Patterns of enrichment deep vs surface, surface vs deep

Pacific vs Atlantic
Atlantic vs Pacific
Comparison of vertical distributions of Al in the oceans

What causes distribution patterns seen in trace elements?

Observed distributions are a combination of the input pattern and the recycling and removal processes.
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

Hydrothermal fluxes
High temperature water-rock reactions lead to enrichments of some chemicals some are removed, e.g. Mg, SO$_4$

Fluxes hard to calculate
Some inputs are large and very diagnostic of vent activity, e.g. Mn, Fe
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) \( \approx 850-900 \times 10^{12} \text{ g yr}^{-1} \)

Rivers:

Suspended load \( \approx 20 \times 10^{15} \text{ g yr}^{-1} \)
Dissolved load \( \approx 3.7 \times 10^{15} \text{ g yr}^{-1} \)
Atmospheric/Riverine \( \approx 4\% \)

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.
Atmospheric deposition is important for Fe
Fe required for biological processes--
phototransport systems, N₂ 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 x 10⁹</td>
<td>360 x 10⁹</td>
</tr>
<tr>
<td>Post estuarine mixing</td>
<td>&lt;3 x 10⁹</td>
<td>&lt;20 x 10⁹</td>
</tr>
<tr>
<td>Dust deposition*</td>
<td>80 x 10⁹</td>
<td>204 x 10⁹</td>
</tr>
</tbody>
</table>

* assumes crustal composition (8% Al, 4.2%Fe and 5% solubility)

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.

Anbar, 1992
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-OH + Me$^{2+}$ = Surface-OMe($^{z-1}$) + H$^+$
Speciation affects scavenging –OH bond
forming elements e.g. Al, Fe, Th
Speciation affects scavenging –OH bond forming elements e.g. Al, Fe, Th

Anions do not form OH bonds e.g. Re, Se

Is a relationship between hydrolysable elements and sediment concentrations
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
Trace element profile shapes reflect involvement in scavenging/regeneration cycles

Can mimic nutrients e.g. Cd for PO₄

Sedimentary records can be used to reconstruct paleo-nutrient distributions
Zn a proxy for Si

Ba mimics Si

Water masses different ratios

Ba in foraminefera
Paleo tracer for Si
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
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
New geochemical initiative

Survey oceans over a 10 year period

Copies available at: