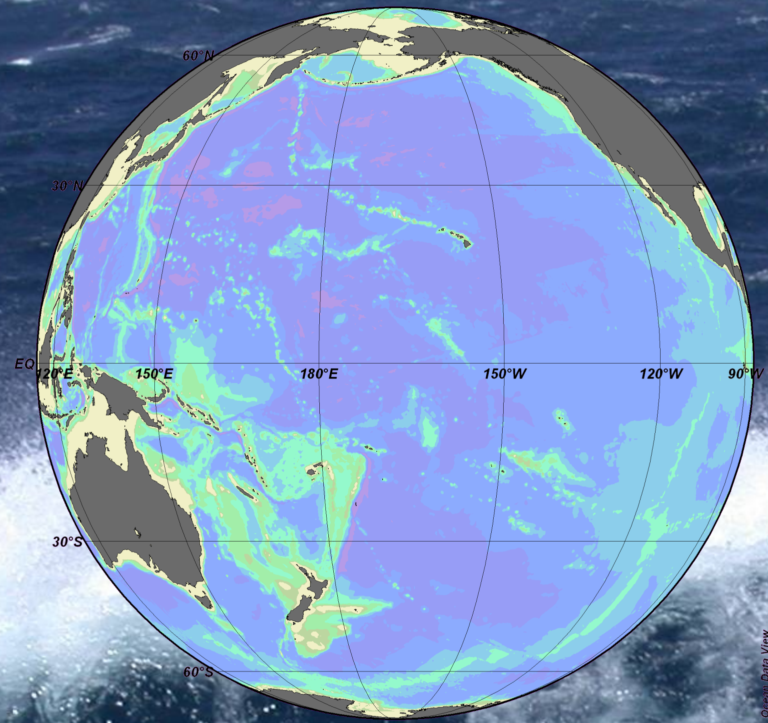
# Transparent exopolymer particles, DOM-POM transformations, and (ir)reversible svavenging: Merging the lessons from different research approaches

NATURAL ENVIRONMENT RESEARCH COUNCIL

THE UNIVERSITY of EDINBURGH

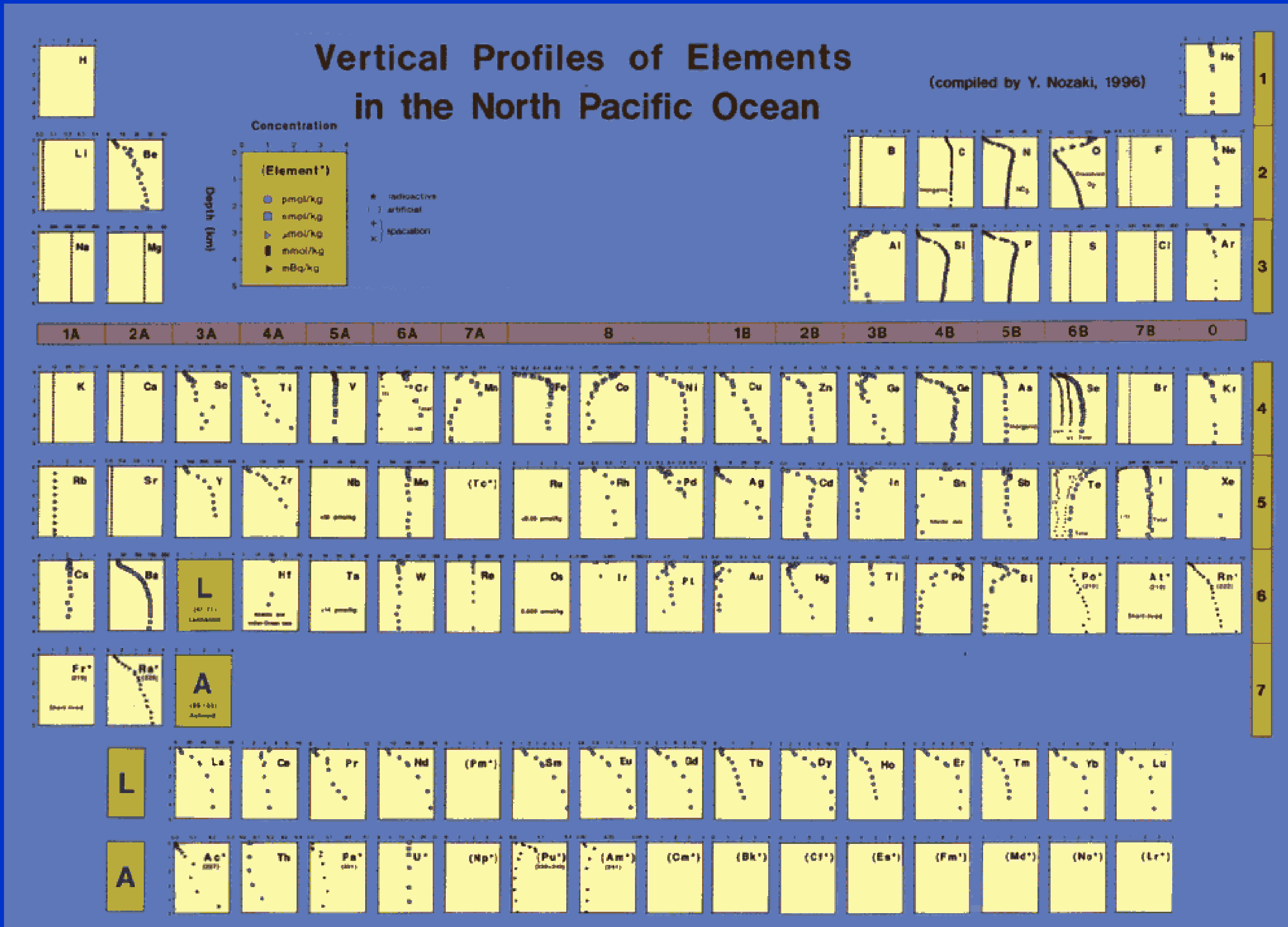



SAGES

Scottish Marine Institute
the home of SAMS

Walter Geibert, University of Edinburgh and Scottish Marine Institute, Oban

# The elemental composition of sea water



# Abundance of selected elements in the ocean

| Element | Concentration (%) | total amount in the oceans estimated (in tons) |
|---|---|---|
| chlorine | 1,95 | $2,57*10^{16}$ |
| sodium | 1,077 | $1,42*10^{16}$ |
| magnesium | 0,129 | $1,71*10^{15}$ |
| sulfur | 0,0905 | $1,2*10^{15}$ |
| potassium | 0,038 | $5,02*10^{14}$ |
| arsenic | 0,00000037 | $4,89*10^{9}$ |
| uranium | 0,00000032 | $4,23*10^{9}$ |
| iron | 0,0000000055 | $7,27*10^{7}$ |
| thorium | 0,000000001 | $1,32*10^{7}$ |
| gold | 0,0000000004 | $5,29*10^{6}$ |
| lead | 0,0000000002 | $2,64*10^{6}$ |
| radium | 0,000000000000011 | 93 |
| actinium | 0,00000000000000000096 | 0,01 – 0.05 |

**The abundance of elements in sea water is controlled by the balance between supply and removal.**

source (except actinium): Ocean, Chemistry and Deep-Sea Sediments, The Open University
actinium: Geibert et al. 2008

## How is the removal of elements linked to organic particulate fluxes?

**Focus: Organic substances forming particles by abiotic processes**

Structure of this talk:

Introduction: experimental results
- Part I: the different approaches
- Part II: natural radionuclides
- Part III: The DOM-POM equilibrium
- Part IV: Analytical advances
- Summary

# Why look into the role of organic matter?

1st attempt to conduct in-vitro experiments with thorium → miserable failure:

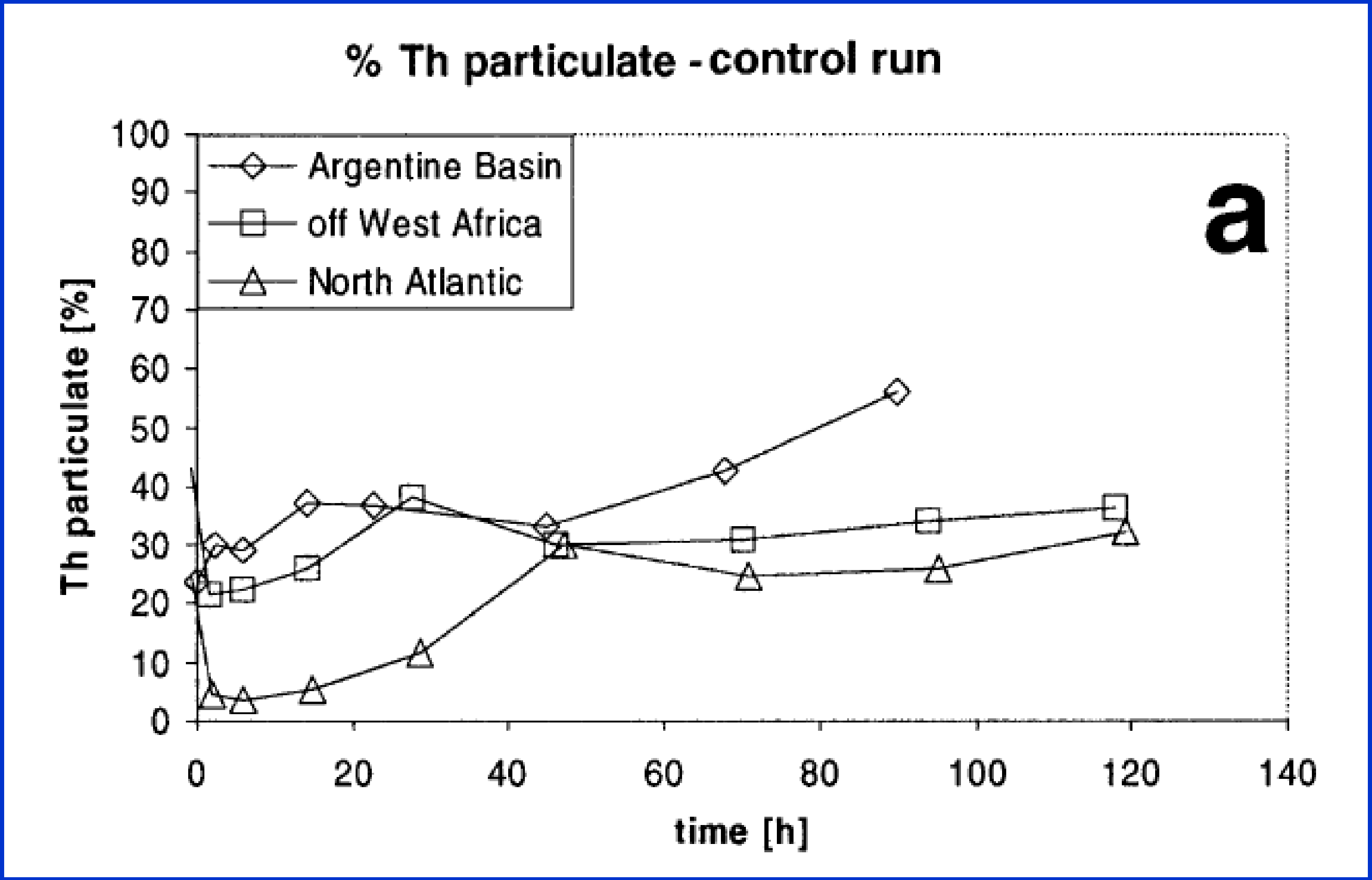
Within minutes, 90% of thorium were lost to the walls (artificial sea water in PTFE)

Alternative approach: assume natural colloids/ligands stabilize Th in solution, repeat experiments with natural sea water

It worked- typical losses were much smaller than 90%.

But

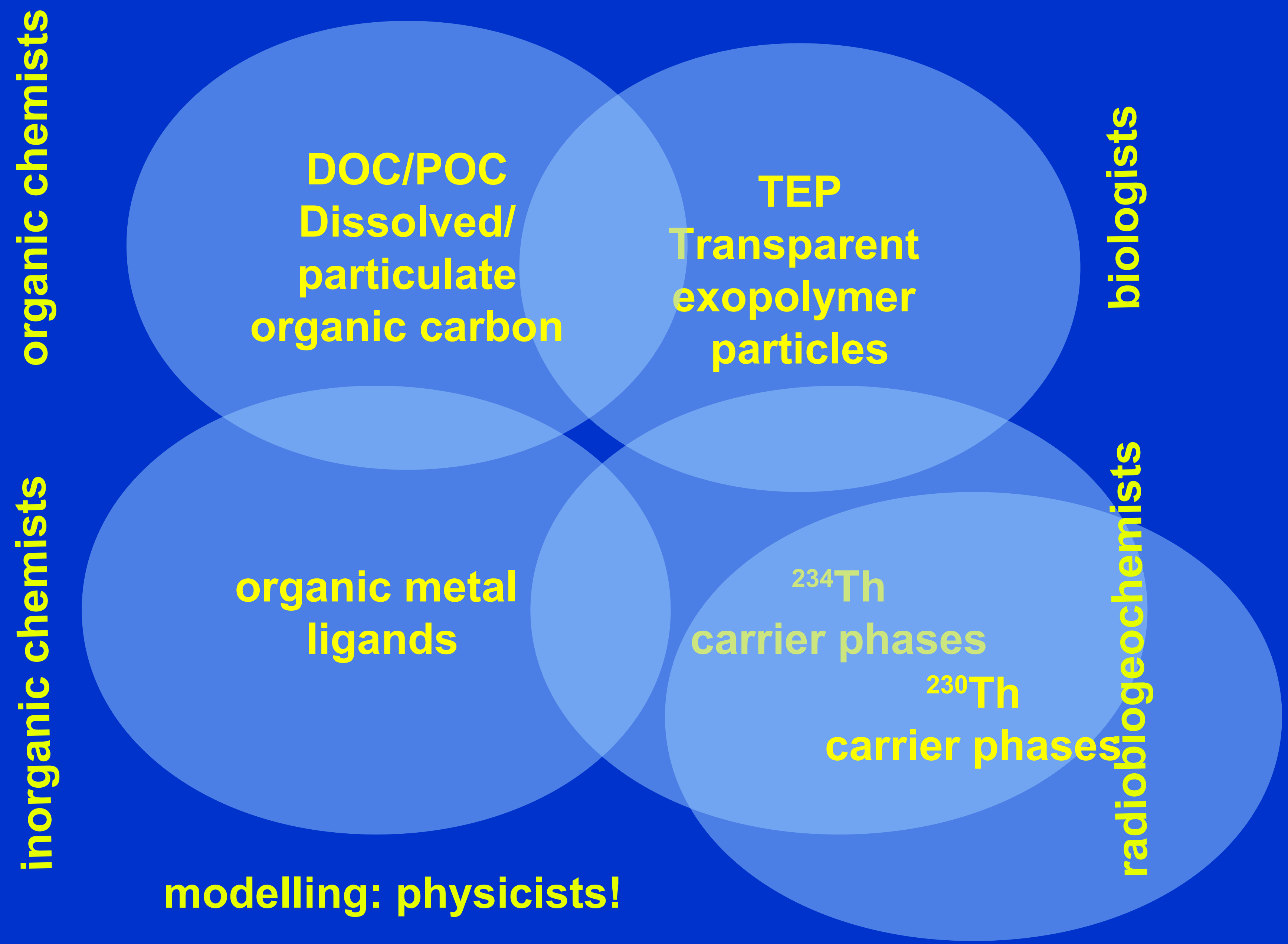
# After 1-2 days, we found around 30% of thorium on particles, in water that had been 0.2 μm filtered



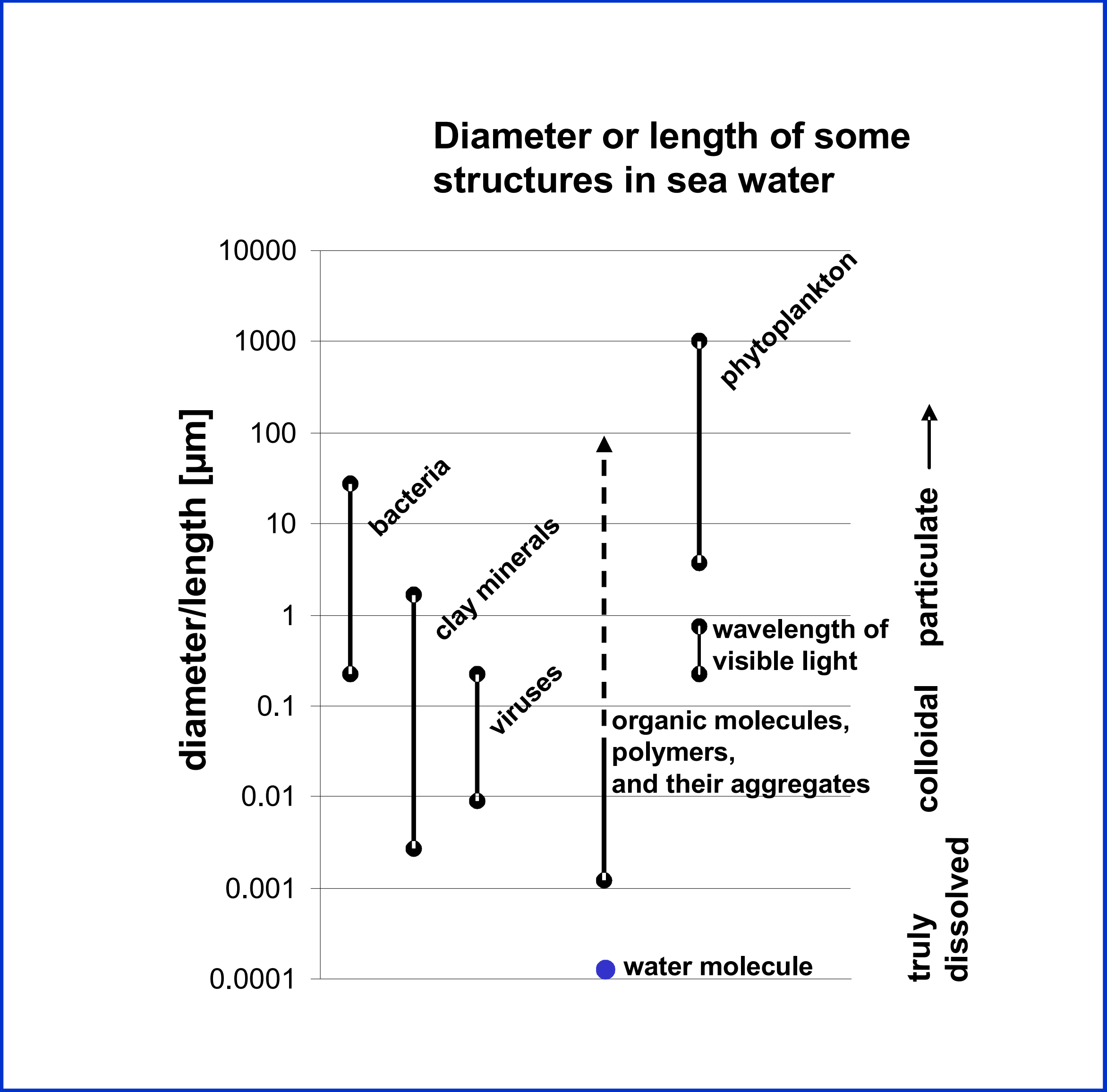

Geibert & Usbeck 2005

## What are these particles?

## Many research disciplines have valuable information to contribute:



# What’s dissolved? What’s a particle?

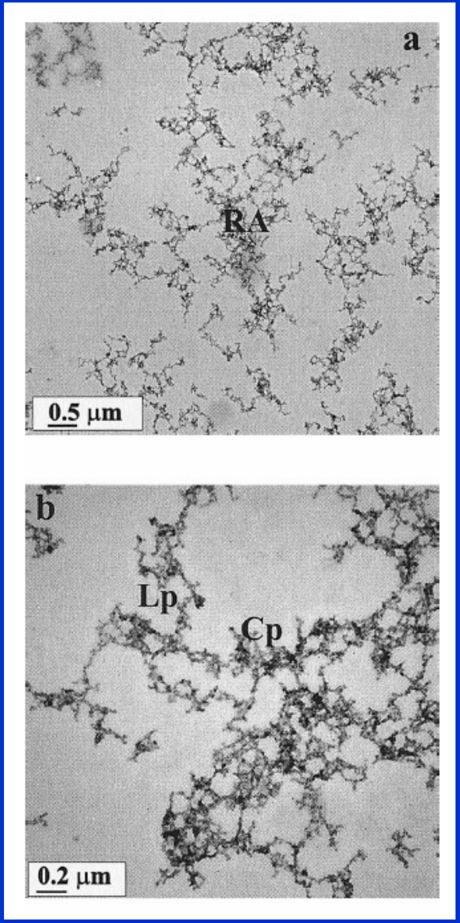



Rutgers van der Loeff and Geibert 2008

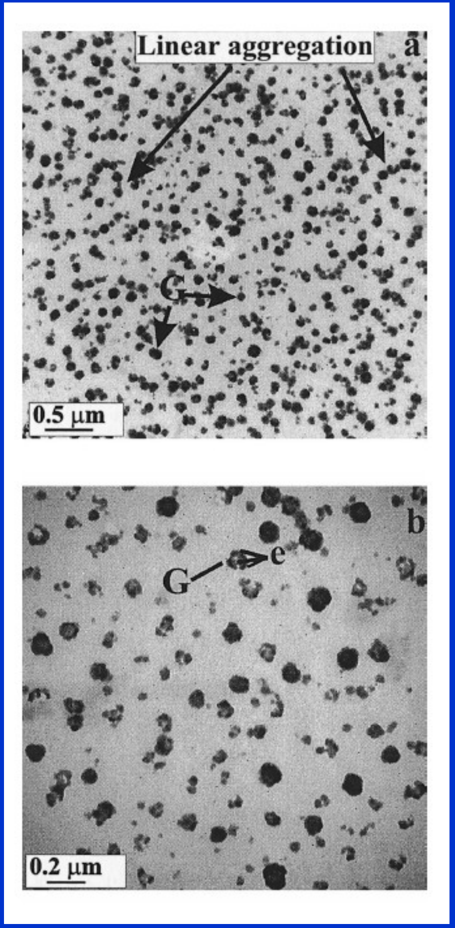
# Some things of colloidal size in sea water

Suttle, 2005: 3,000,000 viruses/ mL in the deep sea
100,000,000 viruses/mL in productive coastal waters

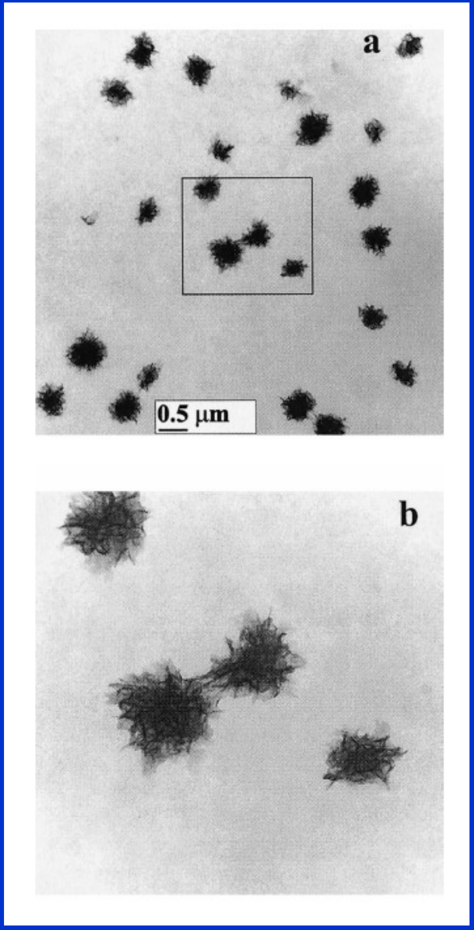
Grout et al. (Mediterranean): other colloidal substances




“Aggregates of rounded entities”




“globule morphotype”

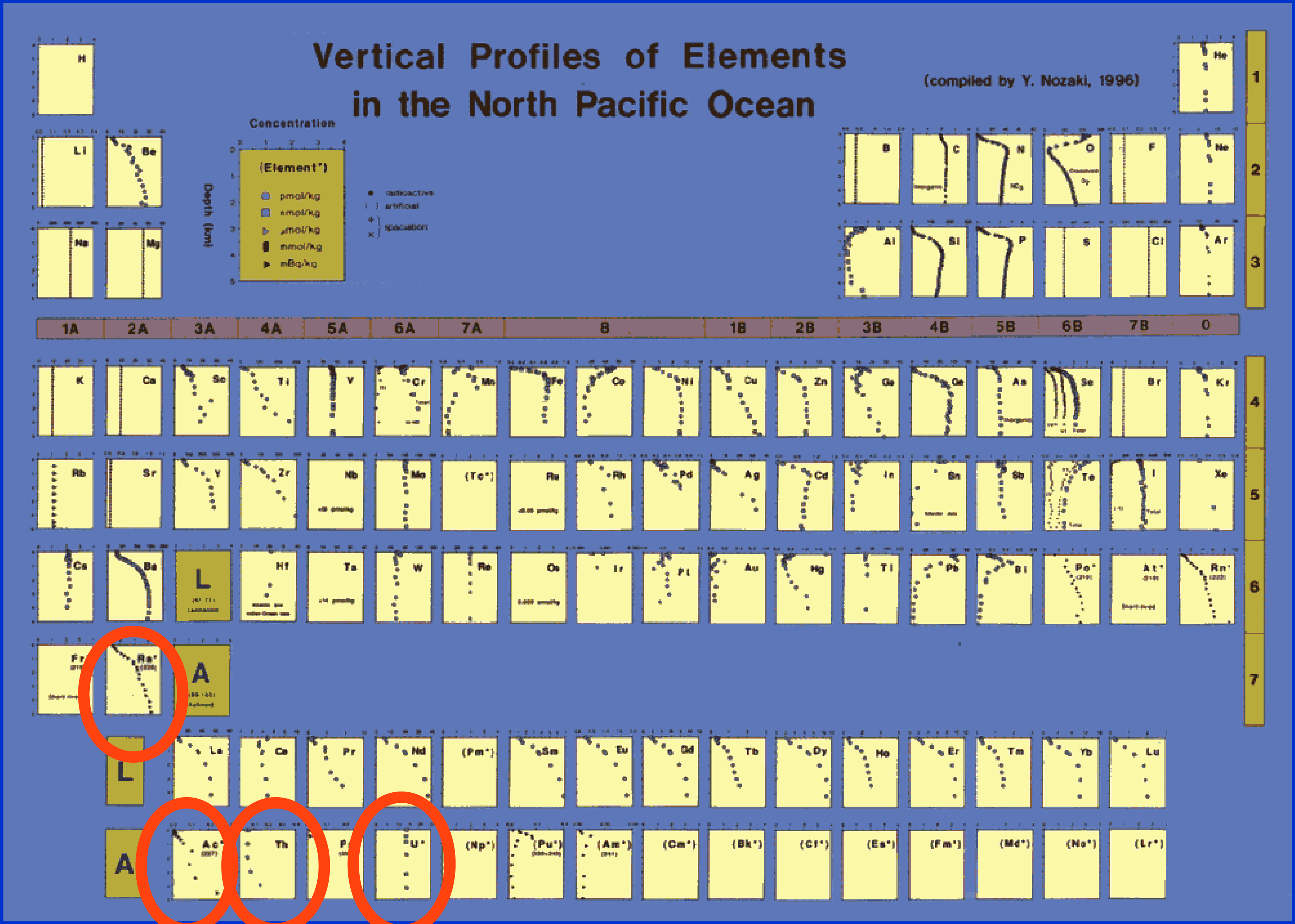



“spherulitic aggregates”

Grout et al. 2001

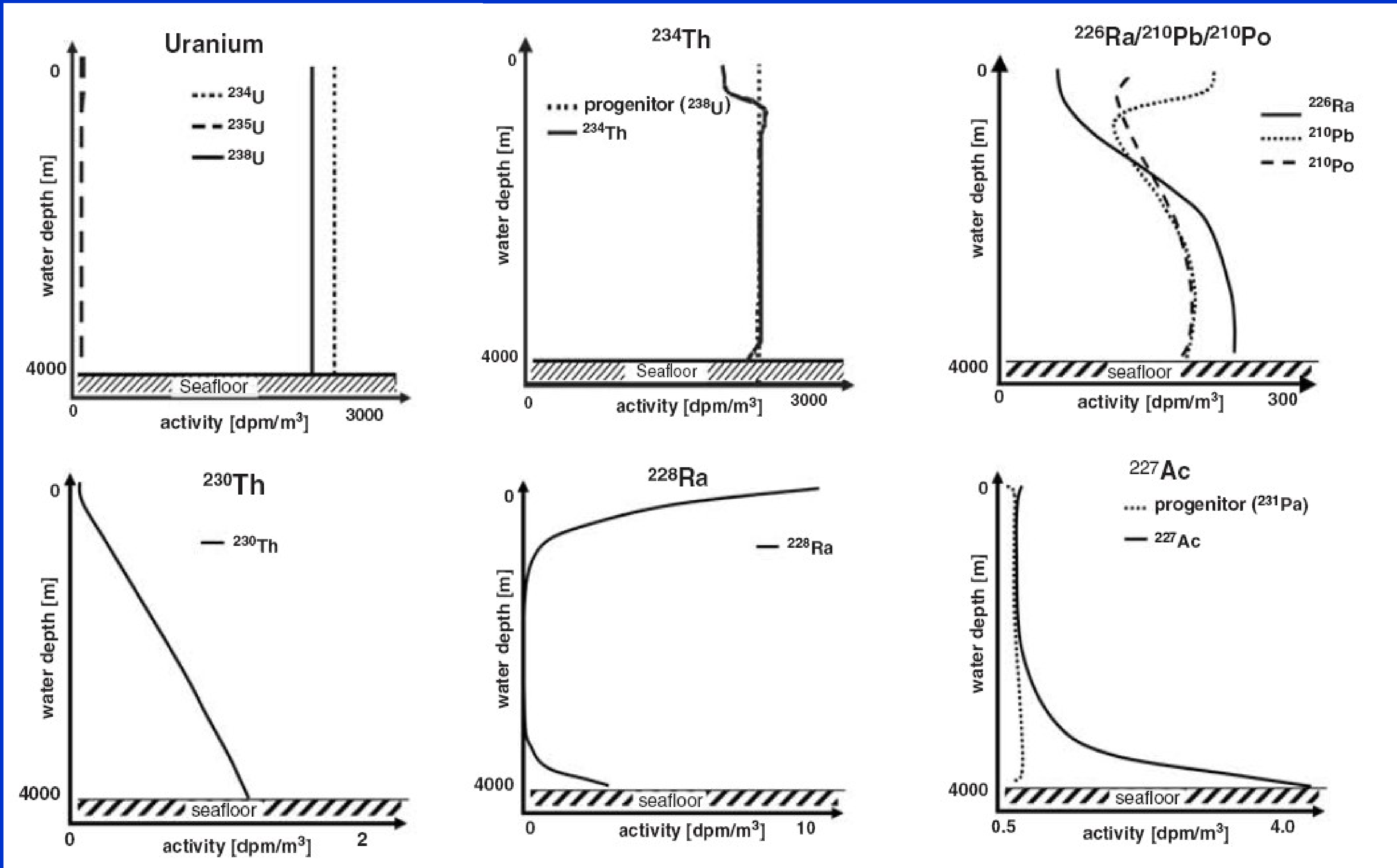
# How can we study particles in the ocean?

| | | |
|---|---|---|
| Bulk optical<br>(light scatter, turbidity) | → | concentration, size (down to large colloids) |
| Microscopy<br>(after prep.) | → | morphology, size (down to bacteria) |
| Electron microscopy<br>(after excessive prep.) | → | down to macromolecules |
| Filtration/ultrafiltration<br>(sample processing) | → | chemical differences |
| natural radionuclides | → | disequilibria- rates of processes |



Vertical Profiles of Elements
in the North Pacific Ocean
(compiled by Y. Nozaki, 1996)
Concentration
(Element*)
Depth (km)
pmol/kg
nmol/kg
μmol/kg
mmol/kg
mBq/kg
radioactive
artificial
speciation
1A
2A
3A
4A
5A
6A
7A
8
1B
2B
3B
4B
5B
6B
7B
0
1
2
3
4
5
6
7
H
He
Li
Be
B
C
N
O
F
Ne
Na
Mg
Al
Si
P
S
Cl
Ar
K
Ca
Sc
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Ga
Ge
As
Se
Br
Kr
Rb
Sr
Y
Zr
Nb
Mo
(Tc*)
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Te
I
Xe
Cs
Ba
L
Hf
Ta
W
Re
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Po*
At*
Rn*
Fr
Ra*
A
L
La
Ce
Pr
Nd
(Pm*)
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
A
Ac*
Th
Pa
U*
(Np*)
(Pu*)
(Am*)
(Cm*)
(Bk*)
(Cf*)
(Es*)
(Fm*)
(Md*)
(No*)
(Lr*)

# Typical profiles of some U-Th series radionuclides




Rutgers van der Loeff and Geibert (2008)

# The Uranium and Thorium Decay Series

of naturally occurring actinides
based on Broecker & Peng,1982

| Element | Uranium-238 decay chain | | | | | | | Th-232 decay chain | | | U-235 decay chain | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Uranium | U-238 4.5*$10^9$ y | | U-234 248000 y | | | | | | | | U-235 7.0*$10^8$ y | | |
| Protactinium | | Pa-234 1.2 min | | | | | | | | | | Pa-231 32500 y | |
| Thorium | Th-234 24.1 d | | Th-230 75200 y | | | | | Th-232 1.4*$10^{10}$ y | | Th-228 1.9 y | Th-231 25.5 h | | Th-227 18.7 d |
| **Actinium** | | | | | | | | | Ac-228 6.1 h | | | Ac-227 21.8 y | |
| **Radium** | | | Ra-226 1620 y | | | | | Ra-228 5.8 y | | Ra-224 3.7 d | | | Ra-223 11.4 d |
| Francium | | | | | | | | | | | | | |
| **Radon** | | | Rn-222 3.8 d | | | | | | | | | | Rn-219 3.96 s |
| Astatine | | | | | | | | | | | | | |
| Polonium | | | Po-218 3.1 min | | Po-214 0.00016 s | | Po-210 138 d | | | | | | Po 215 1.7*$10^{-3}$ s |
| Bismuth | | | | Bi-214 19.7 min | | Bi-210 5.0 d | | | | | | | |
| Lead | | | Pb-214 26.8 min | | Pb-210 22.3 y | | Pb-206 stable | | | Pb-208 stable | | | Pb-207 stable |

$\alpha$ -decay
n: -2
m: -4

$\beta$ -decay
n: +1
m:+/-0

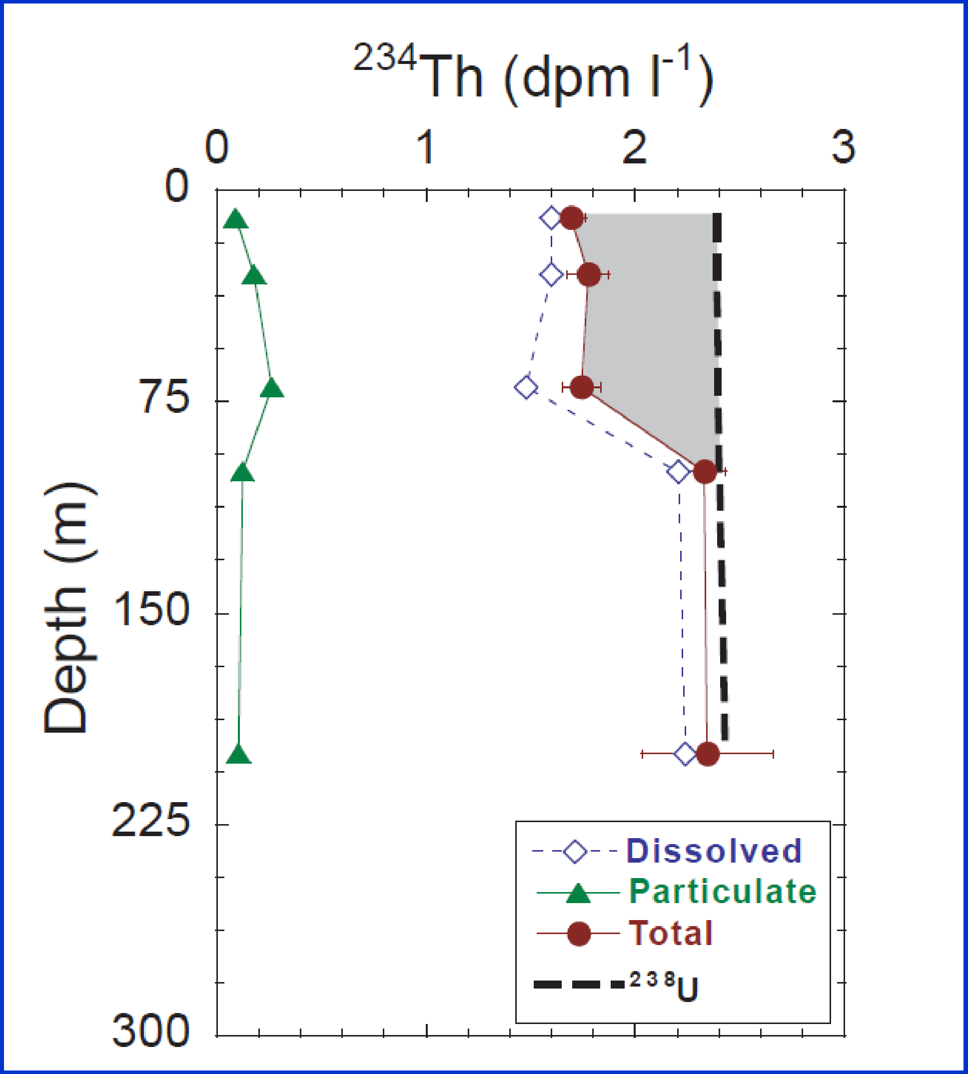
Decay chain
via intermediate nuclides

chem.symbol of the element — Pa-231 — mass
32500 y — half-life

not particle reactive
hardly particle reactive
particle reactive
very particle reactive

modified after Geibert et al. (2002)

# Example of the application of $^{234}$Th to study particle dynamics




Charette and Buesseler 2000

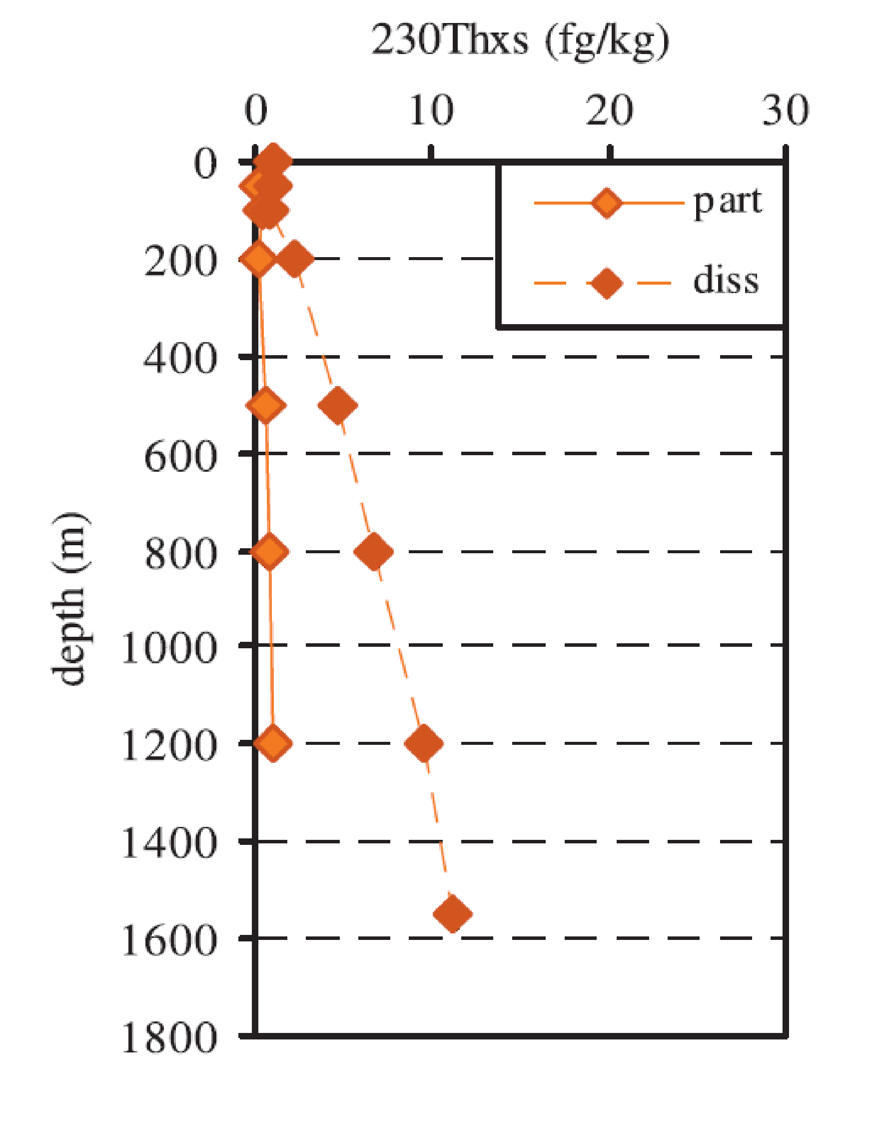
**$^{234}$Th:**
-precisely known production rate
-half-life 24 days
-sticks to particles
-removed by sinking particles

**This example:**
Export of particles from the surface

In equilibrium with $^{238}$U in the deep ocean (except near the sea floor)

Thorium is an analog for other particle-bound elements ($C_{org}$!)

# Example of the application of $^{230}$Th to study particle dynamics




Venchiarutti et al. 2008

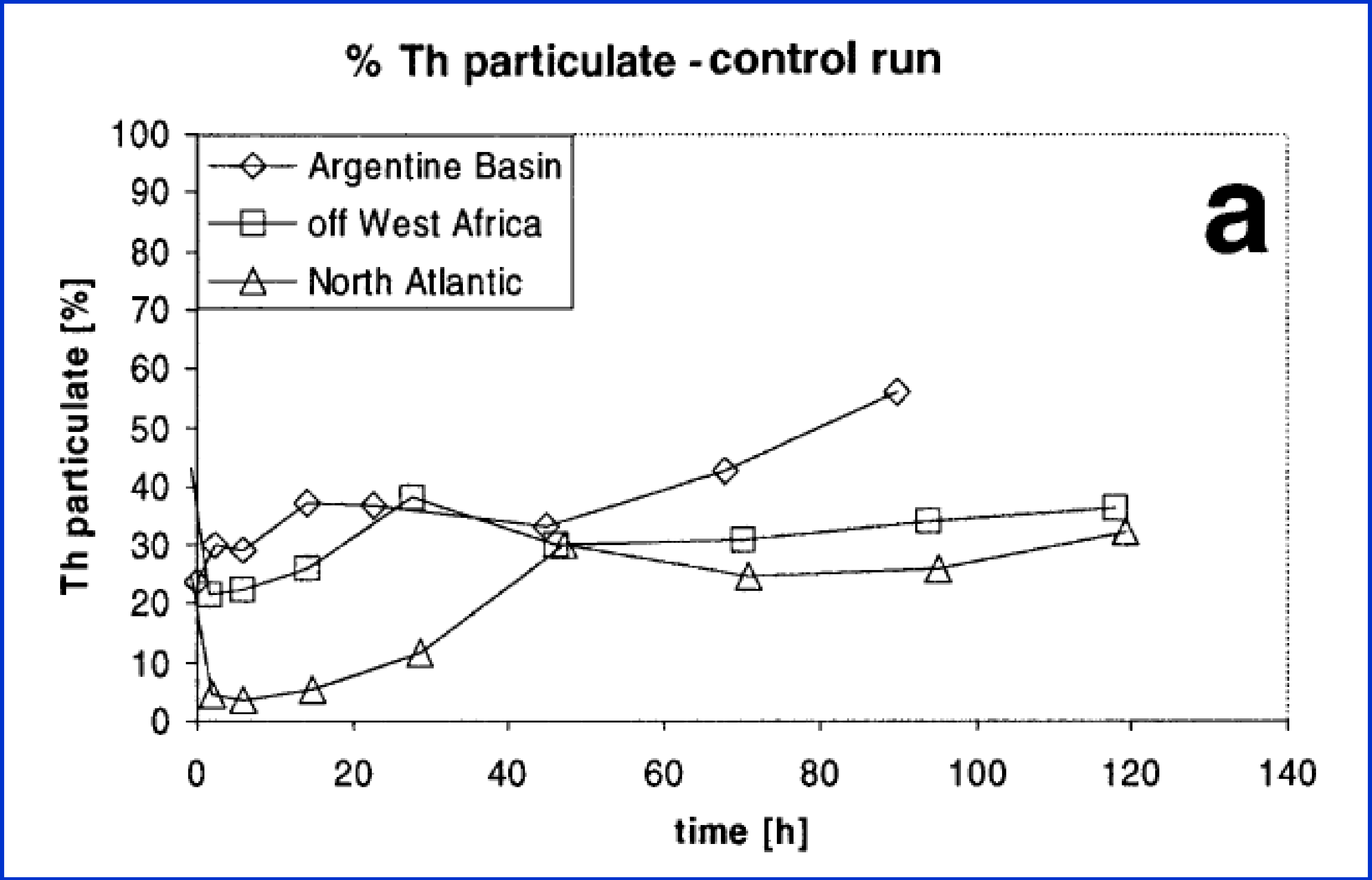
**$^{230}$Th:**
-precisely known production rate
-half-life 75,200 years
-sticks to particles
-removed by sinking particles

**This example:**
average particle sinking velocity
780 m/year

(global deep ocean 300-1000 m/year
= 1-3 m/day)

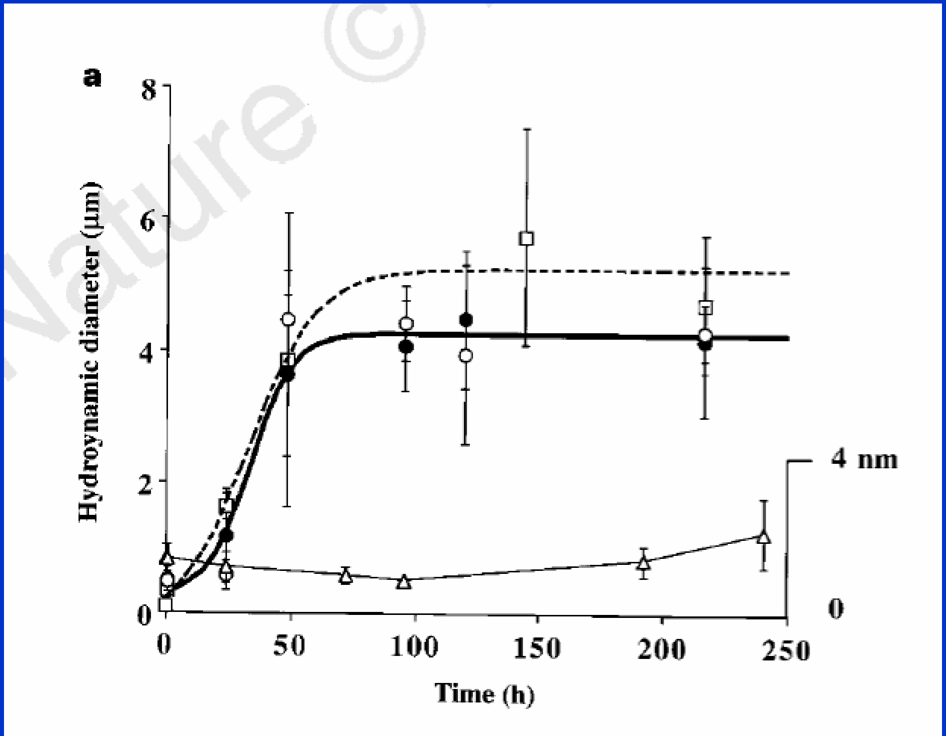
Please note- dissolved Th increases with depth!

# Back to the initial experimental result: What can other approaches tell us?




Geibert & Usbeck 2005

# Explanation:
## Spontaneous assembly of marine dissolved organic matter into polymer gels




**Chin et al. 1998**

Filtered sea water quickly forms particles again, in a reversible process

# The abbreviations in brief

TEP: Transparent exopolymer substances (Alldredge 1993)

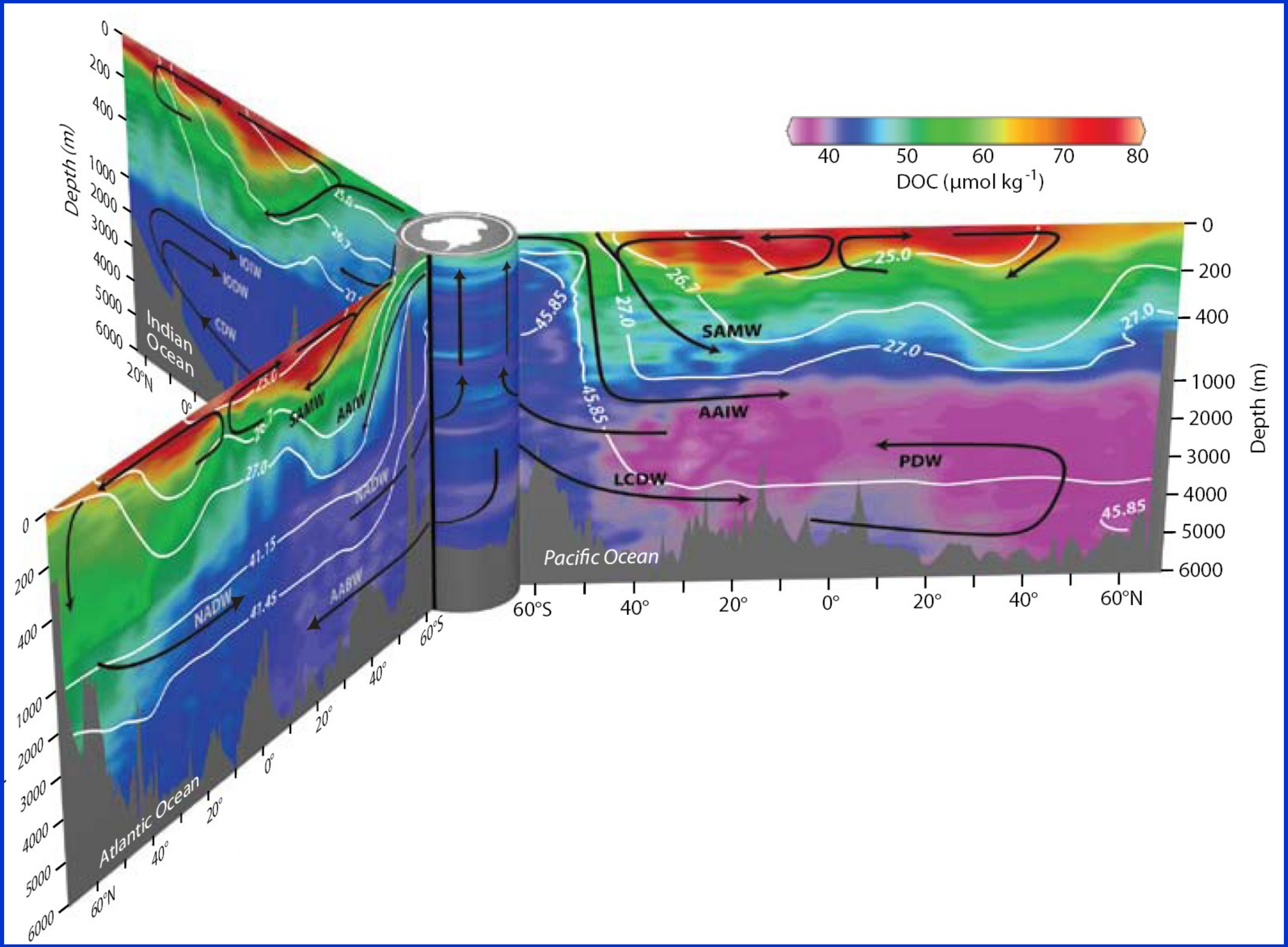
EPS: extracellular polymer substances ( bacteria/environmental studies)

COM: colloidal organic matter (organic chemistry)

SAG: Self-assembling gel (Verdugo & Santschi 2010)

More specific:
acid polysaccharides (Quigley et al. 2002): very strong Th ligand!

# Dissolved organic matter in the deep-sea




Hansell 2009

# The composition of marine dissolved organic matter

Deep sea: ~50 µmol
(Amount is relevant for global carbon budget)

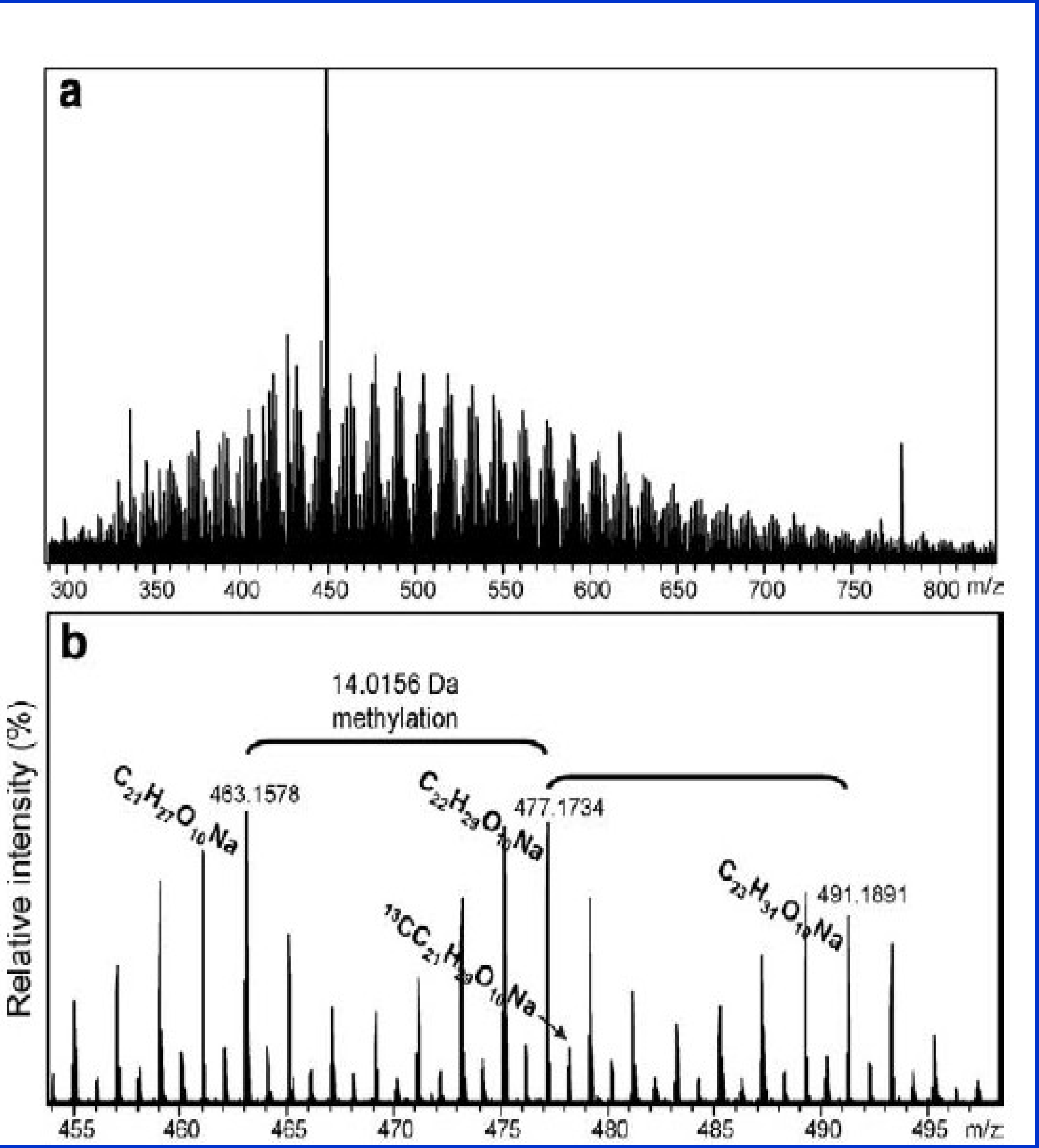
age: several 1000 years

~5% proteins, fats, carbohydrates (including polysaccharides)

~95% unknown until very recently

More information from a quite recent analytical development:

# DOM as seen in ultrahigh resolution mass spectrometry

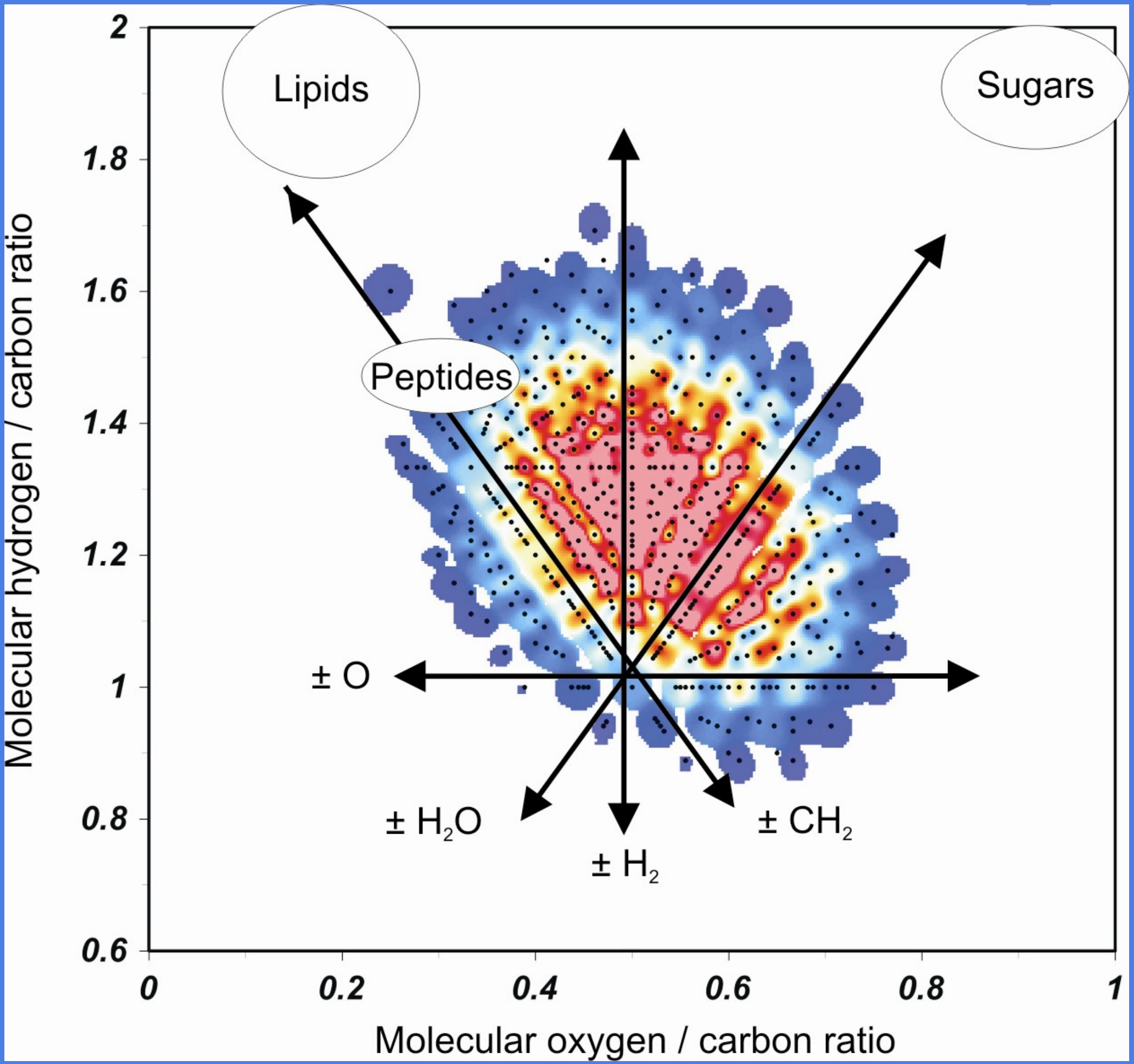



Koch et al. 2005

**Also called FT-ICR-MS**

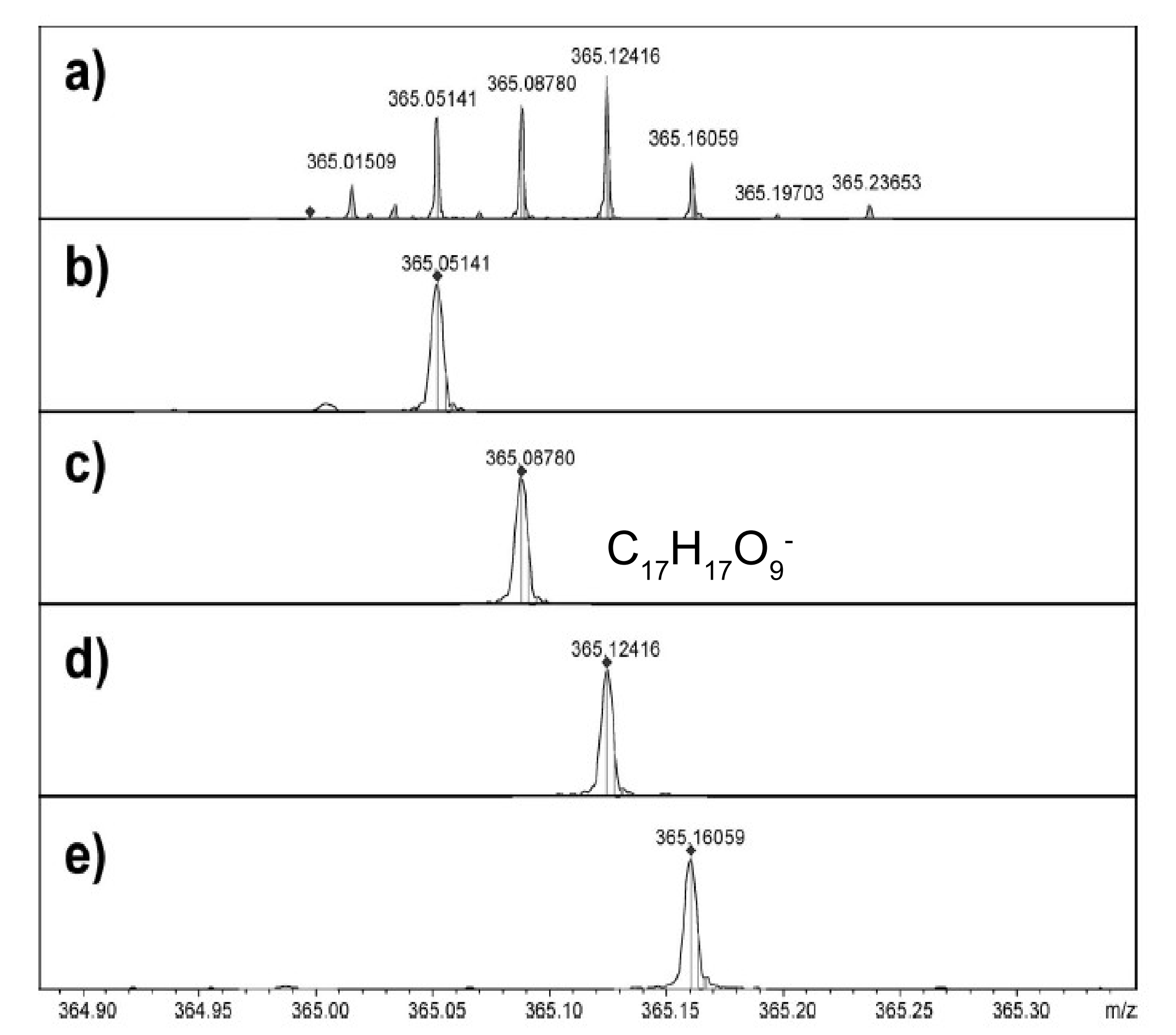
Precision of mass determination allows calculation of contributing atoms

# Dissolved organic matter composition by FT-ICR-MS




Kattner et al. 2011

# Investigating the structure of natural dissolved organic matter




← peaks at mass 365

← isolation of individual compounds by mass

← isolation of individual compounds by mass

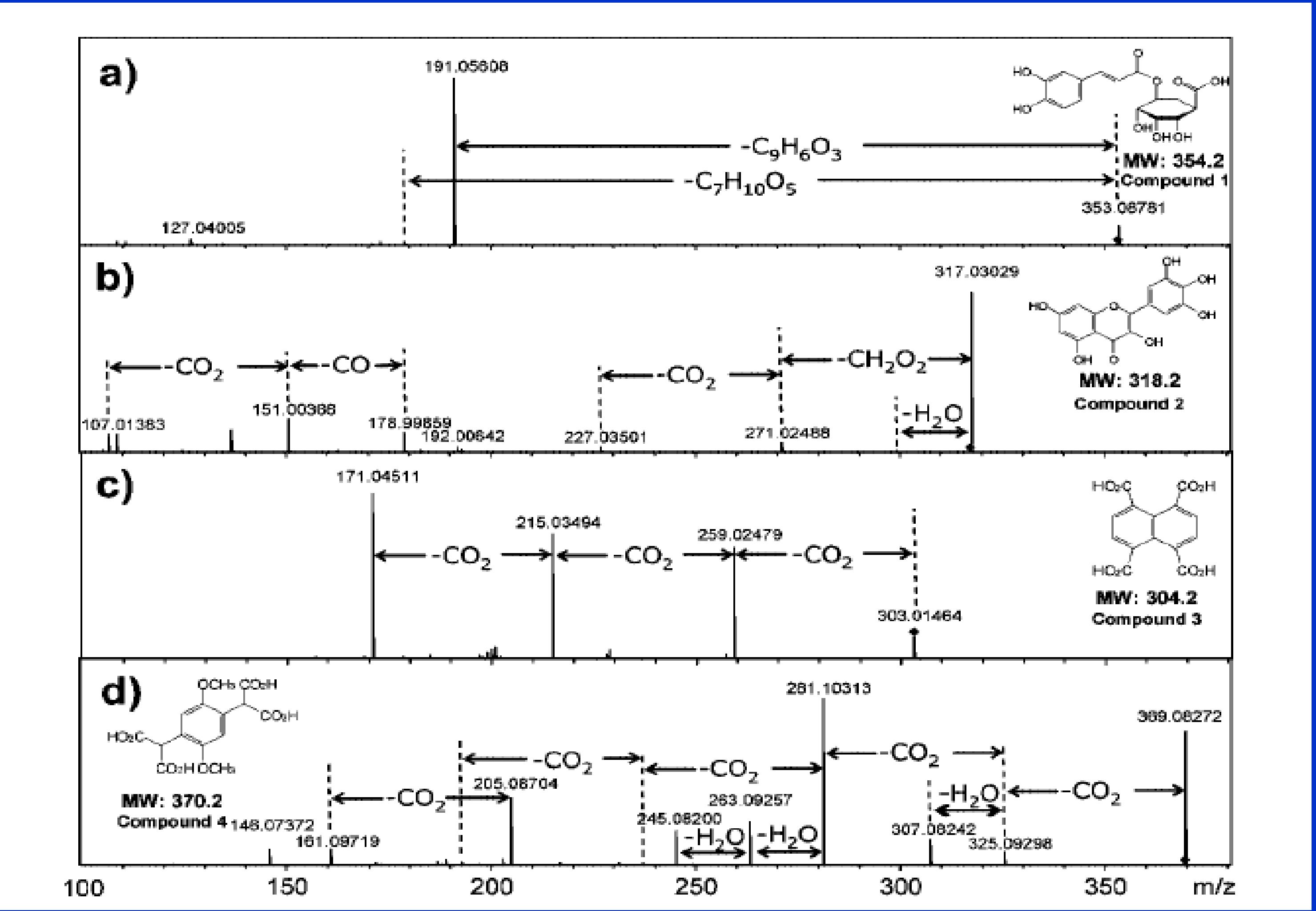
← isolation of individual compounds by mass

← isolation of individual compounds by mass

Witt et al. 2009

→ fragmentation experiments with the isolated compounds to study their structure

# Results of fragmentation of a single compound of dissolved organic matter

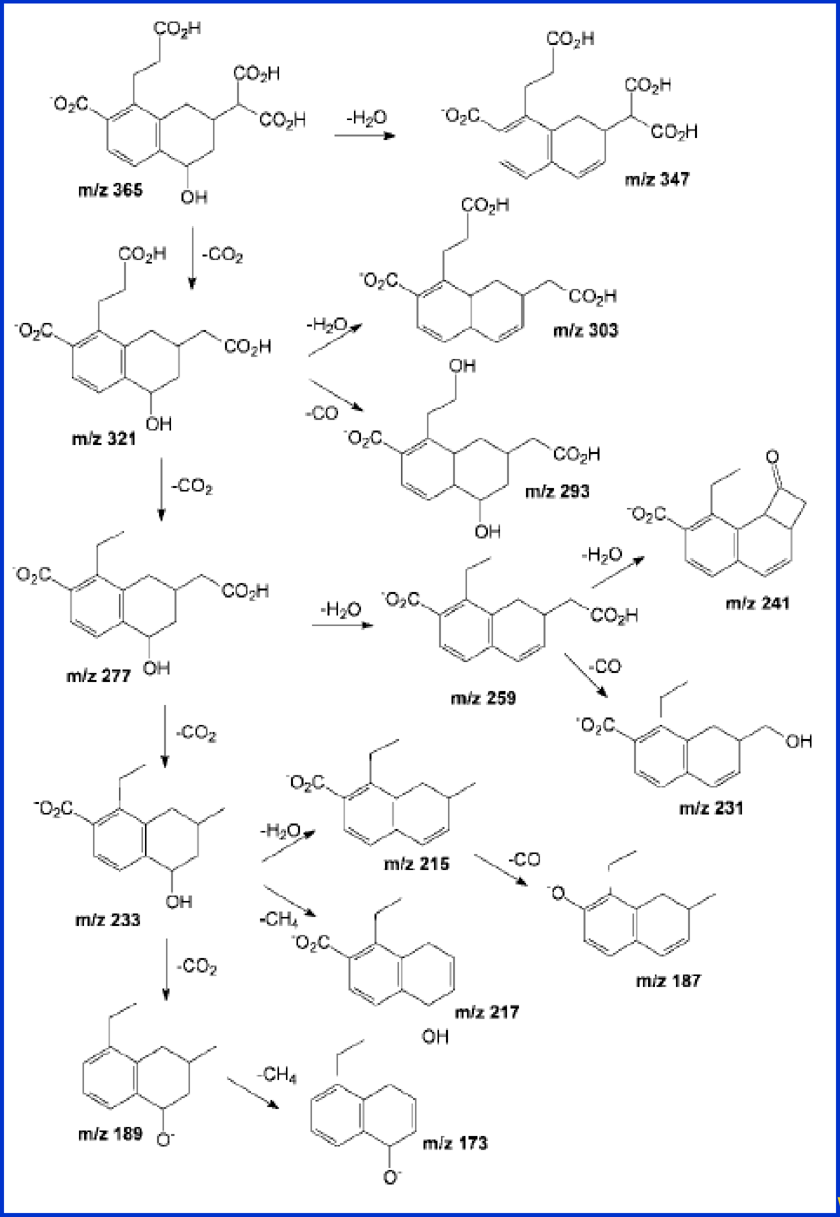


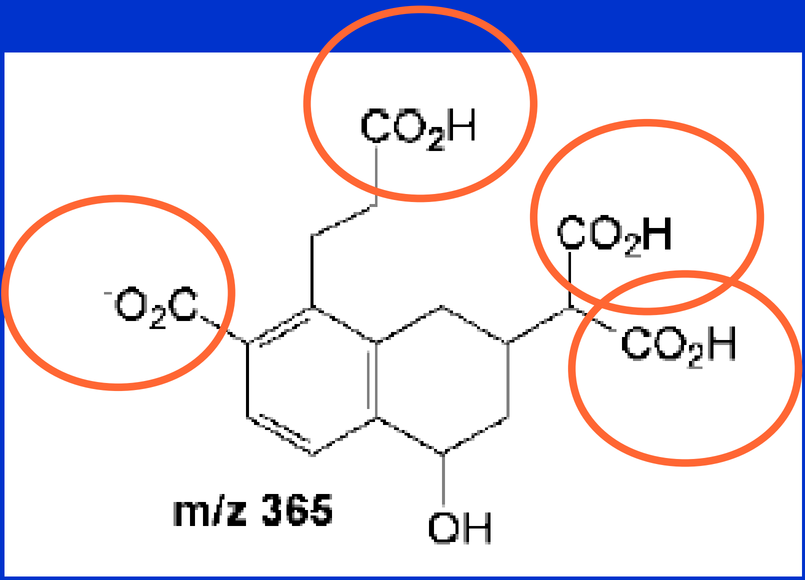

Witt et al. 2009

COOH groups (organic acids)

CO, CH4, H2O groups organised around a ring or condensed ring structure

# Structure of $C_{17}H_{17}O_9^-$ that would be consistent with the observed fragmentation




Four COOH groups (org. acid)

possible complexation of metals

possible polymerization (pH-dependant)

Witt et al. 2009

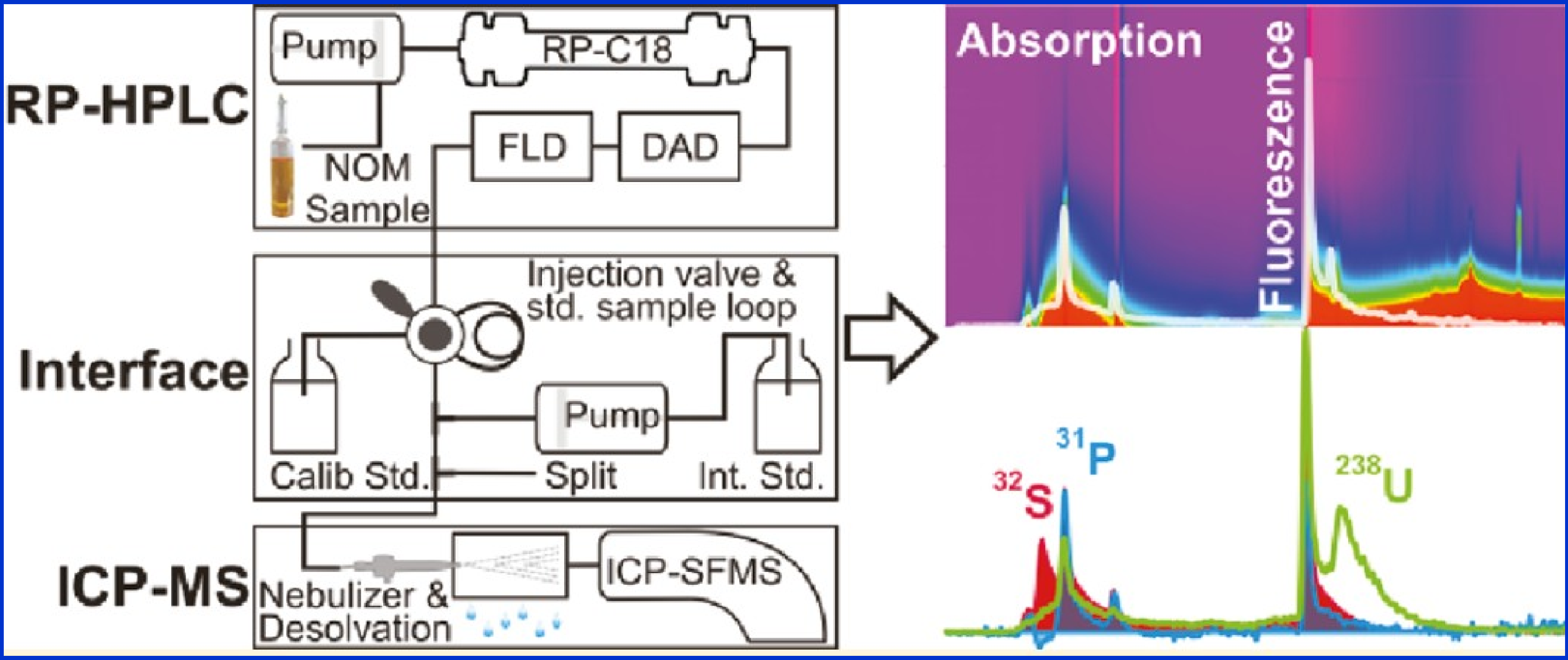
# Main contributors to deep marine DOM:

carboxyl-rich alicyclic molecules (CRAM)

Hertkorn et al. 2006

Approximately one in six C-atoms is carboxylic (acid functional group)

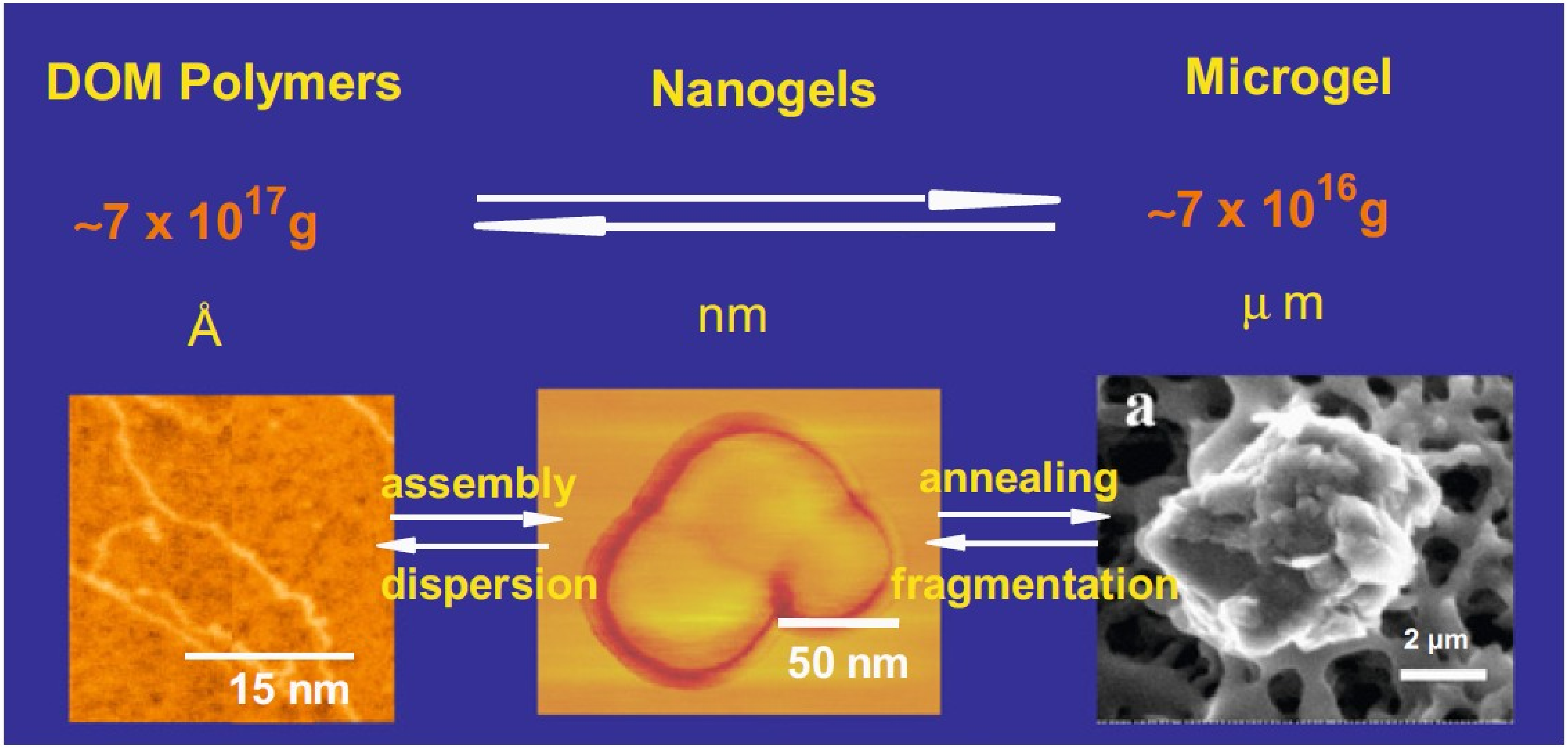
# Coupling of methods




Lechtenfeld et al. 2011

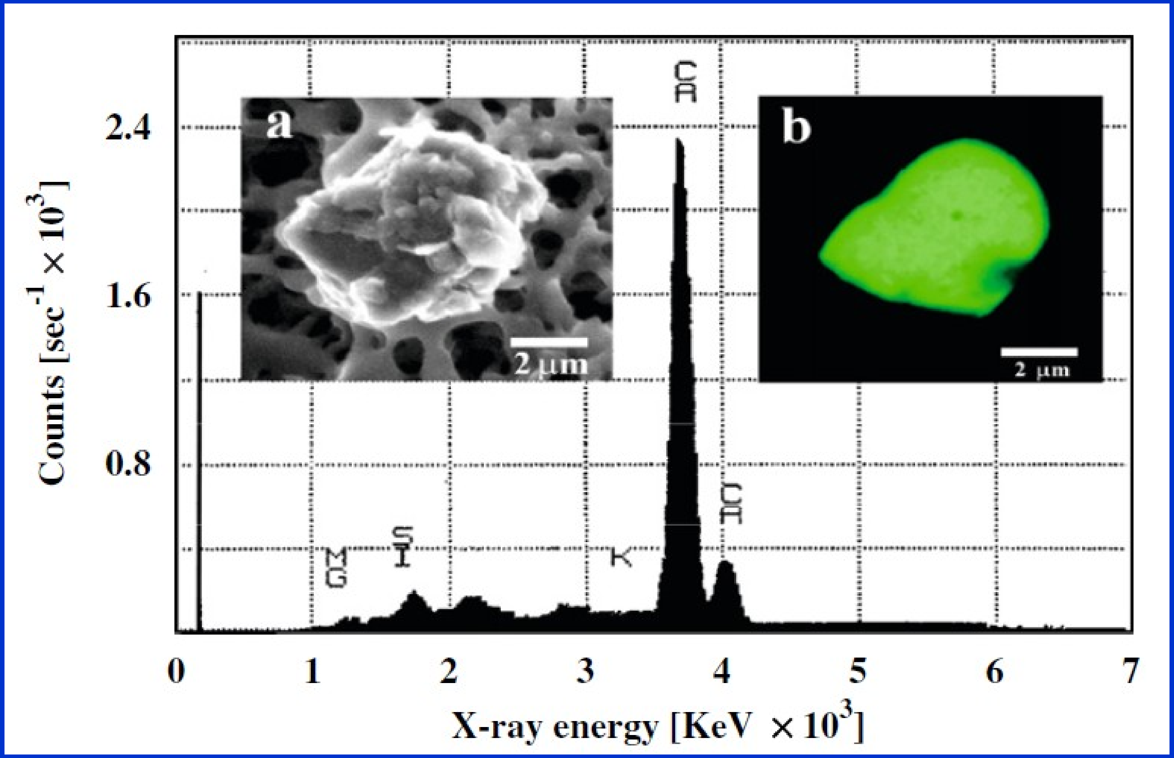
Another new analytical tool to study organic- inorganic interaction: coupling of organic analytical techniques with elemental analysis

# The formation of colloids and particles from dissolved organic matter polymers




Verdugo & Santschi 2010

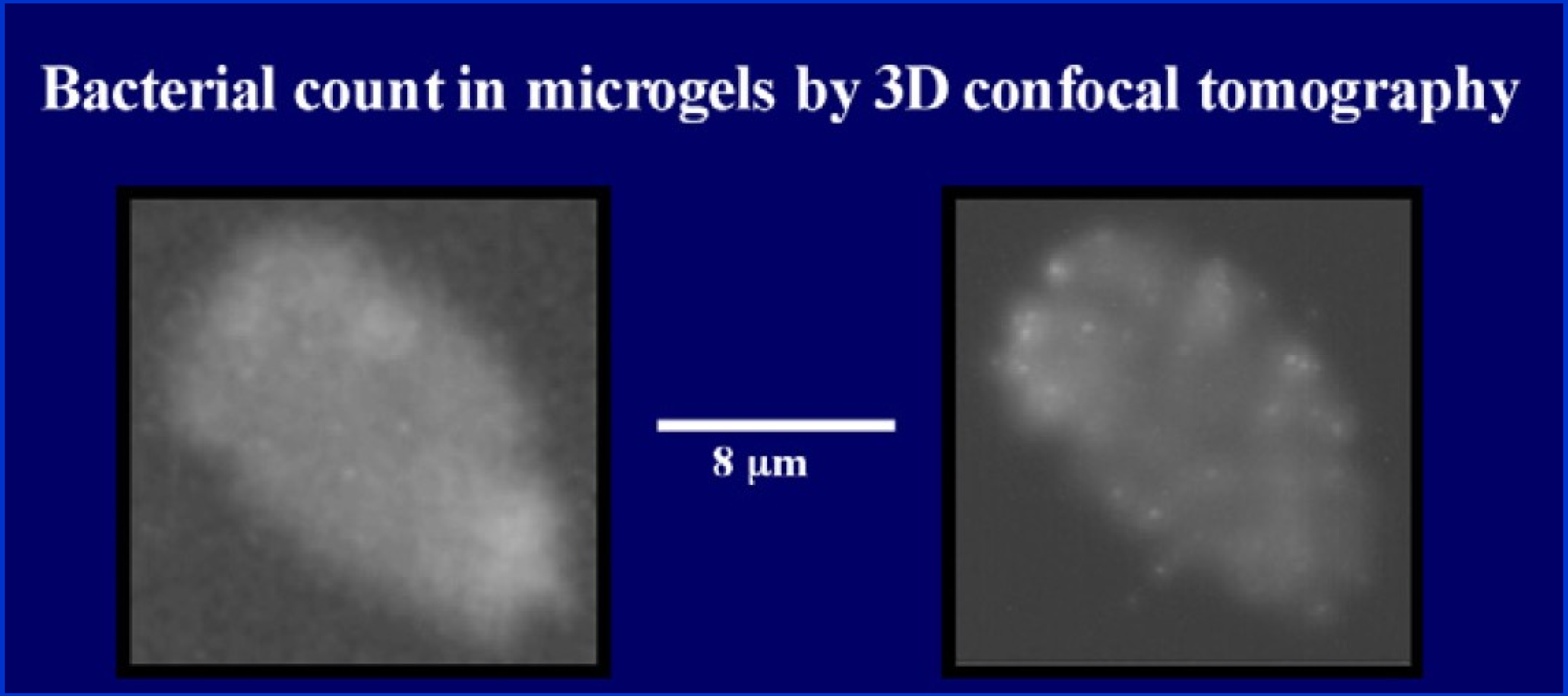
# Metal ions in microgels




Verdugo & Santschi 2010

Please note absence of Mg: The gels are quite selective

# Microgels as an environment for life




Verdugo & Santschi 2010

28 bacteria in this sample
$10^{8}$-$10^{10}$ bacteria/ mL of microgel!

# The reversible combination of DOC-molecules (deep sea)

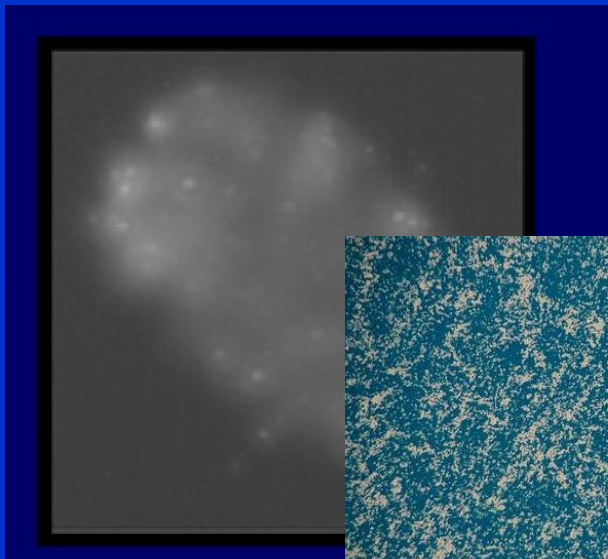
$$\mathrm{DOM1} + \mathrm{DOM2} + \mathrm{DOM3} + \ldots \rightleftharpoons \mathrm{POM}$$

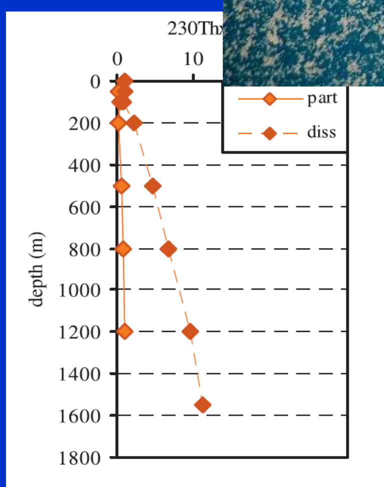
$$\frac{[\mathrm{DOM1}] * [\mathrm{DOM2}] * [\mathrm{DOM3}] * \ldots}{K} = [\mathrm{POM}]$$

**If we remove POM, particles will be regenerated from the DOM pool. (Le Chatelier's principle)**

Square brackets denotate the concentration
DOM: dissolved organic matter
POM: particulate organic matter
K constant

# DOM and POM form a continuum and enable further aggregation



# Summary

Sea water contains a continuum of organic compounds from molecules to marine snow, serving as food, as carriers of elements, or as a microenvironment for bacteria.

Equilibrium between dissolved and organic compounds - if particles (microgels) are removed, they are regenerated

A new exploration of this pool of substances is just beginning for the deep sea

Acid functional groups play a prominent role: polymerisation is pH dependant. Ocean acidification would possibly affect the complexation of metals and particle formation. Strong temperature dependance

Natural radionuclides are a valuable tool to study turnover rates and complexing properties of dissolved organic matter.

# Examples of marine particles (ordered by decreasing size)

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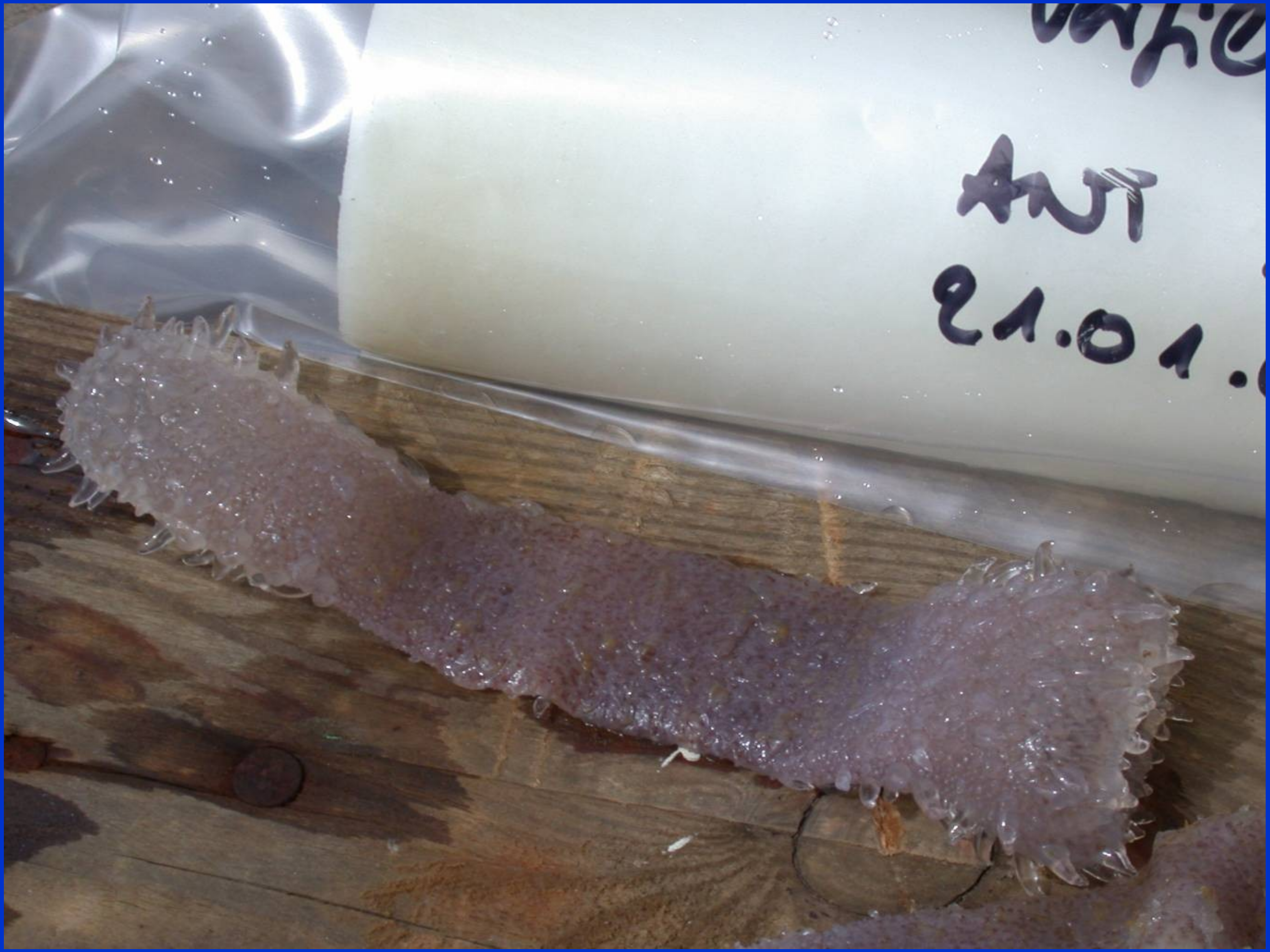
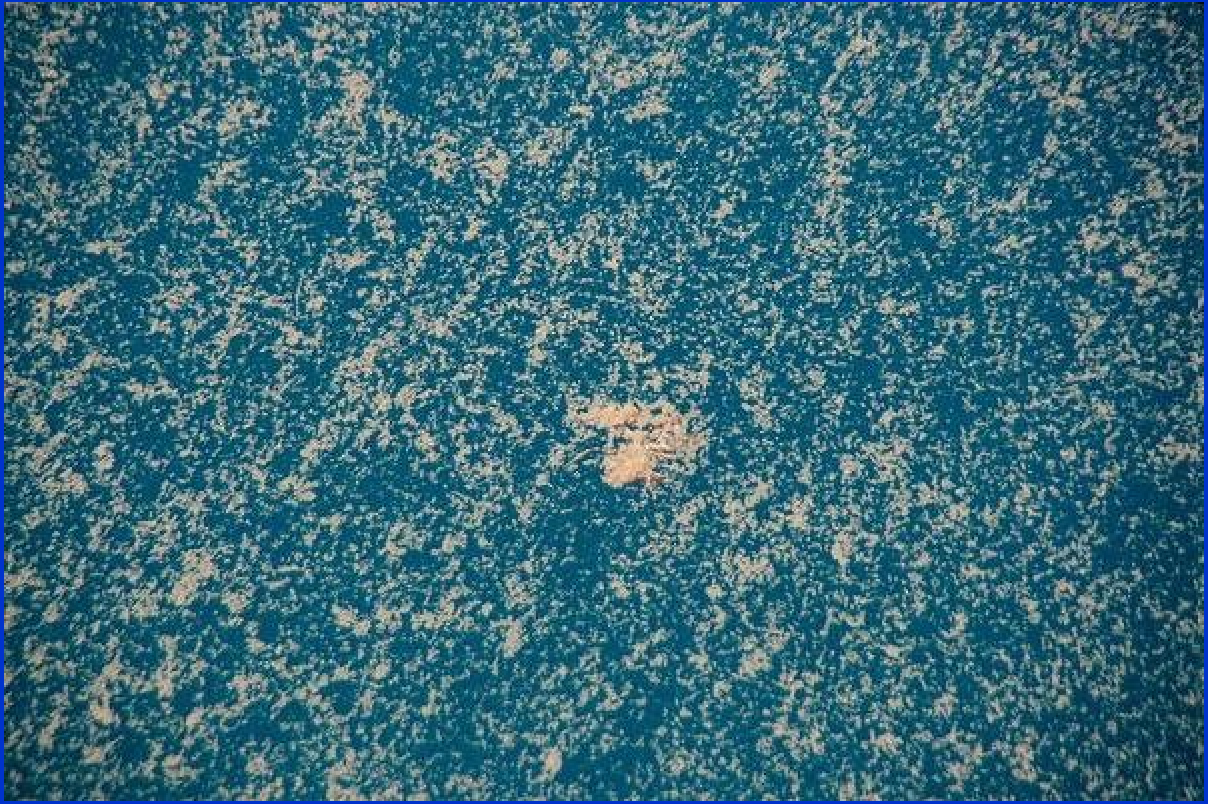
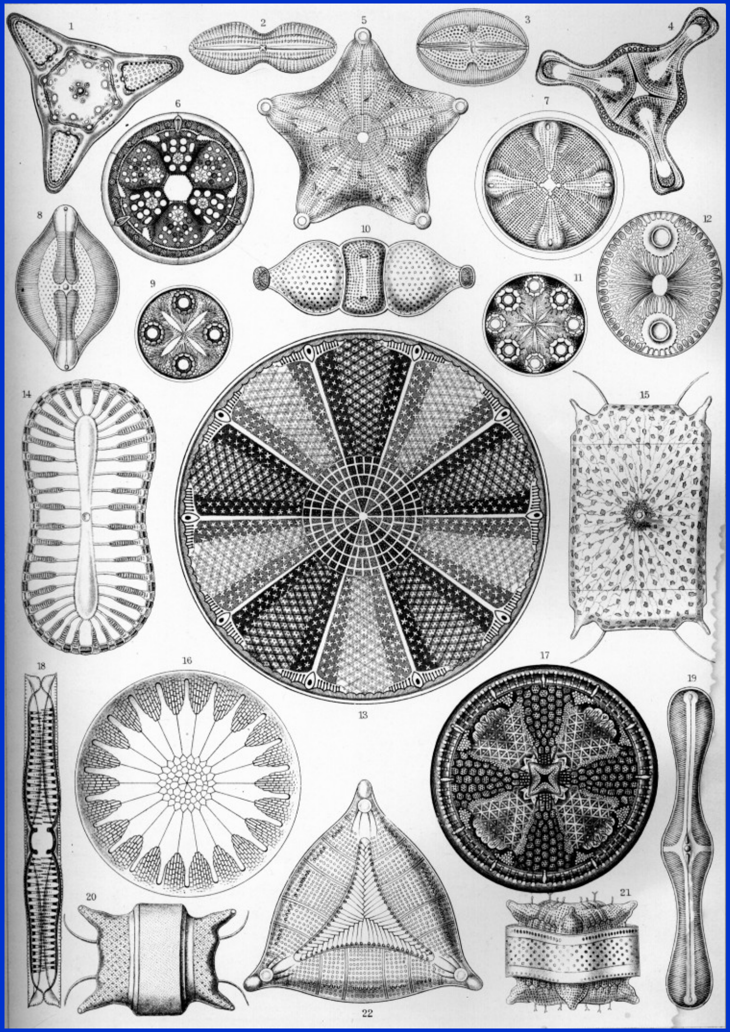


# Marine Snow

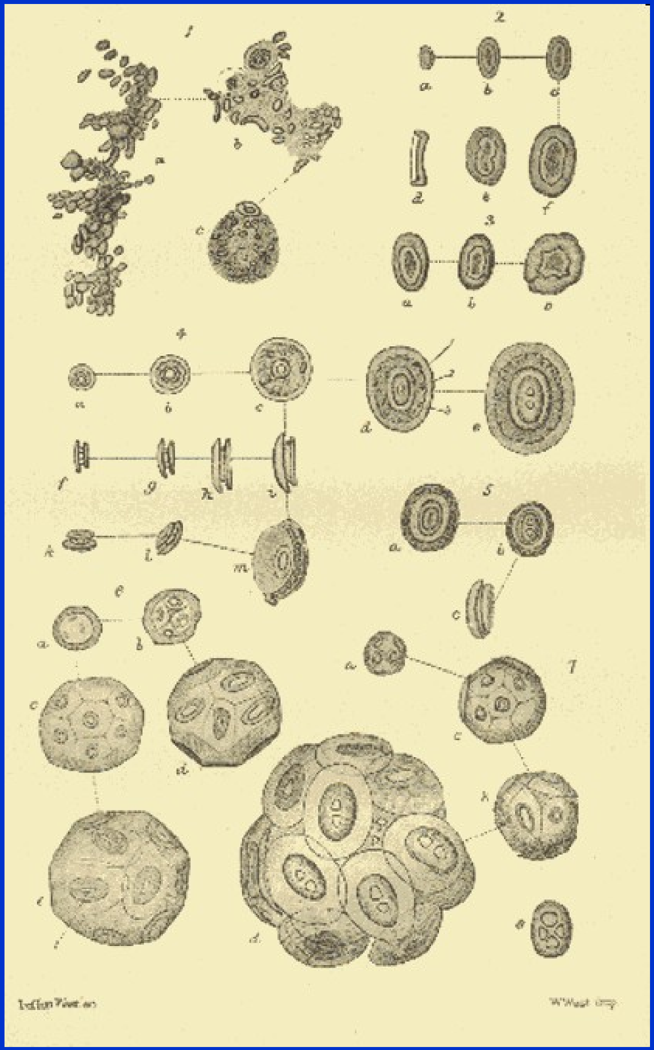


Arne Diercks, from National Geographic

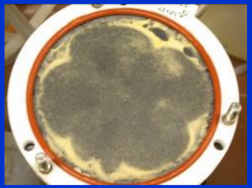
# Examples of marine particles: phytoplankton



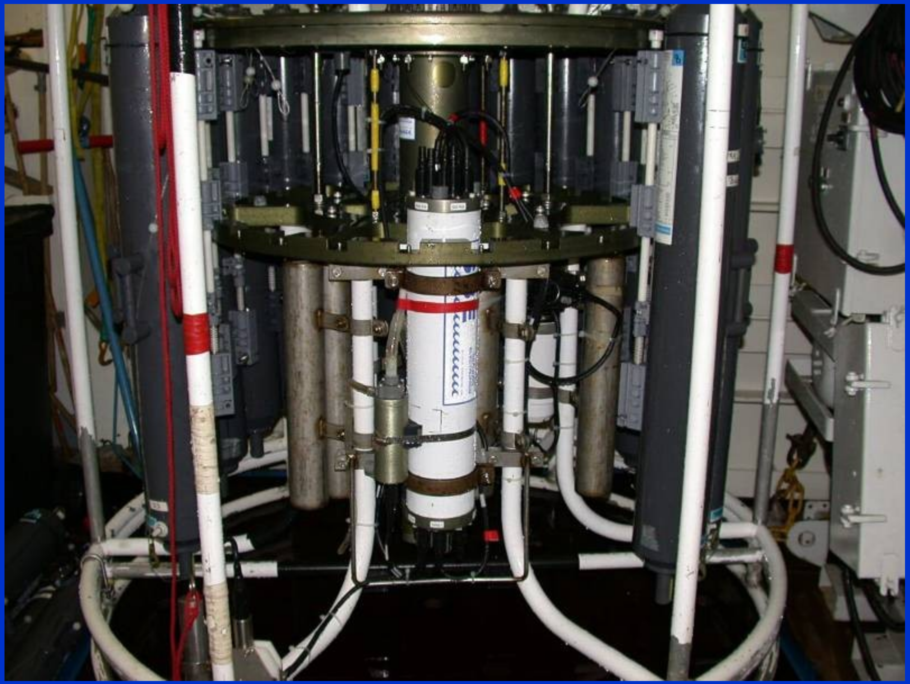
Haeckel 1904



Huxley 1868



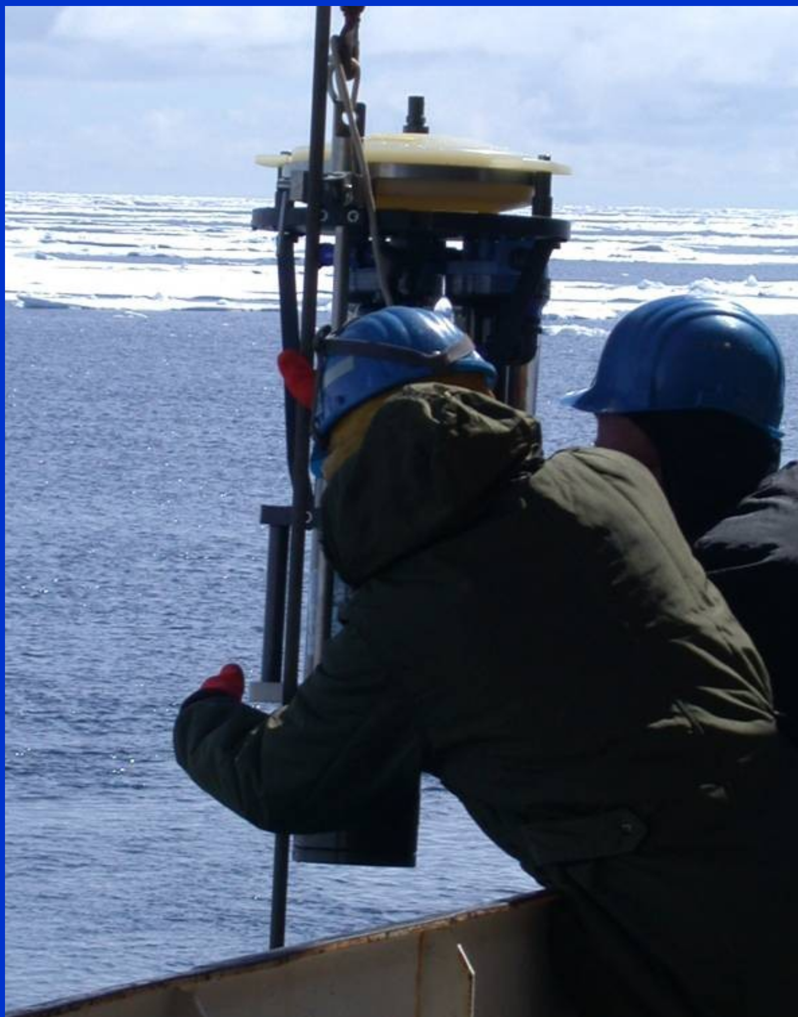
# Sampling devices for particles I



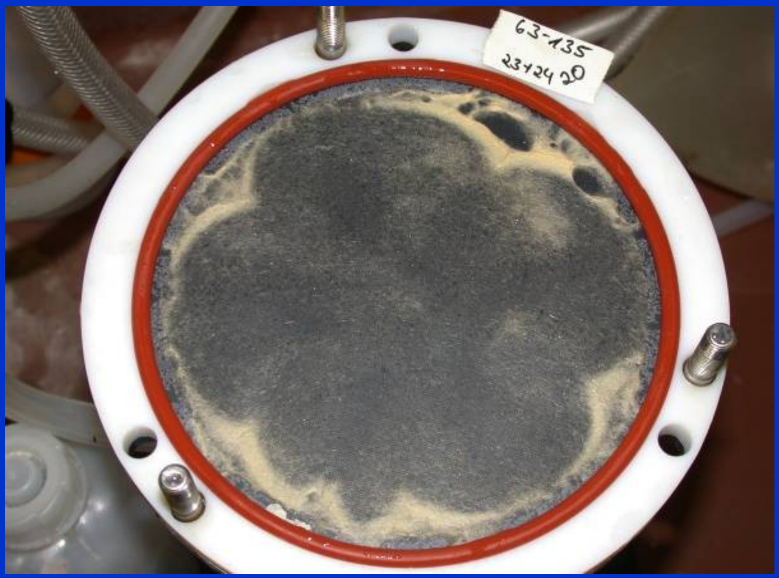
Sensors

Bottles

# Sampling devices for particles II



in situ filtration
(submersible pumps)




Filtration of bottle samples

# Sampling devices for particles III

Large-volume centrifuge