Chemical composition of seawater; Major constituents

OCN 623 – Chemical Oceanography

1/24/2013

Reading

Libes, Chapters 2 - 4

Can skim section 4.3 (Transport of Heat and Salt via Water Movement)

Outline

- Concentration units
- Salinity measurement
- Salinity variability
- Oceanic concentrations of elements
- Element speciation
- Vertical profiles of elements
- Conservative vs. non-conservative elements
- Conditions under which major elements may not be conservative

Concentration Units

Aqueous solutions, gases, and solids

Molar concentration units

1. *Molarity = moles per liter of solution = M*
   - Commonly used terms include:

     mM = millimolar = millimoles per liter = 10^{-3} moles per liter

     μM = micromolar = micromoles per liter = 10^{-6} moles per liter

     nM = nanomolar = nannomoles per liter = 10^{-9} moles per liter

     pM = picomolar = picomoles per liter = 10^{-12} moles per liter

     fM = femtomolar = femtomoles per liter = 10^{-15} moles per liter

2. *Molality = moles per kilogram of solvent = m*
   - No longer in common use except in some computer programs that calculate distribution of chemical species

3. Moles per kilogram of solution
    - The preferred usage in geochemistry, if not in marine chemistry
    - Sometimes defined as "formality"; however, this latter term has been inconsistently defined in the past and is in disuse

4. *Normality = moles of charge equivalents per liter of solution* (analogous to molarity, except that it refers to charge)
    - Can also use equivalents per kg of solution (meq/kg)

5. g-atom/liter = mole/liter (a gram-atom is a mole)

6. Mole fraction (used for mixtures of gases and for solid solutions)

Mass concentration units

1. wt.% = “weight percent” (actually, mass percent)

   = g per 100 g

   - Used for solids

2. ‰ = parts per thousand (ppt)

   = g/kg for liquids and solids

   = mL/L for gas mixtures

3. Per mil = parts per thousand

   - Term is analogous to "per cent“
   - Is used extensively for isotopic analyses – specifies the *deviation* from an isotopic *standard reference material* (SRM)

4. ppm = parts per million

= μg/g or mg/kg for liquids and solids

= μL/L for mixtures of gases = ppmv

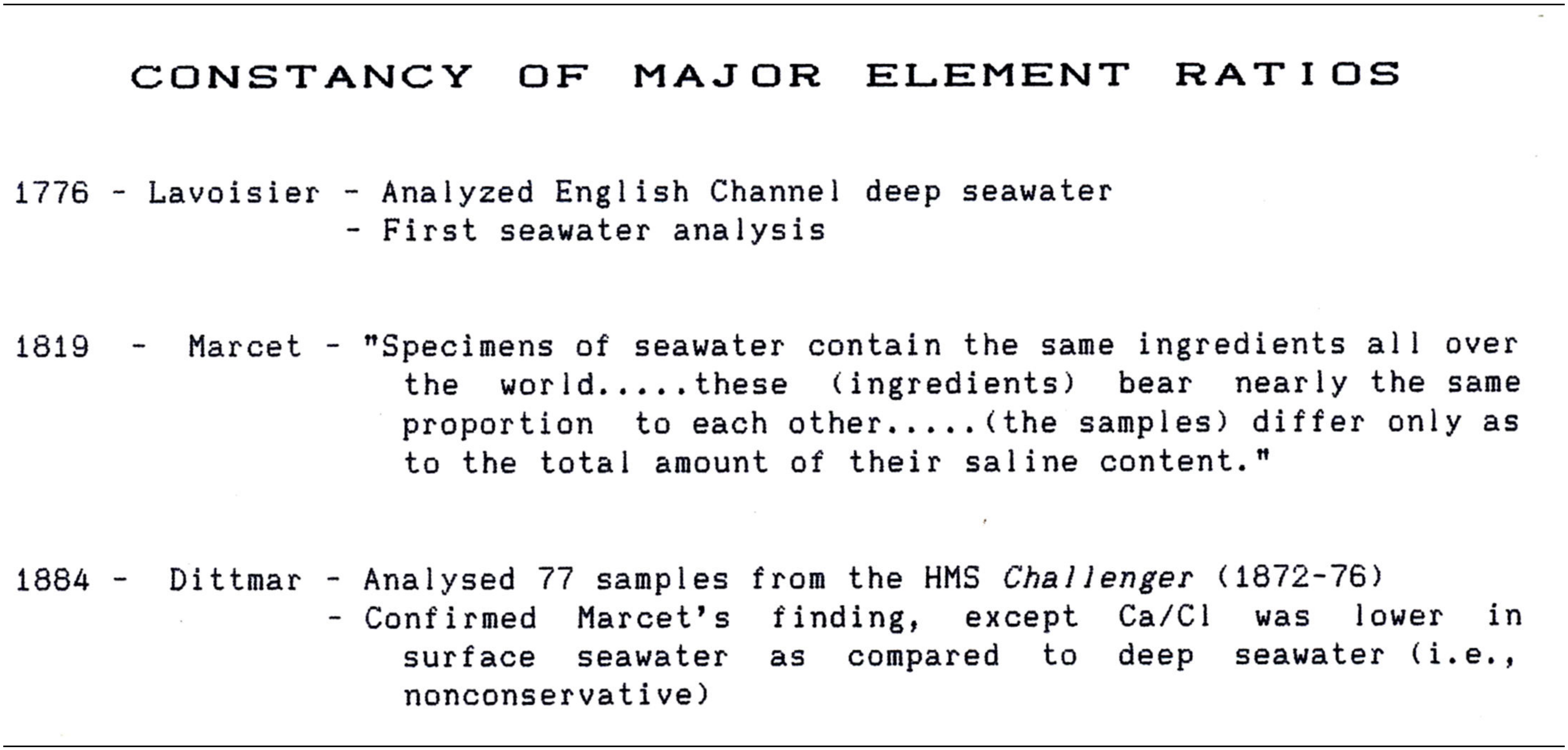
- "ppm" is commonly used for solids, whereas "mg/kg" is generally preferred for liquids

5. ppb = parts per billion

= ng/g or μg/kg

6. mg/L = milligrams per liter

- commonly used for solutions



CONSTANCY OF MAJOR ELEMENT RATIOS

1776 - Lavoisier - Analyzed English Channel deep seawater
- First seawater analysis

1819 - Marcet - "Specimens of seawater contain the same ingredients all over the world.....these (ingredients) bear nearly the same proportion to each other.....(the samples) differ only as to the total amount of their saline content."

1884 - Dittmar - Analysed 77 samples from the HMS *Challenger* (1872-76)
- Confirmed Marcet's finding, except Ca/Cl was lower in surface seawater as compared to deep seawater (i.e., nonconservative)

Thus, there is a need for a measurement of the overall salt content of seawater

Salinity Measurement – The Past

- Salinity is roughly the number of grams of dissolved matter per kilogram of seawater
- Salinity is difficult to measure gravimetrically because many of the salts are hydrophilic, and some decompose on heating to dryness
- From about 1900 to the 1960's, salinity was calculated from *chlorinity Cl*, as determined by titration with silver ion

  Salinity = 1.80655 Cl

- As of 1978, it became standard to calculate "practical salinity" S from measured conductivity (PSS-78)
- Note: <u>practical salinity is unit-less</u>, and is not a SI quantity!

Standard Mean Ocean Water (SMOW): $S \approx 35$, $Cl \approx 19‰$

Salinity Measurement – The Future

www.teos-10.org

A salinity measure (g/kg) that:

- Is more accurate than conductivity-based Practical Salinity
- Handles the spatial variations in the composition of seawater which upset the relationship between
  - Practical Salinity S_P (which is a function of conductivity, temperature and pressure), and
  - Absolute Salinity S_A (defined as the mass of dissolved material (“salt”) per mass of seawater solution....a true “mass fraction”)

Thermodynamic Equation of SeaWater 2010 (TEOS-10) http://www.teos-10.org/

TEOS-10
Thermodynamic Equation Of Seawater - 2010

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TEOS-10 LECTURE SLIDES

HOME

This site is the official source of information about the Thermodynamic Equation Of Seawater - 2010 (TEOS-10), and the way in which it should be used.

TEOS-10 is based on a Gibbs function formulation from which all thermodynamic properties of seawater (density, enthalpy, entropy sound speed, etc.) can be derived in a thermodynamically consistent manner. TEOS-10 was adopted by the Intergovernmental Oceanographic Commission at its 25th Assembly in June 2009 to replace EOS-80 as the official description of seawater and ice properties in marine science.

A significant change compared with past practice is that TEOS-10 uses Absolute Salinity S_A (mass fraction of salt in seawater) as opposed to Practical Salinity S_P (which is essentially a measure of the conductivity of seawater) to describe the salt content of seawater. Ocean salinities now have units of g/kg.

Absolute Salinity (g/kg) is an SI unit of concentration. The thermodynamic properties of seawater, such as density and enthalpy, are now correctly expressed as functions of Absolute Salinity rather than being functions of the conductivity of seawater. Spatial variations of the composition of seawater mean that Absolute Salinity is not simply proportional to Practical Salinity; TEOS-10 contains procedures to correct for these effects.

The document What every oceanographer needs to know about TEOS-10 (the "TEOS-Primer" for short) is a concise summary of the salient theoretical concepts which underpin TEOS-10, while Getting started with the GSW Oceanographic Toolbox of TEOS-10 guides the user through the steps required to process and publish physical oceanographic data using TEOS-10. A detailed explanation of the TEOS-10 thermodynamic description of seawater can be found in the TEOS-10 Manual which has been published by IOC, SCOR and IAPSO. Note that a pdf version of TEOS-10 Lecture Slides is located on the publications page.

Importantly, while Absolute Salinity (g/kg) is the salinity variable that is needed in order to calculate density and other seawater properties, the salinity which should be archived in national data bases continues to be the measured salinity variable, Practical Salinity (PSS-78). To avoid confusion while the use of Practical Salinity in scientific publications is phased out, published values of salinity should be specifically identified as being either Practical Salinity with the symbol S_P or Absolute Salinity with the symbol S_A.

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- Absolute Salinity:
  - Ends the debate in the oceanographic literature about which “salinity” is proper
  - Makes research papers more readable to the outside scientific community
  - Is consistent with SI

- A Reference Composition, consisting of the major components of Atlantic surface seawater, was determined

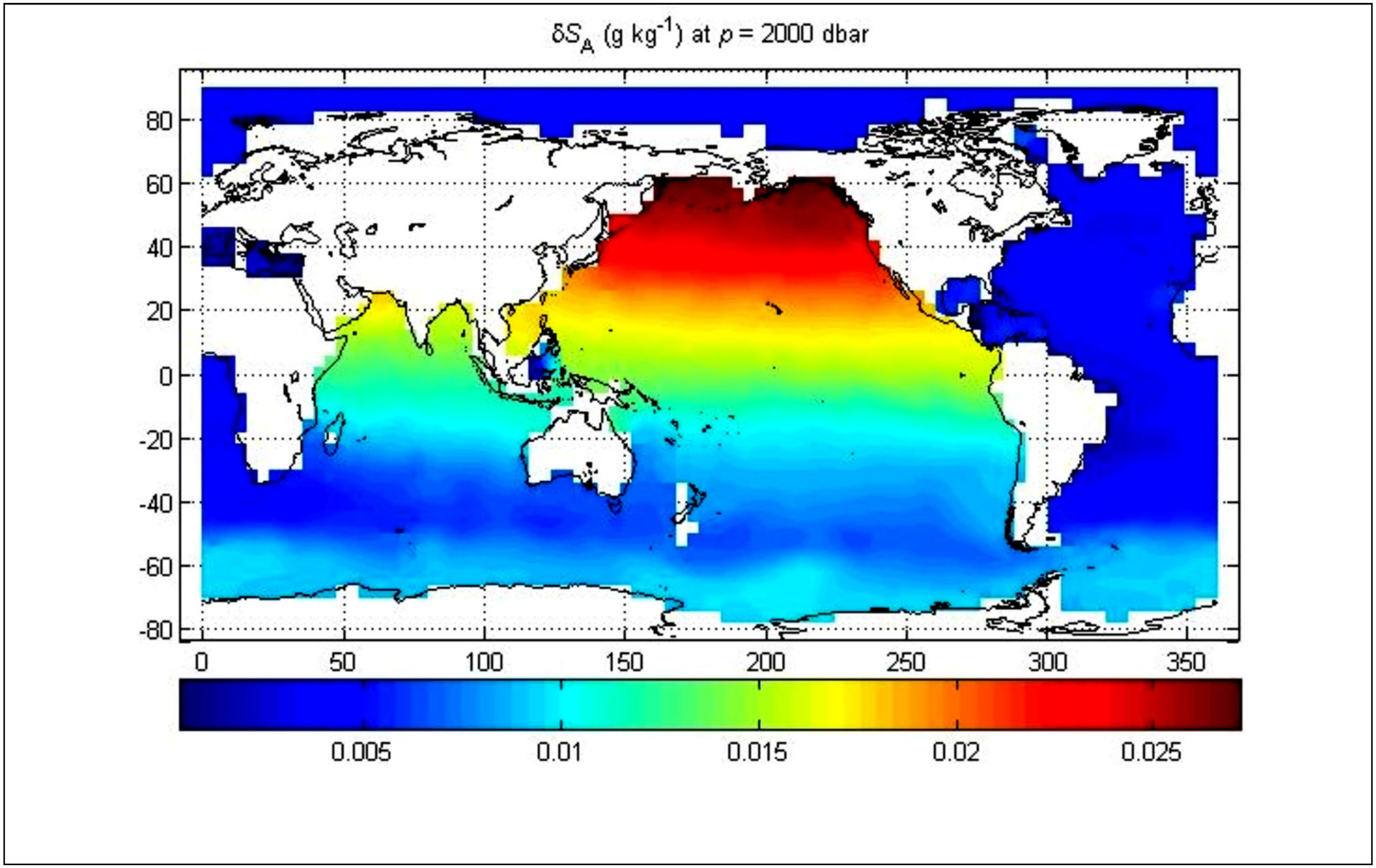
- A new Reference-Composition Salinity S_R is defined to provide the best available estimate of Absolute Salinity

- The value of S_R can be related to Practical Salinity S_P by

$$S_R = (35.165\,04 / 35)\ \mathrm{g\ kg^{-1}} \times S_P$$

- A correction factor (δS_A) accounts for the variation of seawater composition from the standard composition – using either measured parameters (*e.g.*, pH/DIC/ alkalinity/fCO_2, silicate and nitrate) or simply the spatial location (longitude, latitude and pressure)

Spatial distribution of Absolute Salinity Anomaly (δS_A)



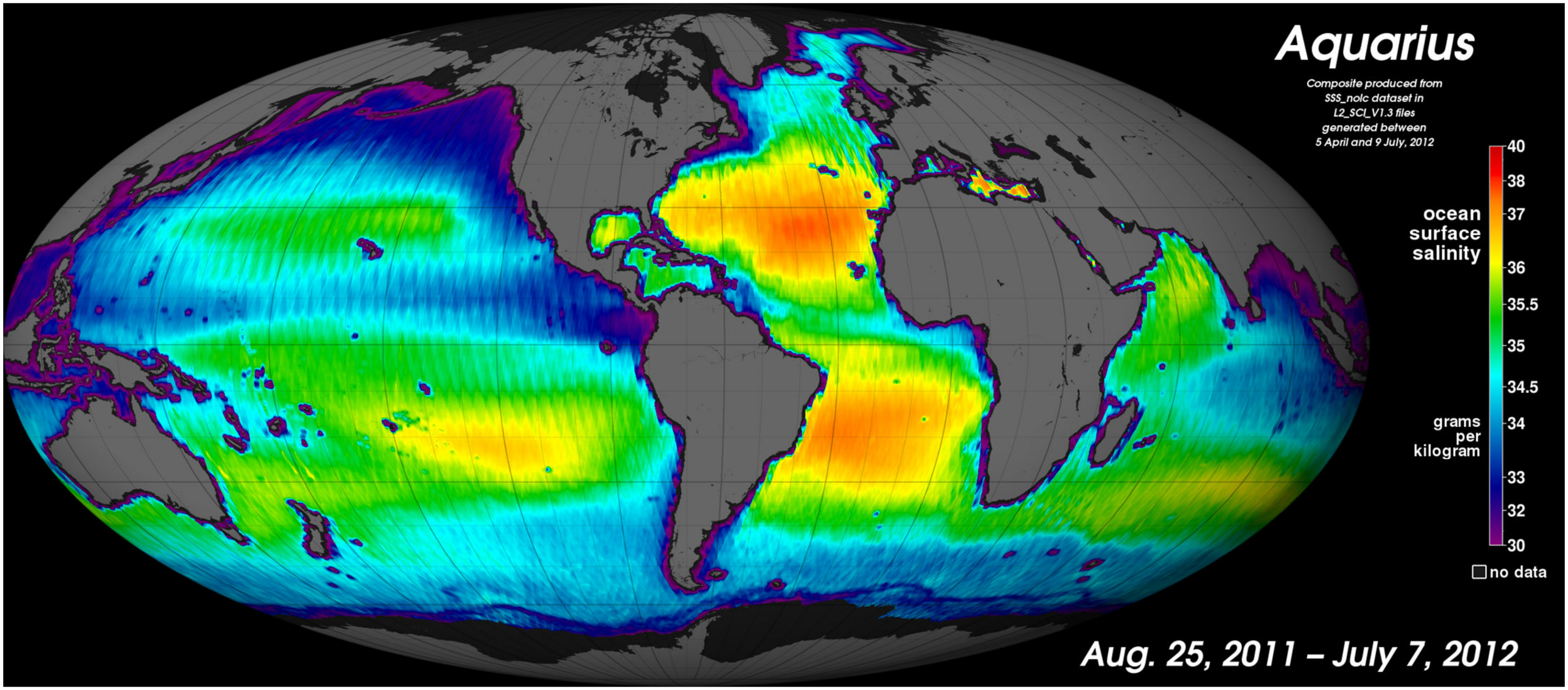
Salinity Variability

- Variations in salinity depend almost entirely on:
    - Balance between evaporation and precipitation
    - Extent of mixing between surface and deeper waters

- The salinity of surface sea water:
    - High (up to 37.5 g/kg) in mid-latitudes due to net evaporation
    - Low at high latitudes (to ~33 g/kg above 40°N and S) and at the equator (~35 g/kg) due to net precipitation

Radiometer-derived sea-surface salinity

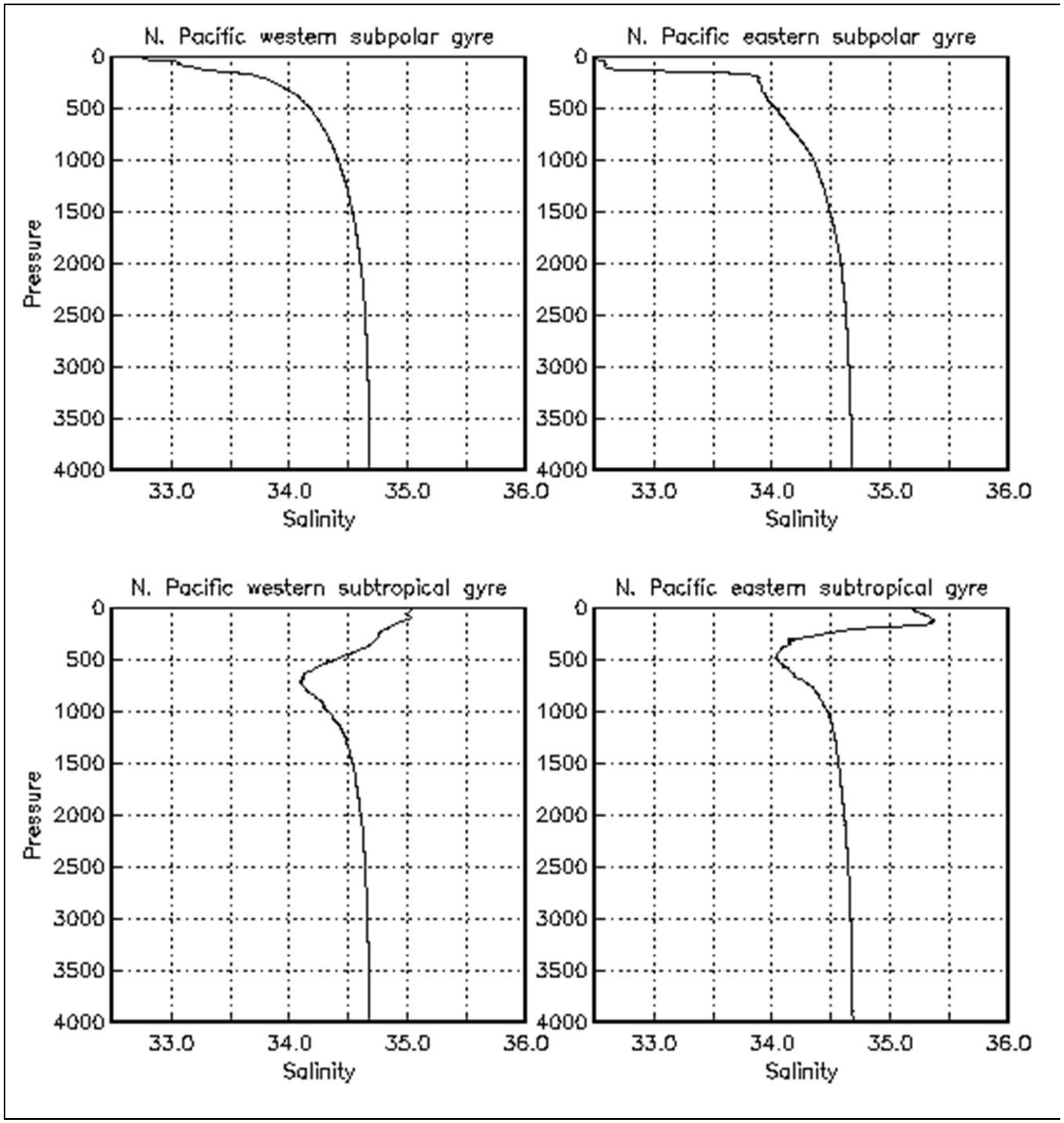
- Aquarius spacecraft



- Set of three radiometers -- sensitive to salinity (1.413 GHz; L-band)
- Scatterometer -- corrects for the surface roughness (1.2 GHz; L-band)

There typically is a *halocline* from the base of the mixed surface layer to about 1000 m depth

- At high latitudes: salinity increases with depth
- At mid and low latitudes: salinity decreases with depth
- Below 1000 m, salinities are generally between 34 and 35 at all latitudes



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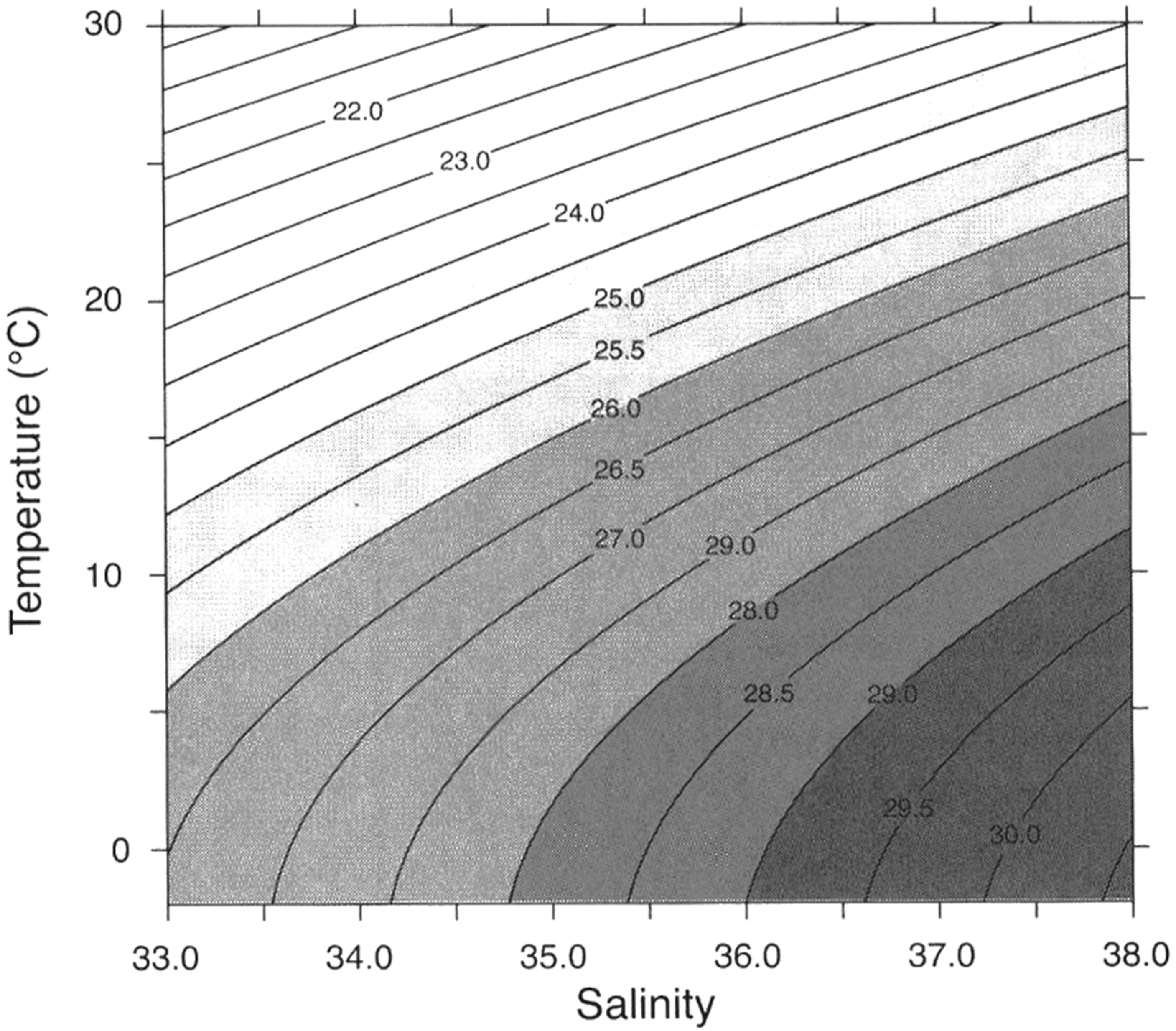
The presence of dissolved salts alters the properties of water:

- The freezing point is lowered from 0° to –1.8°C
- The temperature of maximum density is lowered from +4° to –1.8°C. (Freshwater is less dense at 0°C than at +4°C!)
- This drives the global thermohaline circulation because it causes the coldest (and saltiest) water to sink
  - Temperature and salinity determine the density of seawater →



Sarmiento & Gruber, 2006

The “density anomaly” of seawater in “mass per volume in excess of 1 kg/m^3, multiplied by 1000”, is designated by the symbol “σ” (sigma)

In this notation, a specific gravity of 1.025 kg/m^3 is expressed as σ = 25

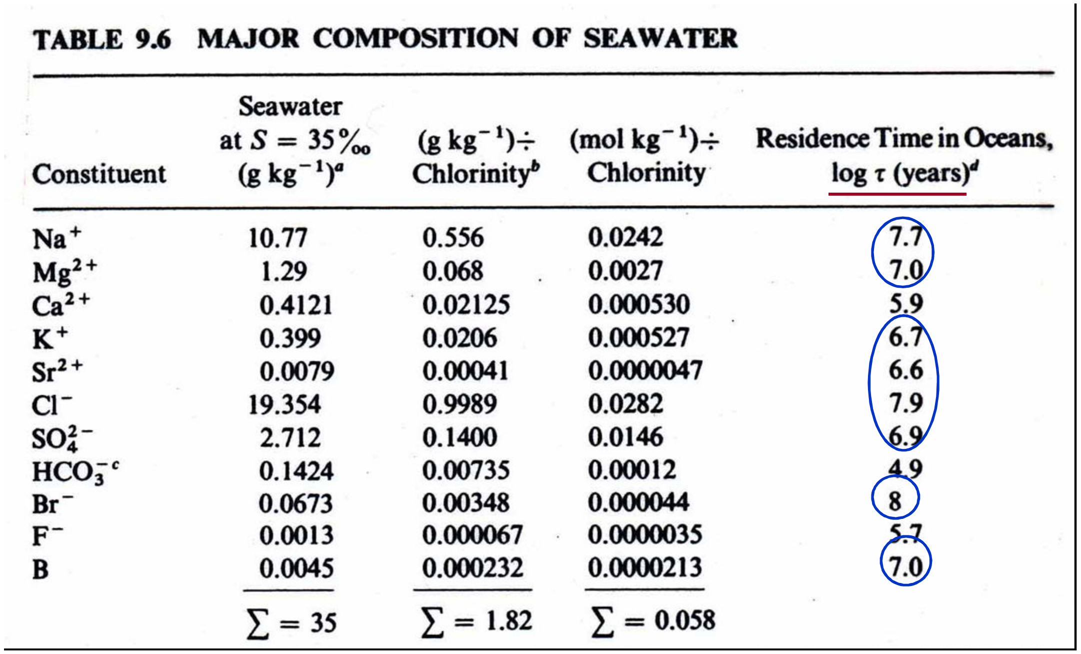


TABLE 9.6 MAJOR COMPOSITION OF SEAWATER

Constituent	Seawater at $S = 35‰$ $(g\ kg^{-1})^a$	$(g\ kg^{-1})\div$ Chlorinity^b	$(mol\ kg^{-1})\div$ Chlorinity	Residence Time in Oceans, $\log \tau$ (years)^d
Na^+	10.77	0.556	0.0242	7.7
Mg^{2+}	1.29	0.068	0.0027	7.0
Ca^{2+}	0.4121	0.02125	0.000530	5.9
K^+	0.399	0.0206	0.000527	6.7
Sr^{2+}	0.0079	0.00041	0.0000047	6.6
Cl^-	19.354	0.9989	0.0282	7.9
SO_4^{2-}	2.712	0.1400	0.0146	6.9
$HCO_3^{-\,c}$	0.1424	0.00735	0.00012	4.9
Br^-	0.0673	0.00348	0.000044	8
F^-	0.0013	0.000067	0.0000035	5.7
B	0.0045	0.000232	0.0000213	7.0
	$\sum = 35$	$\sum = 1.82$	$\sum = 0.058$	

Residence time (y): $\tau \equiv M/Q$

M = mass of element in ocean (mol)

Q = input from rivers ($mol\ y^{-1}$) = c f

c = conc of element in average river water ($mol\ kg^{-1}$)

f = annual flux of river water ($kg\ y^{-1}$)

Note conservation of neutrality

$\log \tau \geq 6.5$

($\tau \geq 3.2 \times 10^6$ y)

Conservative elements

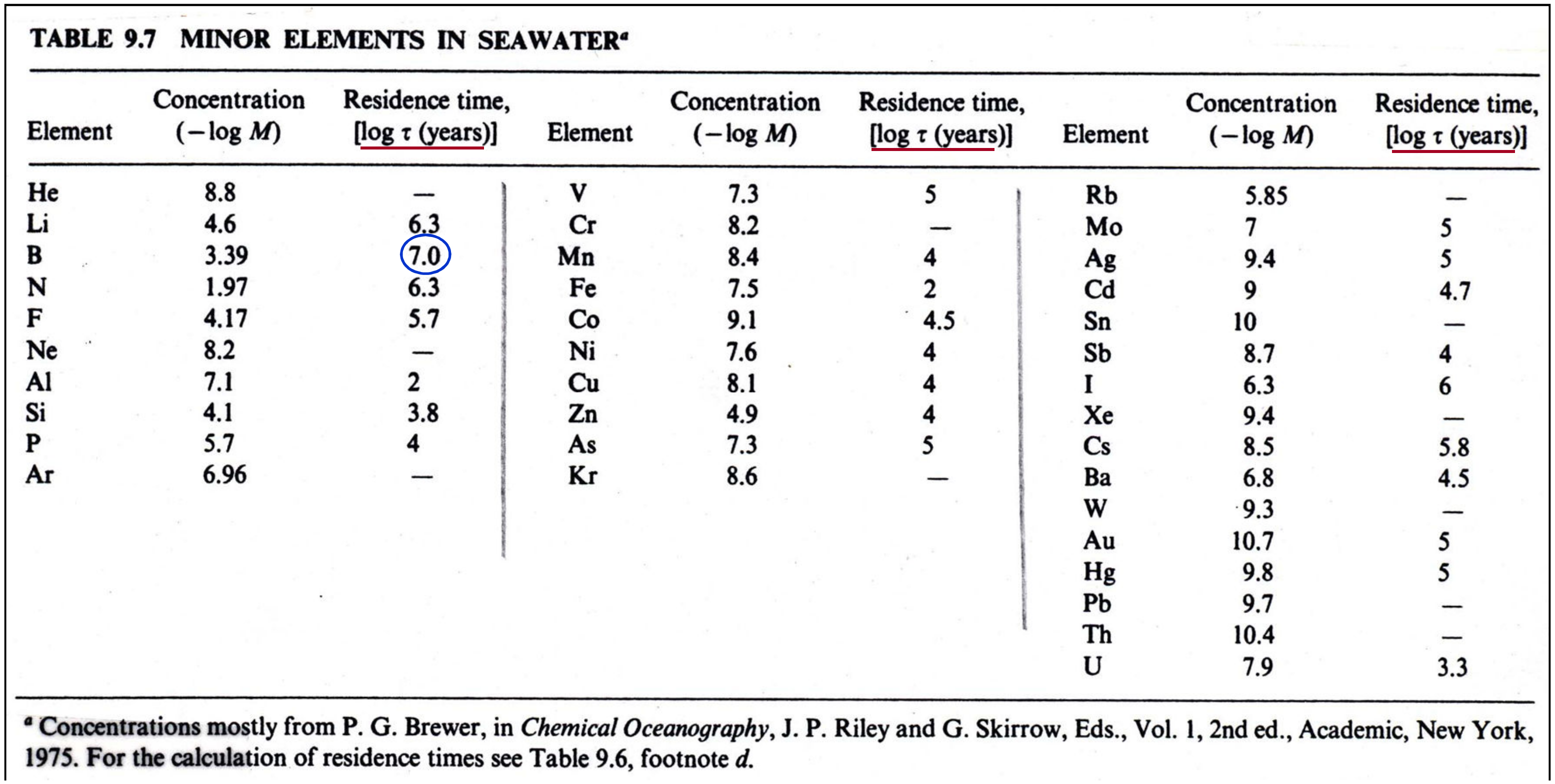


TABLE 9.7 MINOR ELEMENTS IN SEAWATER[a]

Element	Concentration $(-\log M)$	Residence time, $[\log \tau$ (years)$]$	Element	Concentration $(-\log M)$	Residence time, $[\log \tau$ (years)$]$	Element	Concentration $(-\log M)$	Residence time, $[\log \tau$ (years)$]$
He	8.8	—	V	7.3	5	Rb	5.85	—
Li	4.6	6.3	Cr	8.2	—	Mo	7	5
B	3.39	7.0	Mn	8.4	4	Ag	9.4	5
N	1.97	6.3	Fe	7.5	2	Cd	9	4.7
F	4.17	5.7	Co	9.1	4.5	Sn	10	—
Ne	8.2	—	Ni	7.6	4	Sb	8.7	4
Al	7.1	2	Cu	8.1	4	I	6.3	6
Si	4.1	3.8	Zn	4.9	4	Xe	9.4	—
P	5.7	4	As	7.3	5	Cs	8.5	5.8
Ar	6.96	—	Kr	8.6	—	Ba	6.8	4.5
						W	9.3	—
						Au	10.7	5
						Hg	9.8	5
						Pb	9.7	—
						Th	10.4	—
						U	7.9	3.3

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[a] Concentrations mostly from P. G. Brewer, in *Chemical Oceanography*, J. P. Riley and G. Skirrow, Eds., Vol. 1, 2nd ed., Academic, New York, 1975. For the calculation of residence times see Table 9.6, footnote *d*.

Stumm & Morgan (1981)

Mean Oceanic Concentrations of Elements

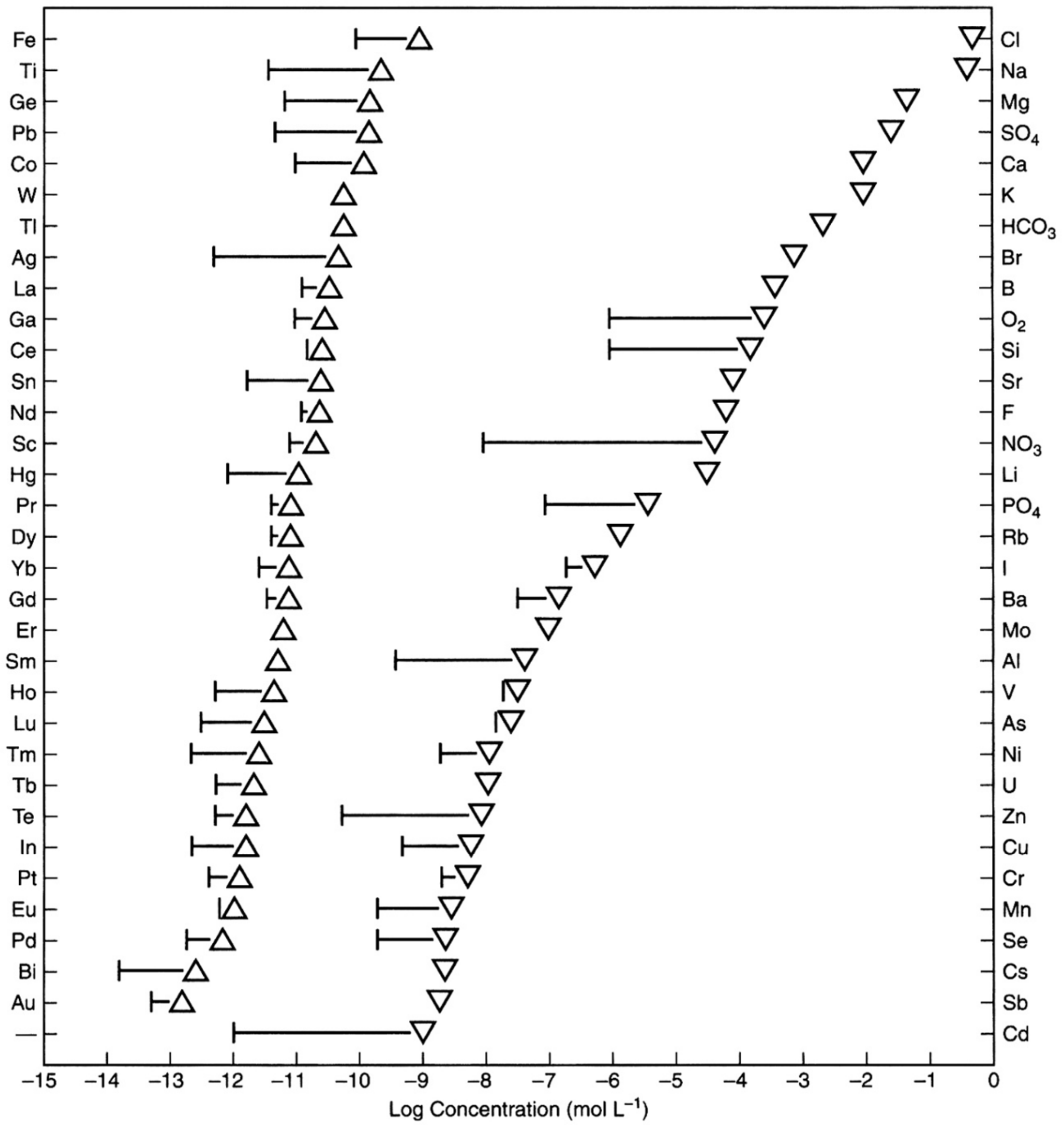


FIGURE 1.1.1: A graphical illustration of the dissolved concentrations of elements and some compounds expressed as log to the base 10 [*Johnson and Jannasch*, 1994]. The higher concentration elements are given on the right-hand side and the lower concentration elements are given on the left-hand side.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

Sarmiento & Gruber 2006

Element Speciation

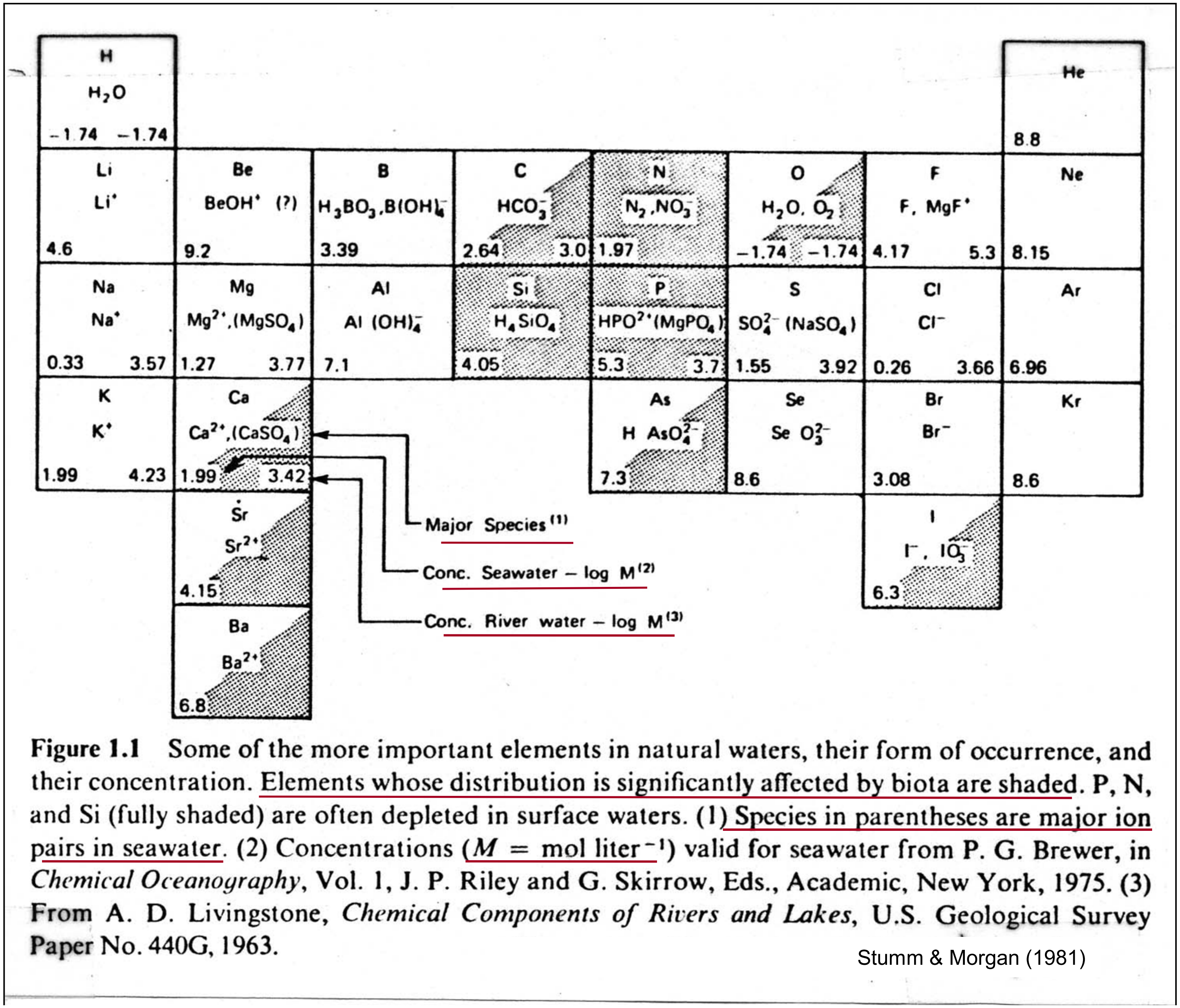
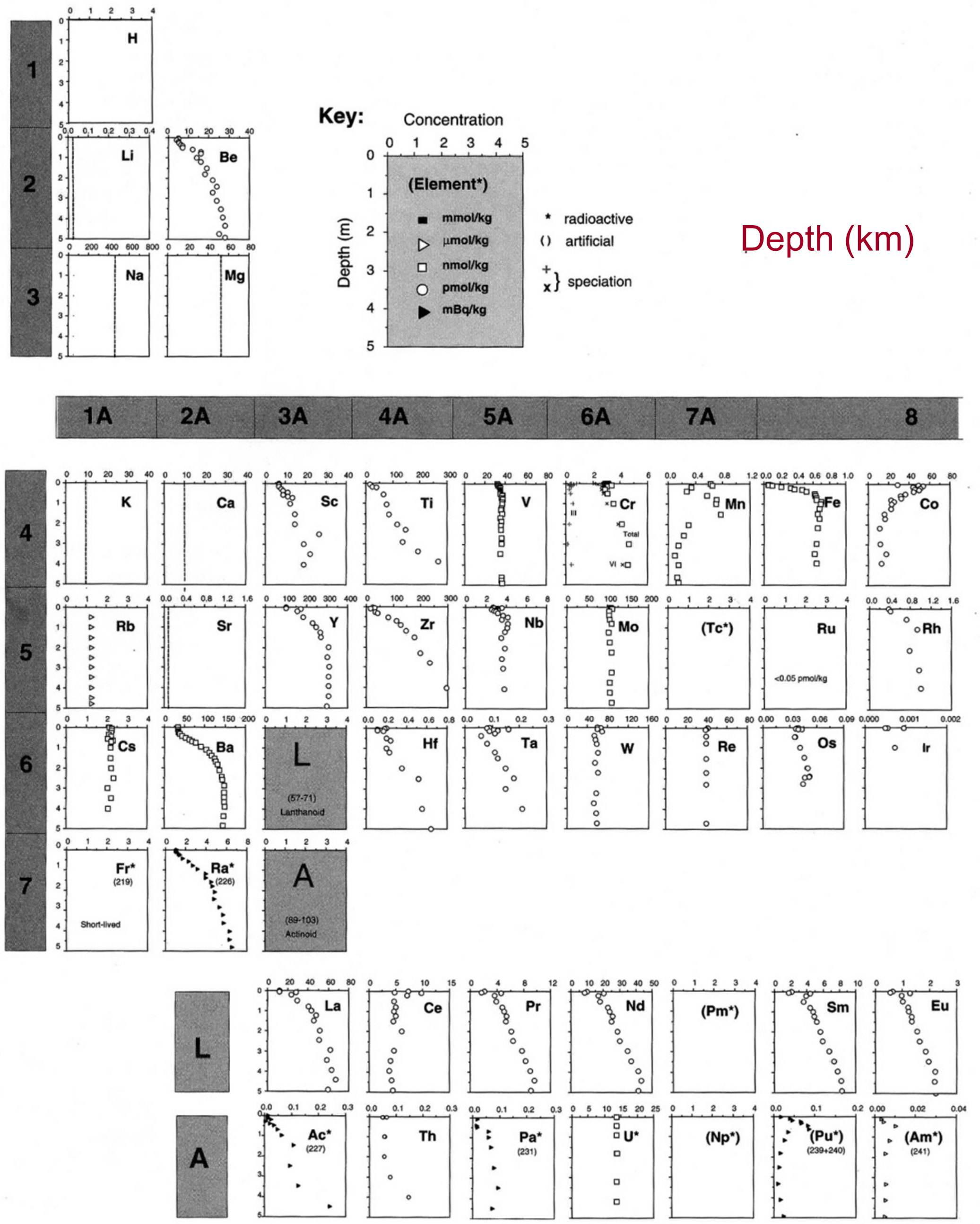


Figure 1.1 Some of the more important elements in natural waters, their form of occurrence, and their concentration. Elements whose distribution is significantly affected by biota are shaded. P, N, and Si (fully shaded) are often depleted in surface waters. (1) Species in parentheses are major ion pairs in seawater. (2) Concentrations (M = mol liter^{-1}) valid for seawater from P. G. Brewer, in *Chemical Oceanography*, Vol. 1, J. P. Riley and G. Skirrow, Eds., Academic, New York, 1975. (3) From A. D. Livingstone, *Chemical Components of Rivers and Lakes*, U.S. Geological Survey Paper No. 440G, 1963.

Stumm & Morgan (1981)

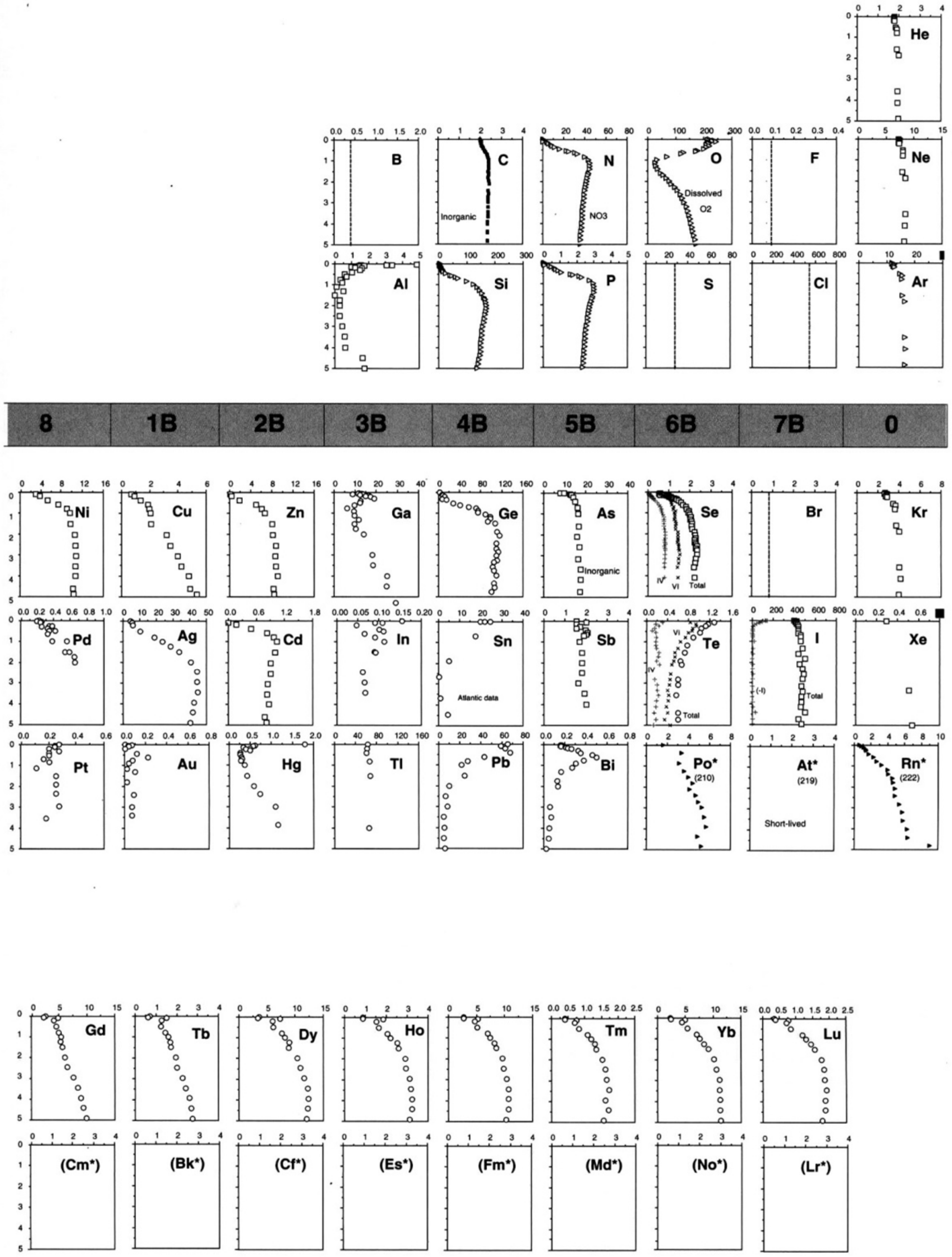
Vertical Profiles of Elements in the Pacific Ocean



Depth (km)

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 ■CO_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

Conservative *vs.* Nonconservative Elements

- *Conservative*
  - Non-reactive
  - Thus, remain in ocean for long periods (long residence time
  - Examples: Na, K, S, Cl, Br, Sr, B ("*conservative major elements*")

- *Nonconservative*
  - Biologically and/or chemically reactive
  - Examples: C, P, Fe

Conditions Under Which Major Elements May Not be Conservative

- Estuaries and Land-locked Seas
  - Examples: Black Sea, Baltic Sea, Chesapeake Bay
  - These element rations are much larger in river water than in seawater:

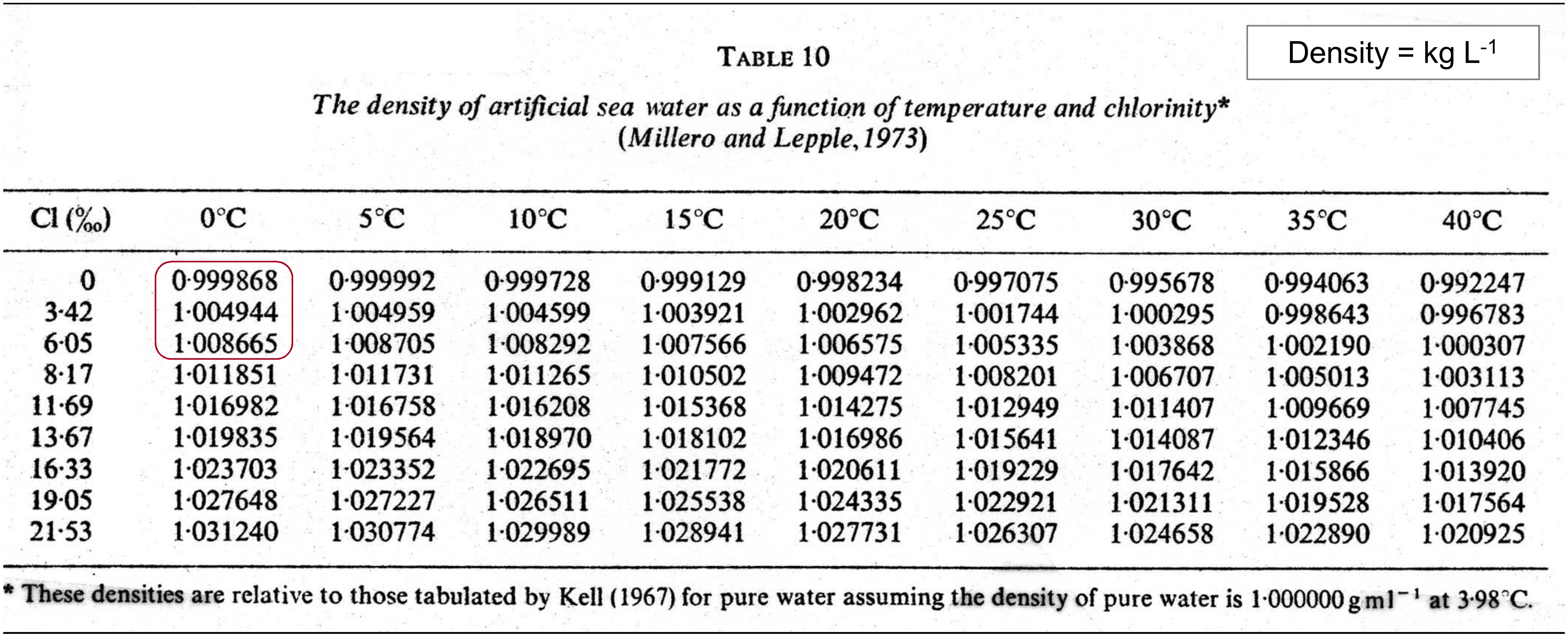
$$\frac{SO_4^{2-}}{Cl^-} \quad \frac{HCO_3^-}{Cl^-} \quad \frac{K^+}{Na^+} \quad \frac{Mg^{2+}}{Na^+} \quad \frac{Ca^{2+}}{Mg^{2+}}$$

  - Runoff can be a major effect for these ions

- Anoxic Basins
  - Sulfate reduction:

$$SO_4^{2-} + CH_2O + 4H^+ + 4e^- \rightarrow HS^- + HCO_3^- + 2H_2O$$

- Freezing
  - Fractionates major ions
  - Example: Sea ice contains proportionally more SO_4^{2-} than Cl^-



Density = kg L^{-1}

TABLE 10

*The density of artificial sea water as a function of temperature and chlorinity**
(Millero and Lepple, 1973)

Cl (‰)	0°C	5°C	10°C	15°C	20°C	25°C	30°C	35°C	40°C
0	0·999868	0·999992	0·999728	0·999129	0·998234	0·997075	0·995678	0·994063	0·992247
3·42	1·004944	1·004959	1·004599	1·003921	1·002962	1·001744	1·000295	0·998643	0·996783
6·05	1·008665	1·008705	1·008292	1·007566	1·006575	1·005335	1·003868	1·002190	1·000307
8·17	1·011851	1·011731	1·011265	1·010502	1·009472	1·008201	1·006707	1·005013	1·003113
11·69	1·016982	1·016758	1·016208	1·015368	1·014275	1·012949	1·011407	1·009669	1·007745
13·67	1·019835	1·019564	1·018970	1·018102	1·016986	1·015641	1·014087	1·012346	1·010406
16·33	1·023703	1·023352	1·022695	1·021772	1·020611	1·019229	1·017642	1·015866	1·013920
19·05	1·027648	1·027227	1·026511	1·025538	1·024335	1·022921	1·021311	1·019528	1·017564
21·53	1·031240	1·030774	1·029989	1·028941	1·027731	1·026307	1·024658	1·022890	1·020925

* These densities are relative to those tabulated by Kell (1967) for pure water assuming the density of pure water is 1·000000 g ml^{-1} at 3·98°C.

Riley & Skirrow (1975) *Chemical Oceanography*, Vol. 3, 2nd Ed.

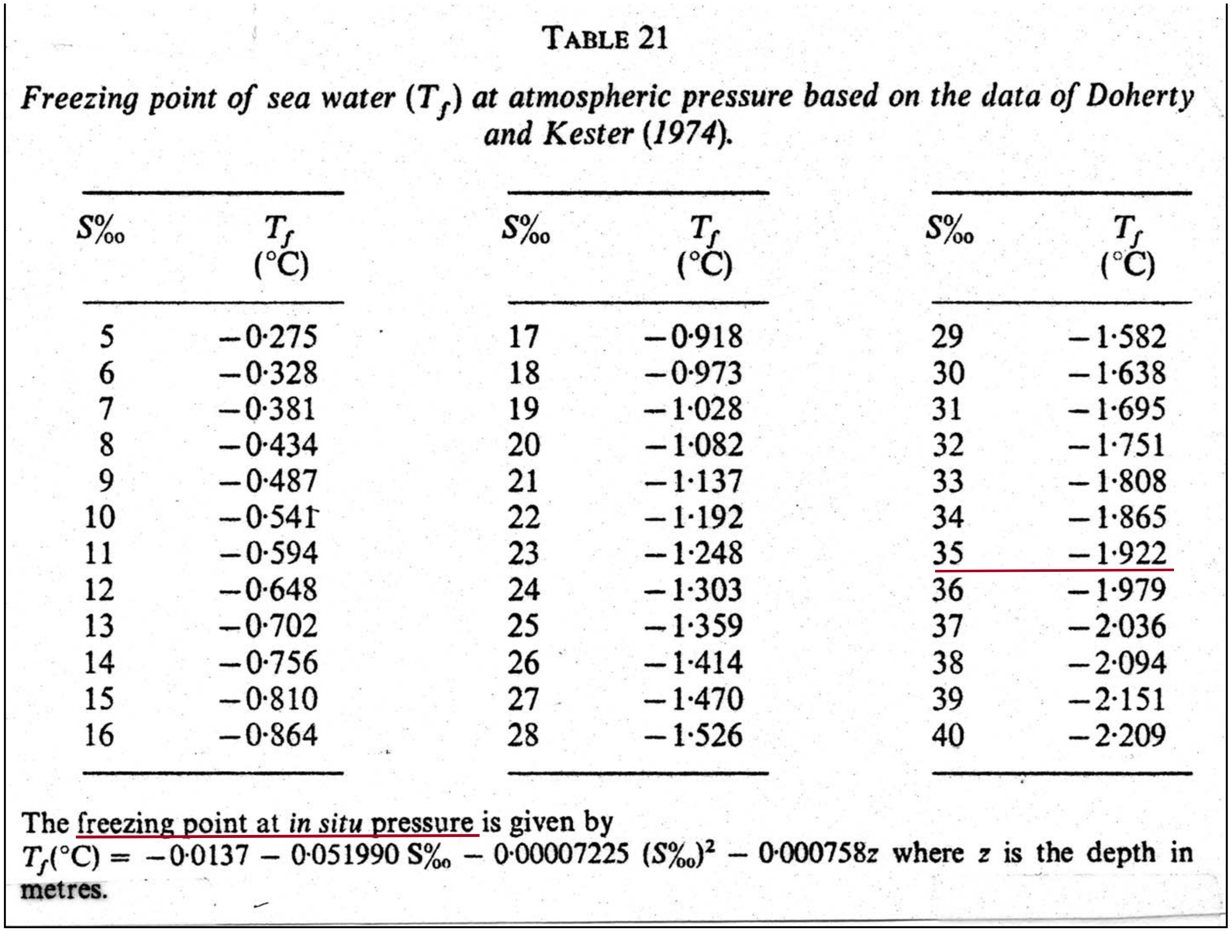


TABLE 21

Freezing point of sea water (T_f) at atmospheric pressure based on the data of Doherty and Kester (1974).

S‰	T_f (°C)	S‰	T_f (°C)	S‰	T_f (°C)
5	−0·275	17	−0·918	29	−1·582
6	−0·328	18	−0·973	30	−1·638
7	−0·381	19	−1·028	31	−1·695
8	−0·434	20	−1·082	32	−1·751
9	−0·487	21	−1·137	33	−1·808
10	−0·541	22	−1·192	34	−1·865
11	−0·594	23	−1·248	35	−1·922
12	−0·648	24	−1·303	36	−1·979
13	−0·702	25	−1·359	37	−2·036
14	−0·756	26	−1·414	38	−2·094
15	−0·810	27	−1·470	39	−2·151
16	−0·864	28	−1·526	40	−2·209

The freezing point at *in situ* pressure is given by $T_f(^\circ\mathrm{C}) = -0{\cdot}0137 - 0{\cdot}051990\,S‰ - 0{\cdot}00007225\,(S‰)^2 - 0{\cdot}000758z$ where z is the depth in metres.

- Note: The “freezing point” of seawater is the ***initial*** freezing point (*i.e.*, the temperature at which an infinitely small amount of ice is in equilibrium with the solution)
- As soon as any ice has formed, the concentration of dissolved material in the remaining brine increases
- Hence, the formation of additional ice can only take place at lower temperature

- Submarine Volcanism
    - Hydrothermal fluids have major- and minor-element ratios different that those of seawater (*e.g.*, higher Si; lower SO_4^{2-} and Mg^{2+})
- Evaporation of Seawater in Isolated Basins

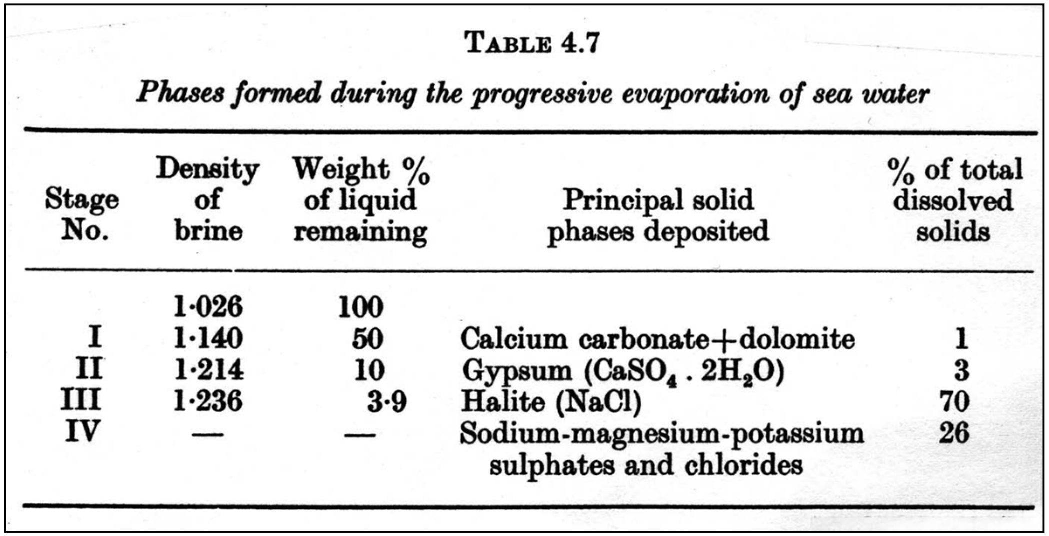


TABLE 4.7

Phases formed during the progressive evaporation of sea water

Stage No.	Density of brine	Weight % of liquid remaining	Principal solid phases deposited	% of total dissolved solids
	1·026	100		
I	1·140	50	Calcium carbonate+dolomite	1
II	1·214	10	Gypsum ($CaSO_4 . 2H_2O$)	3
III	1·236	3·9	Halite (NaCl)	70
IV	—	—	Sodium-magnesium-potassium sulphates and chlorides	26

Lab experiment

- In nature: organic matter oxidation consumes oxygen due to stagnant conditions, then sulfate reduction occurs
- Thus, sulfate minerals are rarely found in natural marine evaporite deposits