Trace elements

OCN 623 – Chemical Oceanography

Ocean Data View

Sitemap Imprint

AWI

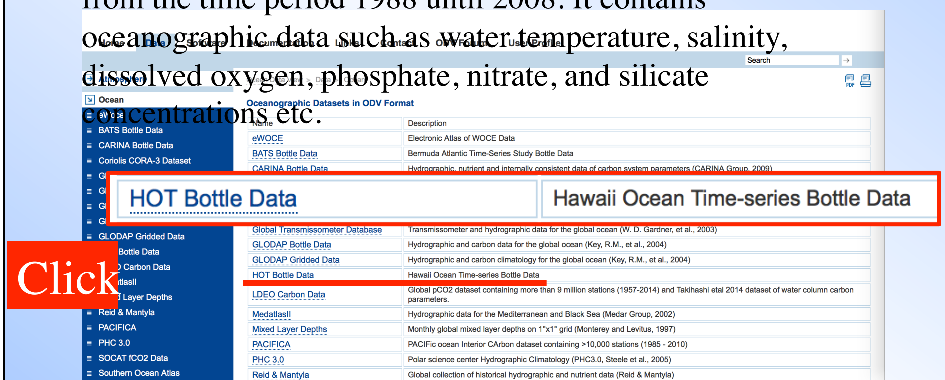
- Download "ODV" from http://odv.awi.de/en/software/download/ and install into your computer (also "Optional Packages"). And bring your computer. You will learn how to use this during the ODV class.

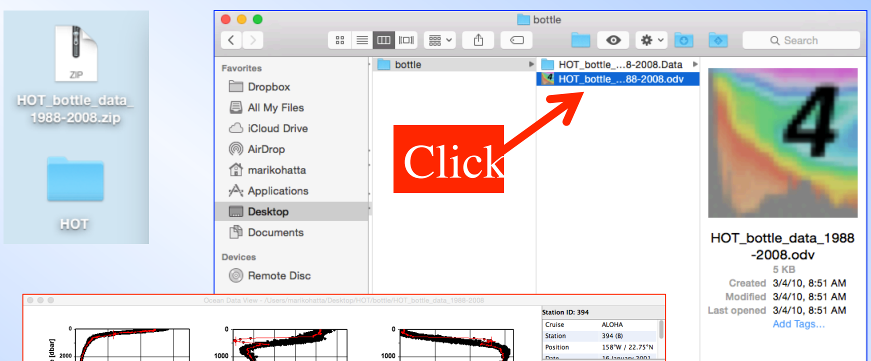
- Download the HOT Bottle Data from http://odv.awi.de/en/data/ocean/

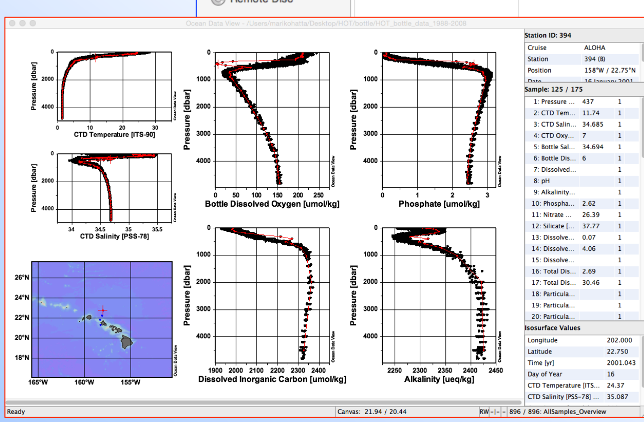
- Download two text files that include data, which you will use to make your own data file during the ODV class.

Downloading data and how to open it!

We will use the "HOT Bottle Data" during next class. Briefly, this data set is an oceanographic data product that was produced by the Hawaii Ocean Time-series (HOT) program from the time period 1988 until 2008. It contains oceanographic data such as water temperature, salinity, dissolved oxygen, phosphate, nitrate, and silicate concentrations etc.







Double chick the odv file (HOT_bottle…..odv) to make sure that you can open the HOT file with ODV software before the class

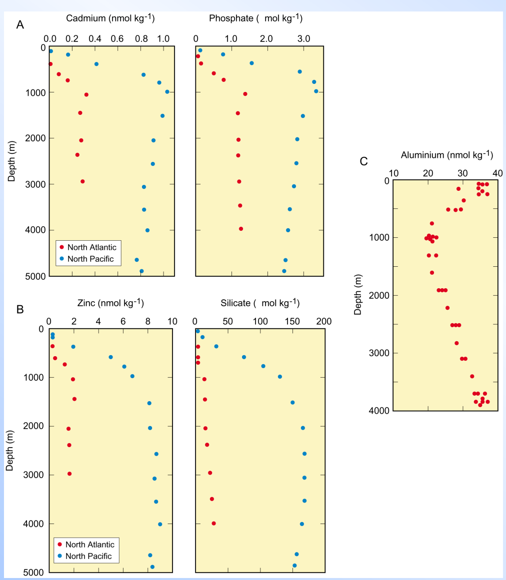
Reading materials

Schlitzer R. (2002) Interactive analysis and visualization of geoscience data with Ocean Data View, Computers & Geosciences 28, 1211–1218.

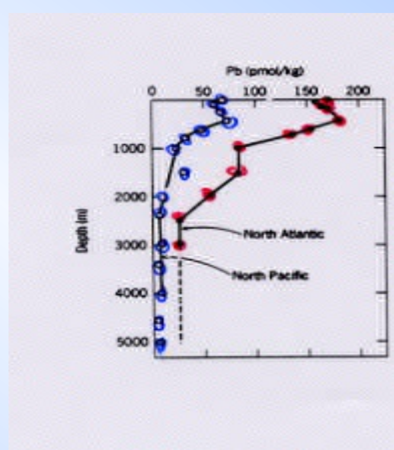
The GEOTRACES Group (2015) The GETORACES Intermediate Data Product 2014, Marine Chemistry 177, 1-8.
http://dx.doi.org/10.1016/j.marchem.2015.04.005

ODV 4 Documentation: https://odv.awi.de/en/documentation/
-Getting Started
-User’s Guide

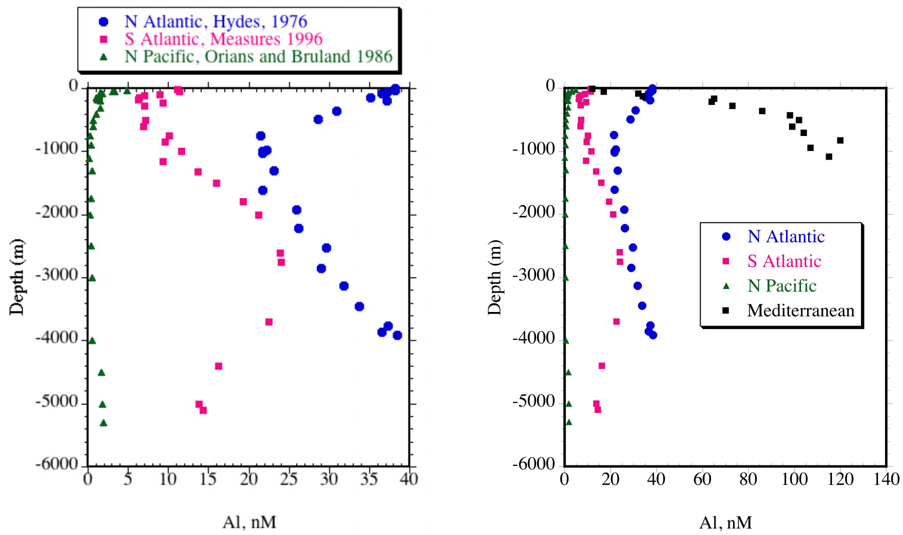
Patterns of enrichment deep vs surface, surface vs deep



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

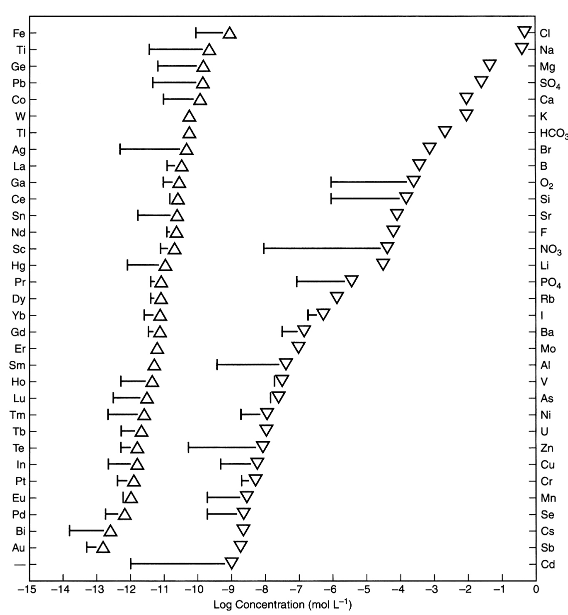
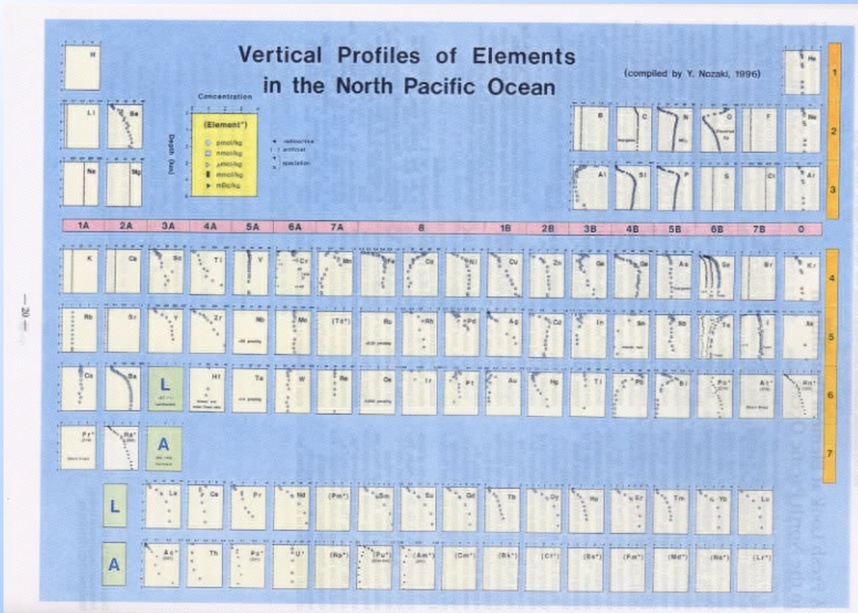


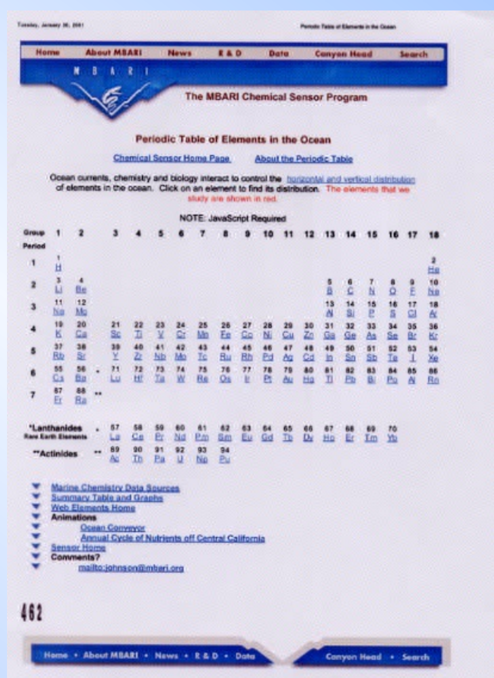
FIGURE 1.1.1: A graphical illustration of the dissolved concentrations of elements and some compounds expressed as log to the base 10 [*Johnson and Jannasch*, 1994]. The higher concentration elements are given on the right-hand side and the lower concentration elements are given on the left-hand side. The bars represent the range of concentrations in the ocean. The full range of concentrations covers almost 12 orders of magnitude.



Ken Johnson's
clickable element
links

http://www.mbari.org/

chemsensor/pteo.htm



Trace elements are dyes, whose colours are a function of speciation

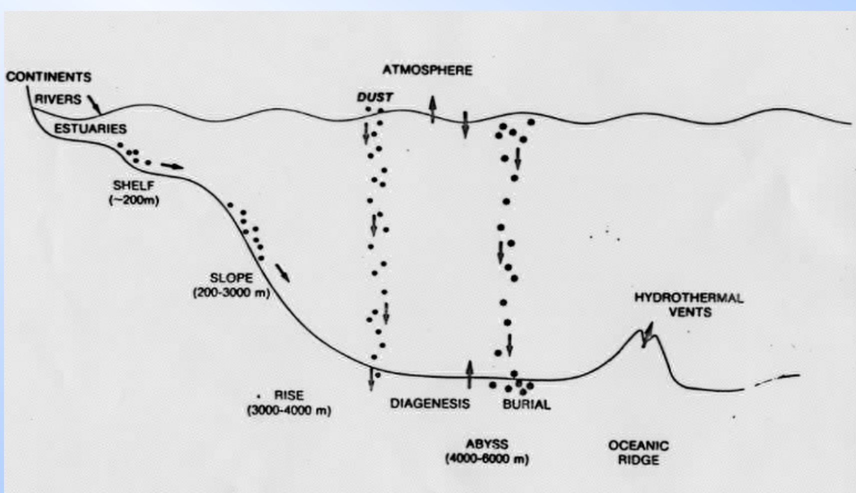
Can be used to trace chemical, biological and physical processes

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

Residence time determines processes they record

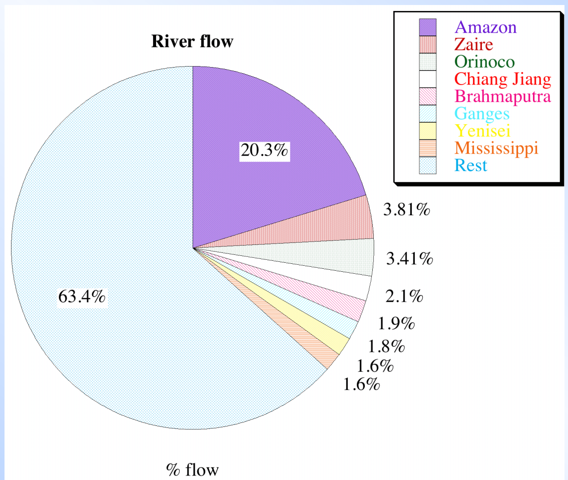
A priori, expect distributions to reflect input function

Principal sources of materials to the oceans



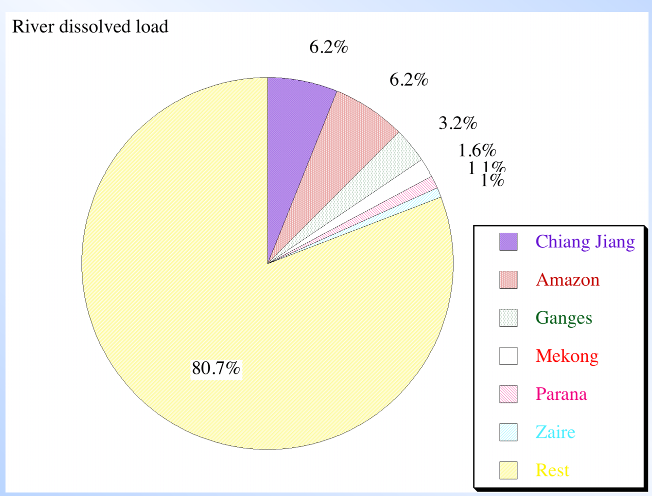
Annual river flow 3.3×10^{16} l/yr

But distribution makes characterisation difficult



Dissolved load not related to flow

Total load 3.6×10^{15} g yr^{-1}



Most large rivers in tropics, weathering limited

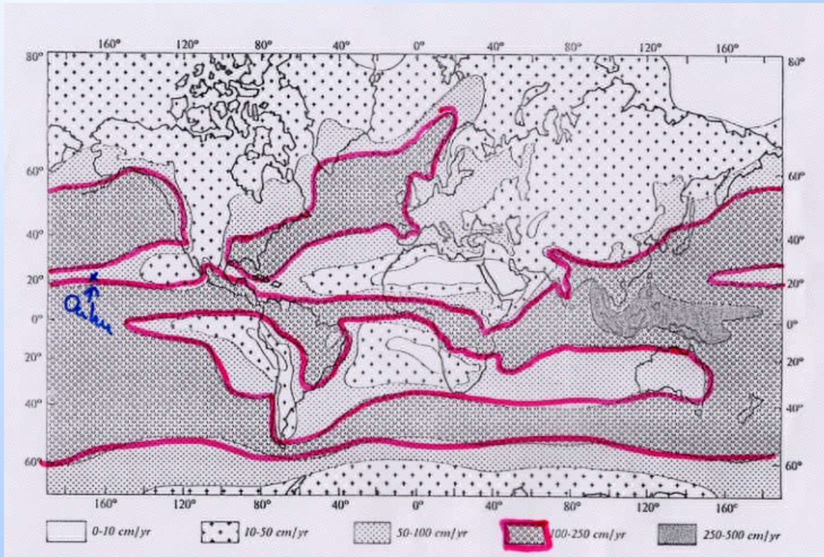
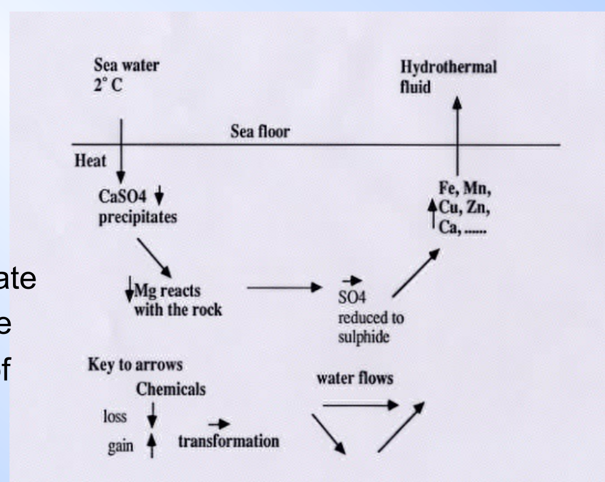


Figure 8-3. Global Rates of Wet Deposition (cm) (Lamb 1972).

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



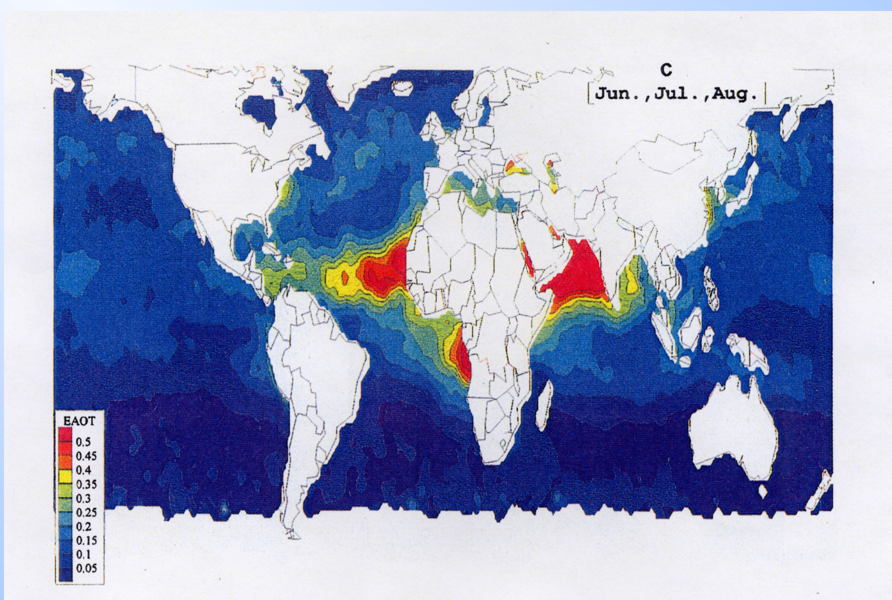
Atmospheric fluxes

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

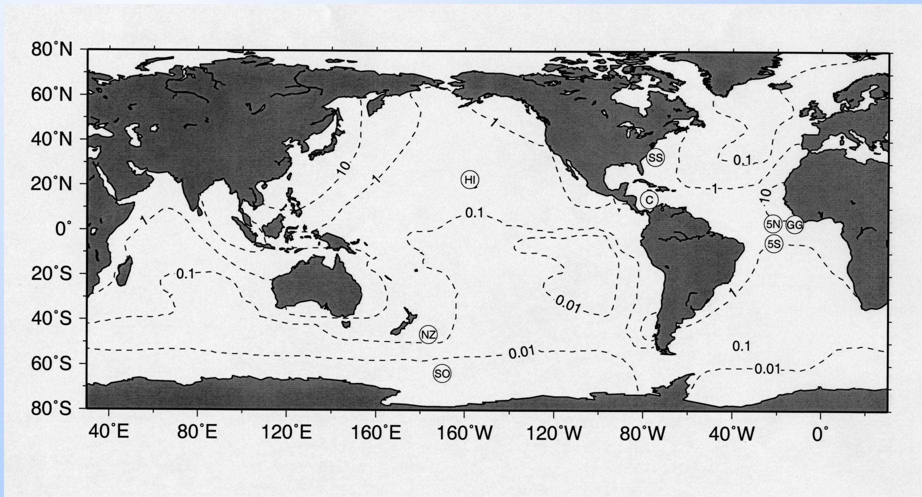
Approximate annual fluxes of material to the oceans

Atmospheric deposition to the surface ocean (particulate flux)	~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%

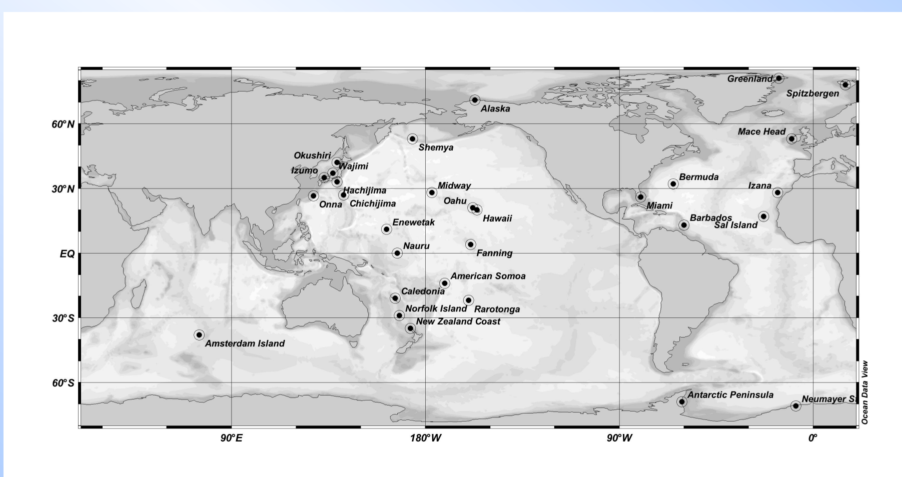
Satellite images show suspended dust clearly



Deposition maps can be produced showing great variations



Cannot sample without land, very difficult to get accurate estimates over the ocean



Atmospheric deposition is important for Fe
Fe required for biological processes--
phototransport systems, N_2 fixation

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

	Al (moles yr^{-1})	Fe (moles yr^{-1})
Riverine load	32×10^9	360×10^9
Post estuarine mixing	$<3 \times 10^9$	$<20 \times 10^9$
Dust deposition*	80×10^9	204×10^9

* 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

Table 1-6. Element concentrations in average river water and in average ocean water. Also given are the corresponding mean oceanic residence times.

Atomic No.	Element	Conc. Mean River[1] (10^{-6} moles/kg)	Conc. Mean Sea[2] (10^{-6} moles/kg)	τ[3] (yrs)
1	H (as H_2O)	-	5.4×10^{7}	-
2	He	-	1.8×10^{-3}	-
3	Li	1.7	2.5×10^{1}	5.7×10^{5}
4	Be	-	(6.5×10^{-5})	-
5	B	1.7	4.2×10^{2}	9.6×10^{6}
6	C (inorganic)	-	2.3×10^{3}	-
	(organic)	-	4	-
7	N (dissolved N_2)	-	5.8×10^{2}	-
	(NO_3)	-	3.0×10^{1}	-
8	O (as H_2O)	-	5.4×10^{7}	-
	(dissolved O_2)	-	2.2×10^{2}	-
9	F	*5.3	6.8×10^{1}	5.0×10^{5}
10	Ne		7.5×10^{-3}	
11	Na	2.2×10^{2}	4.7×10^{5}	8.3×10^{7}
12	Mg	1.6×10^{2}	5.3×10^{4}	1.3×10^{7}
13	Al	1.9	(3×10^{-2})	6.2×10^{2}
14	Si	1.9×10^{2}	1.0×10^{2}	2.0×10^{4}
15	P	1.3	2.3	6.9×10^{4}
16	S	-	2.8×10^{4}	-
17	Cl	-	5.5×10^{5}	-
18	Ar	-	1.5×10^{1}	-
19	K	3.4×10^{1}	10.2×10^{3}	1.2×10^{7}
20	Ca	3.6×10^{2}	10.3×10^{3}	1.1×10^{6}
21	Sc	8.9×10^{-5}	(1.5×10^{-5})	
22	Ti	2.1×10^{-1}	$(<2.0 \times 10^{-2})$	3.7×10^{3}
23	V	2.0×10^{-2}	2.3×10^{-2}	4.5×10^{4}
24	Cr	1.9×10^{-2}	4×10^{-3}	8.2×10^{3}
25	Mn	1.5×10^{-1}	5×10^{-3}	1.3×10^{3}
26	Fe	7.2×10^{-1}	(1×10^{-3})	5.4×10^{1}
27	Co	3.4×10^{-3}	(3×10^{-5})	3.4×10^{2}
28	Ni	3.8×10^{-2}	8×10^{-3}	8.2×10^{3}
29	Cu	1.6×10^{-1}	4×10^{-3}	9.7×10^{2}
30	Zn	4.6×10^{-1}	6×10^{-3}	5.1×10^{2}
31	Ga	1.3×10^{-3}	(3×10^{-4})	9.0×10^{3}
32	Ge	-	7×10^{-5}	-
33	As	2.3×10^{-2}	2.3×10^{-2}	3.9×10^{4}
34	Se	$*2.5 \times 10^{-3}$	1.7×10^{-3}	2.6×10^{4}
35	Br	2.5×10^{-1}	8.4×10^{2}	1.3×10^{8}
36	Kr	-	3.4×10^{-3}	-
37	Rb	1.8×10^{-2}	1.4	3.0×10^{6}
38	Sr	6.9×10^{-1}	8.7×10^{1}	5.1×10^{6}
39	Y	$*7.9 \times 10^{-3}$	(1.5×10^{-4})	7.4×10^{2}
40	Zr	-	(3×10^{-4})	-
41	Nb	-	$(<5 \times 10^{-5})$	-
42	Mo	5.2×10^{-3}	1.1×10^{-1}	8.[illegible] $\times 10^{5}$

Short residence
time = reactive

Mixing time of
ocean 1,000 years.
Residence times
less than this value
not accurate

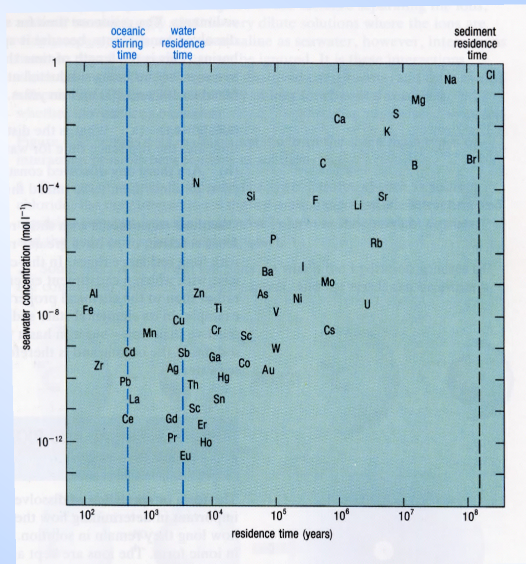
Table 1-6. (continued)

Atomic No.	Element	Conc. Mean River[1] (10^{-6} moles/kg)	Conc. Mean Sea[2] (10^{-6} moles/kg)	τ[3] (yrs)
43	Tc	-	-	-
44	Ru	-	-	-
45	Rh	-	-	-
46	Pd	-	-	-
47	Ag	2.8×10^{-3}	(2.5×10^{-5})	3.5×10^{2}
48	Cd	-	7×10^{-4}	-
49	In	-	(1×10^{-6})	-
50	Sn	-	(4×10^{-6})	-
51	Sb	8.2×10^{-3}	1.2×10^{-3}	5.7×10^{3}
52	Te	-	-	-
53	I	$*5 \times 10^{-2}$	4.4×10^{-1}	3.4×10^{5}
54	Xe	-	5.0×10^{-4}	-
55	Cs	2.6×10^{-4}	2.2×10^{-3}	3.3×10^{5}
56	Ba	4.4×10^{-1}	1.0×10^{-1}	8.8×10^{3}
57	La	3.6×10^{-4}	3×10^{-5}	3.2×10^{3}
58	Ce	5.7×10^{-4}	2×10^{-5}	1.4×10^{3}
59	Pr	5.0×10^{-5}	4×10^{-6}	3.1×10^{3}
60	Nd	2.8×10^{-4}	2×10^{-5}	2.8×10^{3}
61	Pm	-	-	-
62	Sm	5.3×10^{-5}	4×10^{-6}	2.9×10^{3}
63	Eu	6.6×10^{-6}	9×10^{-7}	5.3×10^{3}
64	Gd	5.1×10^{-5}	6×10^{-6}	4.6×10^{3}
65	Tb	6.3×10^{-6}	9×10^{-7}	5.6×10^{3}
66	Dy	$*3.0 \times 10^{-4}$	6×10^{-6}	7.8×10^{2}
67	Ho	6.1×10^{-6}	2×10^{-6}	1.3×10^{4}
68	Er	2.4×10^{-5}	5×10^{-6}	8.1×10^{3}
69	Tm	5.9×10^{-6}	8×10^{-7}	5.3×10^{3}
70	Yb	2.3×10^{-5}	5×10^{-6}	8.5×10^{3}
71	Lu	5.7×10^{-6}	9×10^{-7}	6.2×10^{3}
72	Hf	-	$(<4 \times 10^{-5})$	-
73	Ta	-	$(<1.4 \times 10^{-5})$	-
74	W	$*1.6 \times 10^{-4}$	6×10^{-4}	-
75	Re	2.3×10^{-6}	(2×10^{-5})	7.5×10^{5}
76	Os	-	-	-
77	Ir	-	-	-
78	Pt	250×10^{-9}	250×10^{-9}	1×10^{6}
79	Au	1.0×10^{-5}	(2.5×10^{-5})	9.7×10^{4}
80	Hg	$*3.5 \times 10^{-4}$	(5×10^{-6})	5.6×10^{2}
81	Tl	-	6×10^{-5}	-
82	Pb	4.8×10^{-3}	1×10^{-5}	8.1×10^{1}
83	Bi	-	(1×10^{-4})	-
90	Th		$(<3 \times 10^{-6})$	
92	U	$\sim 1 \times 10^{-3}$	1.3×10^{-2}	$\sim 5 \times 10^{5}$

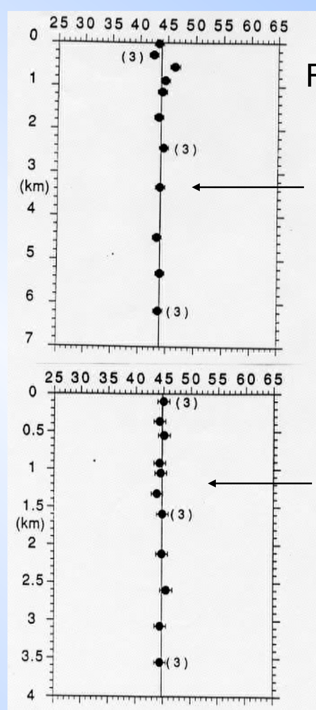
[1]Main source: A summary by Martin and Meybeck (631) with values for F, Se, Y, I Dy, W, and Mg, values with * are taken from Turekian (628).
[2]Main source: A summary by Bruland (456). The values in parenthesis are highly uncertain.
[3]The residence time is obtained by dividing the total amount of the element dissolved in the sea by the amount delivered by rivers each year.

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^{z+} = 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

TABLE 45.1

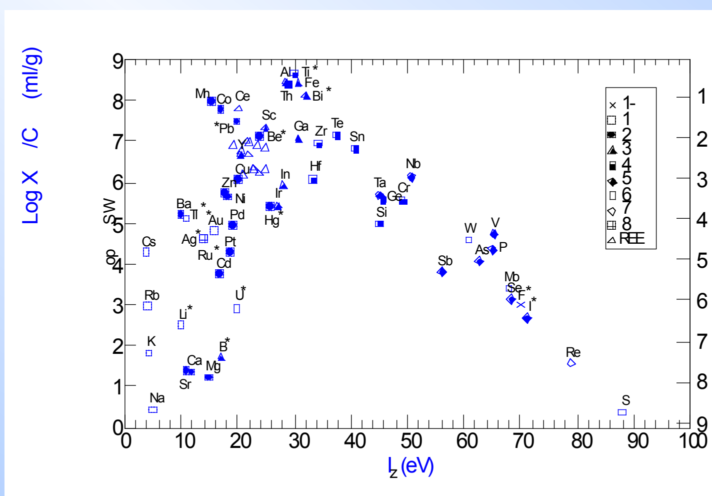
Speciations, concentrations and distribution types c

Element	Probable main species in oxygenated sea-water	Range and average conce at 35‰ salinity†
Li	Li^+	25 μmol kg^{-1}
Be	$BeOH^+$, $Be(OH)_2^0$	4–30 pmol kg^{-1}; 20 pmol k
B	H_3BO_3	0.416 mmol kg^{-1}
C	HCO_3^-, CO_3^{2-}	2.0–2.5 mmol kg^{-1}; 2.3 mm
N	NO_3^- (also as N_2)	<0.1–45 μmol kg^{-1}; 30 μm
O	O_2 (also as H_2O)	0–300 μmol kg^{-1}
F	F^-, MgF^+	68 μmol kg^{-1}
Na	Na^+	0.468 mol kg^{-1}
Mg	Mg^{2+}	53.2 mmol kg^{-1}
Al	$Al(OH)_4^-$, $Al(OH)_3^0$	(5–40 nmol kg^{-1}; 20 nmol k
Si	H_4SiO_4	<1–180 μmol kg^{-1}; 100 μm
P	HPO_4^{2-}, $NaHPO_4^-$, $MgHPO_4^0$	<1–3.5 μmol kg^{-1}; 2.3 μmo
S	SO_4^{2-}, $NaSO_4^-$ · $MgSO_4^0$	28.2 mmol kg^{-1}
Cl	Cl^-	0.546 mol kg^{-1}
K	K^+	10.2 mmol kg^{-1}
Ca	Ca^{2+}	10.3 mmol kg^{-1}
Sc	$Sc(OH)_3^0$	8–20 pmol kg^{-1}; 15 pmol k
Ti	$Ti(OH)_4^0$	(<20 nmol kg^{-1})
V	HVO_4^{2-}, $H_2VO_4^-$, $NaHVO_4^-$	20–35 nmol kg^{-1}; 30 nmol
Cr	CrO_4^{2-}, $NaCrO_4^-$	2–5 nmol kg^{-1}; 4 nmol kg
Mn	Mn^{2+}, $MnCl^+$	0.2–3 nmol kg^{-1}; 0.5 nmol
Fe	$Fe(OH)_3^0$	0.1–2.5 nmol kg^{-1}; 1 nmol
Co	Co^{2+}, $CoCO_3^0$, $CoCl^+$	(0.01–0.1 nmol kg^{-1}; 0.02 n
Ni	Ni^{2+}, $NiCO_3^0$, $NiCl^+$	2–12 nmol kg^{-1}; 8 nmol kg
Cu	$CuCO_3^0$, $CuOH^+$, Cu^{2+}	0.5–6 nmol kg^{-1}; 4 nmol kg

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

Re	ReO_4^-	(14–30 pmol kg^{-1}; 20 pmo
Se	SeO_4^{2-}, SeO_3^{2-}, $HSeO_3^-$	0.5–2.3 nmol kg^{-1}; 1.7 nmol kg^{-1}

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

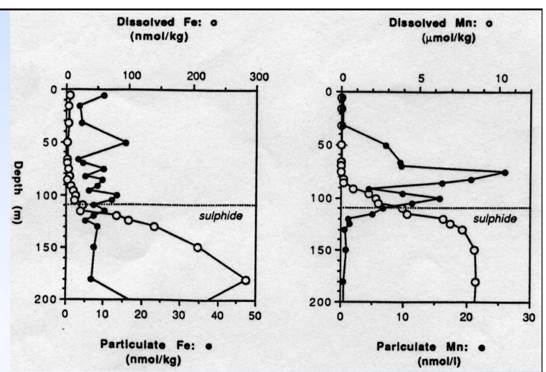
Redox speciation

Change in redox conditions has significant effects on chemical speciation

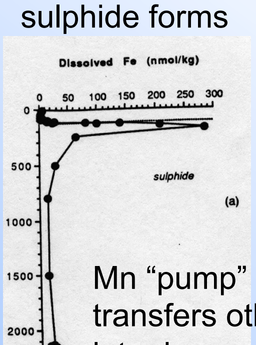
e.g. Mn^{2+} soluble (reduced conditions) to insoluble Mn^{4+} (oxidising conditions)

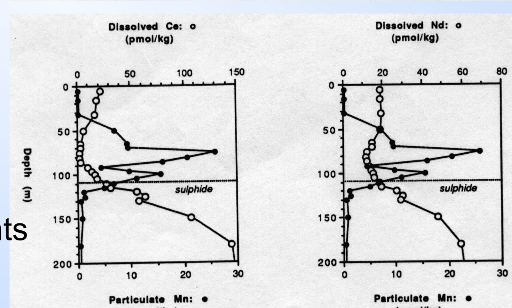
e.g. hydrothermal vent fluid

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

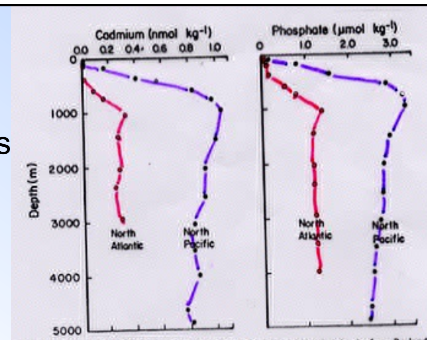
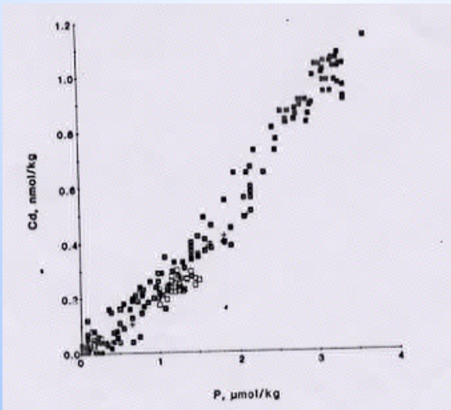


Fig. 45.7. Vertical profiles of cadmium in the North Pacific and North Atlantic, from Bruland (1980) and Bruland and Franks (1983). Profiles of phosphate are also shown for comparison.



Can mimic nutrients e.g. Cd for PO_4

Sedimentary records can be used to reconstruct paleo-nutrient distributions

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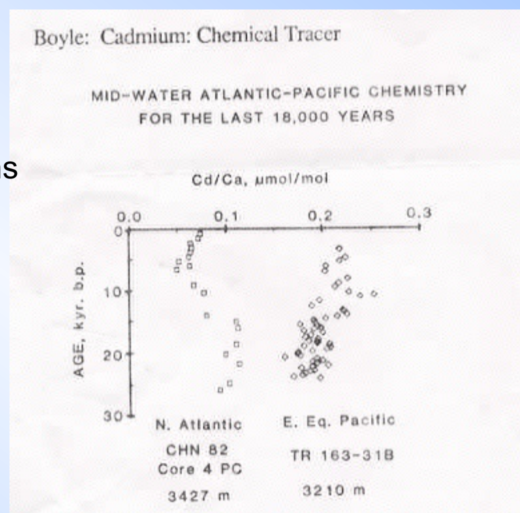
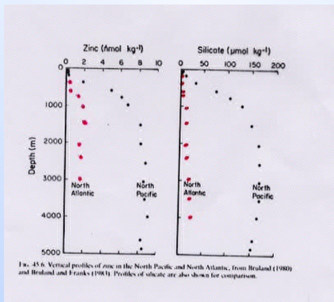
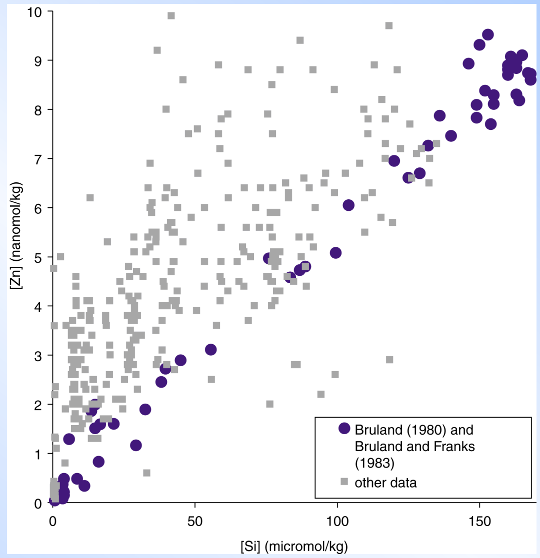
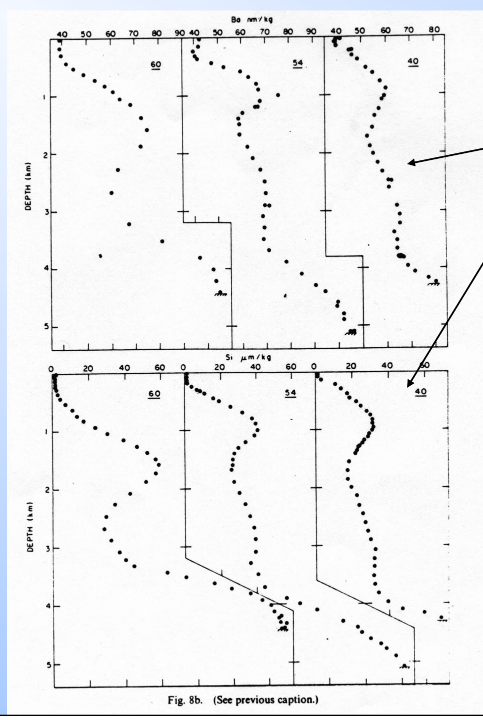


Fig. 8. Benthic Cd records from middepth cores in the Atlantic and Pacific oceans (CHN 82 Sta 24 Core 4PC and TR163-31B), showing the volumetrically compensating Atlantic increase (about a factor of 2) and Pacific decrease (about 12%).

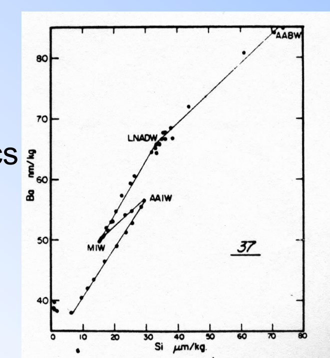
Zn a proxy for Si







Ba mimics Si



Water masses different ratios

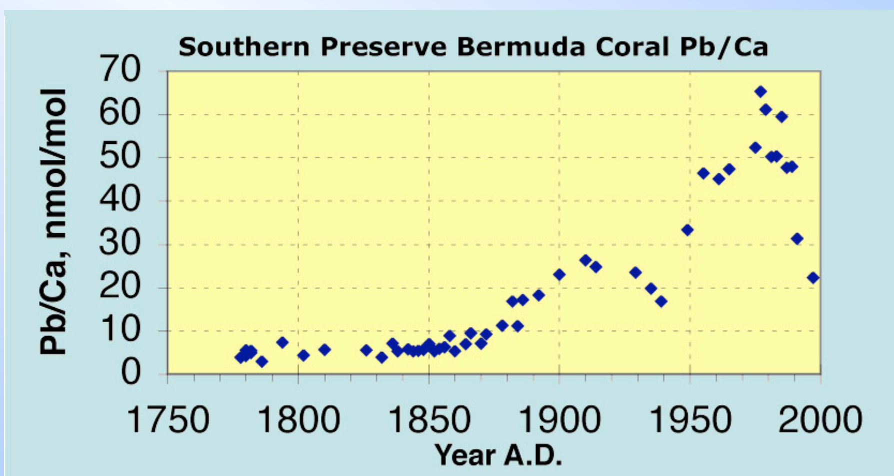
Ba in foraminefera
Paleo tracer for Si

Input patterns

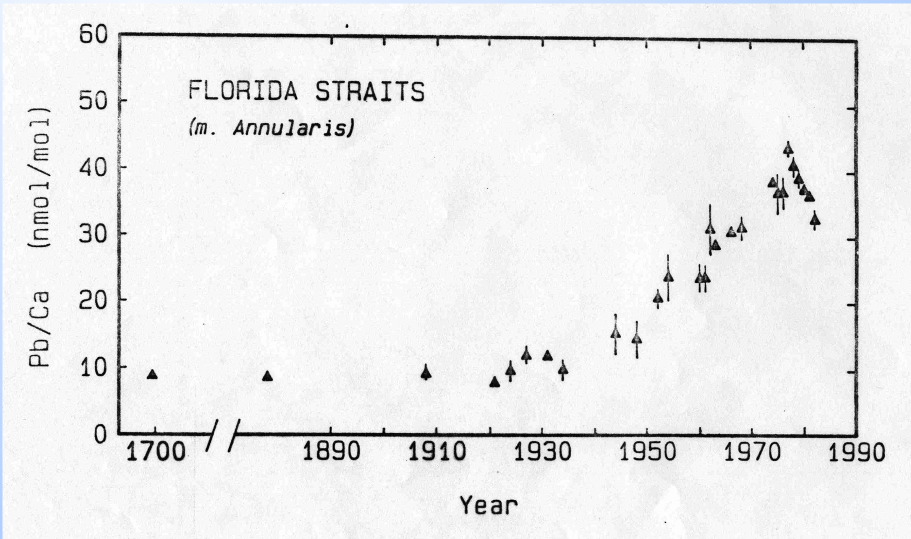
Regional variations in input can track global processes e.g. rivers, hydrothermal,dust

Physical circulation can be tracked, by tracer combinations

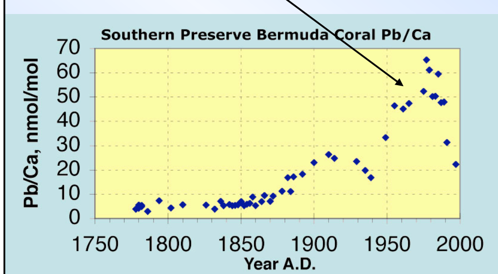
Historical changes in input can be tracked e.g. Pb in corals



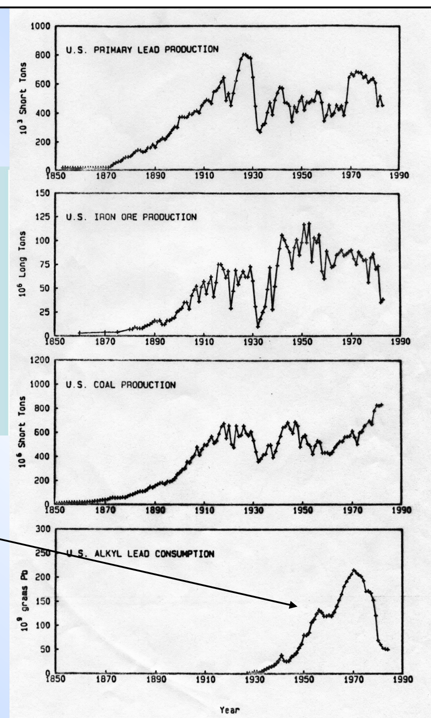
Generality of signal response can be observed with samples from different areas



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