Chemical Oceanography
Metal Geochemistry

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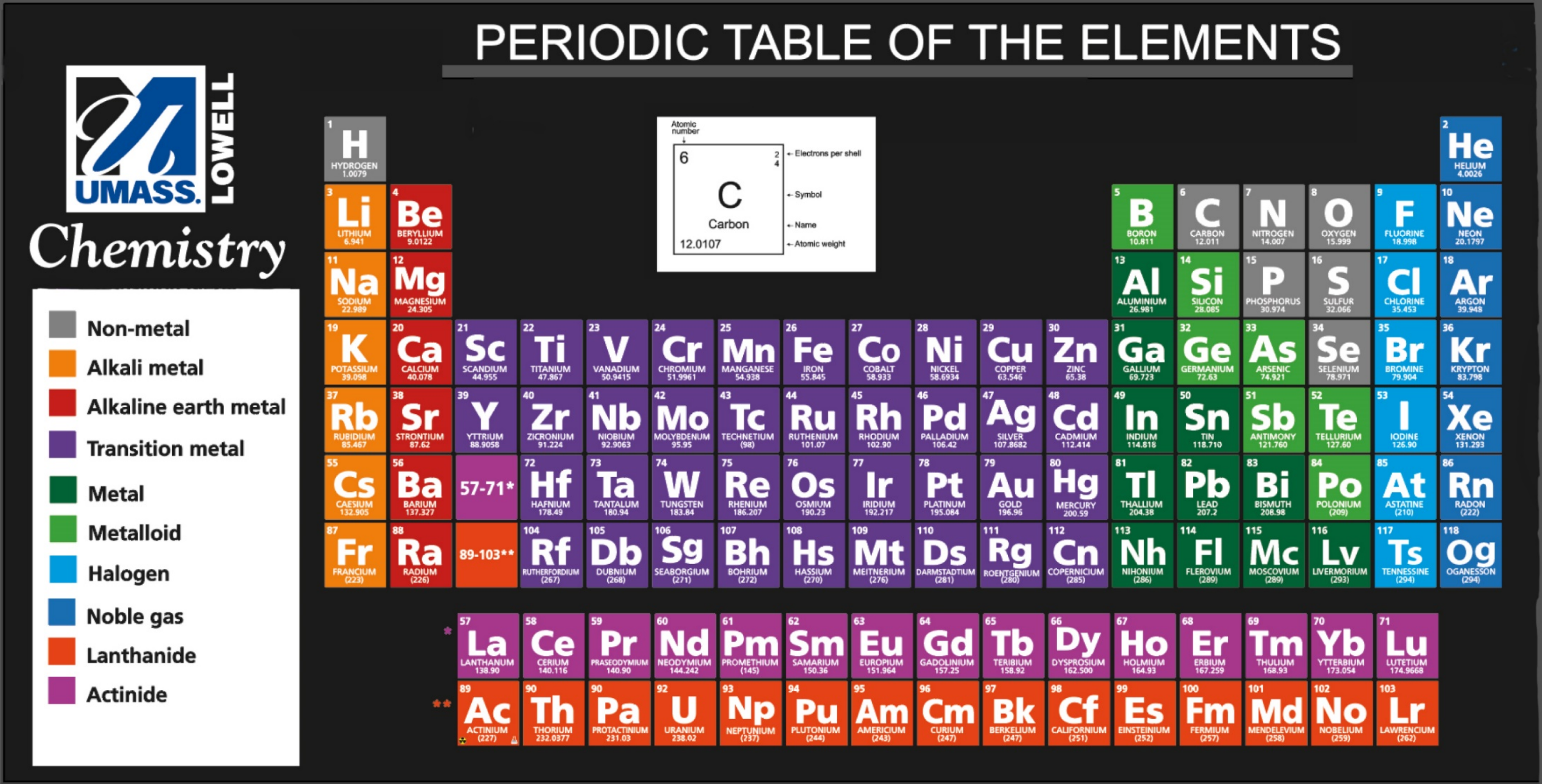
Metal Geochemistry

- Read Emerson & Hedges Chapter 12
- Read paper Donat & Bruland (1995)
- Read paper by Nieboer & Richardson (1980)

(Papers are posted on website for today's class)



PERIODIC TABLE OF THE ELEMENTS
UMASS. LOWELL
Chemistry
Non-metal
Alkali metal
Alkaline earth metal
Transition metal
Metal
Metalloid
Halogen
Noble gas
Lanthanide
Actinide
Atomic number
6
C
Carbon
12.0107
2
4
Electrons per shell
Symbol
Name
Atomic weight
1 H HYDROGEN 1.0079
2 He HELIUM 4.0026
3 Li LITHIUM 6.941
4 Be BERYLLIUM 9.0122
5 B BORON 10.811
6 C CARBON 12.011
7 N NITROGEN 14.007
8 O OXYGEN 15.999
9 F FLUORINE 18.998
10 Ne NEON 20.1797
11 Na SODIUM 22.989
12 Mg MAGNESIUM 24.305
13 Al ALUMINIUM 26.981
14 Si SILICON 28.085
15 P PHOSPHORUS 30.974
16 S SULFUR 32.066
17 Cl CHLORINE 35.453
18 Ar ARGON 39.948
19 K POTASSIUM 39.098
20 Ca CALCIUM 40.078
21 Sc SCANDIUM 44.955
22 Ti TITANIUM 47.867
23 V VANADIUM 50.9415
24 Cr CHROMIUM 51.9961
25 Mn MANGANESE 54.938
26 Fe IRON 55.845
27 Co COBALT 58.933
28 Ni NICKEL 58.6934
29 Cu COPPER 63.546
30 Zn ZINC 65.38
31 Ga GALLIUM 69.723
32 Ge GERMANIUM 72.63
33 As ARSENIC 74.921
34 Se SELENIUM 78.971
35 Br BROMINE 79.904
36 Kr KRYPTON 83.798
37 Rb RUBIDIUM 85.467
38 Sr STRONTIUM 87.62
39 Y YTTRIUM 88.9058
40 Zr ZICRONIUM 91.224
41 Nb NIOBIUM 92.9063
42 Mo MOLYBDENUM 95.95
43 Tc TECHNETIUM (98)
44 Ru RUTHENIUM 101.07
45 Rh RHODIUM 102.90
46 Pd PALLADIUM 106.42
47 Ag SILVER 107.8682
48 Cd CADMIUM 112.414
49 In INDIUM 114.818
50 Sn TIN 118.710
51 Sb ANTIMONY 121.760
52 Te TELLURIUM 127.60
53 I IODINE 126.90
54 Xe XENON 131.293
55 Cs CAESIUM 132.905
56 Ba BARIUM 137.327
57-71*
72 Hf HAFNIUM 178.49
73 Ta TANTALUM 180.94
74 W TUNGSTEN 183.84
75 Re RHENIUM 186.207
76 Os OSMIUM 190.23
77 Ir IRIDIUM 192.217
78 Pt PLATINUM 195.084
79 Au GOLD 196.96
80 Hg MERCURY 200.59
81 Tl THALLIUM 204.38
82 Pb LEAD 207.2
83 Bi BISMUTH 208.98
84 Po POLONIUM (209)
85 At ASTATINE (210)
86 Rn RADON (222)
87 Fr FRANCIUM (223)
88 Ra RADIUM (226)
89-103**
104 Rf RUTHERFORDIUM (267)
105 Db DUBNIUM (268)
106 Sg SEABORGIUM (271)
107 Bh BOHRIUM (272)
108 Hs HASSIUM (270)
109 Mt MEITNERIUM (276)
110 Ds DARMSTADTIUM (281)
111 Rg ROENTGENIUM (280)
112 Cn COPERNICIUM (285)
113 Nh NIHONIUM (286)
114 Fl FLEROVIUM (289)
115 Mc MOSCOVIUM (289)
116 Lv LIVERMORIUM (293)
117 Ts TENNESSINE (294)
118 Og OGANESSON (294)
*
57 La LANTHANUM 138.90
58 Ce CERIUM 140.116
59 Pr PRASEODYMIUM 140.90
60 Nd NEODYMIUM 144.242
61 Pm PROMETHIUM (145)
62 Sm SAMARIUM 150.36
63 Eu EUROPIUM 151.964
64 Gd GADOLINIUM 157.25
65 Tb TERBIUM 158.92
66 Dy DYSPROSIUM 162.500
67 Ho HOLMIUM 164.93
68 Er ERBIUM 167.259
69 Tm THULIUM 168.93
70 Yb YTTERBIUM 173.054
71 Lu LUTETIUM 174.9668
**
89 Ac ACTINIUM (227)
90 Th THORIUM 232.0377
91 Pa PROTACTINIUM 231.03
92 U URANIUM 238.02
93 Np NEPTUNIUM (237)
94 Pu PLUTONIUM (244)
95 Am AMERICIUM (243)
96 Cm CURIUM (247)
97 Bk BERKELIUM (247)
98 Cf CALIFORNIUM (251)
99 Es EINSTEINIUM (252)
100 Fm FERMIUM (257)
101 Md MENDELEVIUM (258)
102 No NOBELIUM (259)
103 Lr LAWRENCIUM (262)

Concerned with Metal Ions (Geochemistry)

- Typically cations (Cu^{2+}, Cd^{2+})
- Some anions (CrO_4^{2-}, MoO_4^{2-}, AsO_4^{3-})
- General properties of interest
  - Reactivity
    - Redox – oxidation/reduction reactions
    - Complexation or Sorption
    - Speciation – forms
  - Cycling – ultimate fate
  - Transport – mobility
  - Toxicity/Bioavailability/Bioaccumulation

Biogeochemical Processes

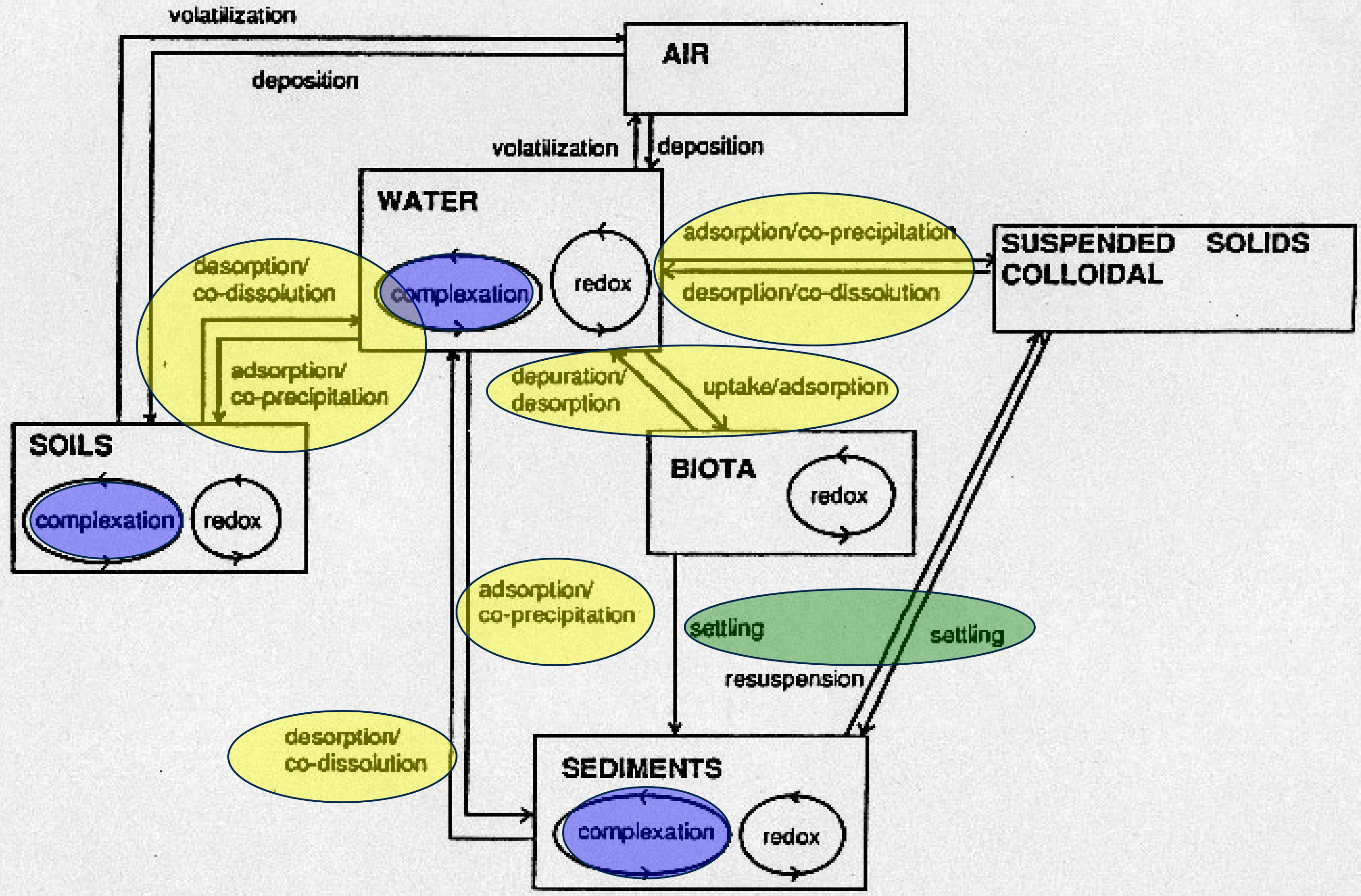


Figure 3.1. Schematic diagram of processes controlling the biogeochemical cycling of metals in aquatic environments.

Classification Schemes for Metals

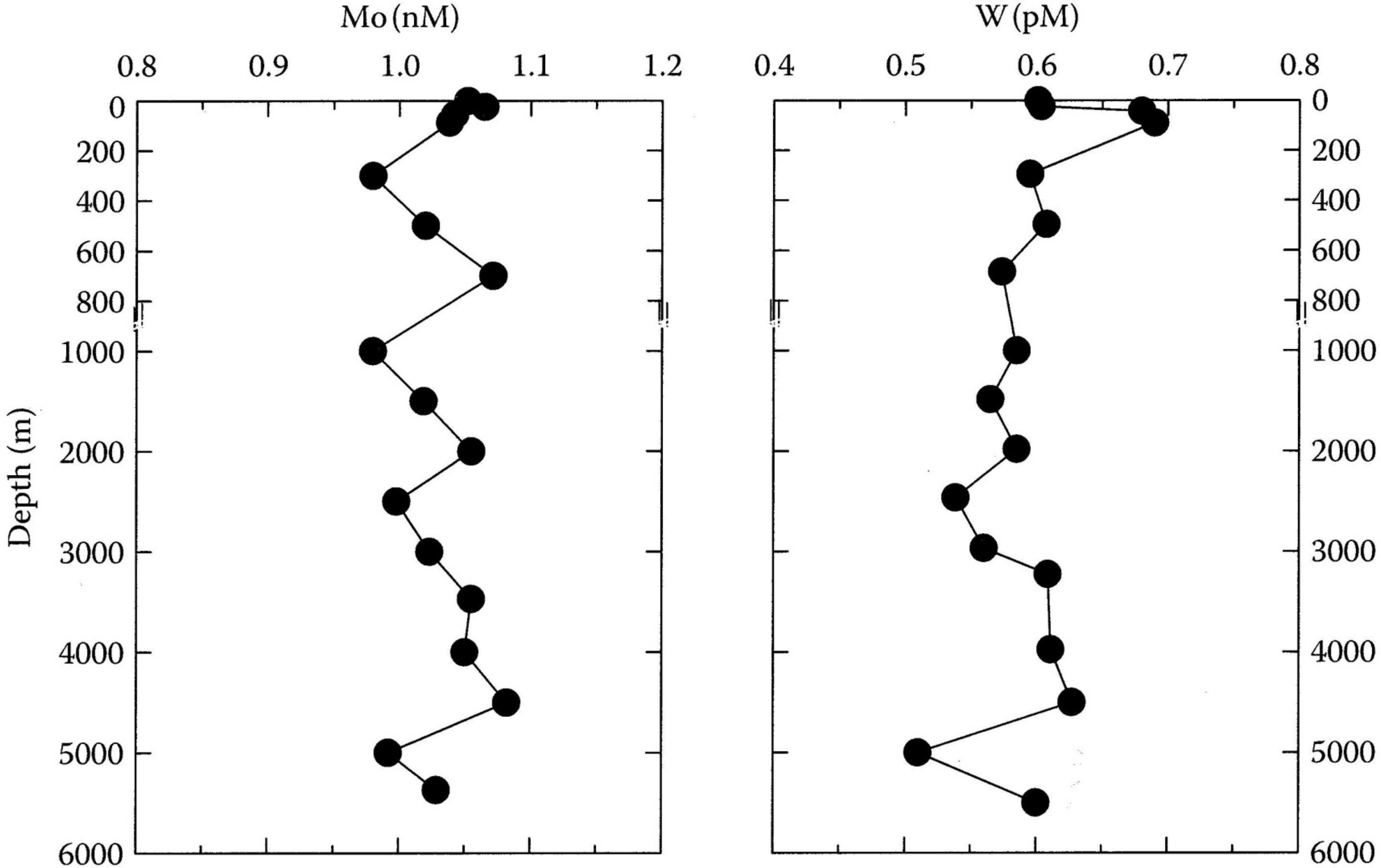
- Concentration – Major, Minor, Trace
- Biological Reactivity – Biolimiting, Biointermediate, Biounlimited, Noncycling
- Chemical Reactivity – d^0, d^{10}, Intermediate or Class A, Class B, Intermediate
- Overall Reactivity – Nutrient Type, Particle Reactive, Other
- Environmental Origin – Crustal, Pollutant (anthropogenic)

Concentration levels

- Major ions – discussed previously
  metals & non metals (Ca^{2+}, Mg^{2+}, Na^{+} , K^{+})
- Minor ions – some mention (Ba^{2+}, Sr^{2+}, etc.)
- Trace ions (Trace Metals) – all the rest
- Millero
  - Major: 0.05 to 750 mM
  - Minor: 0.05 to 50 μM
  - Trace: 0.05 to 50 nM

Depth Profiles for Mo & W

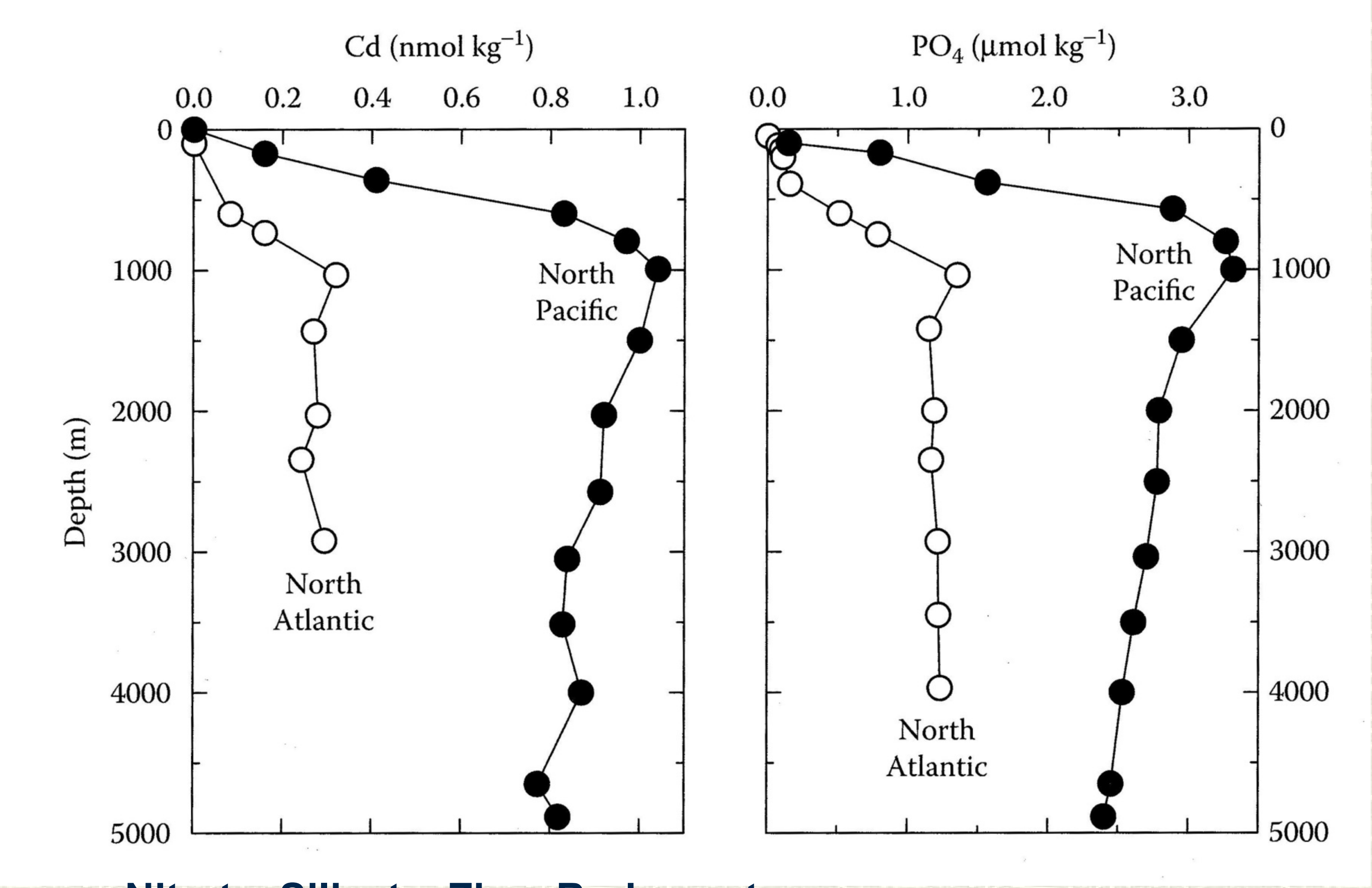
Conservative behavior (Millero 2006)



Major Components, Rb^+, Cs^+, etc.

Depth Profiles for Cd & P

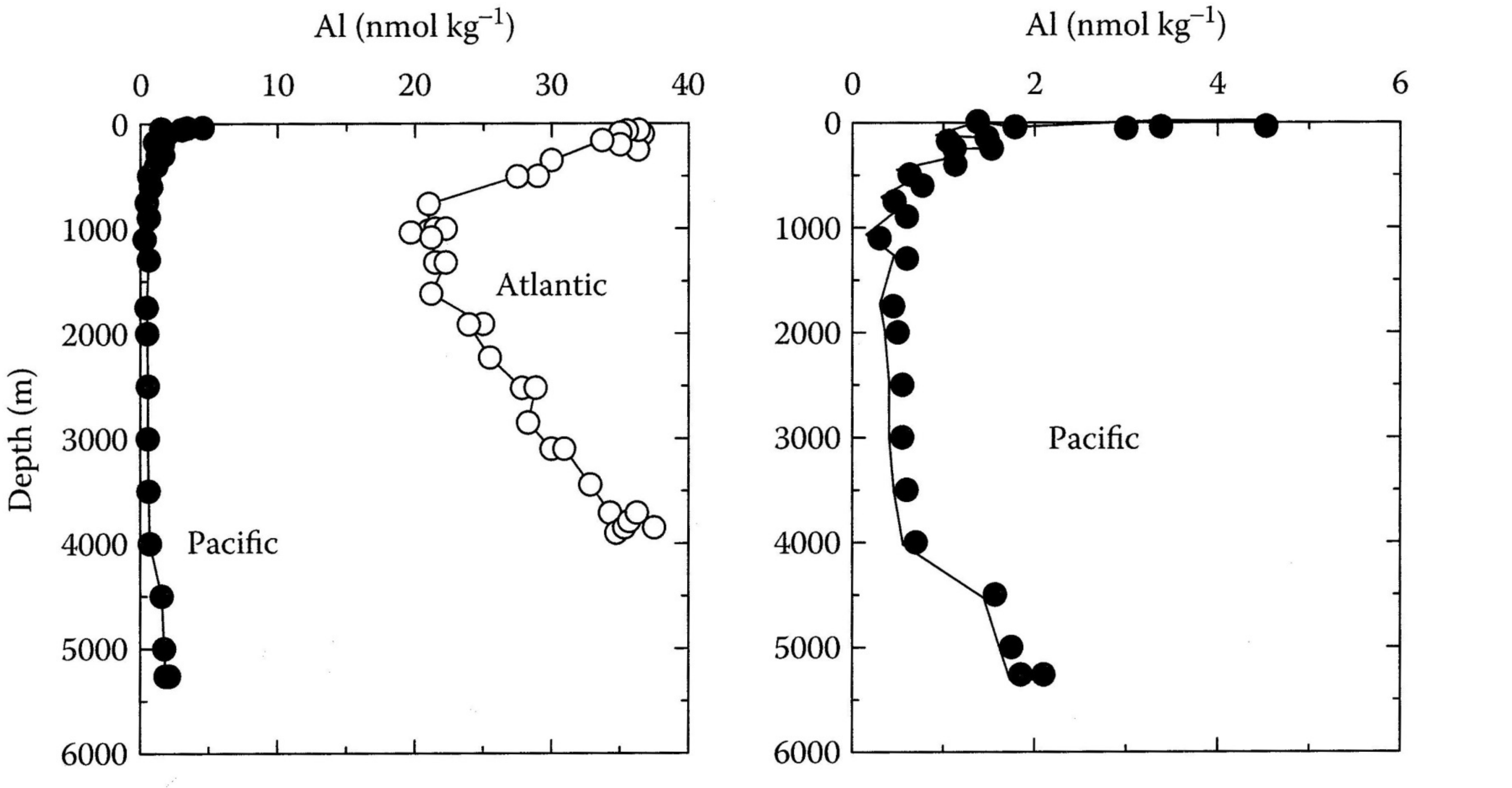
Nutrient behavior (Millero 2006)



Nitrate, Silicate, Zinc, Barium, etc.

Depth Profiles for Al

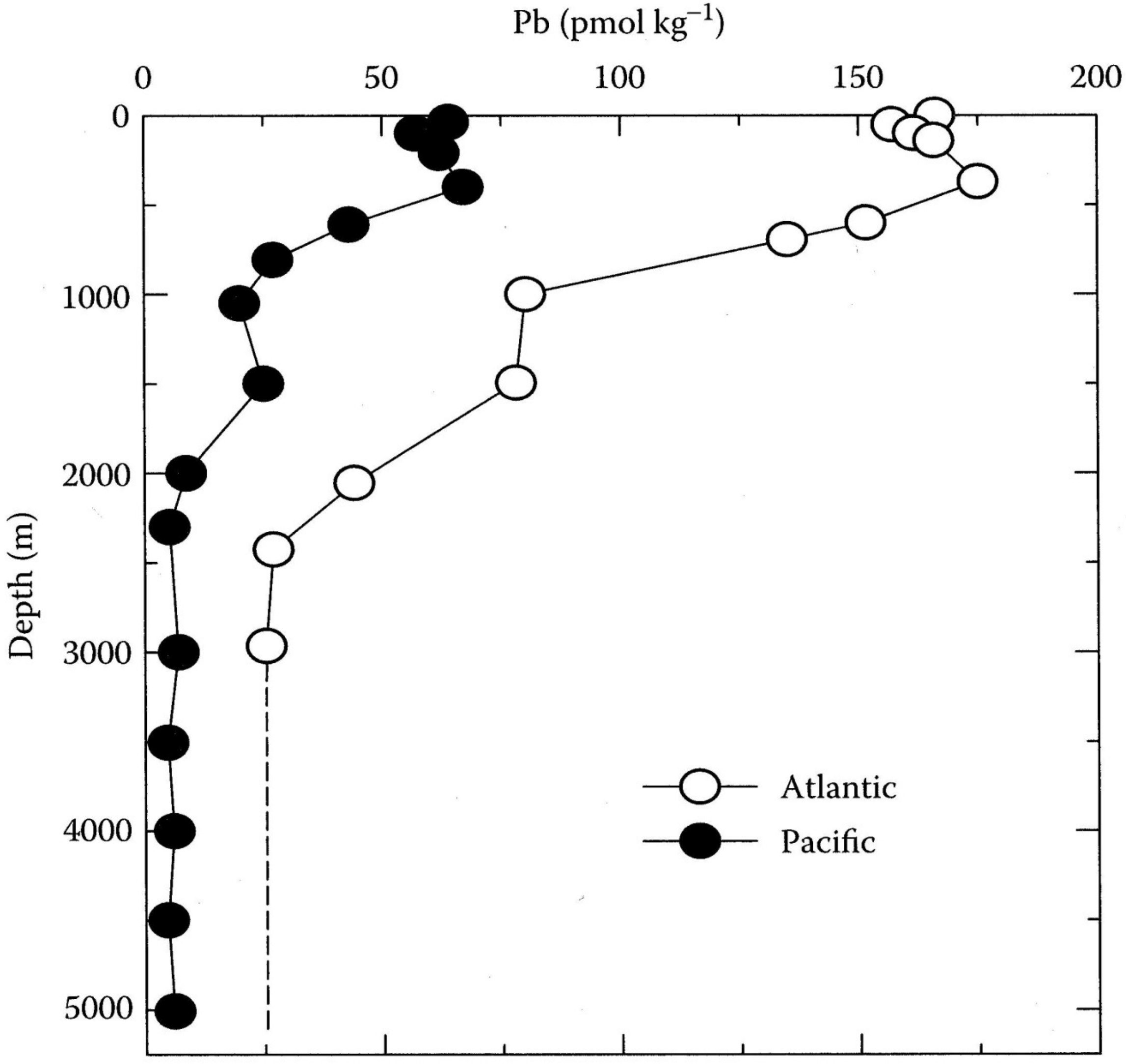
Mid-depth minimum (Millero 2006)

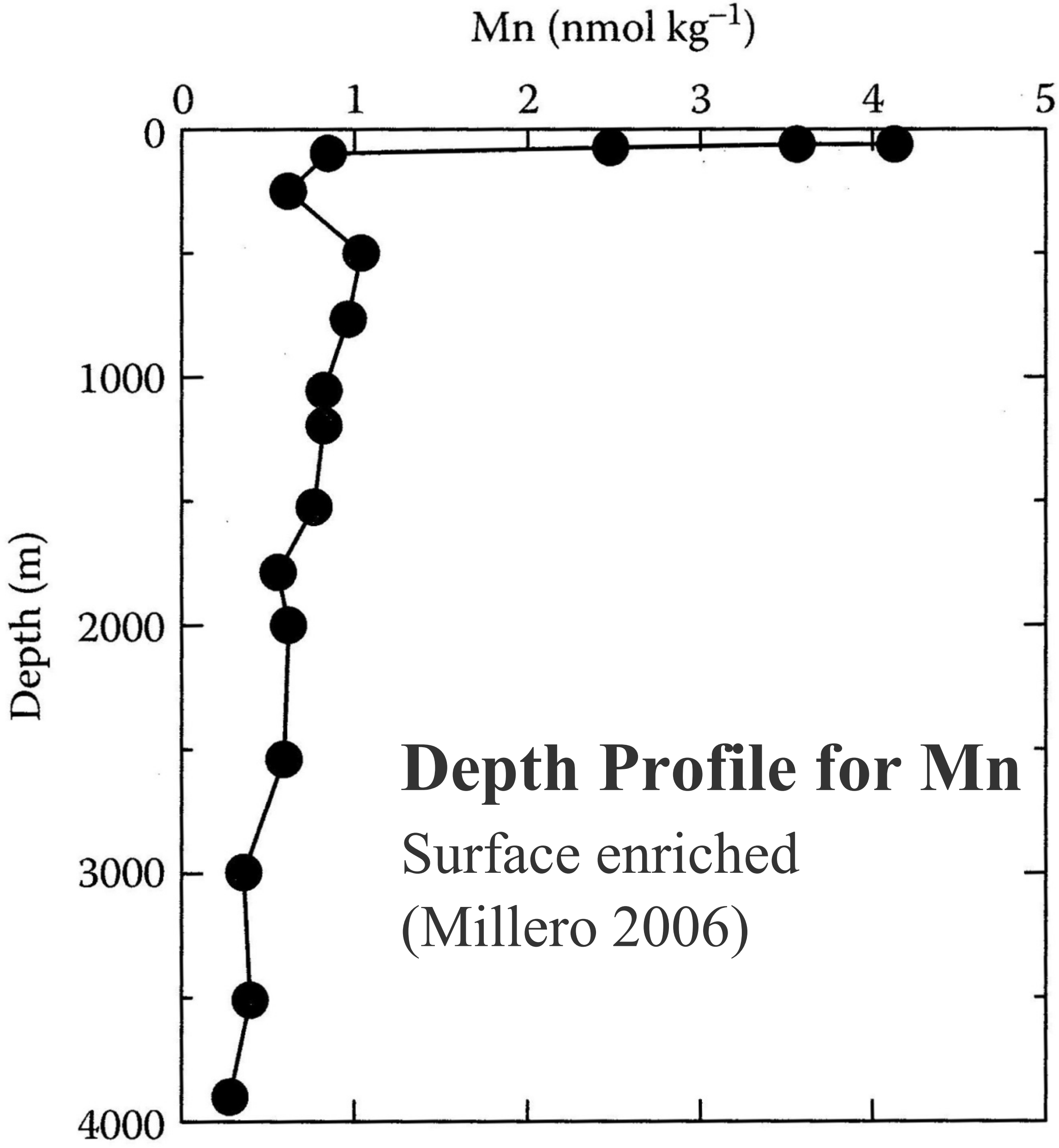


Copper, Tin, etc.

Depth Profiles for Pb

Surface enriched (Millero 2006)





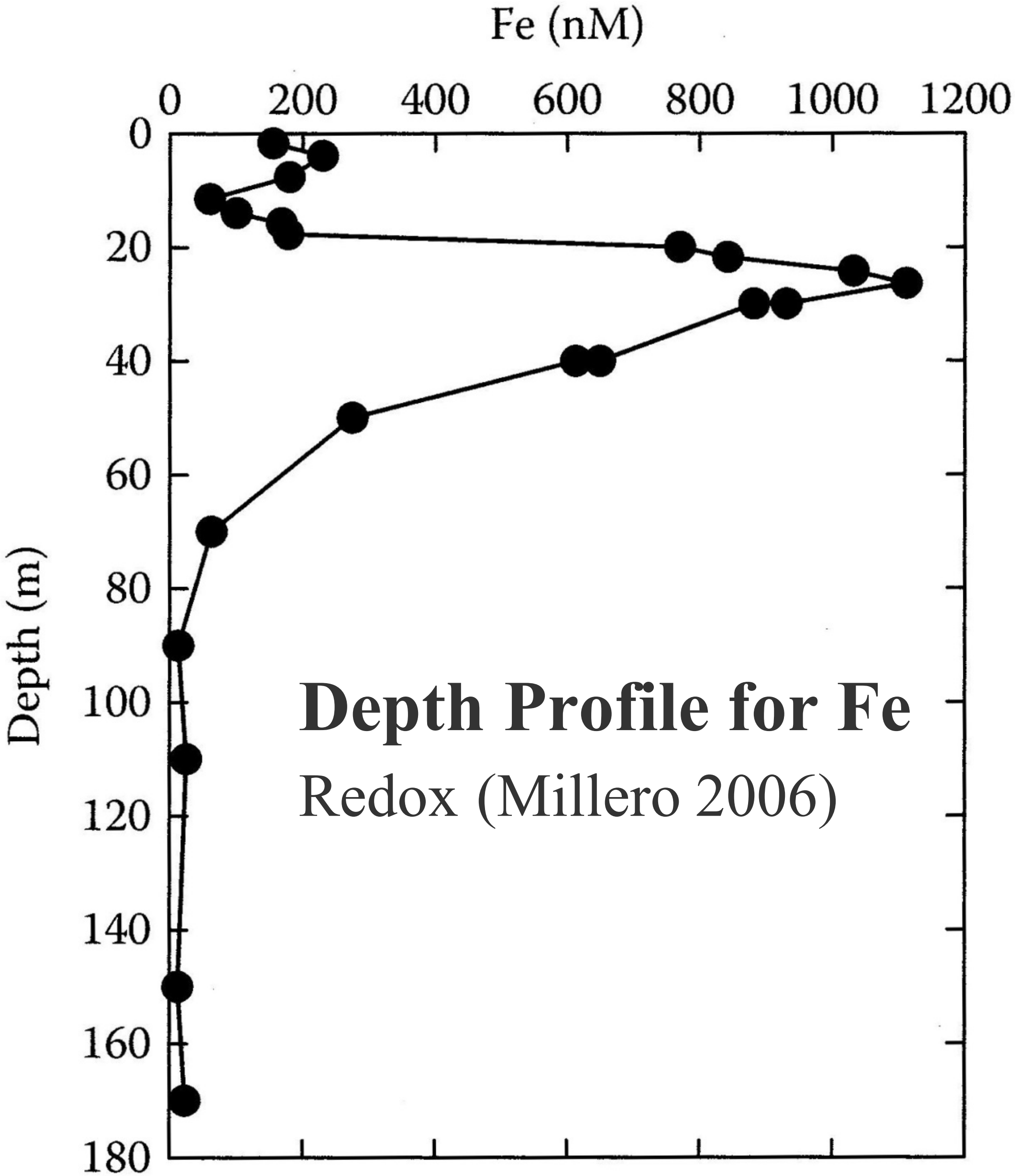
Depth Profile for Mn

Surface enriched

(Millero 2006)

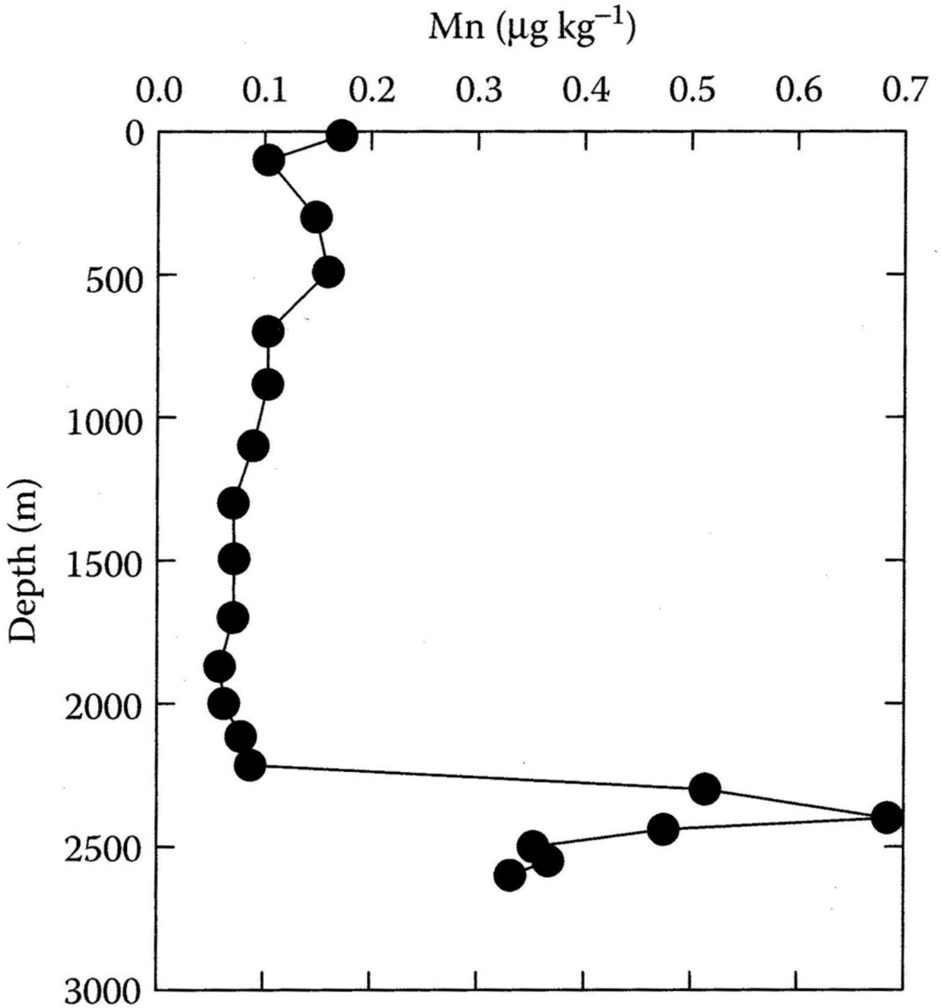
Depth Profile for Fe

Redox (Millero 2006)



Depth Profile for Mn

Anomolous (Millero 2006)



Vertical Profiles of Elements in the Pacific Ocean

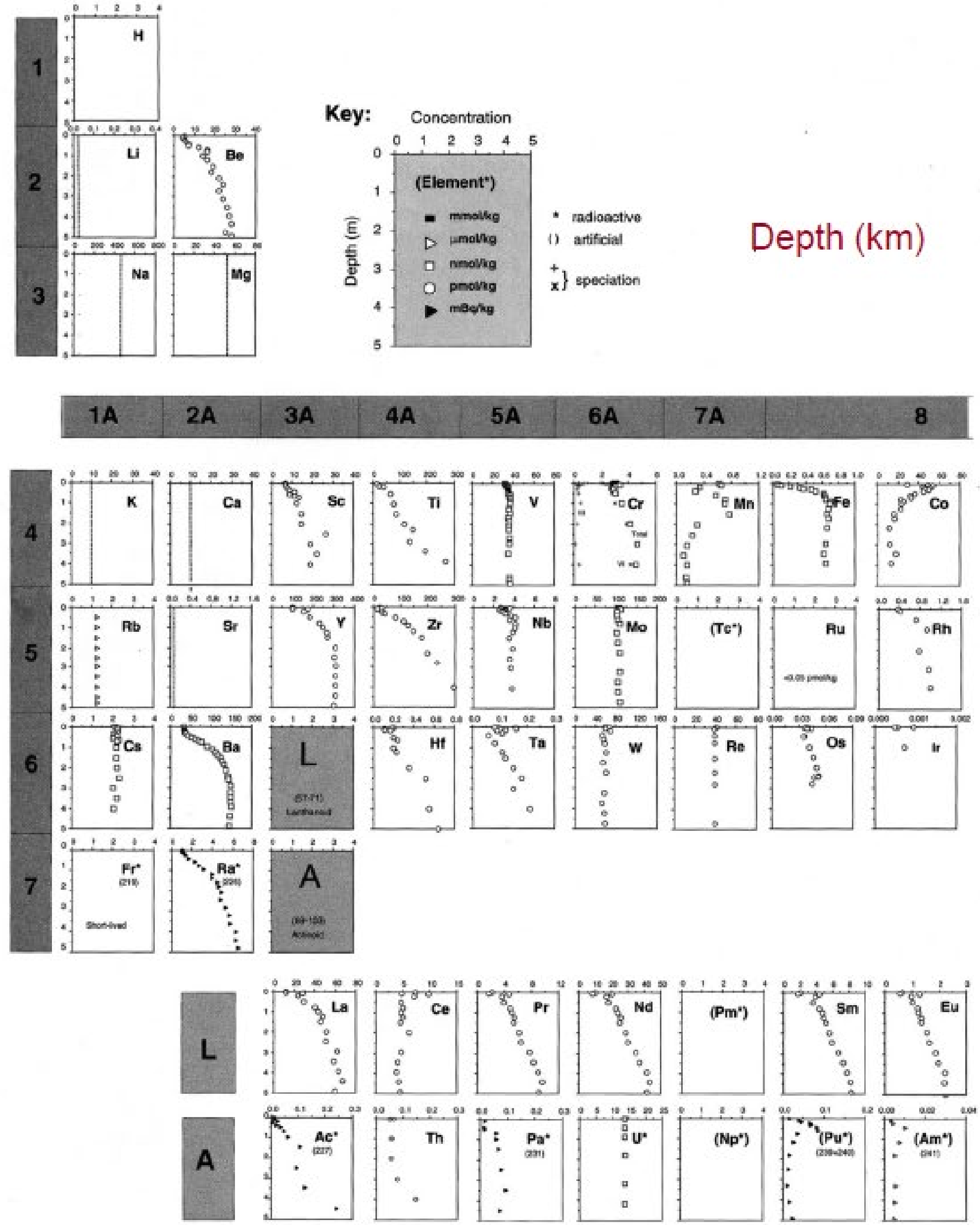
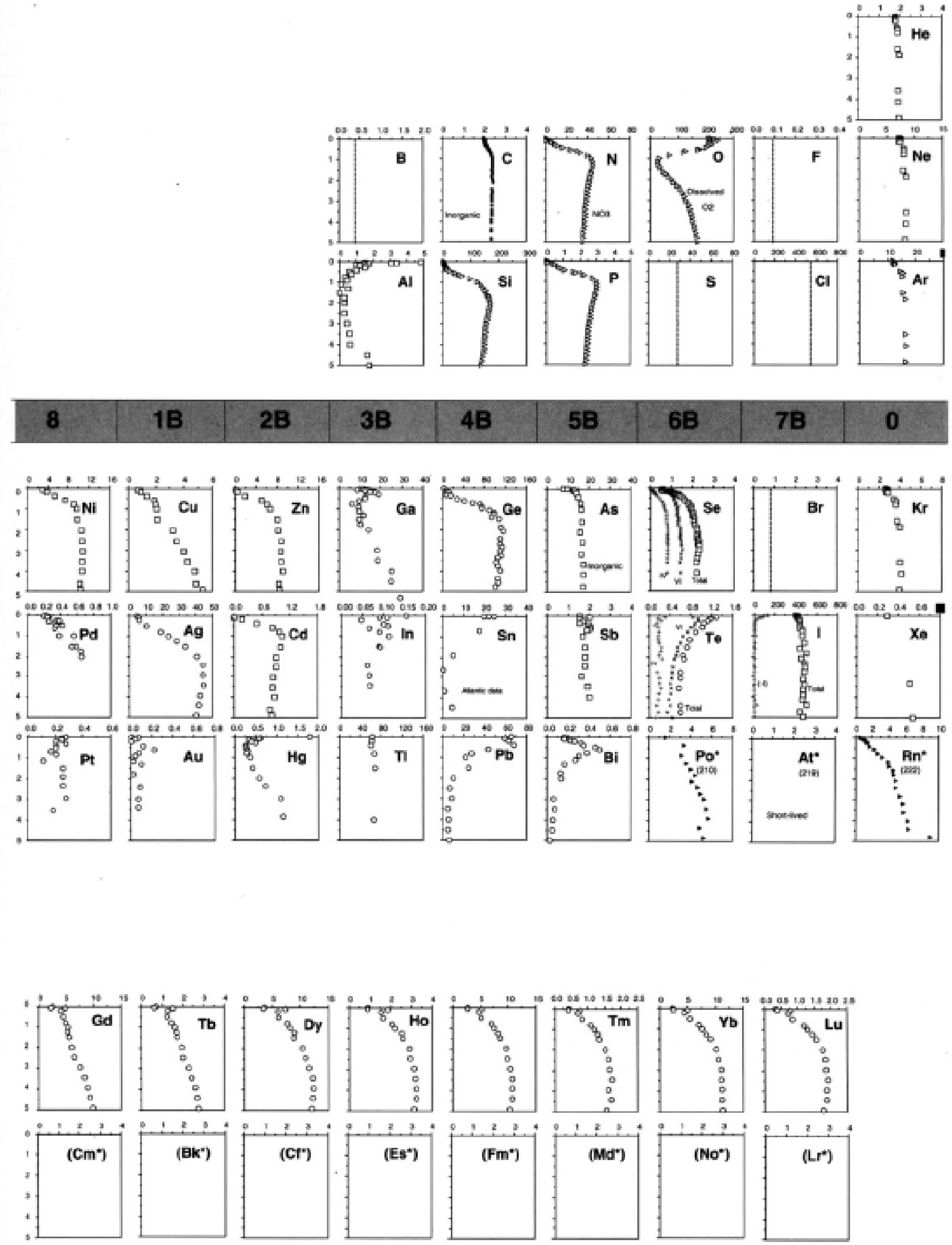


FIGURE 1.2.1: Vertical profiles of elements from the Pacific Ocean arranged as in the periodic table of elements [*Nozaki*, 1997]. The biounlimited elements have nearly uniform concentrations. Most other elements have lower concentrations at the surface than at depth due to biological removal. Biolimiting elements are nearly depleted to 0 mmol m^{-3} at the surface, whereas biointermediate elements show only partial depletion. Oxygen and the noble gases on the right side of the figure are influenced in part by their higher solubility in colder

Sarmiento & Gruber 2006



waters deep in the ocean (see chapter 3) and, in the case of oxygen, by biological production as part of photosynthesis and consumption by respiration. A few elements such as Pb have higher concentrations at the surface due to delivery by dust transport, and lower concentrations at depth due to rapid scavenging from the water column to the sediments.

Sarmiento & Gruber 2006

Table 1. Estimated mean oceanic concentrations of the elements and the references on which the periodic chart (Figure 1) is based.

Atomic Number	Element	Species	Type of Distribution	Oceanic mean Concentration (ng/kg)	Reference
1	Hydrogen	H_2O			
2	Helium	Dissolved gas	c	7.6	Clarke et al. (1970)
3	Lithium	Li^+	c	180×10^3	Stoffyn-Egli and Mackenzie (1984)
4	Beryllium		s+n	0.21	Measures and Edmond (1982)
5	Boron	Borate	c	4.5×10^6	Noakes and Hood (1961)
6	Carbon	Inorganic ΣCO_2	n	27.0×10^6	Broecker and Takahashi (1978)
7	Nitrogen	Dissolved N_2	c	8.3×10^6	Craig et al. (1967)
		NO_3^-	n	0.42×10^6	GEOSECS Operation Group (1987)
8	Oxygen	Dissolved O_2	inverse n	2.8×10^6	GEOSECS Operation Group (1987)
9	Fluorine	F^-	c	1.3×10^6	Bewers et al. (1973)
10	Neon	Dissolved gas	c	160	Craig et al. (1967)
11	Sodium	Na^+	c	10.78×10^9	Millero and Leung (1976)
12	Magnesium	Mg^{2+}	c	1.28×10^9	Carpenter and Manella (1973)
13	Aluminum		s	30	Orians and Bruland (1985)
14	Silicon	Reactive SiO_2	n	2.8×10^6	GEOSECS Operation Group (1987)
15	Phosphorus	Reactive PO_4	n	62×10^3	GEOSECS Operation Group (1987)
16	Sulfur	SO_4^{2-}	c	898×10^6	Morris and Riley (1966)
17	Chlorine	Cl^-	c	19.35×10^9	Wilson (1975)
18	Argon	Dissolved gas	c	0.62×10^6	Craig et al. (1967)
19	Potassium	K^+	c	399×10^6	Culkin and Cox (1966)

Distribution patterns are classified into the following four categories:

conservative, nutrient-type, scavenged, and redox-controlled

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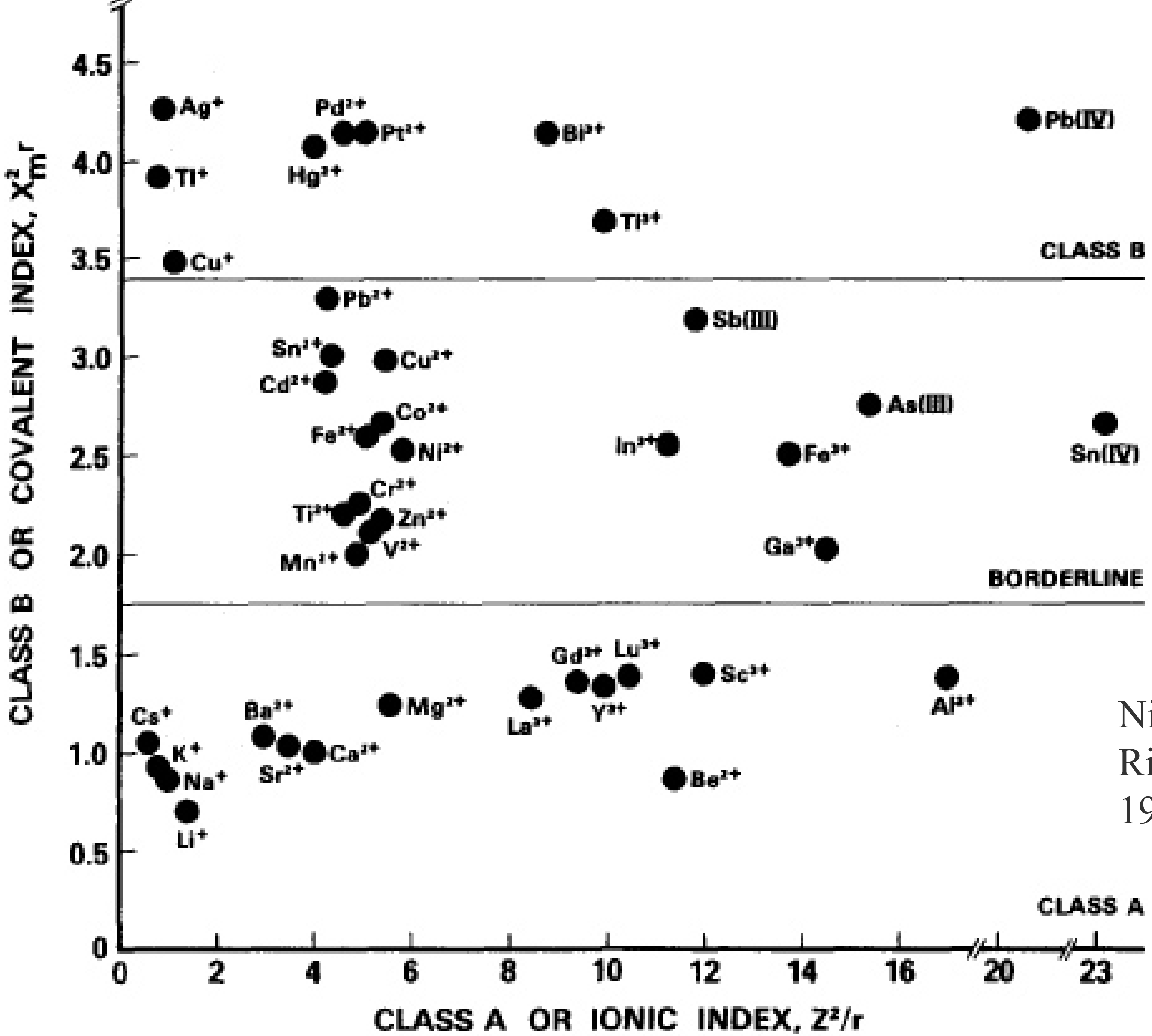
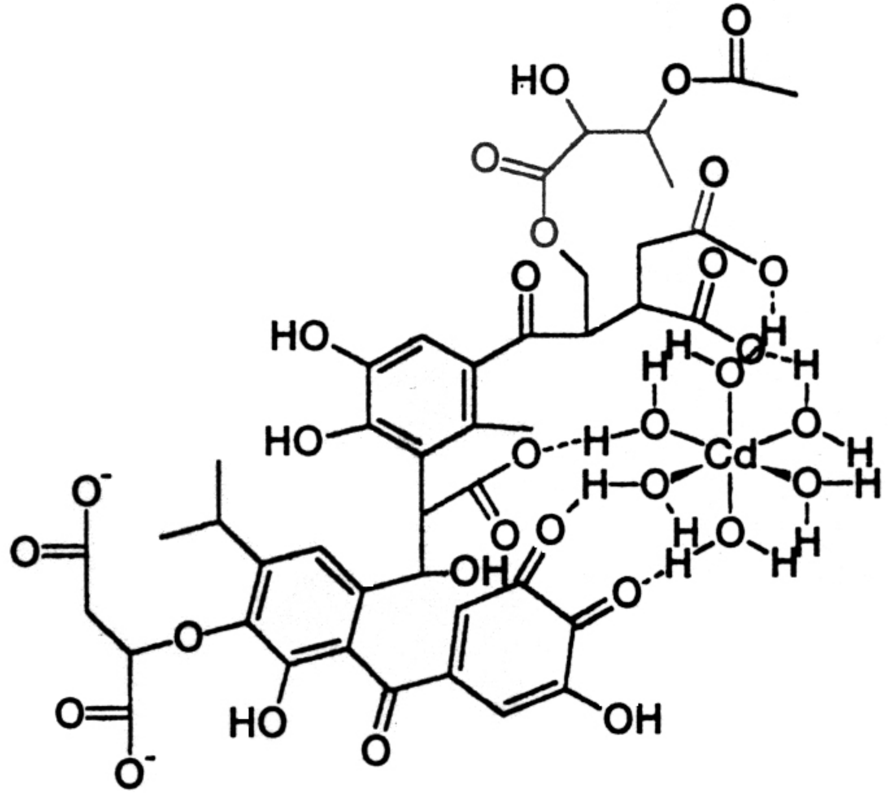


Nieboer & Richardson 1980

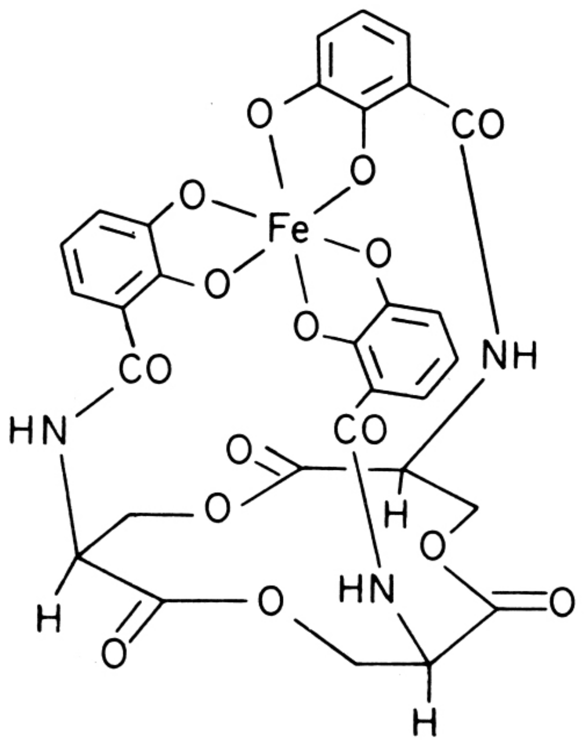
Importance of Humic Materials (Natural Organics)

Global Carbon Reservoir
Take Part in Interfacial Phenomena
Undergo Coagulation and Aggregation
Involved in Photochemical Reactions
Contain Radicals
Known Reducing Agents
Methylate Metals
Form Chlorinated Species, THMs DBPs
Detoxify Metals
Limit Bioavailability of Metals
Alter Solubility
Influence Transport
Bind Metals & Organic Pollutants
Terminal Electron Acceptor for Bacteria

Metal Complexation by Humic Materials



Leenheer et al. (1998)



Morel (1983)

Importance of Humic Materials

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Limit Bioavailability of Metals
Alter Solubility
Influence Transport
Bind Metals & Organic Pollutants
Terminal Electron Acceptor for Bacteria

Humic material will aggregate & may "salt out" with cations

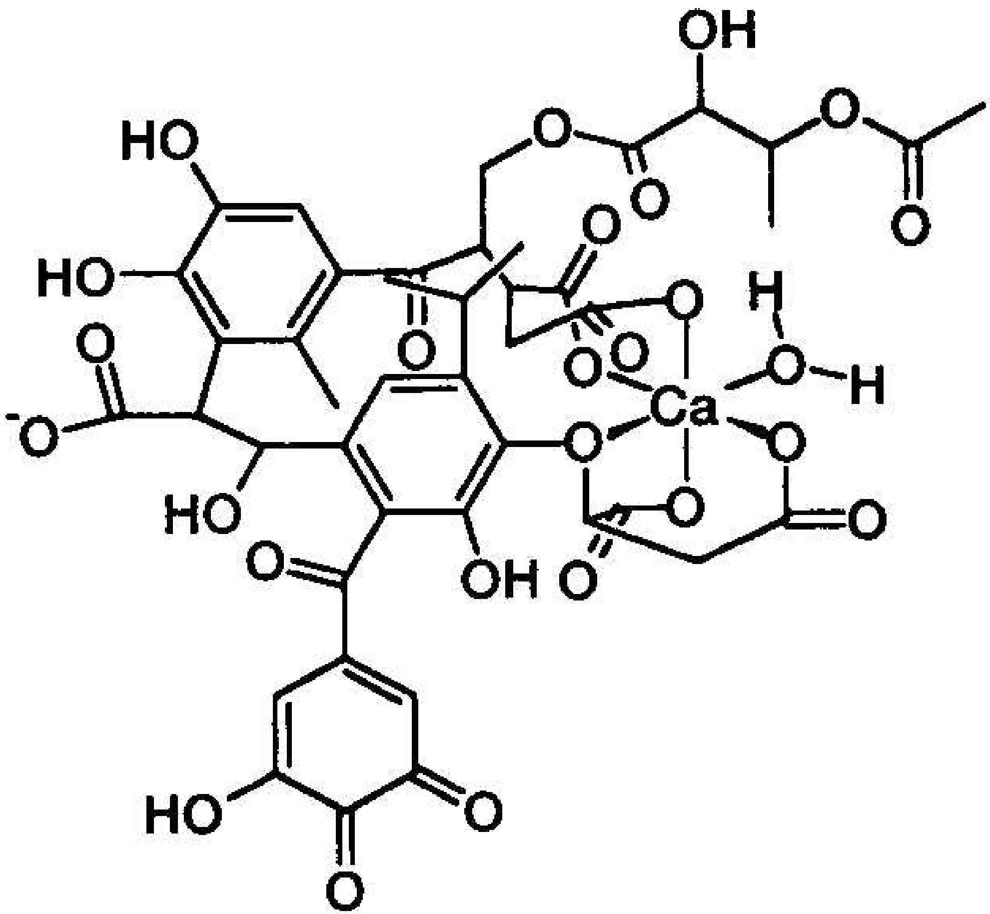
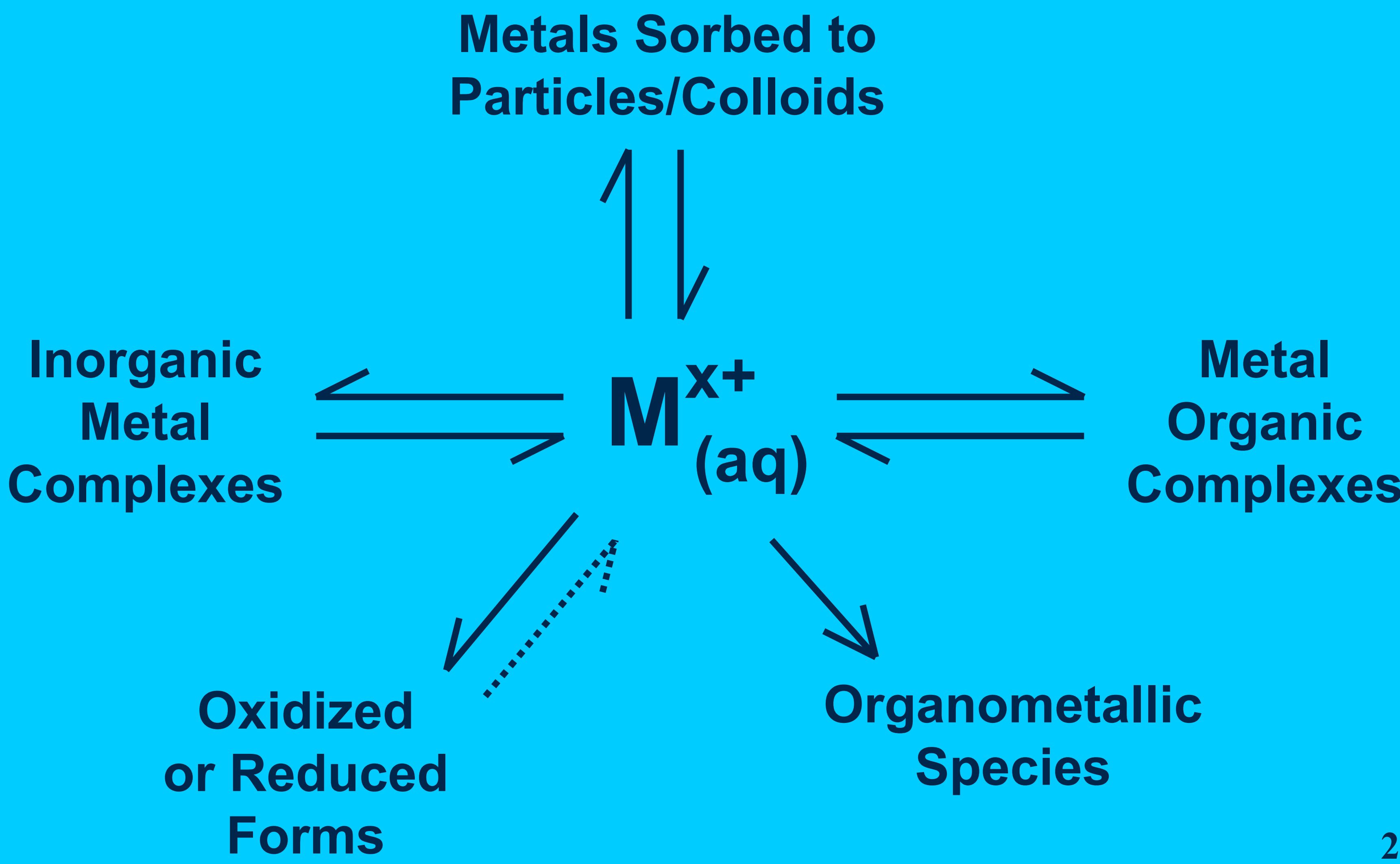


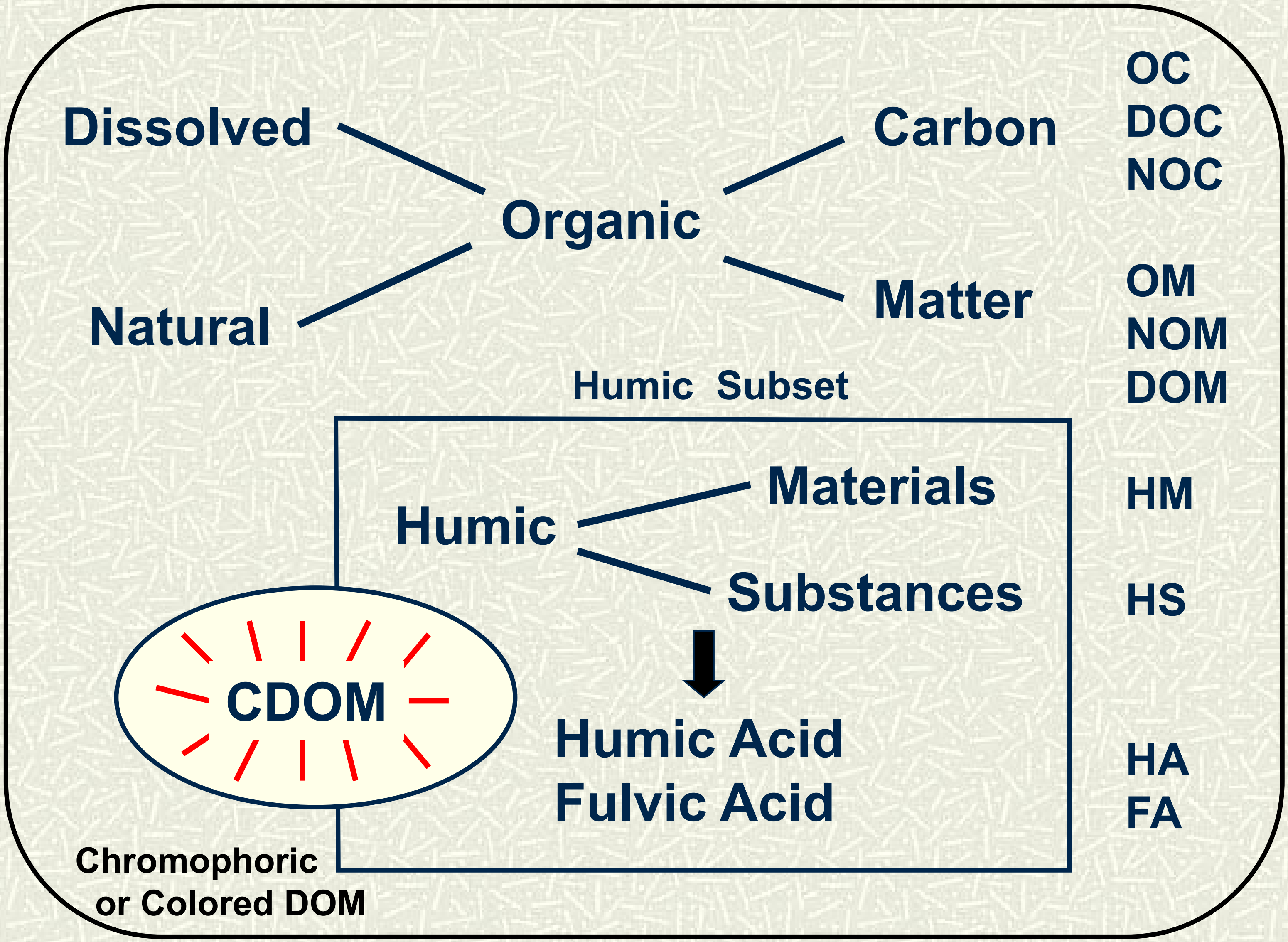
FIGURE 6. Structural model of a calcium inner-sphere complex

Leenheer, J.A. et al. (1998) Environ. Sci. Technol. 32, 2410

Dissolved Metal Species



All Dissolved Organic Compounds



Metal Organic Complexes

M^{x+}

NOM^{y-}

NOM^{y-}

M^{x+} M^{x+}

NOM^{y-}

M^{x+} $M\text{-}NOM^{(x-y)-}$

M^{x+} = metal ion, toxic or non, of charge x+ (e.g., Cu^{2+}, Al^{3+}, etc.)

NOM^{y-} = natural organic matter of varying negative charge y-

$M\text{-}NOM^{(y-x)-}$ = metal complex of natural organic matter