

# Marine Gels: Elucidating the DOM- POM Continuum

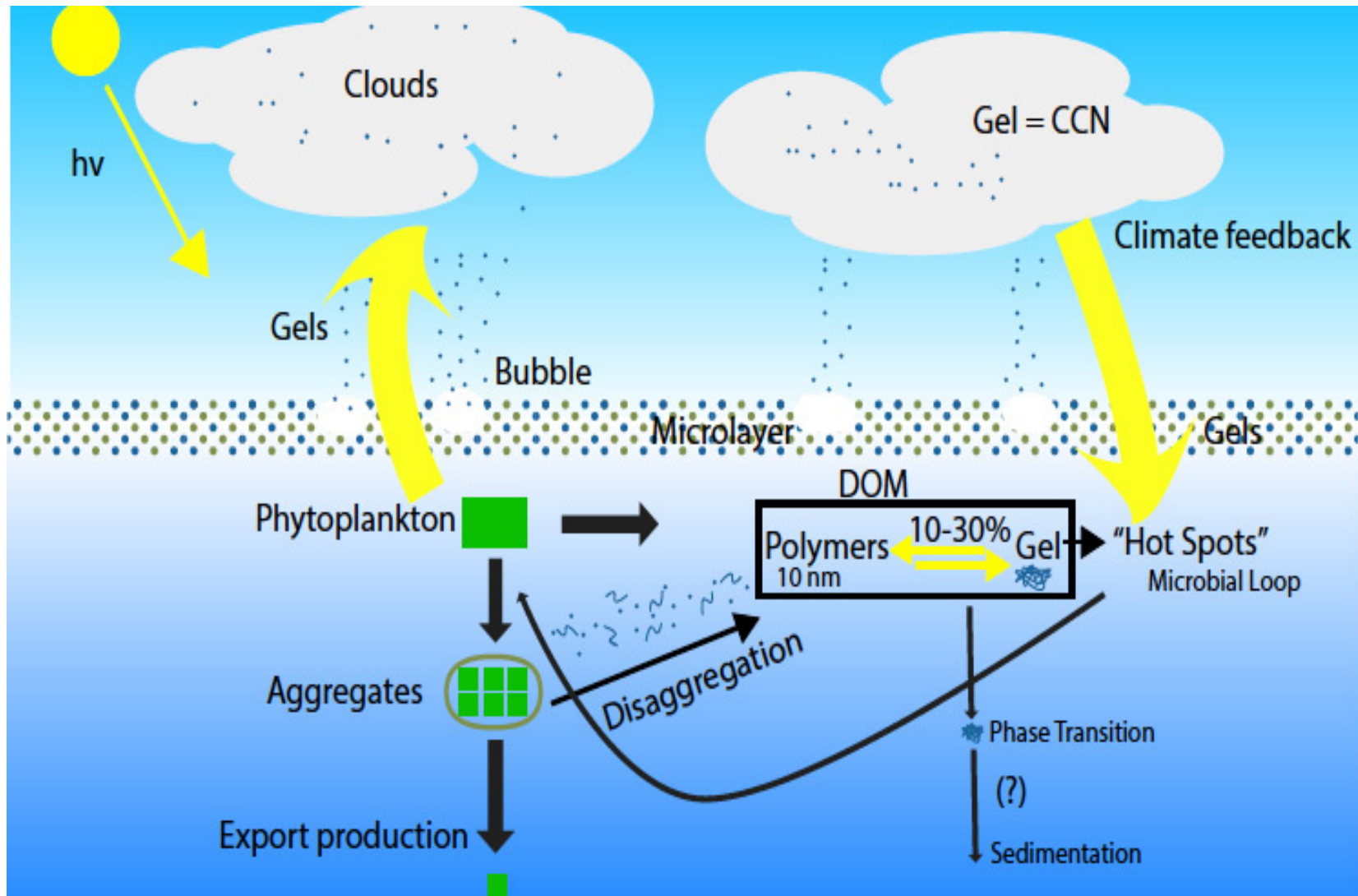


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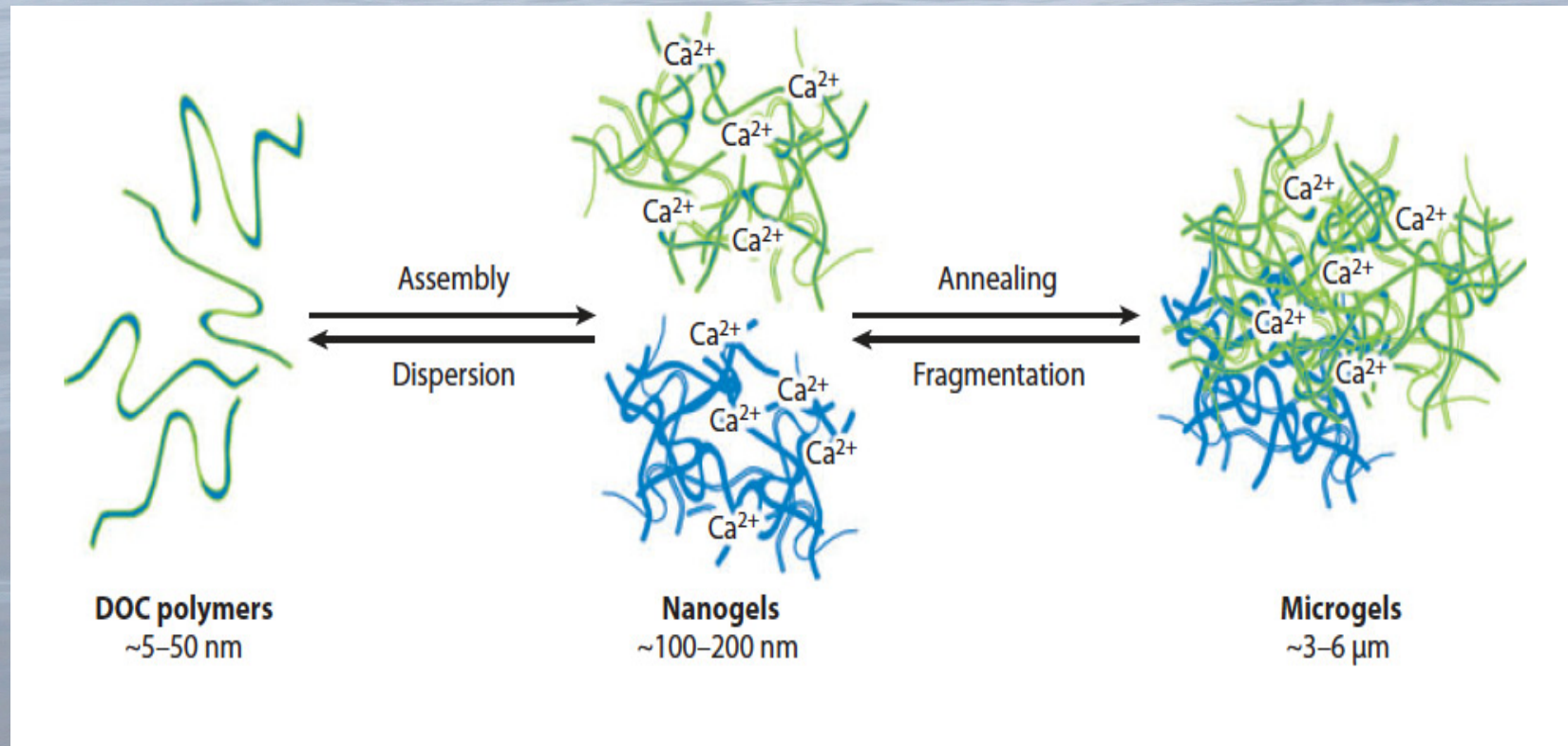
# Marine Microgels



Orellana and Leck, 2015

# The dissolved-particulate continuum

## Thermodynamic yield of assembly



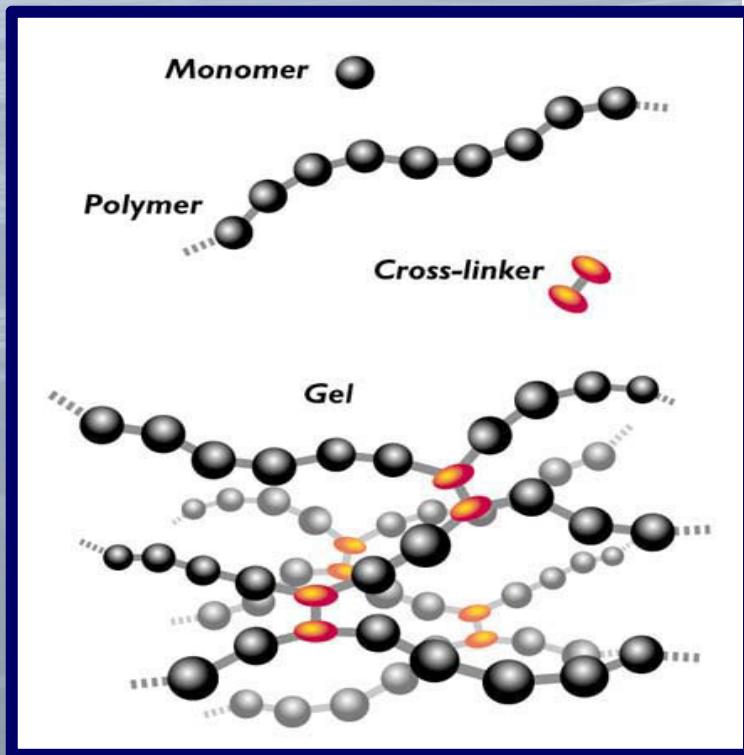
**DOC**

**POC**

Orellana and Verdugo, 2003  
Verdugo, 2012

# Dissolved Organic Matter

662 Pg C (Hansell et al. 2009)



Operationally defined

filter: 0.7, 0.45, 0.22 ( $\mu\text{m}$ )

Complex pool (mostly unknown)

carbohydrates,

proteins

lipids,

nucleic acids

metabolites

lignins

DOC/ DON/CDOM

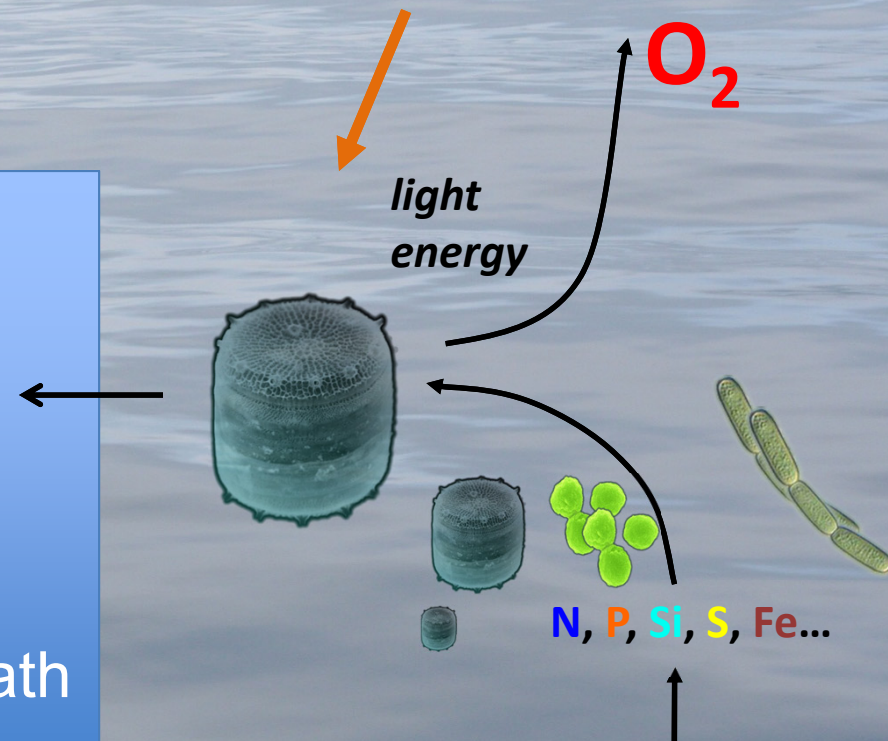
Sources (?) Sinks (?) Dynamics (?)

Role of polymers (?)

Primary Production: 48.5 PgC  
(20-50% ) released as DOM

## Processes: DOM

Extracellular release  
Viral lysis  
Regulated secretion and exocytosis  
Apoptosis, programmed cell death  
Grazing  
Dissolution of large particles

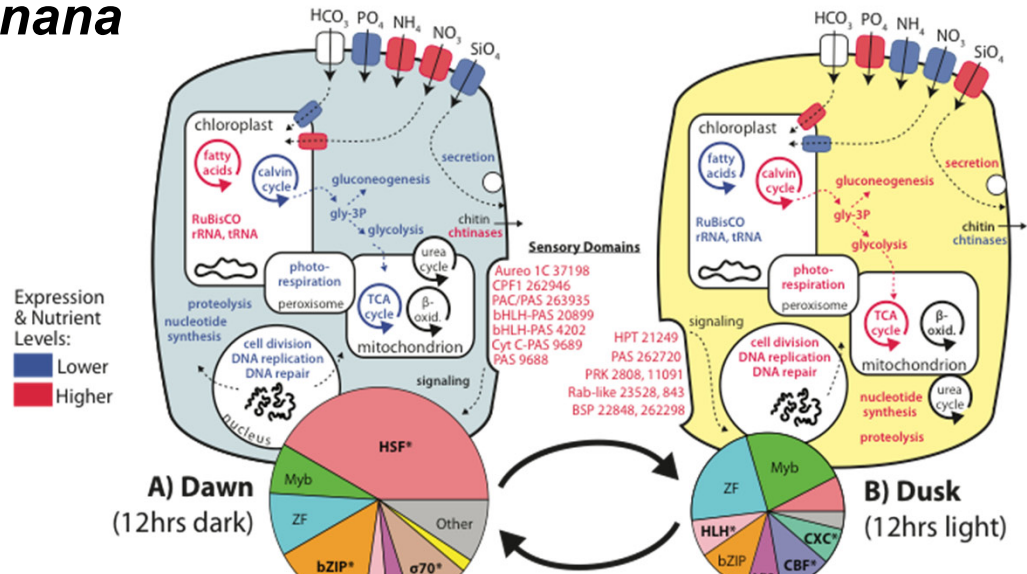


# Mechanisms of biopolymer production by phytoplankton and bacteria

<u>Process</u>	<u>Reference</u>
Direct release	(Decho, 1990),
Viral lysis	(Suttle, 2007; Vardi et al., 2012),
Apoptosis and programmed cell death	(Berman-Frank et al., 2004; Bidle & Falkowski, 2004; Orellana et al., 2013), Biddle 2015.
Microbial degradation of POM	(Nagata and Kirchman, 1997),
Grazing	(Strom, 2008; Strom et al., 1997),
Zooplankton sloppy feeding	(Jumars et al., 1989),
Particle dissolution	(Azam and Long, 2001; Carlson, 2002b; Kiørboe and Jackson, 2001; Nagata et al., 2010; Smith et al., 1992),
Vesicle production and regulated exocytosis	(Biller et al., 2014; Chin et al., 2004)

# Can we predict polymer production?

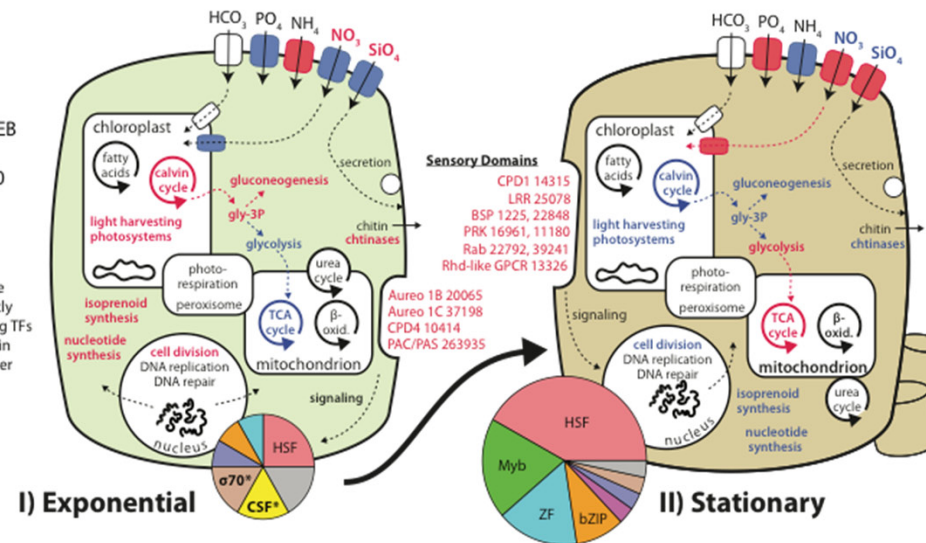
## *T. pseudonana*



### Transcription Factors

- HSF
- Myb
- ZF
- bZIP
- HLH
- AP2\_EREB
- CBF
- Sigma70
- CXC
- CSF
- Other

\*: denotes gene class significantly enriched among TFs with increased in expression under this condition

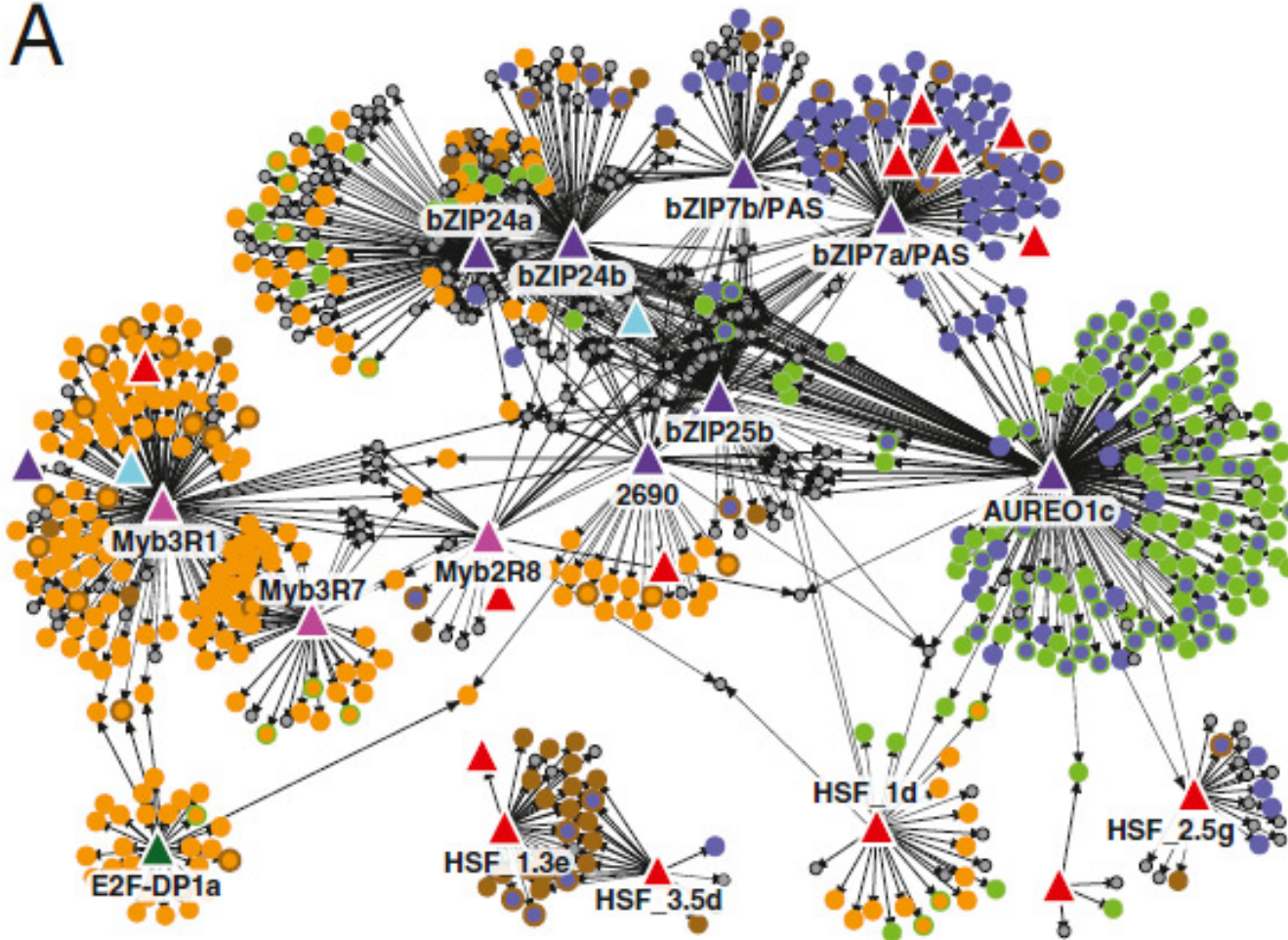


Replete nutrients

Limiting nutrients

# *Thalassiosira pseudonana*

A



Expression states:

- Dawn (12hrs dark)
- Dusk (12hrs light)
- Exponential
- Stationary
- Dawn (dark) & Exponential
- Dusk (light) & Exponential
- Dawn (dark) & Stationary
- Dusk (light) & Stationary

B

TF Family: TFBS searched:

- |        |                         |
|--------|-------------------------|
| ▲ HSF  | GAAN <sub>1-3</sub> TTC |
| ▲ Myb  | GGTAGGTGG               |
| ▲ bZIP | GATGACGTGGC             |
| ▲ AP2  | TGGCGCTCA               |
| ▲ E2F  | TTCCGCGC                |

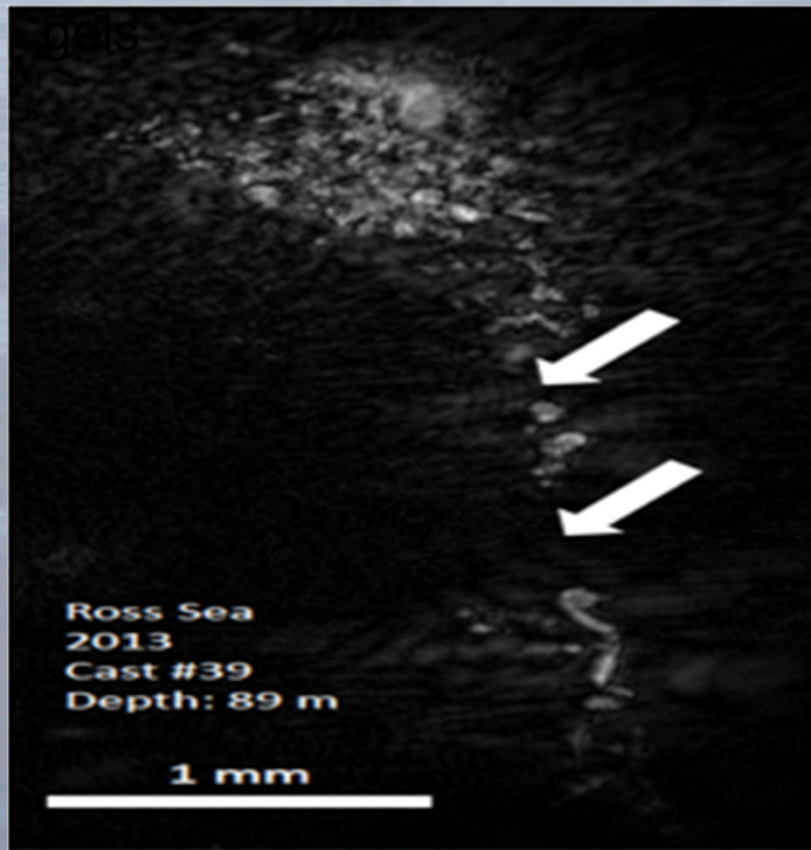
Inferred gene regulatory relationships

Ashworth et al. PNAS 2013

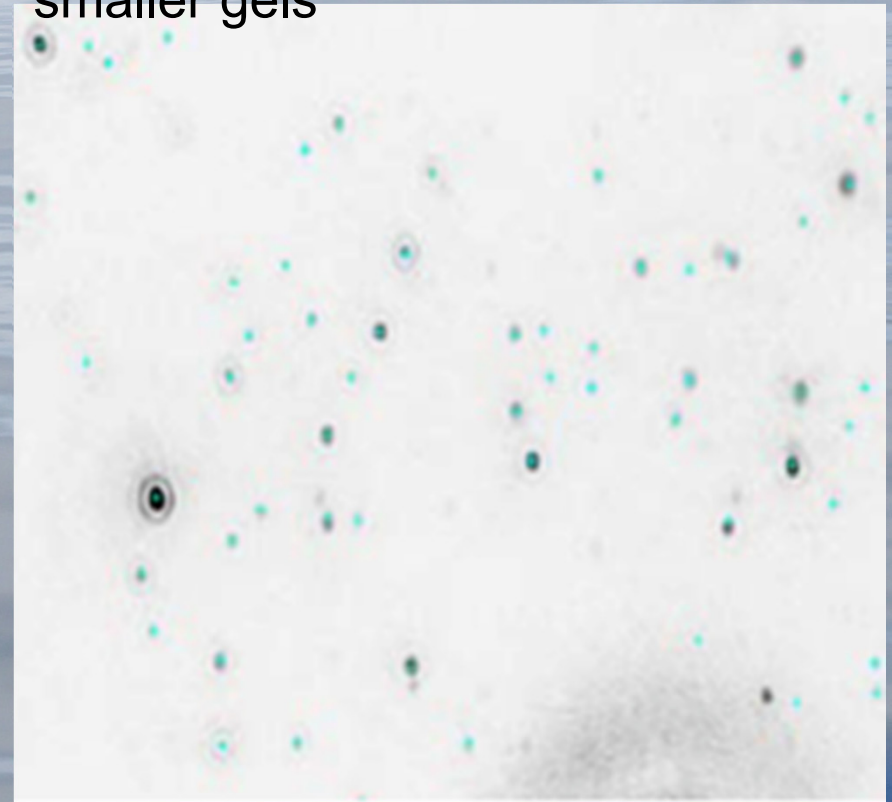


# DOC- POC continuum is influenced by the community structure and metabolic state

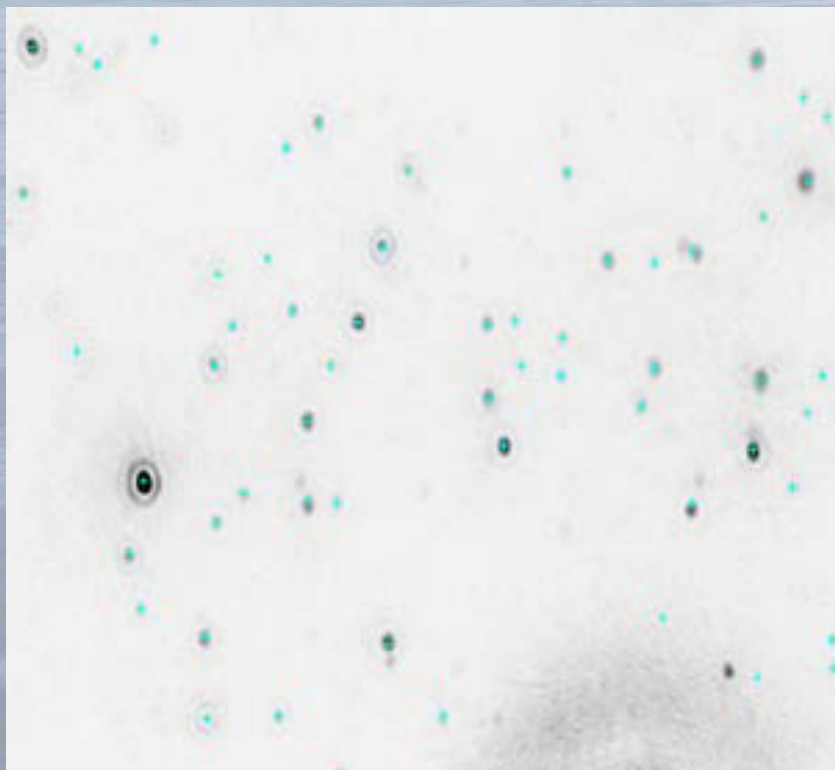
Southern Ocean diatom communities produces larger gels



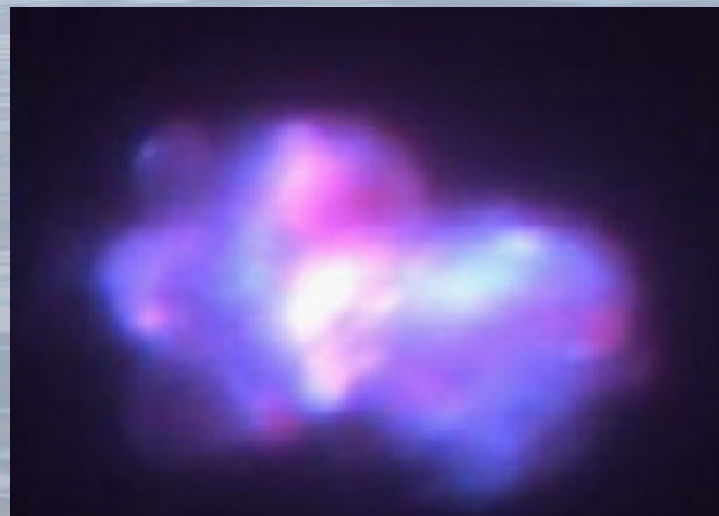
Cyanobacteria and other prokaryote communities produce smaller gels



# How do gels assemble?

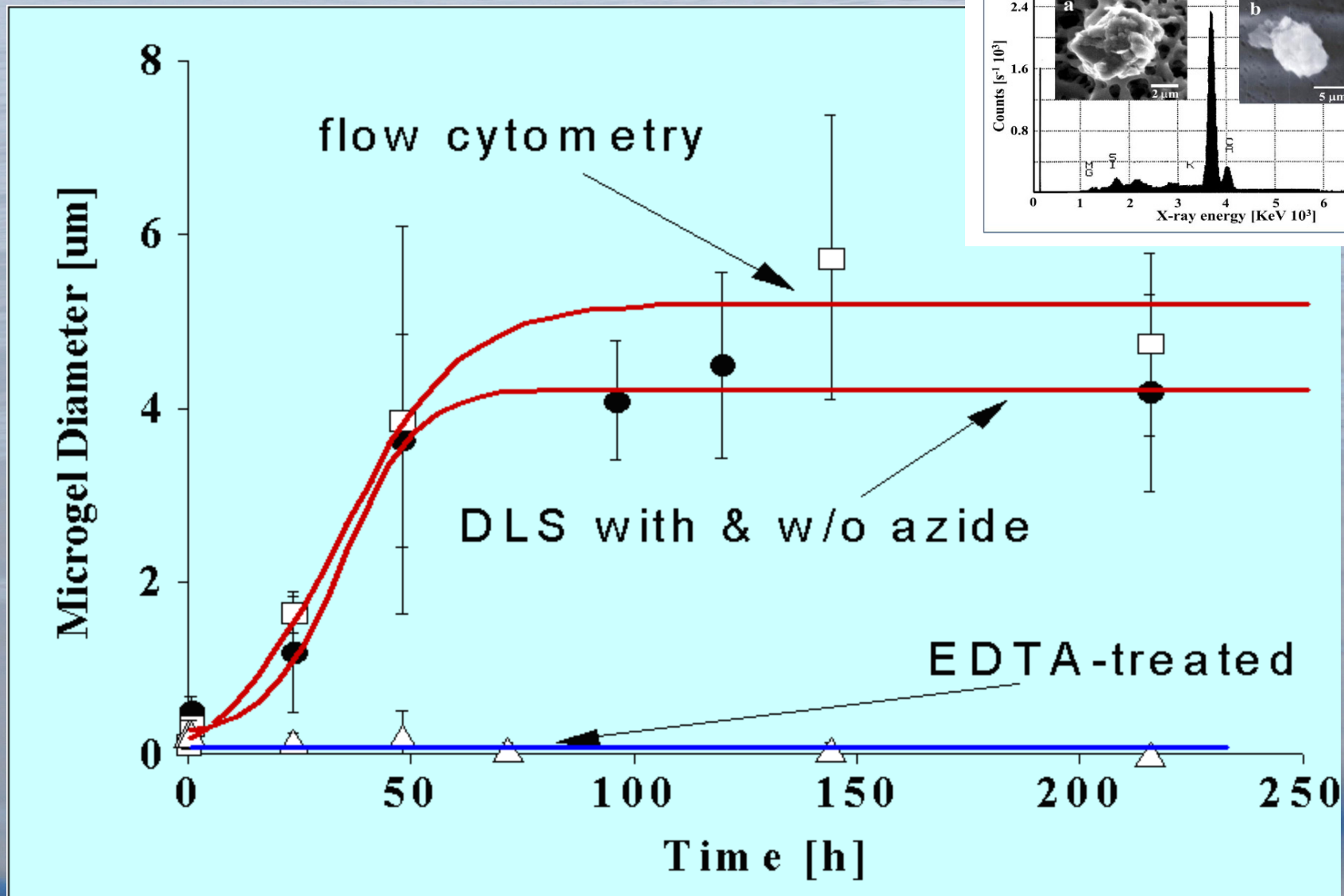


Nanogels  
(20nm)



Microgel  
( $\mu\text{m}$ )

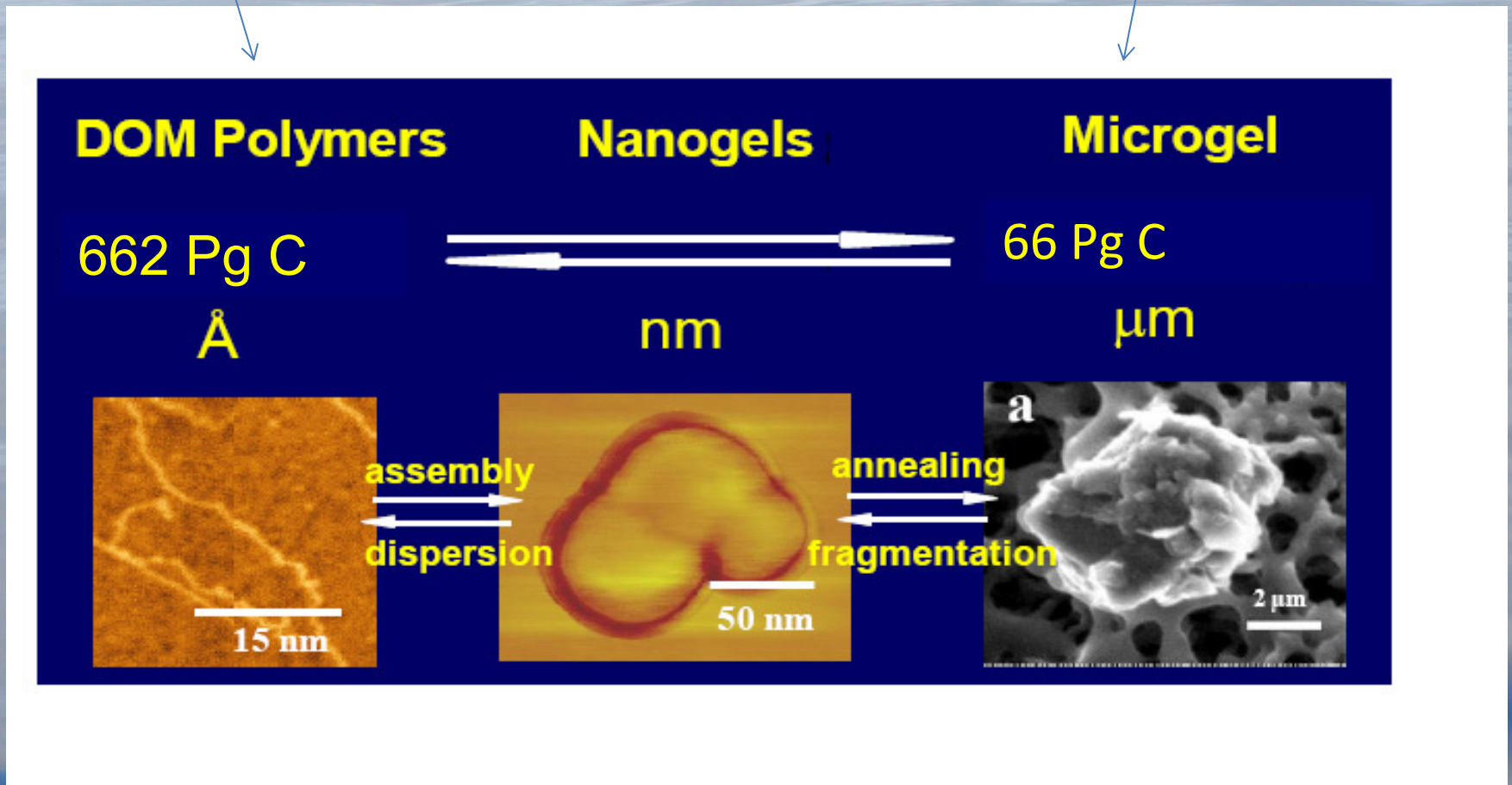
# Microgel spontaneous assembly



Chin et al., 1998 Nature

Atomic Force  
Microscopy

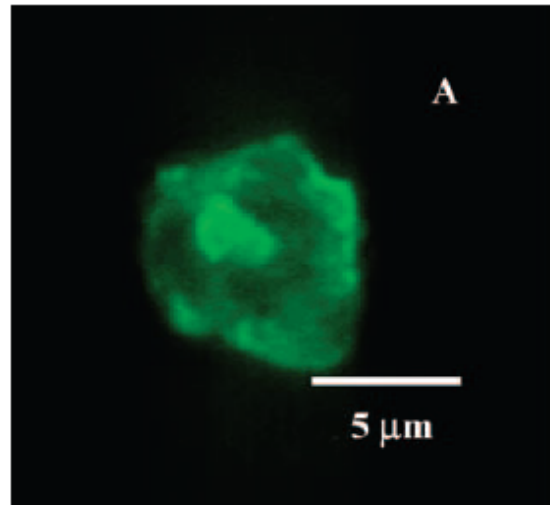
ESEM (environmental  
scanning  
electron) microscope)



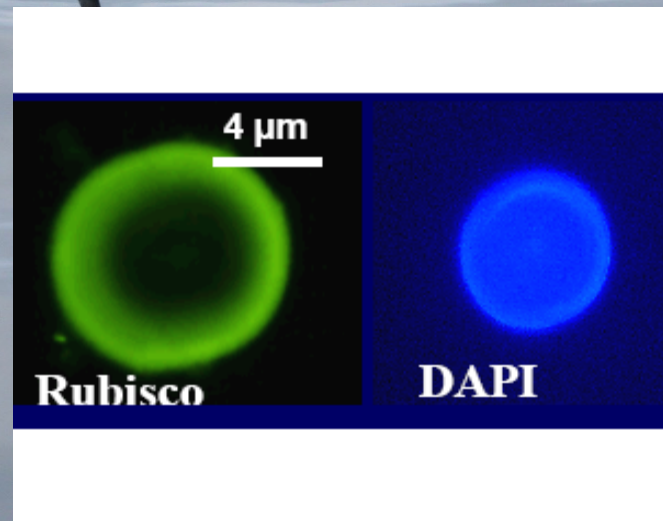
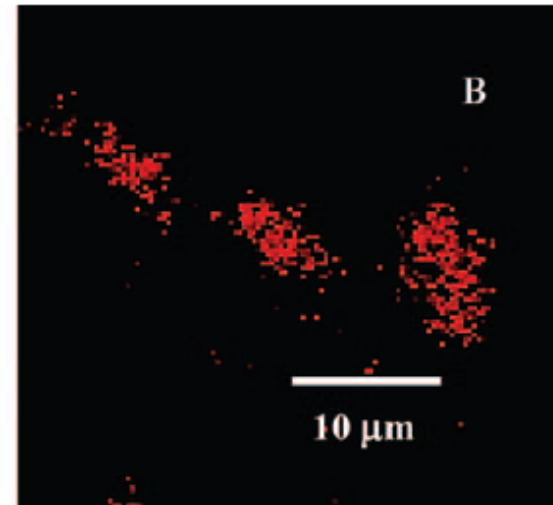
Verdugo and Santschi, 2010

# Chemical composition

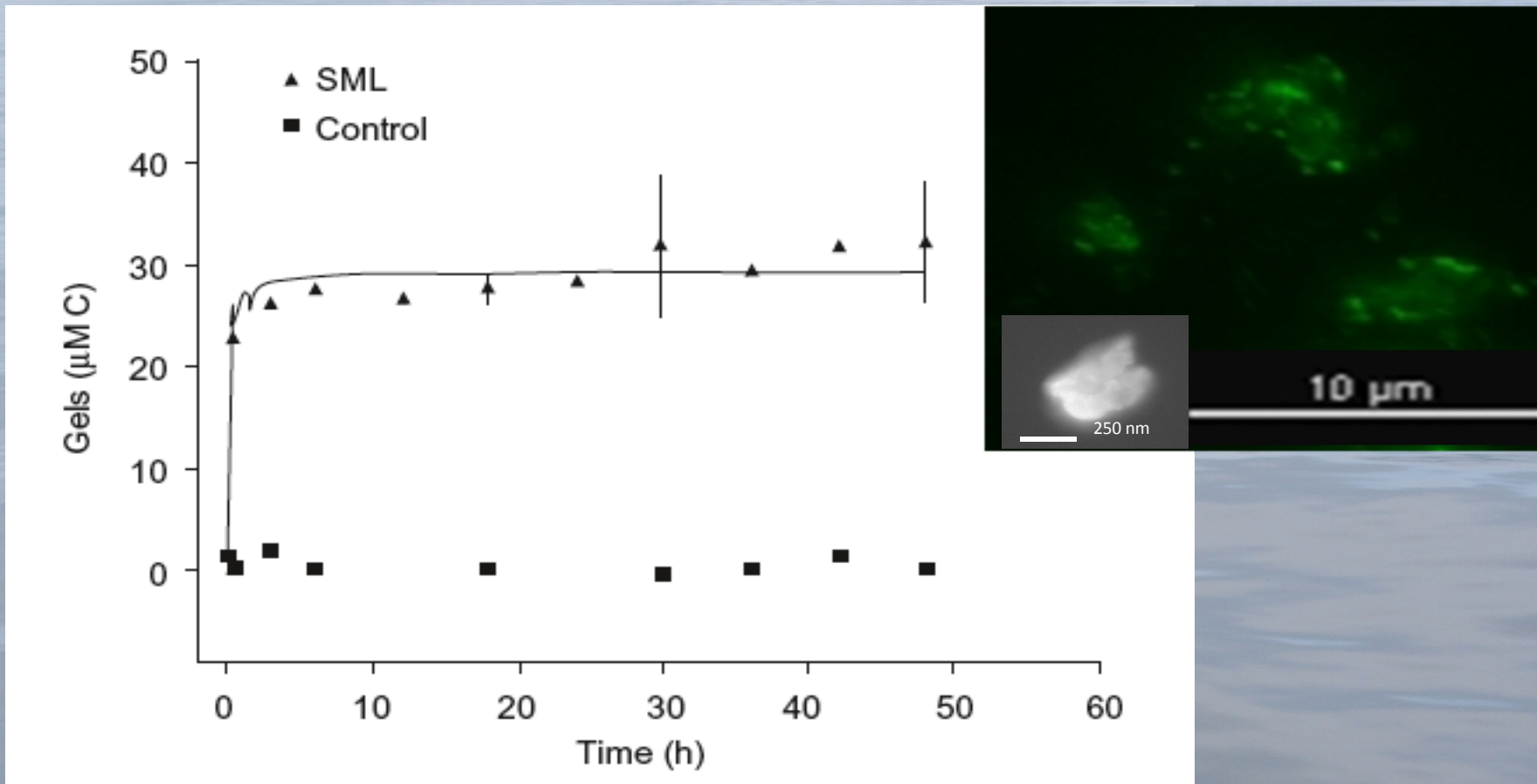
Chlortetracycline



Nile Red

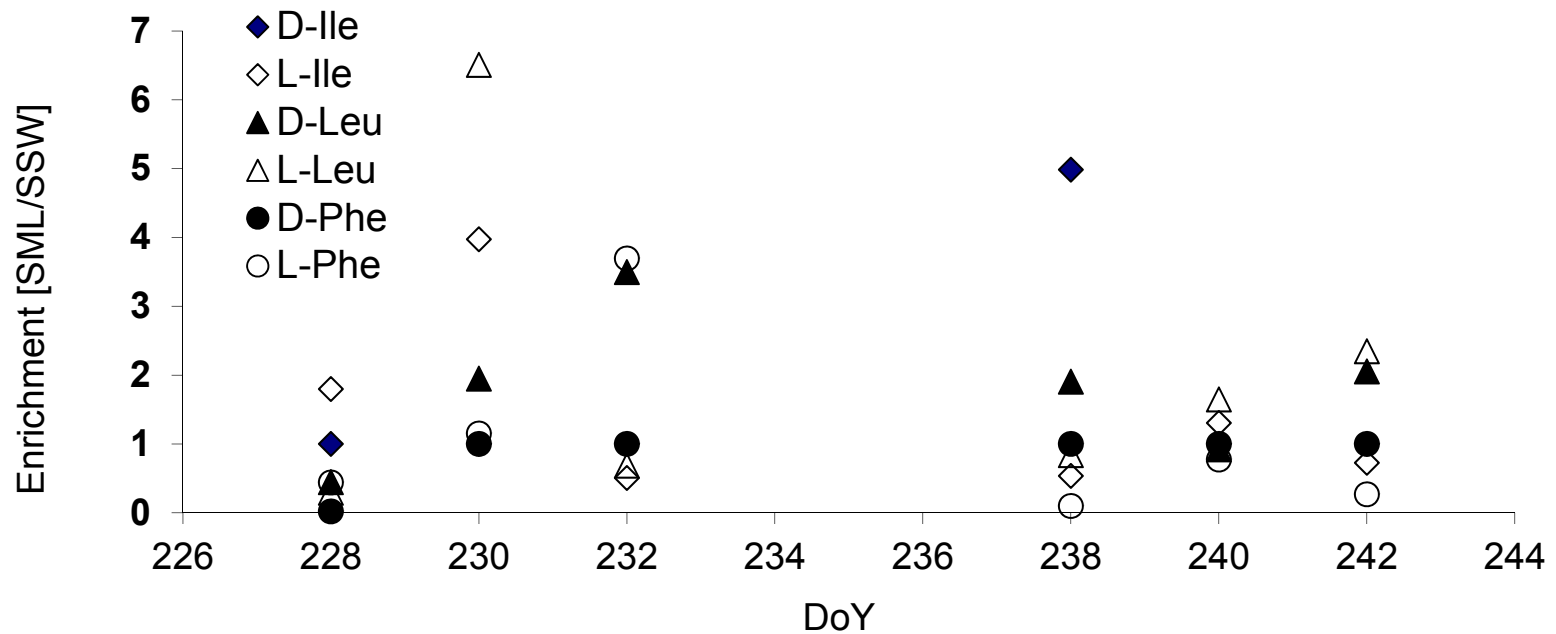
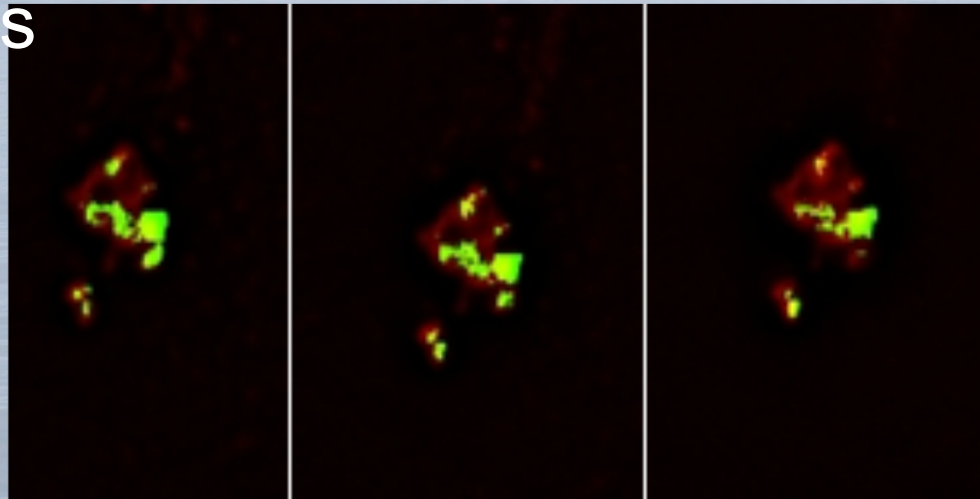


# Does the polymer composition affect assembly?

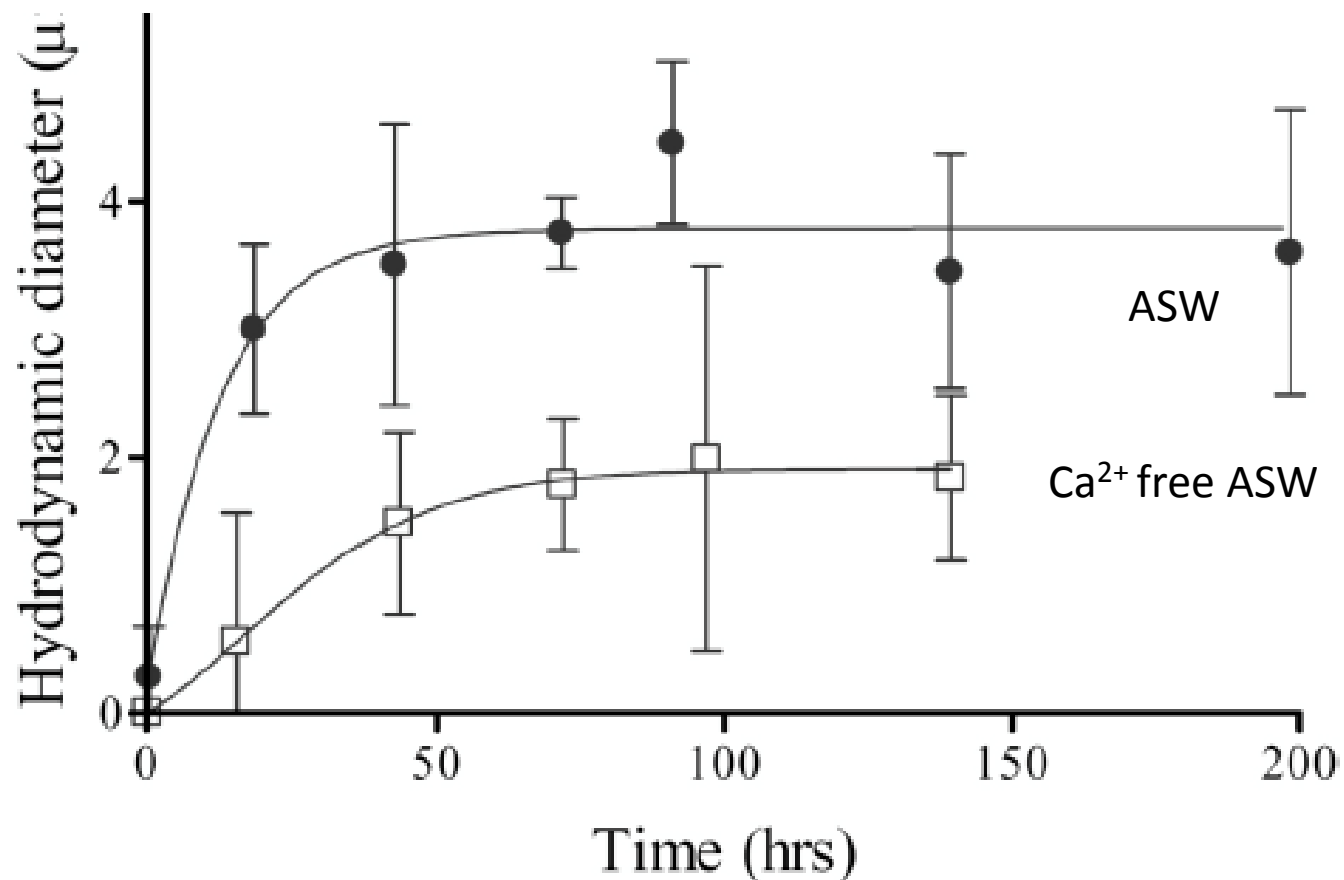


Polymer assembly as a function of time in the high Arctic surface waters (87-88°N, 2-10°W).

# Hydrophobic moieties in polymer gels

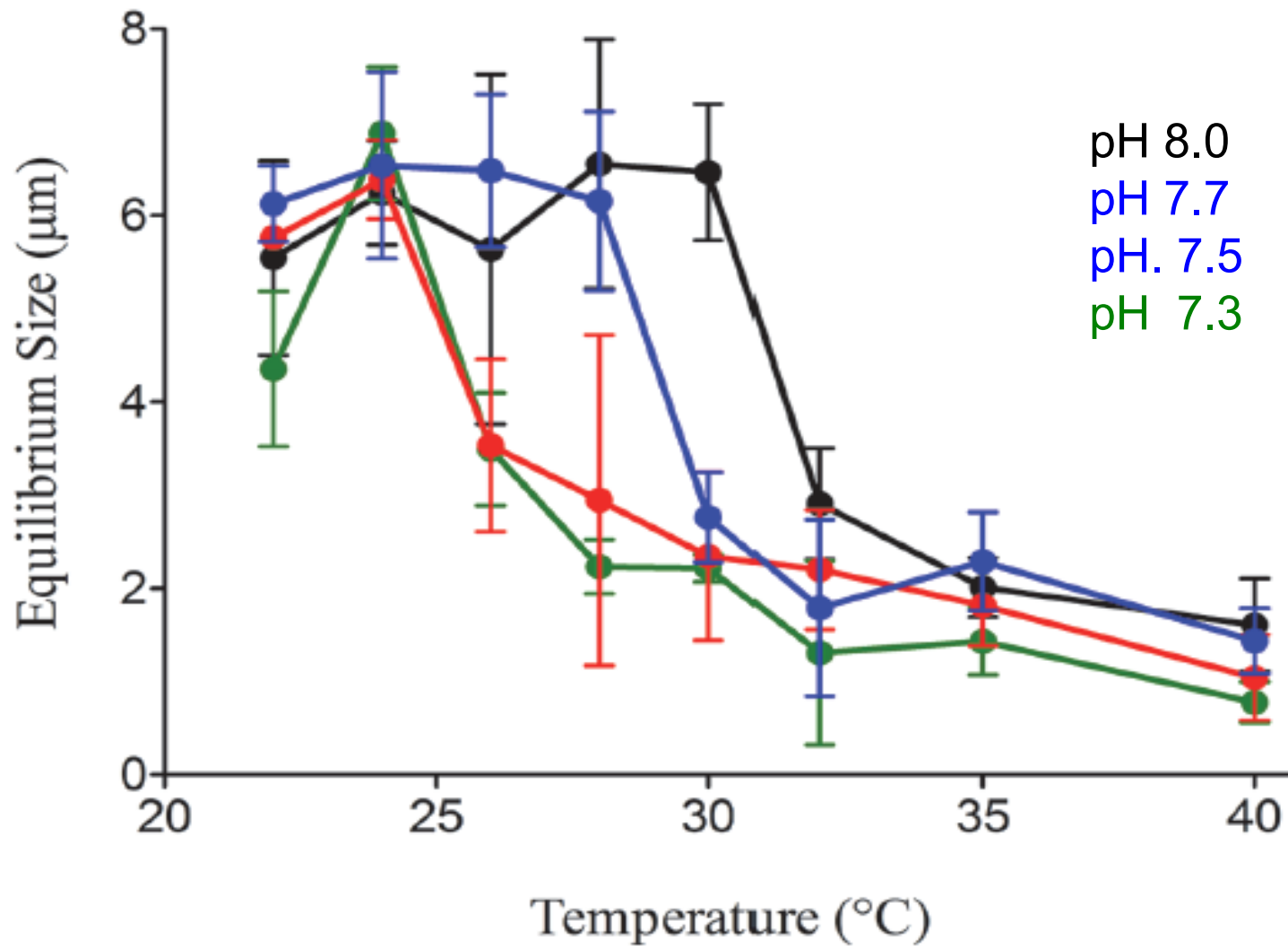


## Spontaneous assembly: hydrophobic moieties in *Emiliana huxleyi*

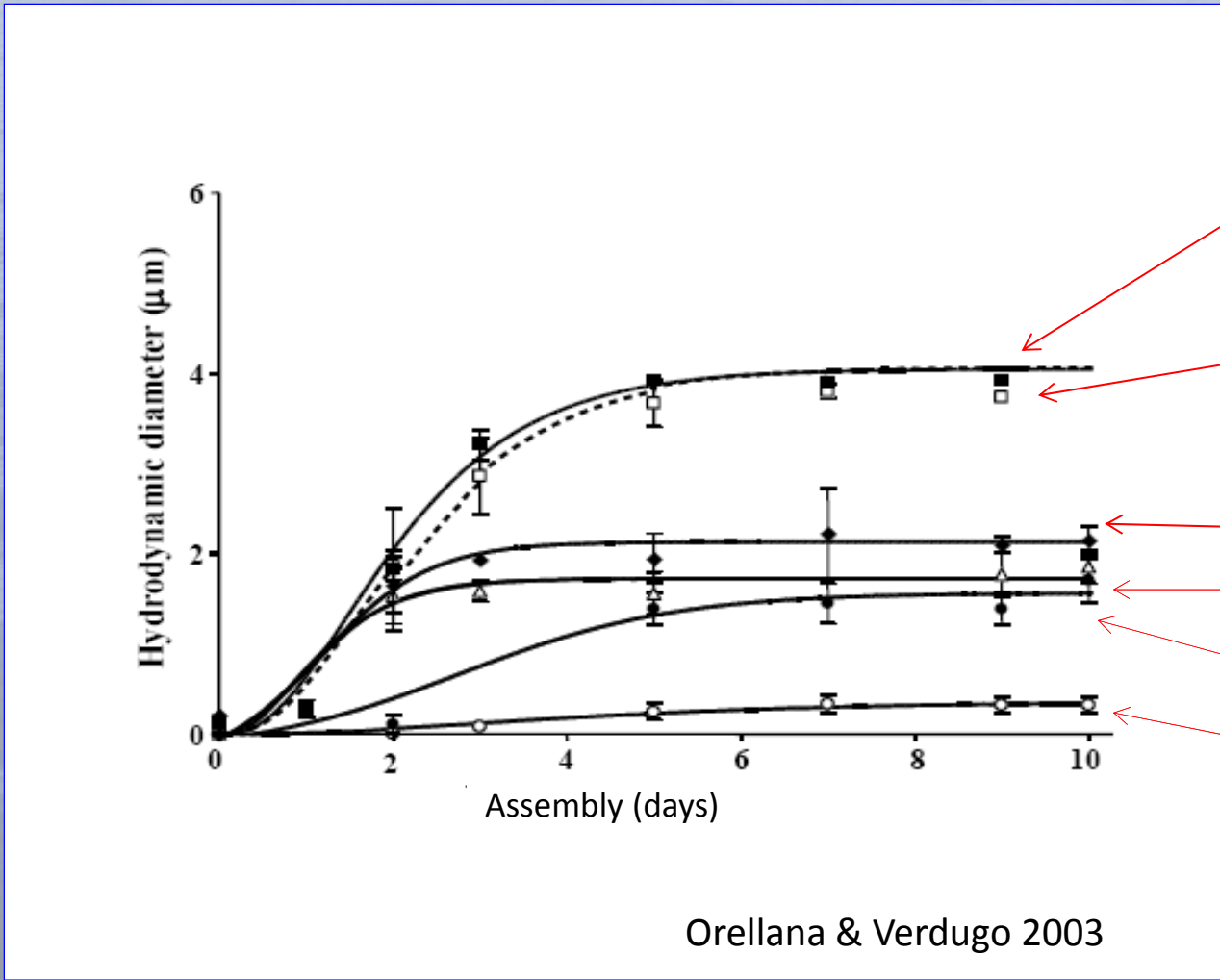




# Dispersion of microgels: synergistic effect of pH and temperature



# Does polymer size matter?



Non radiated

24h UV A

30min UV B

6h

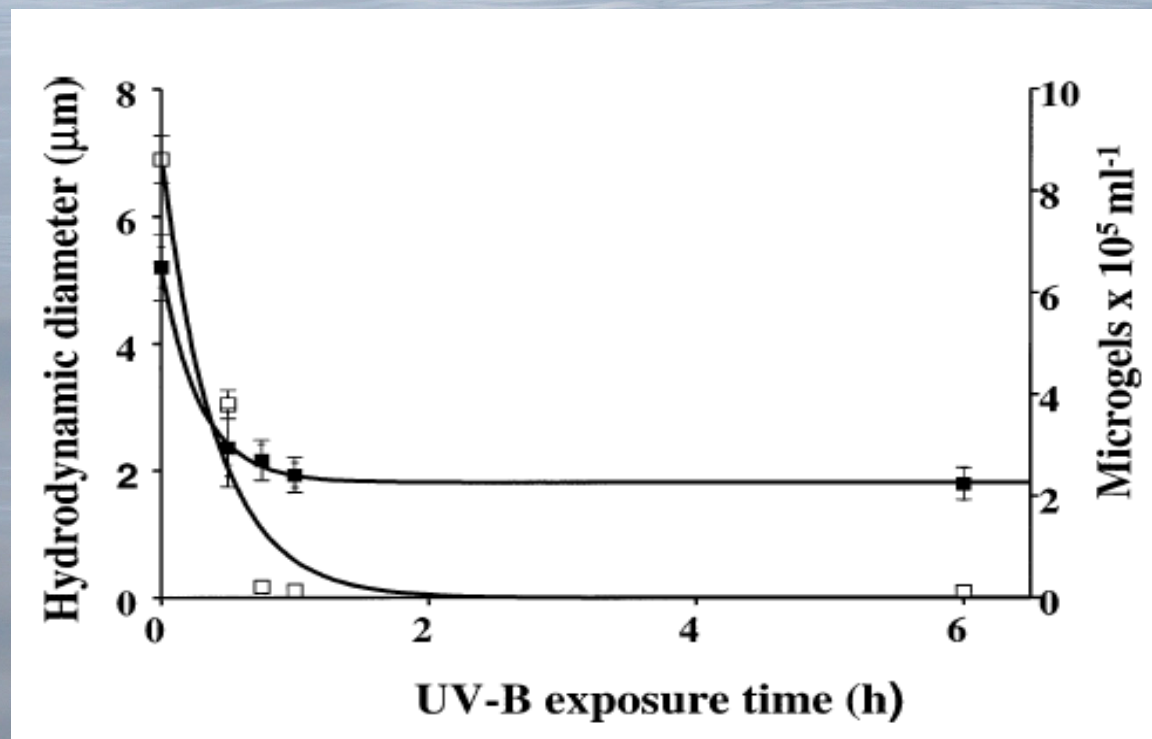
12h

24h

Assembly of marine polymers degraded by UV light exposure

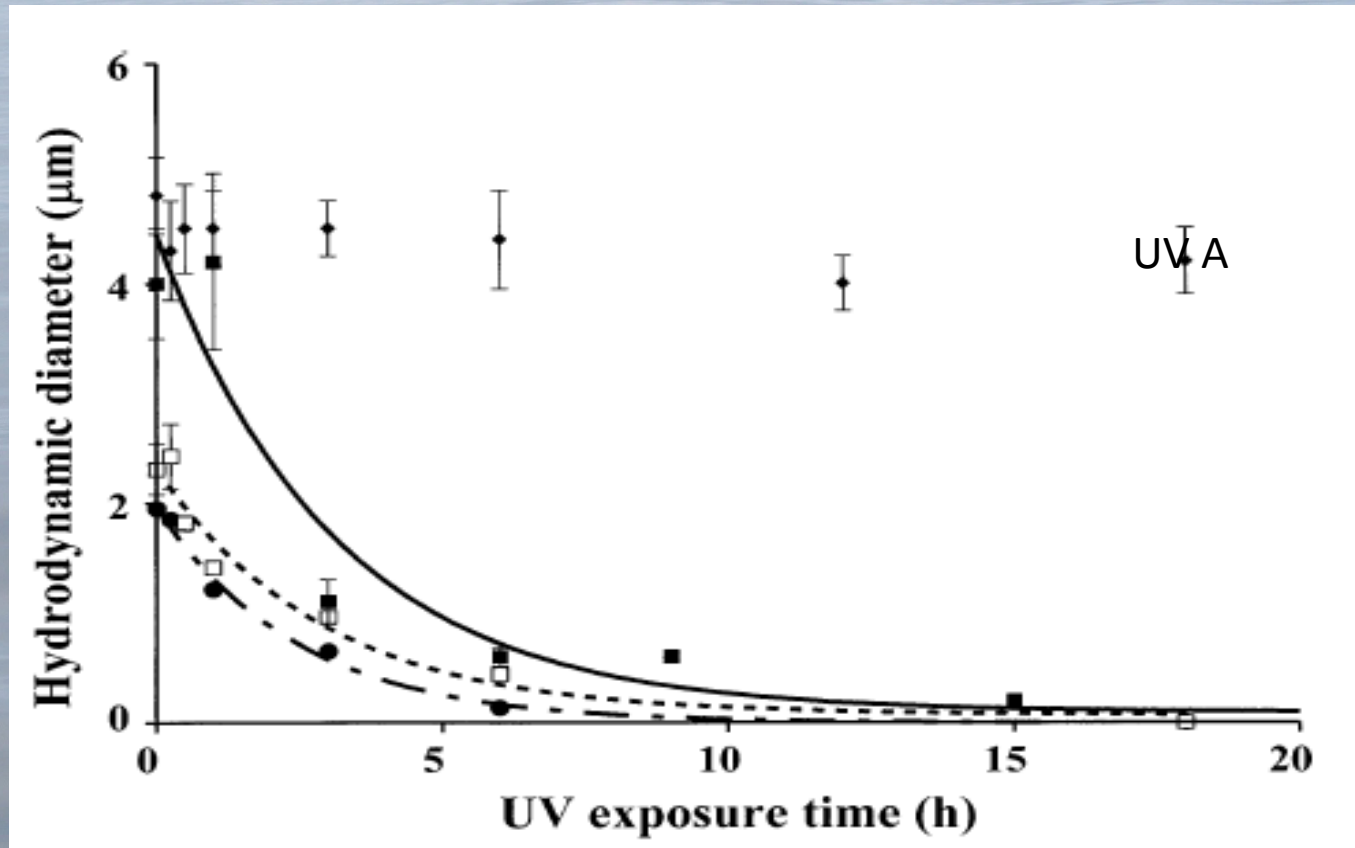
Orellana & Verdugo 2003

Equilibrium polymer size of assembly and concentration of microgels decreases exponentially when irradiated with UV



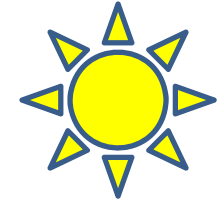
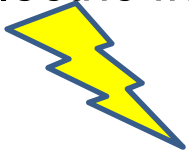
Orellana & Verdugo, L&O 2003

# Exponential decrease of microgels with UVB exposure



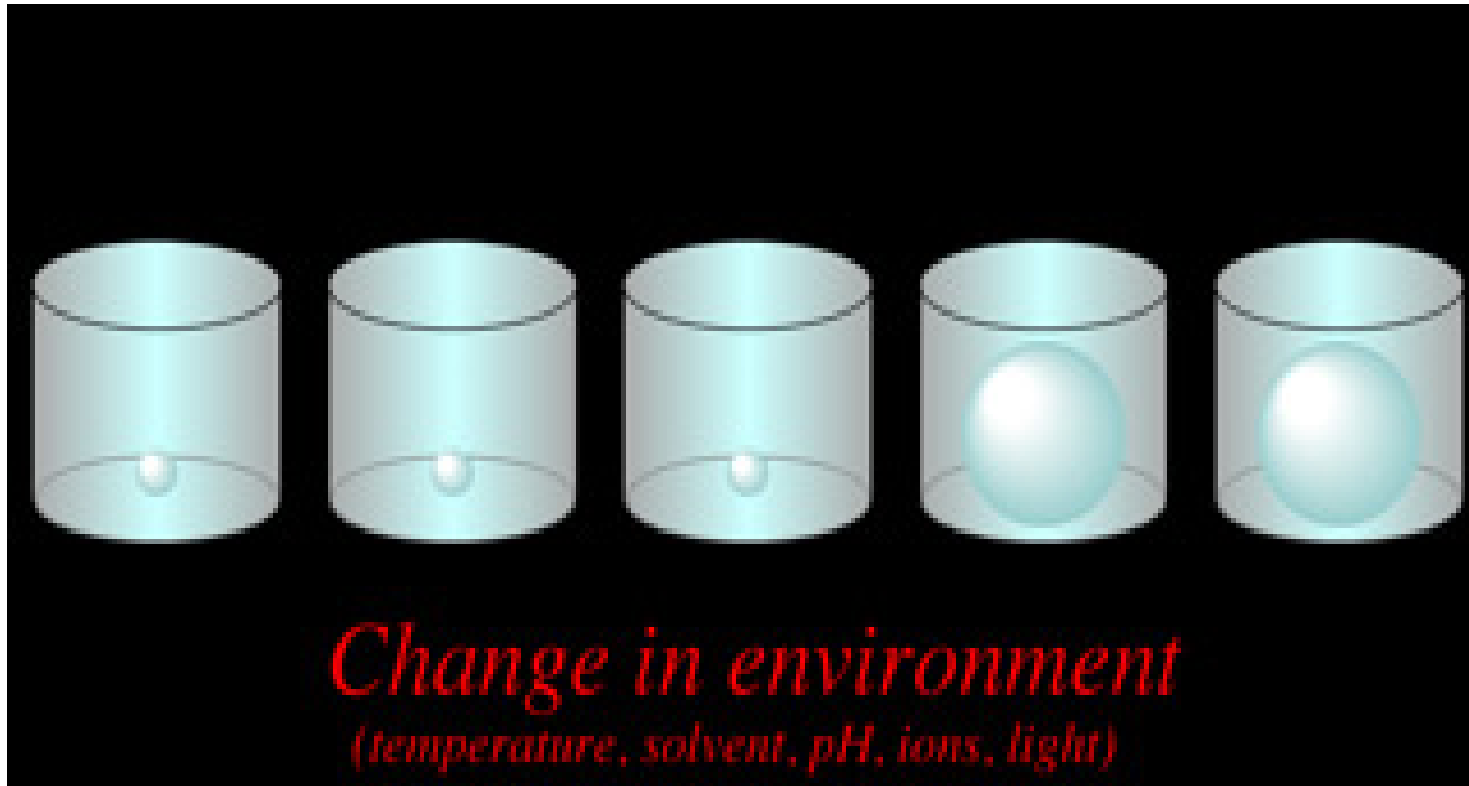
# Volume phase transition

Electric field



light

pollutants



Heat



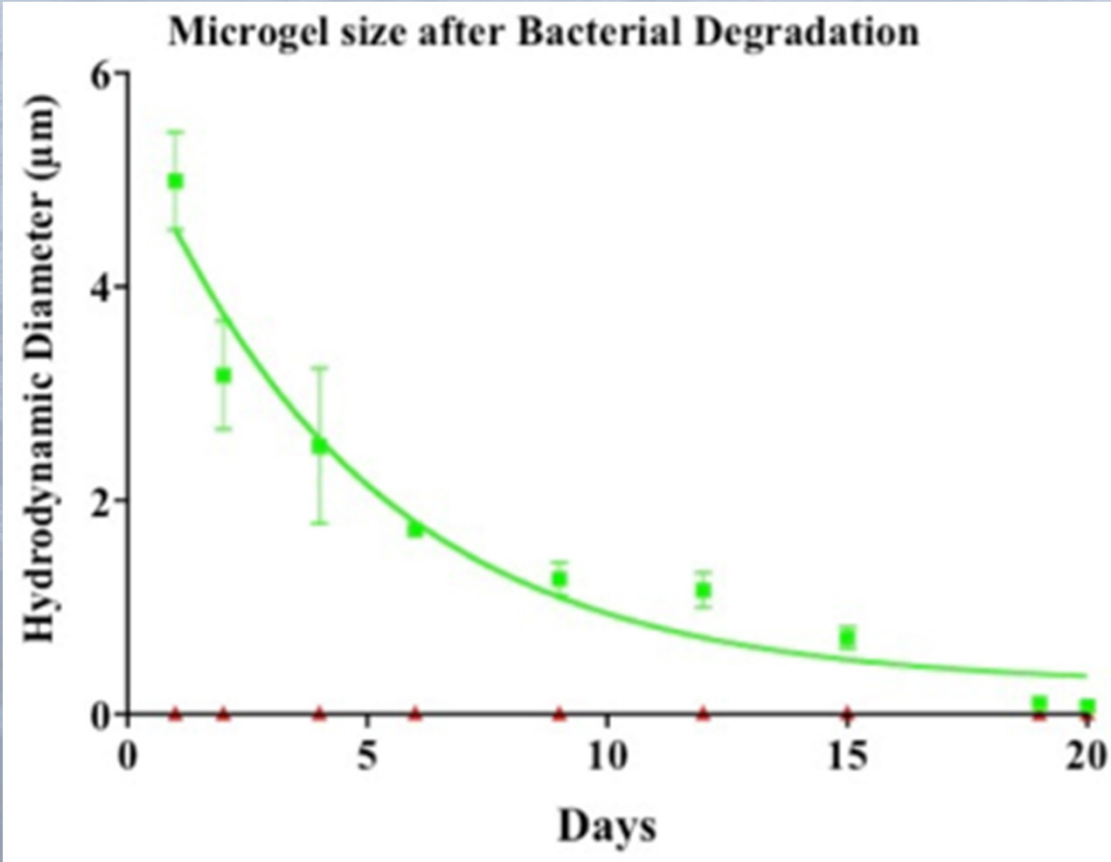
Biochemicals

Ions and pH



T. Tanaka, 1993

# Bacterial degradation



Assembly of microgels after microbial degradation (Orellana et al. unpub.)

South Atlantic

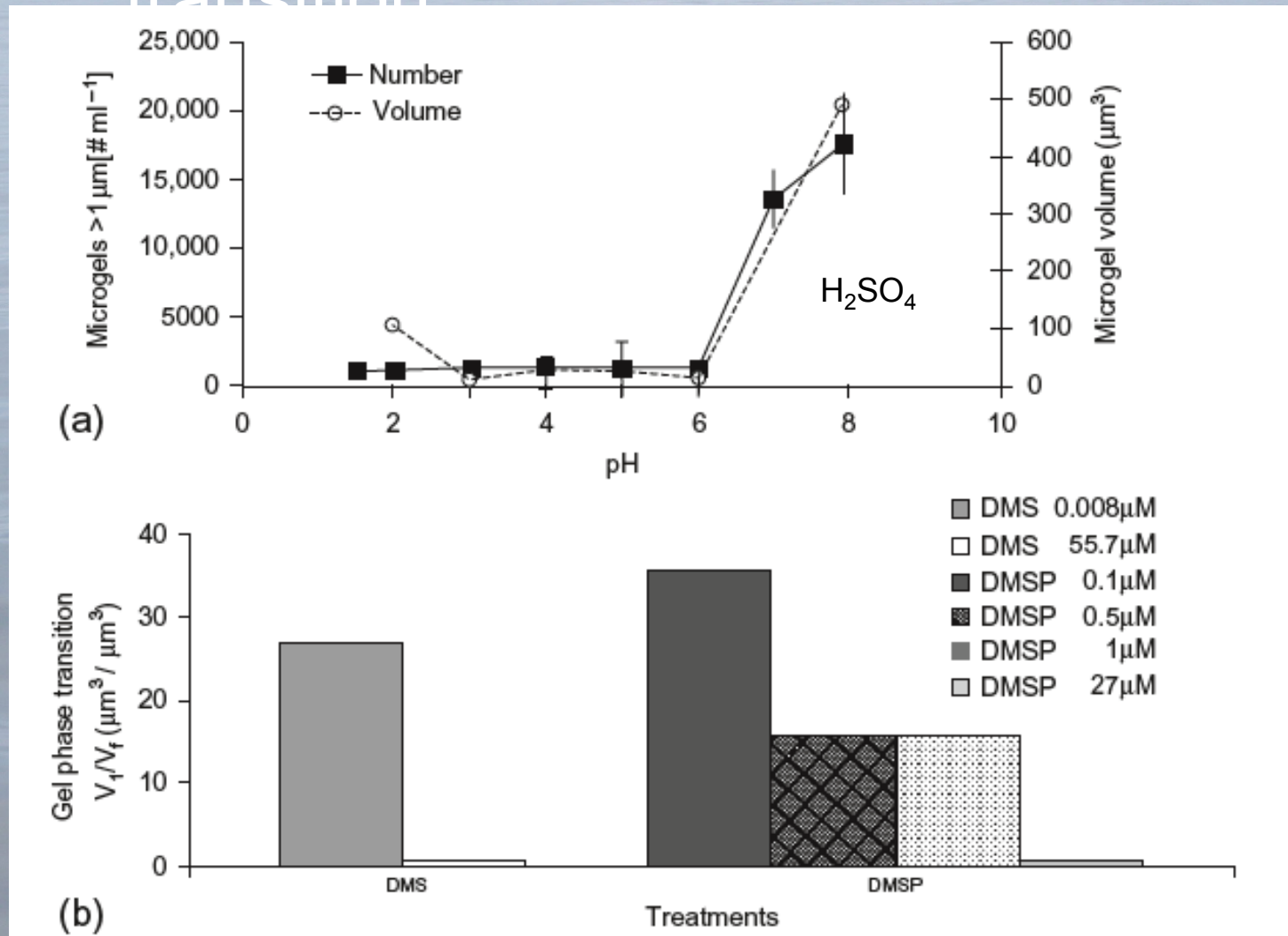
500m

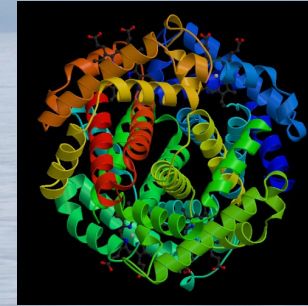
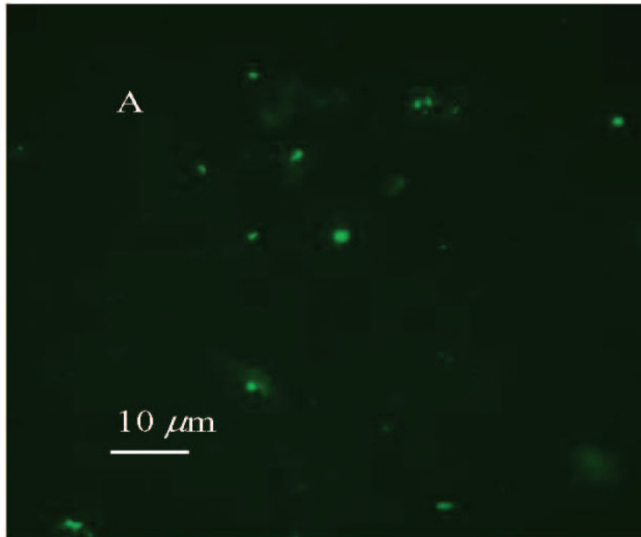
1000 m

4000 m

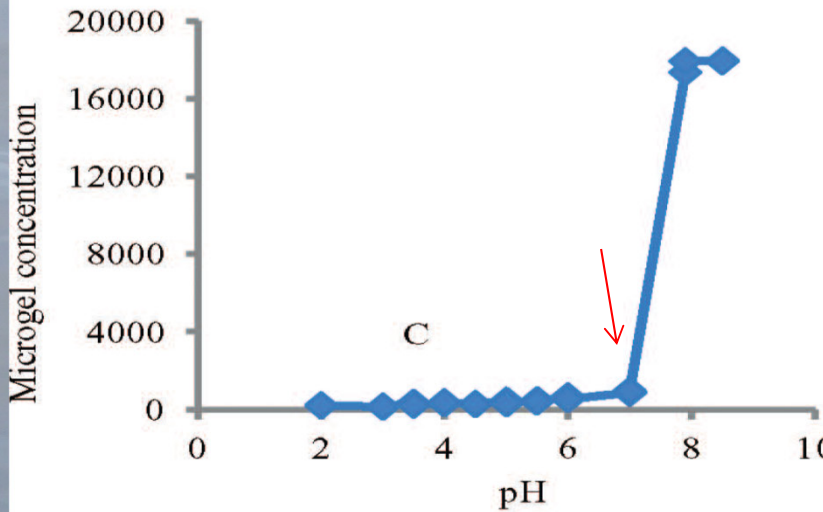
Ditt et al., submitted

# Microgel volume phase transition



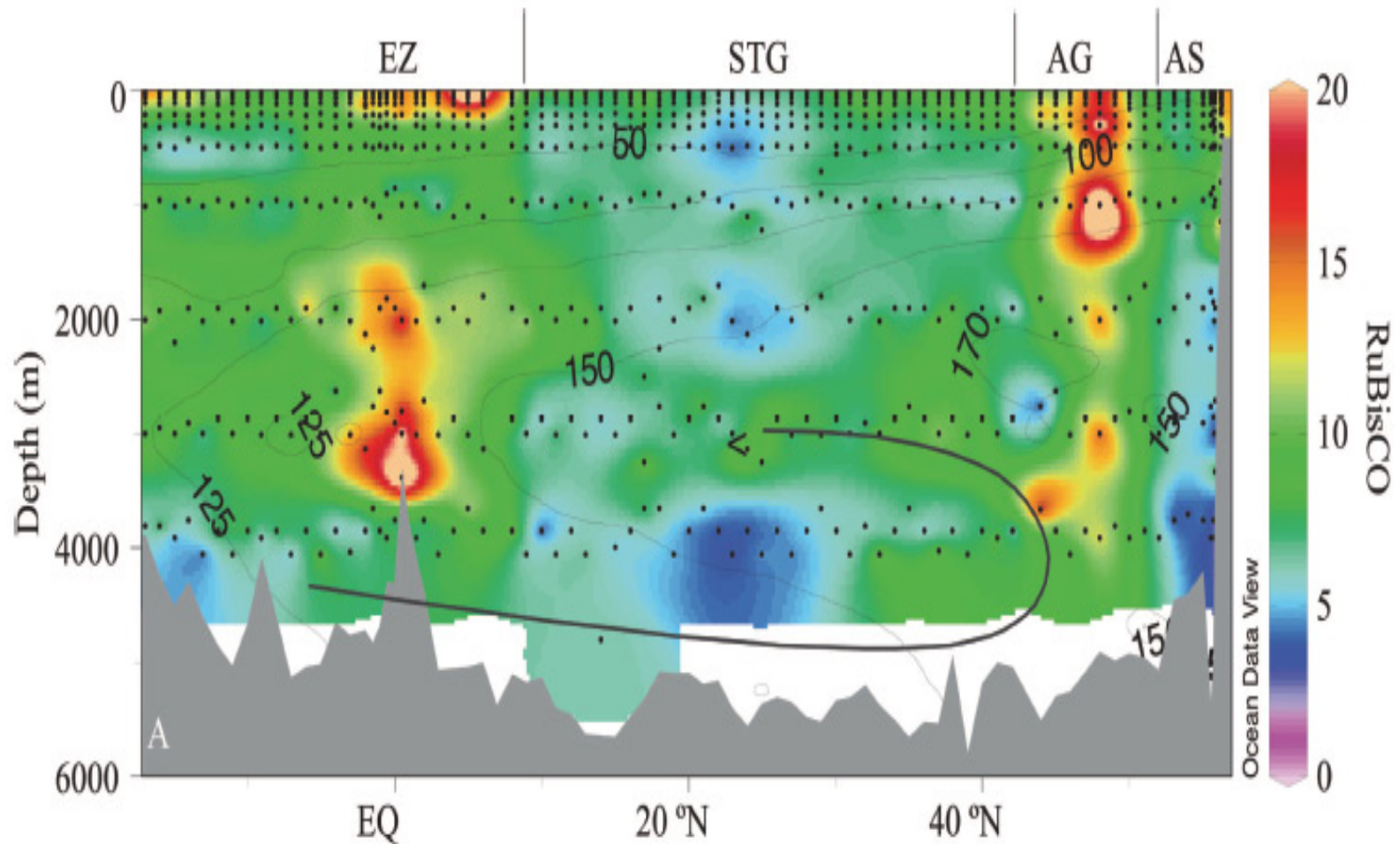


## RuBisCO Microgels Deep Pacific Ocean (3000m)





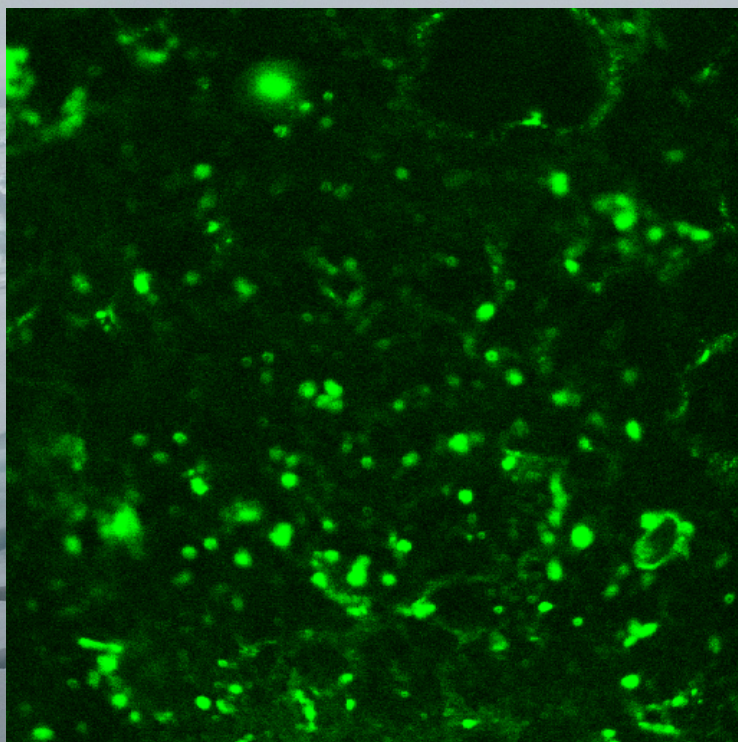
# RuBisCO in the deep Pacific Ocean



Orellana & Hansell 2012

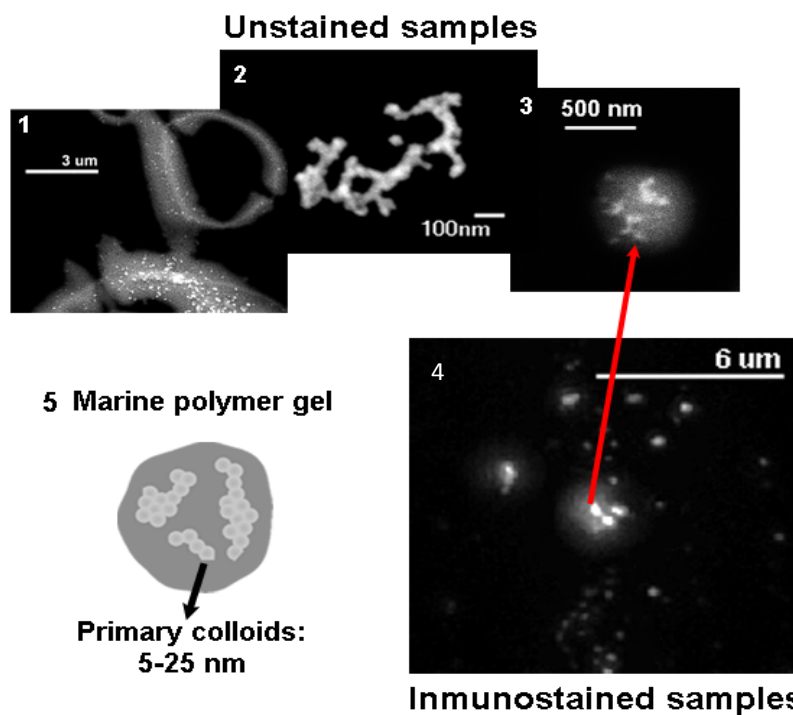
# Microgels in clouds, fog and aerosol particles.

Immunostained cloud microgels



Confocal microscope

Field Emission Scanning microscope



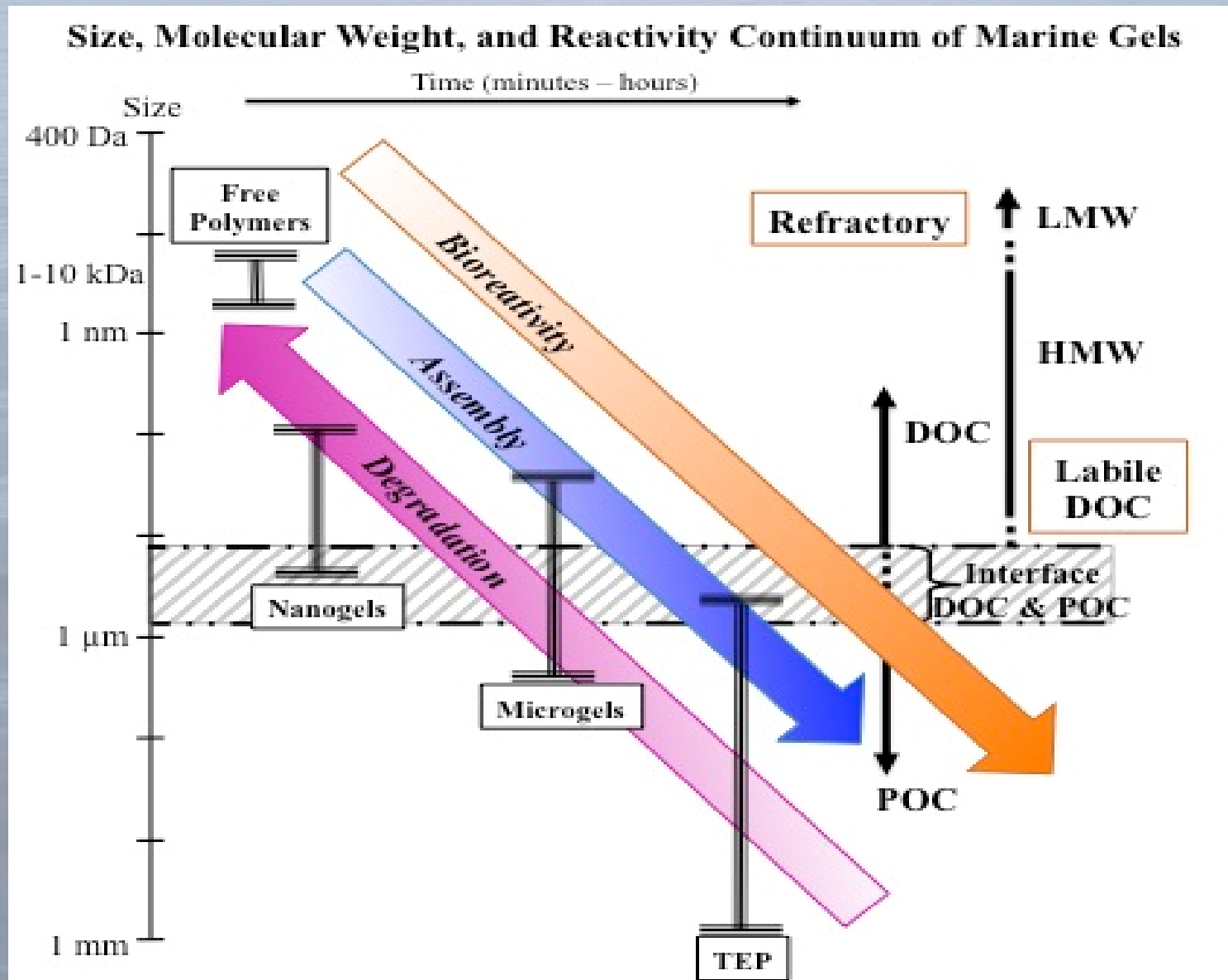
Tangled nanometer sized gels

Fractal structure

## Properties of gels versus solid colloids: Characteristic Features and Reactions

	Gels	Other
Structural units bend, fold, reptate and intertwine	Yes	No
Internal dielectric properties different from the bulk	Yes	No
Non-Newtonian Rheology & porous structure	Yes	?
Defined internal topology of their polymer network	Yes	?
Defined mechanisms of assembly and stability	Yes	No
Defined kinetics of assembly/dispersion and swelling	Yes	No
Characteristic polymer gel phase transitions	Yes	No
Defined ion (Donnan) and hydrophobic partition properties	Yes	No

# DOM-POM continuum



Adapted from Verdugo et al.

# Elucidating the DOM-POM Continuum

- Soft matter physics allows understanding structure and dynamics of DOC biopolymer
- Assembly: explains formation of particles in seawater
- Emergent properties (phase transition) explain chemical landscape

# Thank you!

