Acknowledgements:

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WHERE DISCOVERIES BEGIN

Energy
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Biopolymers as carriers of natural (Th, Pa, Pb, Po, Be) and waste (e.g, Pu, I) radionuclides in aquatic systems

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Objectives

- Relate environmental chemistry of Be to that of other radionuclides.
- Explore role of biopolymeric carriers for radionuclides in the environment.
- Lessons from field and lab studies using 'correlative' and 'extractive' approach.
- Relevance for remediation, interpretation of results from applications, e.g., historical reconstructions, etc.

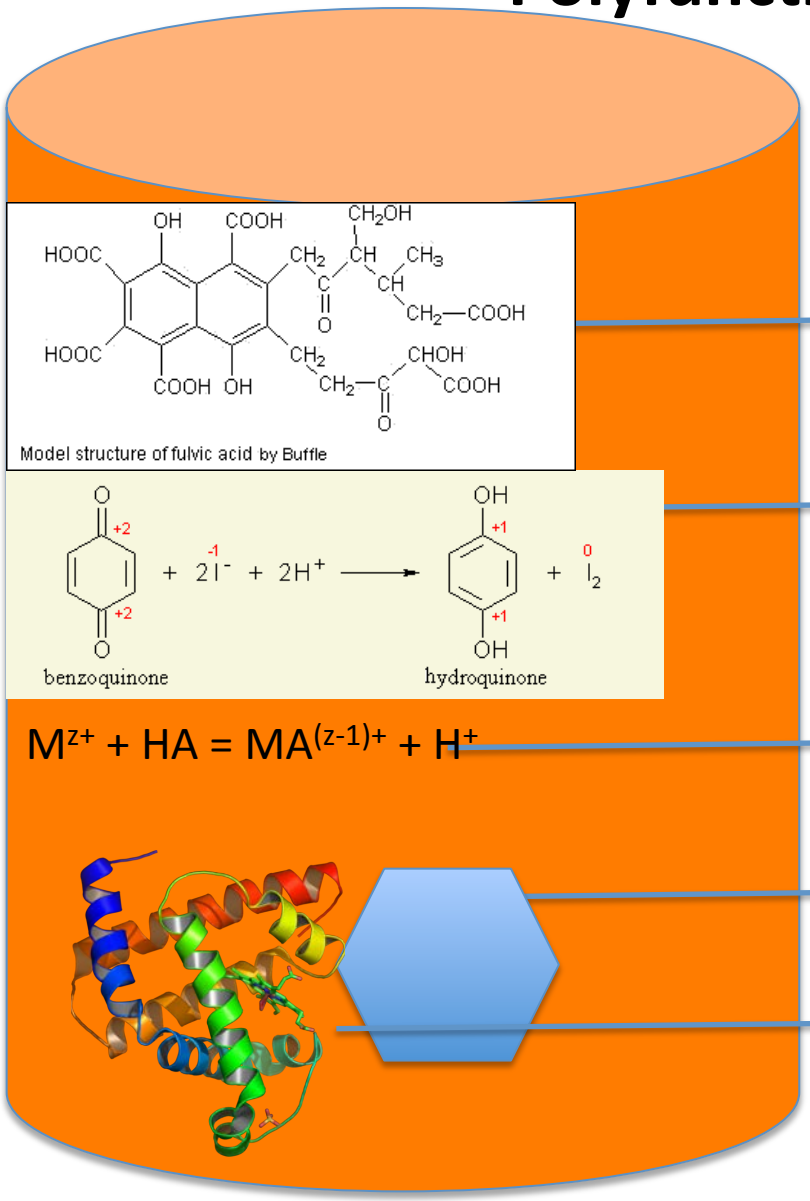
Common Uses of Natural Radionuclides in Environment: Cosmic Ray Produced and Parent-Daughter Radionuclide Pairs allow

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

Common (multiple) oxidation states of environmental radionuclides

- A-type: U(IV,VI), Th(IV), Pa(IV,V), Pu(III,IV,V), Be (II)
- B-type: Pb(II, IV)
- Metalloid: Po(-II, II, IV), I(-I, 0, I, V)

Biomolecules as Carriers of Radionuclides due to their Polyfunctionality



Chelating Site:
Ligand exchange

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

Anionic Site:
Proton exchange

Chemical Reaction Site:
example aromatic C for I

Hydrophobic Reaction Site:
pI, pH and pE dependent folding resulting in 3-dim. structure

Evidence for organic carriers for different colloidal radionuclides

- 'Extractive' Approach: Composition of isolated colloids (e.g., Pu, Th, I)
- 'Correlative' Approach: Relationships between DOC/ PS/APS and colloidal radionuclide concentrations (e.g., Th)
- 'Correlative' Approach: Relationships between POC/ ^{234}Th or Pa/Th ratios in particles and compositional parameters such as acid polysaccharide (APS) concentrations (e.g., Th, Pa)
- 'Correlative' Approach: Relationships between aromatic C and I in colloids

Reasons for Study

- Why do we want to know this?
- -> Remediation , interpretation of results, forecasting, allows decision in controversies
- Requires overarching approaches crossing established disciplines, but limited by “Environmental Heisenberg uncertainty principle”
- High reward, as it might cause a Paradigm shift, but full of potential artifacts.
- Architecture of environmental macromolecules: inside hydrophobic, outside hydrophilic, with chelating and redox active sites → ‘All-in-one’ carrier bio-geo-polymers?

Evidence

from

Correlations

But:

SiO2 is

Weak

sorbent

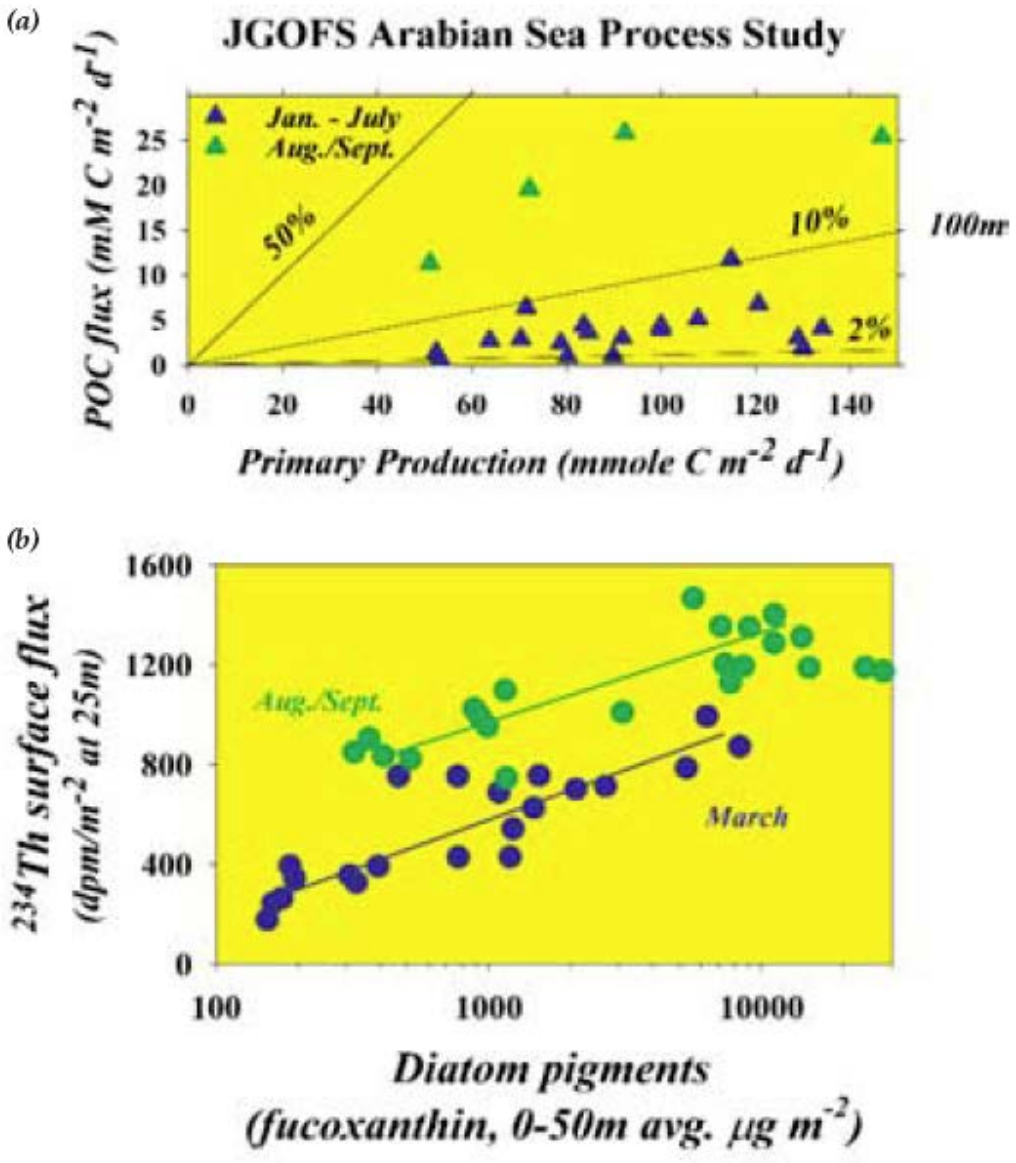
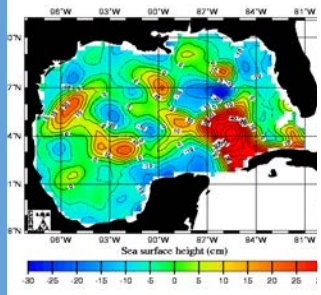
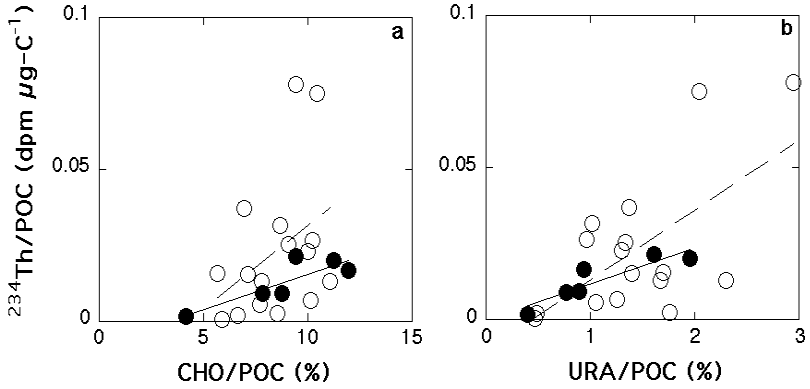


Figure 5. a) Relationship between primary production and Particulate Organic Carbon (POC) export derived from ^{234}Th measurements at 100 m in the Arabian Sea. Note high ratio of POC flux to primary production in August and September. b) Relationship between ^{234}Th export and fucoxanthin (diatom)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

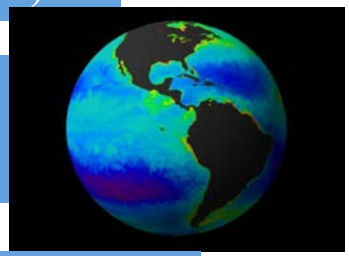
Relationship between ^{234}Th/POC ratio and POC-normalized APS and Carbohydrate Concentrations [Guo et al., 2002, Mar. Chem. 78, 103-119; Santschi et al., GRL.30,C2, 1044]

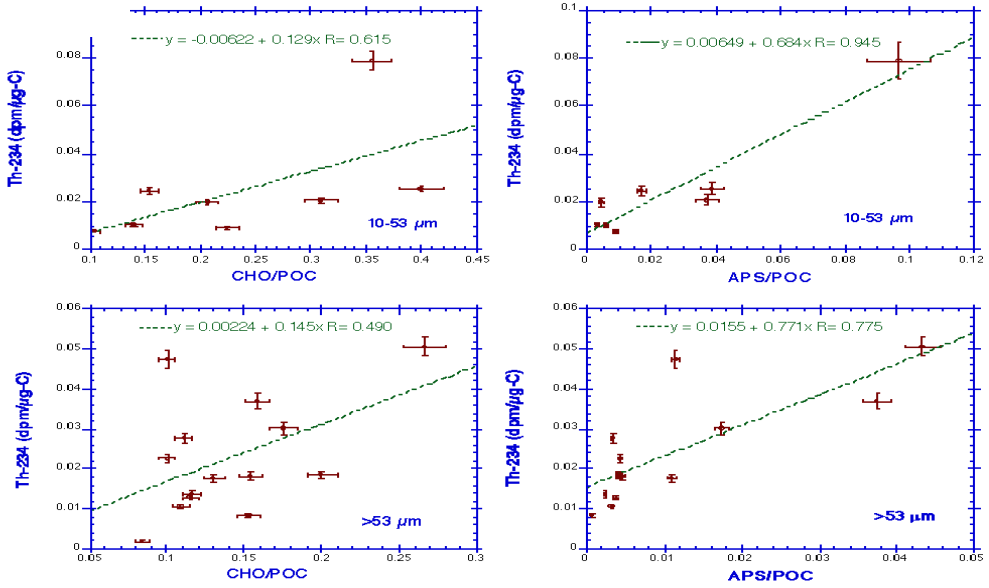
2001 cruise to Gulf of Mexico:
Filled circles: sinking particles
Collected at 65, 90, 120 m depth; Open circles: suspended particles (sum of 0.5, 1, 10, 53 μm fractions)





- CHO /OC~0.1
- URA,APS/OC~0.01

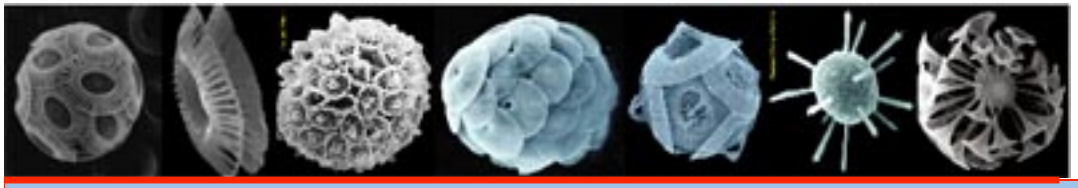


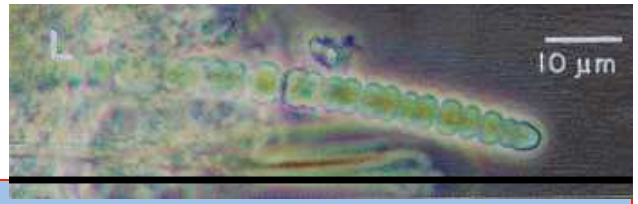


Lig. /POC ~ 0.001 (Hirose, 2004); ^{234}Th/Lig. ~ 10^{-7} – 10^{-12}

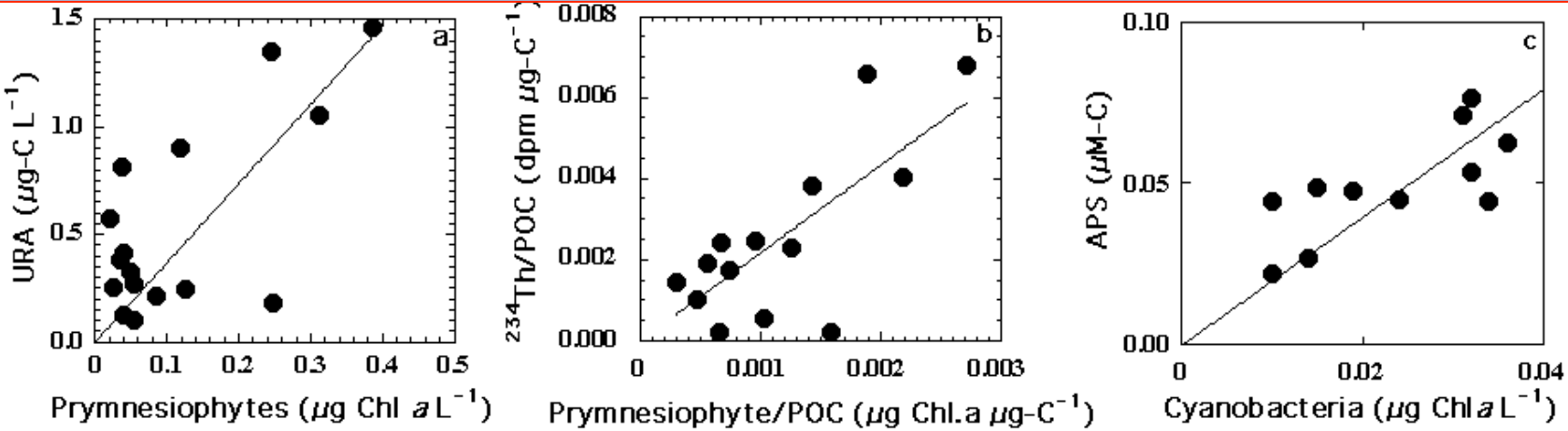
2000 cruise to Gulf of Mexico: Open circles: suspended particles

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



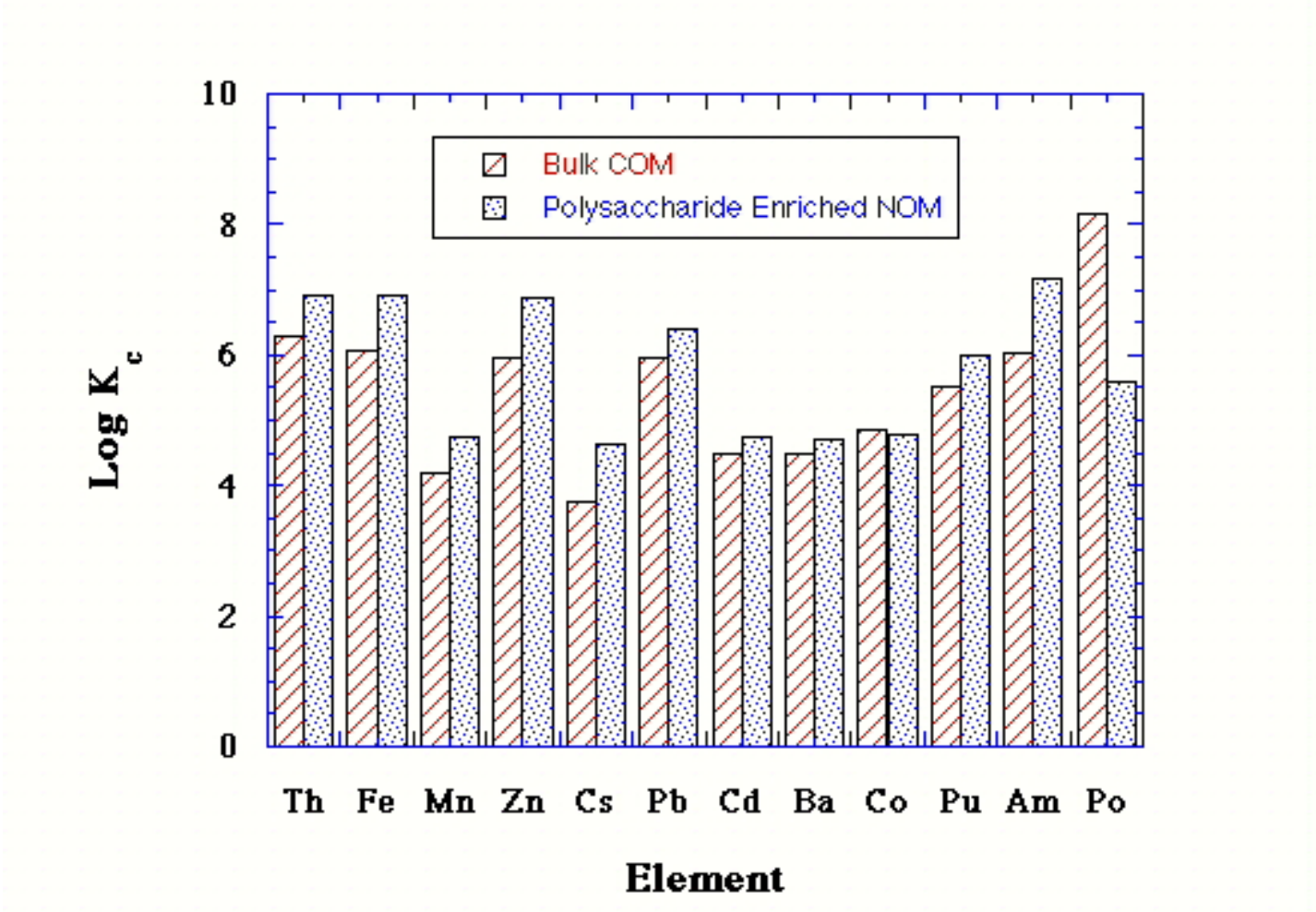


Abundance in ocean: CHO /POC ~ 0.1, APS/POC ~ 0.01, URA/POC ~ 0.01 (all: Santschi et al., 2003; Hung et al., 2003), Lig. /POC ~ 0.001 (Hirose, 2004); ^{234}Th/Lig. ~ 10^{-7} – 10^{-12}

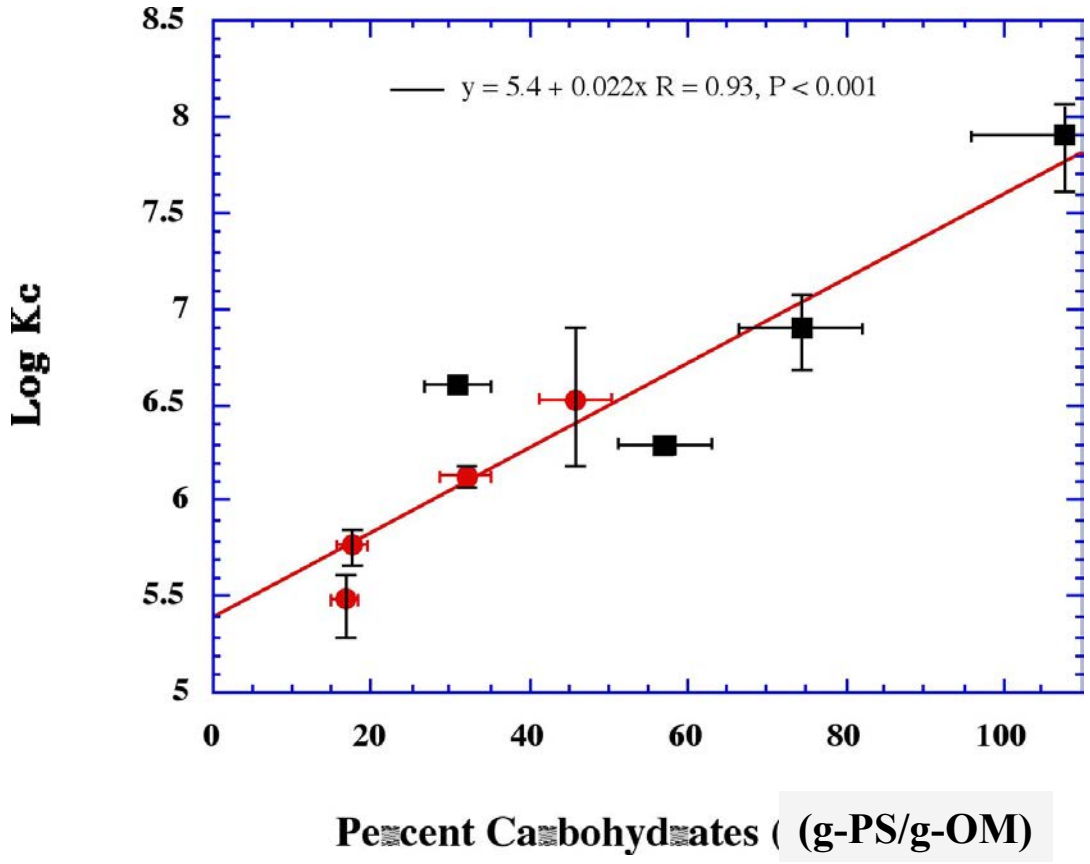


Different phytoplankton species appear, at times, to control acid polysaccharide (APS) e.g., uronic acid (URA), production and ^{234}Th (IV) complexation (-> autoporetic system)

Most Metals Show Enhanced Partitioning Coefficients (K_c) to Polysaccharide Enriched Colloidal Organic Matter (COM) over Unpurified COM (Quigley et al., 2002. L&O, 47, 367)



Colloid-Water Partition Coefficient (Kc) of ^{234}Th(IV) controlled by Polysaccharide Content (Quigley et al., 2002. L&O, 47, 367)



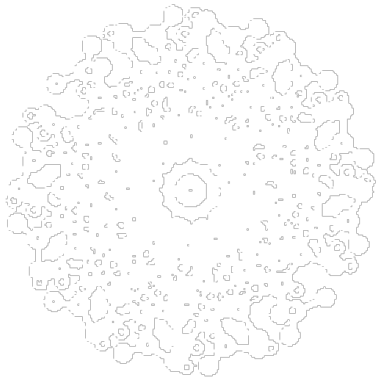
$$K_c = K_c(o)*10^{(2.2f_{PS})}$$

Enrichment through alcohol precipitation

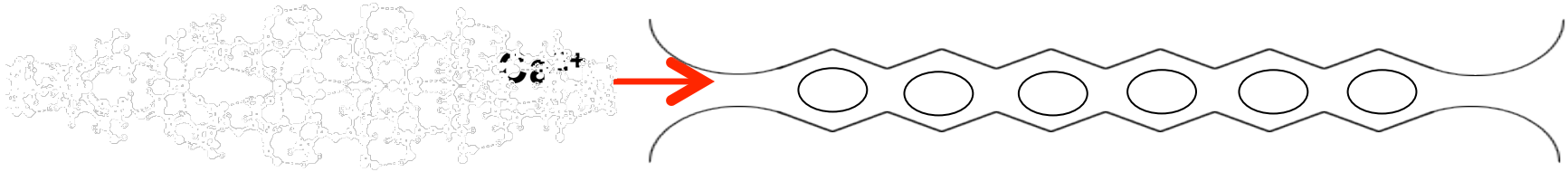
=>Increase in Kc and "freshness' ($\Delta^{14}C$)

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

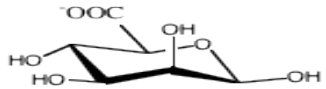
Calcium poly-α-L-guluronate left-handed helix view down axis



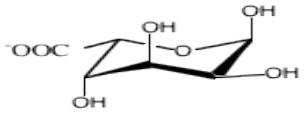
view along axis, showing the hydrogen bonding and calcium binding sites.



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



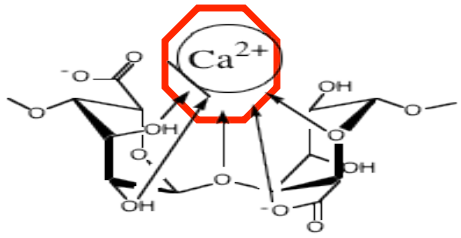
M ($^4C_1$)



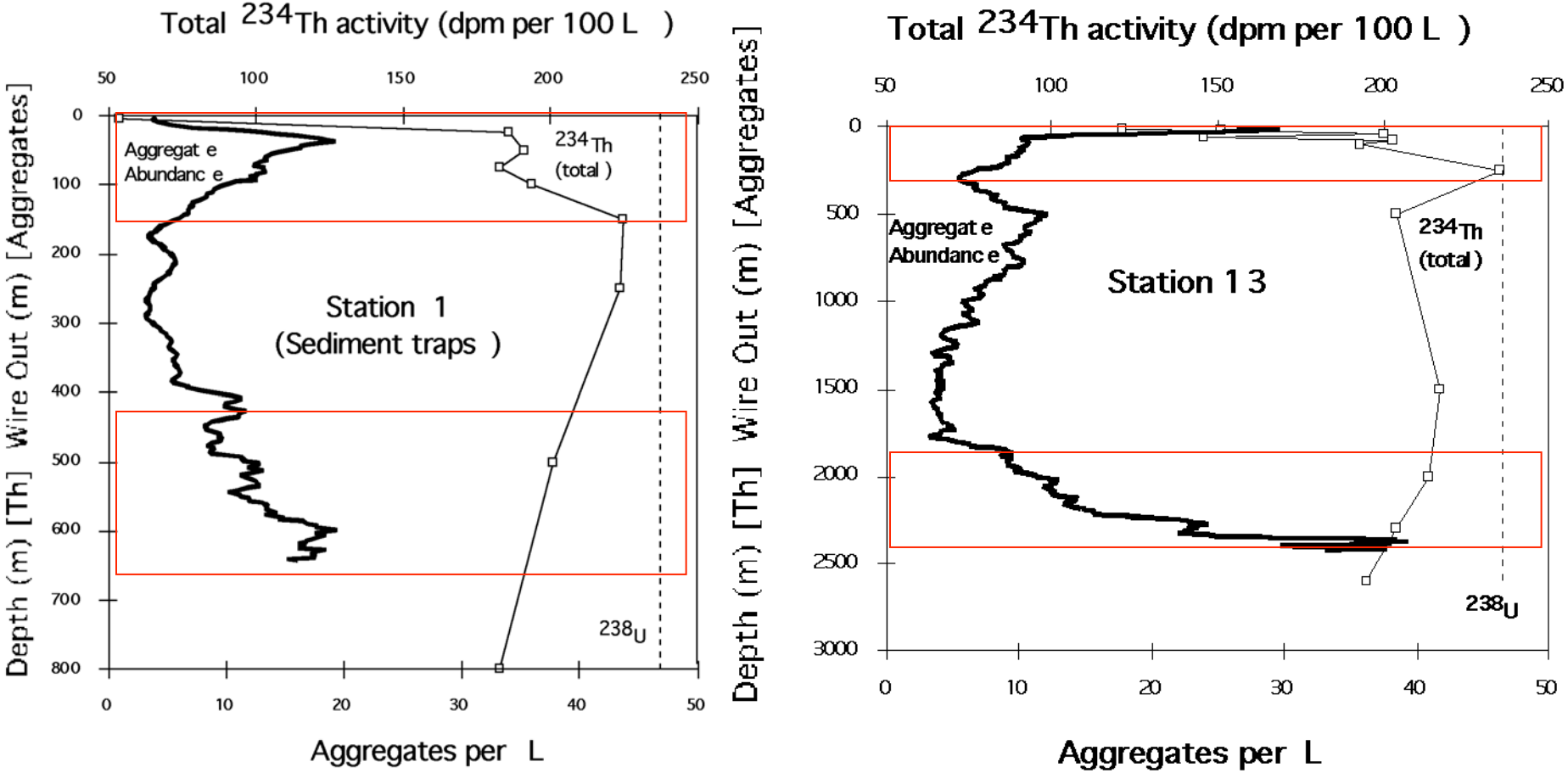
G ($^1C_4$)

Alginic Acid

Double-helix makes Molecule more rigid

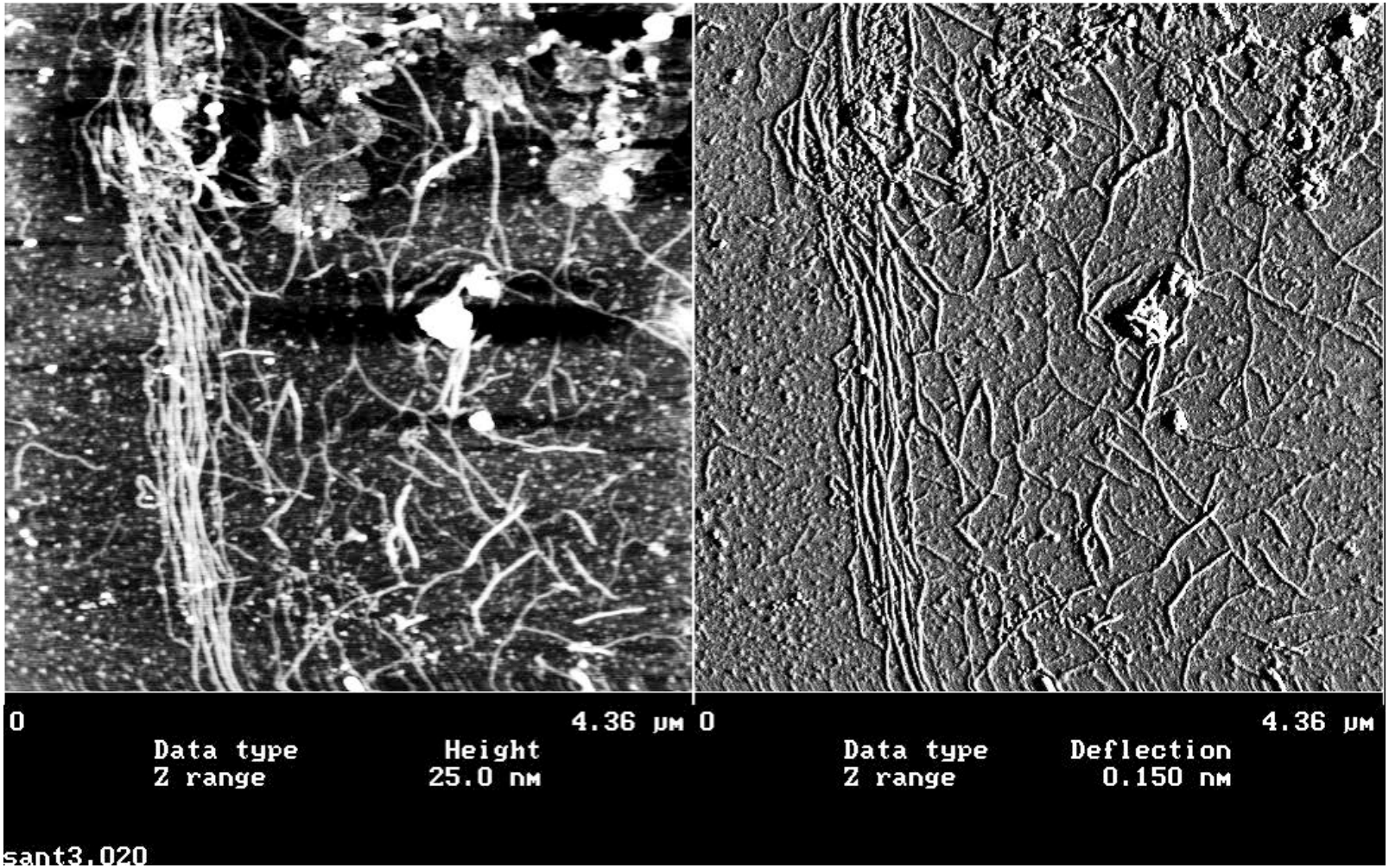


^{234}Th deficiencies ($\sum(^{238}U-^{234}Th)$) in the water column as a measure of particle scavenging intensity from vertical & lateral processes in surface and deep waters (Santschi et al., 1999, Cont. Shelf Res., 19, 609) Aggr~TEP~APS~EPS

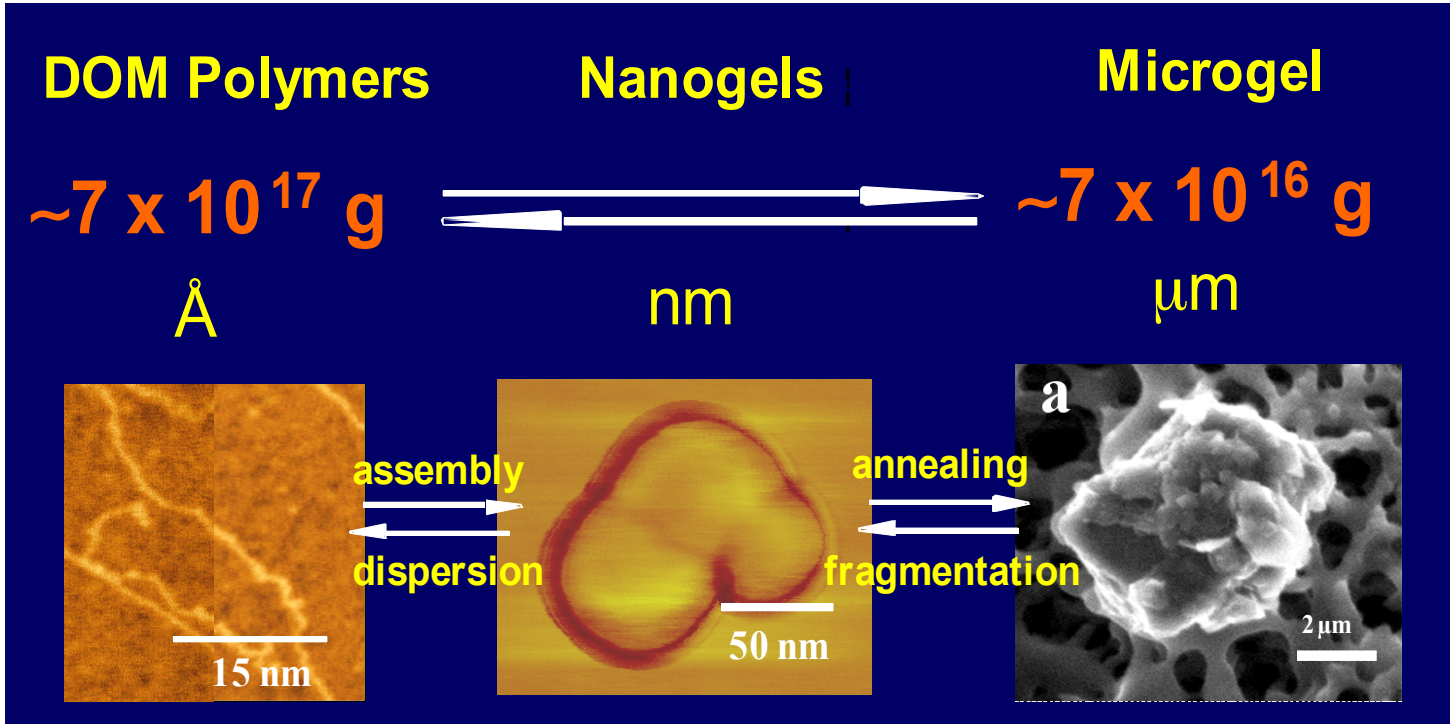


Abundance of Marine Snow Aggregates ≥ 1.5 mm dia α Th-deficiency

AFM image of fibrils from the Gulf of Mexico: Potential for
Gel Phase due to **concentration**/drying effects on the clay substrate (Santschi et al., 1998)



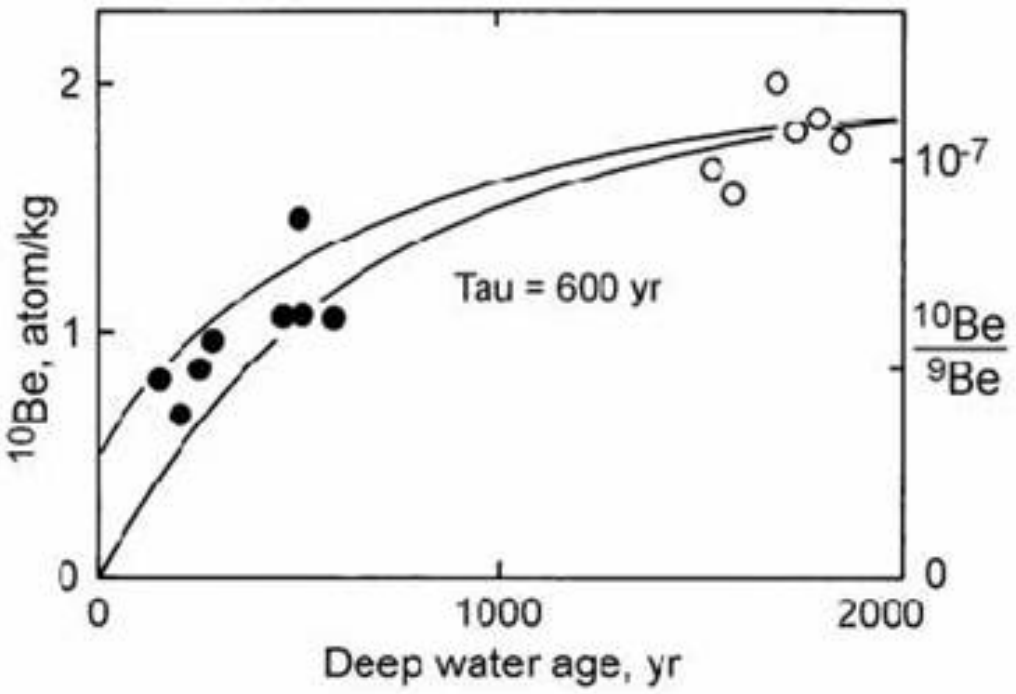
EPS from micro-organisms enhance gel-forming properties; hydrophilic EPSare held together by Ca2+-bridging (EDTA 'dissolves' them), EPS with hydrophobic moieties assemble through hydrophobic bridges; gel self-assembly as a two-step reversible process

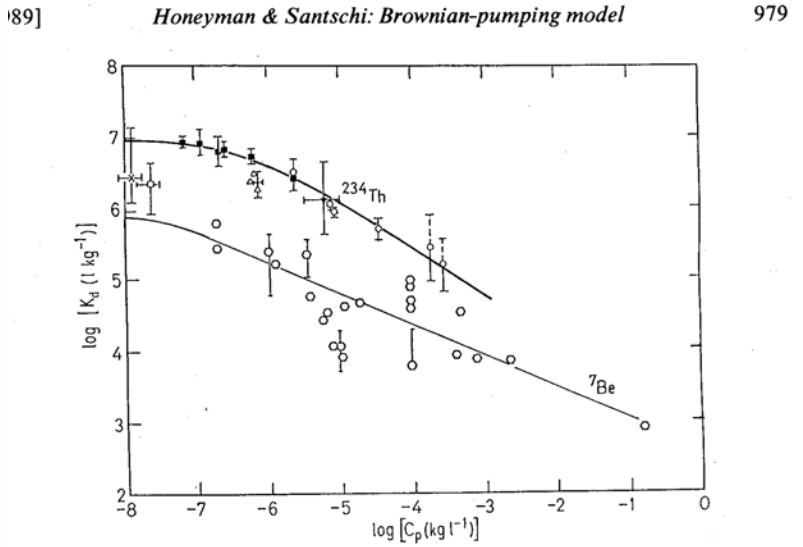


Atomic force microscopy shows that during the first two hours following filtration, 0.2 μm-filtered seawater contain only free polymers that can be readily imaged on mica surface. After5-10 hr nanogels start to appear. After 60 hr, assembly reaches equilibrium, forming microscopic gels of ~4-5 μm that can be filtered and imaged by environmental scanning electron

Relationship between ^{7}Be and ^{234}Th in the ocean.

Oceanic residence time of Be is 10^3 ysr vs. that of Th which is 10^2 yrs





gure 11. Log K_d versus log C_p for ^{230,234}Th and ^{7}Be. Data: for Th: Coale and Bruland, 1985; McKee *et al.*, 1984; Santschi *et al.*, 1979; Minagawa and Tsunogai, 1980; after Honeyman *et al.*, 1988; for ^{7}Be; Li *et al.*, 1984; Nyffeler *et al.*, 1984; Hawley *et al.*, 1986 Buchholtz, 1987; Bloom and Crecelius, 1983; Olson *et al.*, 1984; after Honeyman and Santschi, 1988. Relationships among master variables for model calculations correspond to those of Figure 9.

Left. Plot of ^{10}Be concentration against radiocarbon age in oceanic deep water to show the build-up of ^{10}Be along the Ocean Conveyer Belt. (!) = NADW; (") = Pacific deep water. After von Blankenburg *et al.* (1996).
Right. Plot of particle-water partition coefficient vs. Particle Concentration (Honeyman and Santschi, 1989).

Complexation to Organic Templates?

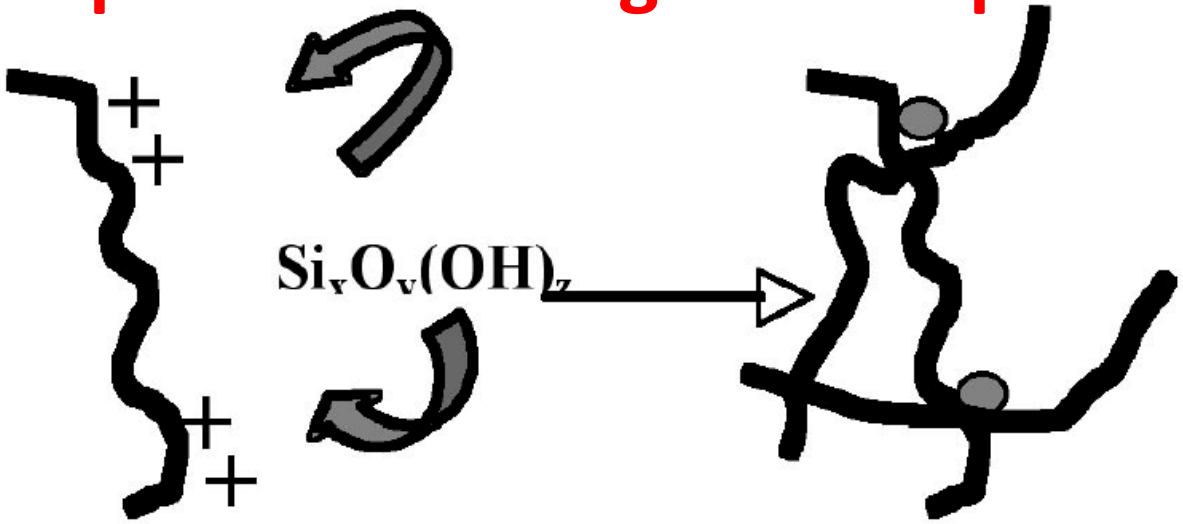


Figure 1:Self-assembling cationic biopolymers interact with anionic silicates to form silica nanoparticles.

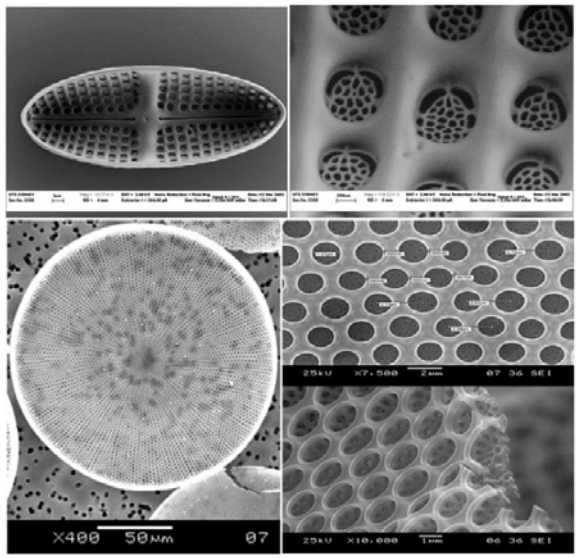


Fig. 4 Hierarchical distribution of pores in diatom frustules; Top: *Achnanthes subsessilis* (reprinted from Materials Science and Engineering C, 25, K.S.A. Butcher *et al.*, A luminescence study of porous diatoms, 659, Copyright (2010), with permission from Elsevier); Bottom: *Coscinodiscus walesii*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

Silaffins as templates for nano-silica growth of diatom shells -> organic residues as binding agents of natural radionuclides to diatoms (rather than pure silica which is a poor sorbent)

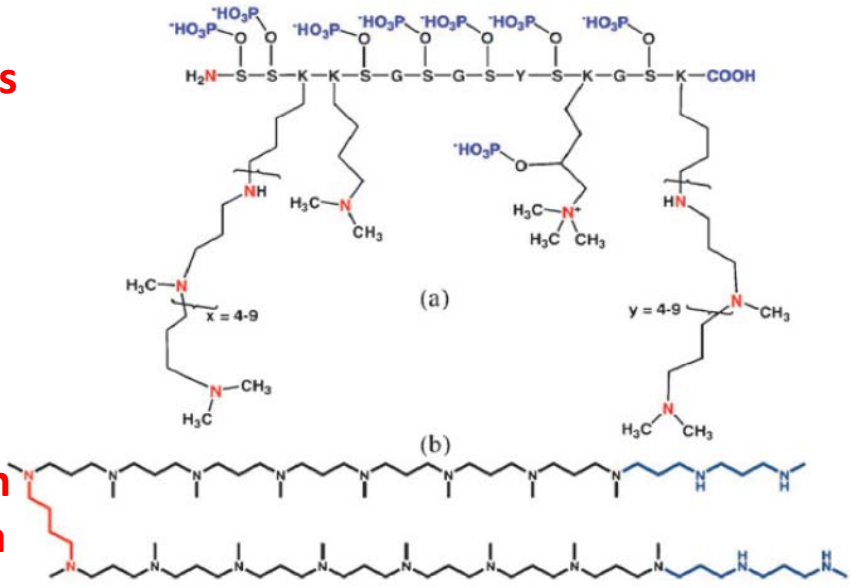


Fig. 5 Molecular structure of (a) silaffins and (b) LPA.

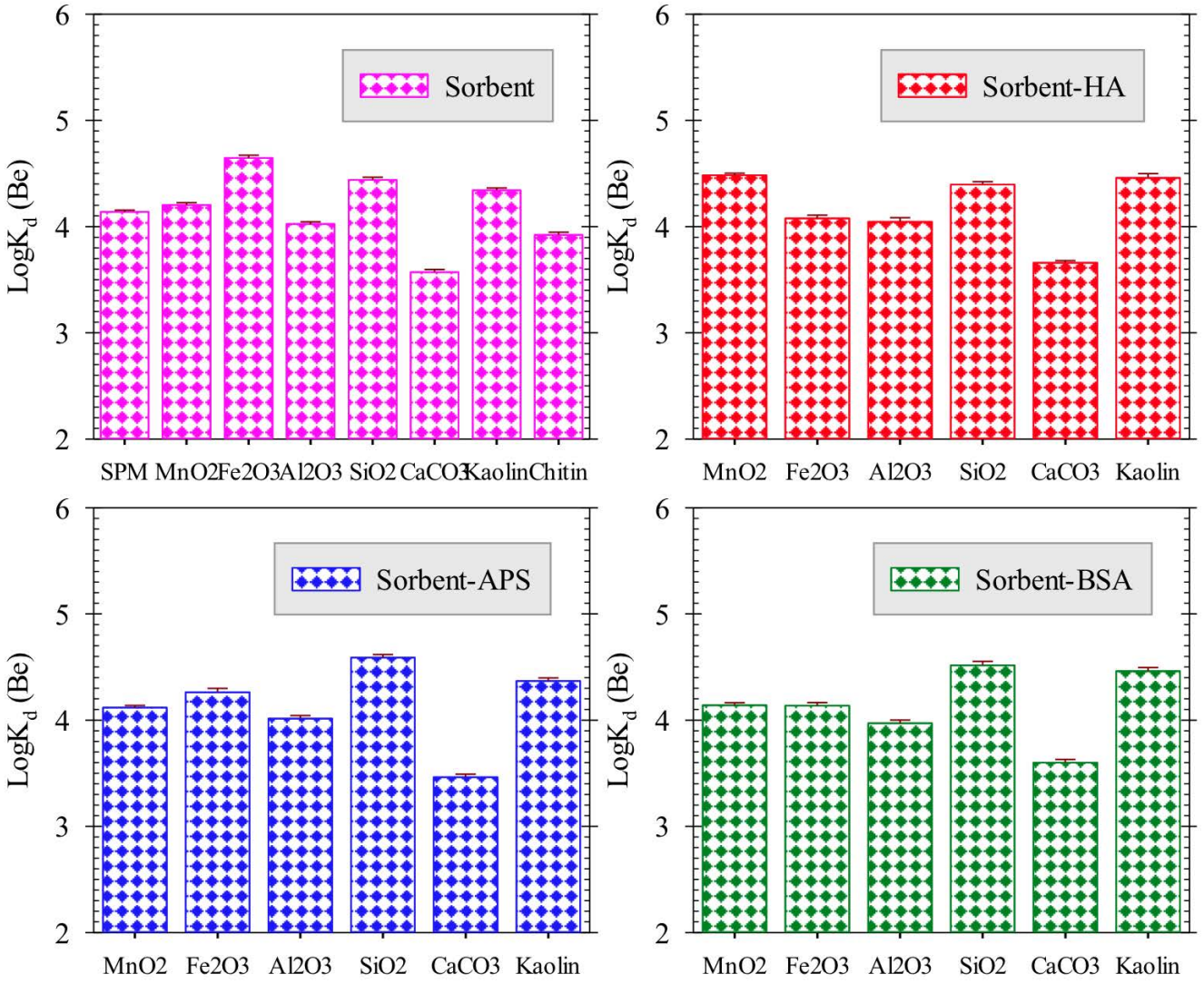
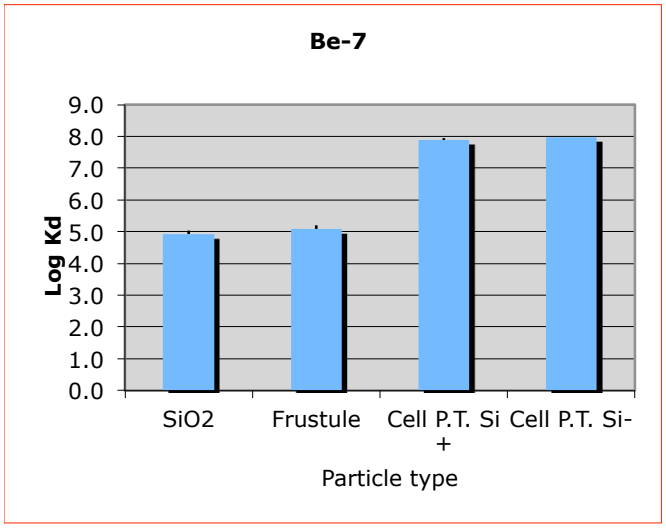
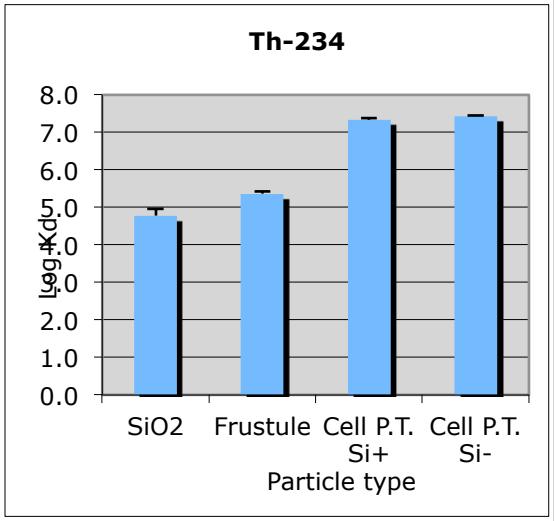
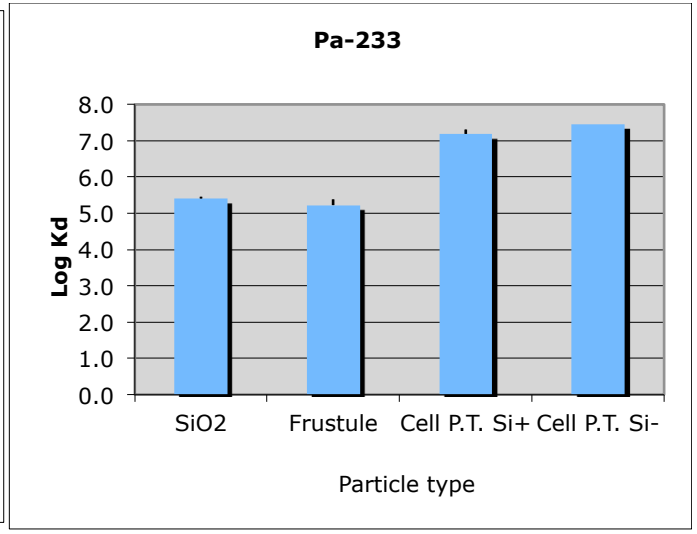


Fig. 3 Partitioning coefficients (K_d) of ^{7}Be on different particle types

Weifeng Yang, Laodong Guo, Peter H. Santschi, unpublished results







- Kd sequence Be>Th>Pa>Pb>Po
- SiO2~cleaned Frustule<Cells P.T.

Treatments

inorganic particle SiO2

Diatom, *Phaeodactylum tricornutum*

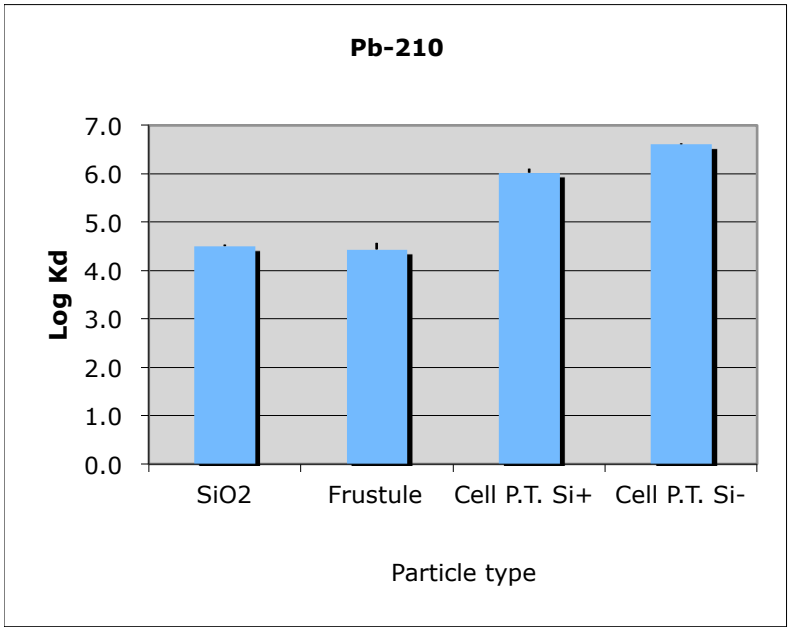
Frustules (Carbon content < 1%)

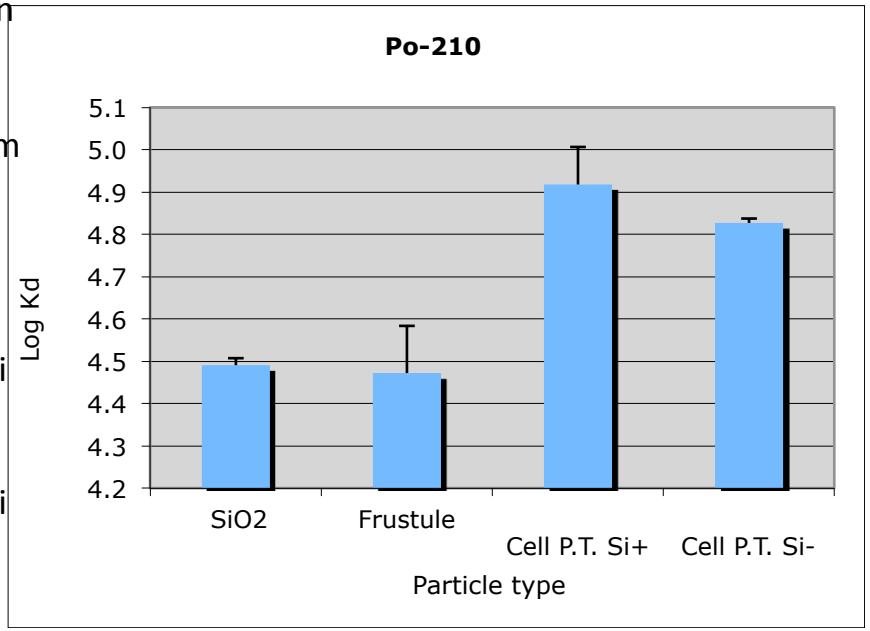
B) Fresh uncleaned diatom cells (P.T. = *Phaeodactylum tricornutum)*

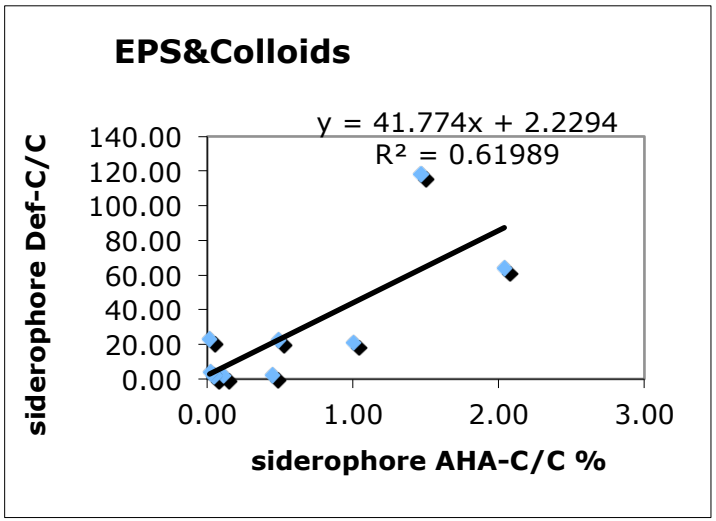
1. diatom cultured under Si + (with Si shell)

2. diatom cultured under Si – (without Si shell)

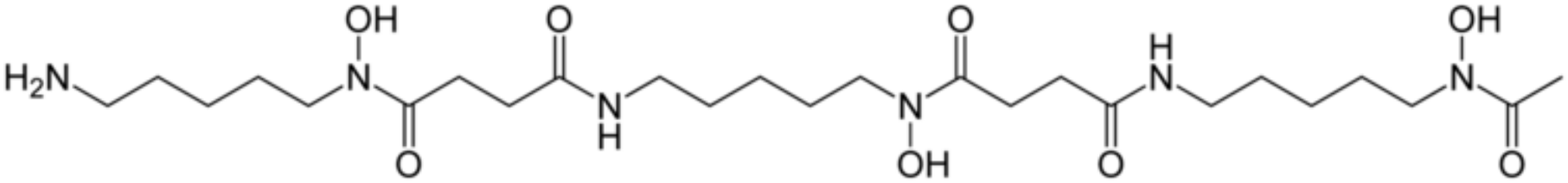
Anderin Chia-Ying Chuang, unpublished results

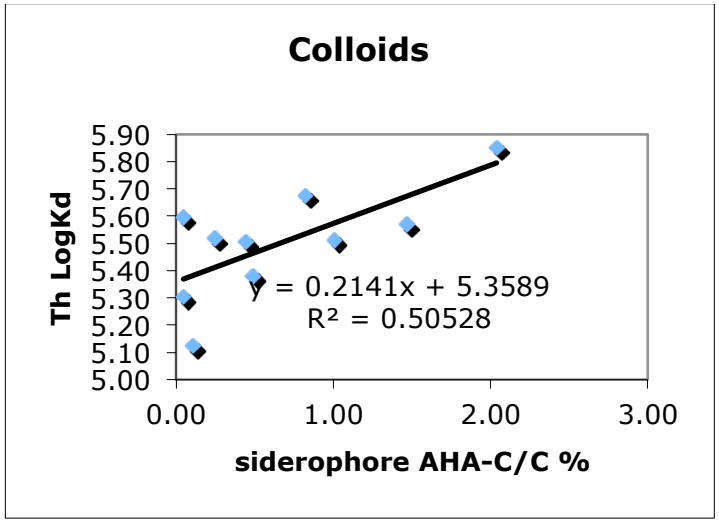


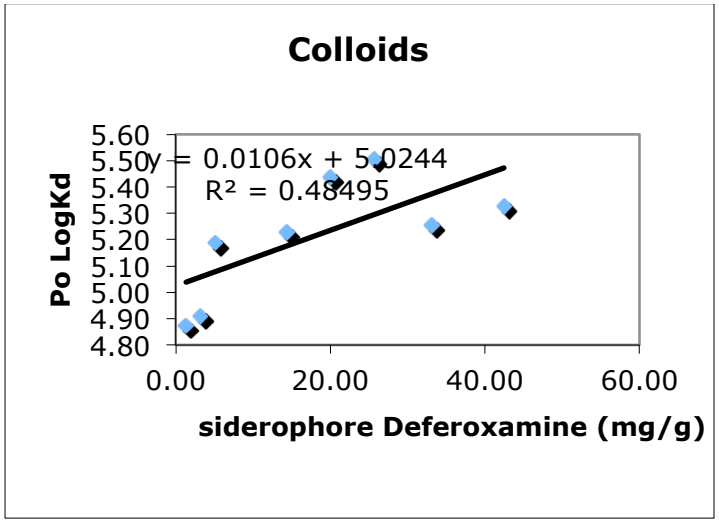




No relationships for Be, Pa and Pb; Anderin Chia-Ying Chuang, unpublished results

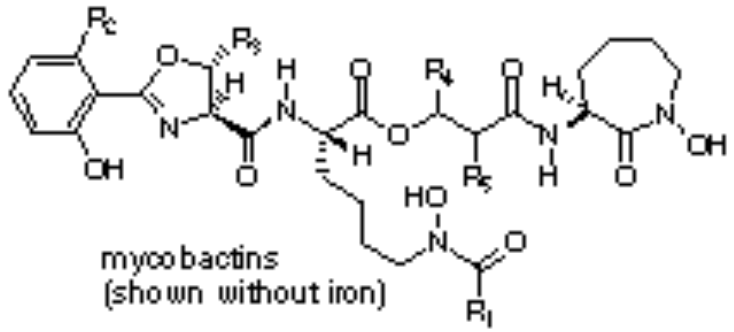




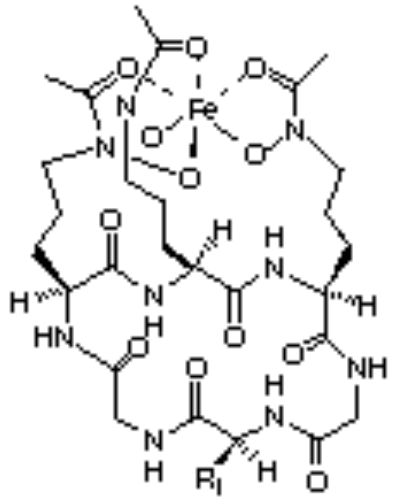


Siderophores

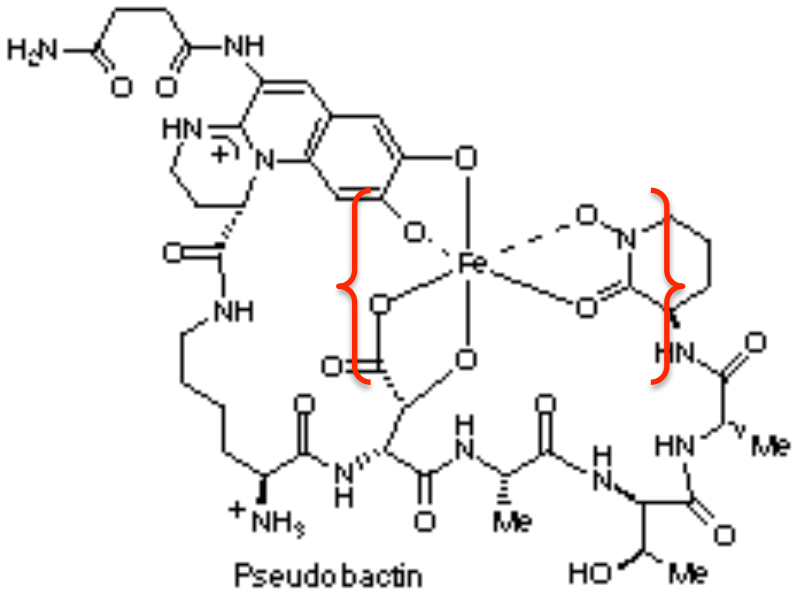
Representative Siderophores:



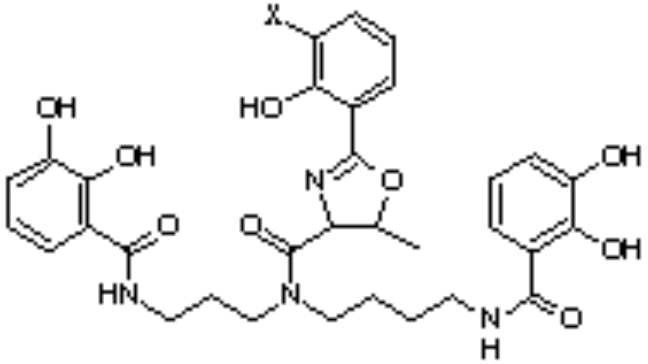
mycobactins
(shown without iron)



ferrichrome



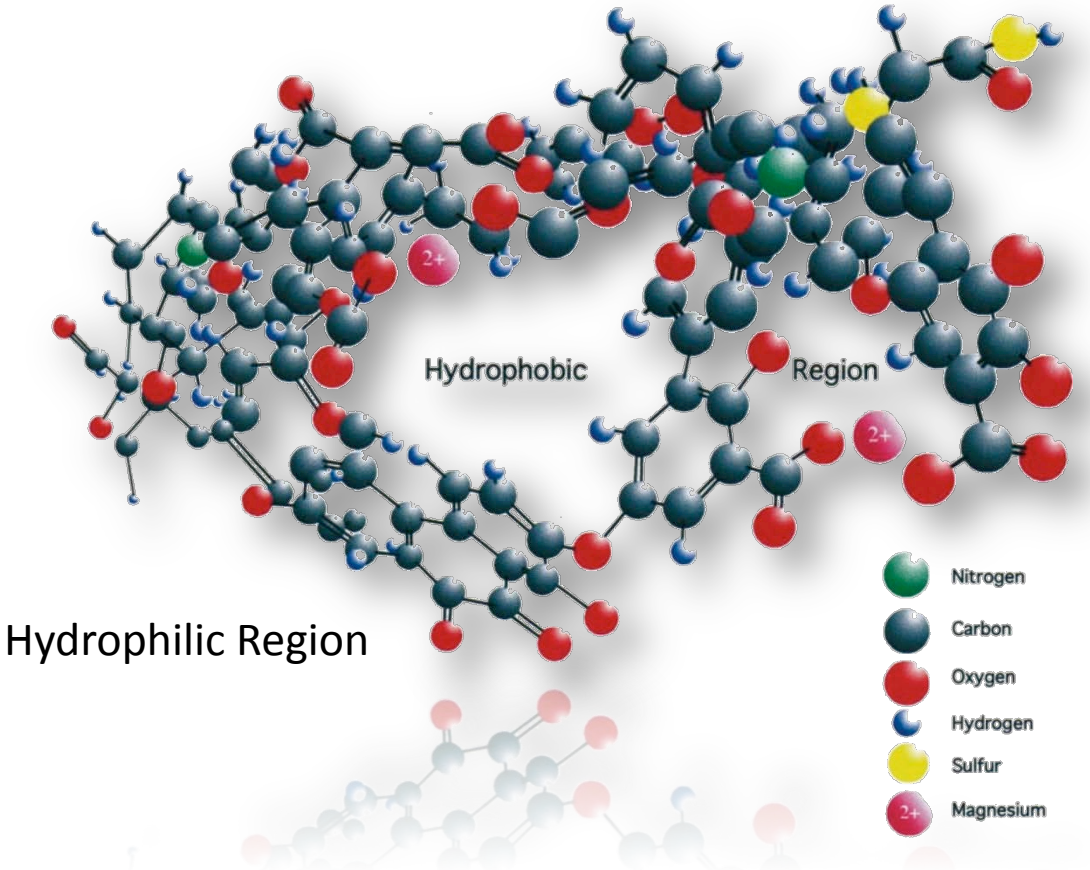
Pseudobactin



agrobactin, X=OH
parabactin, X=H
shown without iron

"All-In-One" Bio-polymers or Geopolymers as carriers of natural (Th, Pa, Pb, Po, Be) radionuclides in aquatic systems

Example: Humic Acid molecule



Hydrophilic Region

- **Have hydrophilic outside, hydrophobic interior**
- **Contain metal binding (chelating) groups**
- **can act as electron shuttles (e.g., quinone-hydroquinone or flavone groups)**

Example: Humic Substance
supramolecular association of self-assembling heterogenous and relatively small molecules derived from the degradation and decomposition of dead biological materials, stabilized predominantly by weak dispersive forces, such as hydrophobic and hydrogen or Ca2+ binding.

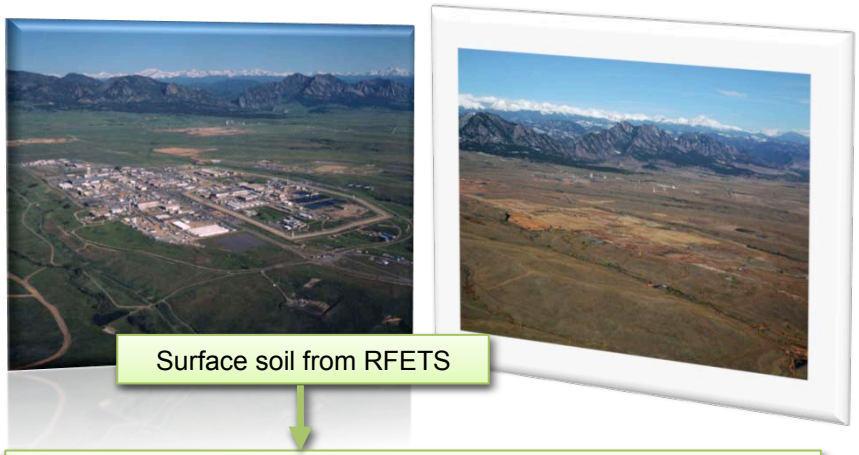
Separation methods and schemes

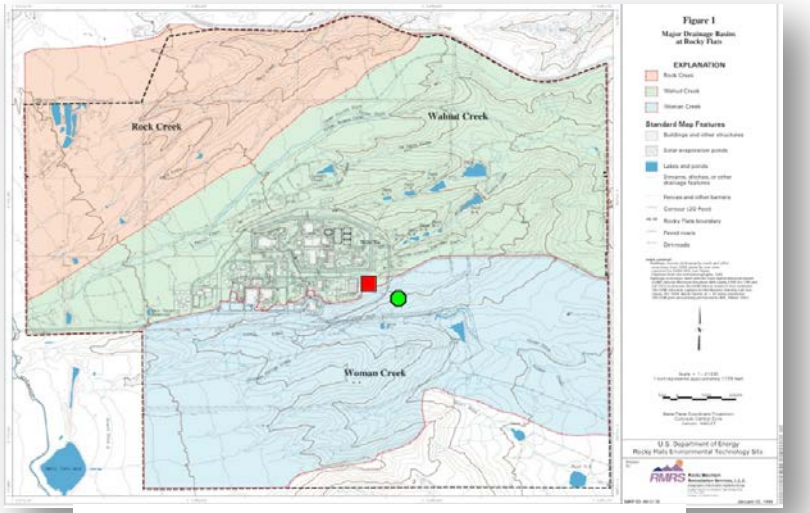
- Isoelectric focusing, Ultrafiltration, HPLC, ion chromatography, alone or in combination.

Chemical Characterization Methods:

- GC-MS, HPLC, ATR-FTIR, NMR, …

Examples for ^{239,240}Pu (and ^{129}I) from contaminated sites: Characterization after IEF, UF, and/or HPLC separation





Surface soil from RFETS

Pass through 1 mm sieve to remove the course components

Re-suspended in D.I water for 3 days (concentration: ~ 5g/L)

Filtered through 0.45μm filter and then the filtrate (<0.45μm) underwent cross-flow ultrafiltration using a 1 KDa Spiral-wound polysulfone cartridge. Retentate further lyophilized.

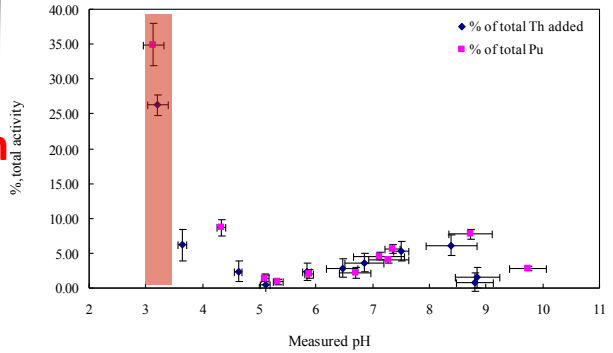
Radiolabelling

IEF experiment

Localizing actinide enriched fraction

^{239,240}Pu and ^{234}Th enriched fraction in the IEF gel extracted and diafiltered. Retentate further lyophilized.

Plutonium Separation Via IEF



HPLC-SEC

Graphite AA (Fe, Mn, Al)

Elemental analysis

Elemental mapping

ATR-FTIR

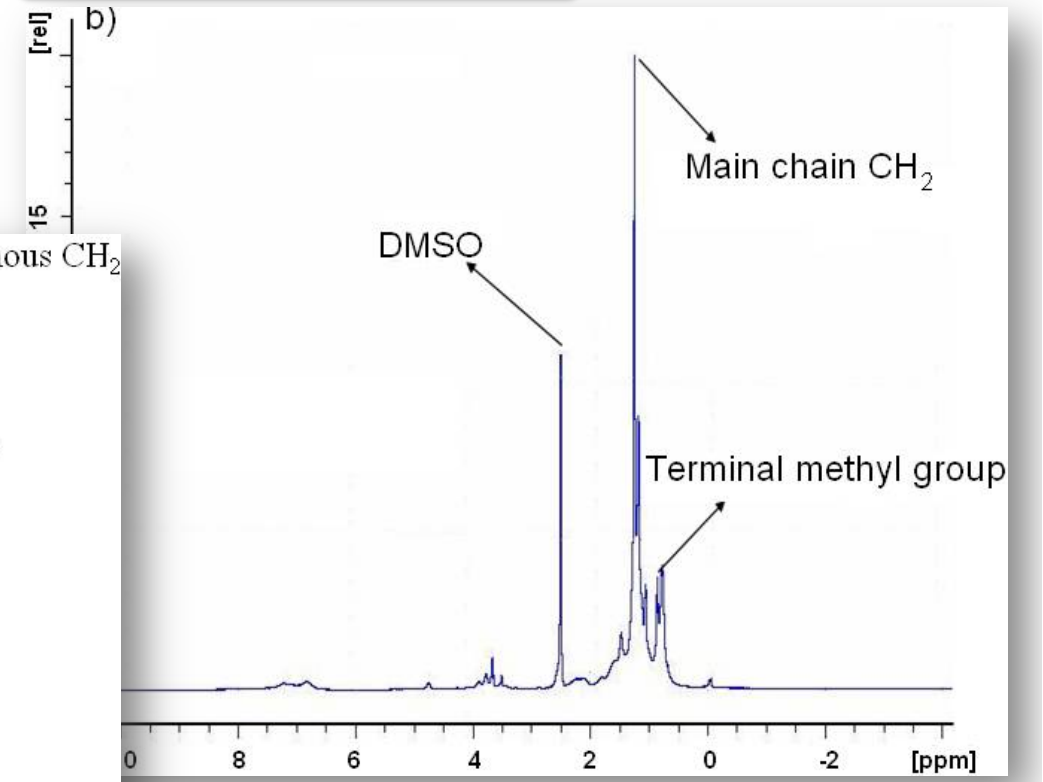
Compositional analysis (TCHO, URA, protein, etc.)

NMR

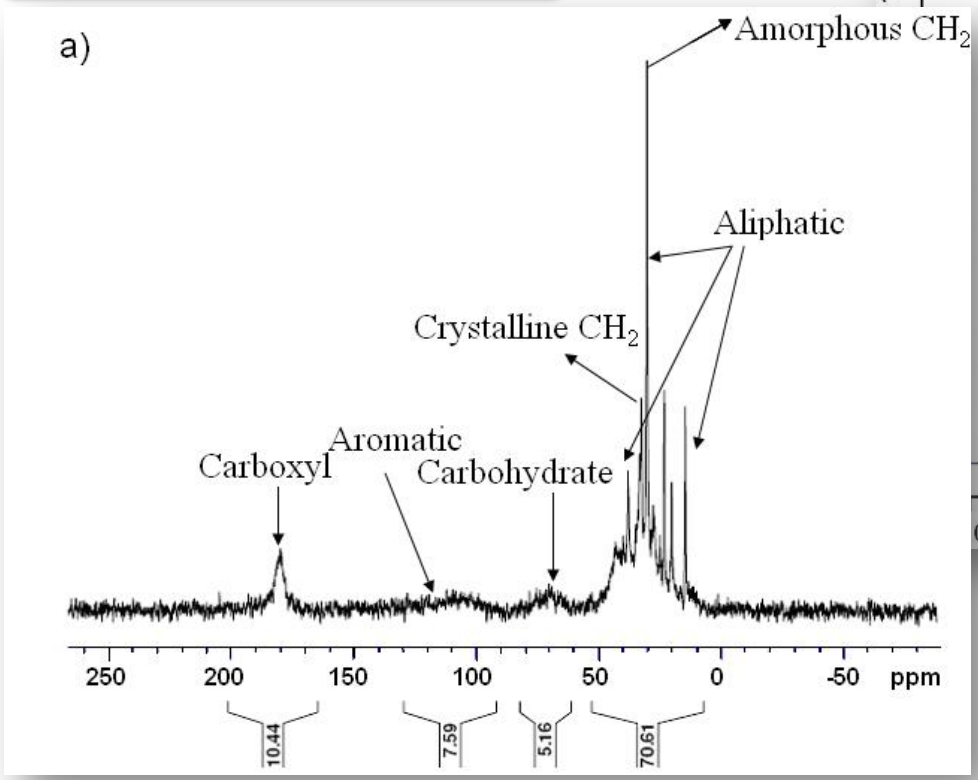
Xu, C., Santschi, P.H.,et al. 2008., 42(22), 8211-8217.

1D ^{13}C and ^{1}H NMR

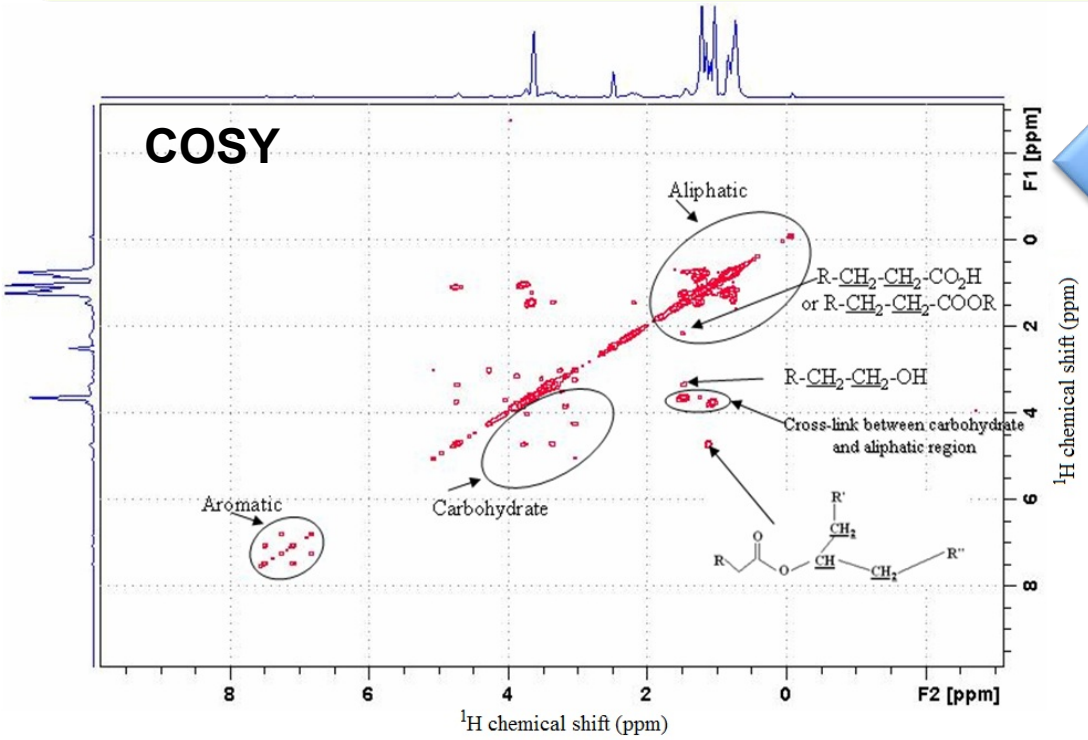
^{1}H HRMAS-NMR



DPMAS ^{13}C NMR



2D NMR

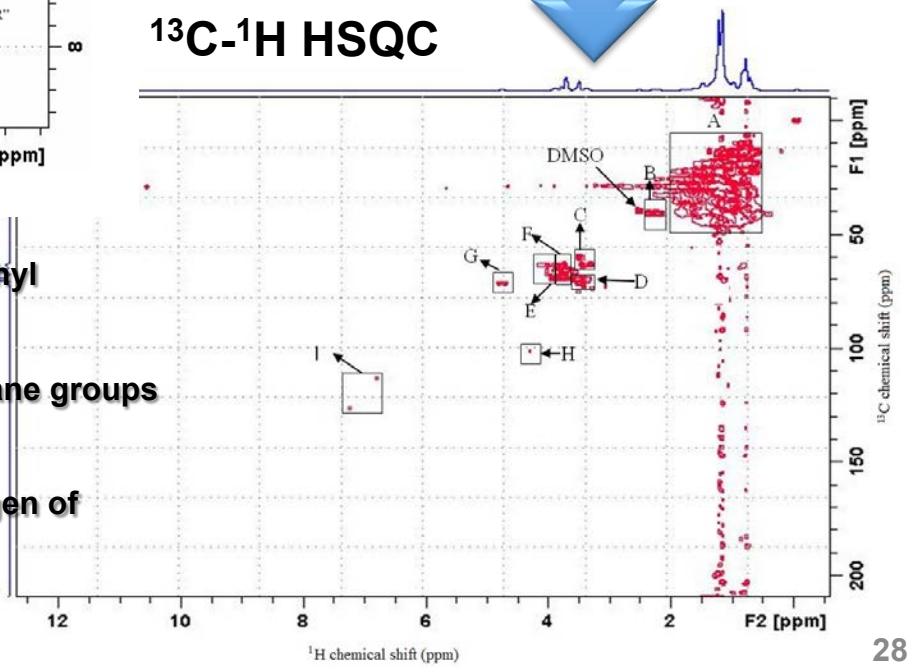


^{1}H-^{1}H coupling

Soil IEF extract swollen in DMSO-d6.

^{13}C-^{1}H coupling

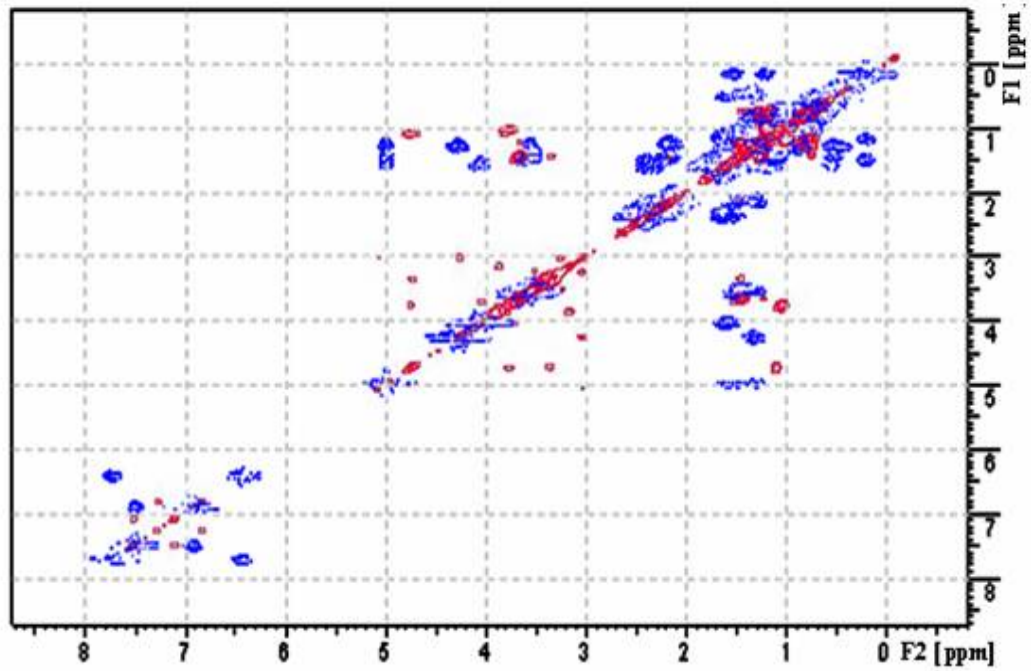
^{13}C-^{1}H HSQC

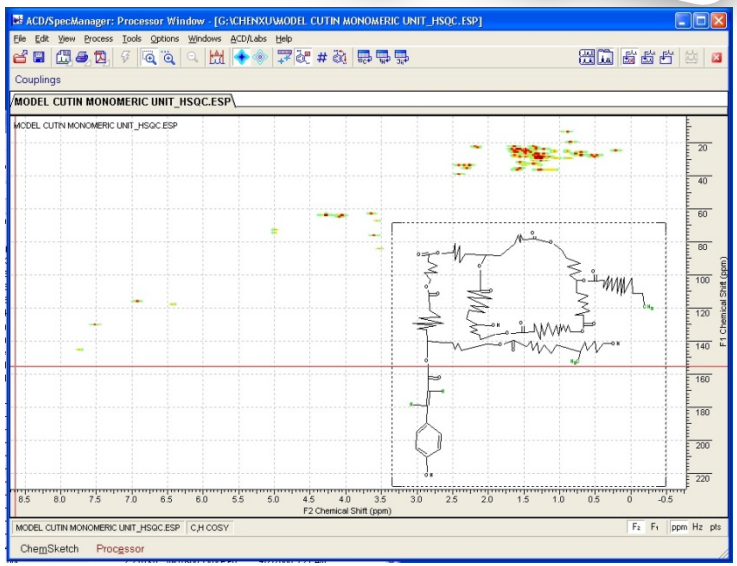


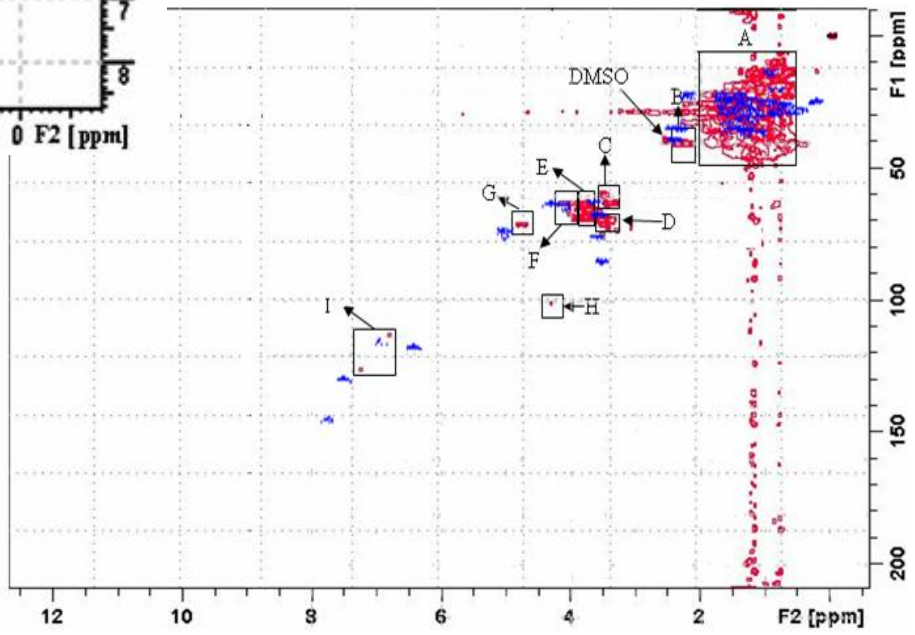
A. terminal methyls and methylene groups
B. methine structures attached to carbonyl groups in α-methyl branched fatty acids and esters
C. methylene structures attached to hydroxyl groups
D. methylene structures attached to ether oxygens or methane groups attached to a secondary alcohol
E. CH groups in carbohydrates
F. methylene structures attached to the singly-bonded oxygen of esters
G. methines attached to the singly-bonded oxygen of esters
H. anomeric carbons in carbohydrates (box H);
I. aromatic structures

Simulation and overlapping

d)



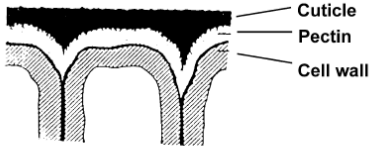




Overlapping with

- published cutin NMR spectra (Kelleher and Simpson, 2006, ES&T; Deshmukh, Simpson and Hatcher, 2003, Phytochem)
- simulated NMR spectra of proposed cutin models (Fang et al., 2001, Phytochem; Kolattukudy, 2001)

Siderophore attached to cutin backbone



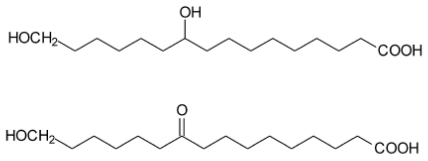
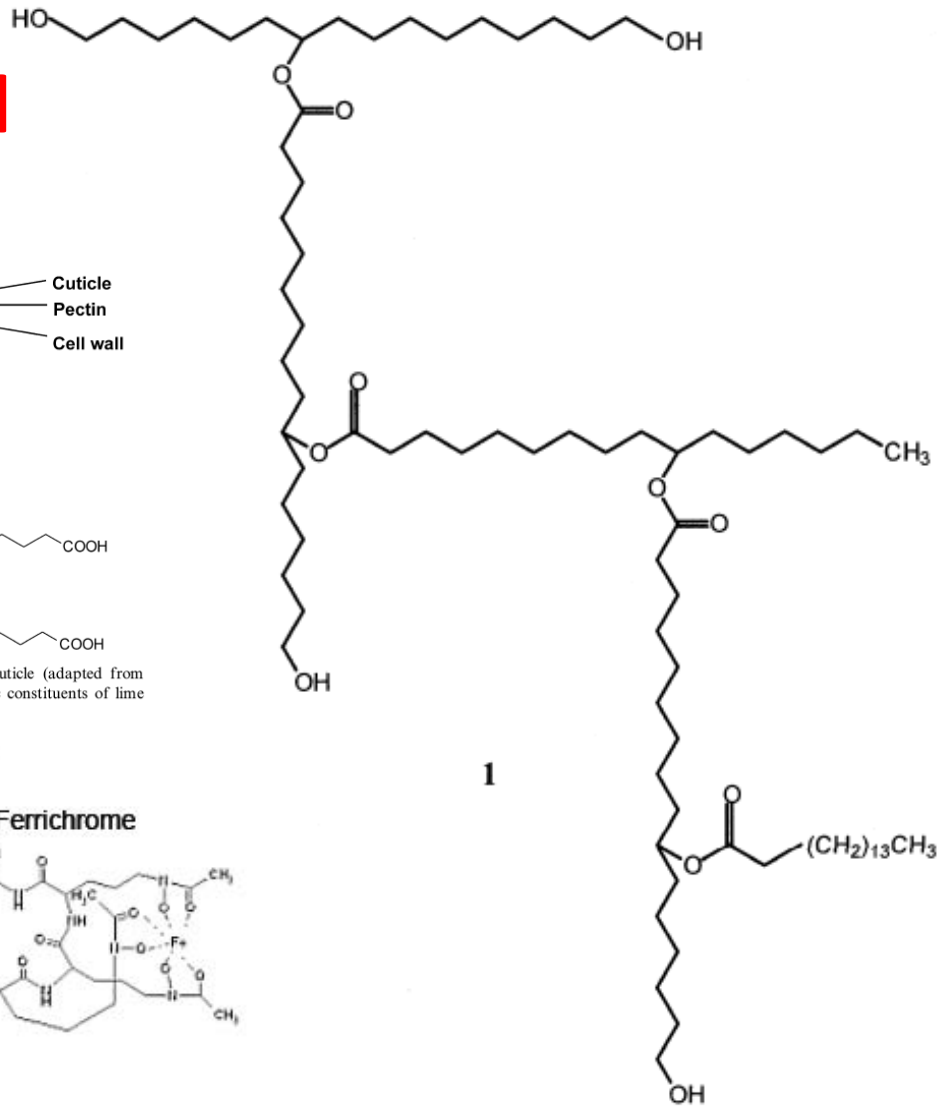


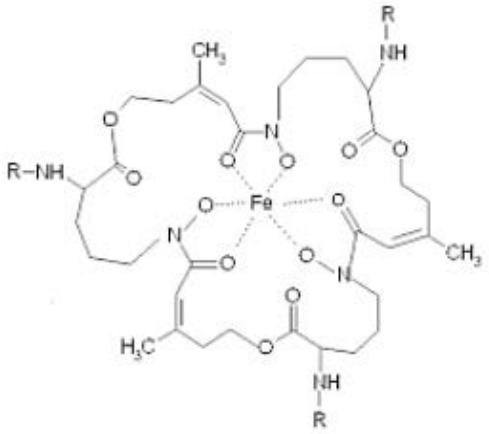
Fig. 1. Schematic organization of the plant cuticle (adapted from Kolattukudy (1984)) and the major monomeric constituents of lime fruit cutin.



1

Common Microbial Siderophores:

Triacetylfusarinine C



Ferrichrome

Coprogen

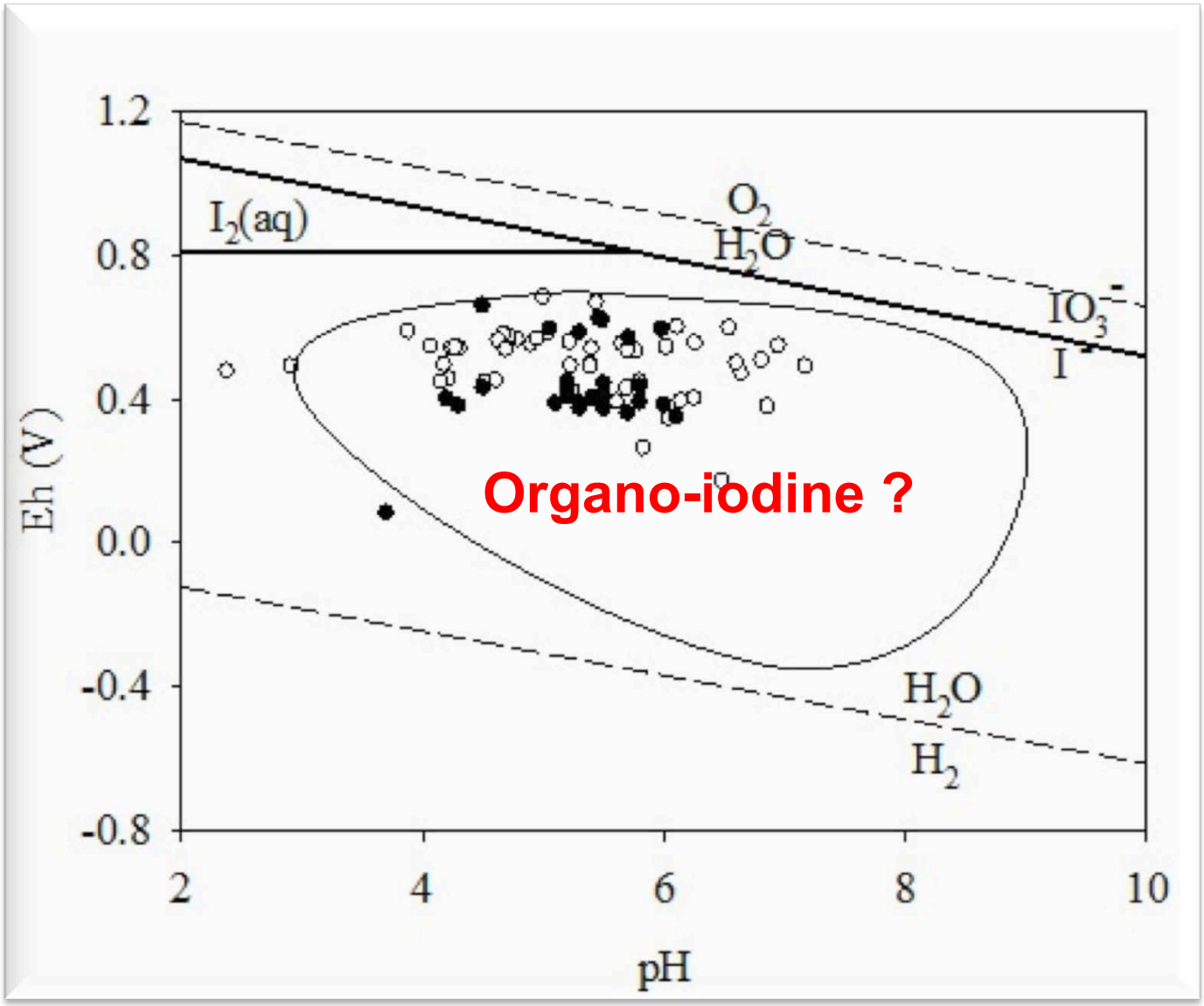
Ferrioxamines

Conclusions

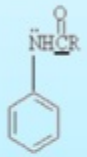
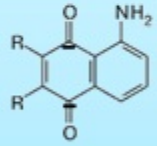
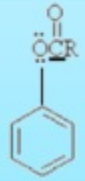
- **Radionuclides in the environment can often find chelating and redox active bio- or geo-polymers because their ultra-low concentrations allow them to find the most energetic sites. For example, ^{7}Be can show high Kd values to diatoms containing silafins.**
- **Separation chemistry combined with organic chemical methods allow identification of carrier molecule(s) for radionuclides (e.g., P, Th, Po) containing strongly chelating groups (hydroxamates, siderophores), anionic coatings (polysaccharides), and hydrophobic backbones (cutins).**
- **Organic carriers of radionuclides in the environment are likely also affecting or could be responsible for observed fate, effects, and interpretation of historical reconstructions.**


Thank you for your attention
Any questions ?

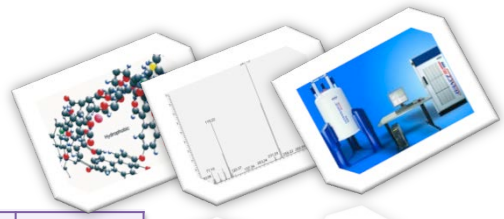
pH-Eh of Iodine.



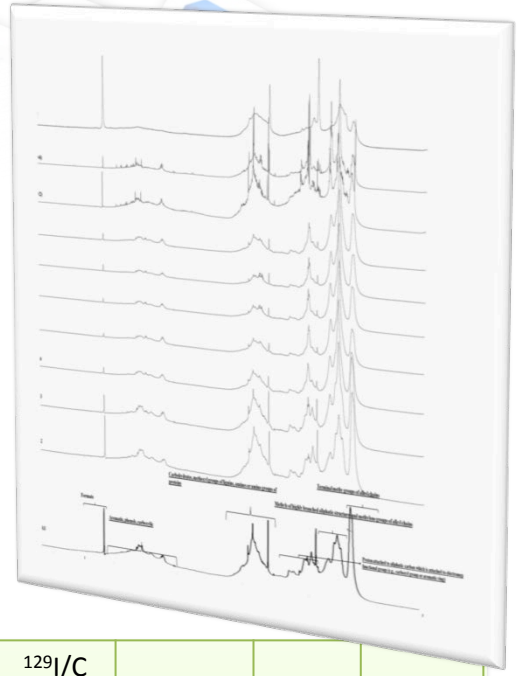
Evidence for Iodine bound to aromatic carbon from NMR and I- (or IO3-) binding (Kd) experiments (Xu et al., 2011a,b)

Proposed active aromatic ring for iodine binding*	^{13}C (ppm)	^{1}H (ppm)
	173.0	7.06-7.41
	171.39	7.08-7.58
	185.2-188.2	7.17-7.65
	160.2	7.92-7.94, 8.29

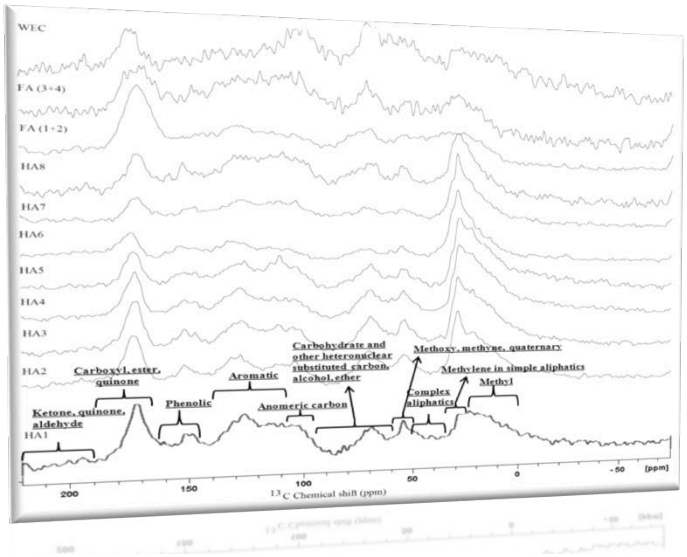
Structural relevances to naturally occurring and laboratory-iodination



Functional group	Chemical shift (ppm)	^{127}I /C μg/g-C		^{129}I/C μg/g-C			Kd (g/ml)
		R^2	p	R^2	p	R^2	p
$C_{Alk-H,C}$	0-60	-0.610	-*	-0.607	-	-0.871	-
C_{Alk-O}	60-108	0.055	-	0.053	-	0.003	-
ΣC_{Alk}	0-96	-0.289	-	-0.339	-	-0.715	-
C_{Ano}	96-108	-0.189	-	-0.020	-	-0.004	-
$C_{Ar-H,C}$	108-145	0.226	-	0.420	-	0.523	0.028
C_{Ar-O}	145-162	-0.186	-	-0.209	-	-0.066	-
ΣC_{Ar}	108-162	0.100	-	0.243	-	0.449	0.048
C_{COO}	162-190	0.774	0.030	0.711	-	0.882	<0.001
$C_{C=O}$	190-220	-0.043	-	-0.196	-	-0.056	-
$C_{Ar-H,C} \times C_{COO}$	(108-145)×(162-190)	0.576	0.017	0.665	0.007	0.890	<0.001

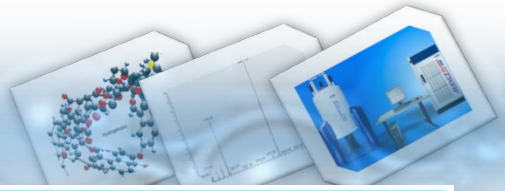


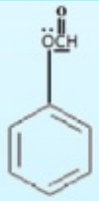
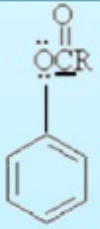
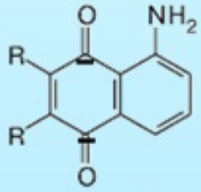
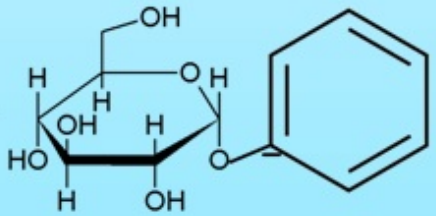
*"-"p values were not reported



Functional group	Chemical shift	^{127}I /C μg/g-C		^{129}I/C μg/g-C		Kd	
	ppm	R^2	p	R^2	p	R^2	p
H_{CH_3}	0-1.67	-0.853	-	-0.714	-	0.660	-
$H_{CH_2, CH}$	1.67-3	-0.219	-	-0.160	-	-0.152	-
H_{CHO}	3-4.5	0.741	0.003	0.650	0.009	0.452	0.047
H_{Ar}	6.0-8.25	0.786	0.002	0.608	0.013	0.843	0.001
H_{HCOO-}	8.29-8.45	0.838	0.001	0.617	0.012	0.648	0.009
H_{Ar}/H_{Al}		0.883	<0.001	0.701	0.005	0.848	<0.001
$H_{CHO} \times H_{lAr}$		0.892	<0.001	0.739	0.003	0.745	0.003

Proposed binding sites for naturally occurring and laboratory iodination at ambient conc.



Proposed active aromatic ring for iodine binding*	^{13}C (ppm)	^{1}H (ppm)
	160.2	7.17-7.36, 8.29
	173.0	7.06-7.41
	185.2-188.2	7.17-7.65
	171.4	7.08-7.58
	158.6	7.03-7.38