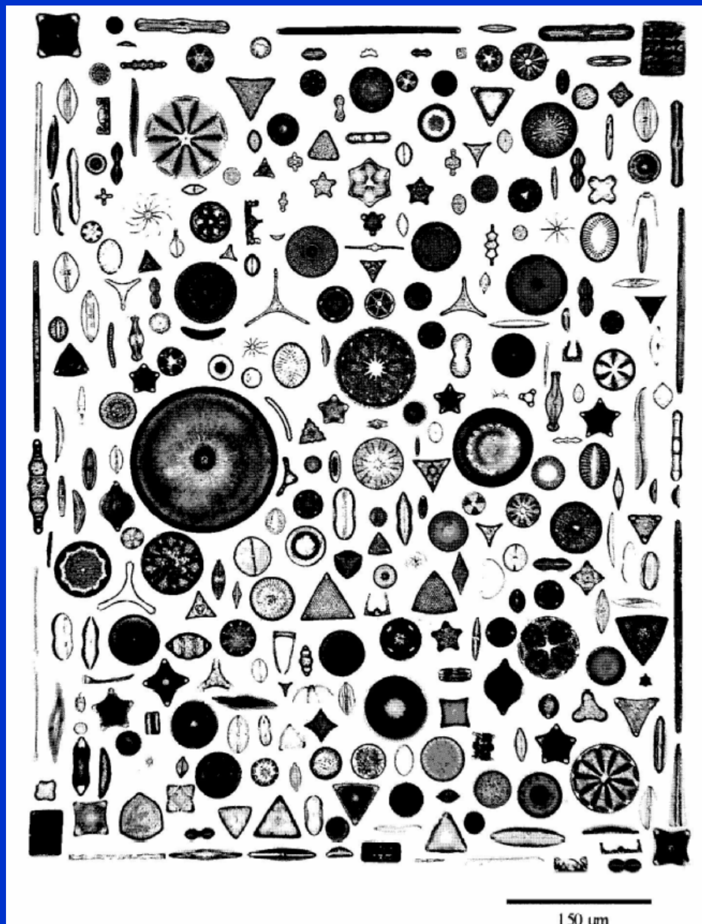
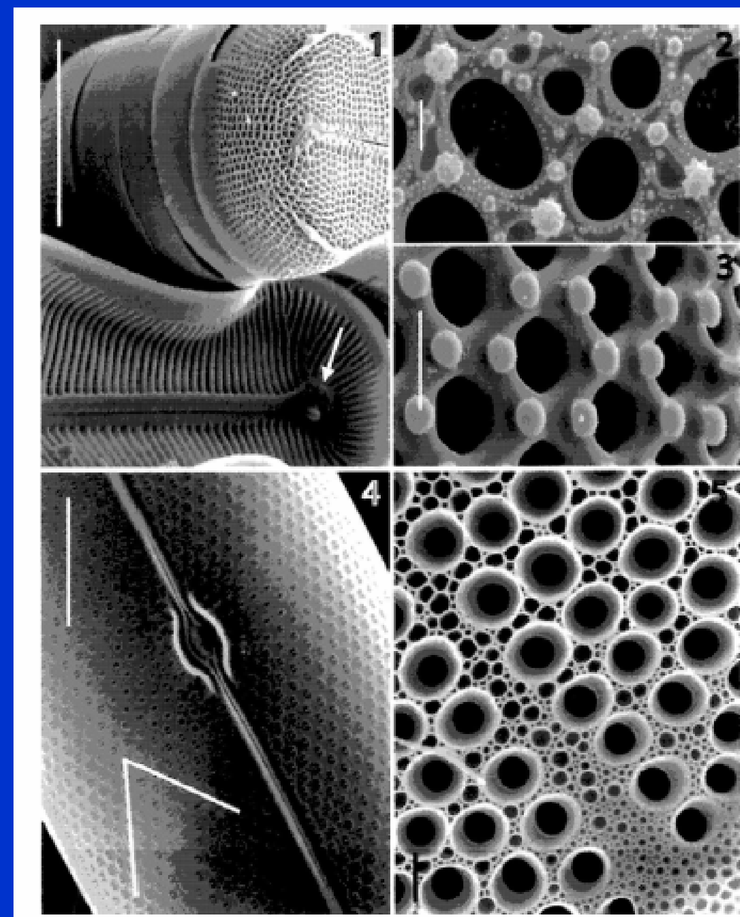
BIOSILICIFICATION: Formation of Amorphous Silica Complex Structures in Biological Systems

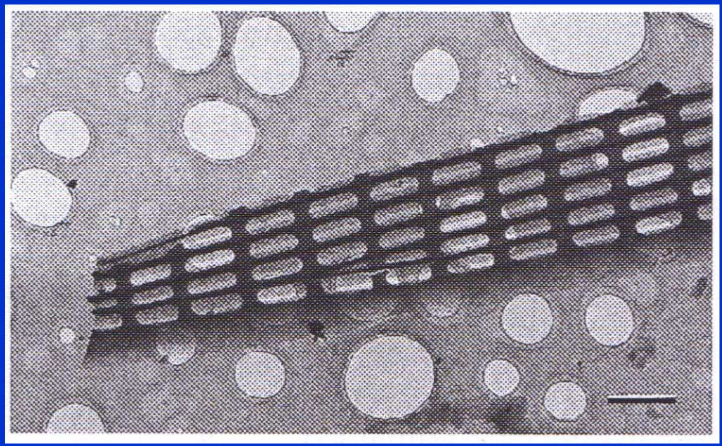




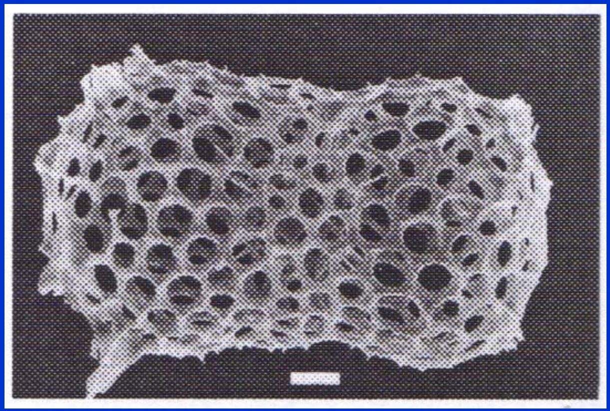
DIATOMS: ***Living in a Constructal Environment, p. 143***

Silica Biominerals

Mineral	Formula	Organism	Location	Function
Silica	$SiO_2 \cdot nH_2O$	Diatoms	Cell wall	Exoskeletons
		Choanoflagellates	Cellular	Protection
		Radiolarians	Cellular	Micro-skeleton
		Chrysophyts	Cell wall scales	Protection
		Limpets	Teeth	Grinding
		Plants	Leaves	Protection

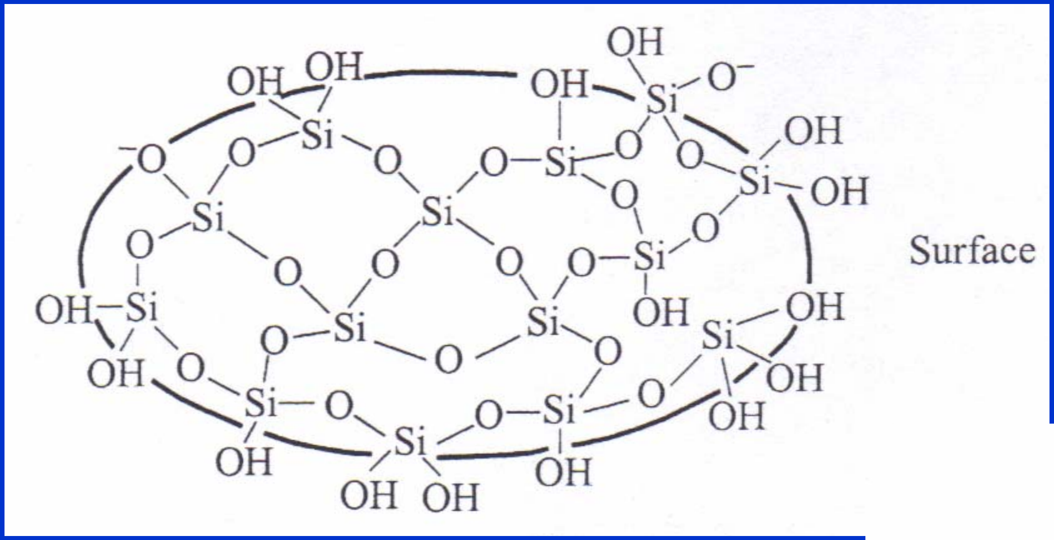


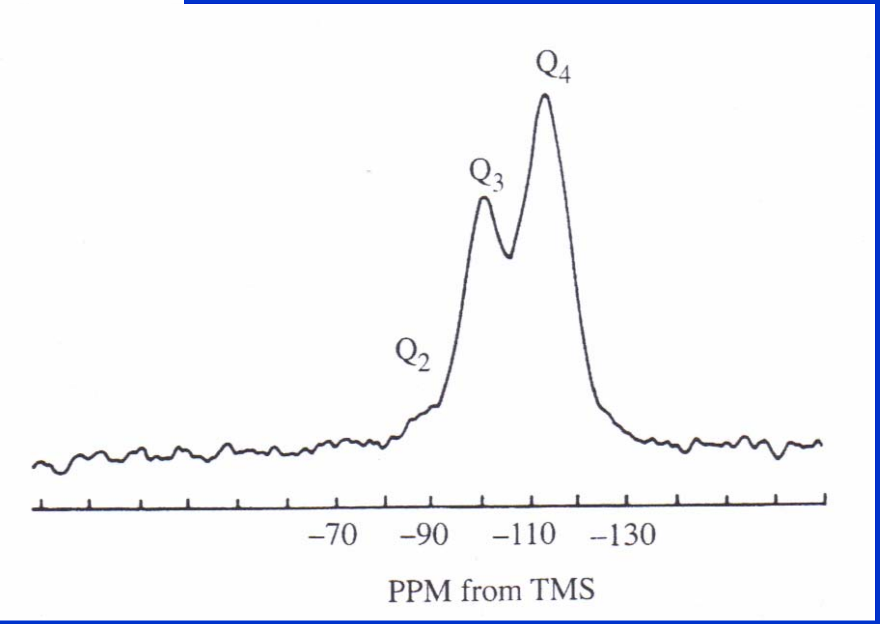
Diatom shell



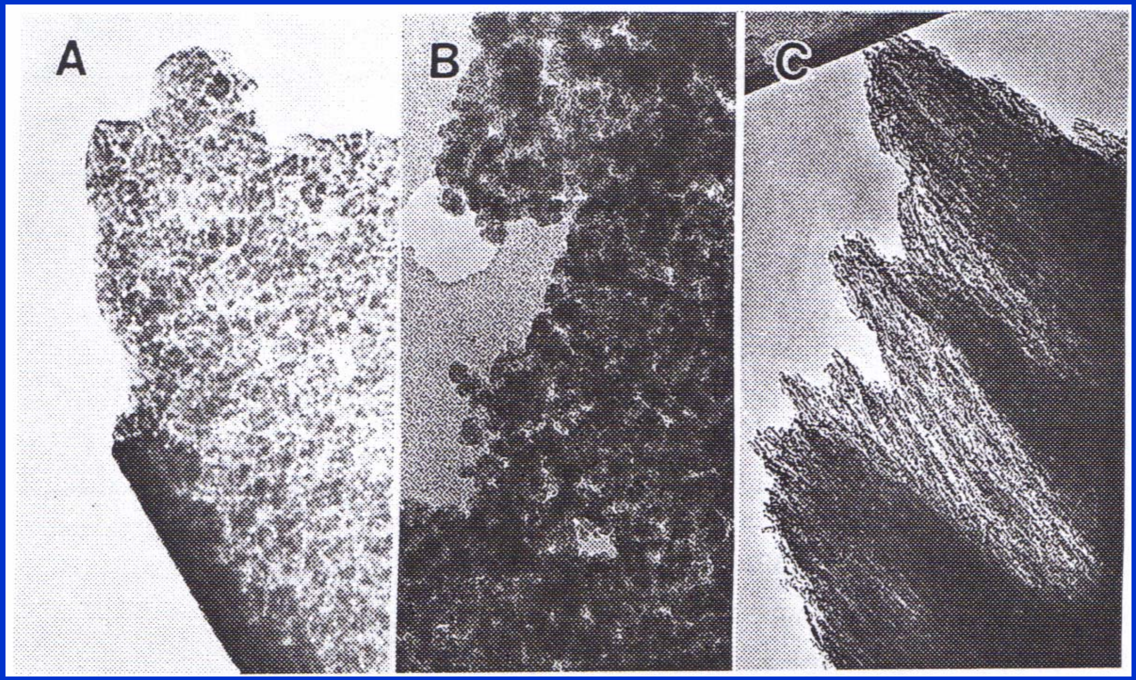
Radiolarian microskeleton

Physicochemical Characterization of Biosilica



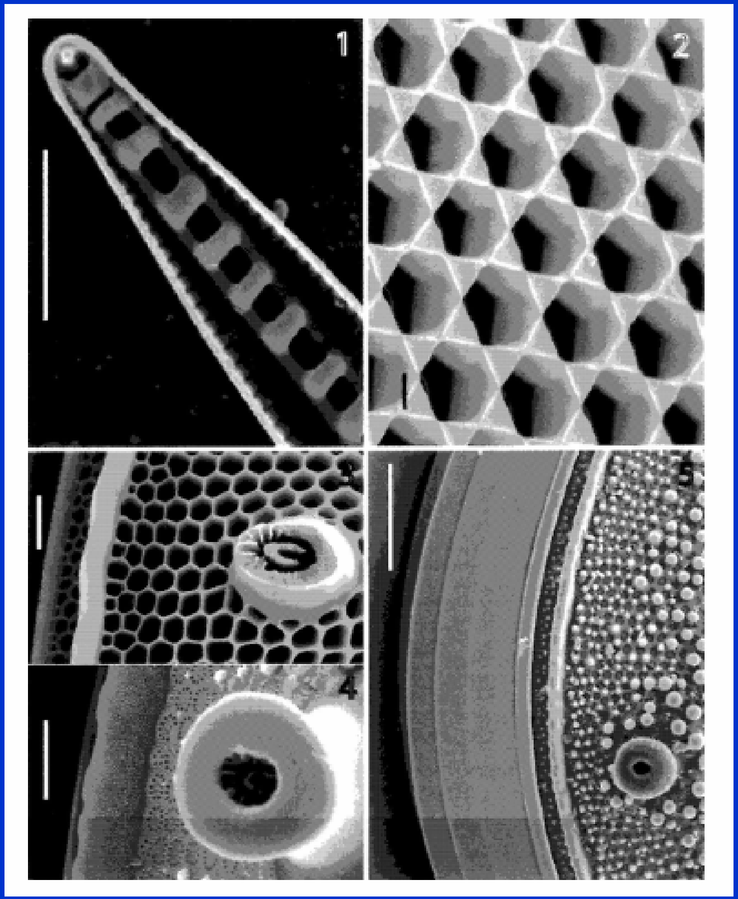


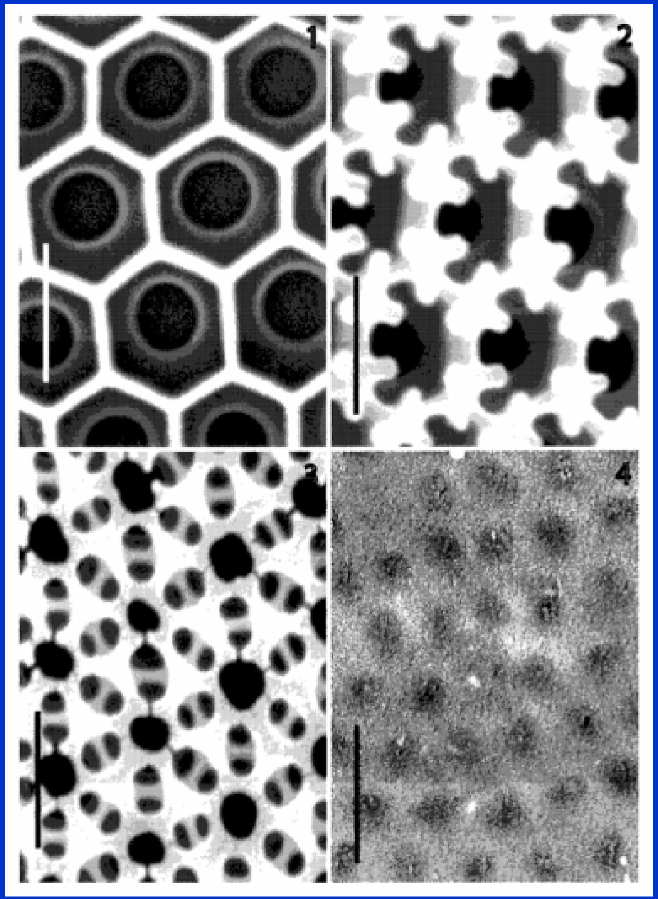
Plant Biosilica



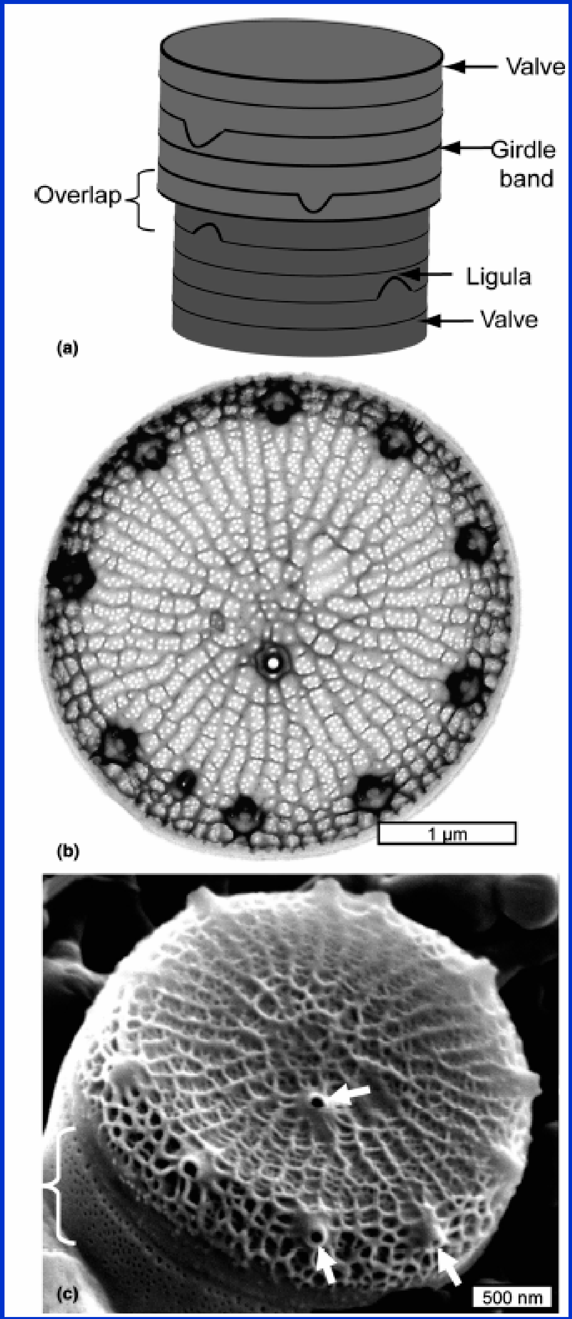
Sheet-like globular fibrilar

BIOSILICIFICATION: Ornate Silica "Super-structures" Not Reproduced by Man

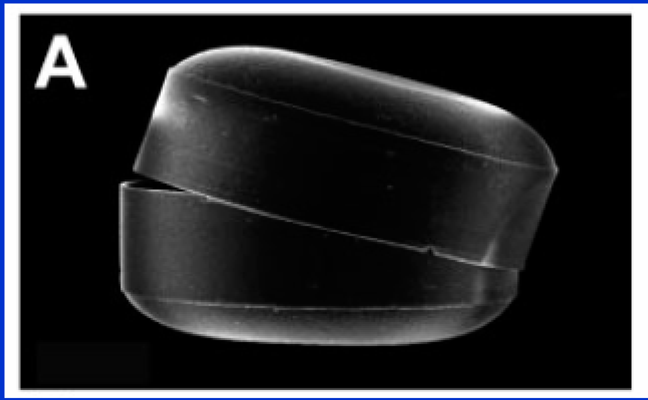


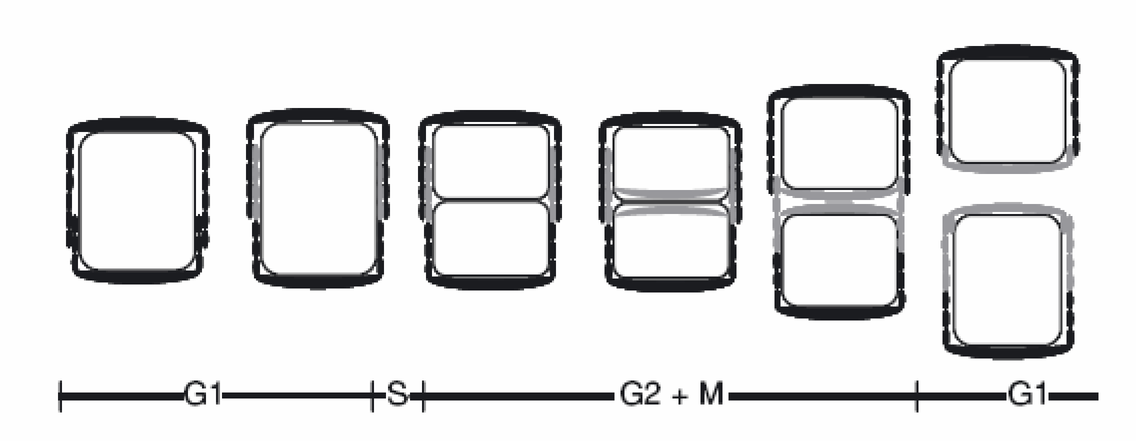


Gross Biogenic Silica Production: ~ 240 ± 40 Tmol "Si"/annum
Silicon Processing: 6.7 Giga tons/annum



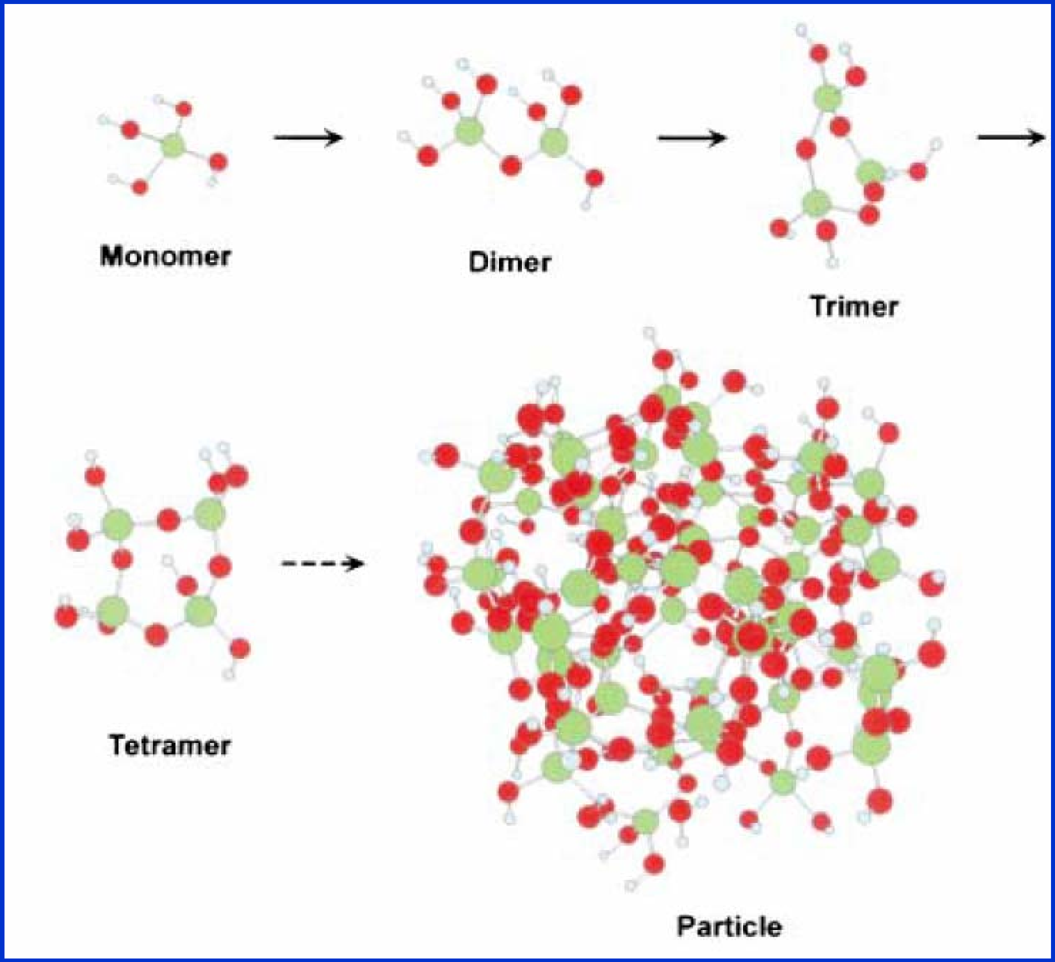
THE DIATOM: An Ideal Protist System for the Study of Biosilicification





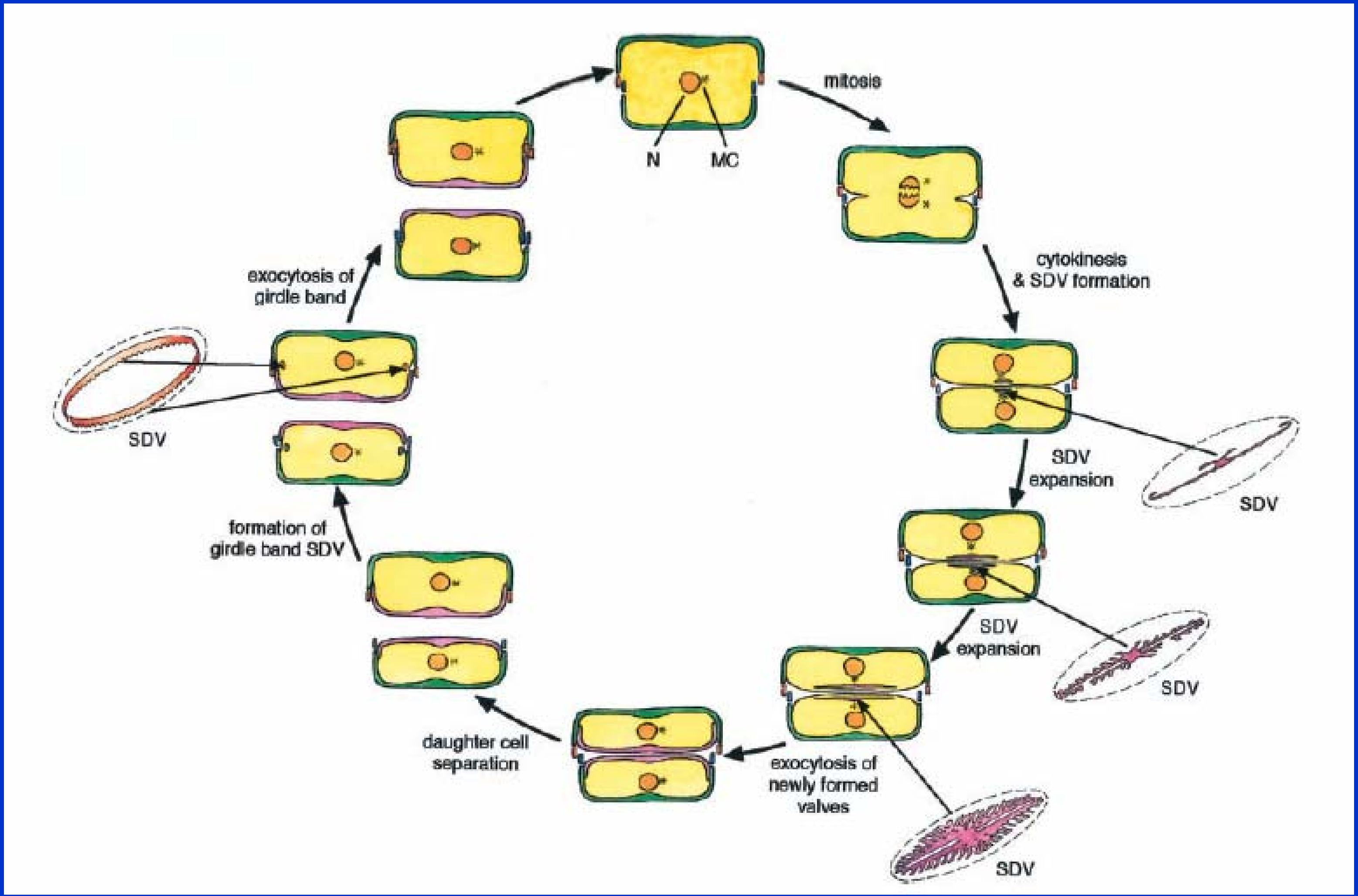
M. Sumper, *Science* **2002**, *295*, 2430.

SILICA FORMATION: Condensation Polymerization Of Silicic Acid at pH ~ 7

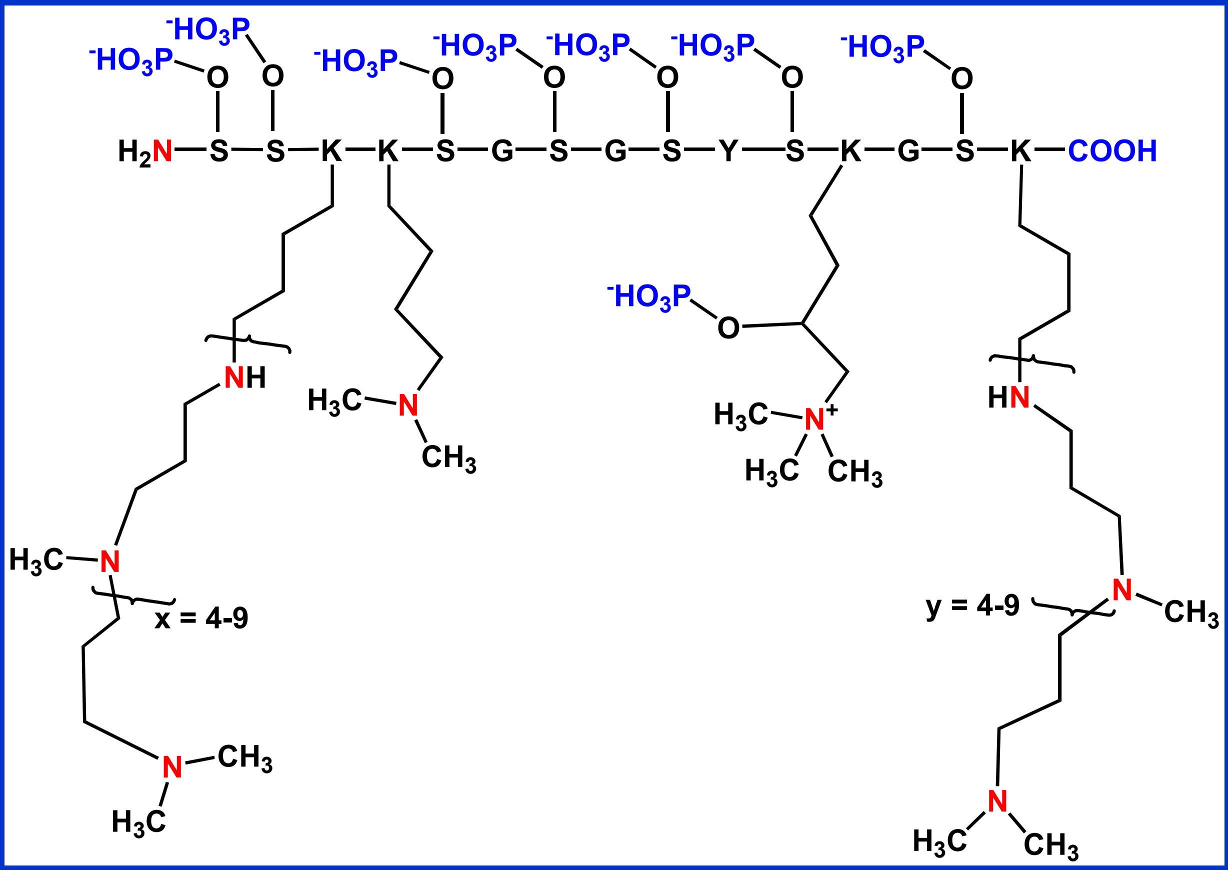


T. Coradin, P. Jean Lopez, *ChemBioChem* **2003**, *4*, 251.

BIOSILICA FORMATION: Inside the Silica Deposition Vesicle (SDV)



THE CATALYTIC ROLE OF BIOMOLECULES ON SILICA FORMATION: Silaffins



N. Kröger, S. Lorenz, E. Brunner, M. Sumper, *Science* **2002**, *298*, 585

SILICA BIOTRANSPORT: How is “Silicon” Transported Inside the SDV?

- *Transport of “soluble” silicate into the SDV*
- *Increase of silicate concentration*
- *Supersaturation in the SDV*
- *Silica formation “at will” and “when needed”*
- *Role of Silica Transport Vesicle (STV)*
- *Role of biomolecules for silicon transport*

GOAL: To identify macromolecules that extend or delay silica formation from soluble silicate

BIOINSPIRED APPROACH

- *Study silicification "in vitro" at pH ~ 7 in the absence of any "additives"*
- *Identify macromolecules that may have a "delay" effect on silicification*
- *Study the inhibitory effect of these macromolecules "in vitro" and compare to "control"*
- *Long-term (3 days) and short-term (8 h) experiments*
- *Monitor "soluble silica"*
- *Study silica formed (if any) by several techniques*
- *Identify mechanisms, structure/function relationships*
- *Ways to improve inhibitory activity*

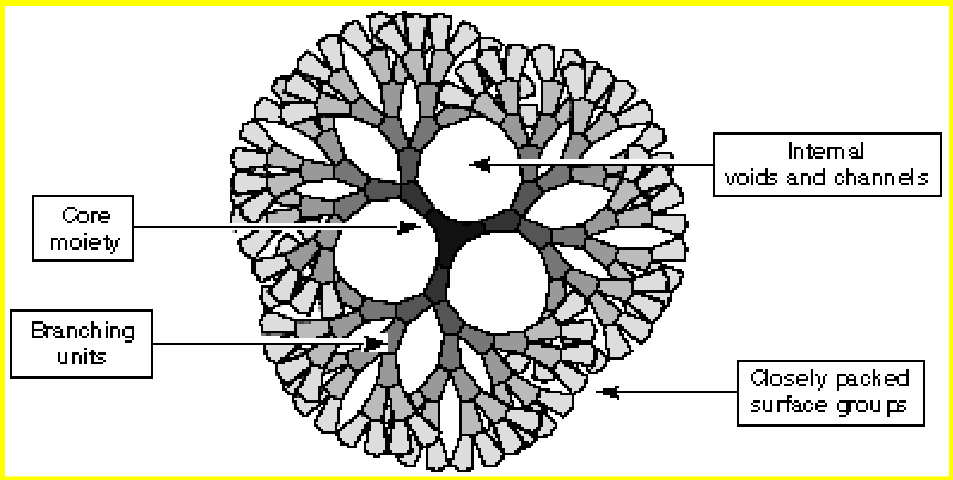
ATTRIBUTES OF MACROMOLECULES THAT AFFECT SILICATE CONDENSATION

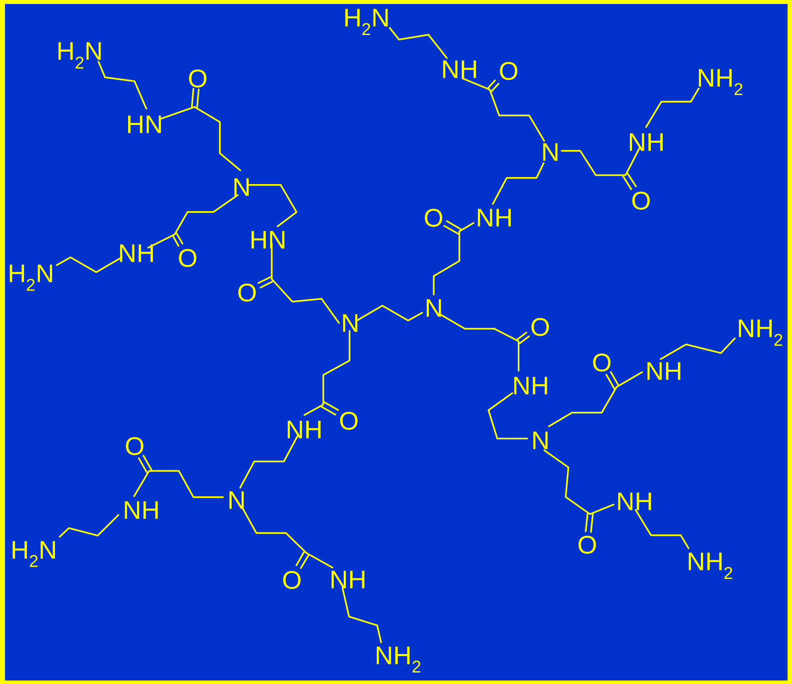
- *Charged polyelectrolytes, water-soluble*
- *Usually Cationic or Partially Cationic*
- *"Proper" extent of Cationic Charge*
- *What Kind of Cationic Groups?*
- *Zwitter-Ions?*
- *What about "neutral" polymers?*

CLASSES OF MACROMOLECULES STUDIED

- *Cationic Dendrimers (-NH_3^+ end-groups)*
- *Cationic, Amine-Containing Polymers (-NH_3^+, -NH_2R^+, -NHR_2^+ groups)*
- *Purely Cationic, Ammonium-Containing Polymers (-NR_3^+ groups)*
- *Copolymers (neutral + cationic groups)*
- *Zwitter-Ions (-NH_2R^+, -NHR_2^+ and –PO_3H^- Groups)*
- *Cationic, Phosphonium-Based oligomers*
- *Neutral Polymers (polyvinylpyrrolidone)*

FUNCTIONALITY OF DENDRIMERS AS SiO_2 INHIBITORS ("*δένδρον*" + "*μέρος*")





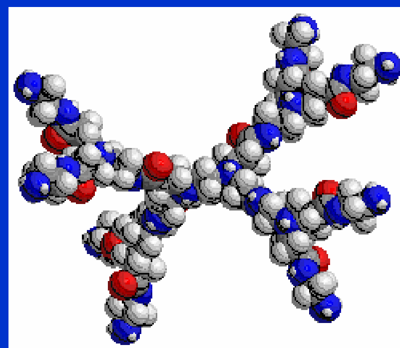
PAMAM = polyaminoamide

Biodegradable by virtue of their amide bonds

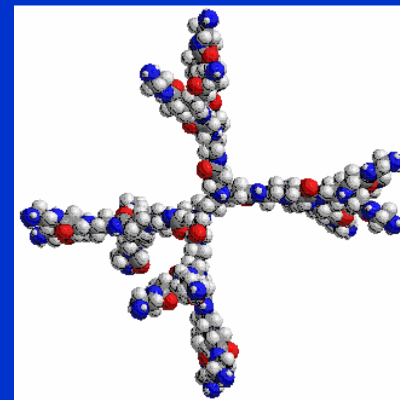
PAMAM generation 1
(8 -NH_2 terminal groups)

Tomalia, D. A., *et al. Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 138.

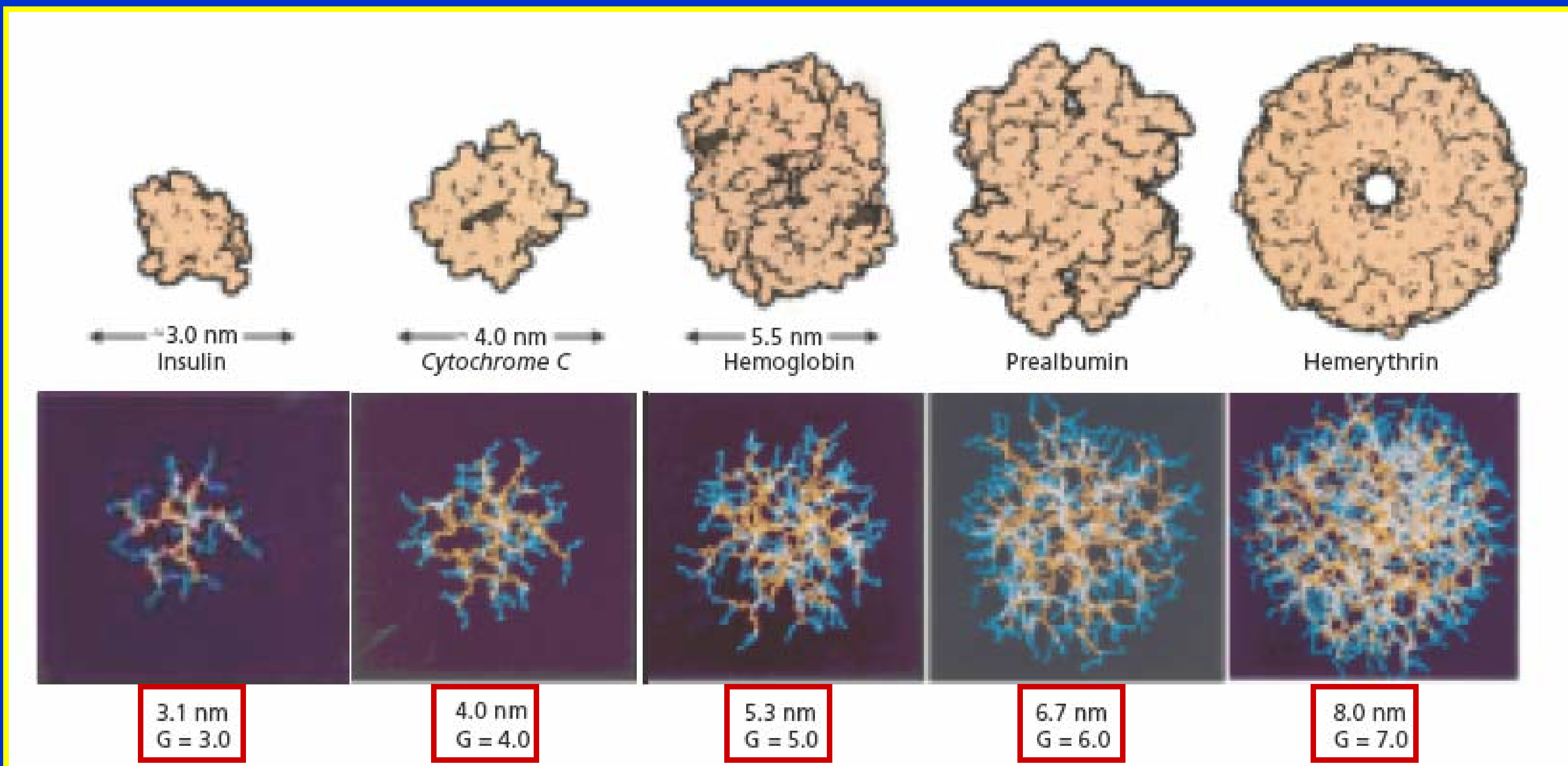
VARIOUS GENERATIONS OF DENDRIMERS



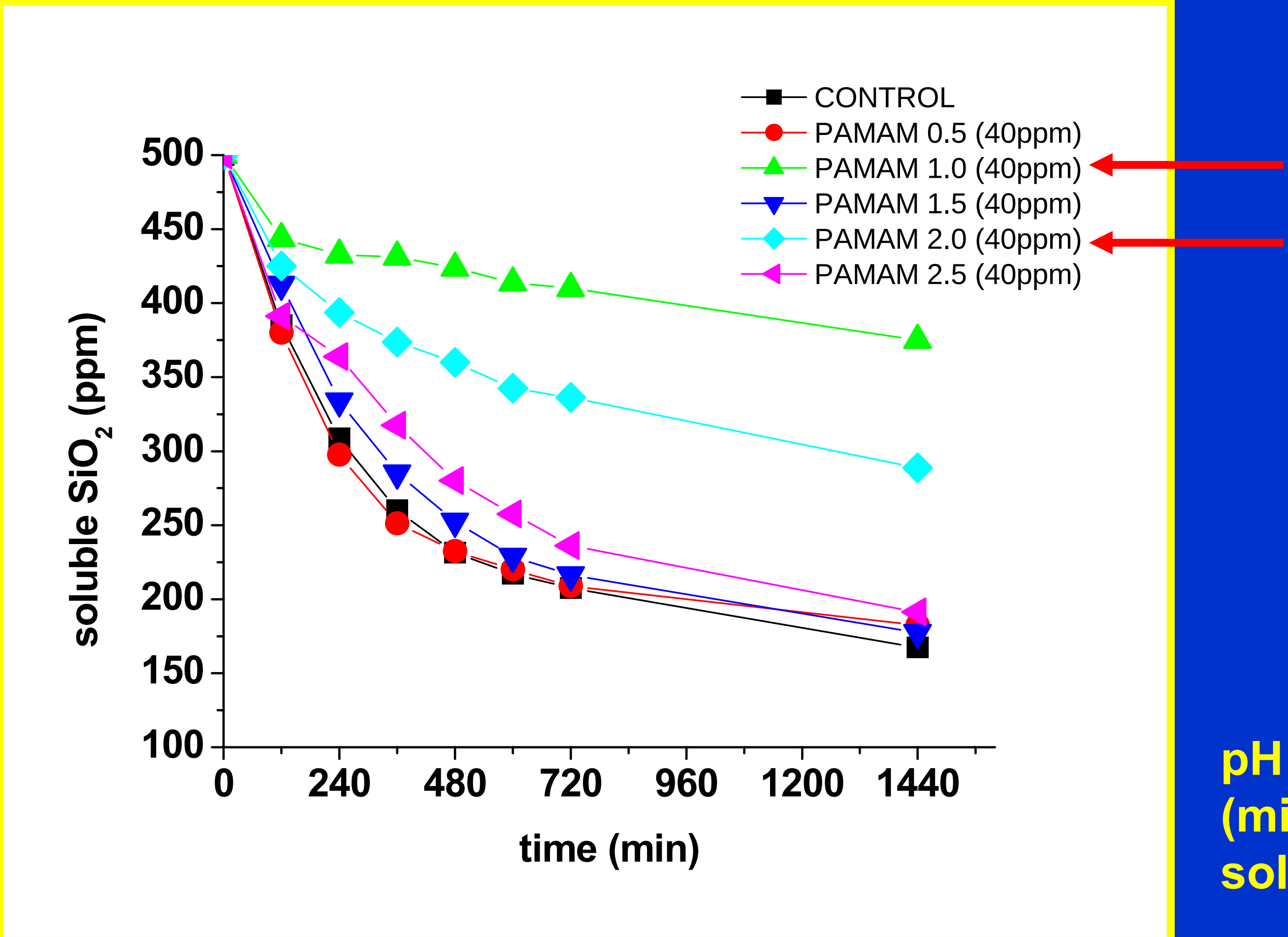
G = 1
2.2 nm



G = 2
2.9 nm



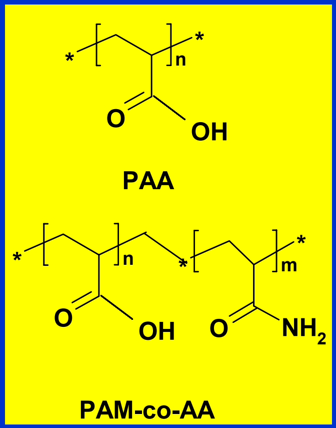
EFFECT OF DENDRIMERS ON SiO_2 FORMATION

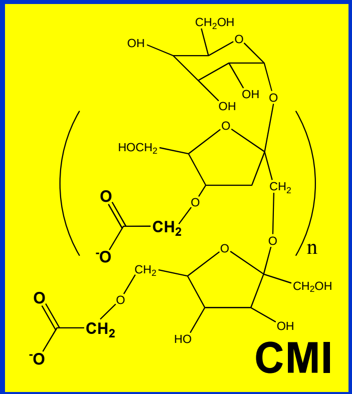


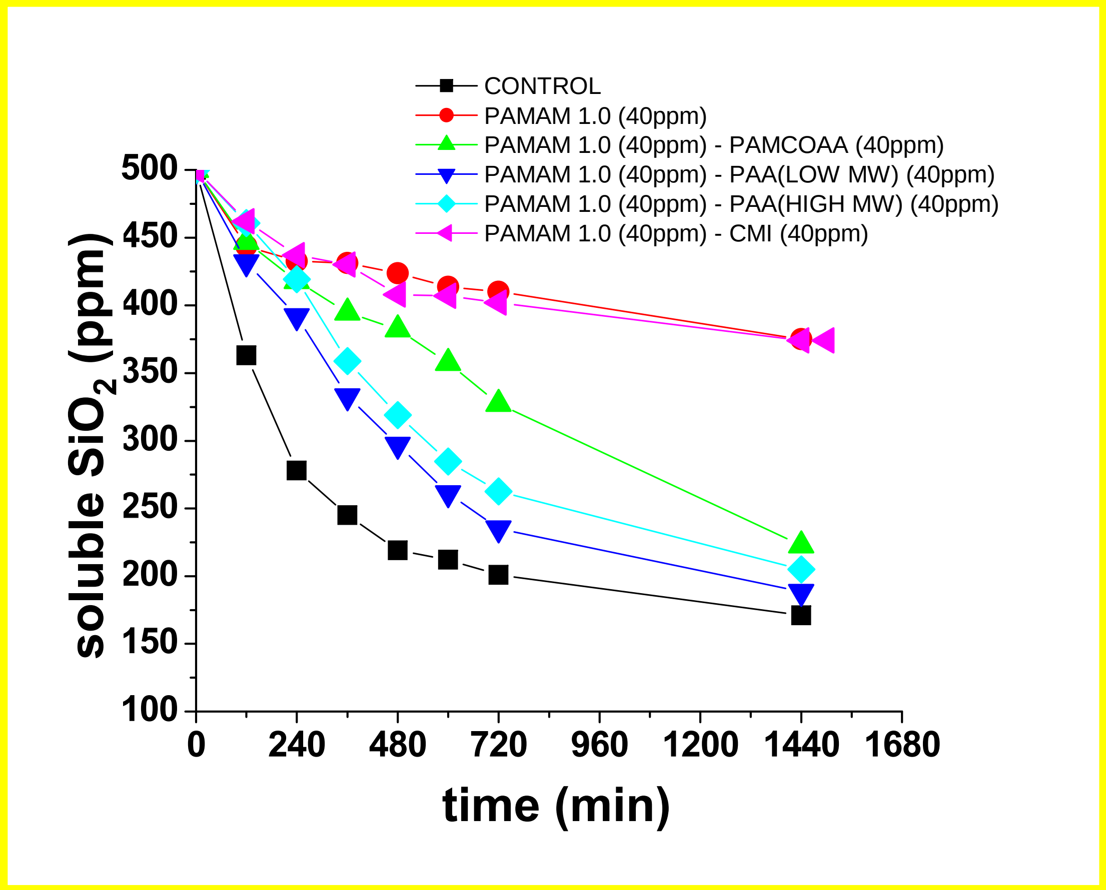
pH = 7.0
(minimum SiO_2 solubility)

Neofotistou, E.; Demadis, K.D. *Coll. & Surf. A: Physicochem. Eng. Asp.* **2004**, *242*, 213.

DISPERSION OF SiO_2 – PAMAM-1 PRECIPITATES USING ANIONIC POLYMERS



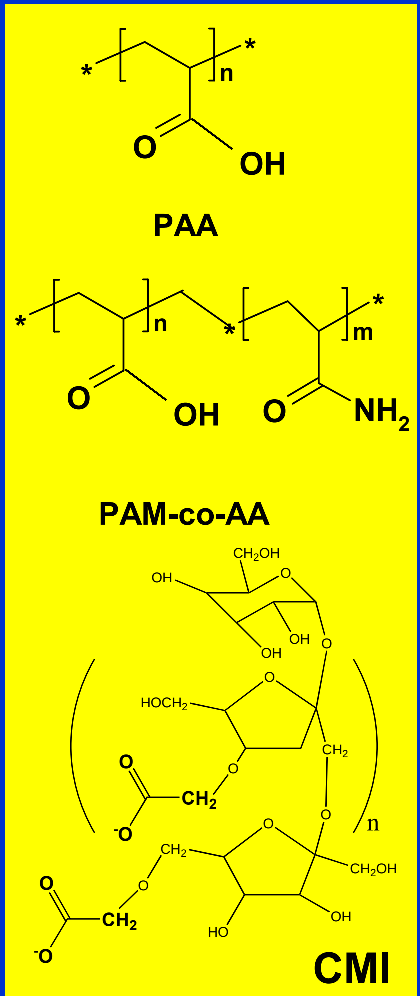


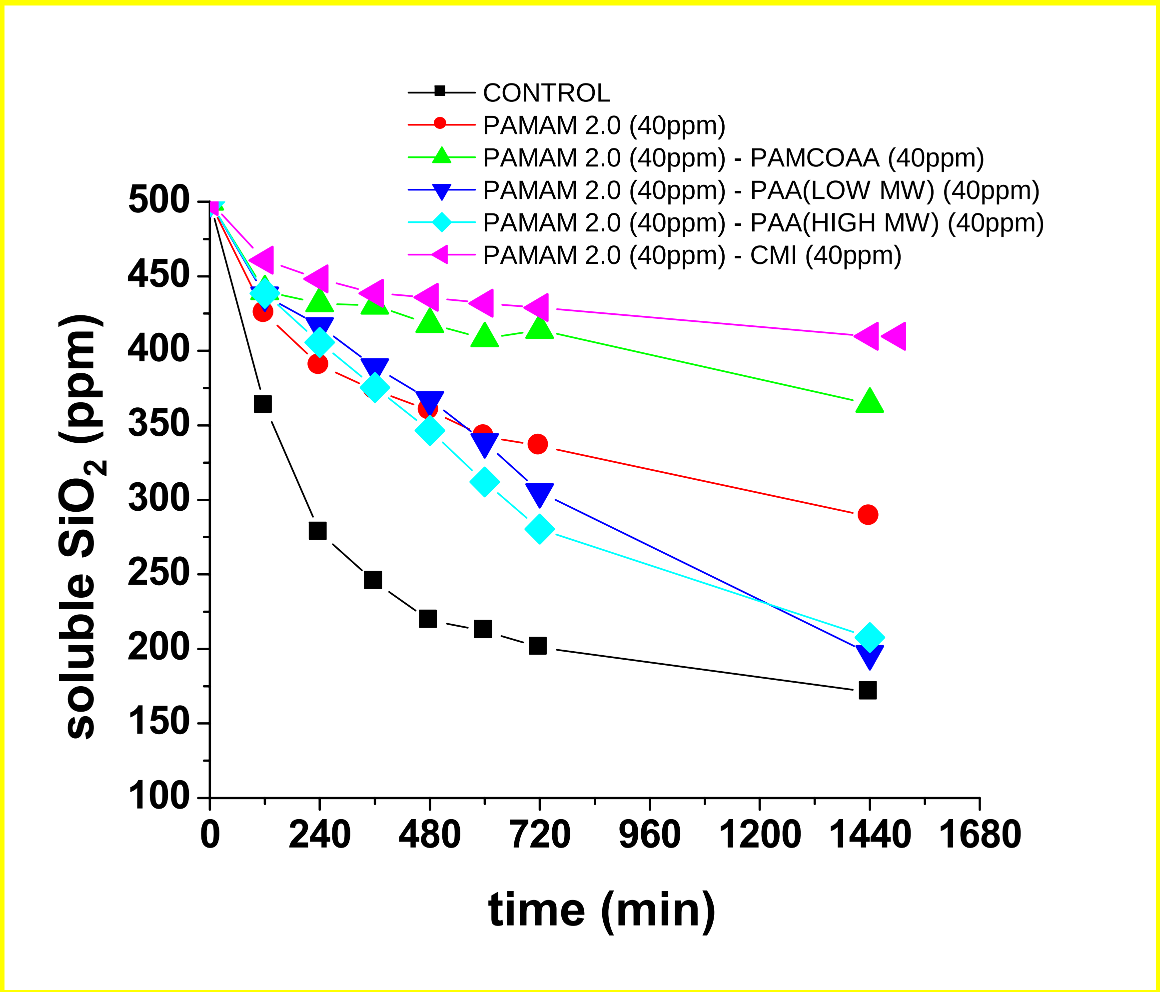


Mavredaki, E.; Neofotistou, E.; Demadis, K.D. *Ind. Eng. Chem. Res.* **2005**, *44*, 7019.

Demadis, K.D.; Neofotistou, E. *Chem. Mater.* **2007**, *19*, 581.

DISPERSION OF SiO_2 – PAMAM-2 PRECIPITATES USING GREEN ANIONIC POLYMERS

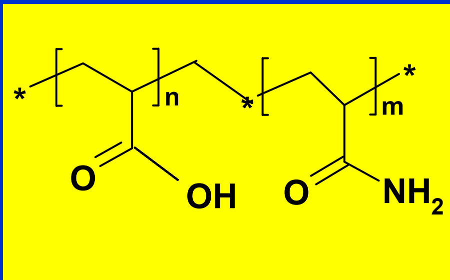




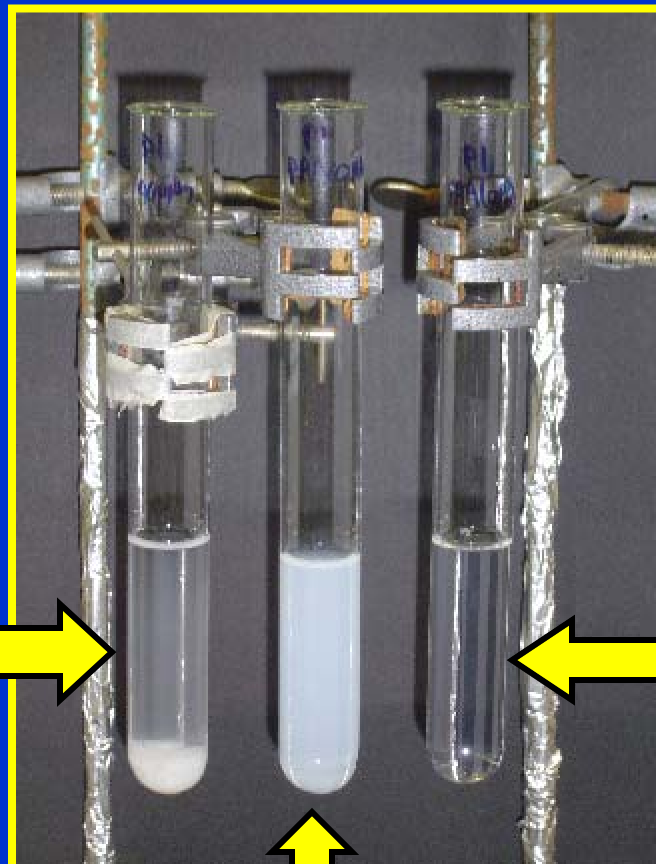
Mavredaki, E.; Neofotistou, E.; Demadis, K.D. *Ind. Eng. Chem. Res.* **2005**, *44*, 7019.

Demadis, K.D.; Neofotistou, E. *Chem. Mater.* **2007**, *19*, 581.

STABLE DISPERSIONS OF SiO_2 – PAMAM PRECIPITATES WITH GREEN ANIONIC POLYMERS



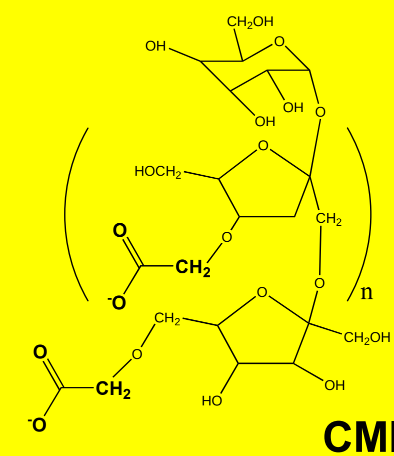
PAM-co-AA



PAMAM

PAMAM + CMI

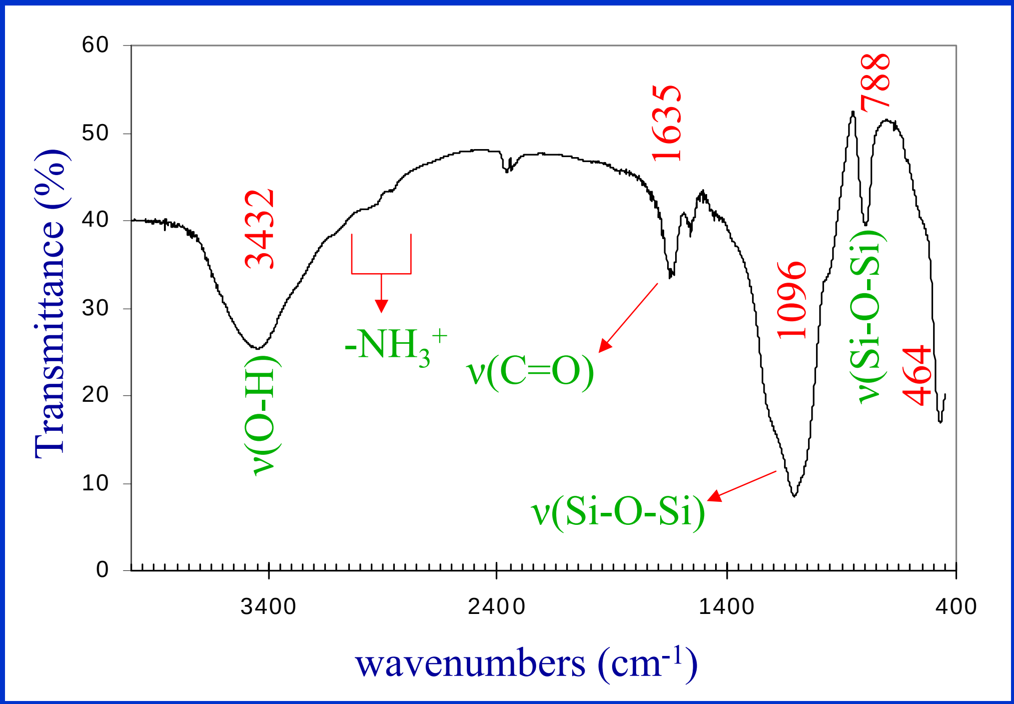
PAMAM + PAM-co-AA

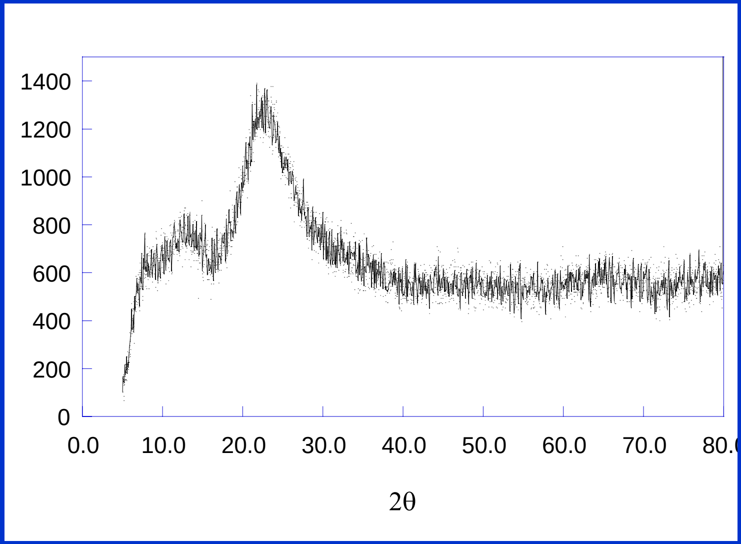


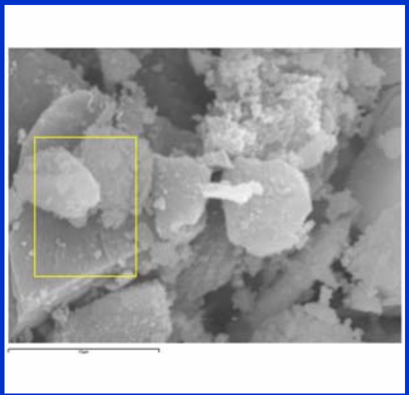
CMI

Mavredaki, E.; Neofotistou, E.; Demadis, K.D. *Ind. Eng. Chem. Res.* **2005**, *44*, 7019.

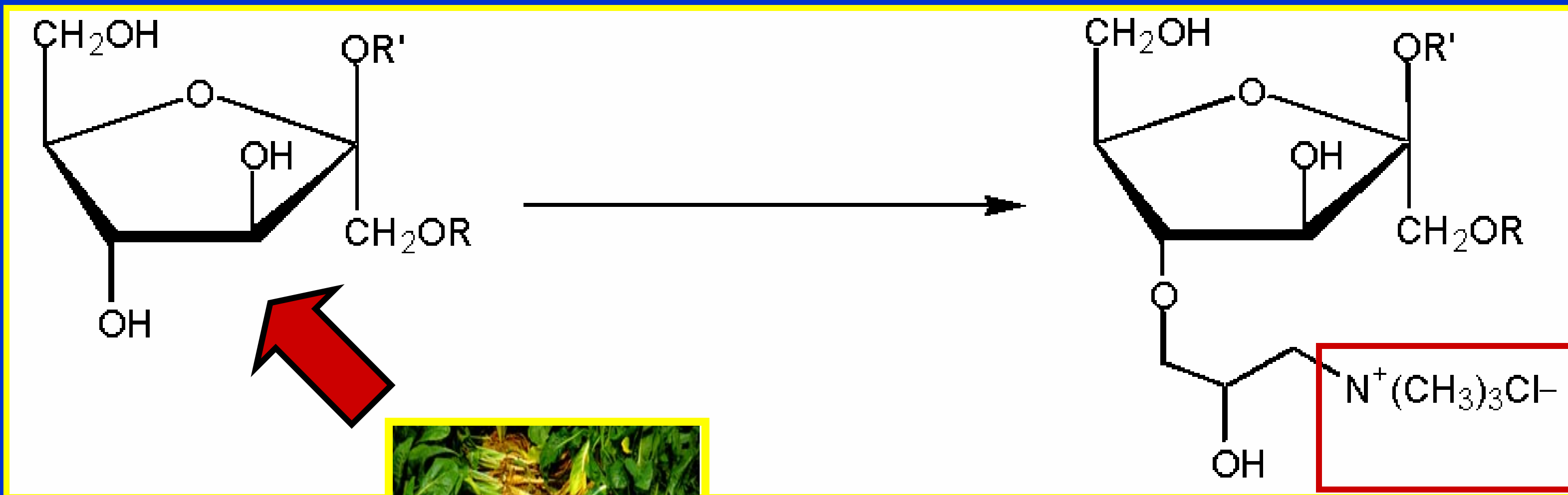
AMORPHOUS SiO_2-PAMAM COMPOSITES







CATIONIC BIO-POLYMERS FOR SiO_2 INHIBITION



inulin
(neutral)

Inulin
(cationic)

chicory roots (Renewable feedstock for non-food applications)

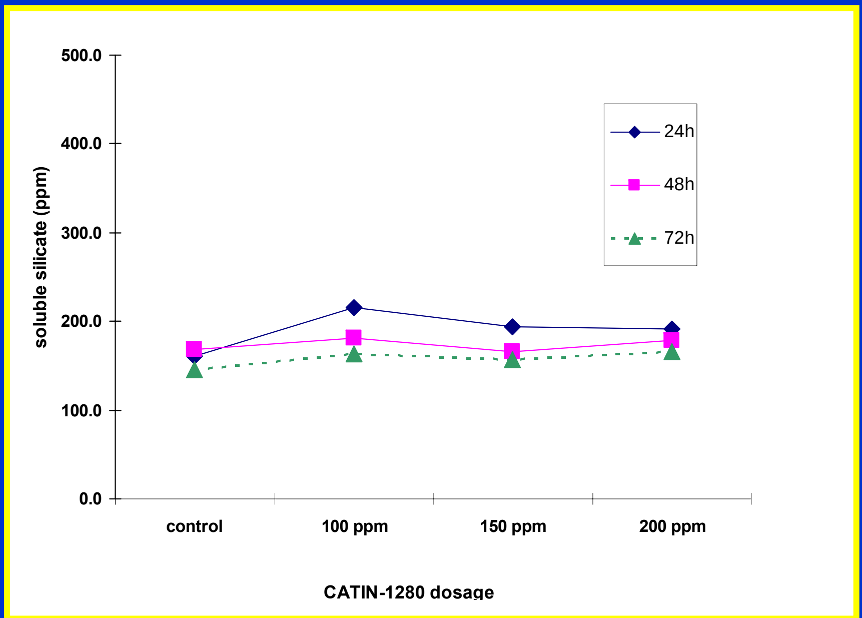
Inulin content:
14.9 - 18.3 %

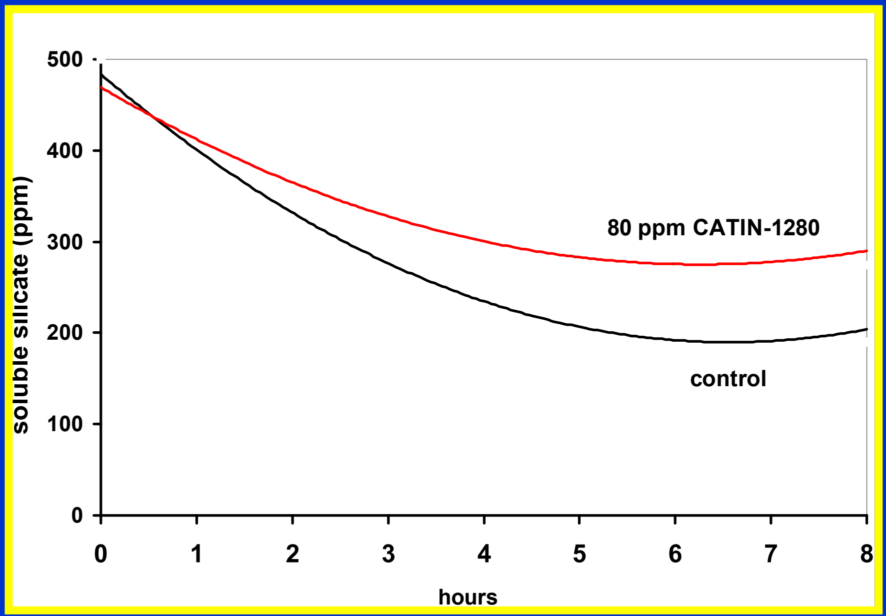
3 cationic inulins:

CATIN-220 (DS = 0.22)
CATIN-860 (DS = 0.86)
CATIN-1280 (DS = 1.28)

DS = degree of substitution)

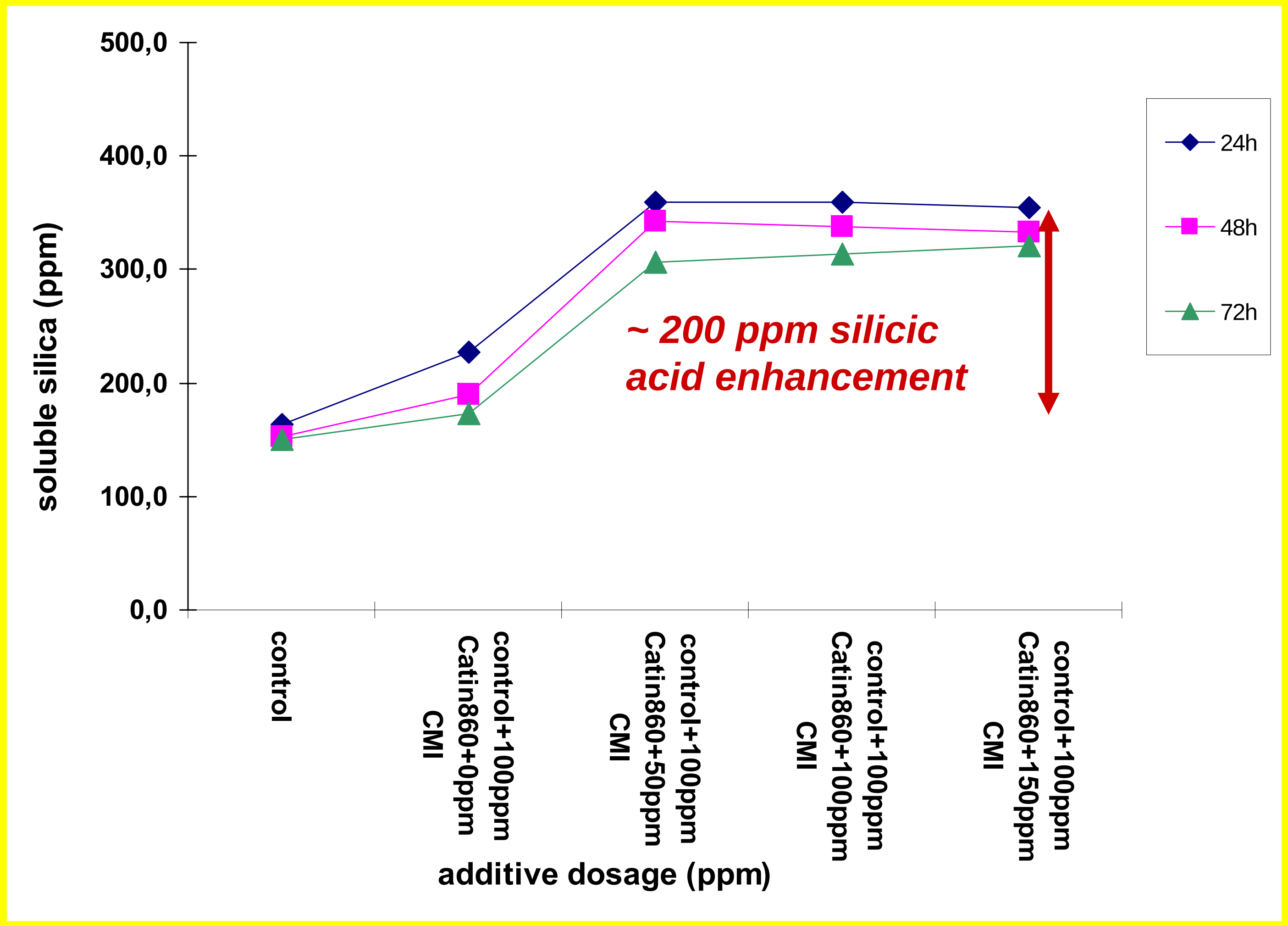
EFFECT OF CATIN-1280 BIO-POLYMER ON SiO_2 INHIBITION





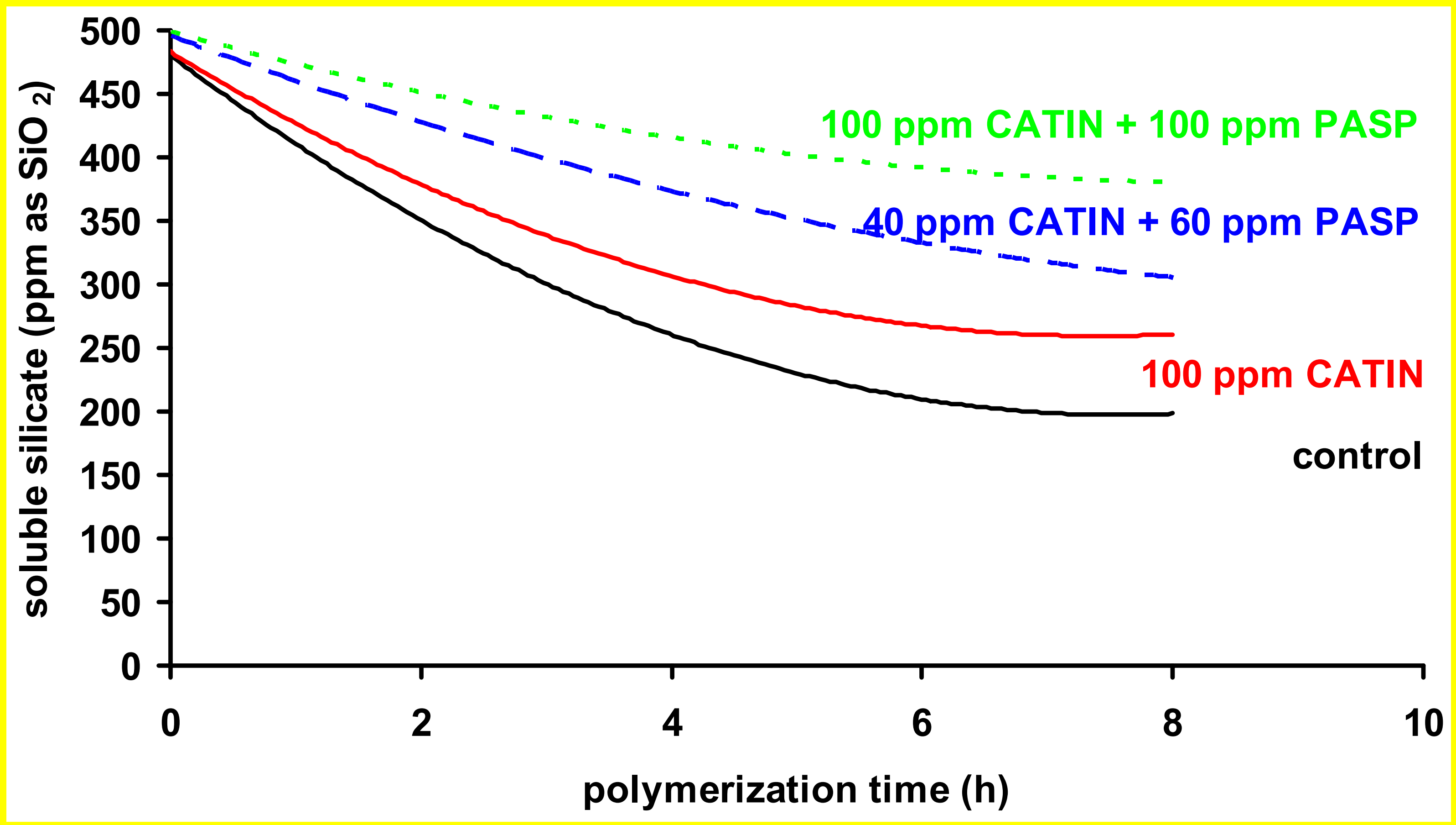
Demadis, K.D.; Ketsetzi, A. *Desalination* **2008**, *223,* 487

SYNERGY BETWEEN CATIN-1280 AND CMI

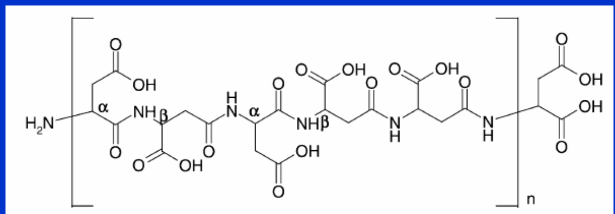


Demadis, K.D.; Ketsetzi, A. *Desalination* **2008**, *223,* 487

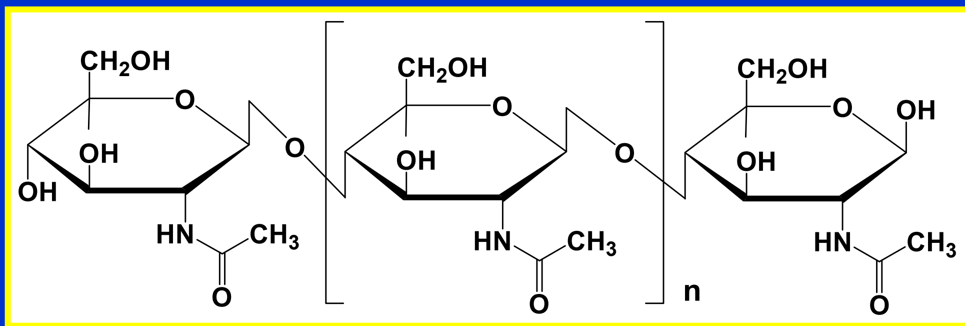
SYNERGISTIC EFFECTS IN SiO_2 INHIBITION: CATIN + PASP



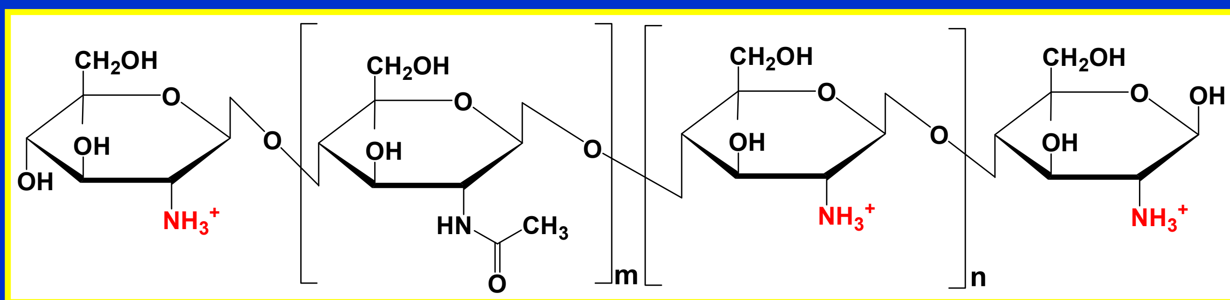
PASP = polyaspartate



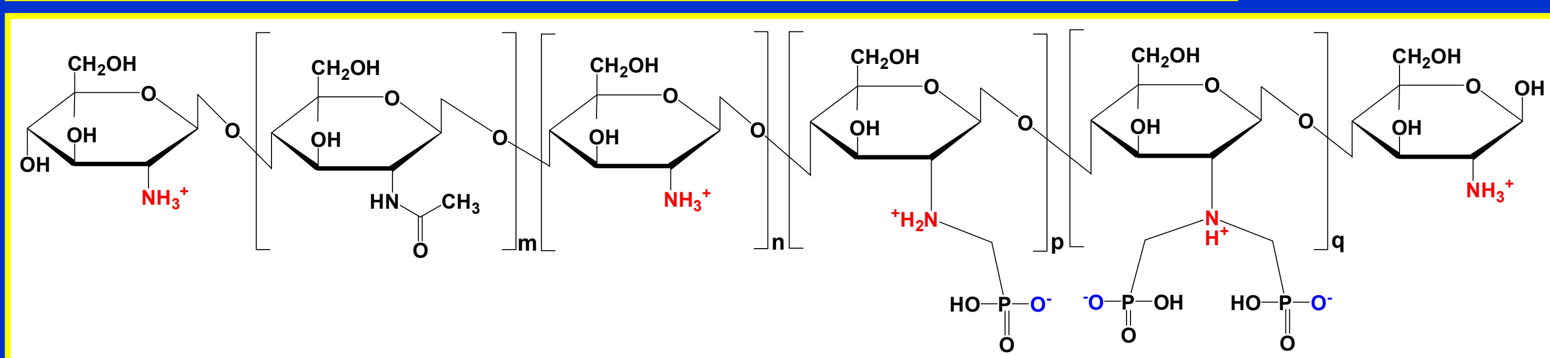
EFFECTS OF ZWITTER-IONIC POLYMERS ON SiO_2 INHIBITION: Phosphonomethylchitosan



CHT



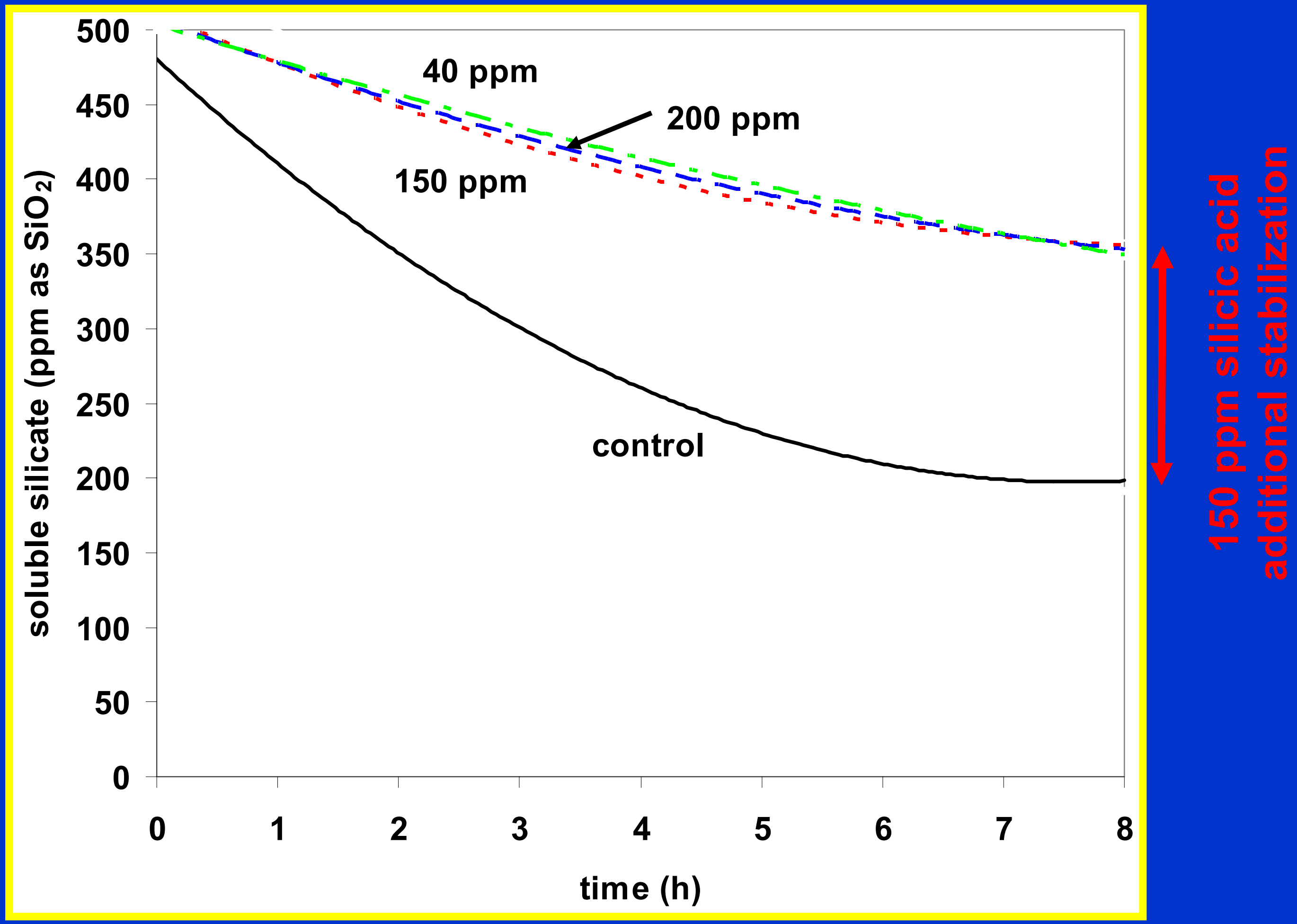
CHS



PCH

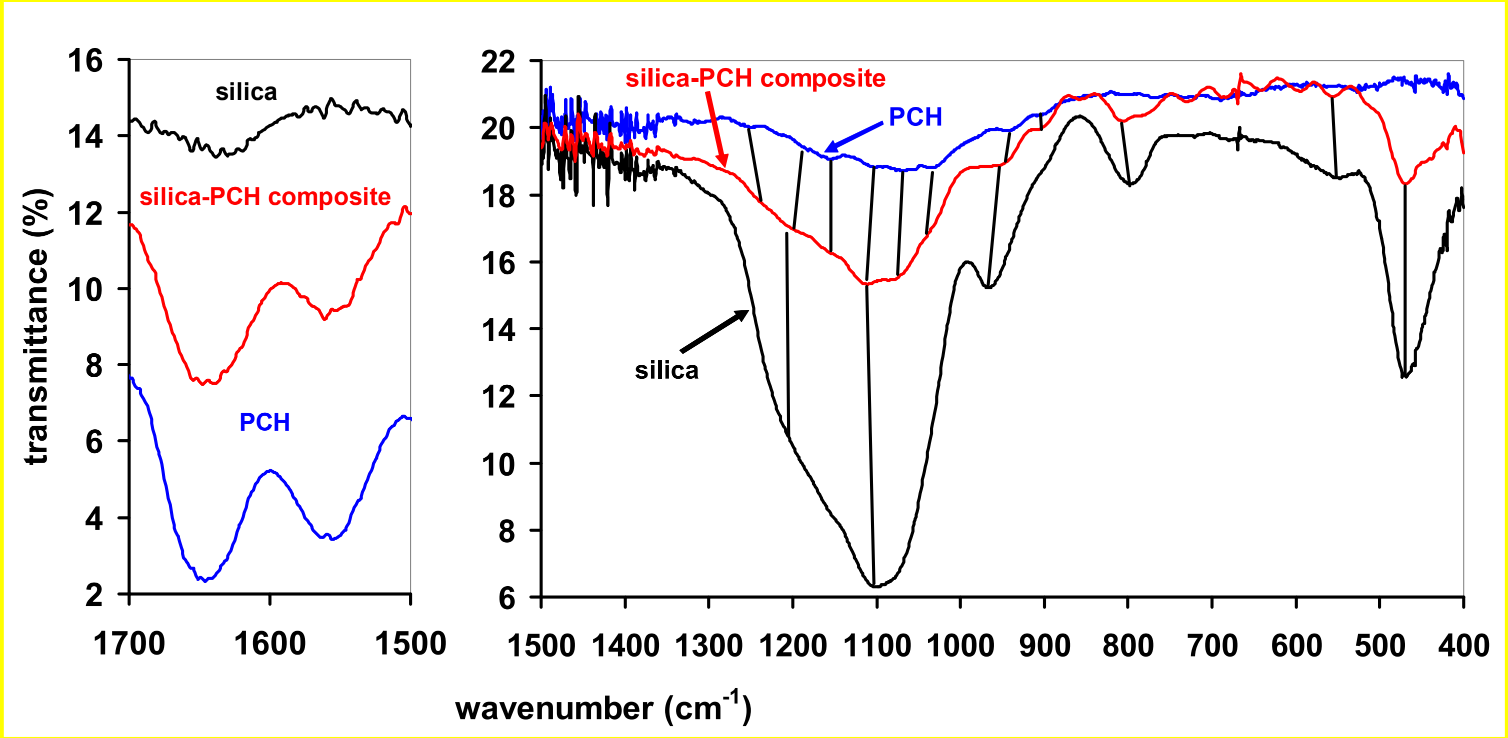
(m = 0.16, n = 0.37, p = 0.24, q = 0.14)

Effect of Phosphonomethylchitosan (PCH) On Silica Formation



Demadis, K.D.; Ketsetzi, K. Pachis; A. Ramos, V.M. *Biomacromolecules* **2008**, *9*, 3288.

Phosphonomethylchitosan (PCH) Entrapment in the Silica Matrix



Demadis, K.D.; Ketsetzi, K. Pachis; A. Ramos, V.M. *Biomacromolecules* **2008**, *9*, 3288.

Conclusions

- Biosilicification is a very complex process (*in vitro* silicification, too!)
- Nature uses silica biominerals for different purposes
- Biosilica is not simple inorganic system
- Biosilica is a composite material
- There are many potential applications of silica