Gulf of Mexico Sediment Evaluations for Microbial-Mineral-Hydrate Associations*

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Abstract

It is known that microbial activities around seafloor gas hydrate accumulations and gas vents far surpass activities remote from hydrates, and the formed hydrates establish a large carbon sink for microbes. This paper reports on investigations into possible roles minerals and microbes, individually and in association, may play in hydrate nucleation, formation rate, induction time and placement. To do this, we have analyzed in the laboratory numerous hydrate-related sediments from Gulf of Mexico cores.

Near-surface sediments and sediments down to 30 m below-surface show interesting trends of hydrate formation propensity. For example, differences in bio-products above and below the sulfate reduction zone may account for the trends. Other sediments were injected with a known biopolymer in the laboratory, the hydrate collected, and the melt analyzed; particles in the melt that had been extracted from the sediments by hydrate crystallization were found to be predominantly about 138 nm diameter and may have acted as hydrate nuclei. The melt from a sample of gas hydrate recovered from an outcrop at MC-118 site from 3000 ft water depth in the Gulf of Mexico was analyzed for particle size by Dynamic Light Scattering and viewed with Scanning Electron Microscope. The melt from this seafloor hydrate showed prolific microbial action that had developed within the interstitial spaces of the hydrate matrix.

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This study makes the hypothesis that microbes promote seafloor hydrate formation via bioproducts and that synergistically the hydrates represent carbon sources for the microbes.

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Hypothesis of microbial influence on seafloor hydrates

Anionic biosurfactants and bioproducts promote gas hydrate formations in sediments of the seafloor. A synergistic effect relates microbes/minerals/hydrates.

Prolific microbial activity around seafloor gas hydrates

Photo: Bacterial mat covers gas hydrate mound protruding from seafloor.

Microbes appear > orders of magnitude more abundant around seafloor hydrate accumulations.

Seafloor gas hydrate mound. Cascadia Margin… Courtesy of Ross Chapman

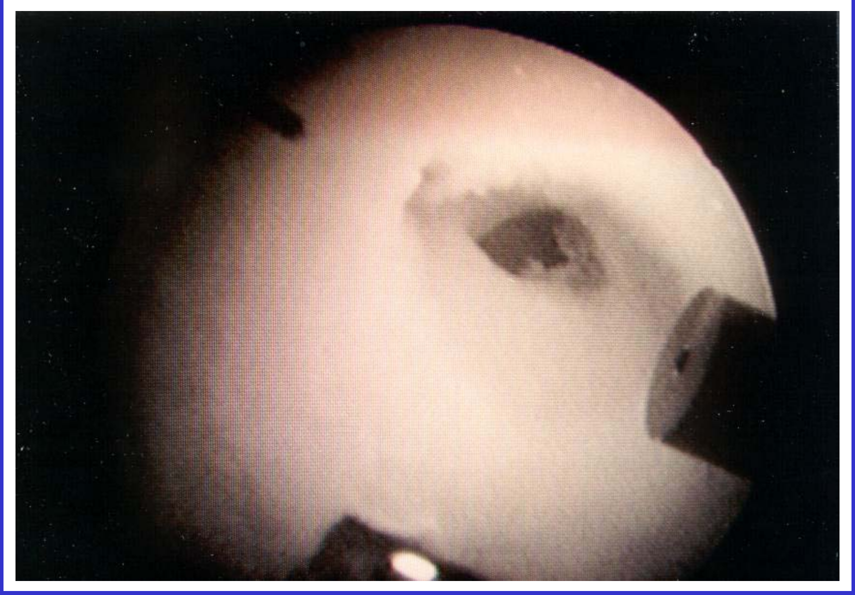
1st Interest: Synthetic anionic surfactants catalyzed gas hydrate formations in laboratory

Small ppm of surfactant caused hydrate short induction time, rapid formation rate, and placement on metal surfaces.

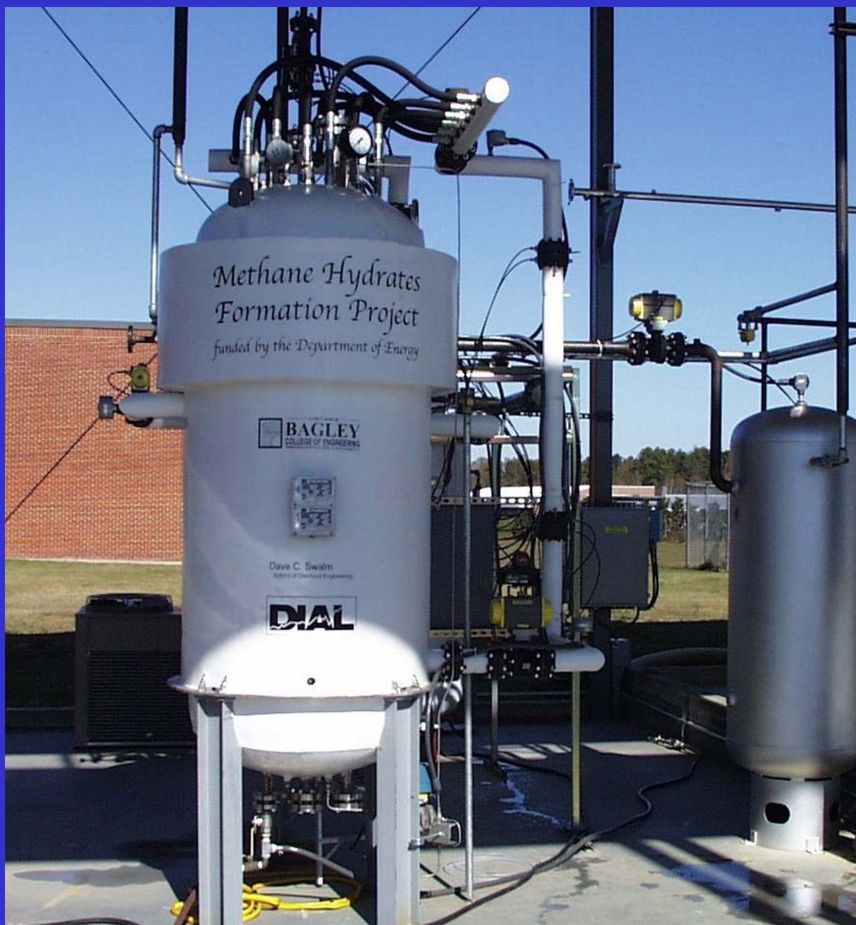
+ 1 hour with 184 ppm surfactant in lab test cell

+ 2 hours w/surfactant

156 vol/vol gas stored in hydrates



Scale-up of anionic surfactant process to store natural gas



5300 ft^3 (stp) natural gas stored in gas hydrates

(1) No stirring

(2) Hydrates self-pack symmetrically

(3) Hydrates-surfactant adsorb on metal surfaces.

Extension of anionic surfactant observations to biosurfactants in seafloor

Fact:	Biosurfactants are anionic.
Known:	Microbes in water of soils emit surfactants to bring insoluble organics into water phase so that carbon can be accessed.
Question:	Could microbial activity around seafloor hydrates produce biosurfactants that would promote seafloor hydrate accumulations?

Anionic Biosurfactant Classifications

Biosurfactant Classifications	Microbe	Biosurfactants Evaluated
Hydroxylated and Crosslinked Fatty Acids	*Corynebacterium lepus*	DL-A-Hydroxystearic acid*
Polysaccharide-lipid-complexes	1. *Pseudomonas syringae* 2. *Acinetobacter calcoaceticus*	1. Snomax 2. Emulsan
Glycolipids	*Pseudomonas aeruginosa*	Rhamnose lipid
Lipoprotein-lipopeptides	*Bacillus subtilis*	Surfactin
Phospholipids	1. *Thiobacillus* species 2. *Corynebacterium* species	DMPC * DPPS * POPC *

Kosaric, 1992; Fujii, 1998

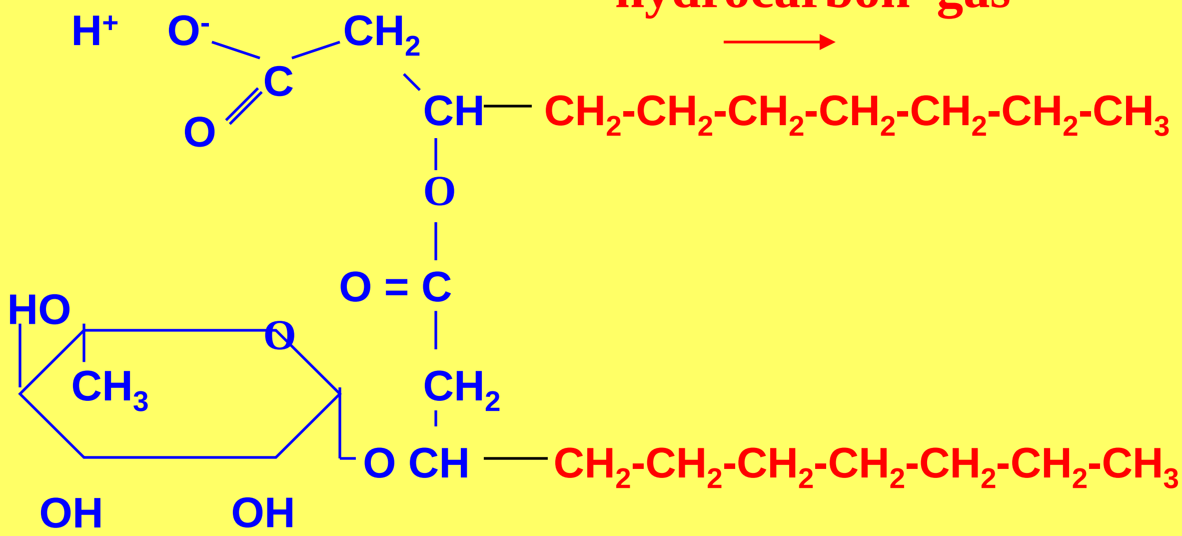
Commercial samples of each category promoted gas hydrates in laboratory porous media!!

Example biosurfactant structure: Rhamnolipid: A Glycolipid (from *Pseudomonas aeruginosa* bacterium)

Note: Anionic

Hydrophilic heads structure water

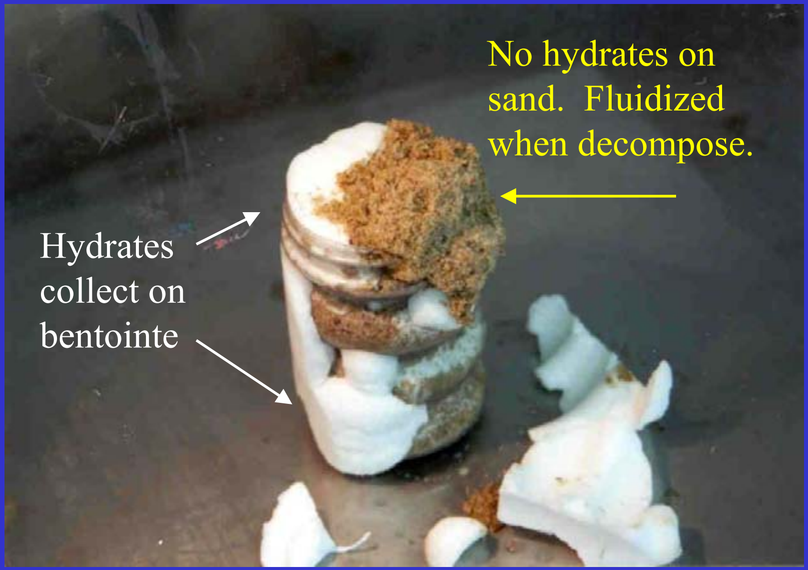
Hydrophobic tails solubilize hydrocarbon gas →



Structure of Rhamnolipid (Bai, 1997)

Note: *Pseudomonas aeruginosa* has been identified on seafloor around gas hydrates. [Lanoil, et al., 2001, *Appl & Envir. Micr.*, 67, 5143]

Biosurfactants especially effective hydrate promoters in presence of smectite clays



Bentonite/Sand saturated with Emulsan/seawater.

Emulsan is an anionic biopolymer.

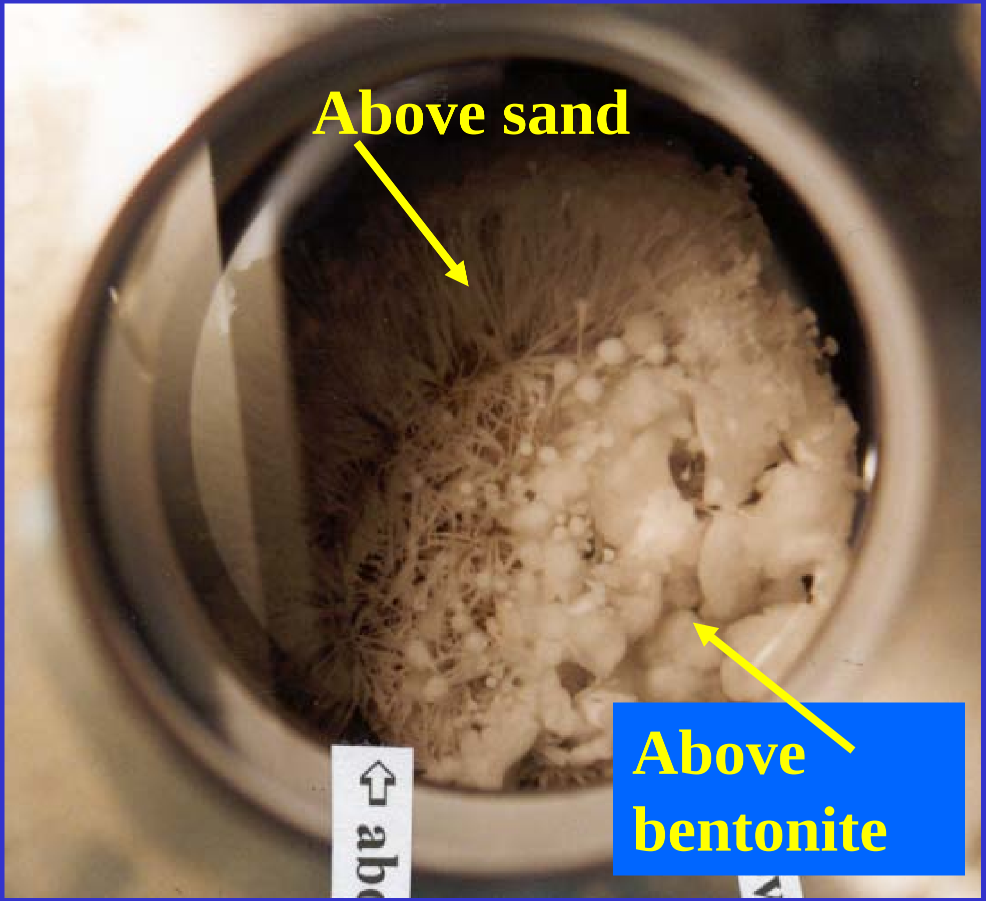
Bentonite/Sand saturated with rhamnolipid/seawater.

Rhamnolipid is an anionic biosurfactant.

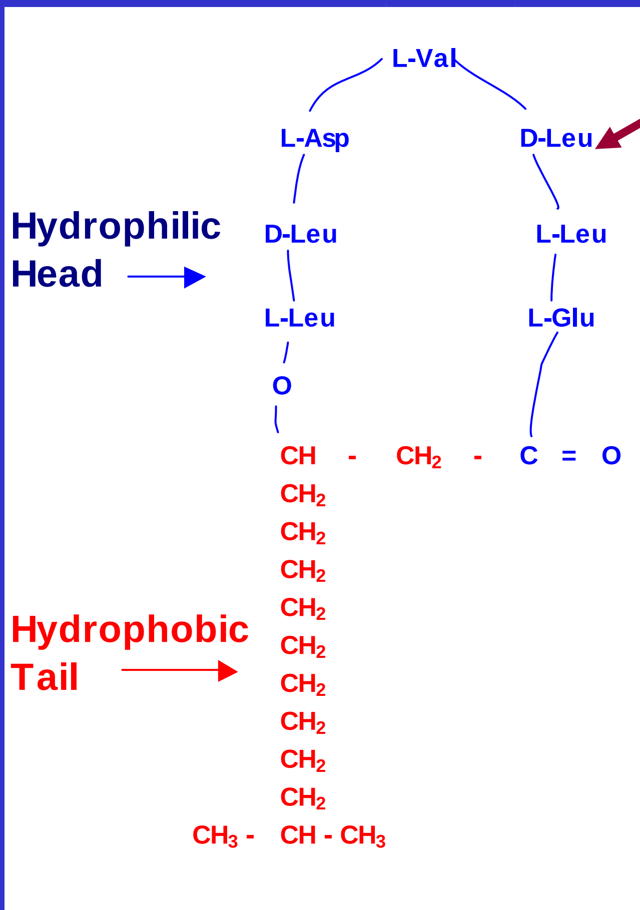
Bioproducts possibly affect hydrate morphology

Photo taken through transparent top of test cell. Cell packed with smectite clay on right and sand on left. Saturated with water/emulsan.

Note hydrate nodules above clay and hydrate whiskers above sand.

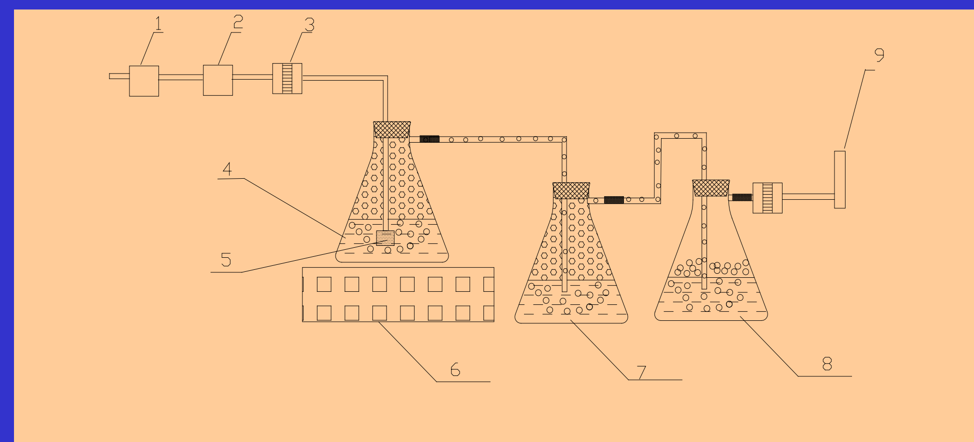


Bacillus subtilis (found in seafloor hydrates) anaerobically cultured in lab. Surfactin removed by bubbling gas. Recovered anionic biosurfactant promoted gas hydrates in porous media.



7 Amino Acids

Separation Process



1. Silica gel drier, 2. Activated carbon, 3. Sterile filter (0.1 microns, 4. Initial broth, 5. Gas distributor, 6. Shaker, 7. and 8. Distilled water solution collecting biosurfactant, 9. Soap-film flow meter.

Surfactin $C_{53}H_{93}N_7O_{13}$ Molecular Weight = 1036

From: Rosenberg, CRC Critical Reviews in Biotechnology

Lab Hydrate Synthesis Investigates Mechanisms (Emulsan/nontronite associate & act as hydrate nuclei)

<u>Analyses based on Dynamic Light Scattering & Scanning Electron Microscope:</u>

Hydrate capillary diameters found to be:

Smallest: 100 – 200 nm

Largest: 1500 nm (approx)

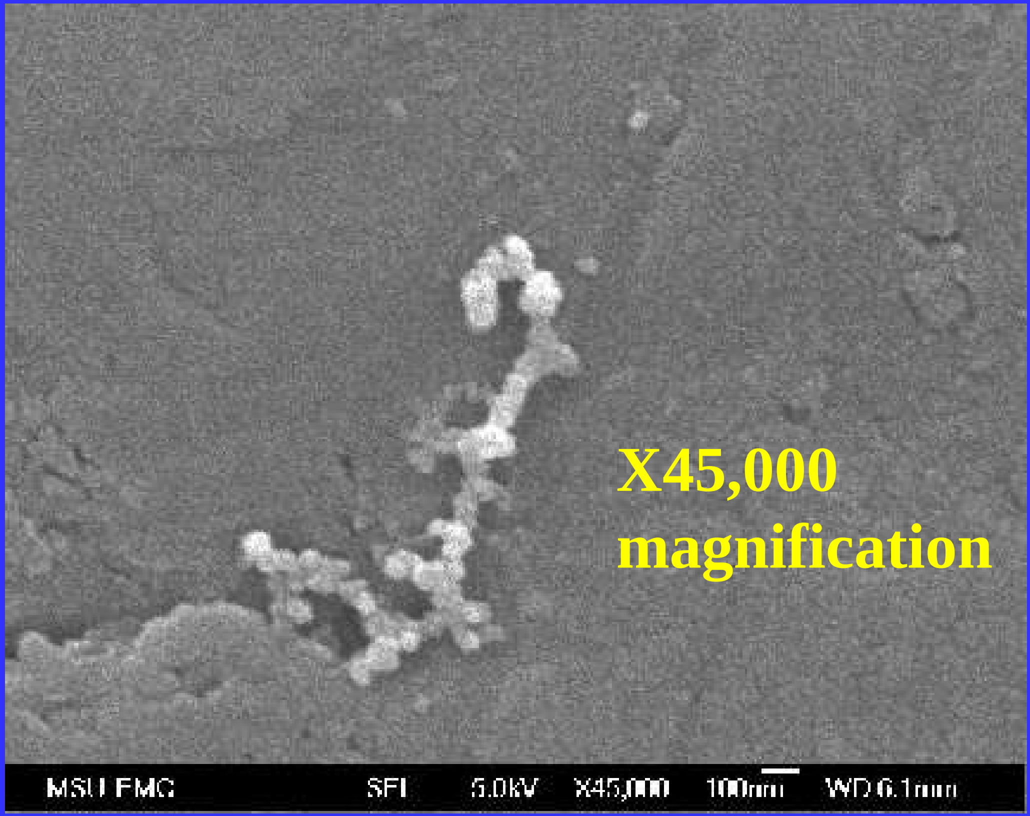
J. Dearman dissertation, MSU, May 2007

Note:

Nontronite is smectite clay.

Emulsan is anionic biopolymer.

These particles diffused through capillaries of hydrates formed in lab porous media.



Nontronite-Emulsan Particle

MC-118 Gas Hydrate Observatory.

(Observatory sponsored by DOE, MMS, NOAA. Bob Woolsey, Director of GOM Gas Hydrate Consortium)

Minerals, microbes, hydrates, and gases to be retrieved from test cells for study.

Data to help resolve mechanisms, determine microbe, mineral, hydrate synergy.

Current experiment, continental slope

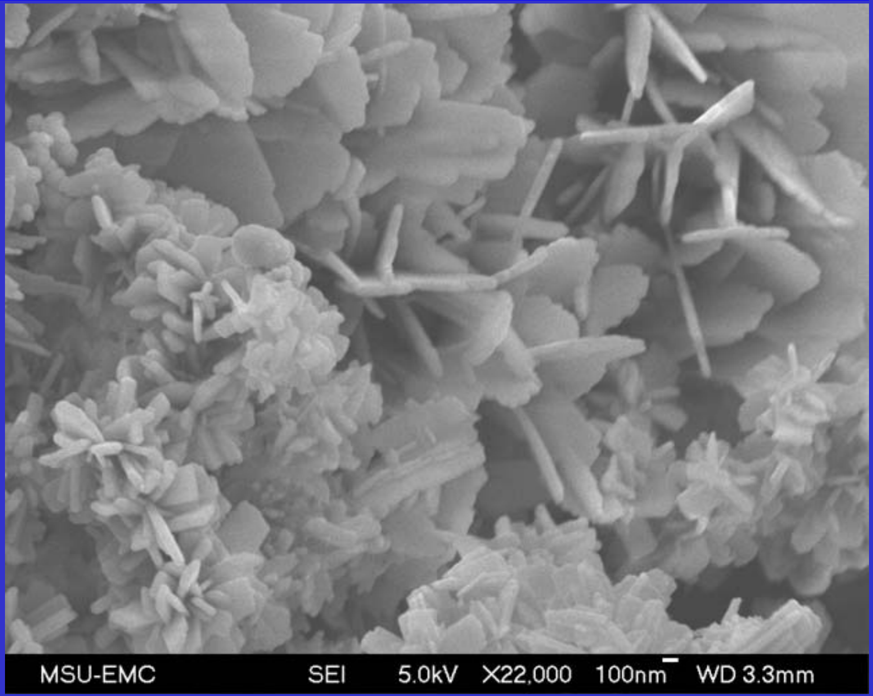
2909 ft water depth. Hydrate mound with carbonates in background. Situated on natural gas vents.

In-Situ hydrates from MC-118 help substantiate hypothesis of microbe/mineral/hydrate synergy

Hydrate from MC-118 for analysis

Photo. Mechanical arm of Research Submersible collecting hydrate from seafloor.

Microbes and clay platelets within seafloor hydrate. SEM



Hydrate melt, X22,000 magnified

Conclusions

1. Anionic (-) synthetic surfactants (ppm) promote hydrates on (+) metal surfaces in Lab.
2. Anionic biosurfactants and biopolymers promote hydrates on mineral nanoparticles, e.g., smectite clay platelets in seafloor.
3. Bioproducts influence rate of hydrate formation and possibly morphology.

Selected References

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