Trace elements

OCN 623 – Chemical Oceanography
New geochemical initiative

Survey oceans over next 10 years

Copies available at:
What causes distribution patterns seen in trace elements?

Observed distributions are a combination of the input pattern and the recycling and removal processes.
Patterns of enrichment deep vs surface, surface vs deep

Pacific vs Atlantic
Atlantic vs Pacific
Within basins
Across multiple basins
Definition of chemical categories:

Major ions Na, K, Mg, SO4, Cl (546-10 mM)
Minor species Sr, B, Br, F, CO2, (2mM- 68µM)
Trace elements everything else except nutrients, dissolved gases, radioactive species
concentration range <50µM-fM
EPA --- less than can be determined!
What about nutrients, trace gases etc?
Definitions are somewhat arbitrary
Trace metals -- often incorrectly defined, metalloids etc.
Concentrations vary from 100 nM (Ba) to < 100 fM Bi. Concentration ranges vary from very small to large.
Ken Johnson’s clickable element links

http://www.mbari.org/chemsensor/pteo.htm
Trace elements are dyes, whose colours are a function of speciation.

Can be used to trace chemical, biological and physical processes.

Act as recorders of paleo conditions -- need to understand contemporary distributions first.

Residence time determines processes they record.

A priori, expect distributions to reflect input function.
Principal sources of materials to the oceans
Annual river flow $3.3 \times 10^{16}$ l/yr
But distribution makes characterisation difficult
Dissolved load not related to flow

Total load $3.6 \times 10^{15}$ g yr$^{-1}$
Most large rivers in tropics, weathering limited
Terrain has large effect on magnitude of dissolved species
Hydrothermal fluxes

High temperature water-rock reactions lead to enrichments of some chemicals; some are removed, e.g., Mg, SO₄
Fluxes hard to calculate
Some inputs are large and very diagnostic of vent activity, e.g. Mn, Fe

Check out Elderfield and Schultz
Ann rev of Ear Sci, 1996 for a review of fluxes and calculation methods

Table 4-1: Comparison of Hydrothermal and River Fluxes

<table>
<thead>
<tr>
<th></th>
<th>21 H1</th>
<th>Guaymas</th>
<th>GSC2</th>
<th>River3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>1.2±1.9x10^{11}</td>
<td>8.6±15x10^{10}</td>
<td>9.5±16x10^{10}</td>
<td>1.4±10^{10}</td>
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<tr>
<td>Na</td>
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<td>-</td>
<td>4.2±5.5x10^{12}</td>
<td>6.9±10^{12}</td>
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<td>K</td>
<td>1.9±2.3x10^{12}</td>
<td>8.0±12x10^{9}</td>
<td>1.3±10^{12}</td>
<td>1.9±10^{12}</td>
</tr>
<tr>
<td>Rb</td>
<td>3.7±4.6x10^{9}</td>
<td>-</td>
<td>1.7±2.8x10^{9}</td>
<td>5x10^{6}</td>
</tr>
<tr>
<td>Be</td>
<td>1.4±5.3x10^{6}</td>
<td>1.7±13x10^{6}</td>
<td>1.6±5.3x10^{6}</td>
<td>3.3±10^{7}</td>
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<td>Mg</td>
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<td>-7.5±10^{12}</td>
<td>-7.7±10^{12}</td>
<td>5.3±10^{12}</td>
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<tr>
<td>Ca</td>
<td>2.4±15x10^{11}</td>
<td>2.4±4.5x10^{12}</td>
<td>2.1±4.3x10^{12}</td>
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<tr>
<td>Sr</td>
<td>-3.1±1.2x10^{9}</td>
<td>1.0±2.4x10^{10}</td>
<td>0</td>
<td>2.2±10^{10}</td>
</tr>
<tr>
<td>Ba</td>
<td>1.1±2.3x10^{9}</td>
<td>2.1±7.7x10^{9}</td>
<td>2.5±6.1x10^{9}</td>
<td>1.0±10^{10}</td>
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<tr>
<td>F</td>
<td>-1.0±10^{10}</td>
<td>n.a.</td>
<td>-31±47.8±10^{12}</td>
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<tr>
<td>Cl</td>
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<td>3.1±10^{12}</td>
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<tr>
<td>SiO2</td>
<td>2.2±2.8±10^{12}</td>
<td>1.3±2.0±10^{12}</td>
<td>3.1±10^{12}</td>
<td>6.4±10^{12}</td>
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<tr>
<td>Al</td>
<td>5.7±7.4±10^{8}</td>
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<td>NH4</td>
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<td>n.a.</td>
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<td>SO4</td>
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<tr>
<td>H2S</td>
<td>9.4±12±10^{12}</td>
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<td>n.a.</td>
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<tr>
<td>Fe</td>
<td>1.0±1.4±10^{11}</td>
<td>1.9±3.4±10^{10}</td>
<td>5.1±16±10^{10}</td>
<td>4.9±10^{9}</td>
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<tr>
<td>Cu</td>
<td>1.1±3.5±10^{11}</td>
<td>2.4±26±10^{9}</td>
<td>+</td>
<td>2.3±10^{10}</td>
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<tr>
<td>Zn</td>
<td>3.1±32±10^{8}</td>
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<td>n.a.</td>
<td>1.1±10^{8}</td>
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<tr>
<td>Ag</td>
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<tr>
<td>Cd</td>
<td>2.3±26±10^{6}</td>
<td>0±6.6±10^{6}</td>
<td>n.a.</td>
<td>8.6±10^{7}</td>
</tr>
<tr>
<td>Pb</td>
<td>2.6±5.1±10^{7}</td>
<td>0±8.9±10^{7}</td>
<td>n.a.</td>
<td>1.5±10^{8}</td>
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<tr>
<td>As</td>
<td>0±6.5±10^{7}</td>
<td>0±1.5±10^{8}</td>
<td>n.a.</td>
<td>7.2±10^{8}</td>
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<tr>
<td>Se</td>
<td>0±1.0±10^{7}</td>
<td>0±1.5±10^{7}</td>
<td>n.a.</td>
<td>7.9±10^{7}</td>
</tr>
</tbody>
</table>

1 All numbers are in moles/yr.
2 GSC data is from Edmond et al. (1979a,b).
3 River concentrations and fluxes are from either Edmond et al. (1979a,b) or Broecker and Peng (1982).
4 n.a. = not analyzed.
<table>
<thead>
<tr>
<th>Element/Vent</th>
<th>Conc moles/kg</th>
<th>Flux moles/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fe</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21N</td>
<td>750-2420 x 10^{-6}</td>
<td>1.7-5.6 x 10^{11}</td>
</tr>
<tr>
<td>13N</td>
<td>3980-10760 x 10^{-6}</td>
<td>9.2-24.7 x 10^{11}</td>
</tr>
<tr>
<td>11N</td>
<td>1640-6470 x 10^{-6}</td>
<td>3.8-14.9 x 10^{11}</td>
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<tr>
<td><strong>Zn</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21N</td>
<td>40-100 x 10^{-6}</td>
<td>9.2-23 x 10^{9}</td>
</tr>
<tr>
<td>13N</td>
<td>2-102 x 10^{-6}</td>
<td>.5-23 x 10^{9}</td>
</tr>
<tr>
<td>11N</td>
<td>44-105 x 10^{-6}</td>
<td>10.1-24. x 10^{9}</td>
</tr>
<tr>
<td><strong>Cd</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21N</td>
<td>17-180 x 10^{-9}</td>
<td>3.9-41 x 10^{6}</td>
</tr>
<tr>
<td>13N</td>
<td>55-70 x 10^{-9}</td>
<td>12.7-16.1 x 10^{6}</td>
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<tr>
<td>11N</td>
<td>&lt;1-43 x 10^{-9}</td>
<td>&lt;0.2-9.9 x 10^{6}</td>
</tr>
<tr>
<td><strong>Al</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21N</td>
<td>4-5.2 x 10^{-6}</td>
<td>0.9-1.1 x 10^{9}</td>
</tr>
<tr>
<td>13N</td>
<td>13.3-20 x 10^{-6}</td>
<td>3.1-4.6 x 10^{9}</td>
</tr>
<tr>
<td>11N</td>
<td>12.9-13.6 x 10^{-6}</td>
<td>2.9-3.1 x 10^{9}</td>
</tr>
</tbody>
</table>

From Campbell et al. JGR, 93, 4537-4549, 1988.
Can be used to find vents e.g. Mn at 13˚N
Methane also a non-conservative tracer
Iron in seawater at Loihi Seamount
Atmospheric fluxes

Are large, but not relative to rivers
Very important source of reactive metals to oceanic gyres

Approximate annual fluxes of material to the oceans

Atmospheric deposition to the surface ocean (particulate flux) ~850-900 x 10^{12} g yr^{-1}

Rivers:

Suspended load ~20 x 10^{15} g yr^{-1}
Dissolved load ~3.7 x 10^{15} g yr^{-1}

Atmospheric/Riverine ~4%
Satellite images show suspended dust clearly.
Deposition maps can be produced showing great variations.
Cannot sample without land, very difficult to get accurate estimates over the ocean.
Use Al distributions as base for model

Works quite well
Atmospheric deposition is important for Fe required for biological processes--phototransport systems, $\text{N}_2$ fixation

Approximate annual fluxes of dissolve Al and Fe to the surface oceans

<table>
<thead>
<tr>
<th></th>
<th>Al (moles yr$^{-1}$)</th>
<th>Fe (moles yr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Riverine load</td>
<td>$32 \times 10^9$</td>
<td>$360 \times 10^9$</td>
</tr>
<tr>
<td>Post estuarine mixing</td>
<td>$&lt;3 \times 10^9$</td>
<td>$&lt;20 \times 10^9$</td>
</tr>
<tr>
<td>Dust deposition*</td>
<td>$80 \times 10^9$</td>
<td>$204 \times 10^9$</td>
</tr>
</tbody>
</table>

* assumes crustal composition (8% Al, 4.2%Fe and 5% solubility)
Concentrations of Fe in upwelling values are too low to use accompanying nutrients. Chemical separation during remobilisation. HNLC regions are where upwelling/deep mixing occurs and eolian deposition is low.
Note low deposition in S. Pacific and equatorial regions
Atmospheric deposition provides external Fe supply
Partial dissolution of dust in surface seawater
Need to know pattern of dust deposition
Temporal variation of deposition very high
Al survey indicates some regions thought to have high dust loads do not -- are HNLC regions

New programs CLIVAR and GEOTRACES
CLIVAR is surveying the oceans for Al and Fe

Proposed program GEOTRACES to map other tracers
UH CLIVAR cruises 2003-2011
Global dust deposition patterns from CLIVAR Al data

gm mineral dust m⁻² yr⁻¹
Southern Ocean very limited deposition
Pb, a good example of an element dominated by eolian deposition.
Residence time
Rate at which the inventory is turning over
\[ T = \frac{A}{\delta A/\delta T} \]
Residence time is inventory, divided by the flux
Assumes ocean at steady state and well mixed
Inventory
Amount in whole ocean (= whole ocean residence time)
Flux
Input or removal rate
Vary from \(~100\) million yrs to \(<100\) yrs
Short residence time = reactive

Mixing time of ocean 1,000 years. Residence times less than this value not accurate
Long residence time tends to lead to high concentrations

Nutrients have residence times from 20-70 thousand years
Some trace elements have long residence times e.g. Re ~ 750,000 years
Can calculate likely river concs. if know residence time

E.g. Pt 230 fM in Pacific, 280 fM in Atlantic

From sediments estimate residence time = 1 million years

Ocean vol = $1.37 \times 10^{21}$ L x 230 fM

= 343 moles Pt in Ocean

River flow = $3.2 \times 10^{16}$ L/yr

Therefore river concentration ~ 10 fM

People who looked for Pt in river water had detection limits of 10-130 pM!
Removal processes

Removal rate determines residence time

Three kinds of processes:

- Inorganic precipitation e.g. Ba, Sr
- Hydrothermal vents e.g. Mg, U, S
- Scavenging: everything else
Scavenging

Active – uptake by organisms (plankton) deliberate e.g. PO$_4$ or adventitious e.g. Cd
sequestration of limiting nutrients e.g. Fe

Passive – interaction with surface functional groups e.g. hydroxyl or carboxyl group

Surface-$\text{OH} + \text{Me}^{z+} = \text{Surface-OMe}^{(z-1)} + \text{H}^+$
Speciation affects scavenging –OH bond forming elements e.g. Al, Fe, Th
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Anions do not form OH bonds e.g. Re, Se
Is a relationship between hydrolysable elements and sediment concentrations

![Graph showing the relationship between hydrolysable elements and sediment concentrations.](image)

Log X / C (ml/g)

Log τ* (years)

I (eV)
anions e.g. SeO$_4^{2-}$, ReO$_4^-$ not scavenged
– wrong charge to be adsorbed onto negatively charged surfaces

Redox speciation
Change in redox conditions has significant effects on chemical speciation
e.g. Mn$^{2+}$ soluble (reduced conditions) to insoluble Mn$^{4+}$ (oxidising conditions)
e.g. hydrothermal vent fluid
Anoxic basin, speciation change across redox boundary particulate to dissolved

Dissolved Fe higher in anoxic layer, but then sulphide forms

Mn “pump” also transfers other elements into deep water
Mn in the Arabian Sea
Cr VI soluble
Cr III scavenged
opposite
behaviour to Mn
Trace element profile shapes reflect involvement in scavenging/regeneration cycles. Can mimic nutrients e.g. Cd for PO$_4$

Sedimentary records can be used to reconstruct paleo-nutrient distributions.
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Fig. 8. Benthic Cd records from middepth cores in the Atlantic and Pacific oceans (CHN 82 Sta 24 Core 4PC and TR163-31B), showing the volumetrically compensating Atlantic increase (about a factor of 2) and Pacific decrease (about 12%).
Zn a proxy for Si
Ba mimics Si

Water masses different ratios

Ba in foraminafera
Paleo tracer for Si
Sedimentary diagenesis produces near bottom enrichments e.g. Cu
Cr undergoes 100 burial cycles before final removal
Input patterns

Regional variations in input can track global processes e.g. rivers, hydrothermal, dust

Physical circulation can be tracked, by tracer combinations
Historical changes in input can be tracked e.g. Pb in corals

Southern Preserve Bermuda Coral Pb/Ca

Pb/Ca, nmol/mol

Year A.D.
Generality of signal response can be observed with samples from different areas.
Observed coral Pb change

Reflects leaded gasoline production, not industrial Pb production
Applications of trace element distributions

Tracking chemical and biological processes in the ocean:
  Hydrothermal plume mapping, Mn, Fe, Al
  Paleo-circulation, Cd for P; Ba for Si, Ge for Si, V for reducing conditions
  Water mass tracing Al, tracking physical circulation features.

Input processes:
  Riverine
  Shelf sediment diagenesis: Mn,
  Eolian: Pb, Al monitoring dust input to the oceans

Biological processes: export production Th
  Fe remobilisation.
Summary

Trace element distributions reflect input, recycling and removal processes.

Large variety of species and oxidation states provides an opportunity to separate the chemical, physical and biological processes in the contemporary ocean.

Understanding the contemporary ocean will allow us to interpret trace species distributions in the sediments as historical changes in chemical, physical and biological cycles.
Sections of Pb(top) and Pb-isotope Ratios in the water column of the Eastern Atlantic Ocean in 1999. The spatial variability of subsurface Pb and Pb-isotope patterns reflects the advection and mixing of surface Waters into the deep sea. Water 500-900m deep to the south of this section sank from the surface decades previously and hence had higher Pb concentrations and a more radiogenic Pb-isotope ratio, consistent with surface-water Pb-isotope ratios at that time (Fig. 5). Deeper waters have less lead because they are dominated by waters that left the surface many decades ago. For example, at ~3000m at the southern end of the section, the Pb-isotope composition reflects lead that was the surface in the 1920s (see Fig. 5). Figure from Reuer (2002).
Is a relationship between hydrolysable elements and sediment concentrations