Acknowledgements:

National Science Foundation
WHERE DISCOVERIES BEGIN

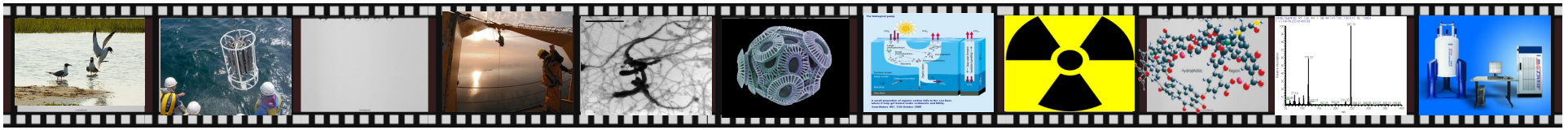
Energy
Office of Biological & Environmental Research
Climate and Environmental Sciences Division | Biological Systems Science Division

Biopolymers as carriers of natural (Th, Pa, Pb, Po, Be) radionuclides in aquatic systems

Peter H. Santschi, Chia-Ying Chuang, Chen Xu, Kathleen A. Schwehr, and Saijin Zhang

Texas A&M University

Galveston, TX, 77553, USA

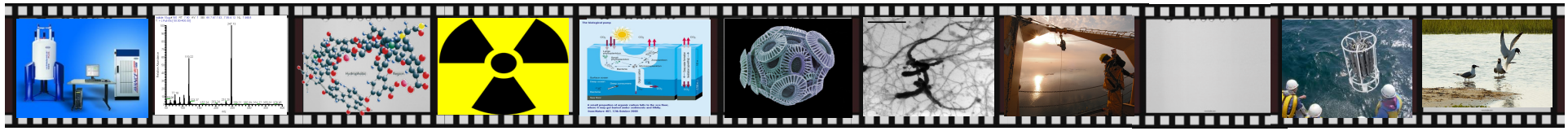


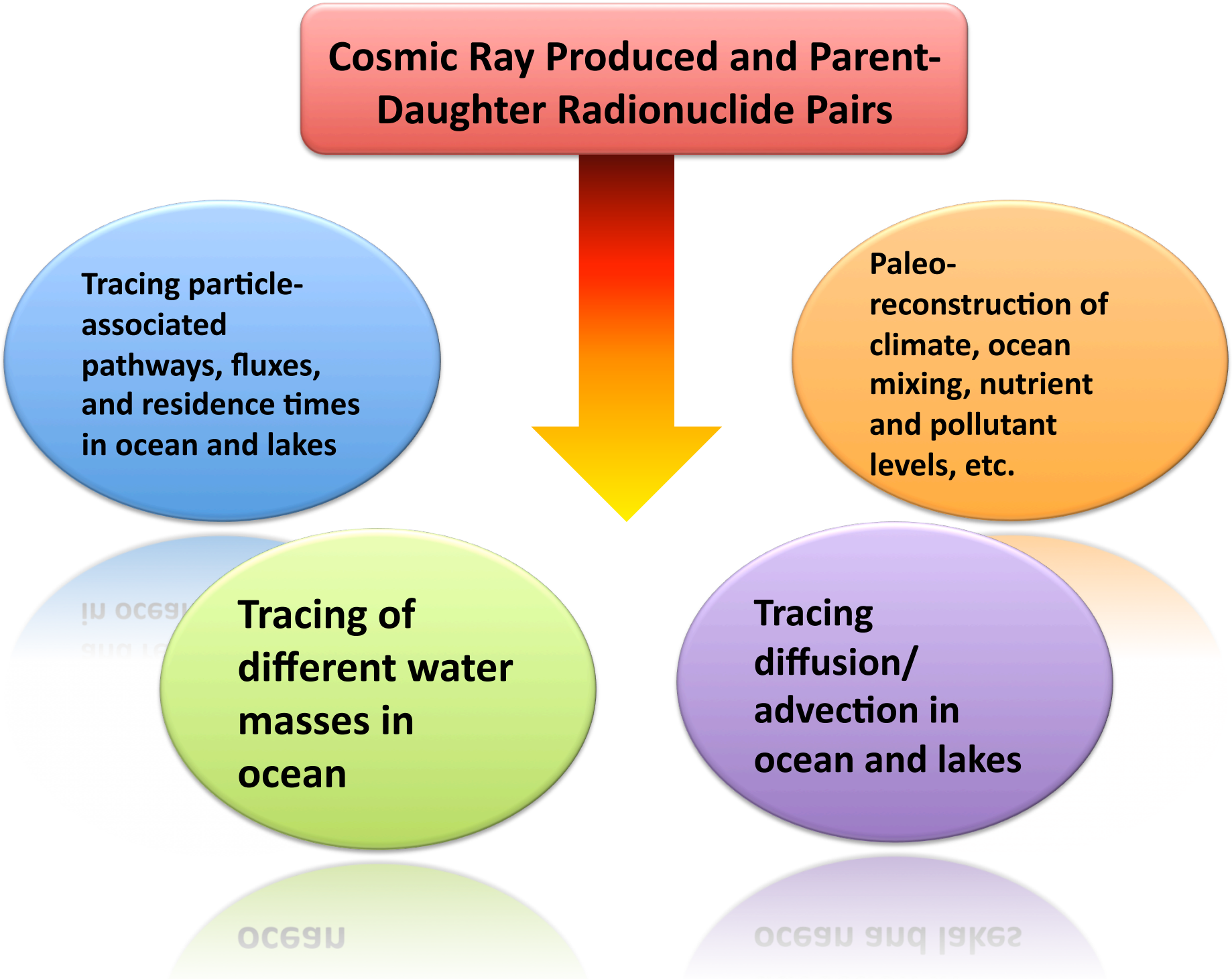
Objectives

Explore the role of biopolymeric carriers (e.g., carbohydrates, proteins in EPS) for radionuclides in the environment.

Lessons from field and lab studies using ‘correlative’ (Chemical Oceanography) leading to ‘extractive’ (Marine Chemistry) approaches.

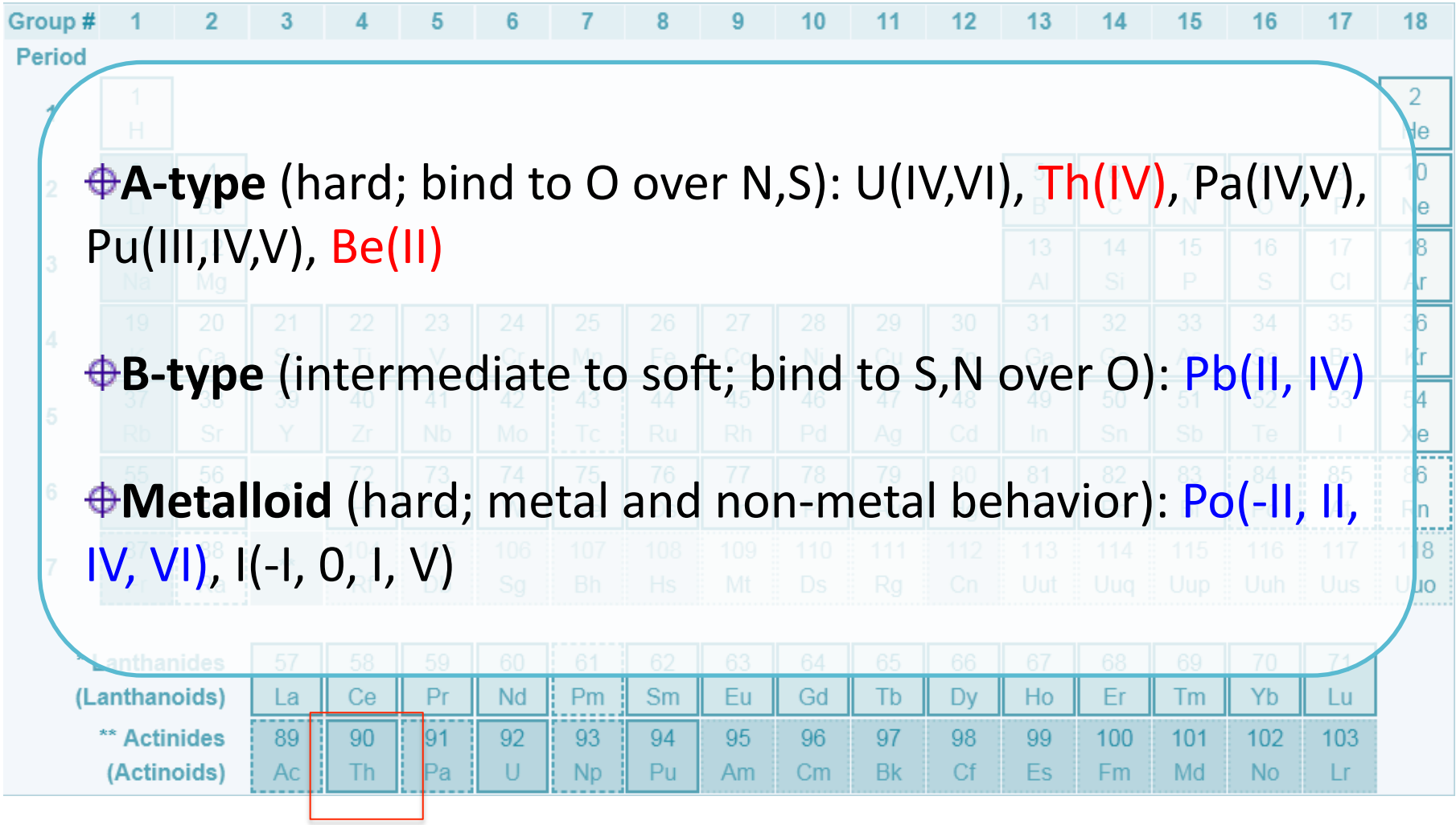
Relevance for remediation, interpretation of results from applications, e.g., historical reconstructions, etc.



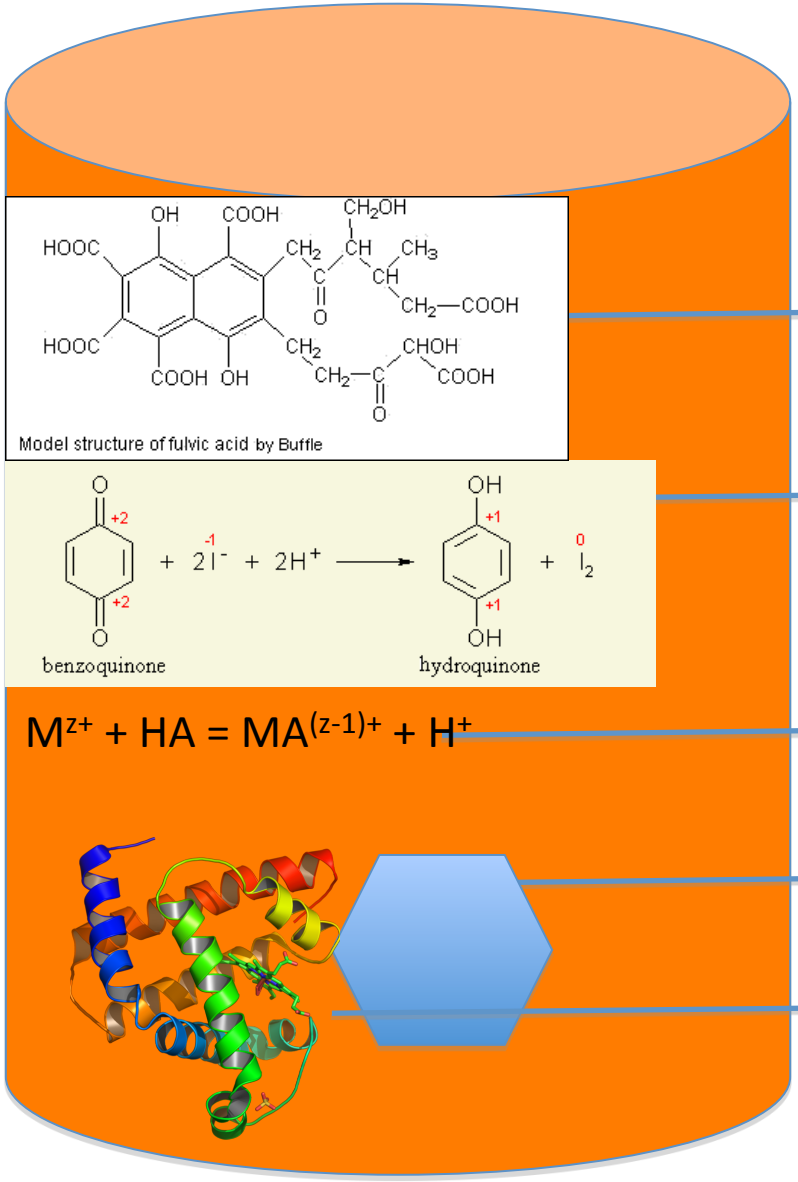

Cosmic Ray Produced and Parent-Daughter Radionuclide Pairs
Tracing particle-associated pathways, fluxes, and residence times in ocean and lakes
Paleo-reconstruction of climate, ocean mixing, nutrient and pollutant levels, etc.
Tracing of different water masses in ocean
Tracing diffusion/ advection in ocean and lakes

Common (multiple) oxidation states of environmental radionuclides

- **A-type** (hard; bind to O over N,S): U(IV,VI), Th(IV), Pa(IV,V), Pu(III,IV,V), Be(II)
- **B-type** (intermediate to soft; bind to S,N over O): Pb(II, IV)
- **Metalloid** (hard; metal and non-metal behavior): Po(-II, II, IV, VI), I(-I, 0, I, V)



Biomolecules as carriers of radionuclides due to their original polyfunctionality (e^-, H^+, Me^{z+} transport)



Site heterogeneity → **Distribution fct of K**

Chelating Site: **Ligand exchange**

Electron-(redox) active Site: **Electron exchange, radical Formation**

Acid/Base Sites: **Proton exchange**

Potential Chemical Reaction Site

Hydrophobic Reaction Site: **pI, pH and pE dependent folding resulting in 3-dim. Structure and "stickiness"**

Potential complications (field data

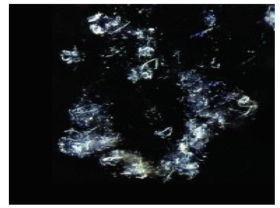
- **Problem of fluid particle-solution boundary, problem of carrier phases for radionuclides that mask their physico-chemical properties in solution, complicates modeling.**

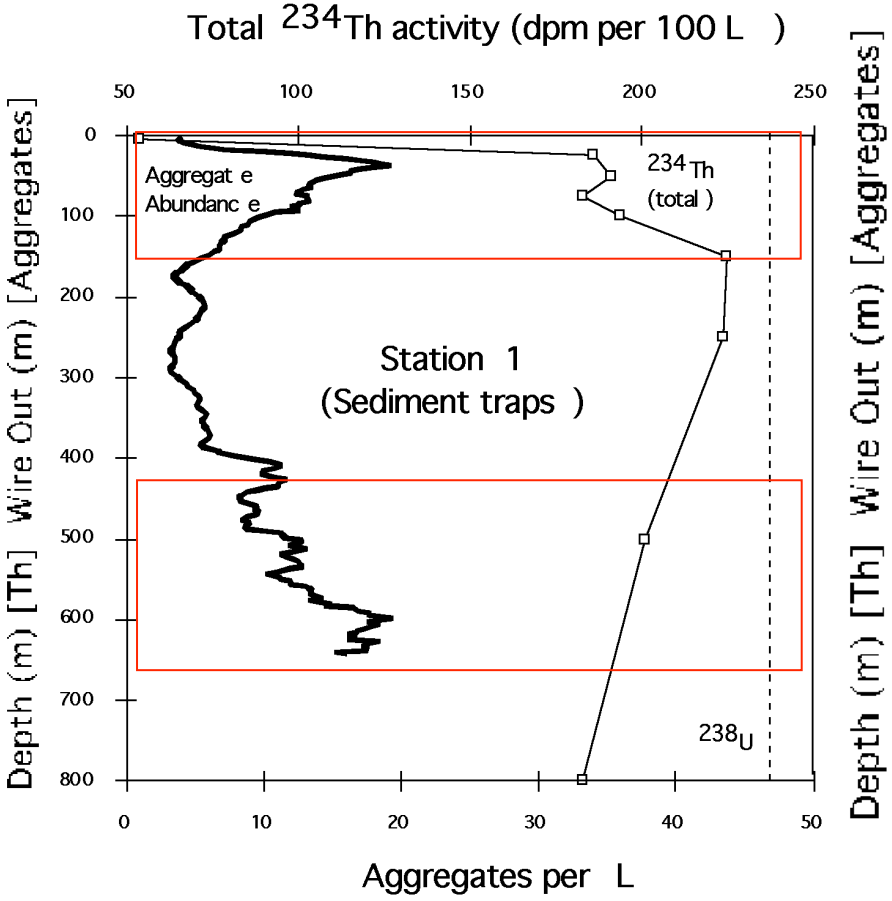
- **Problem of operationally defined procedures and reliance on proxies that can produce paradoxical results and correlations**

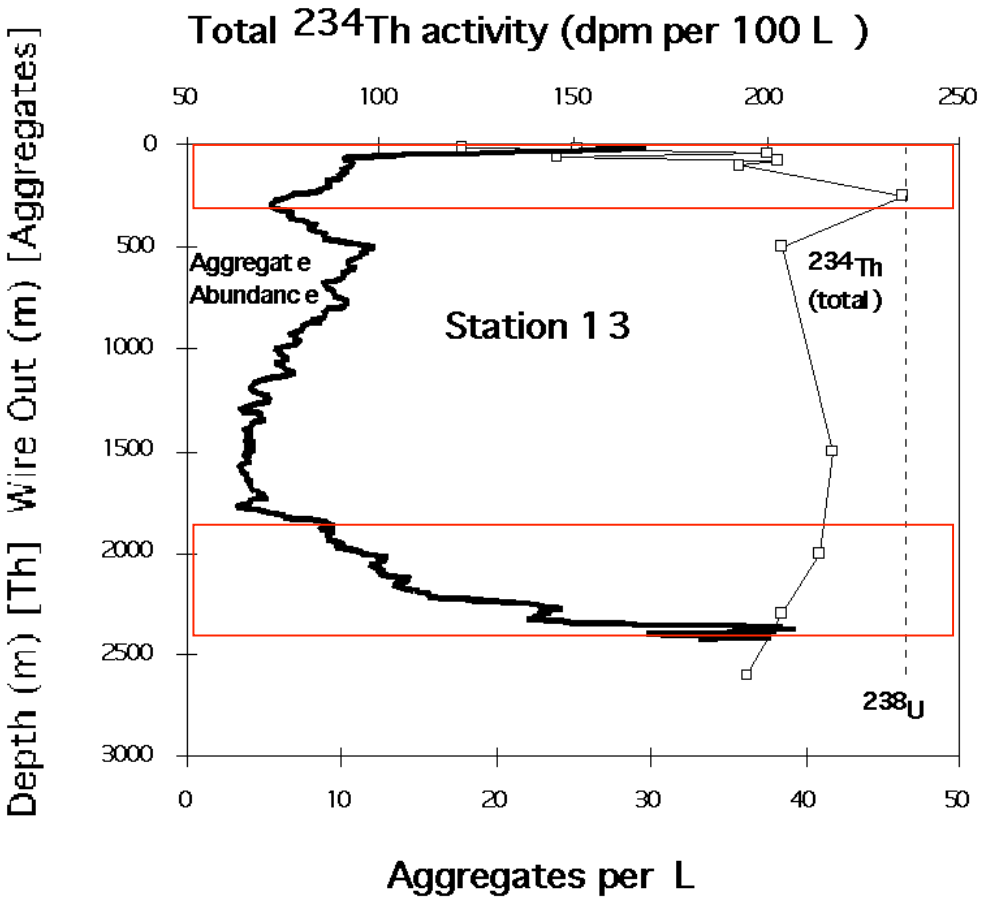
- **All Operational Approaches are limited by "Environmental Heisenberg uncertainty principle"**

^{234}Th deficiencies ($\sum(^{238}U-^{234}Th)$) in the water column as a measure of particle scavenging intensity from vertical & lateral processes in surface and deep waters (Santschi et al., 1999, Cont. Shelf Res., 19, 609).

Correspondence of Th-234 deficiency with abundance of aggregates (Aggr~TEP~APS~EPS), but not with SPM.

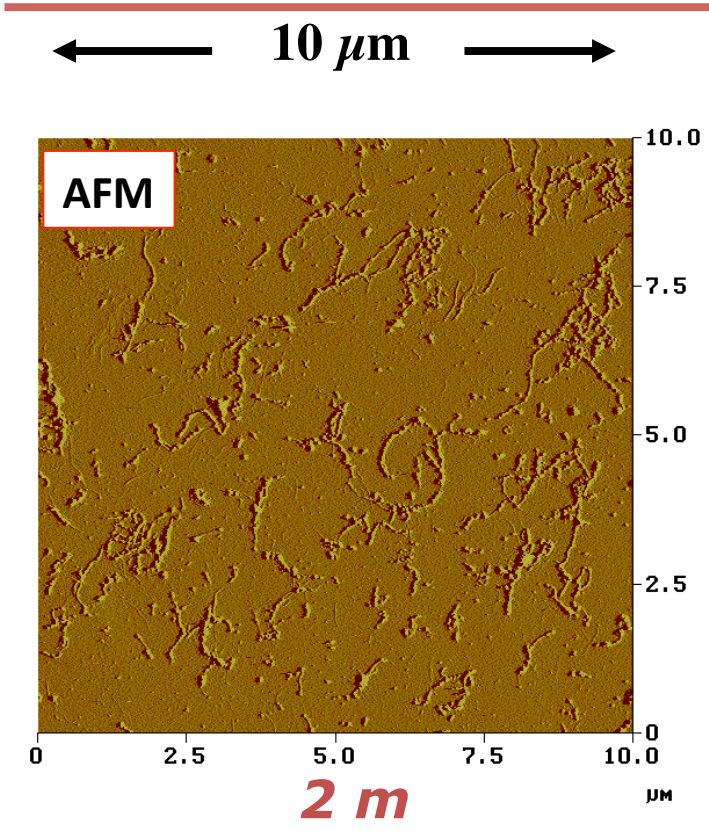


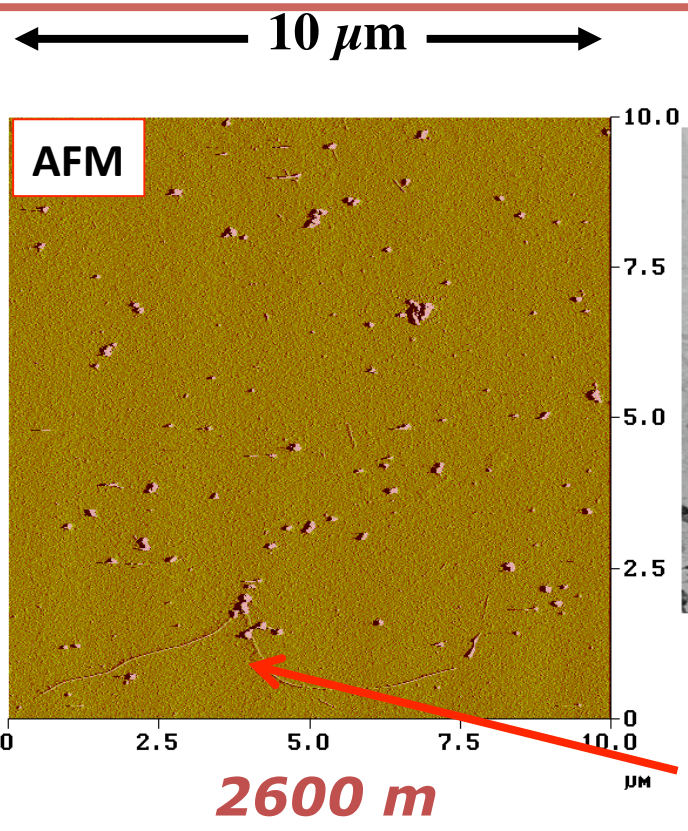


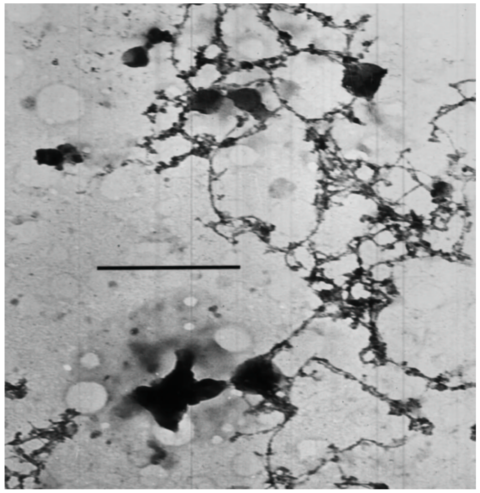


Abundance of Marine Snow Aggregates ≥ 1.5 mm dia α Th-deficiency

Fibrils in 1-200 nm COM from Middle Atlantic Bight, 2m and 2600m depth, documented by Atomic Force Microscopy (AFM, horizontal distance 10 μm) [Santschi et al., 1998. L&O 43, 896]







TEM, after staining

fibril

-> Forms and shapes of colloids: <u>pearls on necklace</u> most common colloidal form

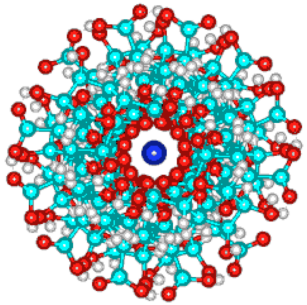
-> "spiderweb"; -> fibrils in surface and bottom waters, but not in mid-depth waters.

-> <u>modern radiocarbon ages of pure fibrils</u> (e.g., ~100% CHO)

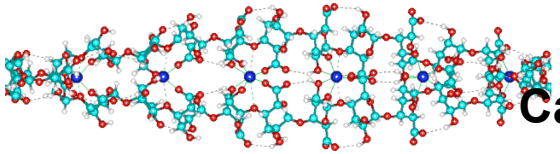
Metal Binding (chelation) to Alginic Acid: Role of Ca^{2+}: Egg Box Model for Trace Metal Complexation in Acid Polysaccharides (-> "sheltering")

Ca^{2+} can be Replaced by other metals, e.g., Fe(III), Th(IV)

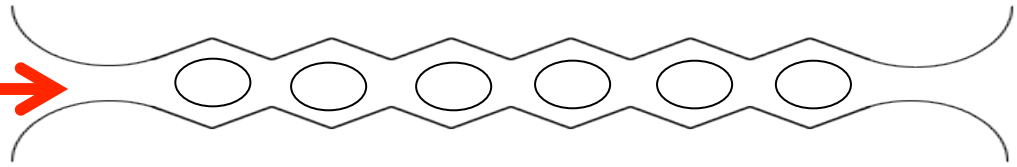
Calcium poly-α-L-guluronate left-handed helix view down axis

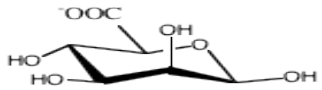


view along axis, showing the hydrogen bonding and calcium binding sites.

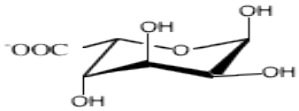


Ca^{2+}

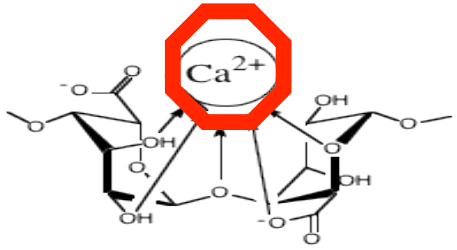




M ($^4C_1$)



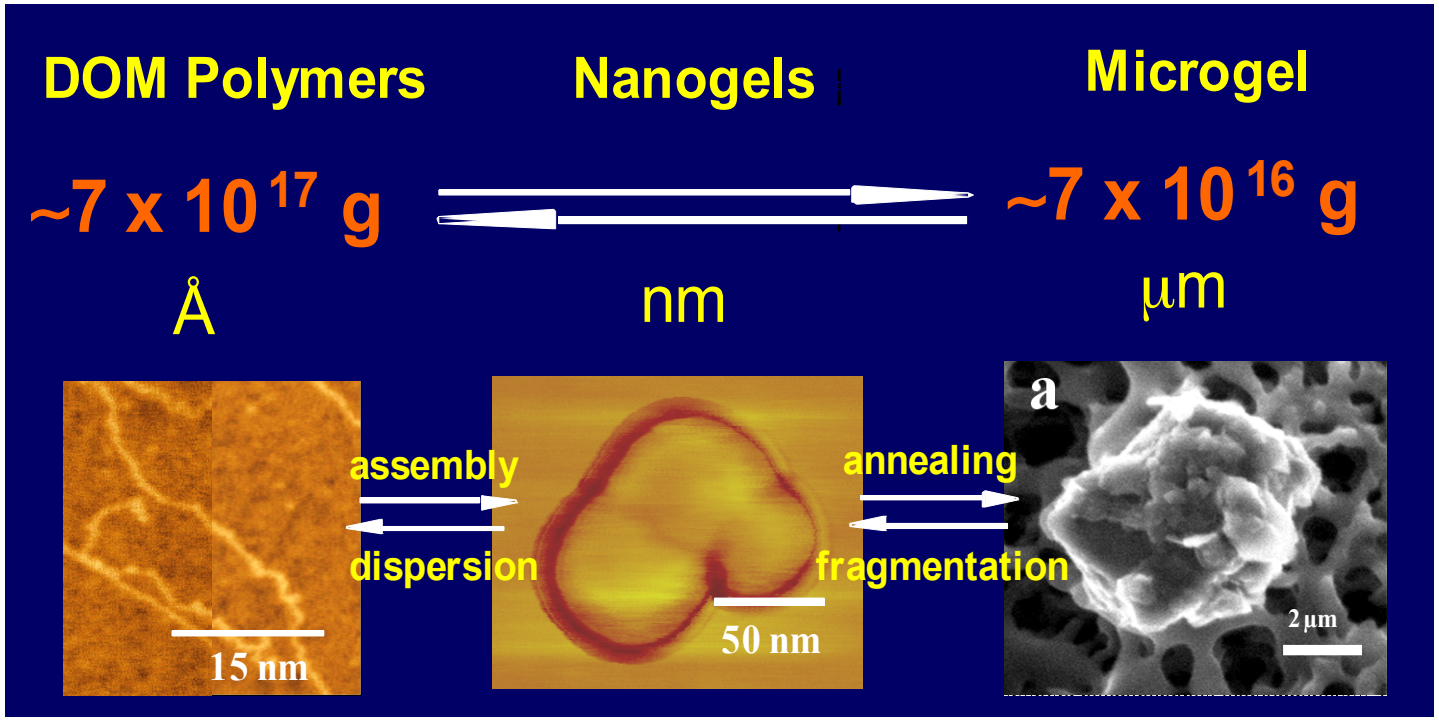
G ($^1C_4$)



Alginic Acid

Double-helix makes Molecule more rigid

EPS from micro-organisms enhance gel-forming properties; hydrophilic EPS are held together by Ca^{2+}-bridging (EDTA 'dissolves' them), EPS with hydrophobic moieties assemble through hydrophobic bridges (EDTA does not 'dissolve' them); gel self-assembly as a two-step reversible process:



AFM shows that during the first two hours following filtration, 0.2 μm-filtered seawater contain only free polymers that can be readily imaged on mica surface. After 5-10 hr nanogels start to appear. After 60 hr, assembly reaches equilibrium, forming microscopic gels of ~4-5 μm that can be filtered and imaged by environmental scanning electron microcopy (ESEM) [see review by Verdugo and Santschi, 2010].

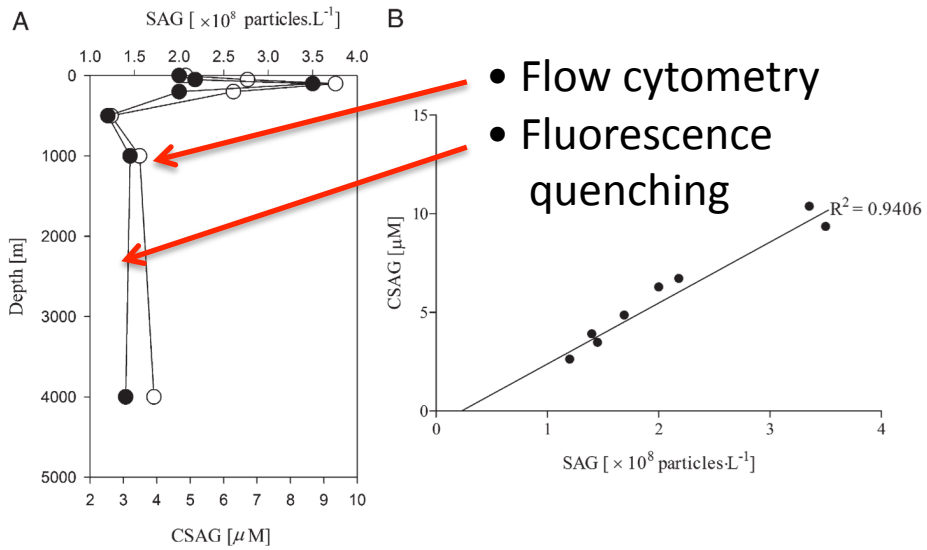


Fig. 3. A) Depth distribution of SAG from transects of samples collected from station ALOHA. Blank circles refer to data obtained by fluorescence quenching. Filled circle data were measured by flow cytometry. B) Comparison and statistical analysis of the results obtained with the fluorescence quenching method and the flow cytometry method. The line is a linear regression of $R^2 = 0.9406$.

Ding, Y.-X., Chin, W.-C., Verdugo, P. 2007. Development of a fluorescence quenching assay to measure the fraction of organic carbon present in self-assembled gels in seawater. Marine Chemistry, 106, 456–462.

Rodriguez et al., 2005. ASLO Mtg Abstract.

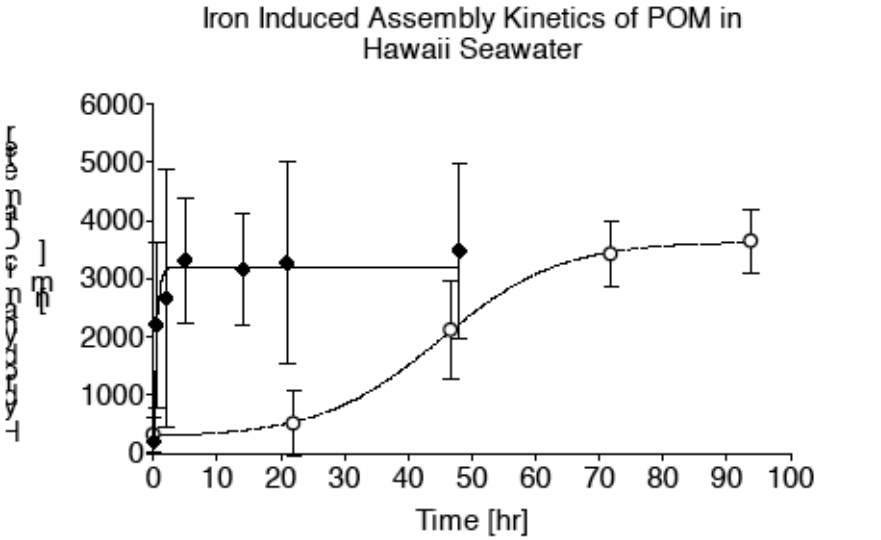
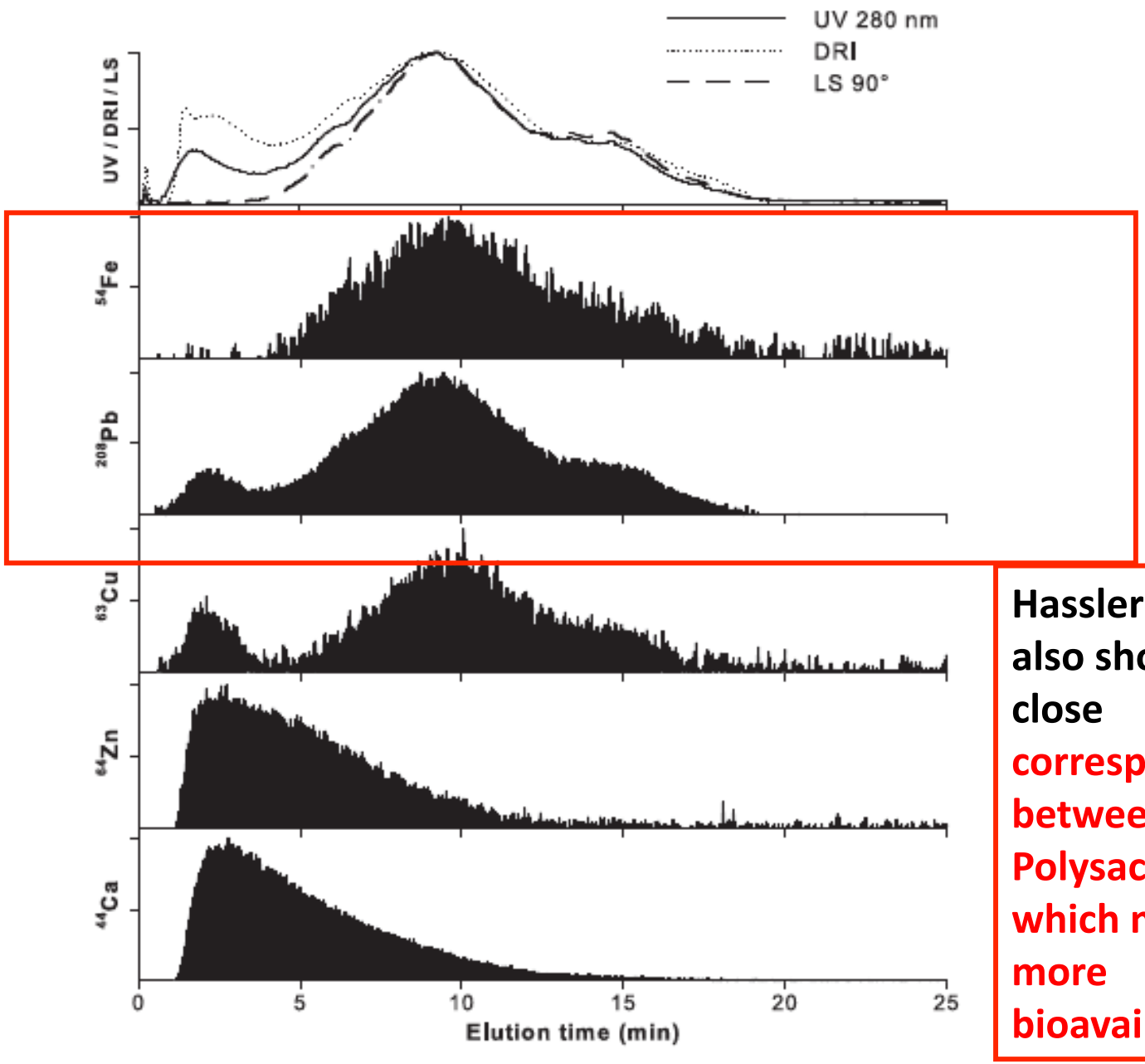


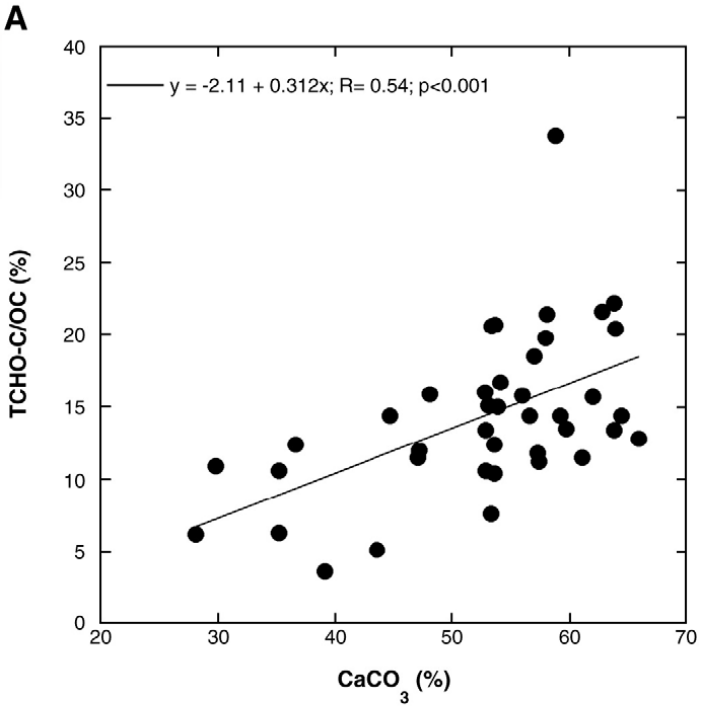
Figure 3a: Here the black diamonds represent the assembly of POM when the concentration of iron is raised about 0.1 nM and the hollow circles represent the assembly of POM under normal Hawaii water conditions.

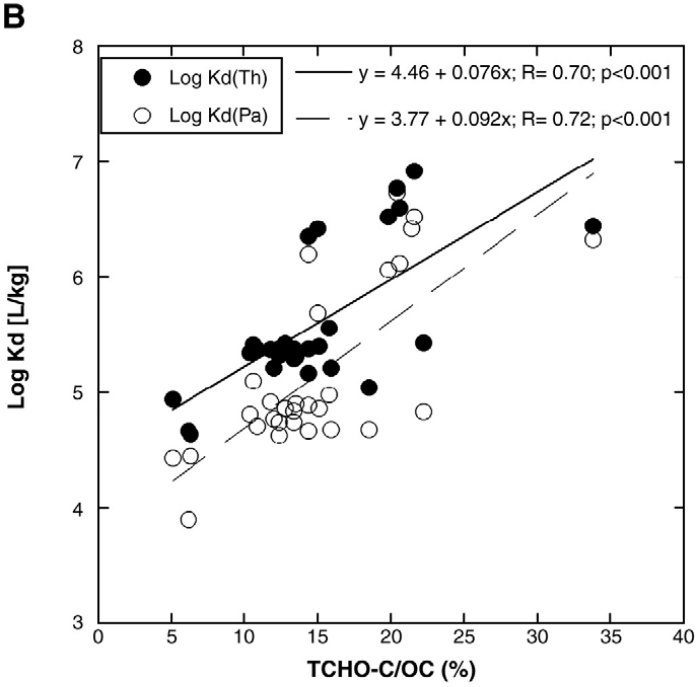
Gels occur throughout the water column, are bacterial hotspots, and their formation is greatly accelarated by Fe



Hassler et al. also showed close correspondence between Fe and Polysaccharides, which makes Fe more bioavailable

Fig. 4. Size distribution of metals associated with the EPS. MALS, UV and selected ICP-MS signals (normalized to the maximum peak height) obtained from the aFlFFF of 500 µL of 0.667 g L^{-1} EPS produced by bacterium CAM036.





Earth and Planetary Science Letters 286 (2009) 131–138

Contents lists available at ScienceDirect

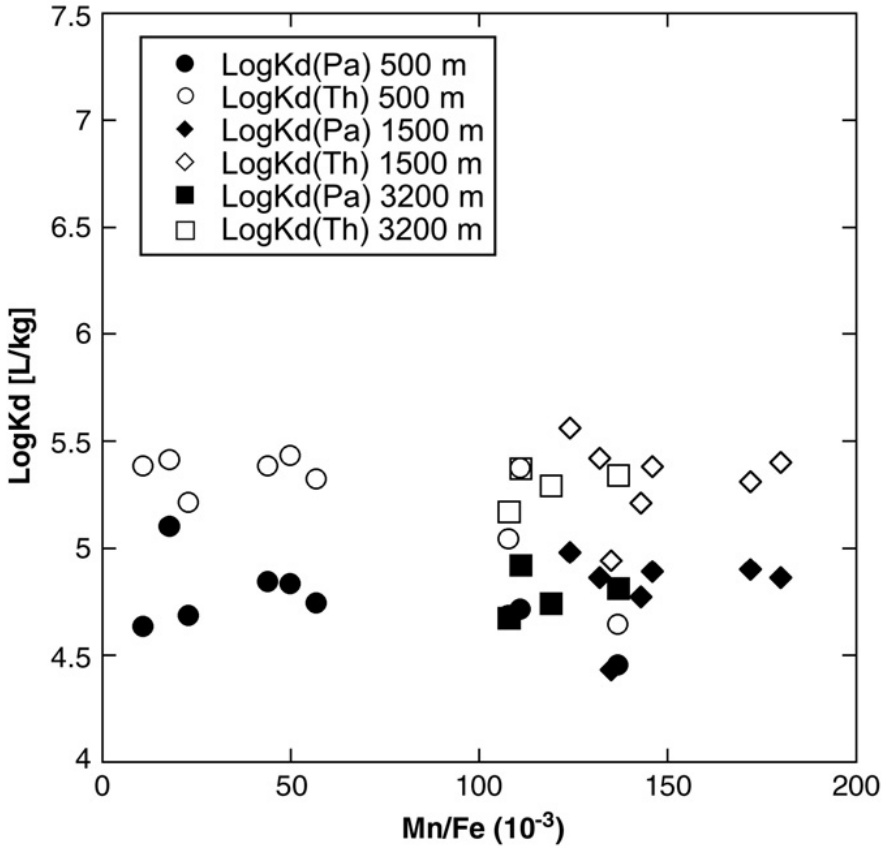
Earth and Planetary Science Letters

journal homepage: www.elsevier.com/locate/epsl

Scavenging and fractionation of thorium vs. protactinium in the ocean, as determined from particle–water partitioning experiments with sediment trap material from the Gulf of Mexico and Sargasso Sea

Kimberly A. Roberts [a,1], Chen Xu [a], Chin-Chang Hung [b], Maureen H. Conte [c], Peter H. Santschi [a,*]

[a] Texas A&M University at Galveston, 5007 Ave U, Galveston, TX 77551, United States
[b] Institute of Marine Environmental Chemistry and Ecology, National Taiwan Ocean University, 2 Pei-Ning Rd, Keelung, 202, Taiwan
[c] Bermuda Institute of Ocean Sciences, 17 Biological Lane, St. George's GE 01, Bermuda



2005, 2006 cruises To GOM

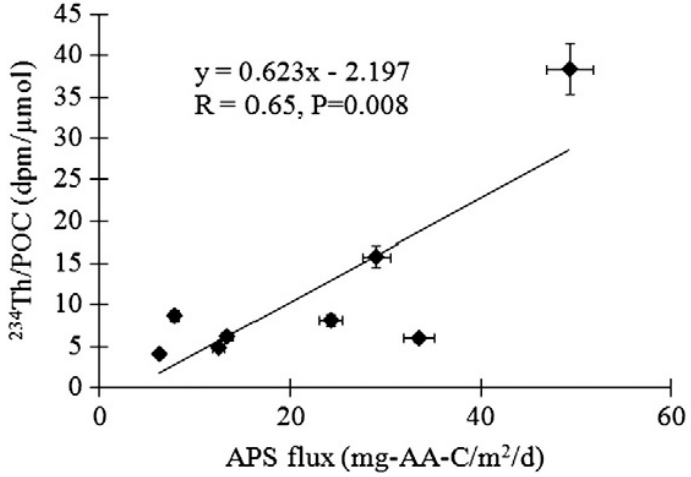
Marine Chemistry 123 (2011) 111–126

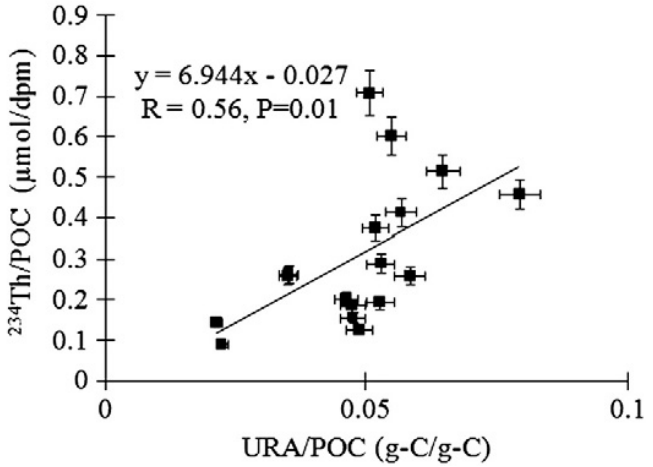
Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem

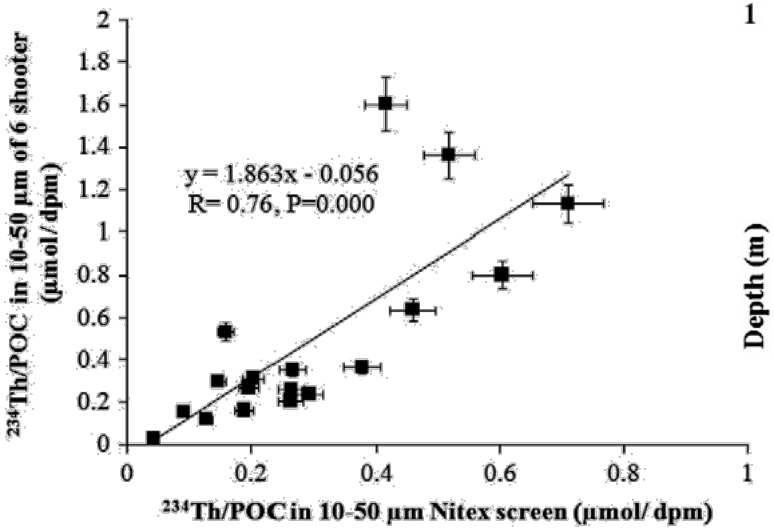
Controls of ^{234}Th removal from the oligotrophic ocean by polyuronic acids and modification by microbial activity

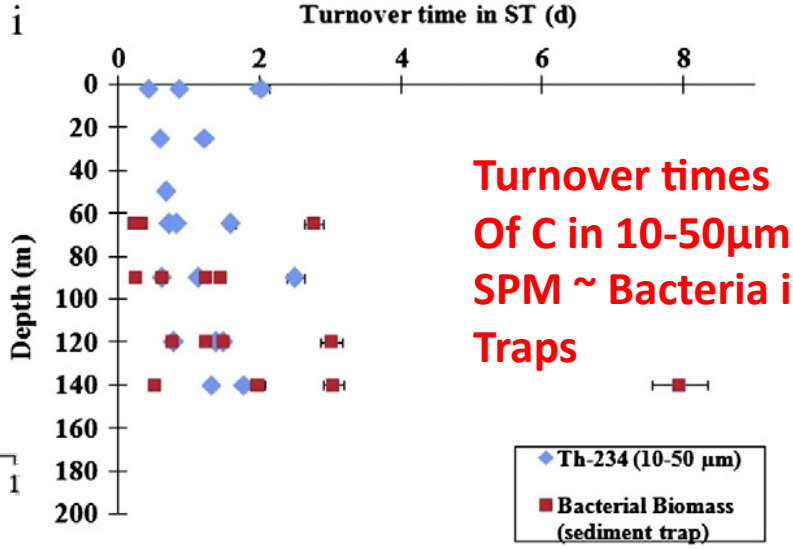
Chen Xu [a], Peter H. Santschi [a,*], Chin-Chang Hung [b], Saijin Zhang [a], Kathleen A. Schwehr [a], Kimberly A. Roberts [a], Laodong Guo [c], Gwo-Ching Gong [b], Antonietta Quigg [a], Richard A. Long [d,e], James L. Pinckney [e,f], Shuiwang Duan [a], Rainer Amon [a], Ching-Ling Wei [g]



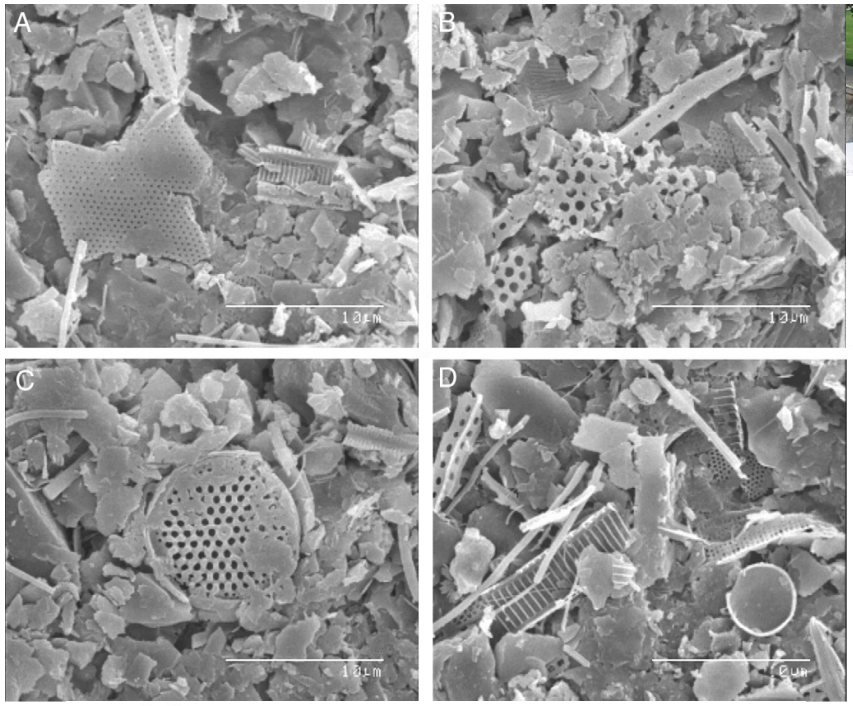


Similar to Guo et al., 2002; Santschi et al., 2003





Turnover times Of C in 10-50µm SPM ~ Bacteria in Traps



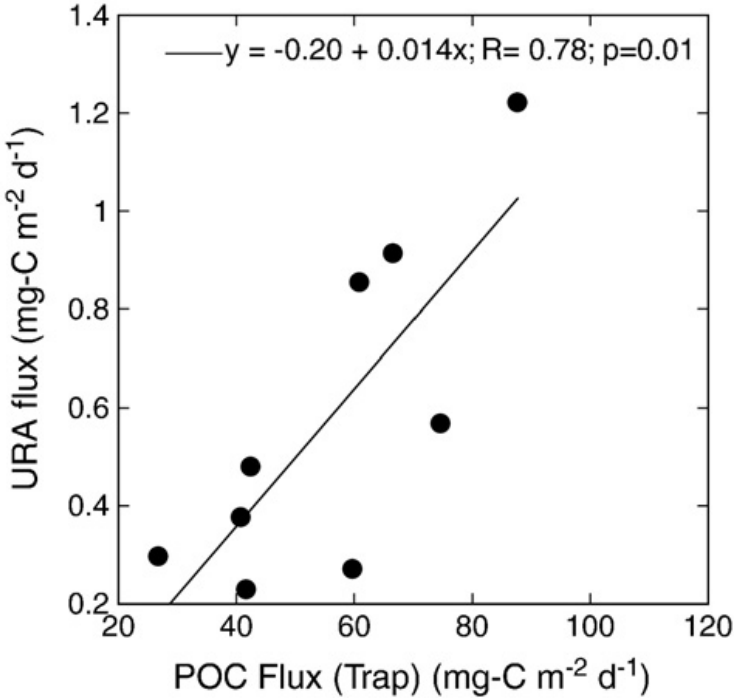
Marine Chemistry 121 (2010) 132–144

Marine Chemistry

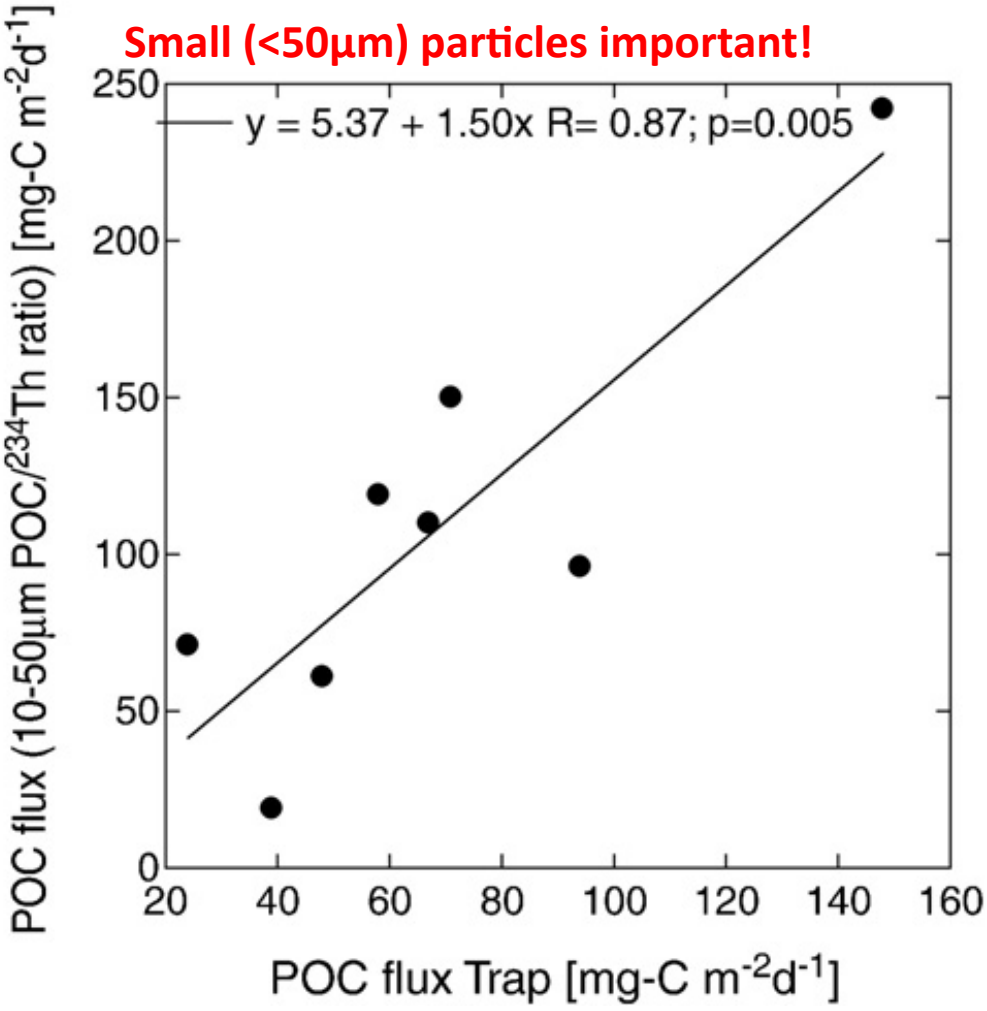
journal homepage: www.elsevier.com/locate/marchem

Comparative evaluation of sediment trap and ^{234}Th-derived POC fluxes from the upper oligotrophic waters of the Gulf of Mexico and the subtropical northwestern Pacific Ocean

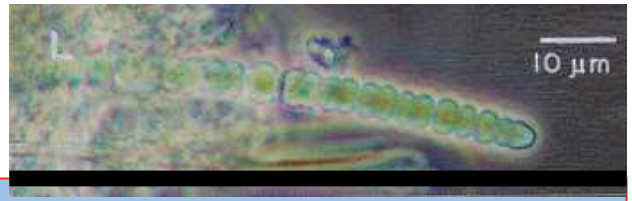
Chin-Chang Hung [a,b], Chen Xu [a], Peter H. Santschi [a,*], Sai-Jin Zhang [a], Kathleen A. Schwehr [a], Antonietta Quigg [a], Laodong Guo [c], Gwo-Ching Gong [b], James L. Pinckney [d], Richard A. Long [e], Ching-Ling Wei [f]



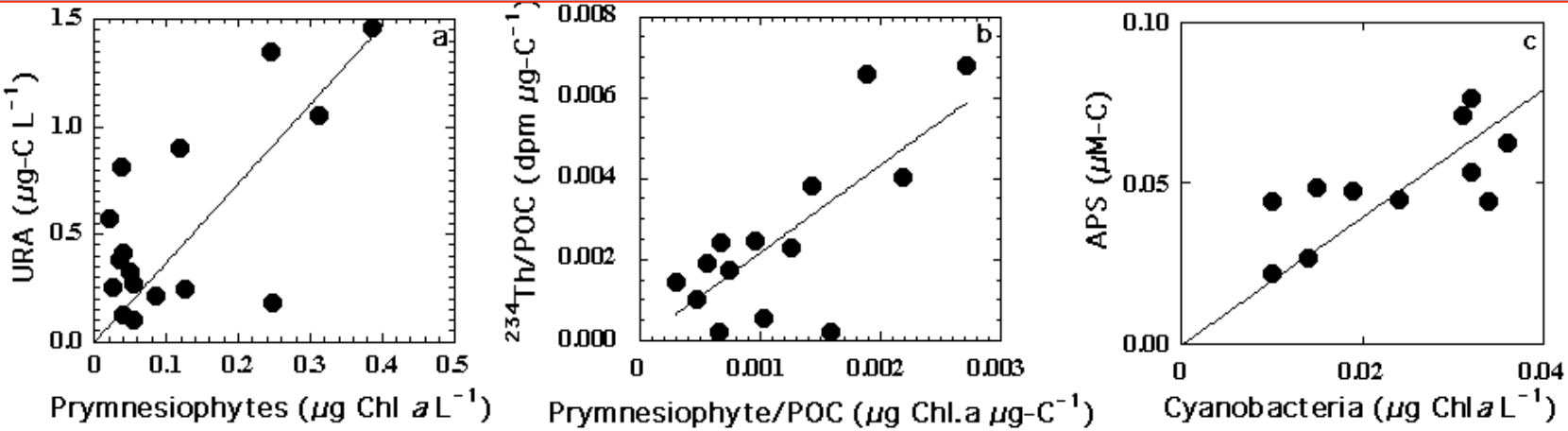
Small (<50µm) particles important!



Importance of Prymnesiophytes in 2001 and Cyanobacteria in 2000 [Santschi et al., 2003, GRL 30, 1044], and Diatoms in 2006



Abundance in ocean: CHO /POC ~ 0.1, APS/POC ~ 0.01, URA/POC ~ 0.01 (all: Santschi et al., 2003; Hung et al., 2003), Lig. /POC ~ 0.001 (Hirose, 2004); ^{234}Th/Lig. ~ 10^{-7} – 10^{-12}



Different phytoplankton species appear, at times, to control acid polysaccharide (APS) e.g., uronic acid (URA), production and ^{234}Th (IV) complexation (-> autoporetic system)

SiO2 as carrier

Evidence for role of diatom-SiO2 From Correlations

But: pure SiO_2 is a Weak sorbent

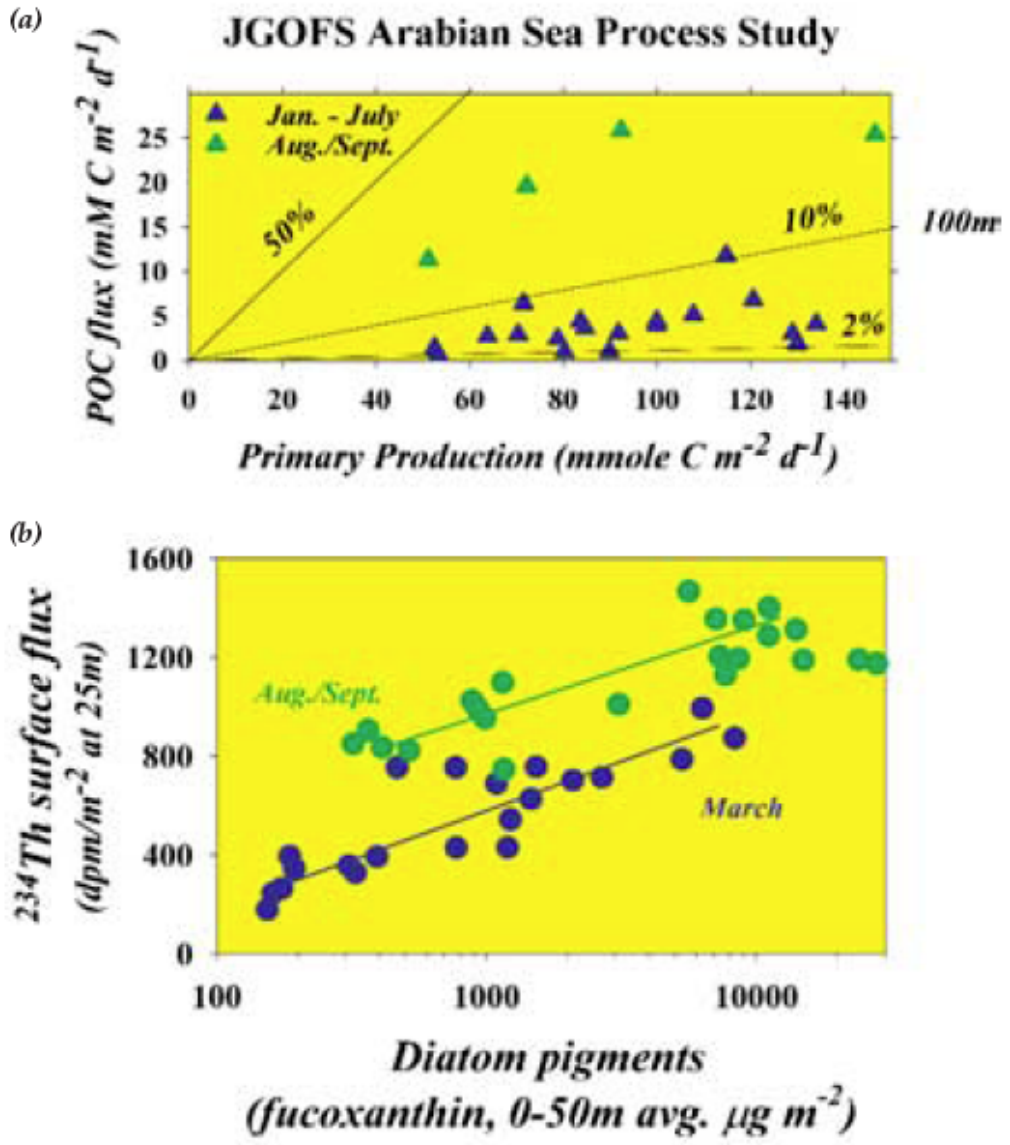
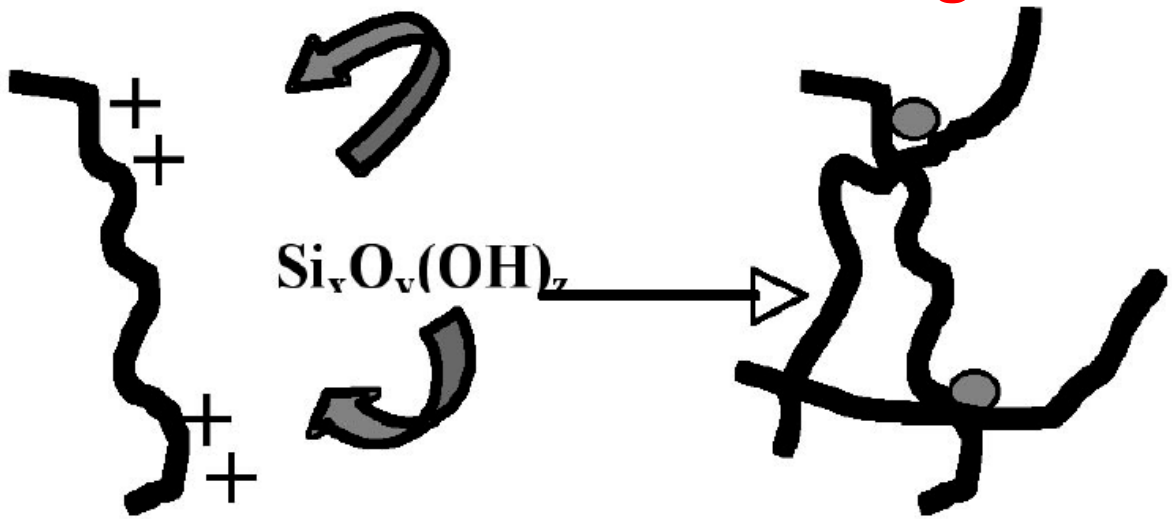


Figure 5. a) Relationship between primary production and Particulate Organic Carbon (POC) export derived from ^{234}Th measurements at 100 m in the Arabian Sea. Note high ratio of POC flux to primary production in August and September. b) Relationship between ^{234}Th export and fucoxanthin (diatom) pigments, showing higher ratio of ^{234}Th export to fucoxanthin flux in August and September during the latter part of the southwest monsoon.

Complexation of trace substances to Organic Templates?



e.g., silaffins that act as templates for the assembly of nano-silica polymers in diatom shells used in paleo-reconstructions

Figure 1:Self-assembling cationic biopolymers interact with anionic silicates to form silica nanoparticles.

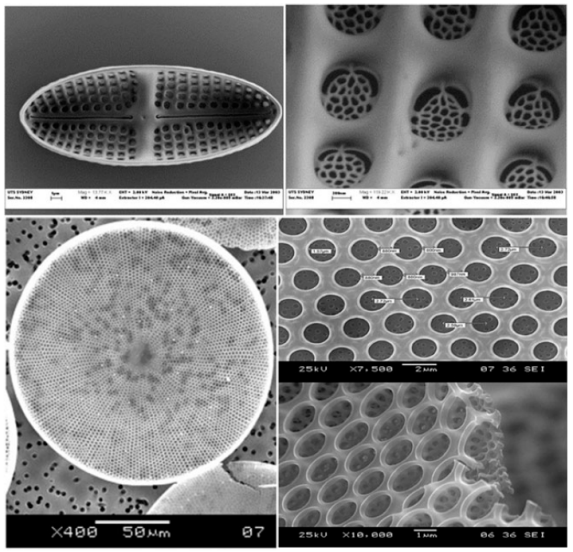


Fig. 4 Hierarchical distribution of pores in diatom frustules; Top: *Achnanthes subsessilis* (reprinted from Materials Science and Engineering C, 25, K.S.A. Butcher *et al.*, A luminescence study of porous diatoms, 659, Copyright (2010), with permission from Elsevier); Bottom: *Coscinodiscus walesii* (reprinted from ref. 77, Copyright (2010), with permission from Elsevier).

-> Can organic residues act as binding agents of natural radionuclides to diatoms (rather than pure silica which is a poor sorbent)?

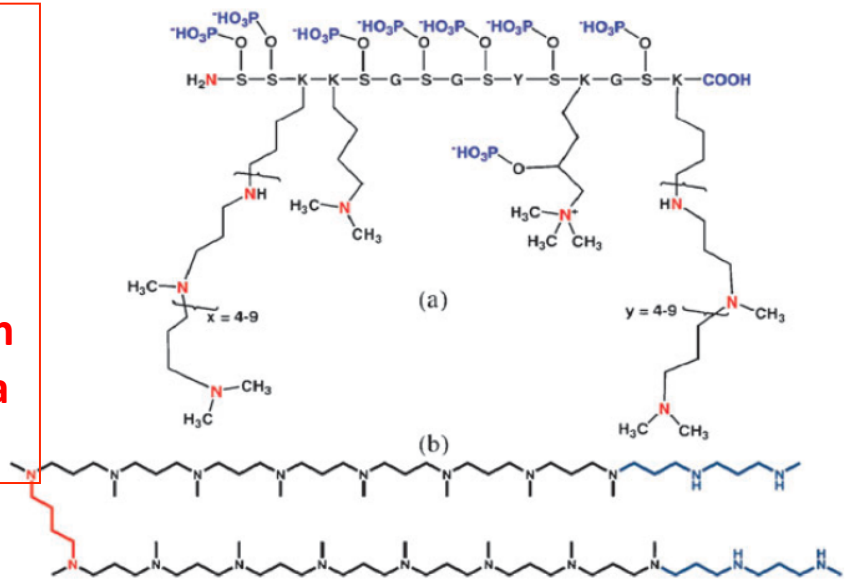
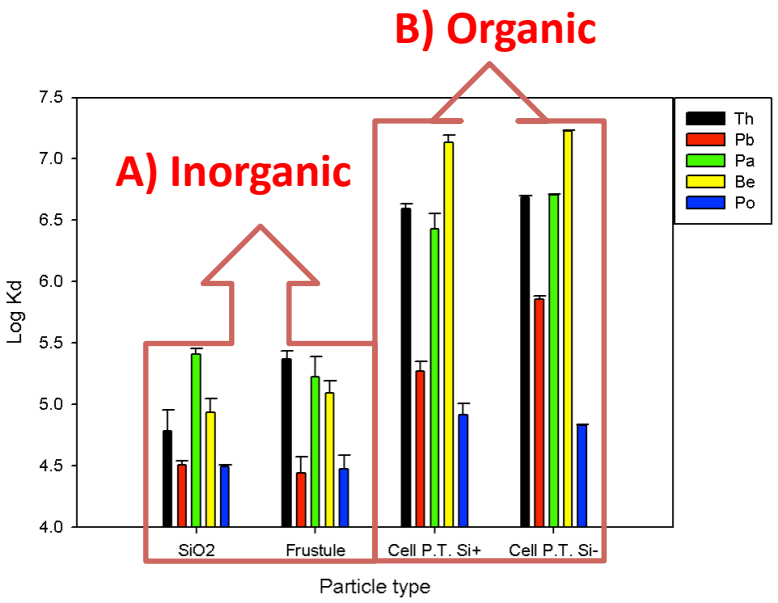
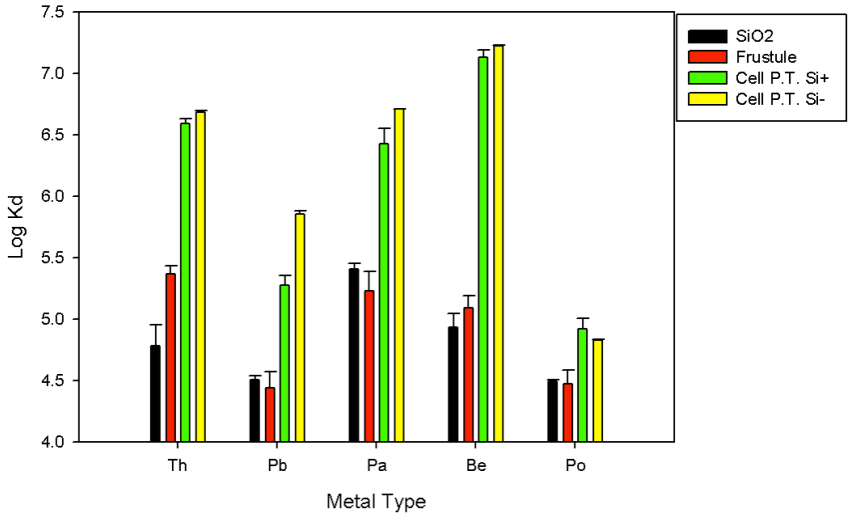


Fig. 5 Molecular structure of (a) silaffins and (b) LPA.





Treatments:

A) Inorganic particle

1. SiO2
2. Diatom, *Phaeodactylum tricornutum* Frustules (Carbon content < 0.1%)

B) Organic particle

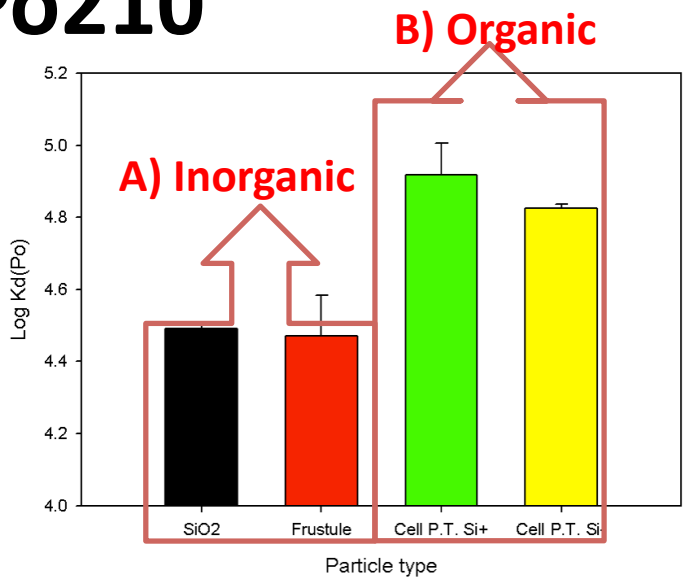
Fresh uncleaned diatom cells (P.T. = *Phaeodactylum tricornutum)*

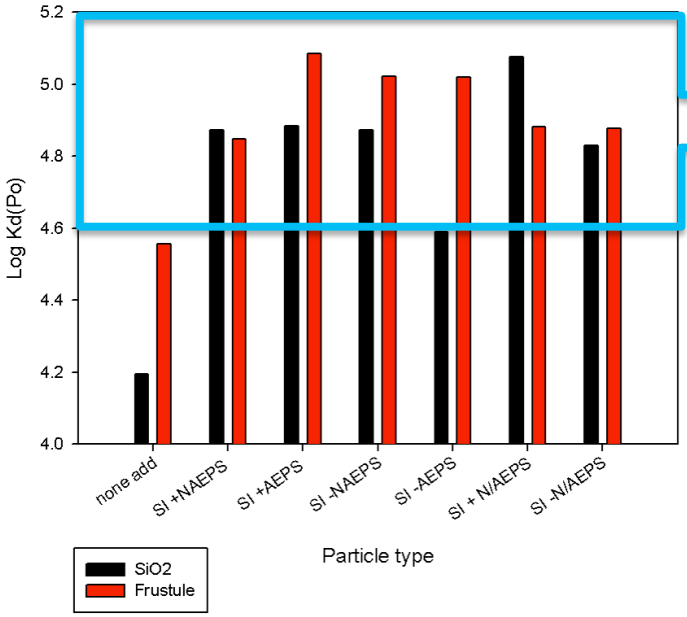
1. diatom cultured under Si + (with Si shell)
2. diatom cultured under Si – (without Si shell)

- Kd sequence: Be>Th~Pa>Pb>Po
- SiO2~cleaned Frustule < Cells P.T.
- high Kd for diatom cells with and without SiO2 shell

Anderin Chia-Ying Chuang, unpublished results

Po210





Treatments:

A) Inorganic particle

1. SiO2
2. Diatom, *Phaeodactylum tricornutum* Frustules (Carbon content < 0.1%)

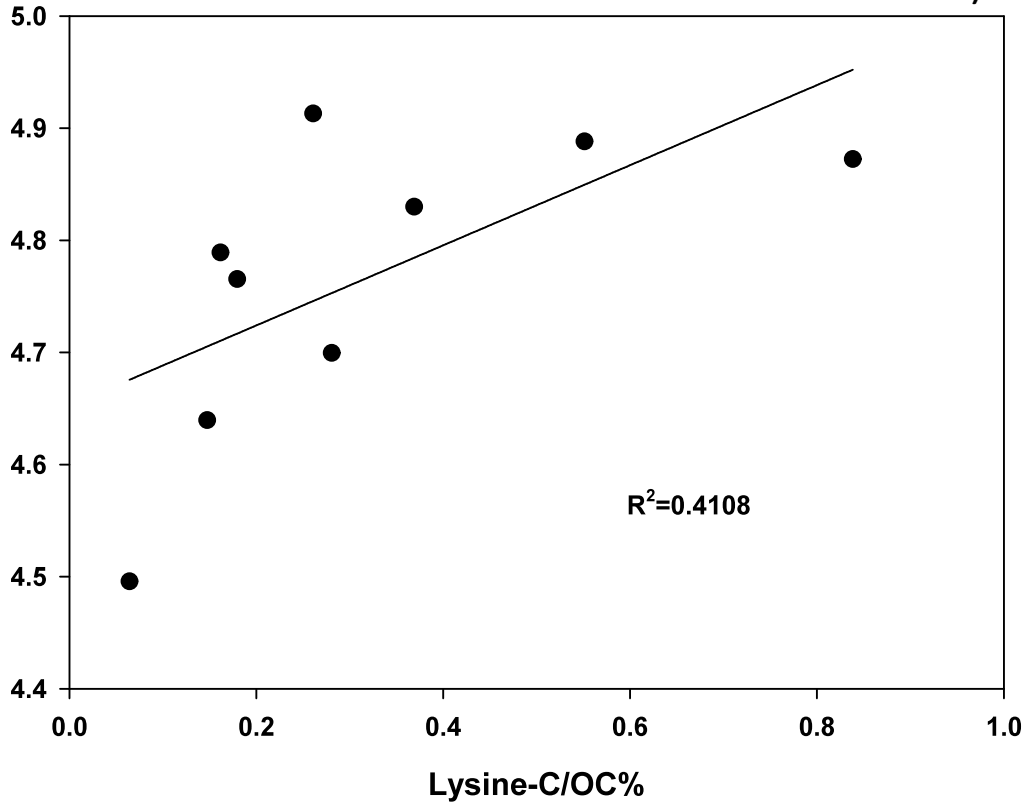
B) Organic particle

Fresh uncleaned diatom cells (P.T. = *Phaeodactylum tricornutum)*

1. diatom cultured under Si + (with Si shell)
2. diatom cultured under Si – (without Si shell)

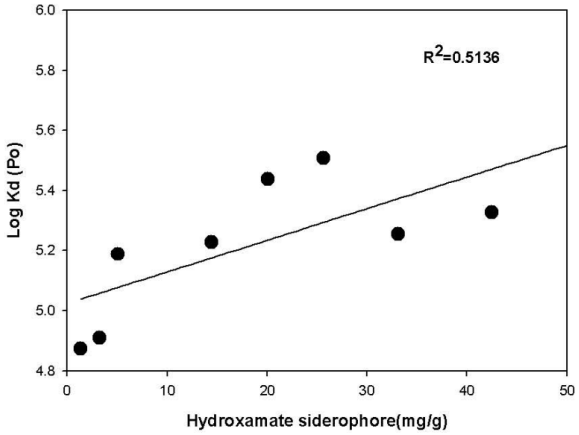
Significant Enhancement observed when organic material present in inorganic particle system

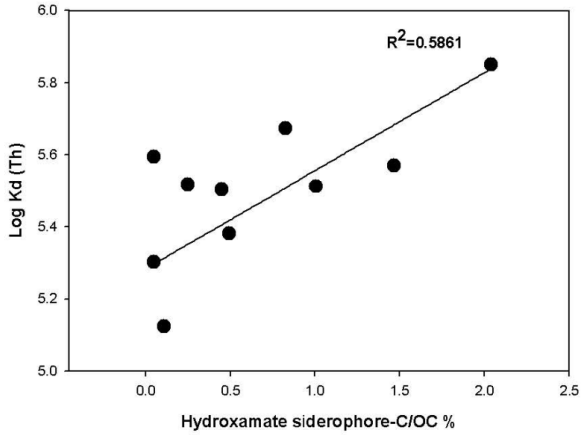
Colloids (collected from Pacific Ocean ; OC:1.50 to 33.45%)



Correlation of Log Kd(Be) with % Lysine-C/OC, the only one among all the amino-acids analyzed.

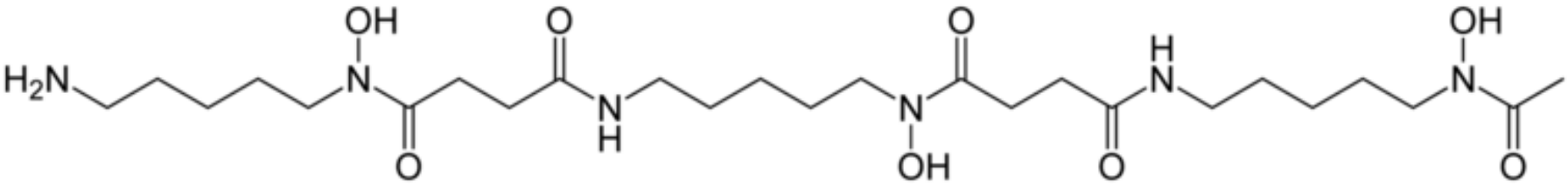
Colloids (collected from Pacific Ocean ; OC:1.50 to 33.45%)



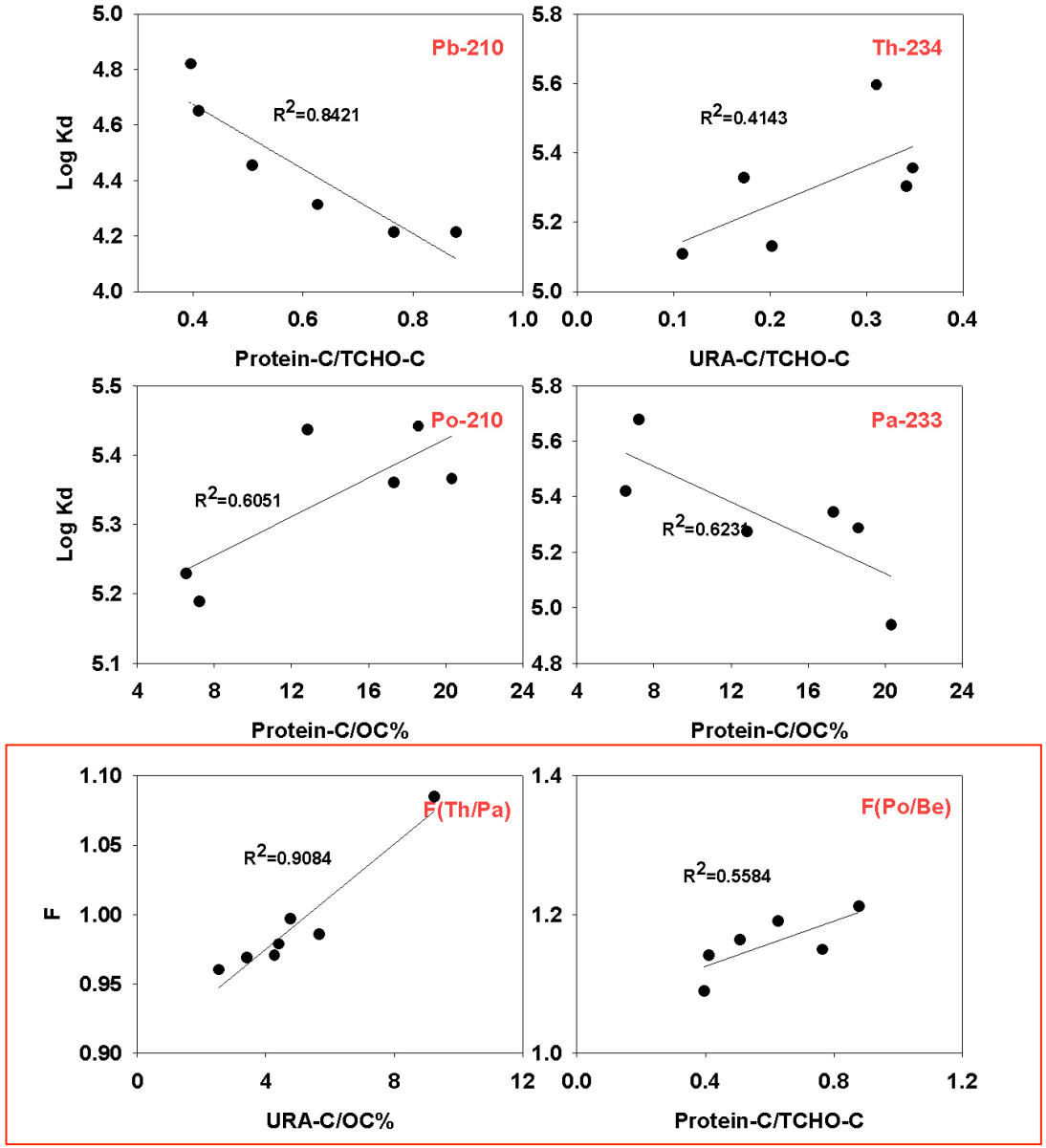


Kd(Th, Po) ~ fct ([siderophore-hydroxamates])

No relationships for Be, Pa and Pb; Anderin Chia-Ying Chuang, unpublished results



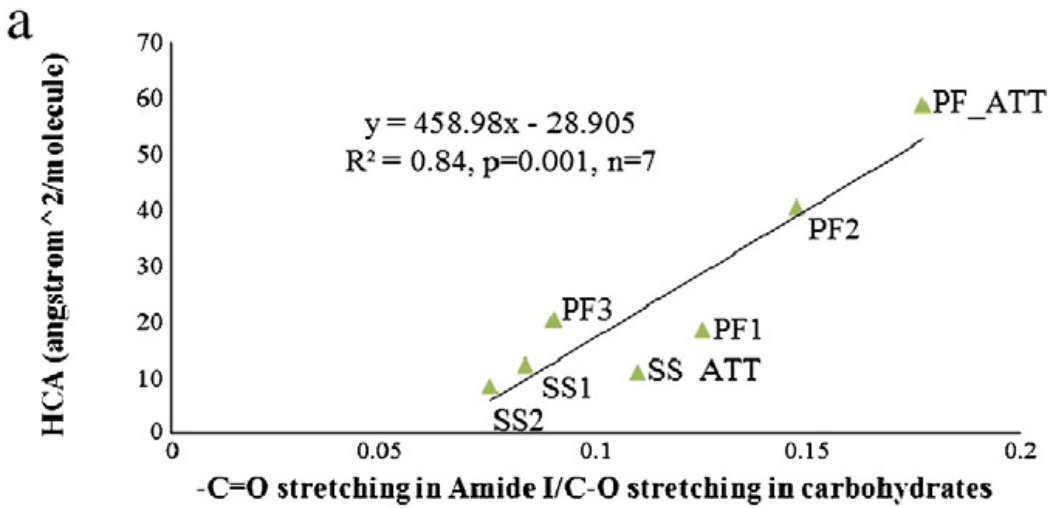
Colloids and EPS (OC%>20 w/w)

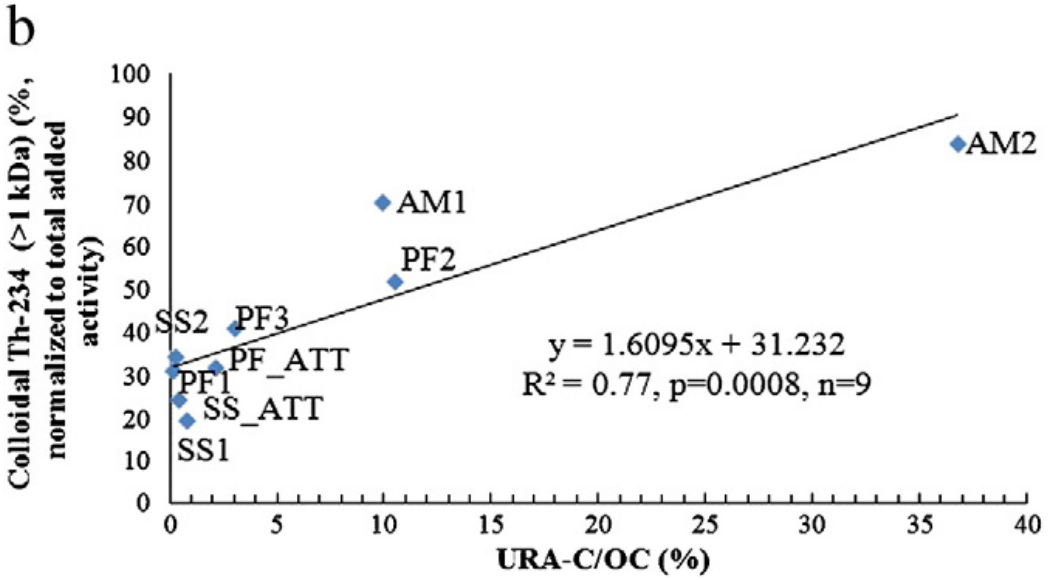


Kd(Po) ~ fct ([Protein]) Kd(Th) and Kd (Th)/Kd(Pa) ~ fct ([Uronic Acids])

Anderin Chia-Ying Chuang, unpublished results

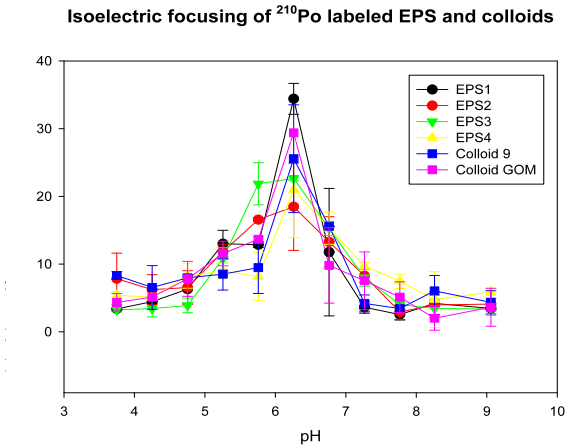
Hydrophobic Contact Area, HCA vs. Protein/Carbohydrate Ratio (FTIR)





Xu, C., Zhang, S., Chuang, C.-Y., Miller, E.J., Schwehr, K.A., Santschi, P.H. 2011. Marine Chemistry, 126, 27-36.

Example for separating radionuclide-tagged organic matter from EPS produced by diatom, *Phaeodactylum tricornutum*
Colloids: Pacific Ocean& Gulf of Mexico



Contrary to:
Th: ~3-4;
Pb: ~3-4;
Pa: ~5;
Be: ~ 8.5

Isoelectric point of many amino acids and iron(II, III) oxide (magnetite).

Future experiments:

Characterization, at molecular levels, using Multi-dim. NMR, ESI-MS in P. Hatcher lab [Xu, C. et al.. 2011. GCA, accepted. Xu, C. et al. 2008. ES&T, 42(22), 8211-8217]**, similar to**

a)a Pu (and Th-) and

b)b) ^{129}I -carrying water-extractable colloids from soil/sediments from contaminated sites, after IEF, UF, and/or HPLC separation and pre-concentration

What we know:

1) concentrations of carbohydrates or uronic acids (or their ratios to C) are good proxies for presence of strongly Th complexing ligand;
2) presence of proteins, or protein/carbohydrate ratio, is a proxy for strongly Po binding amino acids, and of "stickiness" or relative hydrophobicity;
3) Siderophores (hydroxamate) are good proxies for Th- (and Po-?) binding ligand.

What we do not know:

- molecular structure of trace radionuclide binding ligands
- Role of templeting proteins as radionuclide carriers

New Hypotheses:

silaffins, siderophores, poly-lysines, uronic acids are suitable macromolecular carrier ligands for selected radionuclides.

Acknowledgments: it takes a village to be successful!

U.S. Department of Energy
Office of Science
Office of Biological & Environmental Research
Climate and Environmental Sciences Division | Biological Systems Science Division

NSF
OCE-0351559, 0851191