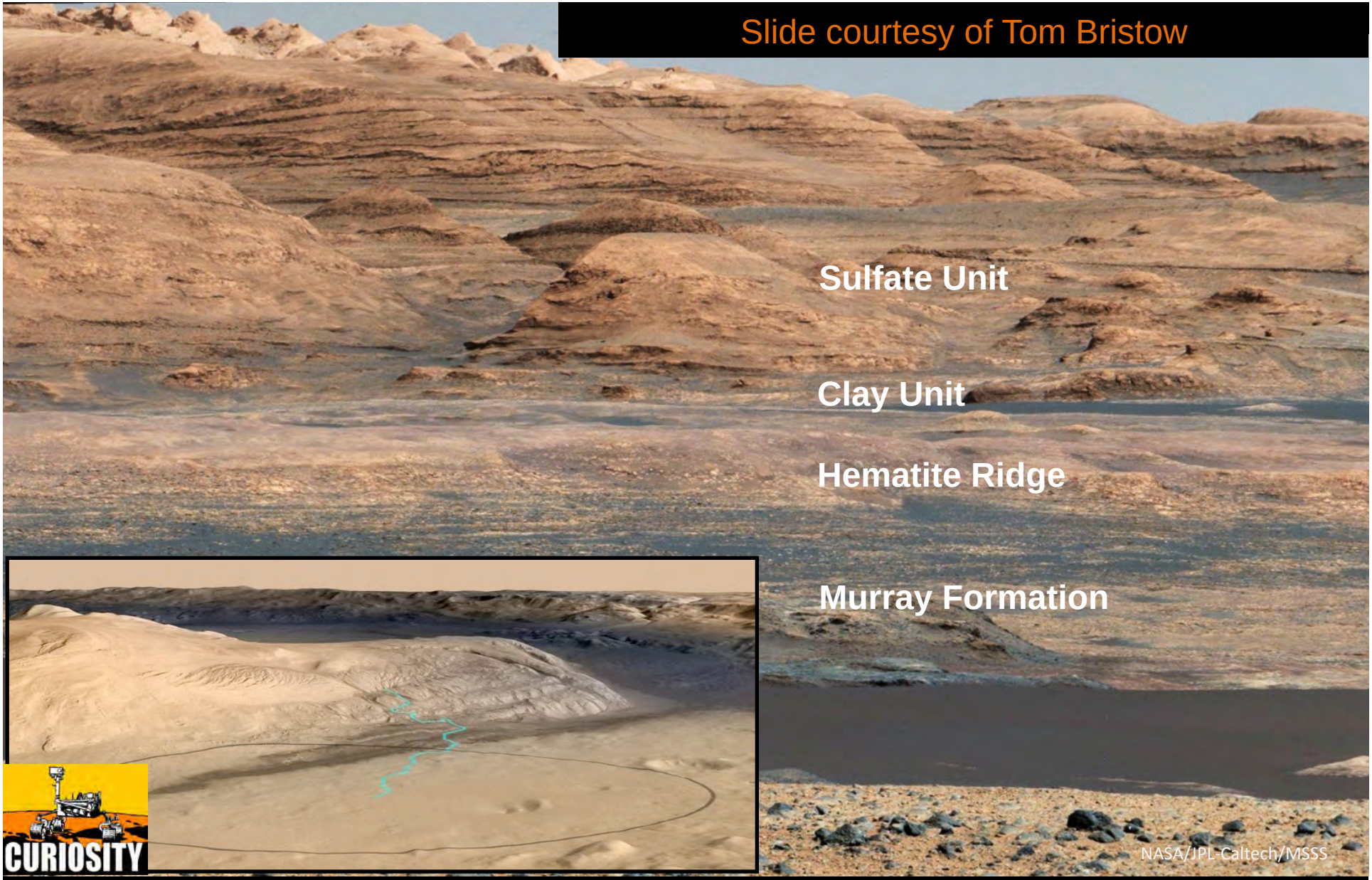
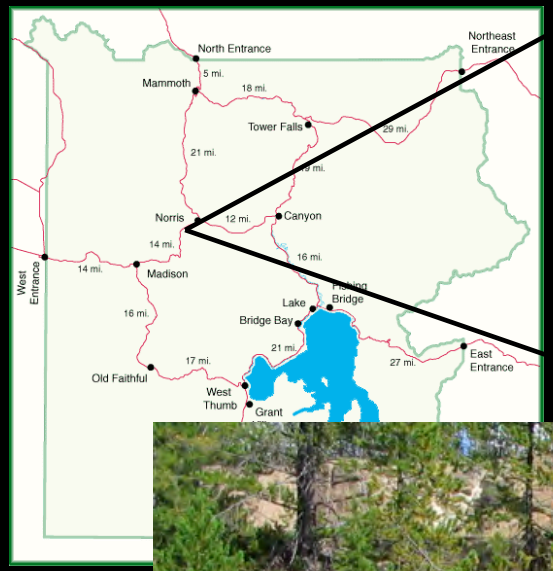
Slide courtesy of Tom Bristow



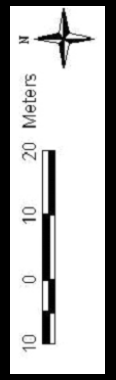


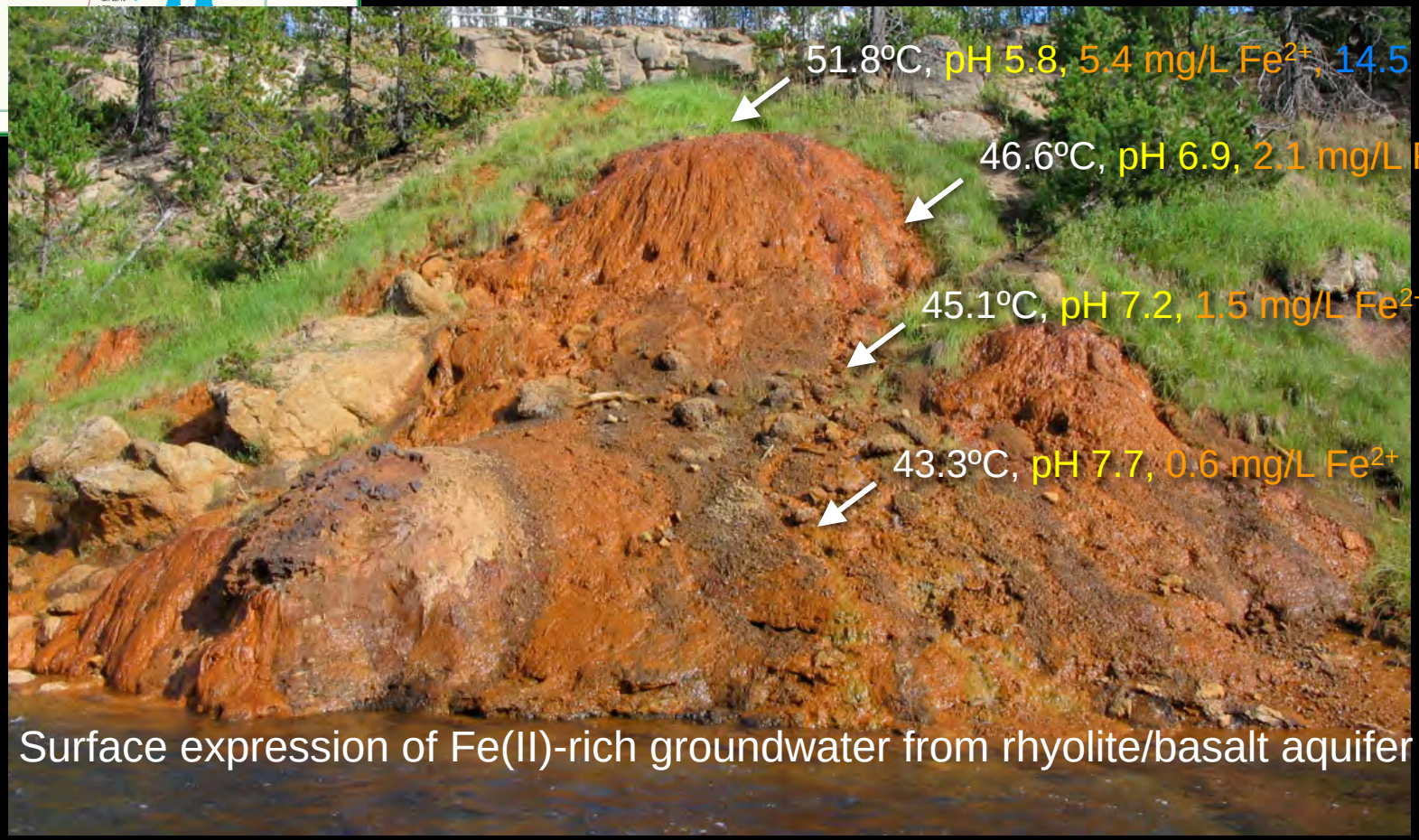


**Curiosity's Extended Mission will explore Mt. Sharp, with an emphasis on understanding the subset of habitable environments that preserve organic carbon**


North Entrance
Northeast Entrance
Mammoth
5 mi.
18 mi.
Tower Falls
29 mi.
21 mi.
Norris
12 mi.
Canyon
14 mi.
16 mi.
West Entrance
14 mi.
Madison
Fishing Bridge
Lake
Bridge Bay
16 mi.
21 mi.
17 mi.
27 mi.
East Entrance
Old Faithful
West Thumb
Grant

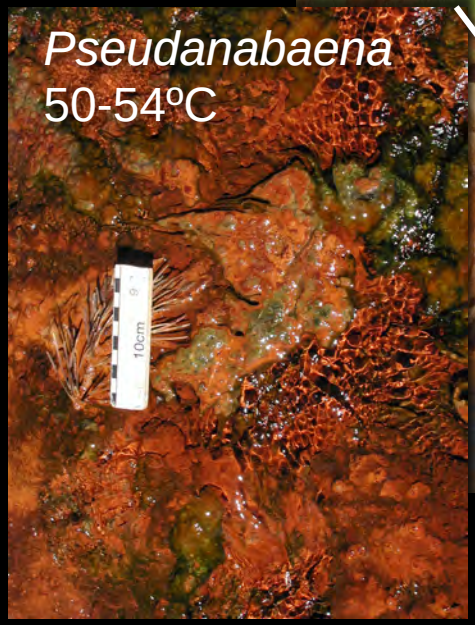

Chocolate Pots


N
Meters
20
10
0
10


51.8ºC, pH 5.8, 5.4 mg/L Fe2+, 14.5 mM DIC
46.6ºC, pH 6.9, 2.1 mg/L Fe2+
45.1ºC, pH 7.2, 1.5 mg/L Fe2+, 5.9
43.3ºC, pH 7.7, 0.6 mg/L Fe2+
Surface expression of Fe(II)-rich groundwater from rhyolite/basalt aquifer

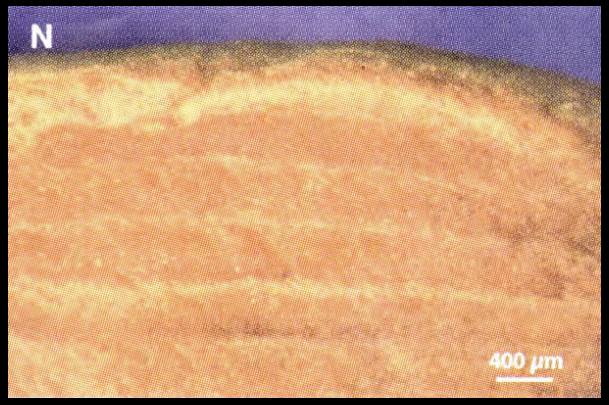
# Microbial mats

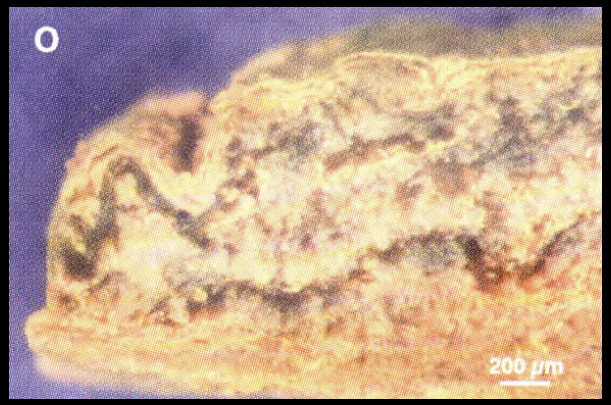






# Microbial biosignatures



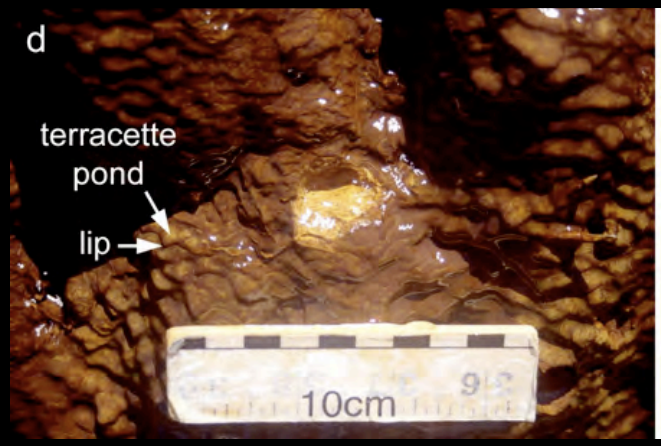



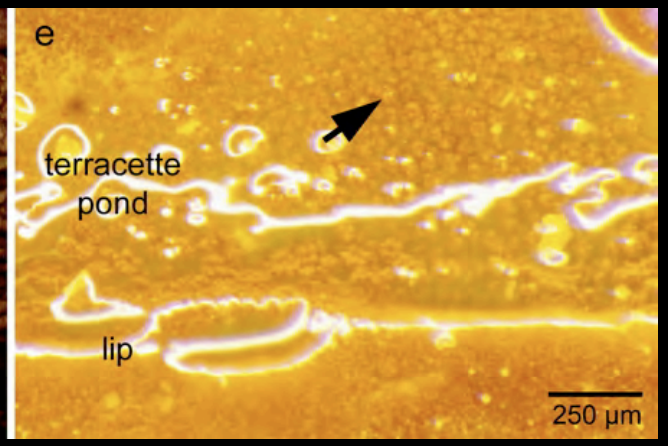

1. Biofabrics, microfossils
    a) OM, SEM, TEM, EDS, ED, XRD
2. Lipids (including lipid biomarkers)
    1. GC-MS (extraction)
    2. ToF-SIMS (*in situ*)
    3. Quantitative analysis of survival of organics in Fe-rich system

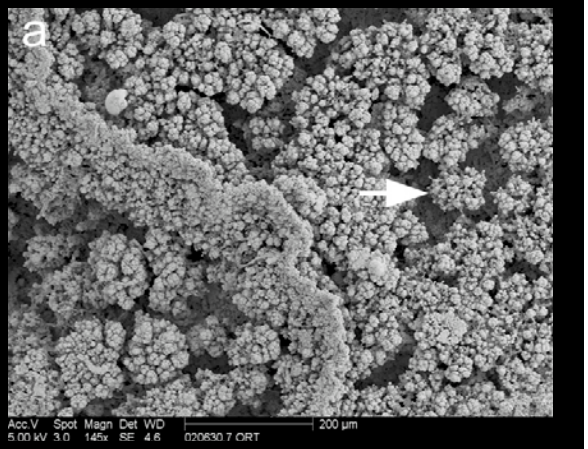
# Biofabrics (poss. visible by camera)

Teracette biofabric mediated by microbes

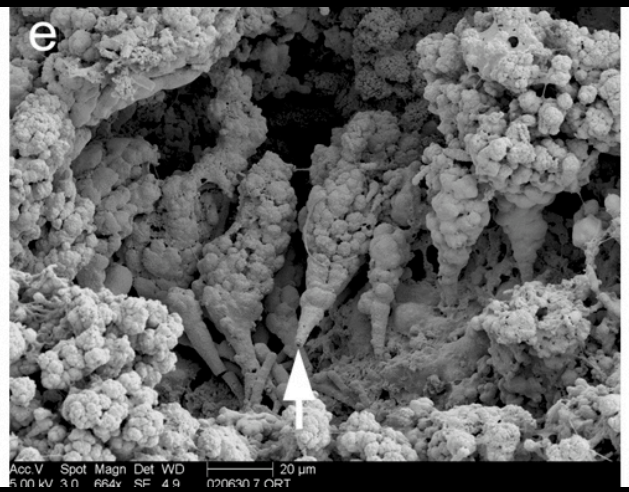
0.4% TOC

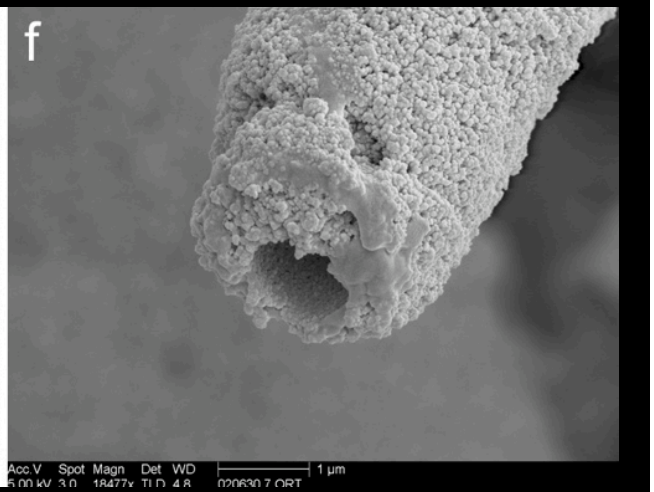




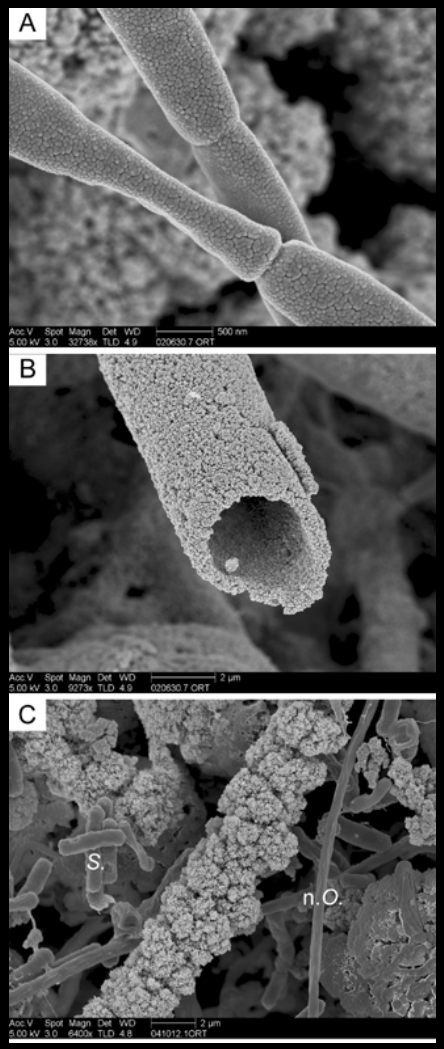


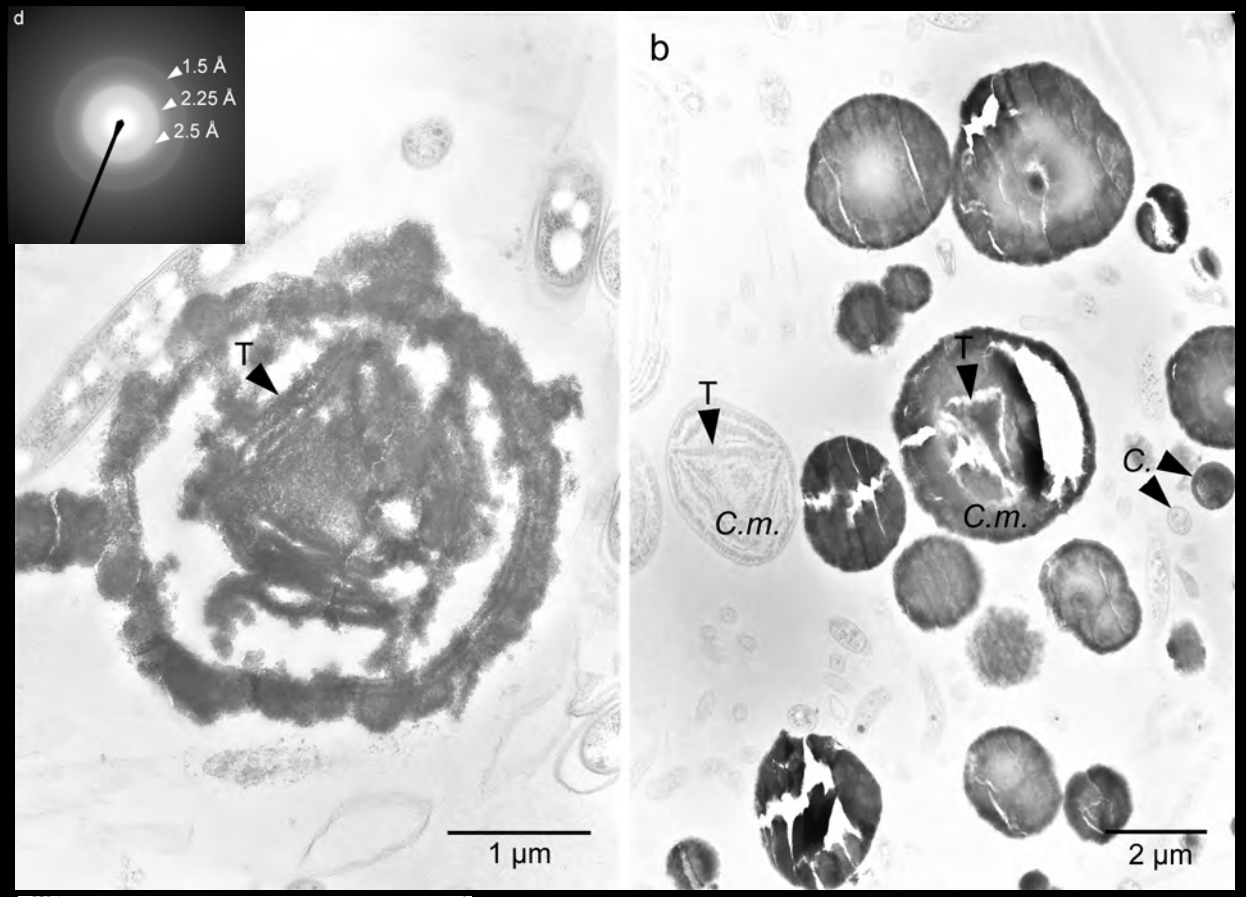

Parenteau and Cady, 2010

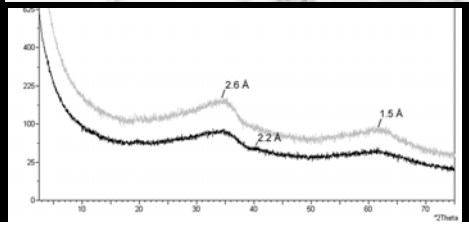
# Microfossils

## Encrustation




## Fe permineralization



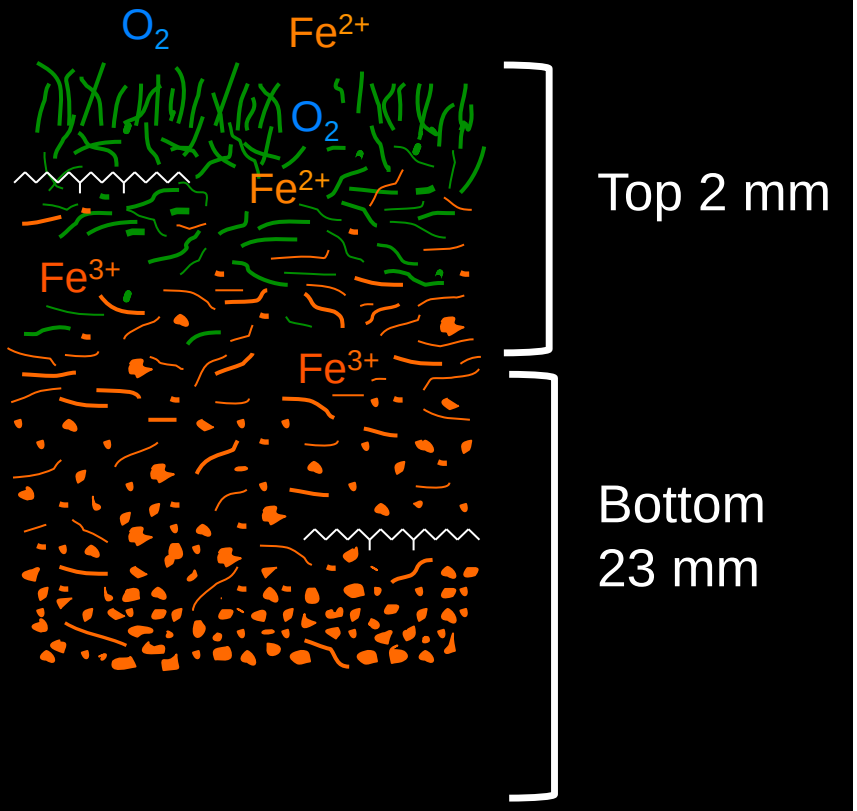




Parenteau and Cady, 2010

# Lipids and lipid biomarkers

Production and preservation of lipids in *Synechococcus*-Chloroflexi mat

- early diagenesis
- quantitative analysis of survival of organics

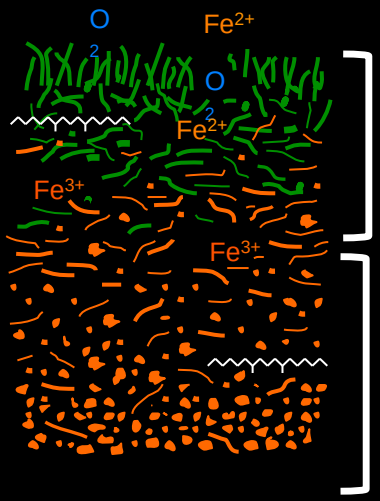



# Labile lipids

- taxonomic information
- not good biomarkers

Phospholipids

Mat and Fh under mat

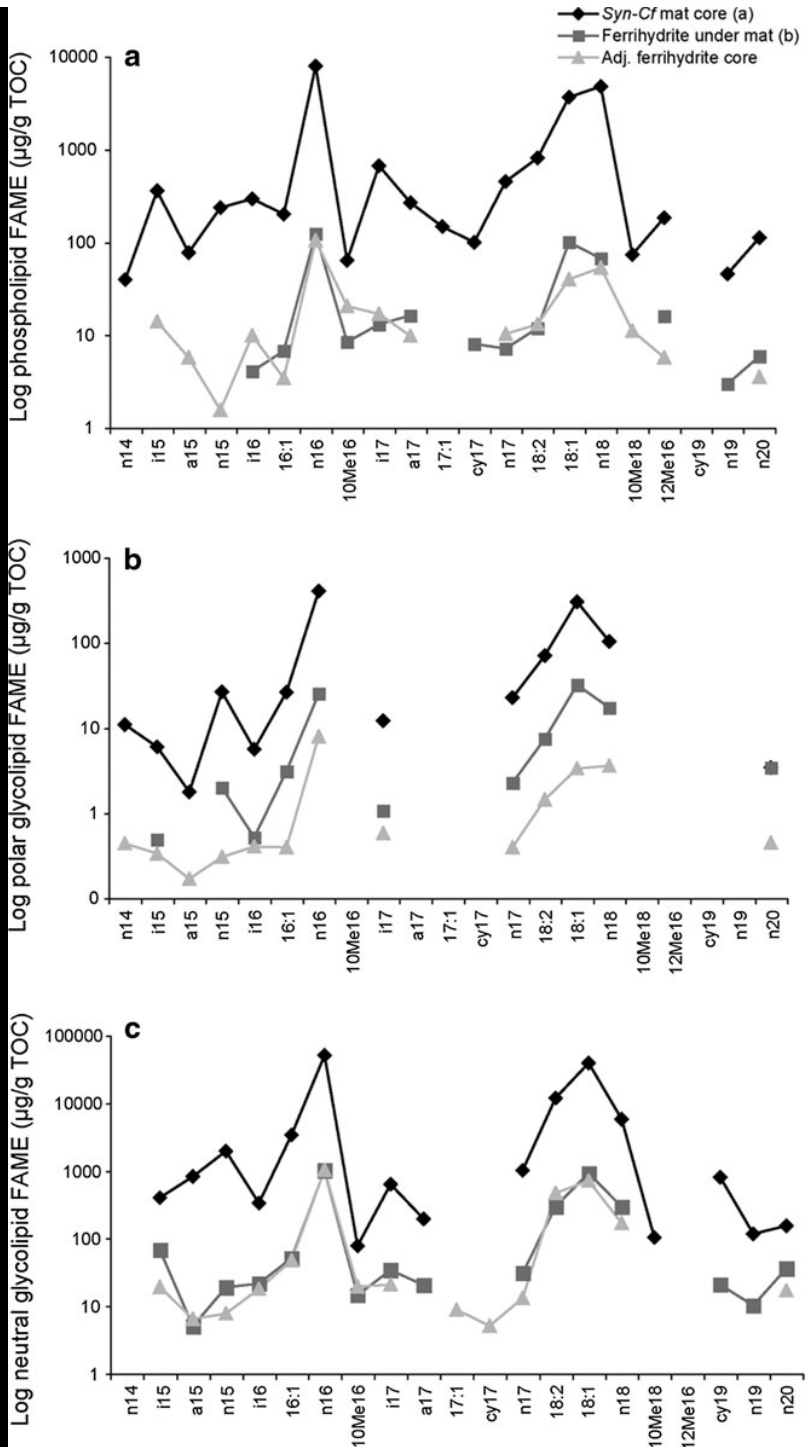



Polar glycolipids

CONTROL:
Fh core with no mat on surface


Neutral glycolipids

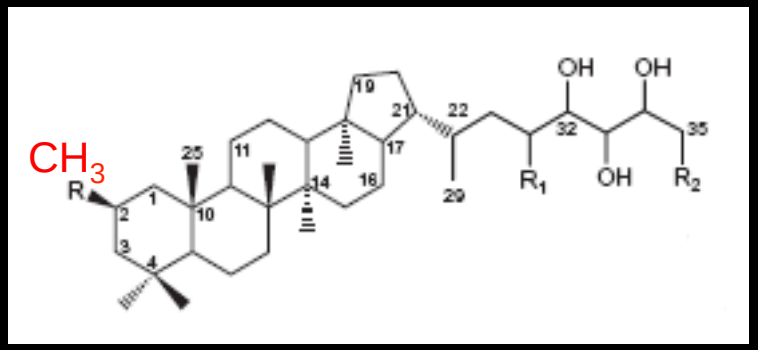
Parenteau et al., 2014



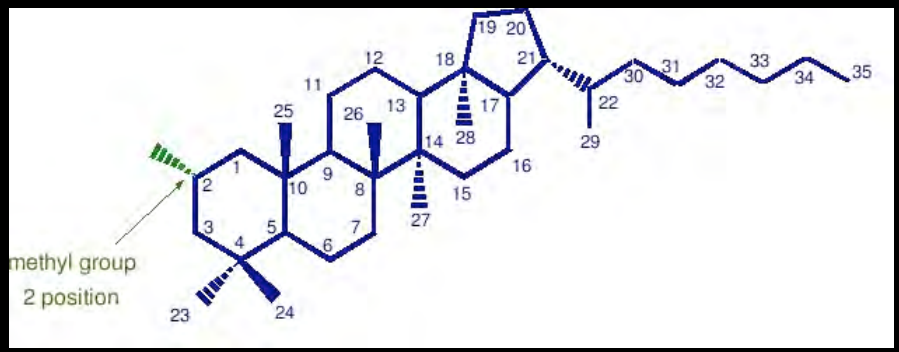
# Lipid biomarkers (geolipids)

## - taxonomic information (e.g., Summons et al., 1999)
## - physiological function in cell (e.g., Rashby et al., 2007

2-Methylbacteriohopanepolyol




2-Methylhopane



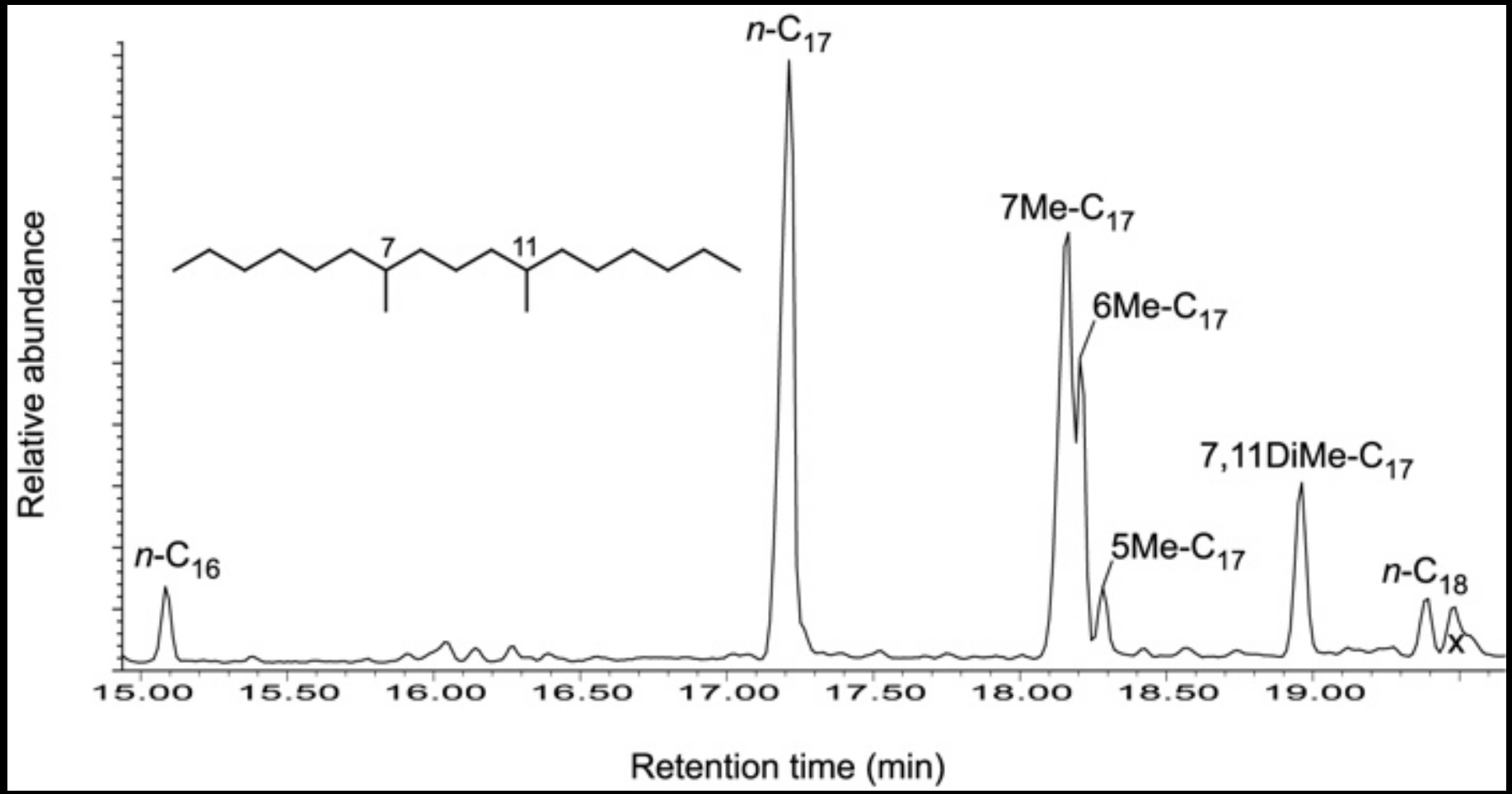

| Lipid biomarker | *Syn-Cf* mat core (a) | Ferrihydrite beneath mat (b) | Adjacent ferrihydrite core | *Pseud-anabaena* mat | *O. princeps* mat | Narrow *Oscillatoria* mat channel | Narrow *Oscillatoria* mat terrace |
|---|---|---|---|---|---|---|---|
| Hopanepolyol products | | | | | | | |
| 2-MeC$_{31}$ | 0.02 | - | - | - | - | - | 10.90 |
| C$_{31}$ | 0.21 | 0.01 | - | 26.50 | - | - | 7.98 |
| 2-MeC$_{32}$ | 0.02 | - | - | - | - | - | - |
| C$_{32}$ | 1.68 | 0.01 | 0.08 | 974.91 | - | 0.03 | 105.51 |

Abbreviations: *Syn-Cf*, *Synechococcus-Chloroflexi* mat; *O. princeps*, *Oscillatoria princeps*; -, not detected.

Parenteau et al., 2014

# Lipid biomarkers (geolipids)

Mid-chain branched mono- and dimethylalkanes

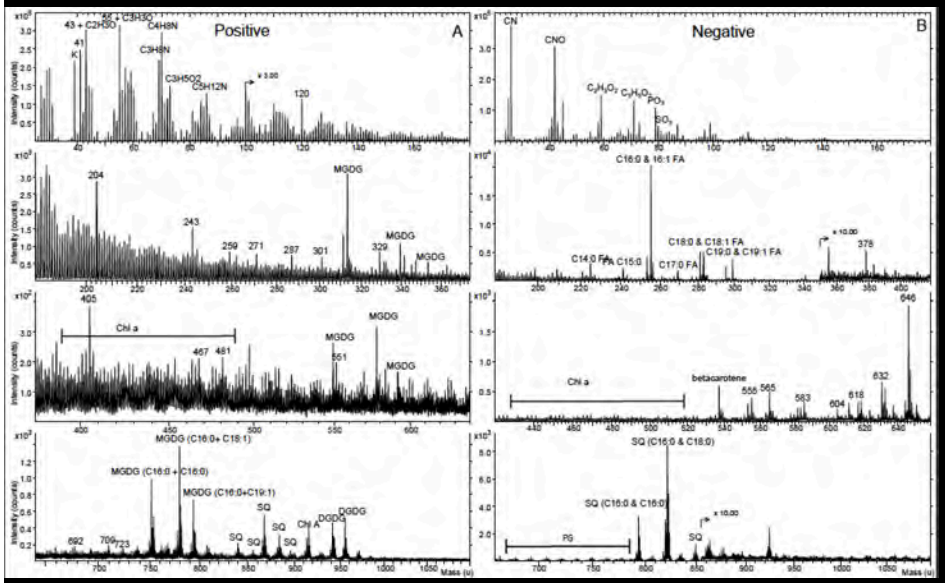


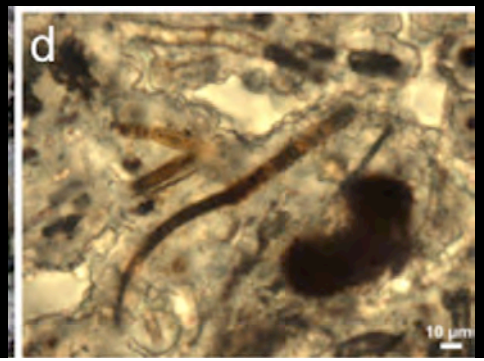

Parenteau et al., 2014

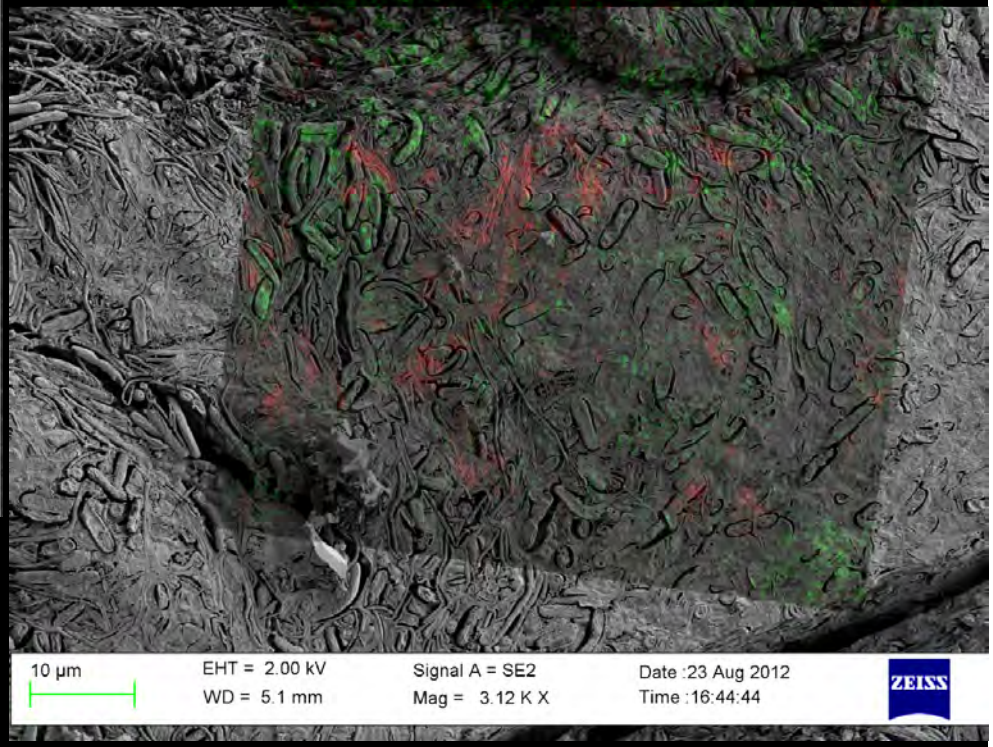
# ToF-SIMS lipid database

Sandra Siljeström SP Technical Research Institute of Sweden
ExoMars MOMA LDI-MS

Can assign lipids to morphotypes
Sulphoquinovosyldiacylglycerol (SQ)

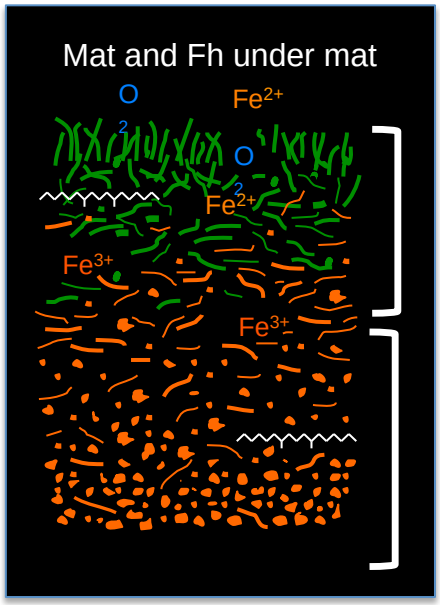


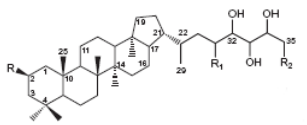

Siljeström et al., in prep.

# Early diagenesis in mats and ferrihydrite




Lipid biomarkers (geolipids)
~30 – 55% destroyed

Labile lipids
~98% destroyed
over ~2 cm

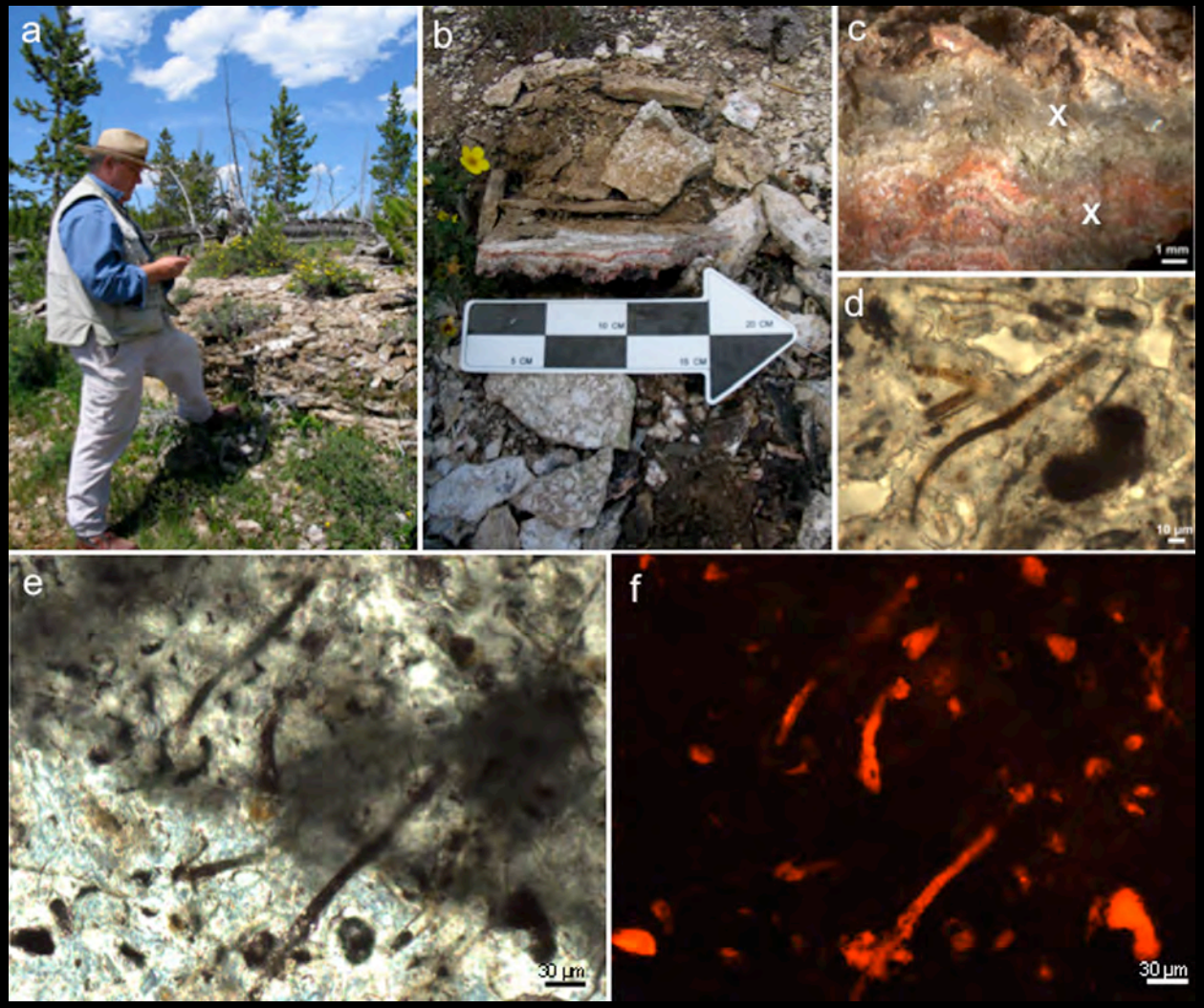


Incomplete
recovery?



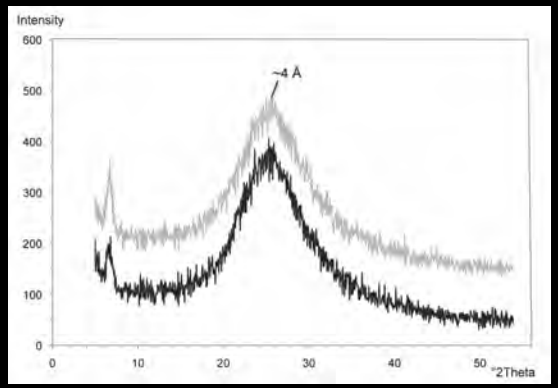

Parenteau et al., 2014

# Later diagenesis in extinct Fe-Si deposits




Younger than 600,000 yr opal-A

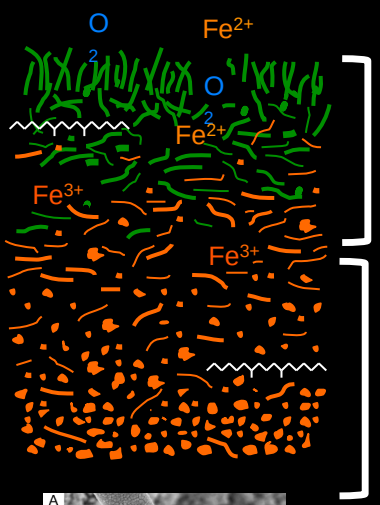
Artist Point sinter opal-A
130,000 – 600,000 yr

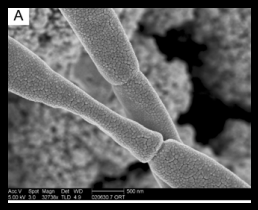



Parenteau et al., 2014

# Enhanced preservation in Fe-Si systems

Mat and Fh under mat





1. Extant mats
   a) 99.9% of organic matter destroyed
      - photoheterotrophy, aerobic respiration, anaerobic respiration, fermentation, methanogensis
        - Fe(II) consumes $O_2$ and depresses aerobic respiration
      - Fe encrustation protects from enzymatic attack, also inhibits enzymatic activity
      - Fe oxidizes organics?
        - Silica blocks surface Fe sites in ferrihydrite
2. Extinct Fe-Si sinter deposits
   a) Recrystallization, pore-filling, later stage redox fluids

# Implications for Mars

1. Biomass production in circumneutral Fe deposits
   a) TOC 1 - 29%
   b) Remember that (slightly) acidic settings are stressful
2. Rate of destruction
   a) Fe(II) depresses aerobic respiration by consuming $O_2$
   b) Rapid mineralization—$Fe^{3+}$ electrostatic interaction with negatively charged cell surfaces
   c) Silica protects organics from Fe oxidation
3. Relevant to study modern settings due to lack of diagenetic alteration at Home Plate
4. Homework: Duration of hydrothermal settings
5. Didn't address: ID of mineral assemblages from orbit, Mars 2020 instrumentation, destruction by radiation (although Fe shields UV)

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