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

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The elemental composition of sea water

Vertical Profiles of Elements in the North Pacific Ocean

(compiled by Y. Nozaki, 1996)
### Abundance of selected elements in the ocean

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (%)</th>
<th>total amount in the oceans estimated (in tons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>chlorine</td>
<td>1,95</td>
<td>$2,57 \times 10^{16}$</td>
</tr>
<tr>
<td>sodium</td>
<td>1,077</td>
<td>$1,42 \times 10^{16}$</td>
</tr>
<tr>
<td>magnesium</td>
<td>0,129</td>
<td>$1,71 \times 10^{15}$</td>
</tr>
<tr>
<td>sulfur</td>
<td>0,0905</td>
<td>$1,2 \times 10^{15}$</td>
</tr>
<tr>
<td>potassium</td>
<td>0,038</td>
<td>$5,02 \times 10^{14}$</td>
</tr>
<tr>
<td>arsenic</td>
<td>0,000000037</td>
<td>$4,89 \times 10^{9}$</td>
</tr>
<tr>
<td>uranium</td>
<td>0,000000032</td>
<td>$4,23 \times 10^{9}$</td>
</tr>
<tr>
<td>iron</td>
<td>0,0000000055</td>
<td>$7,27 \times 10^{7}$</td>
</tr>
<tr>
<td>thorium</td>
<td>0,000000001</td>
<td>$1,32 \times 10^{7}$</td>
</tr>
<tr>
<td>gold</td>
<td>0,0000000004</td>
<td>$5,29 \times 10^{6}$</td>
</tr>
<tr>
<td>lead</td>
<td>0,0000000002</td>
<td>$2,64 \times 10^{6}$</td>
</tr>
<tr>
<td>radium</td>
<td>0,000000000011</td>
<td>$93$</td>
</tr>
<tr>
<td>actinium</td>
<td>0,0000000000000096</td>
<td>$0,01 – 0.05$</td>
</tr>
</tbody>
</table>

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

What are these particles?
Many research disciplines have valuable information to contribute:

- **Organic chemists**
  - DOC/POC
    - Dissolved/particulate organic carbon
  - Organic metal ligands

- **Biologists**
  - TEP
    - Transparent exopolymer particles

- **Inorganic chemists**
  - $^{234}$Th carrier phases
  - $^{230}$Th carrier phases

- **Radiobiogeochemists**

**Modelling**: physicists!
What’s dissolved? What’s a particle?

Diameter or length of some structures in sea water

- **bacteria**
- **clay minerals**
- **viruses**
- **organic molecules, polymers, and their aggregates**
- **water molecule**
- **wavelength of visible light**
- **phytoplankton**

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”
How can we study particles in the ocean?

- **Bulk optical** (light scatter, turbidity) → concentration, size (down to large colloids)
- **Microscopy** (after prep.) → morphology, size (down to bacteria)
- **Electron microscopy** (after excessive prep.) → down to macromolecules
- **Filtration/ultrafiltration** (sample processing) → chemical differences
- **Natural radionuclides** → disequilibria - rates of processes
Typical profiles of some U-Th series radionuclides

Rutgers van der Loeff and Geibert (2008)
# The Uranium and Thorium Decay Series

**Element**

<table>
<thead>
<tr>
<th>Uranium-238 decay chain</th>
<th>Th-232 decay chain</th>
<th>U-235 decay chain</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Uranium</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U-238 4.5*10⁹ y</td>
<td></td>
<td>U-235 7.0*10⁸ y</td>
</tr>
<tr>
<td>Protactinium</td>
<td></td>
<td>Pa-231 32500 y</td>
</tr>
<tr>
<td>Pa-234 1.2 min</td>
<td>Th-232 1.4*10¹⁰ y</td>
<td></td>
</tr>
<tr>
<td>Thorium</td>
<td>Th-231 25.5 h</td>
<td></td>
</tr>
<tr>
<td>Th-234 24.1 d</td>
<td>Th-228 1.9 y</td>
<td></td>
</tr>
<tr>
<td>Actinium</td>
<td>Th-227 18.7 d</td>
<td></td>
</tr>
<tr>
<td>Radium</td>
<td>Rn-222 3.8 d</td>
<td>Rn-219 3.96 s</td>
</tr>
<tr>
<td>Ra-226 1620 y</td>
<td>Ra-228 5.8 y</td>
<td></td>
</tr>
<tr>
<td>Francium</td>
<td>Ra-224 3.7 d</td>
<td></td>
</tr>
<tr>
<td>Radium</td>
<td>Ra-223 11.4 d</td>
<td></td>
</tr>
<tr>
<td>Radon</td>
<td>Rn-222 3.8 d</td>
<td>Rn-219 3.96 s</td>
</tr>
<tr>
<td>Po-218 3.1 min</td>
<td>Po-214 0.00016 s</td>
<td>Po-215 1.7*10⁻³ s</td>
</tr>
<tr>
<td>Polonium</td>
<td>Bi-214 19.7 min</td>
<td></td>
</tr>
<tr>
<td>Po-214 5.0 d</td>
<td>Bi-210 stable</td>
<td></td>
</tr>
<tr>
<td>Bismuth</td>
<td>Pb-206 stable</td>
<td></td>
</tr>
<tr>
<td>Bi-214 19.7 min</td>
<td>Bi-210 5.0 d</td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td>Pb-210 22.3 y</td>
<td>Pb-207 stable</td>
</tr>
<tr>
<td>Pb-214 26.8 min</td>
<td>Pb-210 22.3 y</td>
<td></td>
</tr>
</tbody>
</table>

**Notes:**

- **α-decay:** n: -2, m: -4
- **β-decay:** n: +1, m: +/-0
- **Decay chain via intermediate nuclides**
- **chem.symbol of the element**
- **Pa-231 32500 y**
- **mass**
- **half-life**

*modified after Geibert et al. (2002)*

*Based on Broecker & Peng, 1982*
Example of the application of $^{234}\text{Th}$ to study particle dynamics

$^{234}\text{Th}$:
- 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 $^{238}\text{U}$ in the deep ocean (except near the sea floor)

Thorium is an analog for other particle-bound elements ($\text{C}_{\text{org}}$)

Charette and Buesseler 2000
Example of the application of $^{230}$Th to study particle dynamics

$^{230}$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!

Venchiarutti et al. 2008
Back to the initial experimental result:
What can other approaches tell us?
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: $\sim 50 \ \mu\text{mol}$
(Amount is relevant for global carbon budget)

age: several 1000 years

$\sim 5\%$ proteins, fats, carbohydrates (including polysaccharides)

$\sim 95\%$ unknown until very recently

More information from a quite recent analytical development:
DOM as seen in ultrahigh resolution mass spectrometry

Also called FT-ICR-MS

Precision of mass determination allows calculation of contributing atoms

Koch et al. 2005
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

$\text{C}_{17}\text{H}_{17}\text{O}_9^-$

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

COOH groups (organic acids)
CO, CH4, H2O groups organised around a ring or condensed ring structure

Witt et al. 2009
Structure of $\text{C}_{17}\text{H}_{17}\text{O}_9$ 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)
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

<table>
<thead>
<tr>
<th>DOM Polymers</th>
<th>Nanogels</th>
<th>Microgel</th>
</tr>
</thead>
<tbody>
<tr>
<td>~7 x 10^{17} g</td>
<td>50 nm</td>
<td>~7 x 10^{16} g</td>
</tr>
<tr>
<td>Å</td>
<td>nm</td>
<td>μm</td>
</tr>
</tbody>
</table>

Verdugo & Santschi 2010
Metal ions in microgels

Please note absence of Mg: The gels are quite selective
Microgels as an environment for life

Bacterial count in microgels by 3D confocal tomography

28 bacteria in this sample
$10^8-10^{10}$ bacteria/mL of microgel!
The reversible combination of DOC-molecules (deep sea)

\[
\text{DOM1} + \text{DOM2} + \text{DOM3} + \ldots \rightleftharpoons \text{POM}
\]

\[
[\text{DOM1}] \cdot [\text{DOM2}] \cdot [\text{DOM3}] \cdot \ldots = K [\text{POM}]
\]

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

Square brackets denote 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)
Examples of marine particles (ordered by decreasing size)
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