Updated: 22 January 2020

Print version

CEE 680: Water Chemistry

Lecture #2

Intro: Expressions of Concentrations and Natural Abundance

(Stumm & Morgan, Chapt.1 & 3.4)

(Pg. 4-11; 97-105)

(Pankow, Chapt. 2.8)

(Benjamin, 1.2-1.5)

Elemental abundance in fresh water

From: Stumm & Morgan, 1996; Benjamin, fig 1.4; Langmuir figure 8.12

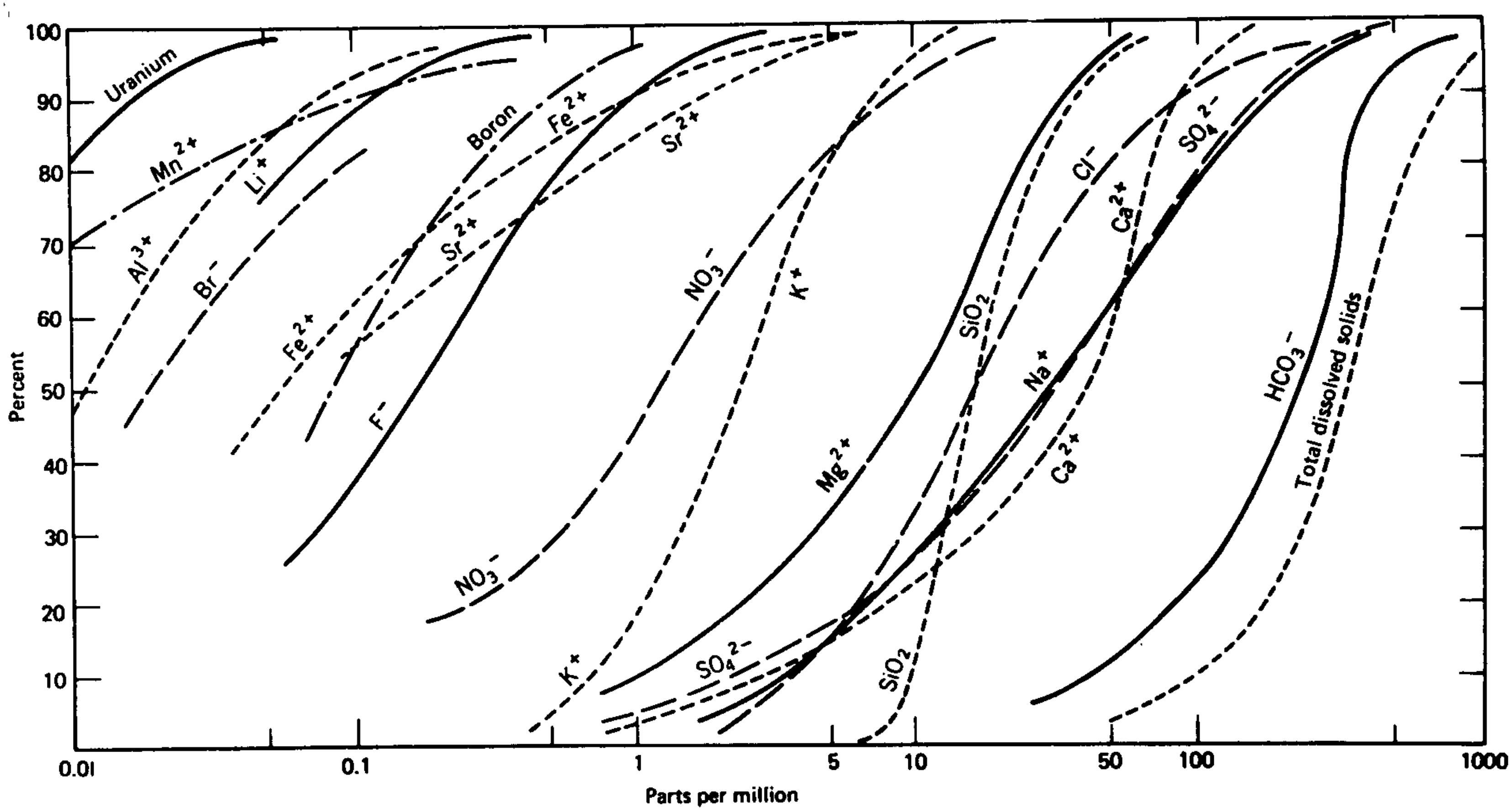
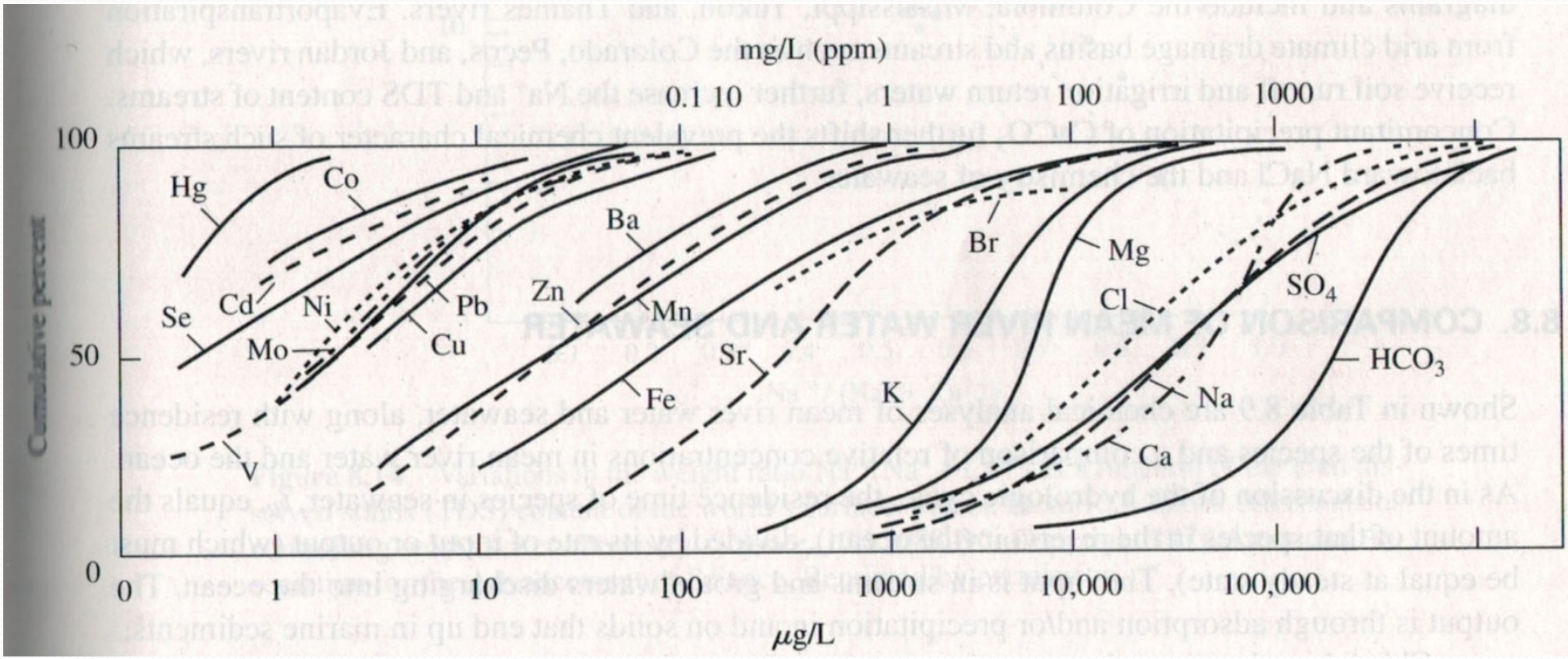


Figure 15.1. Cumulative curves showing the frequency distribution of various constituents in terrestrial water. Data are mostly from the United States from various sources. (Adapted from Davies and DeWiest, 1966.)

Same, but for groundwater

- From Langmuir, figure 8.13
  - Based on Rose et al., 1979, Geochemistry in mineral exploration

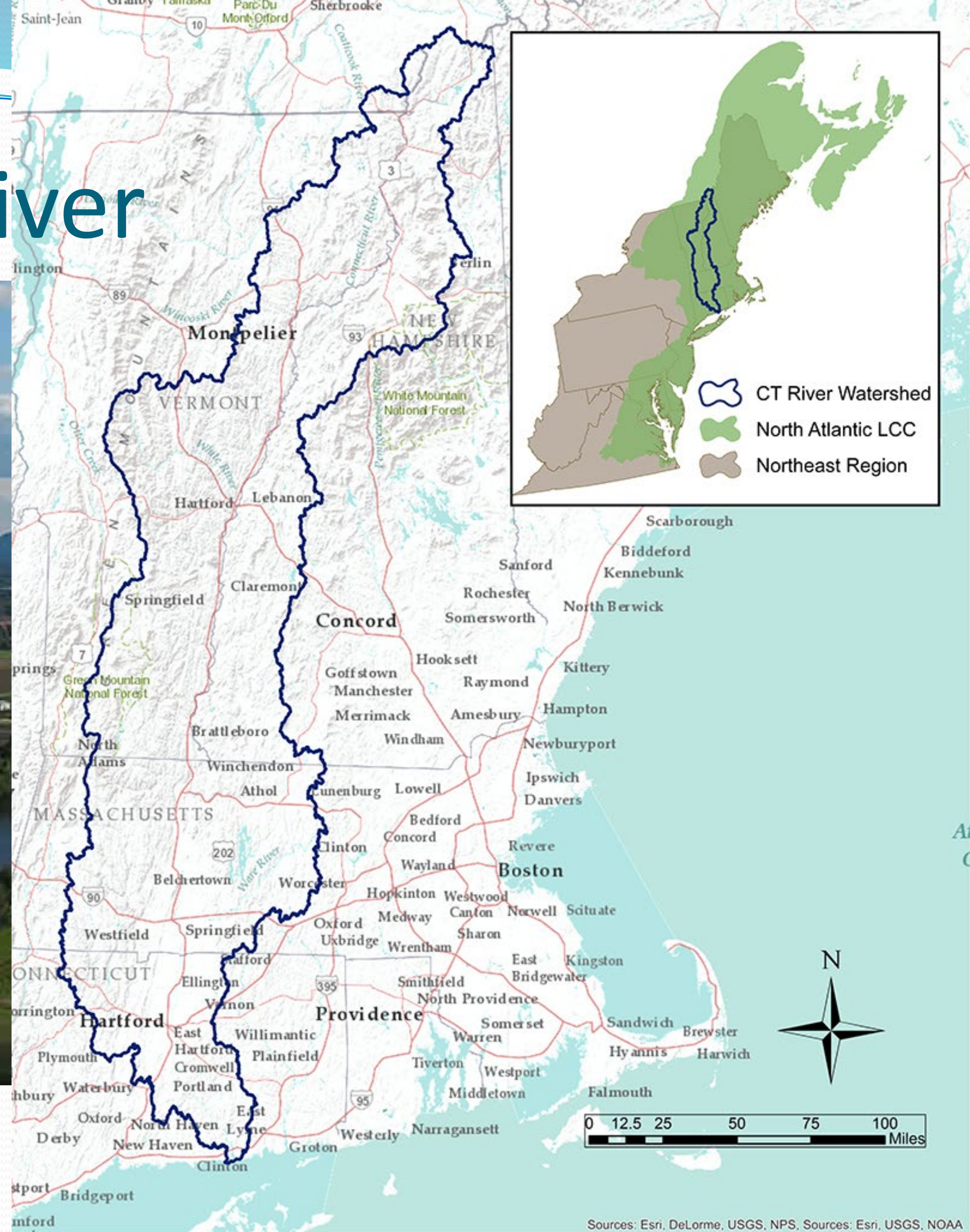


Connecticut River vs Vaal River

- Connecticut River (CT River) watershed
  - Ryder et al., 1981
- Vaal River, site C1H001
  - Mohr, 2015
- Avg (surface water) SW
  - Turekian, 1977 & Langmuir, pg 294
- Precipitation & Sea Water
  - Benjamin, Table 1.1
- All values in mg/L

Parameter	CT River	Vaal River	Avg SW	Precip	Sea Water
Sodium	6.5	4.7	6.3	9.4	10,800
Potassium	1.3	0.9	2.3		395
Calcium	13	7.1	15	0.8	408
Magnesium	3.2	5.5	4.1	1.2	1280
Chloride	10	4.5	7.8	17	19,400
Bicarbonate	22	50	58	2.0	72
Sulfate	27	7.4	3.7	7.6	2710
TDS	113	79	120	38	35,000
Na/(Na+Ca)	0.33	0.40	0.30	0.92	0.96

Connecticut River



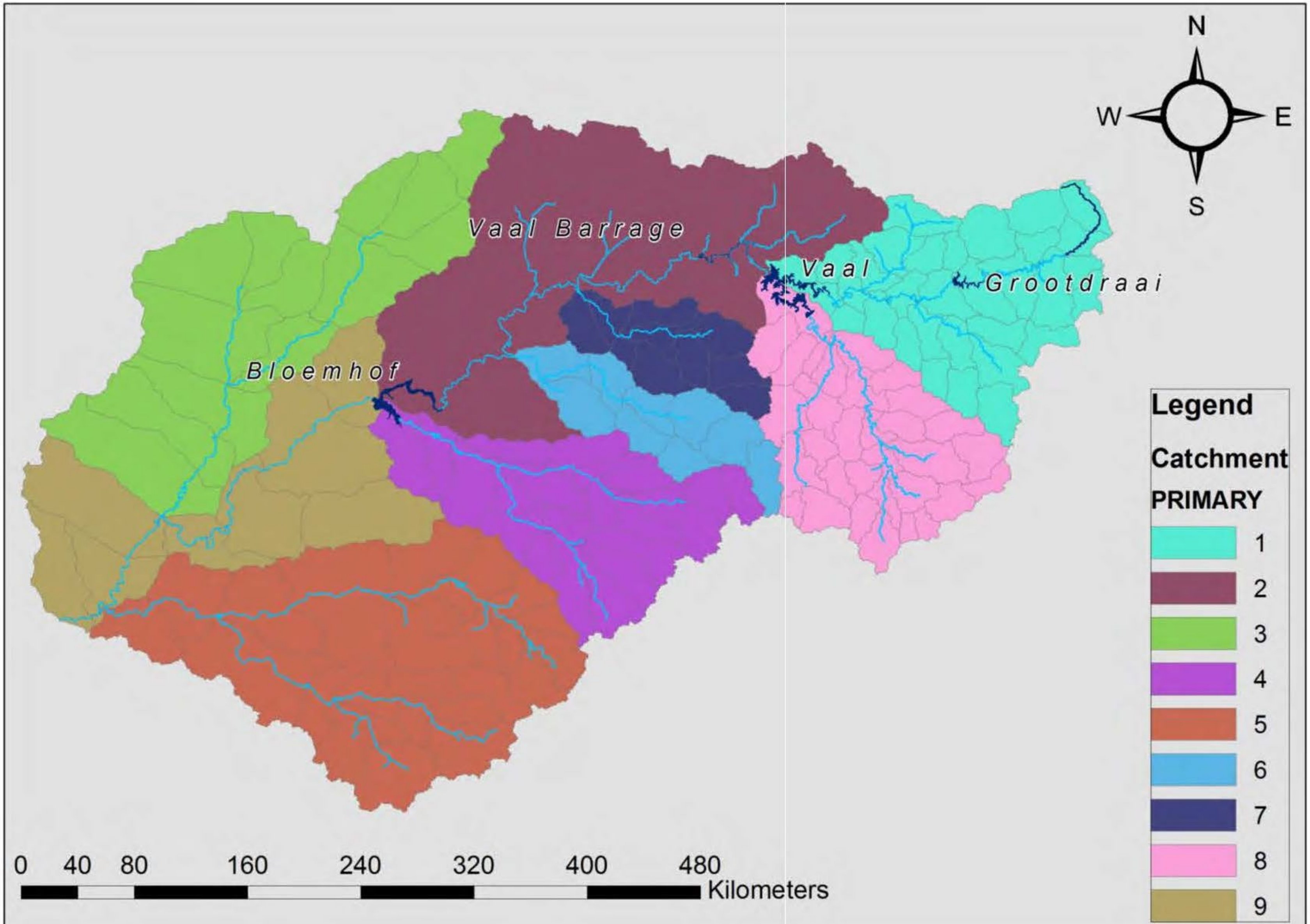
David Reckhow

- sda

Republic of South Africa
Province boundary*
Province capital**
*Province boundaries are subject to change under provisions of the South African Constitution.
**The KwaZulu/Natal provincial legislature has not yet chosen its provincial capital. Press reports indicate that the capital will be either Pietermaritzburg or Ulundi. Final province capitals are to be determined.
0 100 200 Kilometers
0 100 200 Miles
BOTSWANA
ZIMBABWE
MOZAM-BIQUE
NAMIBIA
SWAZILAND
LESOTHO
NORTHERN TRANSVAAL
NORTH-WEST
GAUTENG
EASTERN TRANSVAAL
KWAZULU / NATAL
ORANGE FREE STATE
NORTHERN CAPE
EASTERN CAPE
WESTERN CAPE
South Atlantic Ocean
Indian Ocean
Maun
Bulawayo
Masvingo
Plumtree
Francistown
Ghanzi
Messina
Chicualacuala
Pietersburg
Nylstroom
Gaborone
Chokwe
Lobatse
Rustenburg
Pretoria
Nelspruit
Xai-Xai
Mmabatho
Witbank
Maputo
Mbabane
Johannesburg
Vereeniging
Klerksdorp
Vryburg
Standerton
Keetmanshoop
Kroonstad
Golela
Sishen
Bethlehem
Ulundi**
Upington
Ladysmith
Kimberley
Richards Bay
Bloemfontein
Maseru
Okiep
Pietermaritzburg**
Mafeteng
Durban
De Aar
Kokstad
Port Shepstone
Calvinia
Victoria West
Middelburg
Umtata
Vanrhynsdorp
Queenstown
Beaufort West
Bisho
Saldanha
East London
Worcester
Cape Town
Port Elizabeth
Mosselbaai
Limpopo
Vaal
Orange
Sak
Tugela
Auob
Rio Save
20
25
30

Orange River

- Vaal River sub basin



Vaal Barrage
Vaal
Grootdraai
Bloemhof
N
W
E
S
Legend
Catchment
PRIMARY
1
2
3
4
5
6
7
8
9
0 40 80 160 240 320 400 480
Kilometers

Dav

Connecticut River vs Vaal River

- Connecticut River (CT River) watershed
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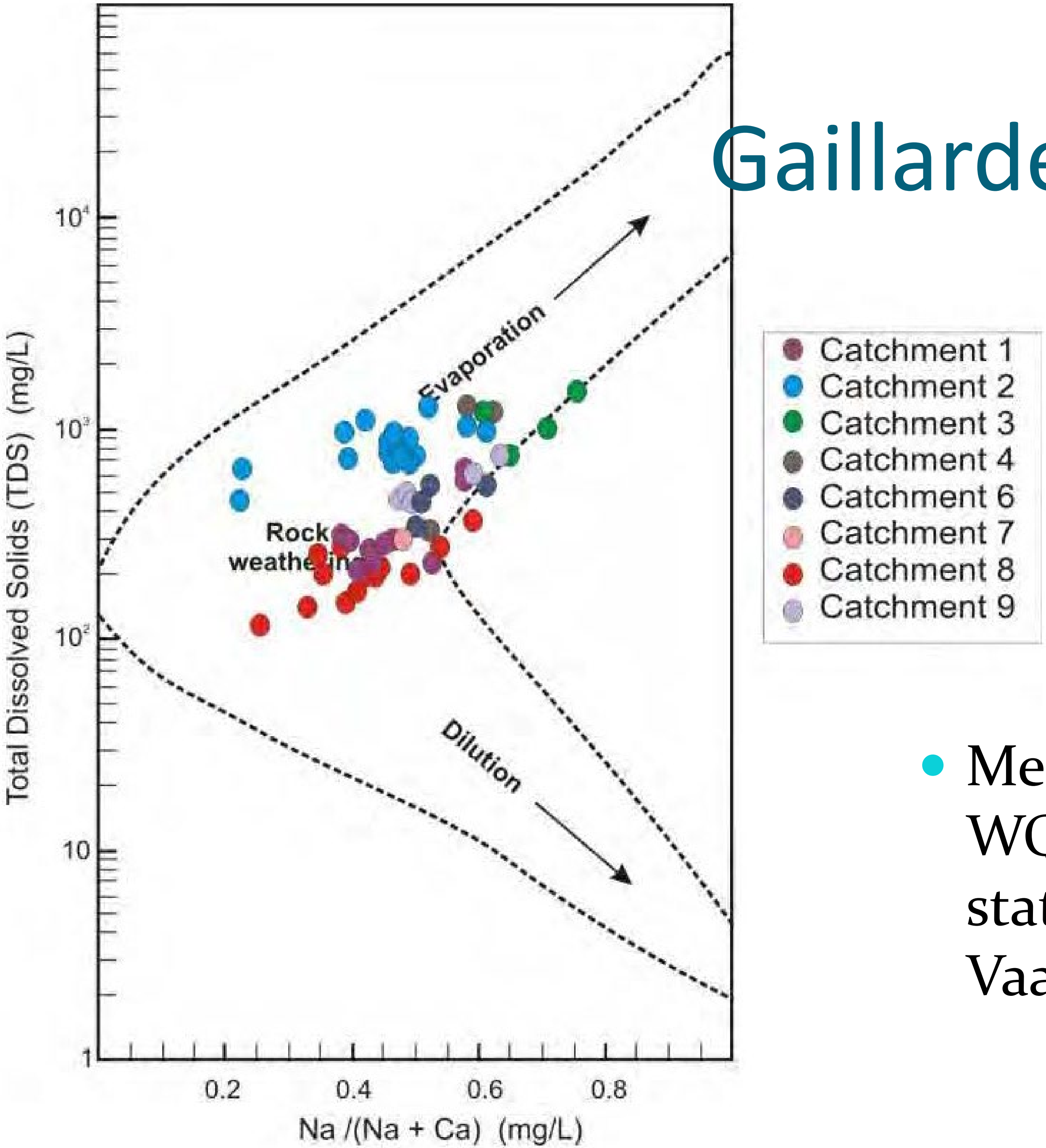
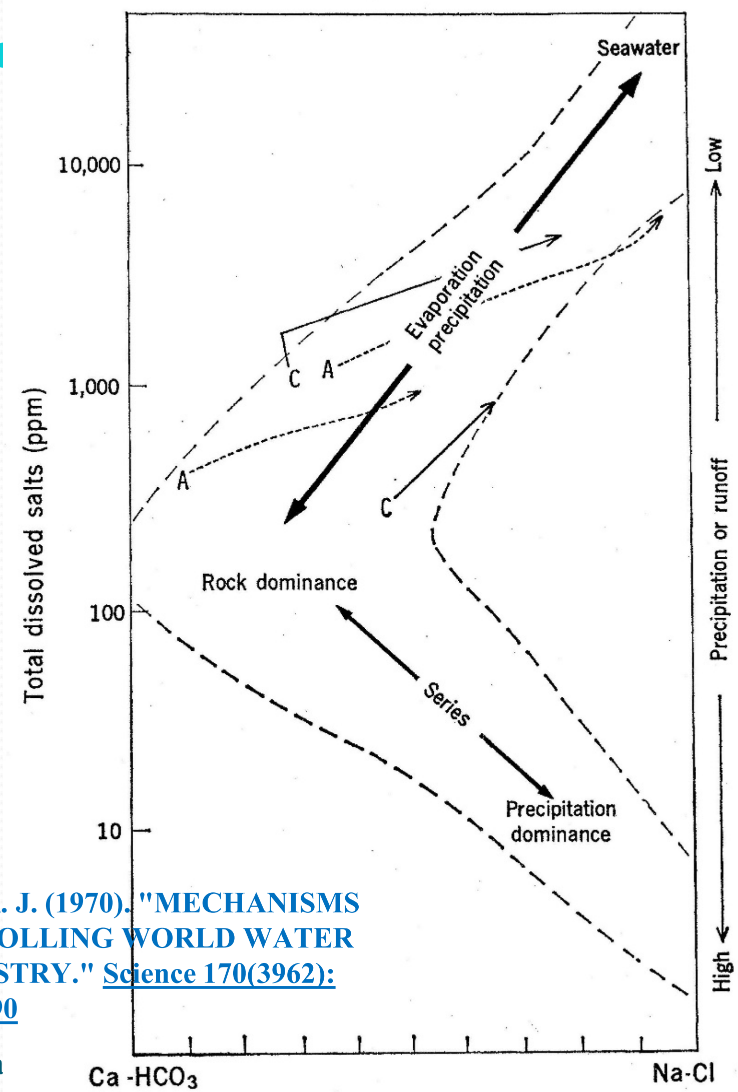
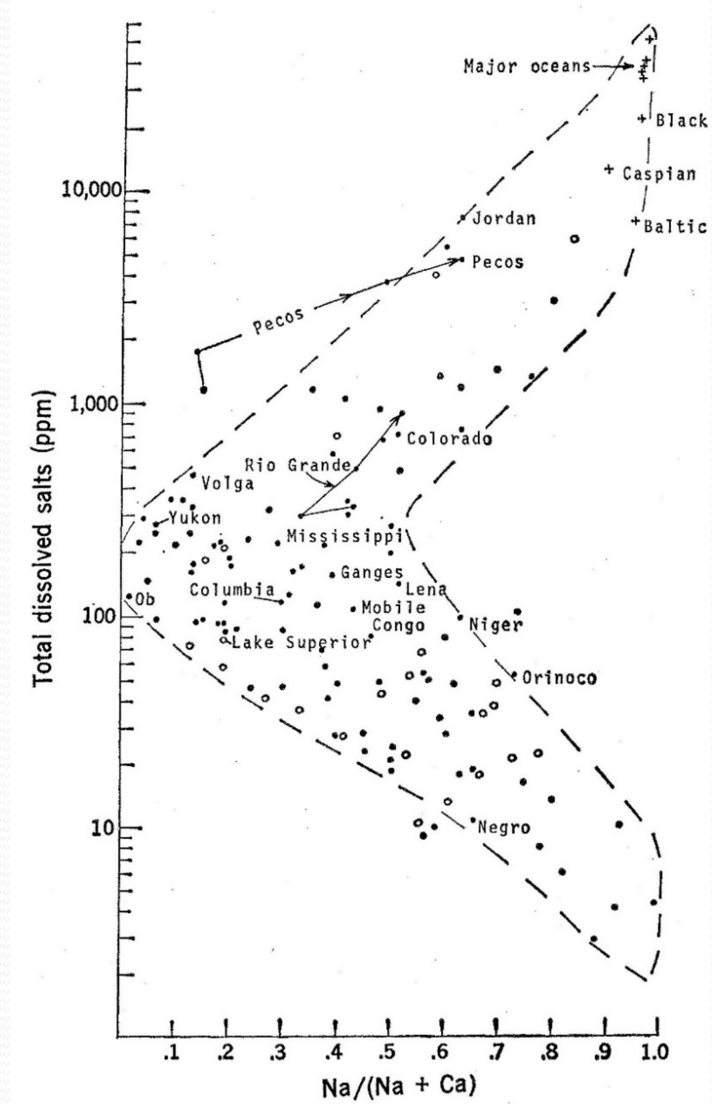
Gaillardet Diagram



- Median values for WQ monitoring stations along the Vaal River

Gibbs view of water composition





Gibbs, R. J. (1970). "MECHANISMS CONTROLLING WORLD WATER CHEMISTRY." Science 170(3962): 1088-1090

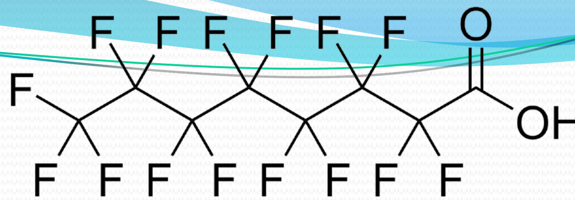
Stoichiometry: Lake Example

- Basic limnology tells us that phosphorus stimulates algal growth, they produce O_2, and bacteria consume O_2 when the algae die
- If we add 1 mg P to a small lake
  - How much algal biomass is produced?
  - How much O_2 is produced?
  - How much O_2 is later consumed?
- Elemental analysis of algae: empirical formula
  - $C_{106}H_{263}O_{110}N_{16}P$

Solution

- Balance equation
  - $106\ CO_2 + 16\ NO_3^- + HPO_4^{-2} + 122\ H_2O + 18\ H^+ = C_{106}H_{263}O_{110}N_{16}P + 138\ O_2$
- Use stoichiometric coefficients
  - Biomass: $$= 1mg-P\left(\frac{1mmole-P}{31mg-P}\right)\left(\frac{3551mg-a\lg ae}{1mmole-a\lg ae}\right)\left(\frac{1mmole-a\lg ae}{1mmole-P}\right)$$ $$= 115mg-a\lg ae$$
  - O_2 production: $$= 1mg-P\left(\frac{1mmole-P}{31mg-P}\right)\left(\frac{32mg-O_2}{1mmole-O_2}\right)\left(\frac{138mmole-O_2}{1mmole-P}\right)$$ $$= 142mg-O_2$$
  - O_2 consumption:

PFOA



In NY village, trail of cancer leads to tap water

By MARY ESCH
Associated Press

HOOSICK FALLS, N.Y. – After his factory worker father died a painful death from kidney cancer at age 68 in 2013, Michael Hickey made it his mission to find out why so many people in his hometown along the Hoosic River were getting sick.

Two years later, the U.S. Environmental Protection Agency has warned residents of Hoosick Falls not to drink or cook with water from municipal wells, and a plastics plant has agreed to install a $2 million carbon filtration system at the village water treatment plant.

Hickey's campaign began with suspicion about industrial pollution in the factory village near the Vermont border. His father had worked for 35 years at a plant that made high-performance plastics similar to Teflon, so Hickey searched online for "cancer" and "Teflon."

What he found: PFOA.

Perfluorooctanoic acid, a water and oil repellent, had been used since the 1940s in products including non-stick cookware, stain-resistant carpeting and microwave popcorn bags. Manufacturers agreed to phase it out by the end of 2015 shortly after DuPont reached a $16.5 million settlement with the EPA over the company's failure to report possible health risks associated with PFOA.

A scientific panel that conducted health studies as part of a DuPont settlement of a West Virginia class-action lawsuit concluded there was a "probable link" between PFOA exposure and kidney cancer, testicular cancer, thyroid disease, high cholesterol, ulcerative colitis and pregnancy-induced hypertension.

In Hoosick Falls, nobody has ever scientifically documented that the village has an unusually high cancer rate, but Hickey and a local doctor had heard enough anecdotal evidence that they felt it should be addressed.

AP PHOTO

A mural of a Grandma Moses painting adorns a building in Hoosick Falls, N.Y.

"There's always been talk around town about how there's a lot of cancer," Hickey said. "When my dad, who didn't drink or smoke, was diagnosed with kidney cancer, that made it more personal."

Dr. Marcus Martinez, the family doctor for many of the village's 3,500 residents, added there certainly seemed to be a high rate of cancer there, particularly rare, aggressive forms. The 44-year-old Martinez himself is in remission from aggressive prostate cancer.

When the two men suggested testing the village water supply, part-time Mayor David Borge at first refused, citing state guidelines. New York state classifies PFOA as an "unspecified organic contaminant" and doesn't require testing for it.

The EPA has a non-enforceable guidance level of 400 parts per trillion — roughly 4 teaspoons in enough water to fill a 10-mile string of rail tankers.

Hickey used his own money in summer 2014 to have water from his kitchen tap and other sources tested. The results showed PFOA at 540 ppt from Hickey's home, exceeding the EPA's guidance. Village officials subsequently tested the municipal supply and found PFOA at similar levels.

Saint-Gobain Performance Plastics, part of a Paris-based global conglomerate, in 1999 became the fifth owner of a plastics factory in Hoosick Falls. It conducted tests in the summer of 2015 and reported a PFOA level of 18,000 ppt in groundwater under its plant, 500 yards from the village's main water wells.

"Saint-Gobain Performance Plastics is committed to helping the village of Hoosick Falls with this situation," company spokesman Carmen Ferrigno said. While the source of the PFOA contamination hasn't been identified, Saint-Gobain has been paying for bottled water for residents since November and has agreed to pay for filtration to remove the chemical from the public water supply, he said.

Hickey and Martinez, along with Albany environmental lawyer David Engel, weren't satisfied. They wanted people to be told not to drink the tap water, as well as a full investigation and remediation.

Engel contacted Judith Enck, who heads the EPA region that includes New York. She issued a statement in December warning residents not to drink or cook with village water. Until then, state and village officials had told residents the water was unlikely to cause health problems.

On Jan. 14, Enck and a panel of leading EPA scientists addressed a standing-room-only crowd at Hoosick Falls' high school auditorium. The same day, New York officials asked the EPA to add the Saint-Gobain plant and other possible sources of contamination in Hoosick Falls to the Superfund priorities list. The state health department also recently announced plans to study cancer rates in the village and vicinity.

"We are giving this contamination problem a high priority," Enck said. "A very detailed study of groundwater is needed in Hoosick Falls to know what we are dealing with and how to best address it."

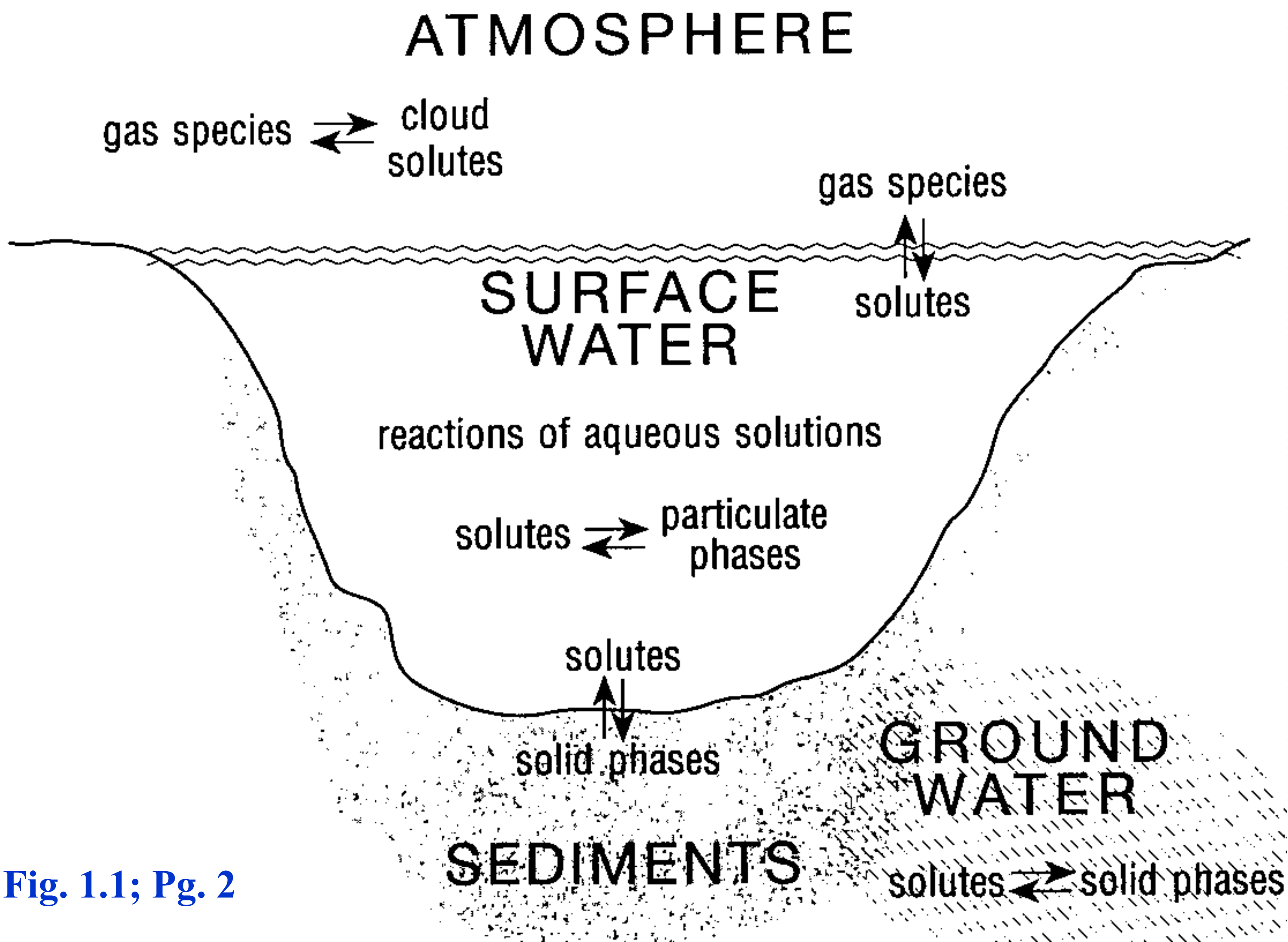
Perfluorooctanoic acid (**PFOA**), also known as **C8** and **perfluorooctanoate**, is a synthetic compound. One industrial application is as a surfactant in the production of fluoropolymers. It has been used in the manufacture of such prominent consumer goods as polytetrafluoroethylene (commercially known as Teflon). PFOA has been manufactured since the 1940s in industrial quantities.

PFOA persists indefinitely in the environment. It is an animan carcinogen. PFOA has been detected in the blood of more than 98% of the general US population in the low and sub-ppb range, and levels are higher in chemical plant employees and surrounding subpopulations. How general populations are exposed to PFOA is not completely understood. PFOA has been detected in industrial waste, stain resistant carpets, carpet cleaning liquids, home dust, microwave popcorn bags, water, food, some cookware and PTFE such as Teflon.

Daily Hampshire Gazette, 27 January 2016

Natural Water Environment

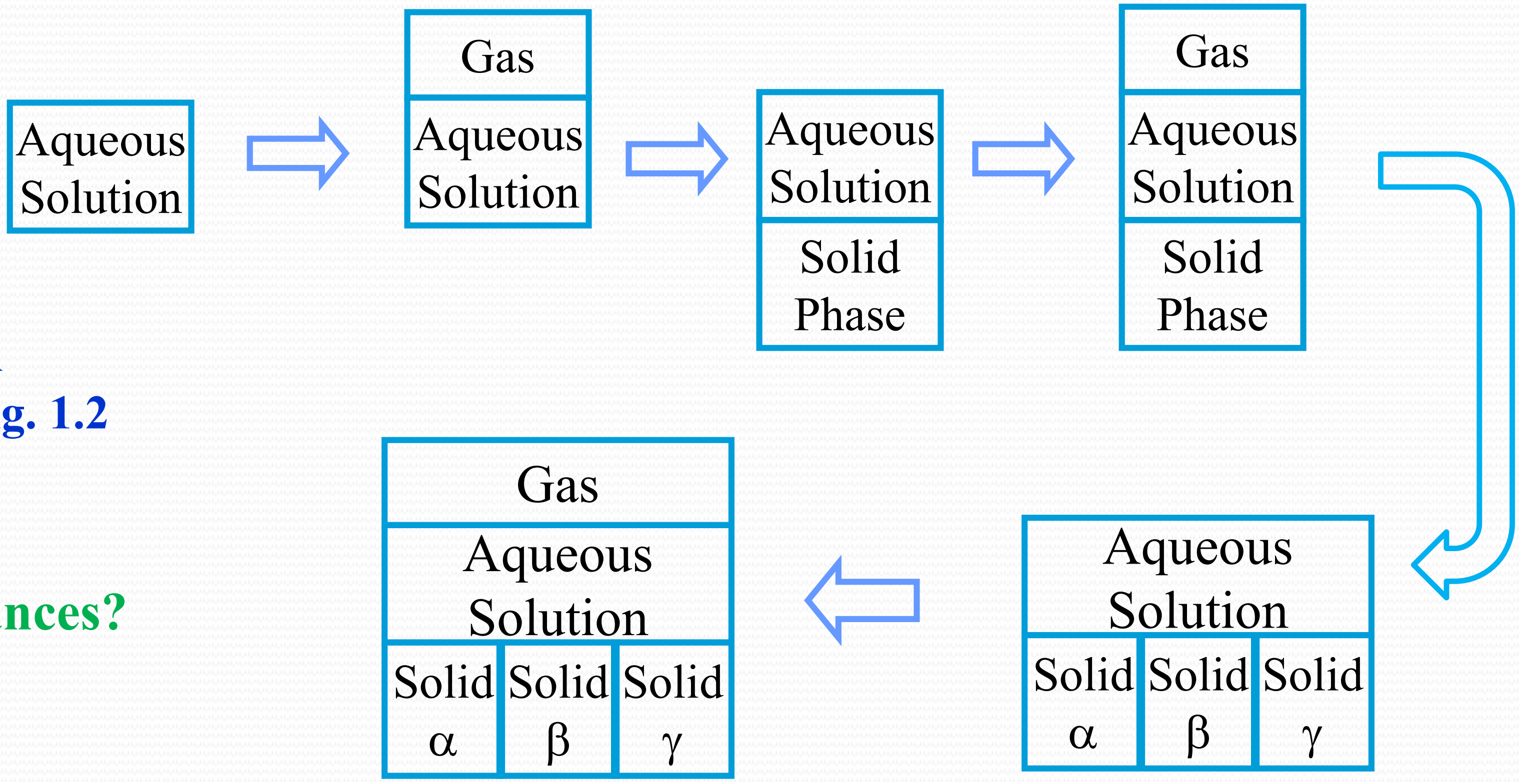
- C



S&M: Fig. 1.1; Pg. 2

Model Complexity: Phases

- Single Phase to multi-phase



Based on S&M: Fig. 1.2 Pg. 4

Abundances?

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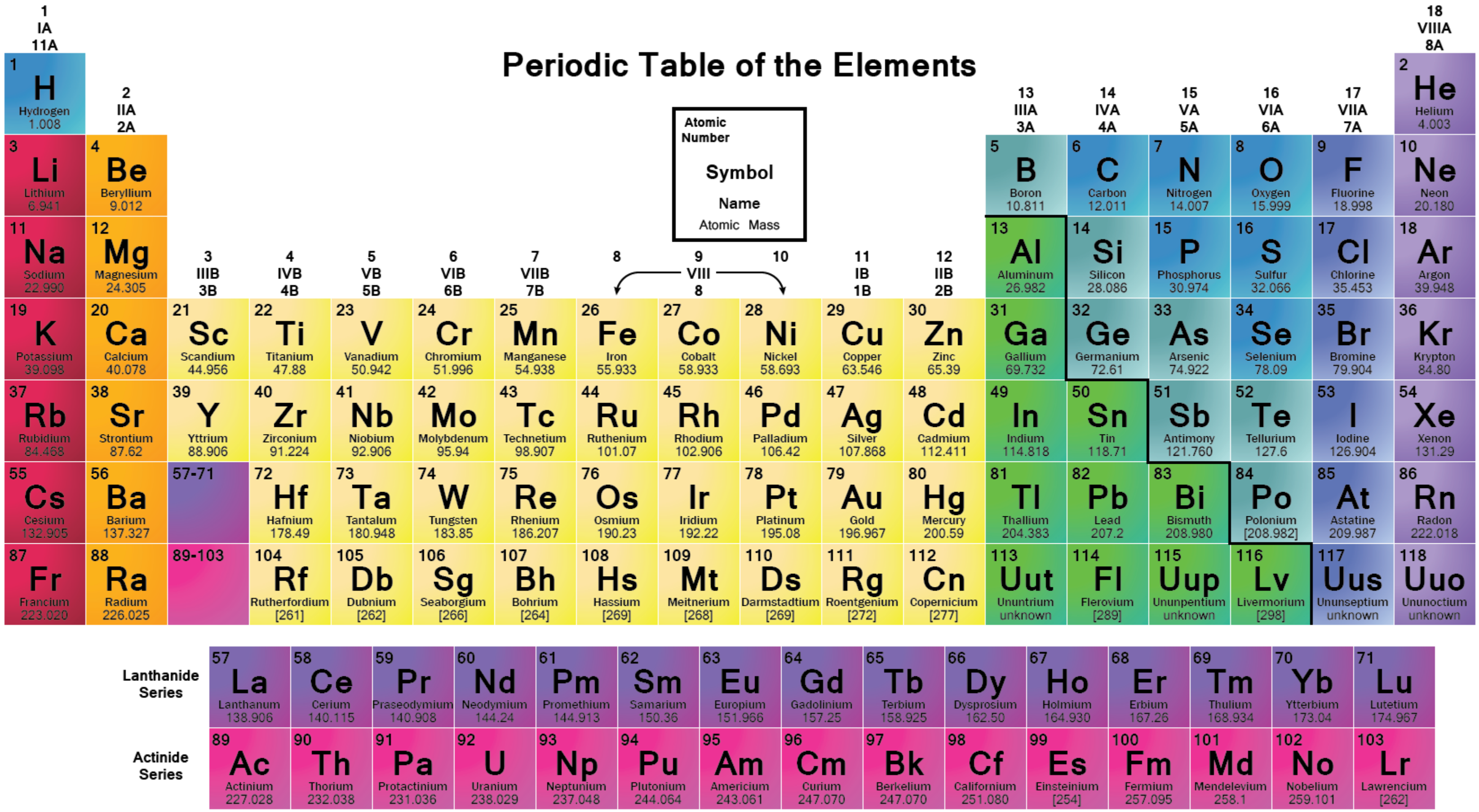
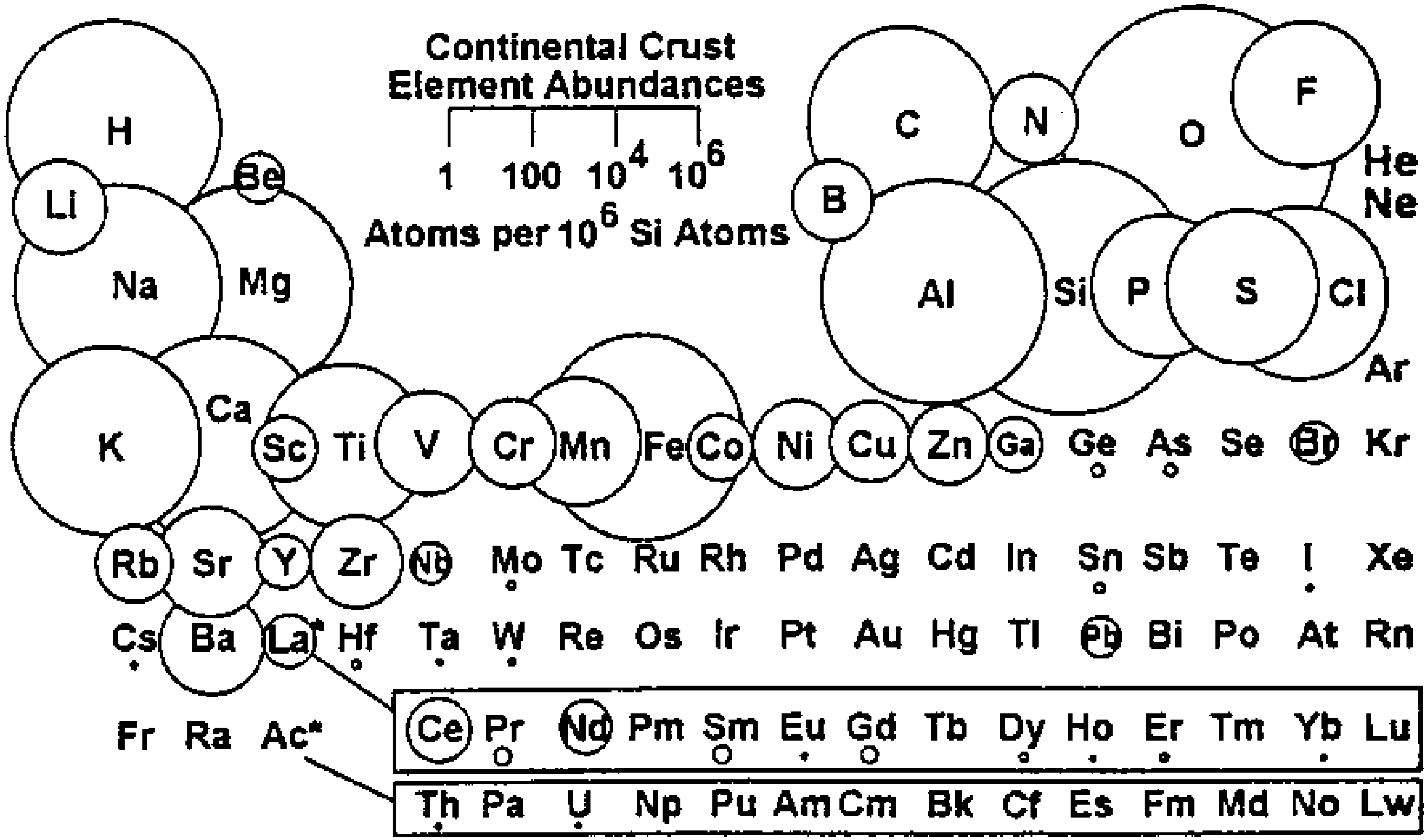


Periodic Table of the Elements
Atomic Number
Symbol
Name
Atomic Mass
1 IA 11A
2 IIA 2A
3 IIIB 3B
4 IVB 4B
5 VB 5B
6 VIB 6B
7 VIIB 7B
8
9 VIII 8
10
11 IB 1B
12 IIB 2B
13 IIIA 3A
14 IVA 4A
15 VA 5A
16 VIA 6A
17 VIIA 7A
18 VIIIA 8A
1 H Hydrogen 1.008
2 He Helium 4.003
3 Li Lithium 6.941
4 Be Beryllium 9.012
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 20.180
11 Na Sodium 22.990
12 Mg Magnesium 24.305
13 Al Aluminum 26.982
14 Si Silicon 28.086
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 44.956
22 Ti Titanium 47.88
23 V Vanadium 50.942
24 Cr Chromium 51.996
25 Mn Manganese 54.938
26 Fe Iron 55.933
27 Co Cobalt 58.933
28 Ni Nickel 58.693
29 Cu Copper 63.546
30 Zn Zinc 65.39
31 Ga Gallium 69.732
32 Ge Germanium 72.61
33 As Arsenic 74.922
34 Se Selenium 78.09
35 Br Bromine 79.904
36 Kr Krypton 84.80
37 Rb Rubidium 84.468
38 Sr Strontium 87.62
39 Y Yttrium 88.906
40 Zr Zirconium 91.224
41 Nb Niobium 92.906
42 Mo Molybdenum 95.94
43 Tc Technetium 98.907
44 Ru Ruthenium 101.07
45 Rh Rhodium 102.906
46 Pd Palladium 106.42
47 Ag Silver 107.868
48 Cd Cadmium 112.411
49 In Indium 114.818
50 Sn Tin 118.71
51 Sb Antimony 121.760
52 Te Tellurium 127.6
53 I Iodine 126.904
54 Xe Xenon 131.29
55 Cs Cesium 132.905
56 Ba Barium 137.327
57-71
72 Hf Hafnium 178.49
73 Ta Tantalum 180.948
74 W Tungsten 183.85
75 Re Rhenium 186.207
76 Os Osmium 190.23
77 Ir Iridium 192.22
78 Pt Platinum 195.08
79 Au Gold 196.967
80 Hg Mercury 200.59
81 Tl Thallium 204.383
82 Pb Lead 207.2
83 Bi Bismuth 208.980
84 Po Polonium [208.982]
85 At Astatine 209.987
86 Rn Radon 222.018
87 Fr Francium 223.020
88 Ra Radium 226.025
89-103
104 Rf Rutherfordium [261]
105 Db Dubnium [262]
106 Sg Seaborgium [266]
107 Bh Bohrium [264]
108 Hs Hassium [269]
109 Mt Meitnerium [268]
110 Ds Darmstadtium [269]
111 Rg Roentgenium [272]
112 Cn Copernicium [277]
113 Uut Ununtrium unknown
114 Fl Flerovium [289]
115 Uup Ununpentium unknown
116 Lv Livermorium [298]
117 Uus Ununseptium unknown
118 Uuo Ununoctium unknown
Lanthanide Series
57 La Lanthanum 138.906
58 Ce Cerium 140.115
59 Pr Praseodymium 140.908
60 Nd Neodymium 144.24
61 Pm Promethium 144.913
62 Sm Samarium 150.36
63 Eu Europium 151.966
64 Gd Gadolinium 157.25
65 Tb Terbium 158.925
66 Dy Dysprosium 162.50
67 Ho Holmium 164.930
68 Er Erbium 167.26
69 Tm Thulium 168.934
70 Yb Ytterbium 173.04
71 Lu Lutetium 174.967
Actinide Series
89 Ac Actinium 227.028
90 Th Thorium 232.038
91 Pa Protactinium 231.036
92 U Uranium 238.029
93 Np Neptunium 237.048
94 Pu Plutonium 244.064
95 Am Americium 243.061
96 Cm Curium 247.070
97 Bk Berkelium 247.070
98 Cf Californium 251.080
99 Es Einsteinium [254]
100 Fm Fermium 257.095
101 Md Mendelevium 258.1
102 No Nobelium 259.101
103 Lr Lawrencium [262]

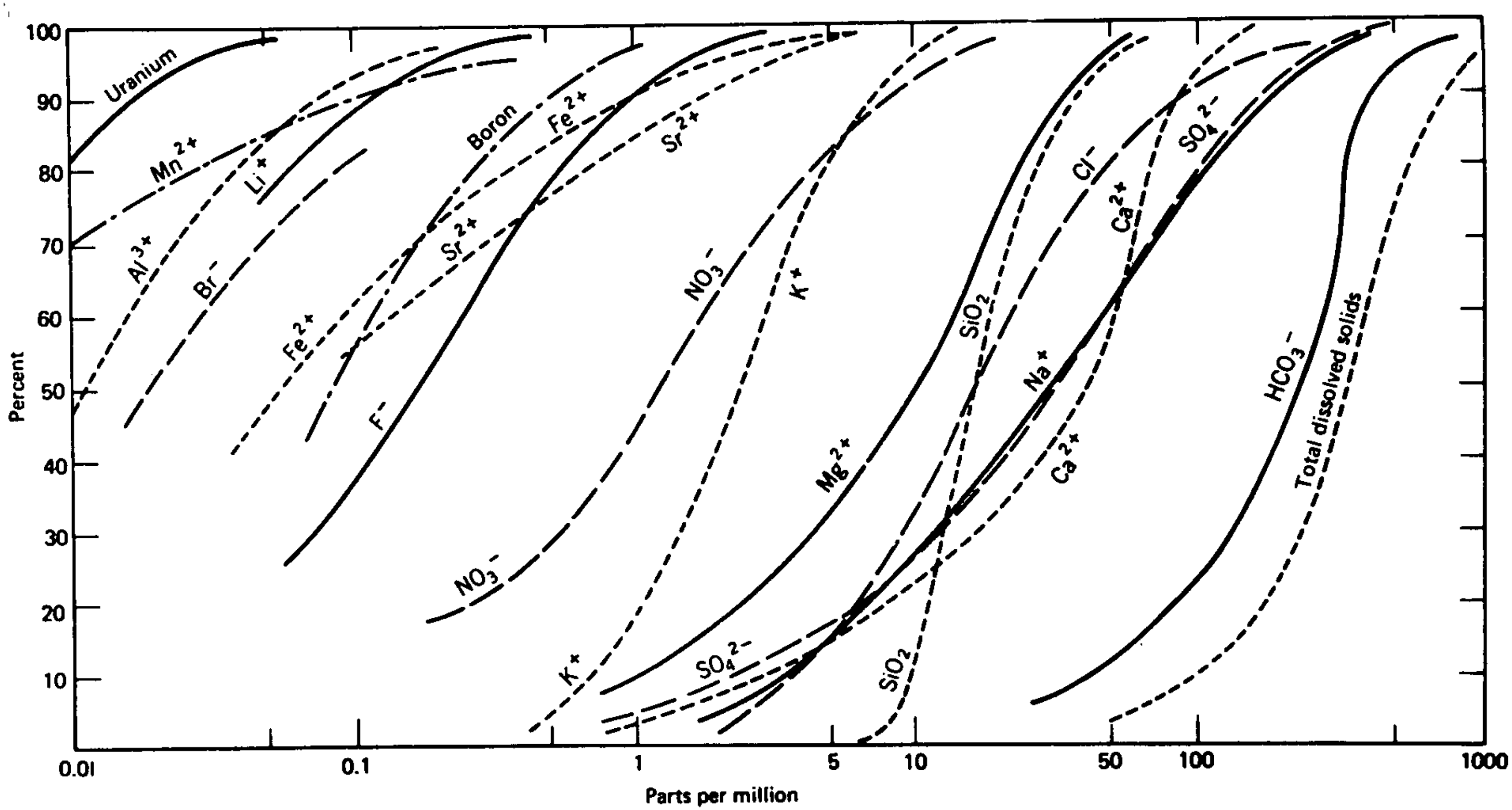
Elemental abundance in crust



- O
- Si
- Al
- Fe
- Ca
- Na
- Mg
- K
- Ti
- H
- P
- Mn
- F

Elemental abundance in fresh water

From: Stumm & Morgan, 1996; Benjamin, 2002; fig 1.1



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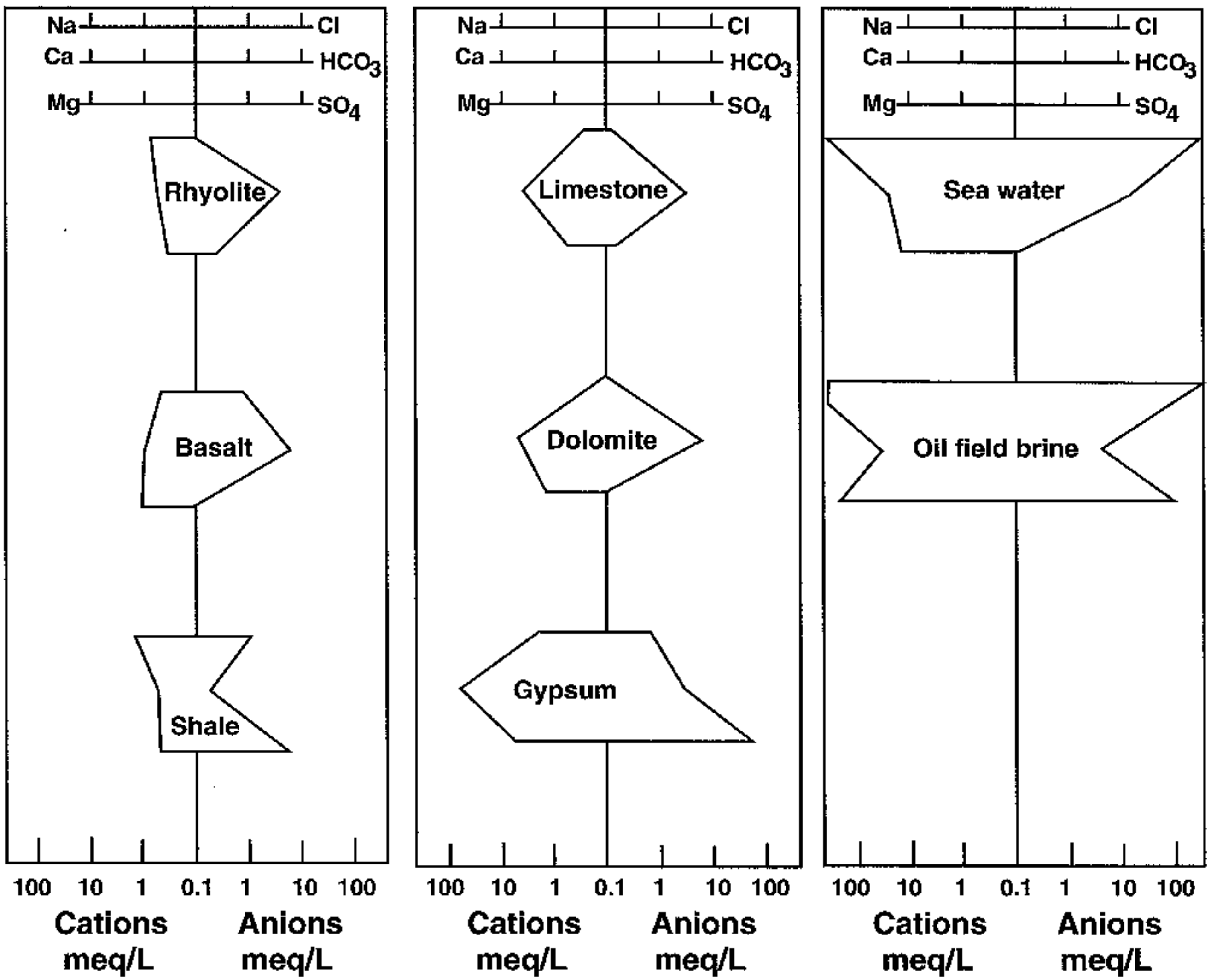
Rock-WQ Connection



- Water Solutes reflect rock mineralogy; e.g.
  - Limestone
    - $CaCO_3$, mostly
  - Dolomite
    - $CaMg(CO_3)_2$, mostly
  - Gypsum
    - $CaSO_4$

"Stiff diagram"
From Hounslow, 1995
Water Quality Data; Analysis and Interpretation

Review

- Units
  - Mass based
  - Molarity
  - Molality
  - Normality
  - Mole fraction
  - Atmospheres
- Chemical Stoichiometry
  - mass balance
  - balancing equations
- Thermodynamics
  - law of mass action
  - types of equilibria

SI Unit prefixes

Factor	Prefix	Symbol
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p
10^{-15}	femto	f
10^{-18}	atto	a

Factor	Prefix	Symbol
10^{1}	deka	da
10^{2}	hecto	d
10^{3}	kilo	k
10^{6}	mega	M
10^{9}	giga	G
10^{12}	tera	T
10^{15}	peta	P
10^{18}	exa	E

Mass Based Concentration Units

- Solid samples

$$\frac{17.5mg\ \text{Pb}}{1kg\ \text{soil}} = \frac{17.5x10^{-3}\ \text{g Pb}}{1\text{x}10^{3}\ \text{g soil}} = 17.5g\ \text{Pb} \Big/ 10^{6}\ g\ \text{soil}$$

$$= 17.5\ \text{ppm}_\text{m}\ \text{Pb in soil}$$

$$1mg / kg = 1\,ppm_m$$
$$1\mu g / kg = 1\,ppb_m$$

- Liquid samples

$$\frac{0.35mg\ \text{Fe}}{1L\ \text{water}}\ x\ \frac{1L\ \text{water}}{10^3\ \text{g water}}$$

Density of Water at 5ºC

$$= \frac{0.35mg\ \text{Fe}}{10^3\ \text{g water}} = \frac{0.35x10^{-3}\ \text{g Fe}}{10^3\ \text{g water}} = 0.35g\ \text{Fe} \Big/ 10^6\ g\ \text{water}$$

$$= 0.35\ \text{ppm}_\text{m}\ \text{Fe in water}$$

Mass/Volume Units	Mass/Mass Units	Typical Applications
g/L (grams/liter)	(parts per thousand)	Stock solutions
mg/L (milligrams/liter) 10^{-3}g/L	**ppm** (parts per million)	Conventional pollutants (DO, nitrate, chloride)
µg/L (micrograms/liter) 10^{-6}g/L	**ppb** (parts per billion)	Trihalomethanes, Phenols.
ng/L (nanograms/liter) 10^{-9}g/L	**ppt** (parts per trillion)	PCBs, Dioxins
pg/L (picograms/liter) 10^{-12}g/L		Pheromones

Gas phase concentration

- Gas samples (compressible)

$$\frac{0.056mg \text{ Ozone}}{1m^3 \text{ air}}$$

  - Could be converted to a ppm_m basis
    - But this would change as we compress the air sample
  - Could also be converted to a ppm_v basis
    - Independent of degree of compression
    - But now we need to convert mass of ozone to volume of ozone

By definition:

$$n = \frac{mass(g)}{GFW}$$

Ideal Gas Law

- An ideal gas
  - Will occupy a certain fixed volume as determined by:

$$PV = nRT$$

$$V = n\frac{RT}{P} = \frac{mass(g)}{GFW}\frac{RT}{P}$$

regardless of the nature of the gas

$\frac{RT}{P}$ =22.4 L at 1 atm, 273.15ºK

  - Where:
    - P=pressure
    - V=volume
    - n=number of moles
    - T=temp
    - R=universal gas constant=0.08205 L-atm/mole-ºK
    - GFW=gram formula weight

Convert mass to moles

- Now we know that ozone's formula is O_3
  - Which means it contains 3 oxygen atoms
  - Therefore the GFW = 3x atomic weight of oxygen in grams or 48 g/mole

$$\frac{0.056mg \text{ Ozone}}{1m^3 \text{ air}}$$

- n=mass(g)/GFW
- $n=0.056x10^{-3}g/(48\ g/mole)$
- $n=0.00117x10^{-3}$ moles

$$\frac{0.00117x10^{-3} moles \text{ Ozone}}{1m^3 \text{ air}}$$

Now determine ppm_v

$$ppm_v = \frac{volume_{ozone}}{volume_{air}}$$

$$= \frac{0.00117x10^{-3}\,moles\ x22.4L/mole}{1m^3\ \text{air}}$$

$$= \frac{0.026x10^{-3}\ \text{L Ozone}}{1\text{x}10^3\ \text{L air}}$$

$$= 0.026\ \text{ppm}_\text{v}\ \text{O}_3\ \text{in air}$$

$$= 26\ \text{ppb}_\text{v}\ \text{O}_3\ \text{in air}$$

Mole & volume fractions

$$\frac{V_i = n_i \frac{RT}{P}}{V_{total} = n_{total} \frac{RT}{P}}$$

- Based on the ideal gas law:
  - The volume fraction (ratio of a component gas volume to the total volume) is the same as the mole fraction of that component
  - Therefore:

$$\frac{V_i}{V_{total}} = \frac{n_i}{n_{total}}$$

Defined as: Volume fraction ($\frac{V_i}{V_{total}}$)

Defined as: mole fraction ($\frac{n_i}{n_{total}}$)

  - And since the fraction of the total is one-millionth of the number of ppm:

$$10^{-6} ppm_v \equiv \frac{V_i}{V_{total}} = \frac{n_i}{n_{total}}$$

$$PV = nRT$$

Partial pressures

$$P = \frac{n}{V}RT$$

- Based on the ideal gas law:
  - And defining the partial pressure (P_i) as the pressure a component gas (i) would exert if all of the other component gases were removed.
  - We can write: $P_i = \frac{n_i}{V_{total}}RT$ and $P_{total} = \frac{n_{total}}{V_{total}}RT$
  - Which leads to: $\frac{P_i}{P_{total}} = \frac{n_i}{n_{total}}$
  - And: $P_i = P_{total}\frac{n_i}{n_{total}} = P_{total}10^{-6}\,ppm_v$

Earth's Atmosphere

Divide by 100 and you get the partial pressure for a total pressure of 1 atm.

Table 2-2. Composition of the Atmosphere*

Compound	Concentration (% volume or moles)	Concentration (ppm_V)
Nitrogen (N_2)	78.1	781,000
Oxygen (O_2)	20.9	209,000
Argon (Ar)	0.93	9,300
Carbon dioxide (CO_2)	0.035	350
Neon (Ne)	0.0018	18
Helium (He)	0.0005	5
Methane (CH_4)	0.00017	1.7
Krypton (Kr)	0.00011	1.1
Hydrogen (H_2)	0.00005	0.500
Nitrous oxide (N_2O)	0.000032	0.316
Ozone (O_3)	0.000002	0.020

Data from Graedel and Crutzen, 1993.

*Values represent concentrations in dry air at remote locations.

- To next lecture