Physical and Molecular Biosignature Preservation in Hydrous Ferric Oxides: Implications for Detection on Mars with MSL and Future Missions
-or-
A Tale of Two Biosignatures

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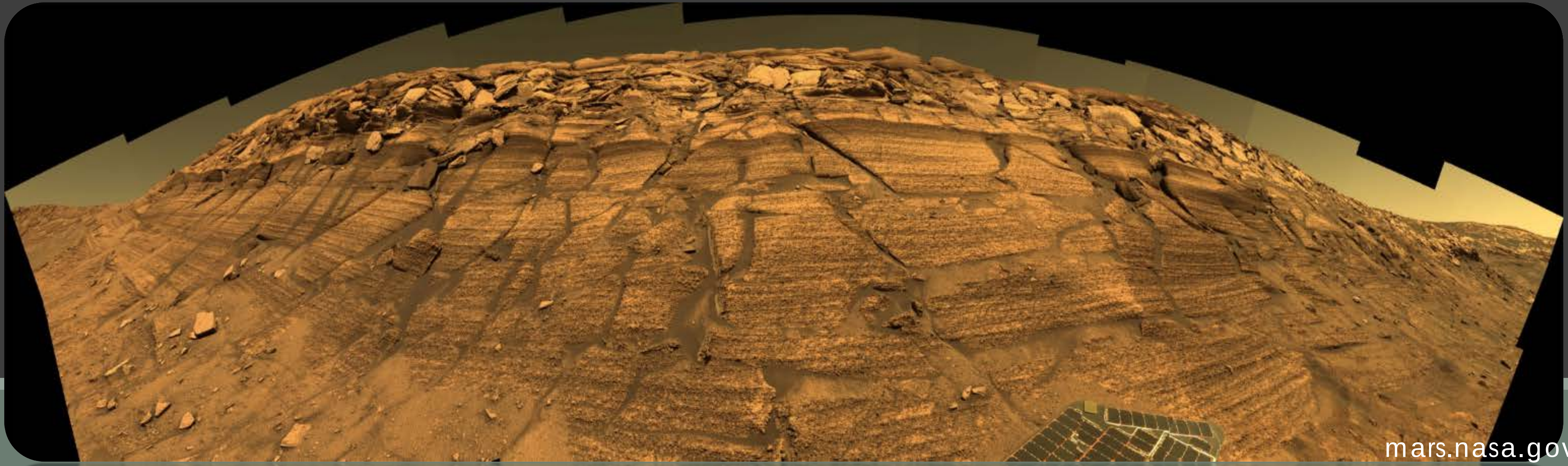
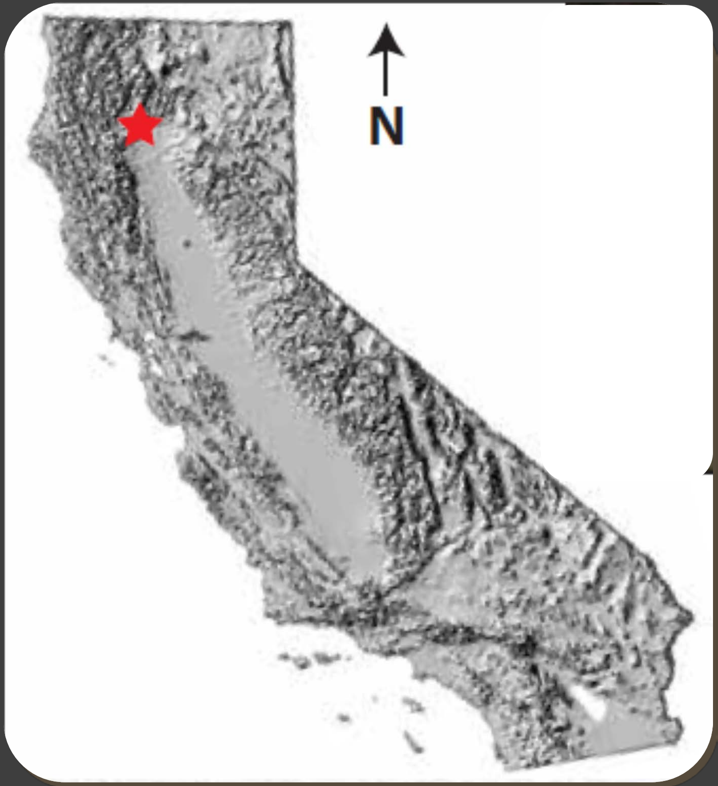
Iron oxides make Mars the “Red Planet”

- Iron oxides can preserve physical biosignatures
- There are challenges with preserving molecular biosignatures in iron oxides over long time periods
- This study demonstrates preservation of both biosignature categories in iron rocks from Iron Mountain, CA, and how to detect them in Martian environments



mars.nasa.gov

Iron Mountain, CA



ca.water.usgs.gov

Iron Mountain, CA

- Gossan-like environments (e.g. Burns 1987) and banded iron formations (e.g. Fallacaro & Calvin) have been predicted on Mars

Iron Mountain, CA

- Analogous mineral environment:
  - ✓ Hematite
  - ✓ Goethite
  - ✓ Jarosite
  - ✓ Fe-SO_4 salts
  - ✓ (Schwertmannite)
- Jarosite indicates an acidic environment, pH<3
- Fe(III) minerals indicate oxidizing environments

Iron Rocks from Iron Mountain

Modern Iron Oxides

- Microbially mediated iron precipitate (months to years old)
- Schwertmannite

Older Iron Oxides & Sulfides

- Iron rocks from the oxidized sulfide deposit (100’s-1000’s years old)
- Goethite + hematite, pyrite, quartz

Iron Mountain Biosignatures

PHYSICAL

- Environmental Context
- Morphology
- Morphometrics (quantify bending & flexibility)

MOLECULAR

- Presence and preservation of lipids (e.g. fatty acids)

MODERN VS “OLDER”

What biosignatures can we look for?

Physical

Criteria	
Mineral precipitating environment	✓
Visible in cross section	
Differ from surrounding mineral matrix	
Biological Morphology	
Cell lumina	
Uniform diameters	
Biological size ranges	
Flexibility	
Criteria from Williams et al 2015, 2016; Hofmann et al 2008; Schopf et al 2007; Cady et al 2003; Buick 1990	

Modern

Older

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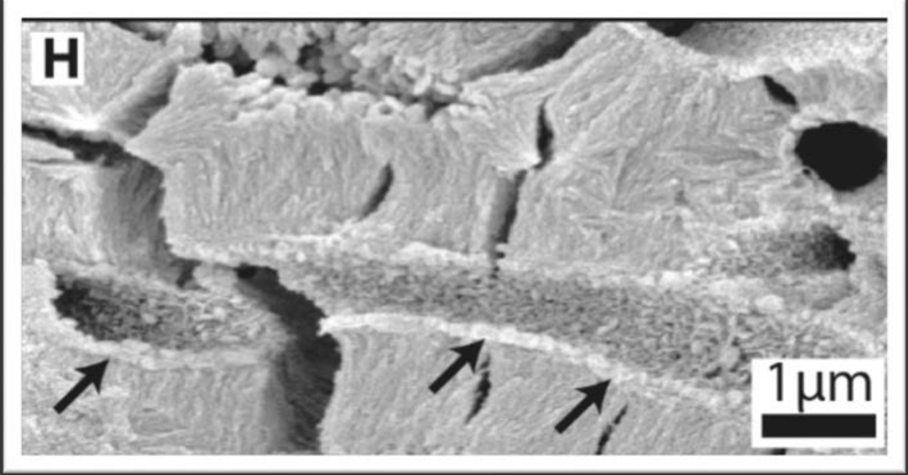

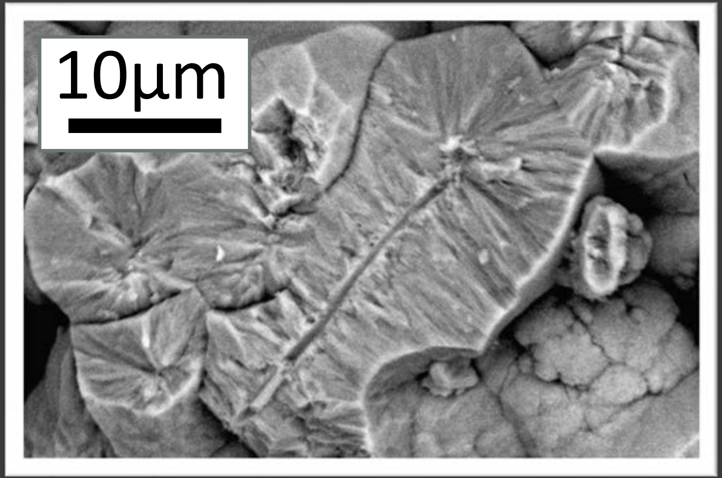

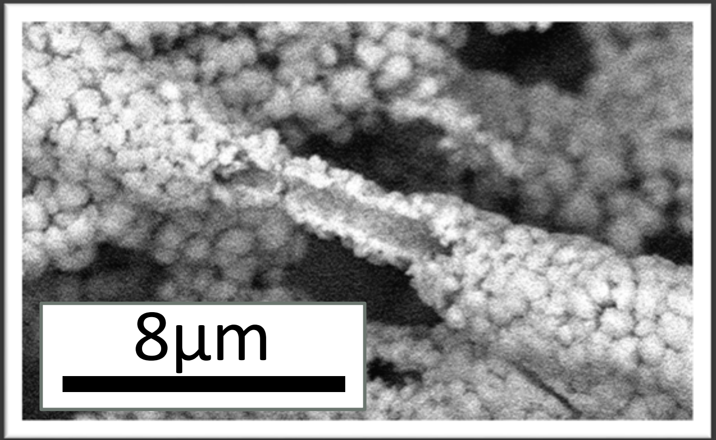

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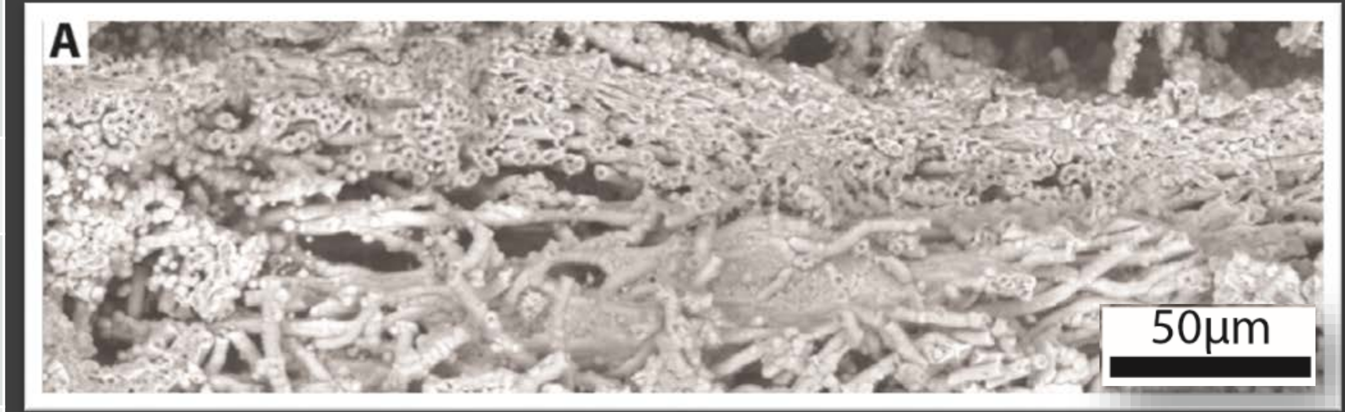

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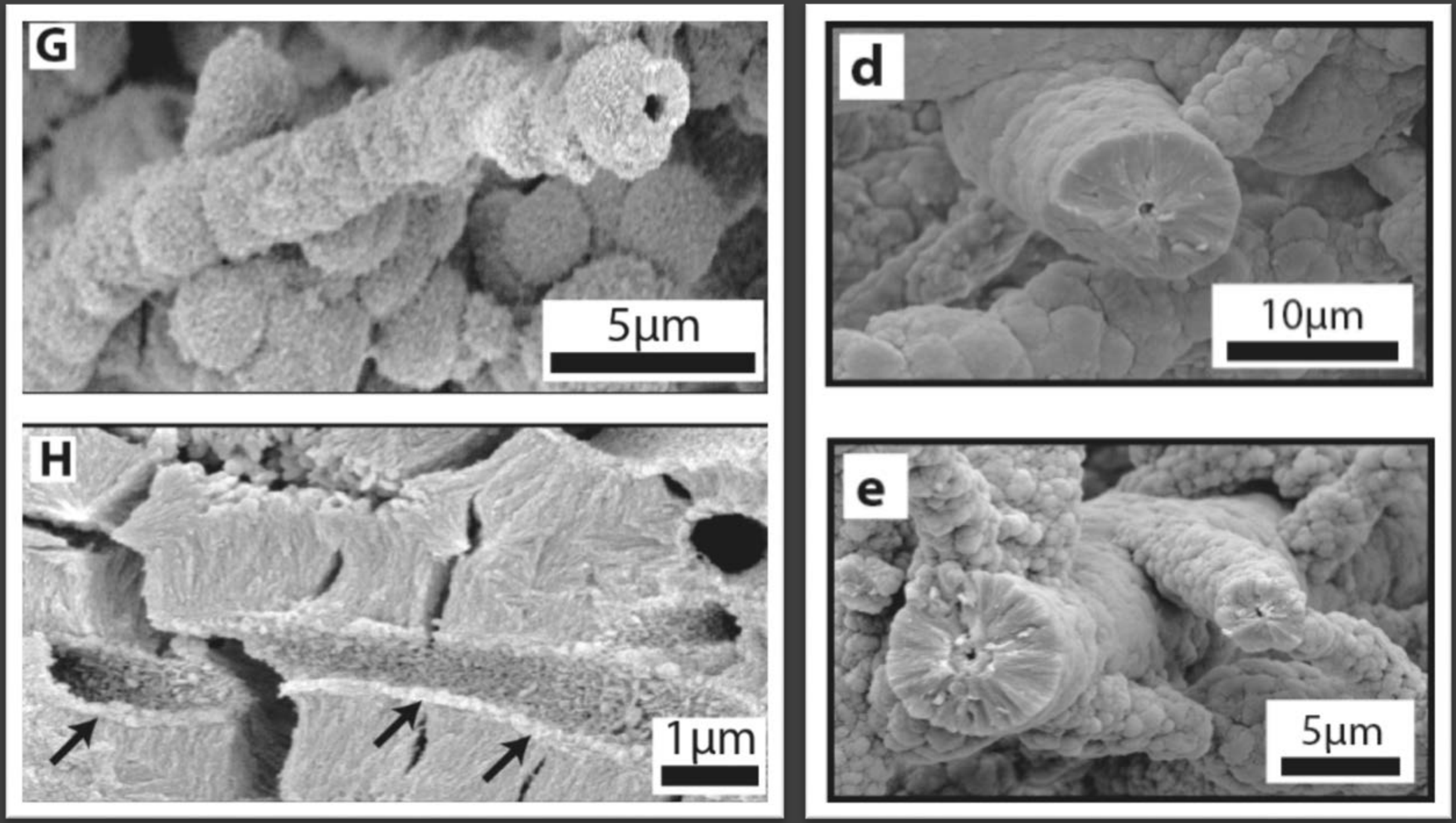

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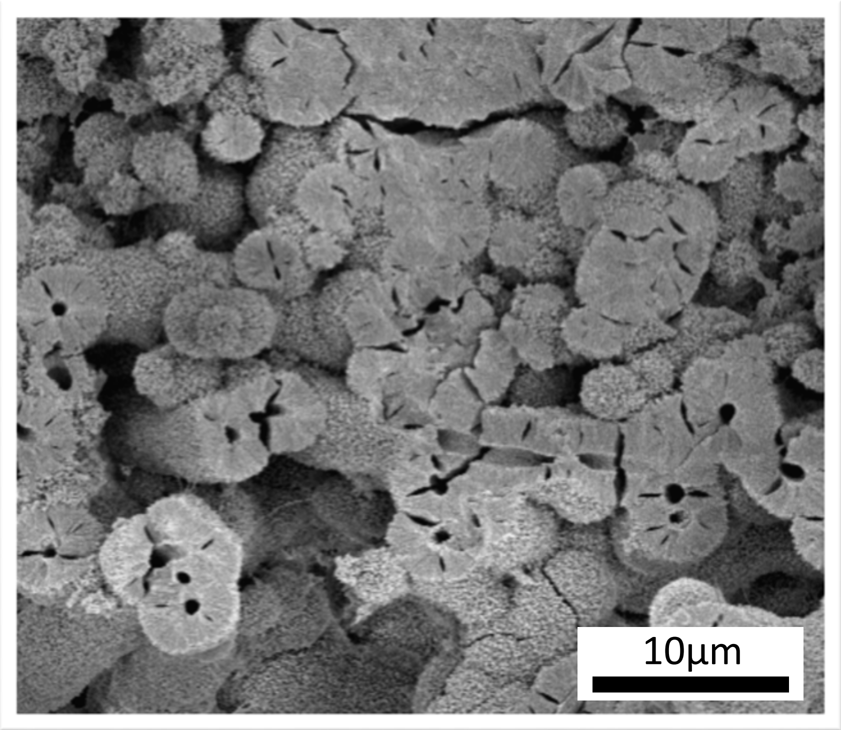

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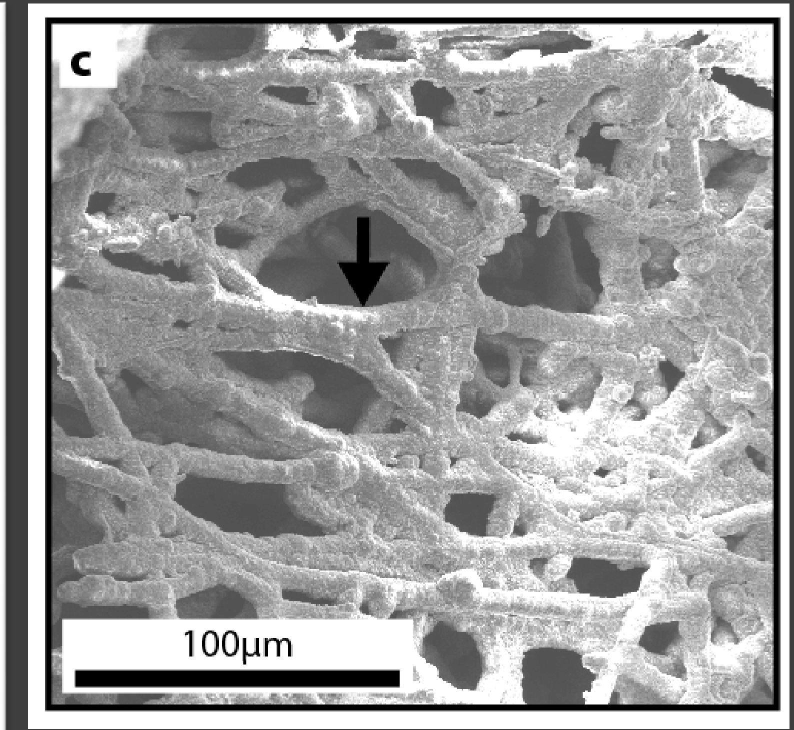

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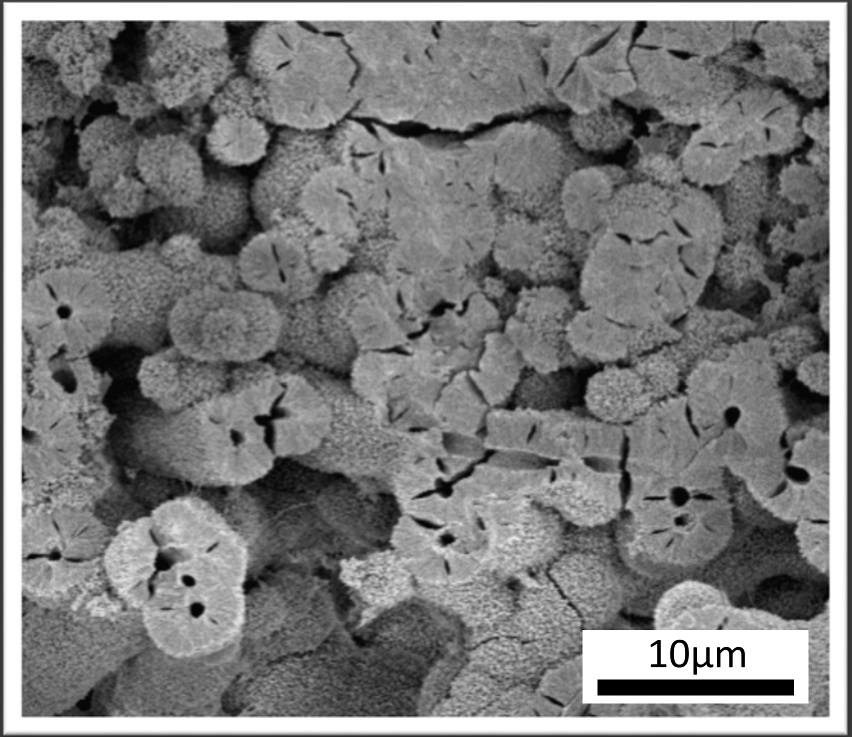
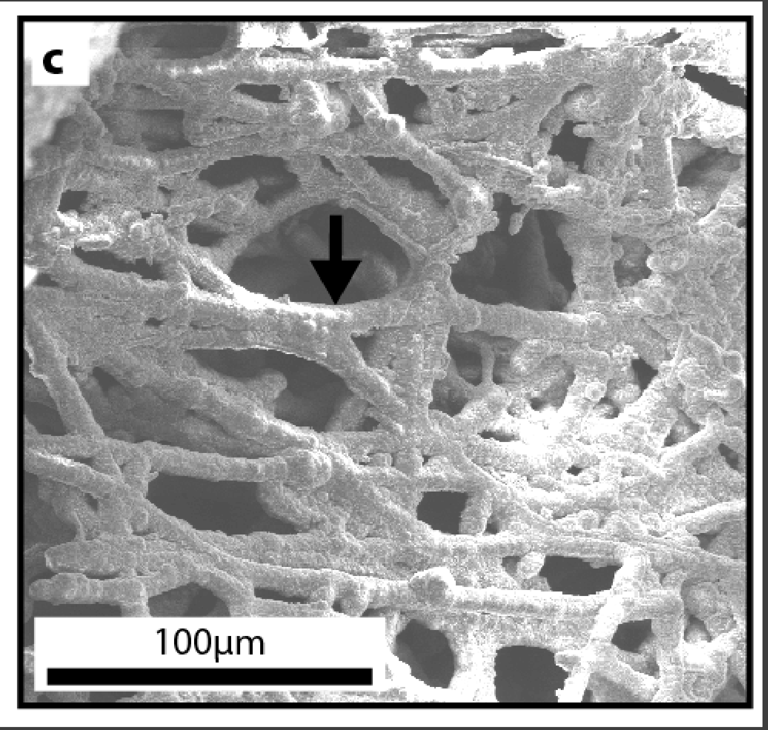


Microbial filament: avg=0.3µm
Filament lumina: avg=0.6µm

Modern



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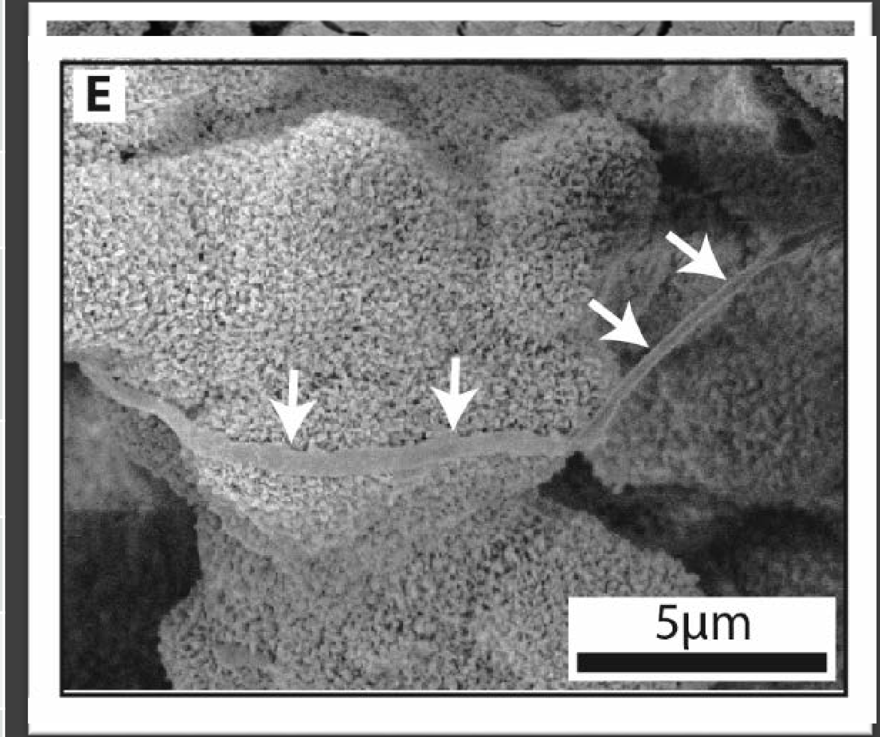

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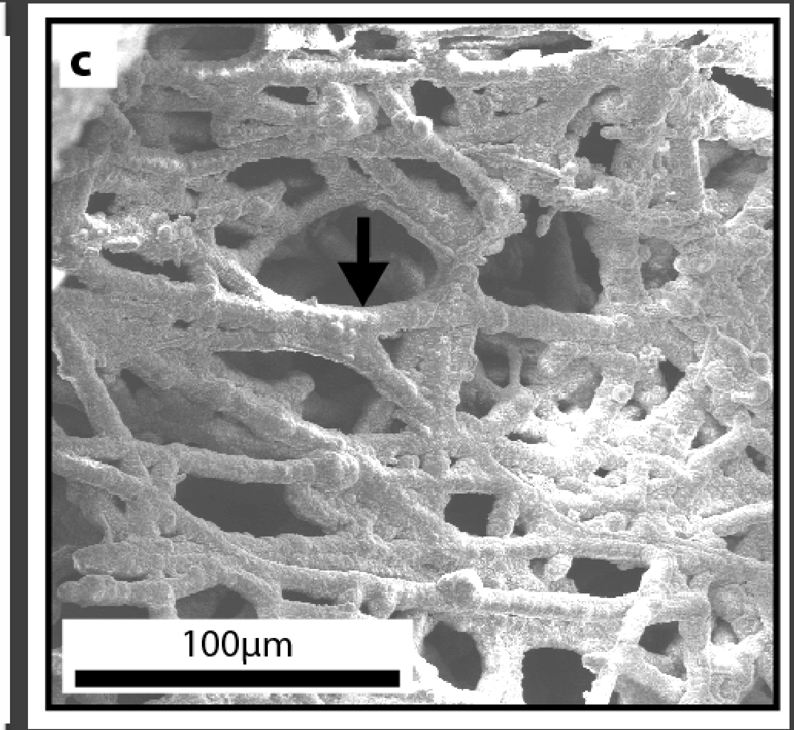

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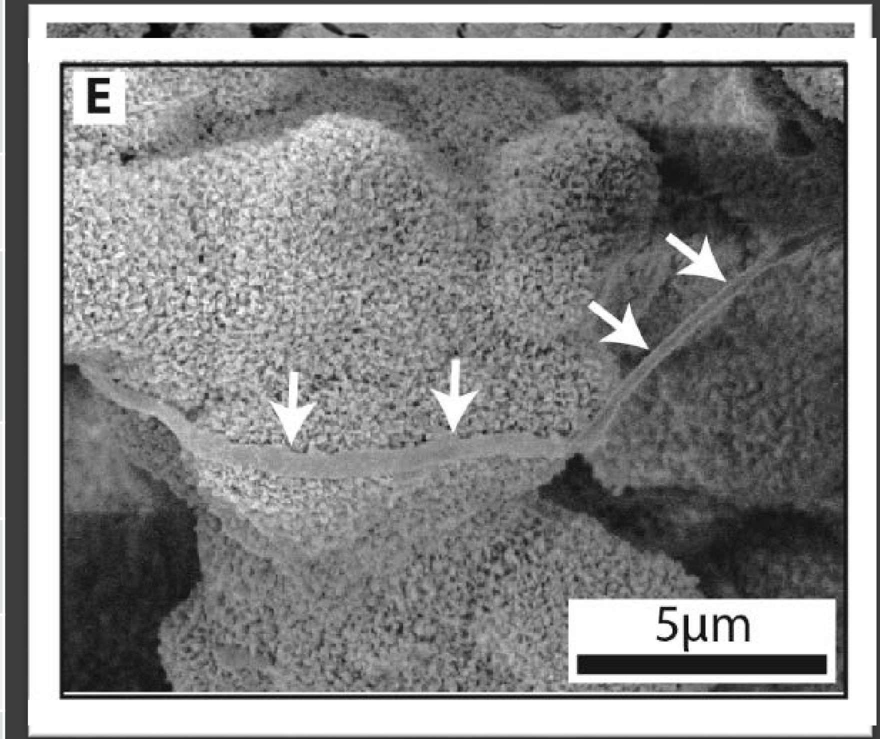

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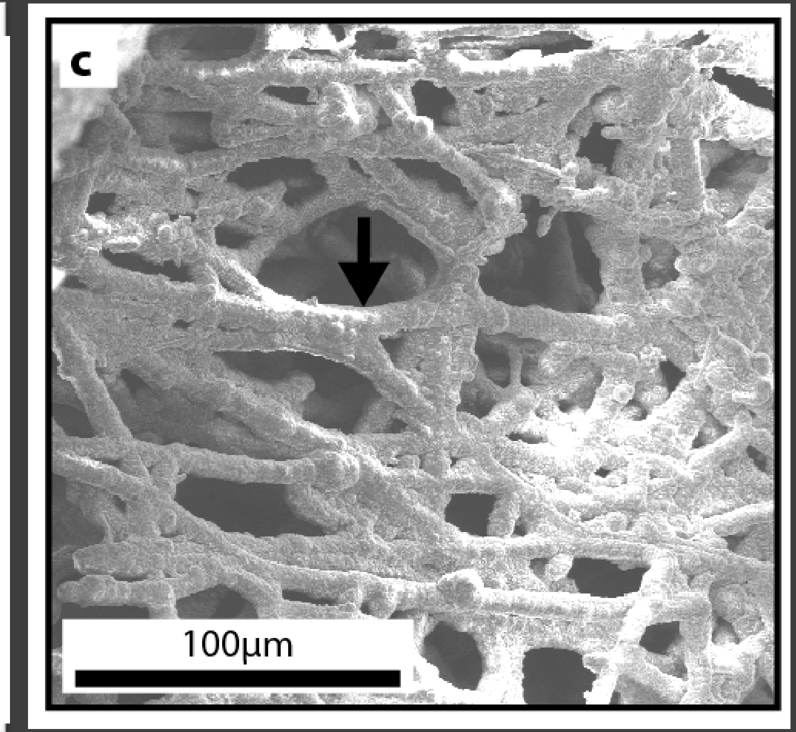

No interior microbes detected
Filament lumina: avg=0.5µm

Older

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Differ from surrounding mineral matrix	✓
Biological Morphology	
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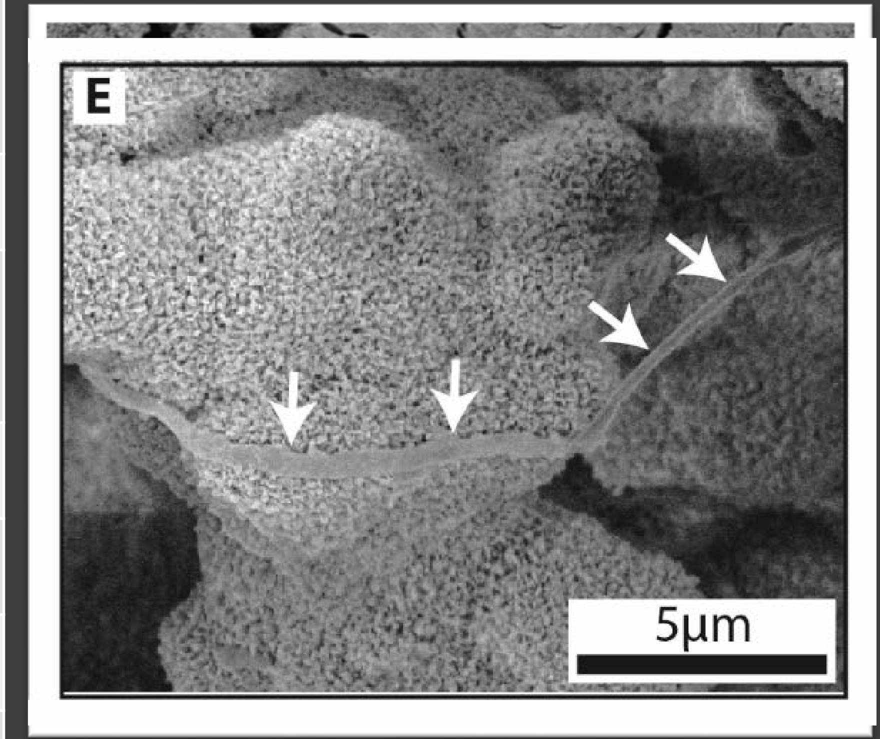

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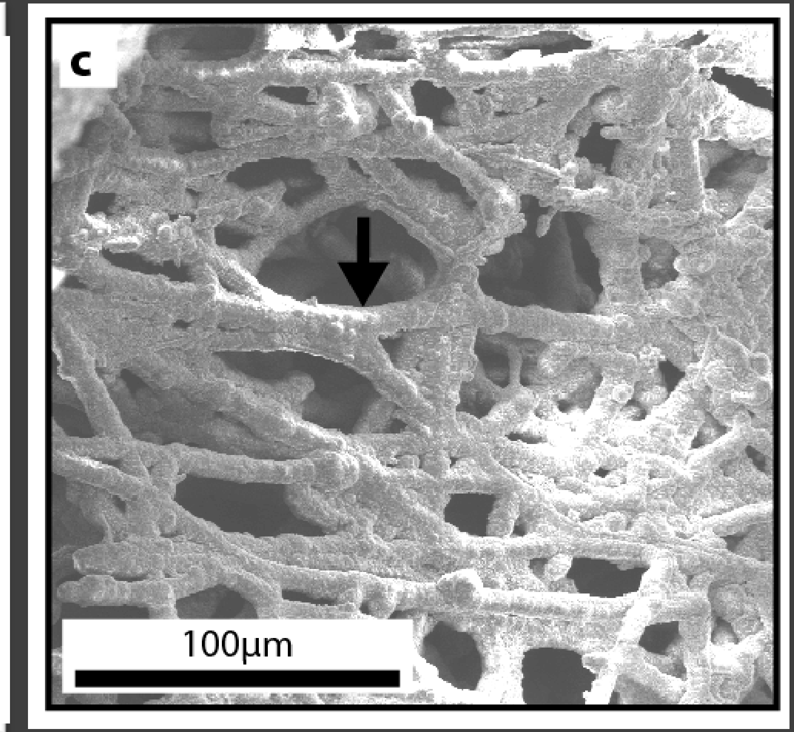

No interior microbes detected
Filament lumina: avg=0.5µm

Microbial average diameter *A. ferrooxidans* and *Leptothrix* sp. 0.4 to 0.8µm

Modern

Older

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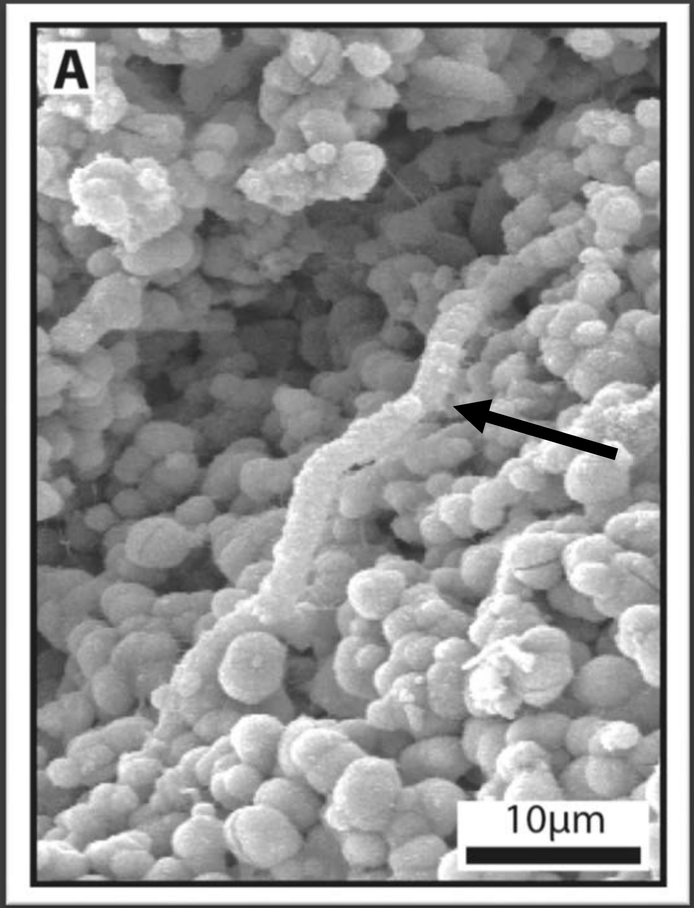

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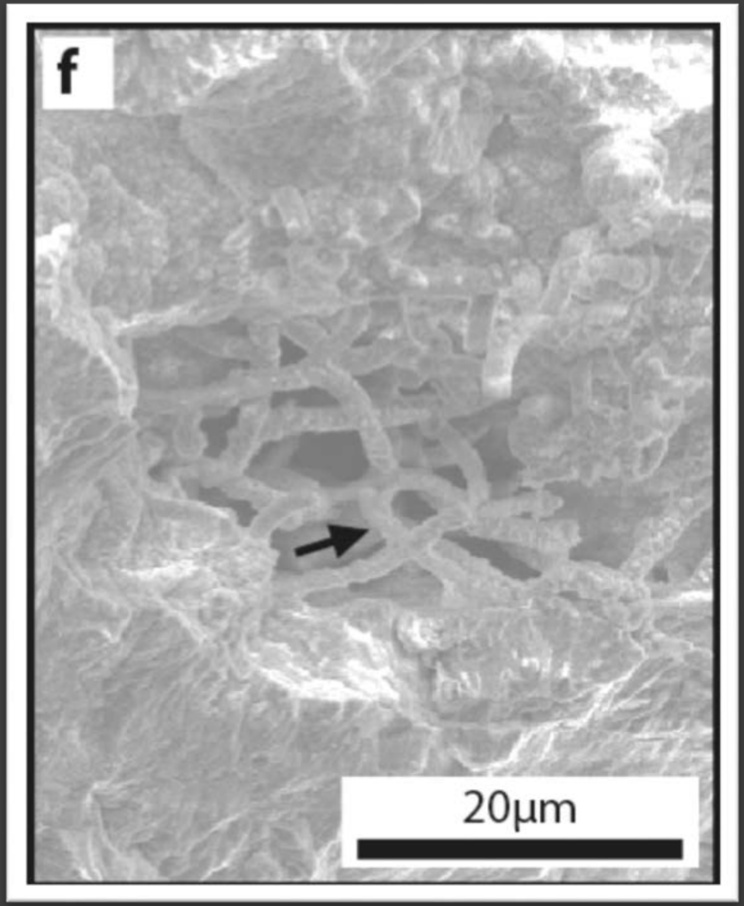

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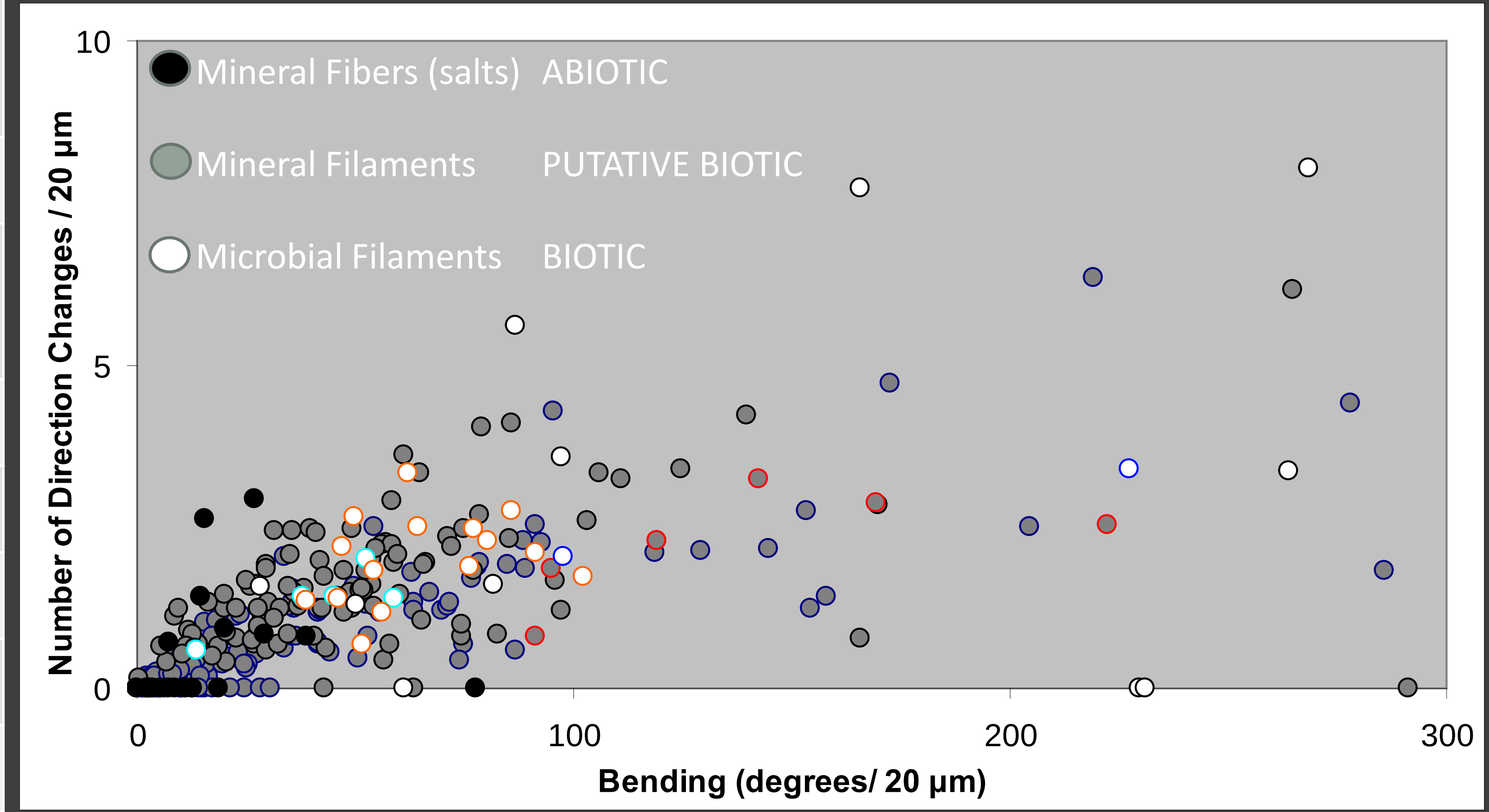

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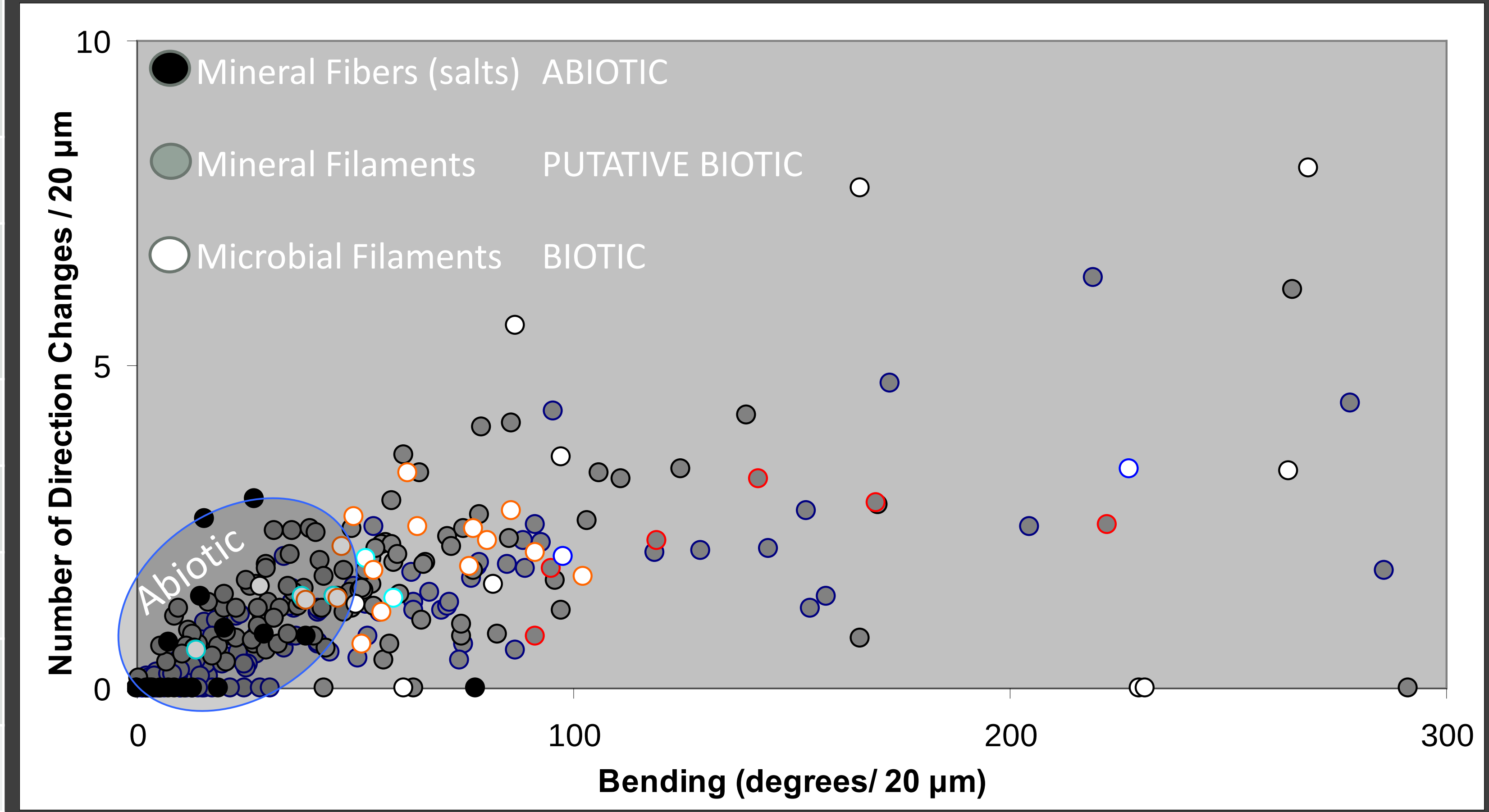

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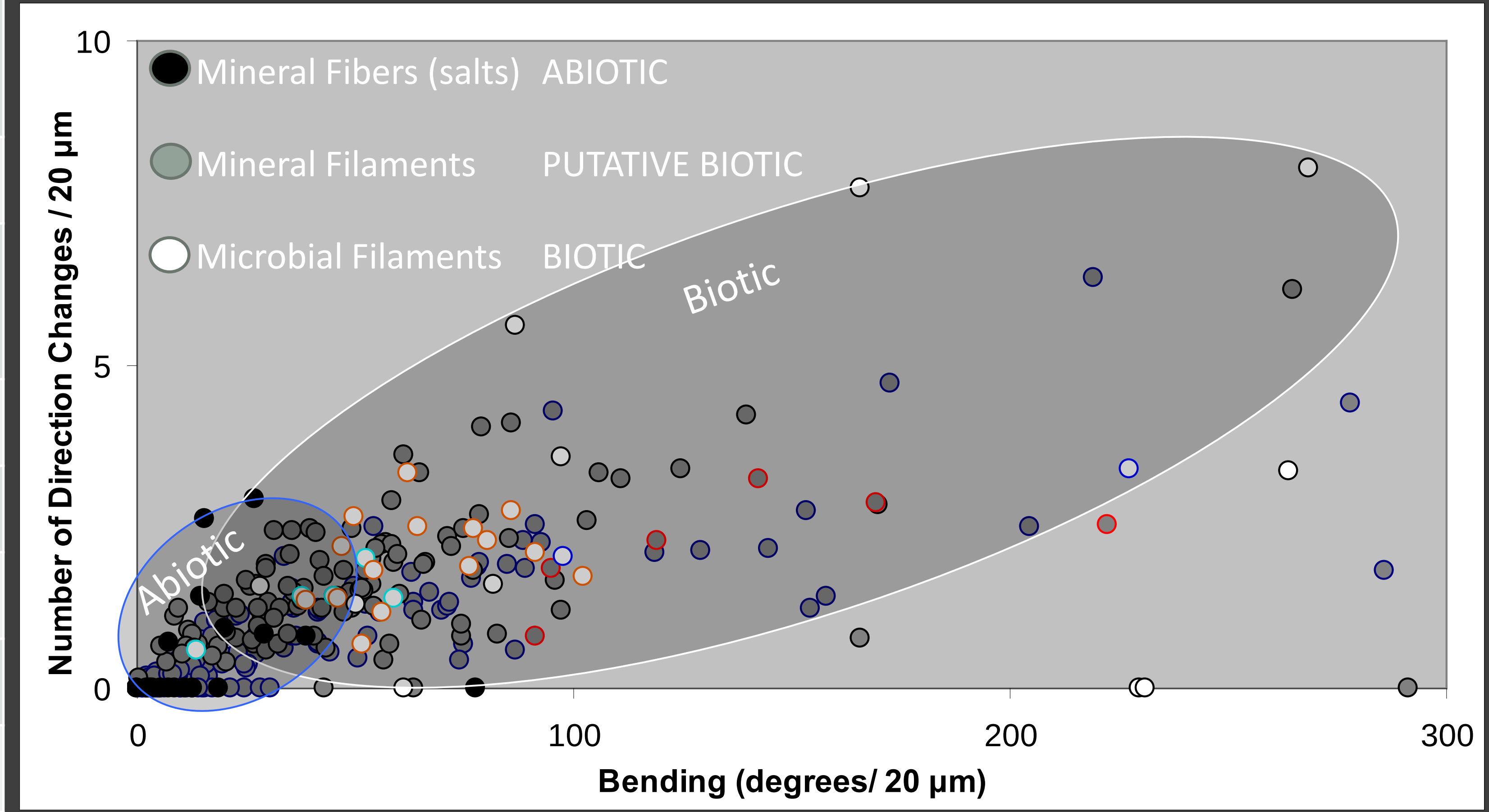

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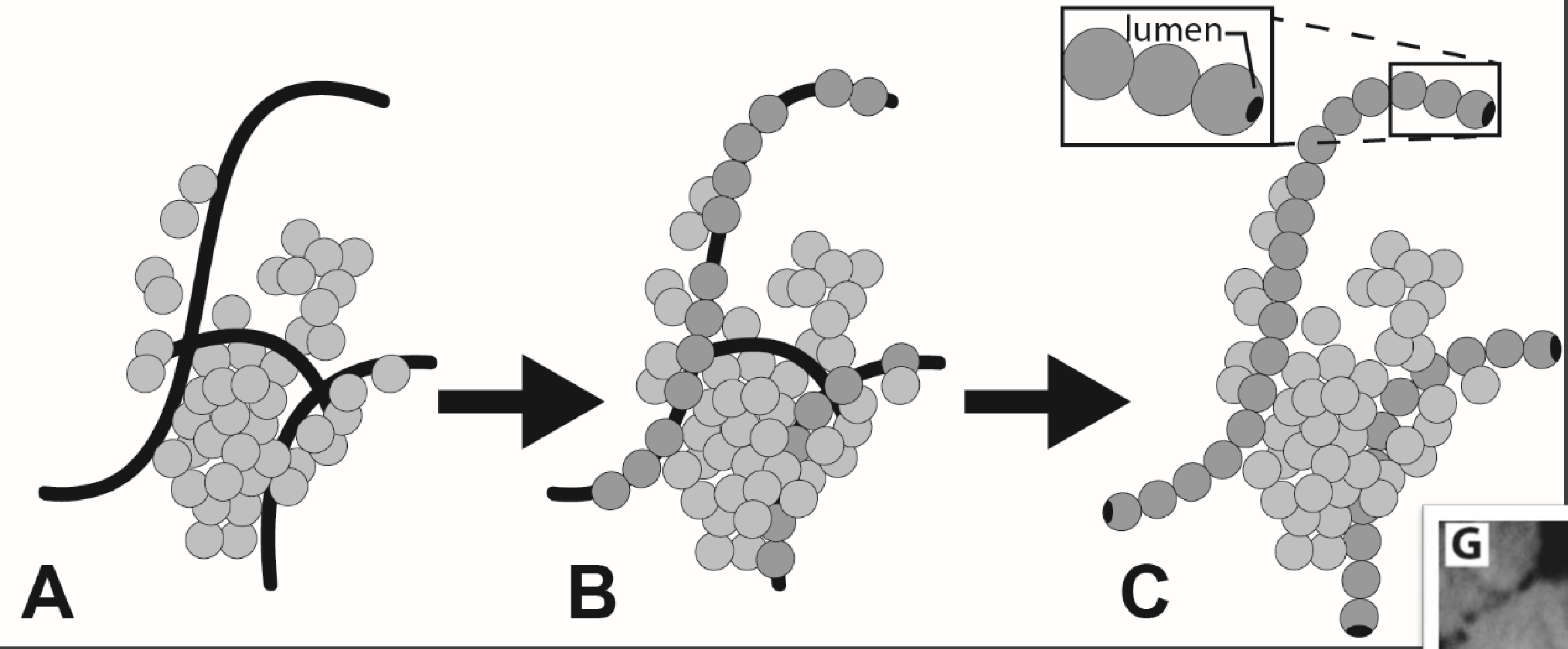

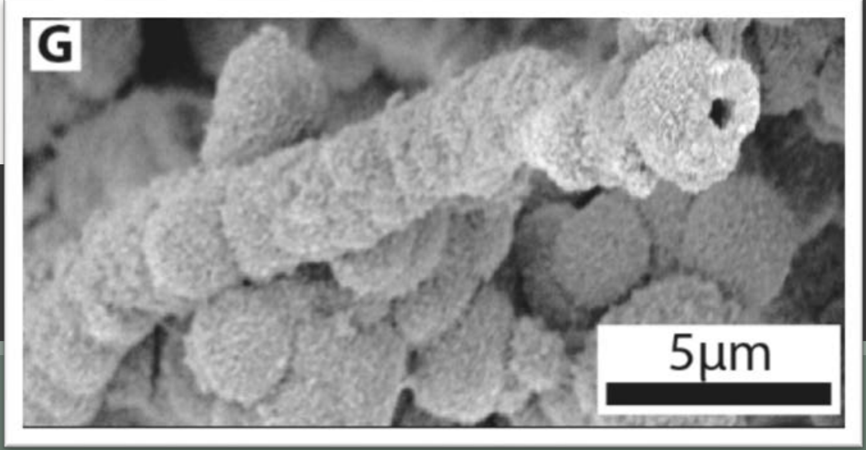

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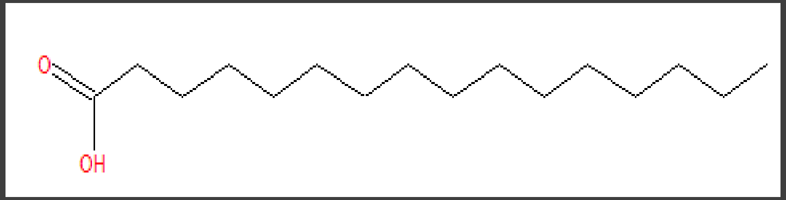
Molecular



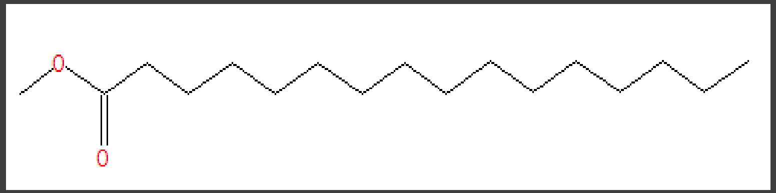
fatty acid

ΔT

→

TMAH

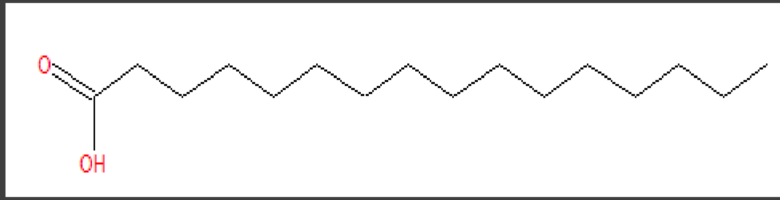
$$CH_3-N^+(CH_3)_3 \quad OH^-$$



fatty acid methyl ester (FAME)
+
trimethylamine

- Thermochemolysis with TMAH (tetramethylammonium hydroxide) reacts with labile H on fatty acids, hydrolyzing and methylating the molecule with CH_3

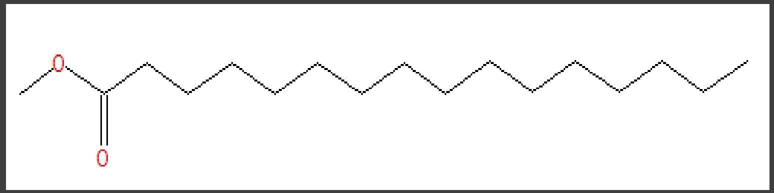
What biosignatures can we look for? Molecular



fatty acid

ΔT → TMAH

$$(CH_3)_4N^+\ OH^-$$



fatty acid methyl ester (FAME)
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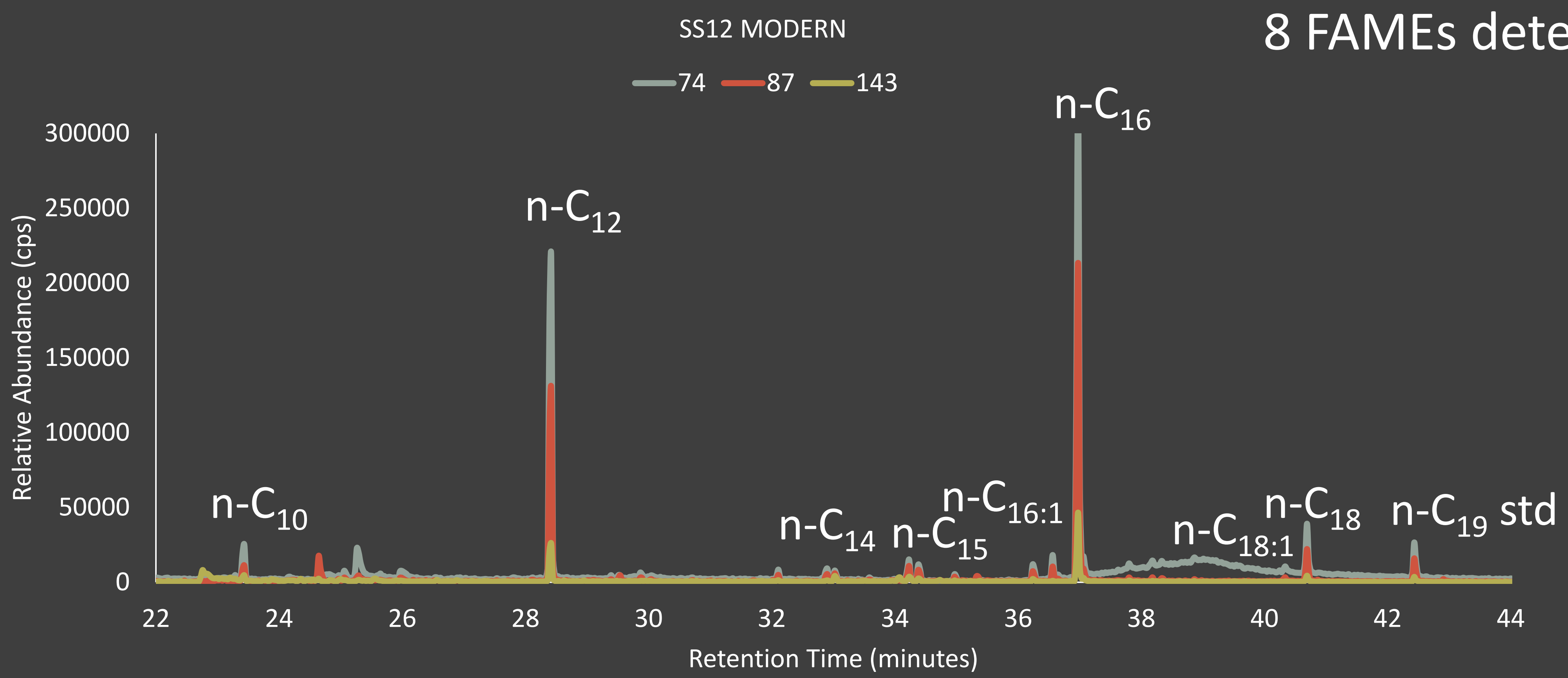
- ❑ At elevated temperatures (during pyrolysis), this produces fatty acid methyl esters (FAMEs), detectable to GCMS

What biosignatures can we look for?
Molecular

8 FAMEs detected



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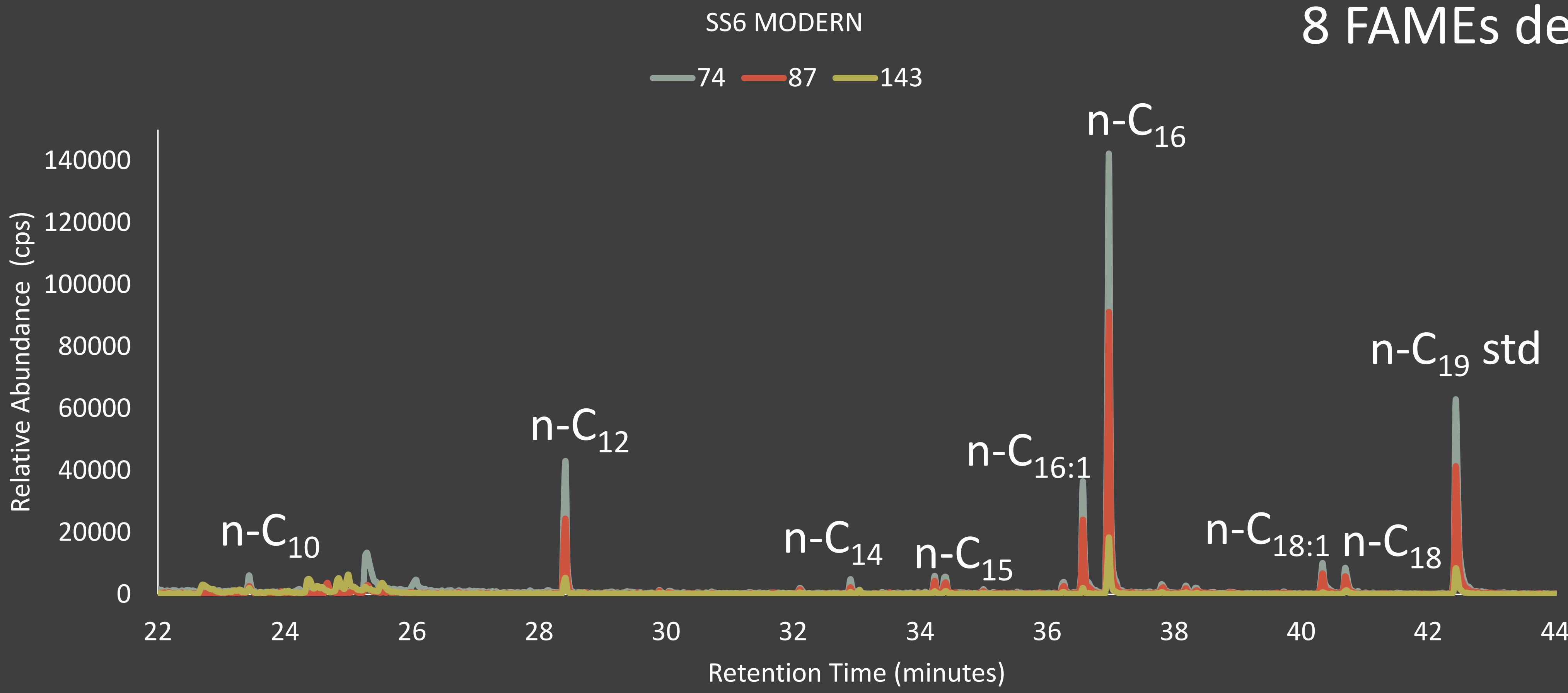
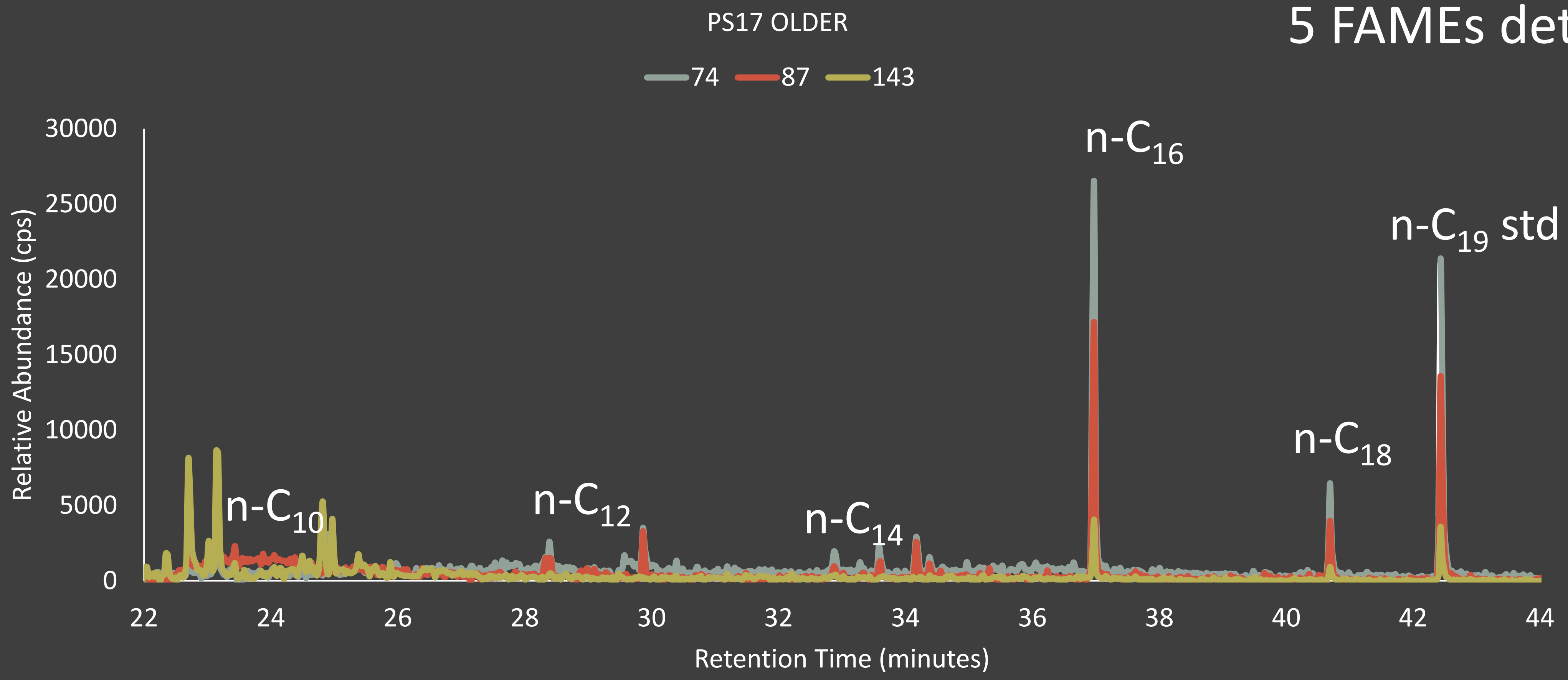


What biosignatures can we look for?
Molecular

5 FAMEs detected



Summary of Iron Mountain Biosignatures

PHYSICAL

MOLECULAR

MODERN

OLDER

Summary of Iron Mountain Biosignatures

PHYSICAL

MOLECULAR

MODERN

- First identification of microbial filaments coated with iron minerals to form physical mineral filament biosignatures at Iron Mtn.

OLDER

Summary of Iron Mountain Biosignatures

PHYSICAL | MOLECULAR

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- First identification of microbial filaments coated with iron minerals to form physical mineral filament biosignatures at Iron Mtn.
- Filamentous microbes and mineral filament biosignatures present and being preserved
- Biosignatures fulfill established criteria

OLDER

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OLDER

- Mineral filament biosignatures preserved in older gossan
- Biosignatures fulfill established criteria

Summary of Iron Mountain Biosignatures

	PHYSICAL	MOLECULAR
	❑ First identification of microbial filaments coated with iron minerals to form physical mineral filament biosignatures at Iron Mtn.	❑ Fatty acids are preserved in iron oxides and detectable using TMAH detection methods
MODERN	❑ Filamentous microbes and mineral filament biosignatures present and being preserved ❑ Biosignatures fulfill established criteria	
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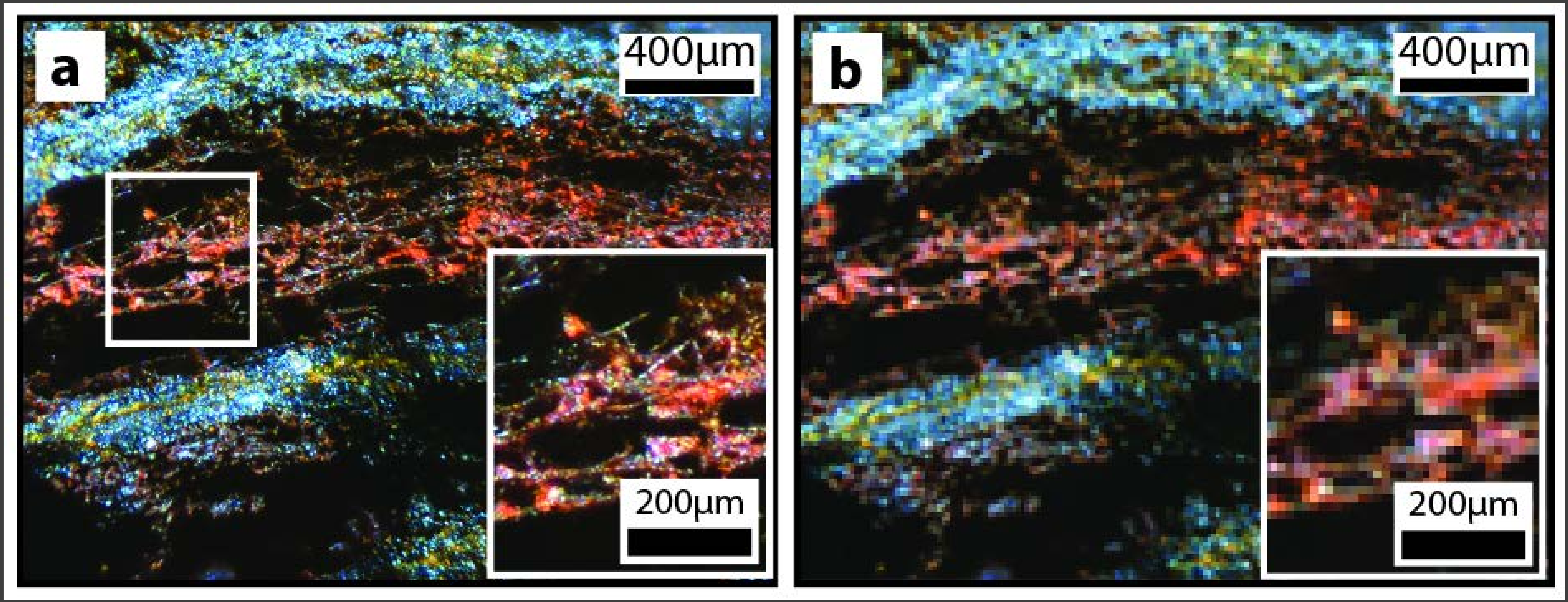
OLDER	❑ Mineral filament biosignatures preserved in older gossan ❑ Biosignatures fulfill established criteria	❑ >1000s year old ❑ No/limited interior microbial community ❑ Detected FAMEs = 4 to 5

How can we look for **physical** biosignatures on Mars?

- So far, there are no payloads with SEM capabilities on Mars
- Individual filaments are below the resolution of high resolution optical flight cameras, but sinuous filaments forming mat-like textures are resolvable



High resolution Z-stack

0.8 μm / pixel

MAHLI resolution

13.9 μm / pixel

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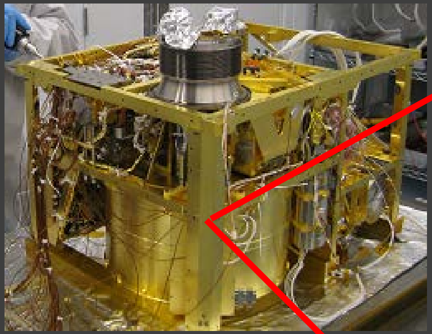
- Curiosity Rover: MAHLI (Mars Hand Lens Imager)
- ExoMars Rover: CLUPI (Close Up Imager)
- Mars 2020 Rover: WATSON (Wide Angle Topographic Sensor for Operations and eNgineering)

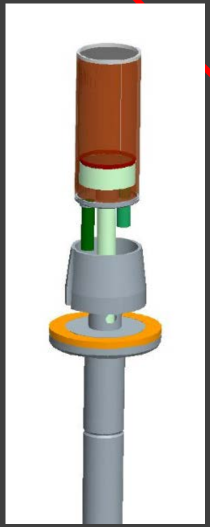
How can we look for **molecular** biosignatures on Mars?

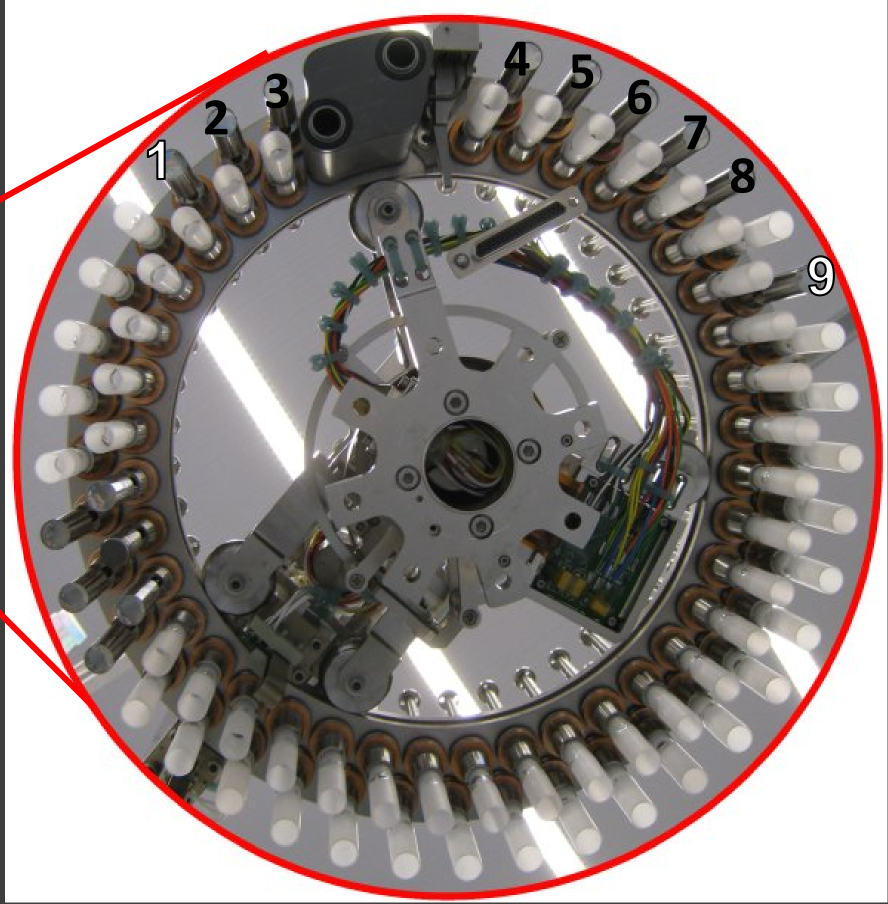
- Molecular biosignatures like long chain fatty acids are detectable with TMAH thermochemolysis

SAM wet chemistry cups

Two TMAH cups for low temperature extraction targeting less volatile organic compounds



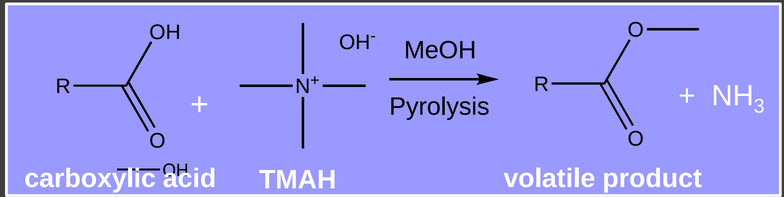




Foil cap designed for puncture using pin – Mars sample dropped into solvent filled cup through inlet tube

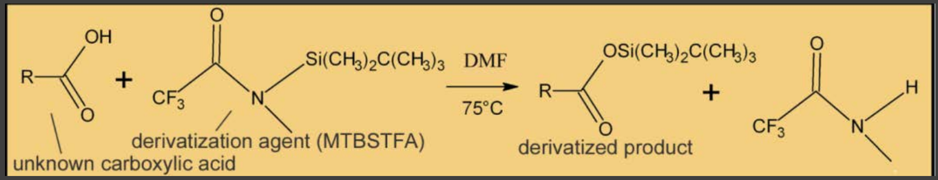
TMAH Thermochemolysis

Tetramethylammonium hydroxide



MTBSTFA Derivatization

N-(*tert*-butyldimethylsilyl)-*N*-methyltrifluoroacetamide



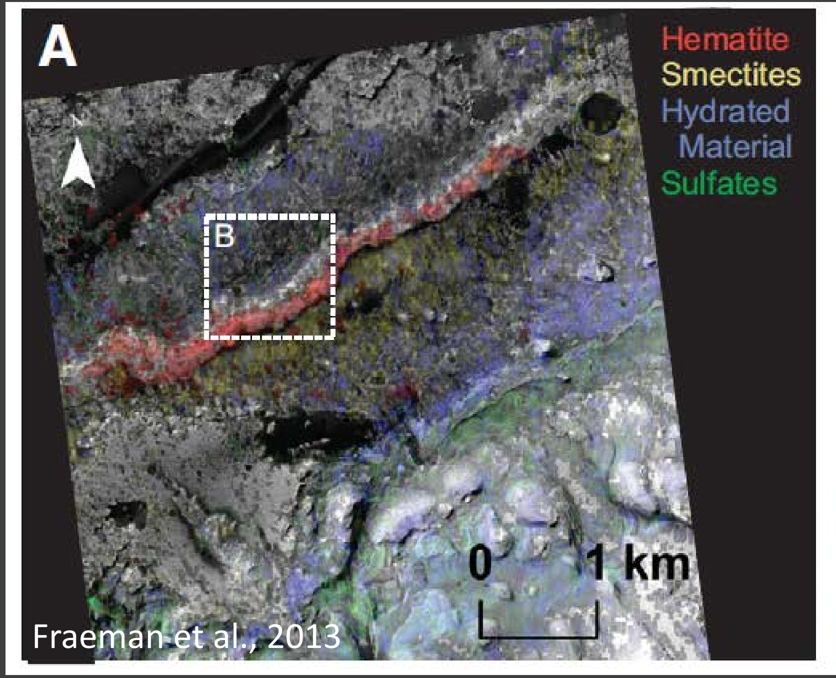
How can we look for **molecular** biosignatures on Mars?

- Molecular biosignatures like long chain fatty acids are detectable with thermochemolysis or derivitization:
- Curiosity Rover: SAM (Sample Analysis at Mars)
- ExoMars Rover: MOMA (Mars Organic Molecule Detector)

- Mars 2020 Rover: SHERLOC (Scanning Habitable Environments with Raman & Luminescence for Organics & Chemicals) – aliphatic and aromatic organics with deep UV resonance Raman

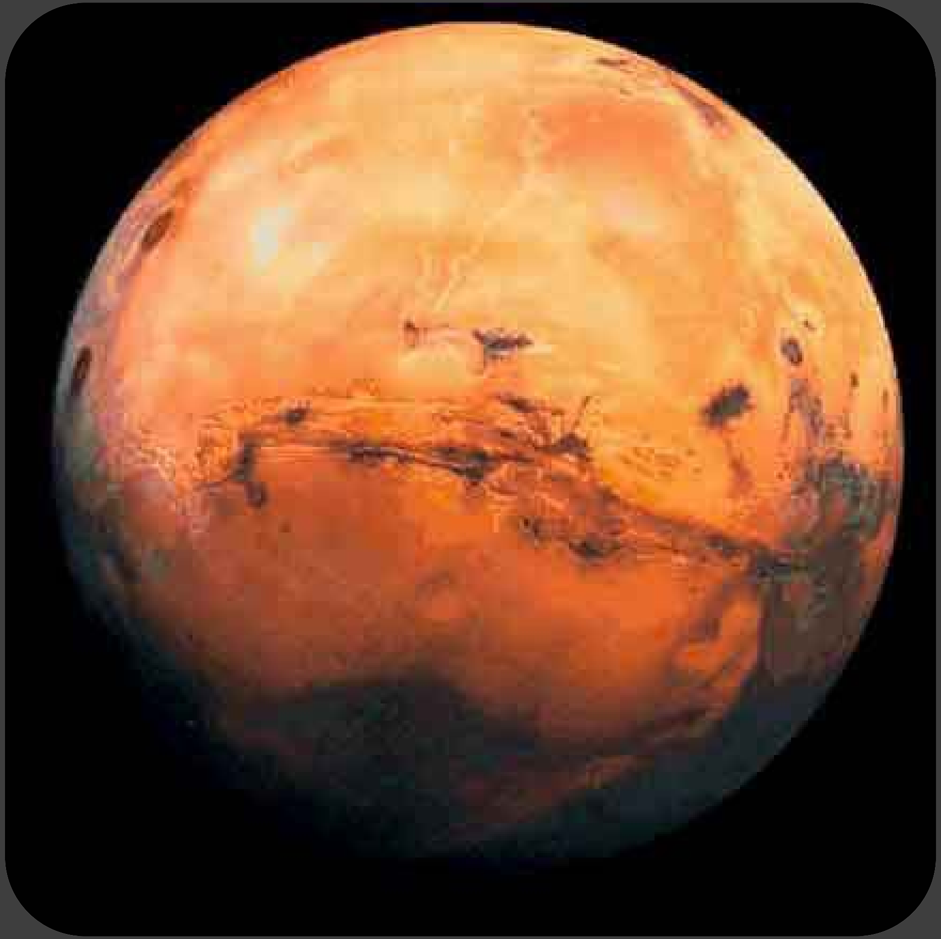
Where do we look for our tale of two biosignatures on Mars?

- Iron oxide-bearing units can have high biosignature preservation potential
- Hematite Ridge in Gale Crater
  - Formed from interaction of Fe(III)-bearing fluids
  - Was a redox front and an actively-precipitating mineral environment
  - A GREAT place to look for physical and molecular biosignatures



Where do we look for our tale of two biosignatures on Mars?

- A landing site with multiple habitable environments with high preservation potential gives the greatest opportunities for success.



Back ups

What biosignatures can we look for?
Molecular