An Outline

of Marine Chemistry

W. G. Breck

THE OCEAN AS A CHEMICAL ENVIRONMENT

Marine chemistry is one of the interdisciplines concerned with the total science of the oceans, others being marine geology, physical oceanography, marine biology, and more recently a separate study called biological oceanography. The word "marine", strictly speaking, refers to salt water, which is important in that about 71 percent of our planet's area is covered by salt seas. So marine chemistry is planetary science in scope and outlook and in seeking planetary relations goes far beyond the mere analysis of water samples. Fresh waters have importance, too, especially in Canada, and more especially in this area, but an understanding of marine chemistry includes the same principles for fresh waters. Besides, fresh waters grade into and interact with the oceans, for rivers and glaciers bring burdens of continental material whose reactions are part of the study of marine chemistry.

The student of marine science must be prepared to cross the boundaries of traditional science. And he must also be ready to cross the physical boundaries of the sea; for to understand the sea water itself requires an appreciation of its interaction with the surroundings: the cosmosphere, the atmosphere, the lithosphere and the biosphere, including the effects of man's activities.

```
┌─────────────┐            ┌──────────┐              ┌──────┐
│ CONTINENTS  │            │ATMOSPHERE│              │COSMOS│
│ - weathering│            └──────────┘              └──────┘
│ - erosion   │                                   Transport
│ - volcanism │                                   processes:
└─────────────┘                                   - rivers
                                                   - glaciers
                                                   - winds
```

$$\text{THE SEAS (including marine life)}$$

$$\begin{pmatrix}\text{dissolved}\\ \text{phases}\end{pmatrix} \qquad \begin{pmatrix}\text{particulate}\\ \text{phases}\end{pmatrix}$$

$$+\ \frac{dA}{dt}$$

$$-\ \frac{dA}{dt}$$

THE SEDIMENTS
(Pore solutions, Hydrogenous, Biogenous,
Lithogenous, Cosmogenous sediments)

Residence time $T = \dfrac{A}{dA/dt}$, at steady state,
where A is the concentration of any
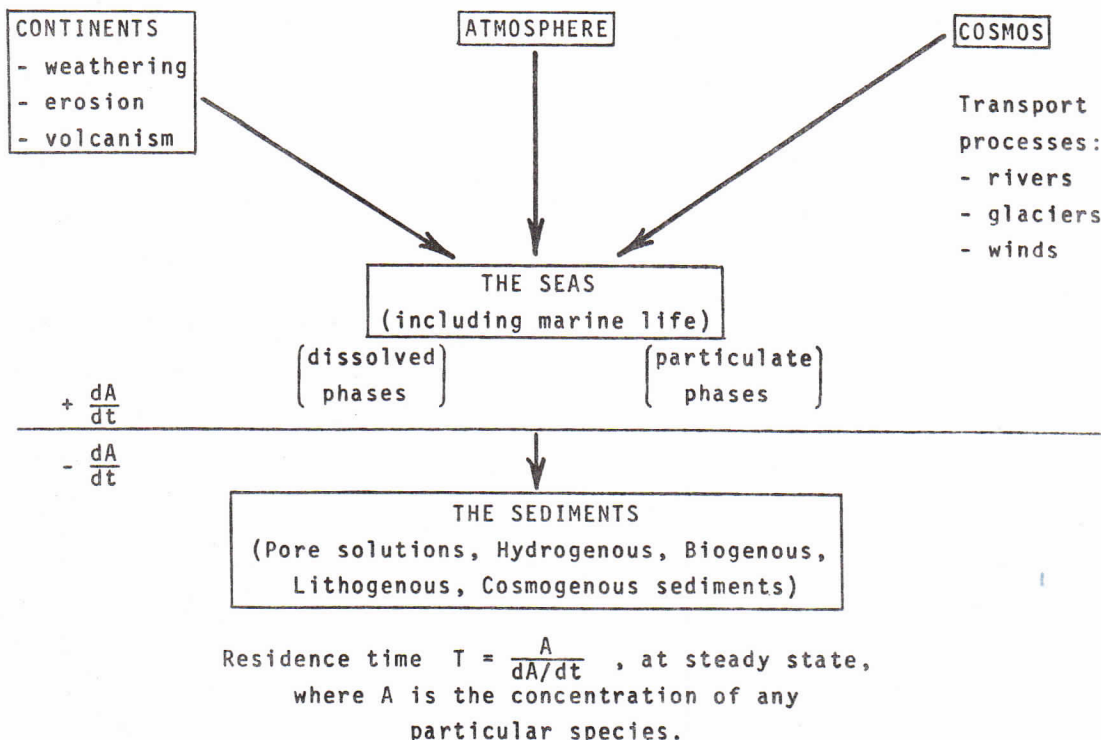particular species.

FIGURE 1. DEPOSITION OF SEDIMENTS IN THE SEAS (taken from Dr. E.D. Goldberg, lecture material).

Most chemical systems can be described by three variables: temperature, pressure and composition. For the seas there is little variation in temperature (-1° to 35 °C), but the pressure range is enormous (1 to 1000 atm) with an average of about 400 atm. There is much to be learned about the high pressure chemistry of the ocean depths. However, it is known that at high pressure some important solutes like $MgSO_4$ are more dissociated into the separate ions (Mg^{2+}, SO_4^{2-}), a fact which has great importance in the study of sound transmission in sea water. Furthermore, high pressures have important effects on the transport properties (e.g. viscosity) of the water itself.

Most of all the chemist is interested in the composition of sea water which in an overall way is characterized by the salinity (S) expressed in grams of the total amount of solid material dissolved in one kilogram of sea water. The units are g./kg., termed "per mille" and indicated by the symbol S °/$_{oo}$. Less commonly used is the chlorinity (Cl °/$_{oo}$) in grams

of total chloride contained in one kilogram of sea water (with all bromide and iodide converted to chloride). It is one of the most important properties of the oceans that although there is considerable variation in salinity, from low values for the Baltic Sea (where drainage of fresh water is great and evaporation low) to high values for the Mediterranean Sea (where rivers are scarce and evaporation high), the proportions of the major species relative to one another remain reasonably constant. This constancy of individual proportions in spite of variability of salinity was recognized very early by such marine scientists as Marcet, Forchammer, Maury, and Dittmar and the principle is sometimes identified with one or other of these names. A more modern trend is to characterize the total composition of the sea water solutes by electrical conductivity, the magnitude of which reflects the total ionic content.

The Water Itself

The most important chemical in the sea is, of course, water. In sea water of normal salinity, say 35 S $^o/_{oo}$, there are 965 g. of H_2O for 35 g. of all other substances. Nevertheless, the dissolved substances are able to change significantly the physical properties such as freezing point, boiling point, viscosity, but particularly electrical conductivity, from the values for pure water. Properties such as electrical conductivity which depend almost totally on ionic solutes, are much more affected than, for example, viscosity, which depends chiefly on the behaviour of the solvent content.

Pure water is a remarkable substance, a fact of which sight should not be lost even if it is such a common material. In their book, *The Oceans*, Sverdrup, Johnson and Fleming (1942) have listed the following exceptional properties of pure water:

(i)   highest heat capacity of all solids and liquids, except NH_3
(ii) highest heat of fusion, except NH_3
(iii) highest heat of evaporation
(iv) has maximum density at 4 °C, below which it expands on cooling
(v)   highest surface tension of all liquids
(vi) highest dielectric constant of all liquids (i.e. good insulator between dissolved ions)
(vii) most versatile solvent
(viii)highest thermal conductivity of common liquids
(ix) great transparency for visible light
(x)   is neutral in pH with equal but low molarities (10^{-7}) of H^+, OH^-.

Most of the above can be explained by the notable property of water molecules to form H-bonds with one another because of the tendency for two

small electronegative atoms such as O, F, or N to hold an electropositive H atom between them by electrostatic attraction. This accounts for the anomalously great tendency for water molecules to hold together against disruptive stress applied in the form of physical force (viscosity) or elevated temperature.

There is no mystery about the composition or architecture of the individual H_2O molecule as it would exist in the vapour phase. It has been determined spectroscopically that two H's are bonded to the O atom at a bond angle of 105° and bond distance 0.96 angstrom. H-bonding enters the picture when a H atom becomes shared between molecules but not at equal distances, as shown below:
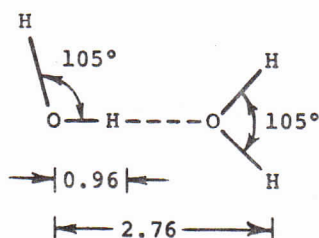
The centres of positive and negative charge in the water molecule do not coincide, so the molecule acts as an electric dipole or is said to have a dipole moment which affects its electrical interaction and orientation with other molecules and ions.

In the gaseous state H-bonding is mostly absent and the molecules randomly oriented. In the solid state there are known at least nine different arrangements of water molecules with extensive H-bonding between them. The intermolecular structure in the liquid state is intermediate in nature and has not been exactly defined. In order to conform to the recognized physical properties for water in bulk several proposed structural theories have been offered, the most important of which are:

(1) that water structure is a form of "broken-down ice structure" being a variable mixture of two different H-bonded solids which could be two different ice structures.

(2) that "flickering clusters" of water molecules are H-bonded in regions or clusters which are constantly changing and migrating.

Though the intermolecular structure of liquid water is not definitely established, the effects on it of change of temperature, pressure and addition of solutes are known by experiment. Increase of temperature disrupts structure by increased molecular motion; increase of pressure causes structural water to be broken down into denser monomeric water; while with addition of some ions (K^+, Br^-, Cl^-) structure is broken, most ions are structure makers (Na^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, Li^+).

The Major Dissolved Ions

The 35 g. of dissolved species with 965 g. of 35 S $^o/_{oo}$ sea water is composed almost entirely in quantity by weight in g. of the following cations and anions:

Na^+	10.7	Cl^-	19.3
Mg^{2+}	1.3	SO_4^{2-}	2.7
Ca^{2+}	0.4	HCO_3^-	0.1
K^+	0.4	Br^-	0.1

The above figures are too rough to allow for trace elements to be shown.

It is not possible easily to pair the above cations with anions to make partners for whole salts nor is it required to do so unless one were to evaporate the water to have the salts crystallize out in turn. In solution the ions can be separate and mostly are, or they may complex with one another, or form ion pairs. For example, it is obvious that the amount of Na^+ does not match the amount of Cl^-, so sea water is no such simple system as NaCl dissolved in water with some lesser additions, and should not be considered as such. The Na content of sea water will be mostly as Na^+ (hydrated), along with much lesser amounts of the ion pairs $NaHCO_3$ and $NaSO_4^-$. In the case of Mg there is rather more $MgSO_4$ as an ion pair. Among the major constituent ions of sea water the problem of deciding exactly what species are to be expected in what proportions is not an easy one, but has been treated by Garrels and Thompson as outlined later.

The Minor Constituents and Traces - Elemental Compositions

An up-to-date compilation which shows elemental compositions for minor constituents and traces (as well as for major elements) has been given by Goldberg et al (1971) and is represented by Table 1. The abundances are shown in the table in micrograms per litre or parts per billion (ppb). It can be seen that although some of the concentrations are exceedingly low, the ocean is known to contain almost all known elements in some amount, and concentrations of some species although low can be highly

TABLE 1: GEOCHEMICAL CHARACTERISTICS OF THE ELEMENTS[a]

Element	Seawater Concentration (μg/liter)	Principal Dissolved Species	Category[b]	Concentration Dissolved in Stream Waters (μg/liters)	Residence Time in Ocean (yr)
H	1.1×10^8	H_2O	A	-	-
He	7×10^{-3}	He(gas)	A	-	-
Li	1.7×10^2	Li^+	A	3	2.3×10^6
Be	6×10^{-4}	-	-	-	-
B	4.5×10^3	$B(OH)_3, B(OH)_4^-$	A	10	1.8×10^7
C	2.3×10^4	HCO_3^-, CO_3^{-2}	A	-	-
C(org.)	1×10^2	-	A	-	-
N	1.5×10^4	N_2(gas)	A	-	-
N	6.7×10^2	NO_3^-	B	-	-
O	8.8×10^8	H_2O	A	-	-
O	6×10^3	O_2	B	-	-
O	1.8×10^6	SO_4^{-2}	A	-	-
F	1.3×10^3	F^-	A	100	5.2×10^5
Ne	0.12	Ne(gas)	A	-	-
Na	1.1×10^7	Na^+	A	6,300	6.8×10^7
Mg	1.3×10^6	Mg^{+2}	A	4,100	1.2×10^7
Al	1	-	-	400	1.0×10^2
Si	3×10^3	$Si(OH)_4, SiO(OH)_3^-$	B	6,500	1.8×10^4
P	90	$HPO_4^{-2}, H_2PO_4^-, PO_4^{-3}$	B	20	1.8×10^5
S	9.0×10^5	SO_4^{-2}	A	-	-
Cl	1.9×10^7	Cl^-	A	1,800	1×10^8
Ar	4.5×10^2	Ar(gas)	A	-	-
K	3.9×10^5	K^+	A	2,300	7×10^6
Ca	4.1×10^5	Ca^{+2}	A	15,000	1.0×10^6
Sc	$<4 \times 10^{-3}$	$Sc(OH)_3^0$	-	0.004	$<4 \times 10^4$
Ti	1	$Ti(OH)_4^0$	-	3	1.3×10^4
V	2	$VO_2(OH)_3^{-2}$	-	0.9	8.0×10^4

Element	Seawater Concentration (μg/liter)	Principal Dissolved Species	Category[b]	Concentration Dissolved in Stream Waters (μg/liters)	Residence Time in Ocean (yr)
Cr	0.5	CrO_4^{-2}, Cr^{+3}	-	1	2.0×10^4
Mn	2	Mn^{+2}	C	7	1.0×10^4
Fe	3	-	-	670	2.0×10^2
Co	0.4	Co^{+2}	C	0.1	1.6×10^5
Ni	7	Ni^{+2}	C	0.3	9.0×10^4
Cu	3	Cu^{+2}	C	7	2×10^4
Zn	10	Zn^{+2}	C	20	2×10^4
Ga	3×10^{-2}	-	-	0.09	1×10^4
Ge	7×10^{-2}	$Ge(OH)_4$	-	-	-
As	2.6	$HAsO_4^{-2}$, $H_2AsO_4^-$	-	2	5×10^4
Se	9×10^{-2}	SeO_4^{-2}	C	0.2	2×10^4
Br	6.7×10^4	Br^-	A	20	1×10^8
Kr	0.2	$Kr(gas)$	A	-	-
Rb	1.2×10^2	Rb^+	A	1	5×10^6
Sr	8×10^3	Sr^{+2}	A	70	4×10^6
Y	1×10^{-3}	$Y(OH)_3^0$	C	-	-
Zr	3×10^{-2}	-	-	-	-
Nb	0.01	-	-	-	-
Mo	10	MoO_4^{-2}	A	0.6	7×10^5
Ru	-	-	-	-	-
Rh	-	-	-	-	-
Pd	-	-	-	-	-
Ag	0.3	$AgCl_2^-$	C	0.3	4×10^4
Cd	0.1	Cd^{+2}	-	-	-
In	<20	-	-	-	-
Sn	0.8	-	-	-	-
Sb	0.3	-	C	2	7,000

Element	Seawater Concentration (μg/liter)	Principal Dissolved Species	Category[b]	Concentration Dissolved in Stream Waters (μg/liters)	Residence Time in Ocean (yr)
Te	-	-	-	-	-
I	60	IO_3^-, I	A	7	4×10^5
Xe	5×10^{-2}	Xe(gas)	A	-	-
Cs	0.3	Cs^+	A	0.02	6×10^5
Ba	20	Ba^{+2}	C	20	4×10^4
La	3×10^{-3}	$La(OH)_3^0$	C	0.2	6×10^2
Ce	1×10^{-3}	$Ce(OH)_3^0$	C	-	-
Pr	0.6×10^{-3}	$Pr(OH)_3^0$	C	-	-
Nd	3×10^{-3}	$Nd(OH)_3^0$	C	-	-
Sm	0.5×10^{-3}	$Sm(OH)_3^0$	C	-	-
Eu	0.1×10^{-3}	$Eu(OH)_3^0$	C	-	-
Gd	0.7×10^{-3}	$Gd(OH)_3^0$	C	-	-
Tb	1.4×10^{-3}	$Tb(OH)_3^0$	C	-	-
Dy	0.9×10^{-3}	$Dy(OH)_3^0$	C	-	-
Ho	0.2×10^{-3}	$Ho(OH)_3^0$	C	-	-
Er	0.9×10^{-3}	$Er(OH)_3^0$	C	-	-
Tm	0.2×10^{-3}	$Tm(OH)_3^0$	C	-	-
Yb	0.8×10^{-3}	$Yb(OH)_3^0$	C	-	-
Lu	0.1×10^{-3}	$Lu(OH)_3^0$	C	-	-
Hf	$< 8 \times 10^{-3}$	-	-	-	-
Ta	$< 3 \times 10^{-3}$	-	-	-	-
W	0.1	WO_4^{-2}	-	0.03	1.2×10^5
Re	0.008	-	-	-	-
Os	-	-	-	-	-
Ir	-	-	-	-	-
Pt	-	-	-	-	-
Au	1×10^{-2}	$AuCl_2^-$	C	0.002	2×10^5

Element	Seawater Concentration (μg/liter)	Principal Dissolved Species	Category[b]	Concentration Dissolved in Stream Waters (μg/liters)	Residence Time in Ocean (yr)
Tl	<0.1	Tl^+	-	-	-
Pb	0.03	$PbCl_2^-, PbCl^+, Pb^{+2}$	C	3	4×10^2
Bi	0.02	-	-	-	-
Po	-	-	-	-	-
At	-	-	-	-	-
Rn	6×10^{-13}	Rn(gas)	-	-	-
Ra	1×10^{-7}	Ra^{-2}	C	-	-
Ac	-	-	-	-	-
Th	$<5\times10^{-4}$	$Th(OH)_4^0$	-	0.1	<200
Pa	2.0×10^{-6}	-	-	-	-
U	3	$UO_2(CO_3)_3^{-4}$	A	0.04	3×10^6

[a]Compiled from Goldberg (1965) and Turekian (1969)
[b]See text for explanation of letters.

important as, for example, to living organisms. As well the table shows
the principal dissolved species for each element, not an easy matter to
determine in some cases.

Categorization of Elements as to Reactivity, Residence Time

In the same table Goldberg et al (1971) have put the elements into
various categories A, B, C in column 4 according to the following descript-
ions:

A. conservative elements with concentrations proportional to S $^\circ/_{\circ\circ}$
B. variable elements with concentrations dependent on depth, location
C. elements with variation in concentration, but not correlated with
    S $^\circ/_{\circ\circ}$, depth or location in ocean basin.

TABLE 2: PERIODIC TABLE OF THE ELEMENTS. SEE TEXT FOR EXPLANATION.

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB	VIIIB	VIIIB	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1 H 1.00797 (–)																	2 He 1.0026 (A)
3 Li 6.939 (A)	4 Be 9.0122 (–)											5 B 10.811 (A)	6 C 12.0115 (A)	7 N 14.0067 (A,B)	8 O 15.9994 (A,B)	9 F 18.9984 (A)	10 Ne 20.183 (A)
11 Na 22.9898 (A)	12 Mg 24.312 (A)											13 Al 26.9815 (–)	14 Si 28.086 (B)	15 P 30.9738 (B)	16 S 32.064 (C)	17 Cl 35.453 (A)	18 Ar 39.948 (A)
19 K 39.102 (A)	20 Ca 40.08 (A)	21 Sc 44.956 (C)	22 Ti 47.950 (–)	23 V 50.942 (–)	24 Cr 51.996 (–)	25 Mn 54.9380 (C)	26 Fe 55.847 (–)	27 Co 58.9332 (C)	28 Ni 58.71 (C)	29 Cu 63.546 (C)	30 Zn 65.37 (C)	31 Ga 69.72 (–)	32 Ge 72.59 (–)	33 As 74.9216 (–)	34 Se 78.96 (C)	35 Br 79.904 (A)	36 Kr 83.80 (A)
37 Rb 85.47 (A)	38 Sr 87.62 (A)	39 Y 88.905 (C)	40 Zr 91.22 (–)	41 Nb 92.906 (–)	42 Mo 95.904 (A)	43 Tc (99) (–)	44 Ru 101.07 (–)	45 Rh 102.905 (–)	46 Pd 106.4 (–)	47 Ag 107.868 (A)	48 Cd 112.40 (–)	49 In 114.82 (–)	50 Sn 118.69 (–)	51 Sb 121.65 (–)	52 Te 127.60 (A)	53 I 126.9044 (A)	54 Xe 131.30 (A)
55 Cs 132.905 (A)	56 Ba 137.34 (C)	57 La 138.91 (C)	72 Hf 178.49 (C)	73 Ta 180.948 (–)	74 W 183.85 (–)	75 Re 186.2 (–)	76 Os 190.2 (–)	77 Ir 192.2 (–)	78 Pt 195.09 (–)	79 Au 196.967 (–)	80 Hg 200.59 (C)	81 Tl 204.37 (C)	82 Pb 207.19 (C)	83 Bi 208.980 (C)	84 Po (209) (–)	85 At (210) (–)	86 Rn (222) (–)
87 Fr (223) (–)	88 Ra (226) (C)	89 Ac (229) (–)															

58 Ce 140.12 (C)	59 Pr 140.907 (C)	60 Nd 144.24 (C)	61 Pm (147) (–)	62 Sm 150.35 (C)	63 Eu 151.96 (C)	64 Gd 157.25 (C)	65 Tb 158.924 (C)	66 Dy 162.50 (C)	67 Ho 164.930 (C)	68 Er 167.26 (C)	69 Tm 168.934 (C)	70 Yb 173.04 (C)	71 Lu 174.97 (C)
90 Th 232.038 (C)	91 Pa (231) (–)	92 U 238.03 (A)	93 Np (237) (–)	94 Pu (244) (–)	95 Am (243) (–)	96 Cm (247) (–)	97 Bk (247) (–)	98 Cf (251) (–)	99 Es (254) (–)	100 Fm (257) (–)	101 Md (256) (–)	102 No (254) (–)	103 Lw (257) (–)

Also shown is a periodic table in which the elements are designated according to the above categories. It can be seen that most of the A elemental species come from the alkali cations, the alkaline earth cations, the halide anions and the atomic noble gases. Such elemental species are extremely stable from the point of view of electronic configuration (having completed p orbitals) and in the forms shown in column 3 in the table are quite unreactive. The B elemental species are nutrients and elements on which life depends; as such these are among the most reactive and variable with planetary biological processes such as photosynthesis and decay, and according changes in depth and position. The C elements are also more reactive but rather in a geochemical way, and consist of transition elements, lanthanides and actinides. Their behaviour is not so well under-stood, but there is an obvious connection between Goldberg's categories and the periodic table.

Assuming that the elemental species are fed into the seas by rivers and streams at reasonably known rates, dA/dt and that in time they will precipitate out in the sediments at an equal rate, causing a steady-state inventory in the sea, it is possible to calculate their residence times, T, in the sea (with time in years) as

$$T = \frac{A}{dA/dt}$$

These residence times are also a mark of reactivity, short residence times being associated with a highly reactive nature and vice versa. The penult-imate column shows content of stream waters, and the last column the calcu-lated residence times. A-type elements generally have long residence (up to 10^8 years) while B-and C-types have shorter residence in the sea. Professor Goldberg is at the Scripps Institution of Oceanography, La Jolla, California.

Quite another problem is that of determining just what species of the elements are present in the sea - termed speciation. In the case of trace elements this can be very difficult and in some cases impossible. On the assumption that certain equilibria are in effect it is possible to make logical decisions as to speciation. This has been done for the major ionic species in the sea by Garrels and Thompson in their classic model sketched below.

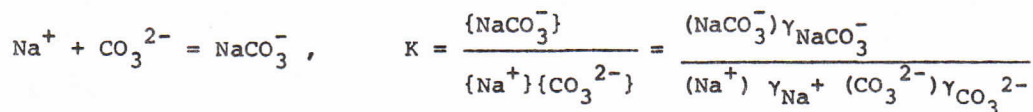## The Garrels and Thompson Model for Major Ionic Species

To begin with, activities are used instead of concentrations. The activity of a species is an idealized concentration related to the real concentration by an activity coefficient (γ), e.g.

$$\{Cl^-\} = \gamma (Cl^-)$$

where $\{Cl^-\}$ means activity of Cl^- and (Cl^-) means molality of Cl^-. Certain main assumptions are axiomatic to their development.

(1) Values for γ as calculated from theory are taken as 0.7 for monovalent ions, and 0.1 for divalent.

(2) The model applies only to the major ions: Na^+, Mg^{2+}, Ca^{2+}, K^+, and Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}.

(3) Cl^- and other halides do not significantly form ion pairs with the above cations, as do SO_4^{2-}, HCO_3^-, CO_3^{2-}.

Equilibria of ion pair formation are considered, such as

$$Na^+ + CO_3^{2-} = NaCO_3^- , \qquad K = \frac{\{NaCO_3^-\}}{\{Na^+\}\{CO_3^{2-}\}} = \frac{(NaCO_3^-)\gamma_{NaCO_3^-}}{(Na^+)\,\gamma_{Na^+}\,(CO_3^{2-})\gamma_{CO_3^{2-}}}$$

The above is only one of ten such combinations among the ions. The other nine ion pairs are: $NaHCO_3$, $NaSO_4^-$, $CaHCO_3^+$, $CaCO_3$, $CaSO_4$, $MgHCO_3^+$, $MgCO_3$, $MgSO_4$, and KSO_4^-. ($KHCO_3$ and KCO_3^- are neglected). In addition to the ten above combinations there are the seven free ions mentioned above for which there are seven equations of type,

$$(Na)_{total} = (Na^+) + (NaHCO_3) + (NaCO_3^-) + (NaSO_4^-).$$

The total concentration of Na is established by analysis. With known equilibrium constants this gives 17 equations in 17 unknowns which the authors have solved to give the results shown in Table 3.

The above is doubtless a highly significant contribution to our understanding of the ultimate nature of the oceans. Professor Garrels is now at the University of Hawaii and Dr. Thompson at the Canada Centre for Inland Waters.

TABLE 3: OCCURRENCE OF MAJOR IONIC SPECIES ACCORDING TO THE GARRELS AND THOMPSON MODEL

CATIONS	Molality	% free ion	% cation SO_4	% cation HCO_3	% cation CO_3
Na^+	0.4752	99	1.2	0.01	-
Mg^{2+}	0.0540	87	11	1	0.3
Ca^{2+}	0.0104	91	8	1	0.2
K^+	0.0100	99	1	-	-

ANIONS	Molality	% free ion	% Ca anion	% Mg anion	% Na anion	% K anion
SO_4^{2-}	0.0284	54	3	22	21	0.5
HCO_3^-	0.0024	69	4	19	8	-
CO_3^{2-}	0.0003	9	7	67	17	-

Acid-Base Control in the Sea

The rapid, immediate control of acidity in the open sea is considered to be chiefly by the carbonate system,

$$CO_2 \overset{H_2O}{\rightleftharpoons} H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$
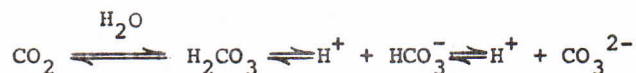
All the above species are present in the sea but HCO_3^- predominates at the usual pH (~8). These bicarbonate ions can either gain or lose protons (H^+) as required without the pH changing much. Such a substance is called a buffer, tending to maintain the pH status relatively constant. Less important systems which can assist the carbonate system as buffers are the borate and phosphate systems:

$$H_3BO_3 \rightleftharpoons H^+ + H_2BO_3^- \quad \text{(at pH 8, dominant form } H_3BO_3\text{)}$$

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$$

$$\text{(at pH 8 dominant form } HPO_4^{2-}\text{)}$$
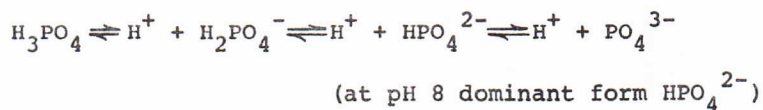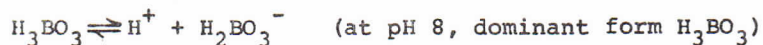
Ultimately any stress causing addition or removal of protons is transmitted
to the clays in the sediments, but this is a slow process if only for
physical reasons. Clays are natural ion-exchange resins which are capable
of exchanging Na^+ for H^+ or vice versa over a period of time and so con-
stitute a reservoir for protons to back up the carbonate system in buffer-
ing. These abundant clays are formed by the weathering of igneous rock by
water and carbon dioxide. They undergo a sequence of changes in the sea
which, depending on conditions such as latitude, can produce kaolinite,
illite, montmorillonite and chlorite. Clay chemistry provides important
information which is being used to unravel planetary chemical cycles. A
most effective ion-exchanger of a different type is the feldspar philip-
site, found in quantity in the Pacific basins.

An intensive measurement of the acidity condition of the ocean is
obtained by using a glass electrode along with a reference electrode to
read the pH on an electronic voltmeter. Increasingly, however, scientists
are paying more attention to extensive measurements wherein the alkalinity
of the sea water is determined by titration with standard acid to a suit-
able end point, a procedure which determines the uptake of H^+ by such
entities in the water as HCO_3^-, CO_3^{2-}, $H_2BO_3^-$, $H_2PO_4^-$, HPO_4^{2-}, $H_3SiO_4^-$.

The pH of the open sea does not differ much from 8; however, in
the sediments and in certain stratified waters in fiords or deep basins
with sills which prevent mixing, decay of organic matter may use up O_2 and
produce CO_2, with a reduction in pH.

Redox Control in the Sea

Sillen (1965) has made a fundamental study of the origin, history
and present equilibrium conditions of what he considers to be the major
redox elements on the planet: H, O, C, N, S, Fe and Mn. From mass bal-
ances of Goldschmidt and Horn on a planetary scale for the above elements
and the available thermodynamic data Sillen has estimated the abundance of
these redox elements and decided on the likely oxidation states to be found
in various environments. Over the course of geological time the earth is
thought to have evolved from a much more reduced condition when such com-
pounds as CH_4, H_2 and NH_3 were prevalent along with H_2O. H_2 tended to grad-
ually escape from the planet only to be fed by the photodecomposition of
H_2O according to

$$H_2O \xrightarrow{h\nu} H_2 + \frac{1}{2} O_2 ,$$

leaving a residue of O_2 in the atmosphere and producing an oxidized outer
layer with oxidation of CH_4 to C and CO_2 and NH_3 to N_2 and NO_3^-. But prob-
ably a greater contribution to the inventory of atmospheric O_2 is attribut-

able to the process of photosynthesis wherein, with solar energy of sufficient frequency ($h\nu$), CO_2 is reduced in the presence of H_2O to produce natural carbohydrates and O_2. A gross attempt to represent this process is,

$$CO_2 + H_2O \xrightleftharpoons{h\nu} \frac{1}{n} (CH_2O)_n + O_2 \ .$$

The process can be reversed in sense by what is termed respiration or decay. For example most plants photosynthesize in daylight hours and respire at night. The planetary inventory of O_2 must correspond roughly to the amount of carbohydrate, with allowance for the different weights. Thus photosynthesis tends to keep the outer skin of the earth pumped up to a high oxidation state and decay processes tend to reduce it. The presence of O_2 is essential to most life as we know it and oxic conditions in air and water are healthy; anoxic conditions are lethal, except to certain bacteria.

When O_2 is used up or absent, redox control is usually taken over by the sulphur system and is recognized by the odor of H_2S from the sulphides present. Under still more reduced conditions CO_2 and carbonates are reduced to solid carbon and ultimately to hydrocarbons such as CH_4 and its homologues. By such a process petroliferous deposits are thought to be produced from decayed organic matter from plankton and other living matter.

Considering the planet as a whole, the major element is iron and the earth's core is thought to consist chiefly of an alloy of this element, being, of course, in a highly reduced state at the centre. The outside of the planet, by contrast, is in a highly oxidized state by virtue of photosynthesis. The earth's crust consists chiefly of silica, silicates, alumino-silicates, oxides of iron (usually between the II and III oxidation states). The intervening mantle must be intermediate in oxidation state between crust and centre and is roughly considered to consist of various layers of more or less dense silicates of iron and magnesium.

Most of the ocean waters are well mixed and oxygenated and so are able to support life. In the sediments, in land-locked bays, fiords, and certain basins, O_2 may become depleted and not renewed quickly enough to prevent the water going anoxic, and dropping in oxidation level.

In the open sea H exists mostly as H_2O; O as H_2O and dissolved O_2; N as dissolved N_2 and small amounts of NO_3^-, NO_2^-, NH_4^+, NH_3; C mostly as HCO_3^- with lesser amounts of CO_2, H_2CO_3, and CO_3^{2-}; S stably as SO_4^{2-}; Fe mostly as particulate FeOOH; and Mn as Mn^{2+} and some particulate MnO_2. Under anoxic conditions O_2 is absent; C may be as solid C or a homologue of CH_4; N as NH_4^+ or NH_3; S mostly as HS^- with some H_2S and S^{2-} and polysulphides; Fe as FeS or FeS_2; and Mn as MnS.

In assessing the quality of the environment, the determination of the oxidation state (as Eh or pE) is a prime criterion, but it is a difficult measurement to make and interpret. For most purposes a measurement of the dissolved O_2 will serve to indicate whether the water is healthy. The presence of species of the ubiquitous redox elements Fe and Mn can also serve as a useful indicator of the state of oxidation of a particular environment.

SEA WATER AS A PLANETARY RESOURCE

Apart from its physical utility (for cooling, hydro power, and navigation) sea water has great importance for the chemicals it contains. Of these the water itself is the most abundant and important as being the trademark of our planet. With fresh water supplies no longer adequately available where needed, desalination processes based on various physico-chemical principles are now in operation on ships and in dry regions. If hydrogren fusion were to become a viable source of energy then the sea would provide a virtually inexhaustible supply of this element. If solar energy were to become feasible on a large scale then the water of the seas would in some way be required since they cover most of the earth's surface and supply one of the key molecules for photosynthesis, as well as constituting a benign medium for living processes. However caution should be exercised in crediting what has been said about the sea providing an abundance of food by proper aquaculture. The limiting factor (apart from light) is ultimately the distribution of the proper mix of nutrients (nitrate, phosphate, silica and trace elements) and of course the production is limited chiefly to surface waters. Many areas of the sea are already overfished for certain species, although admittedly underfished for others, and much better use could be made of the protein available on the planet did people's tastes only make it more acceptable on the market in the form of concentrates, meals and pastes. Even poor people prefer TV sets to fish meal.

Another area of economic importance which has been overrated is the bonanza of mining the seas. Most of the exploration and recovery under way on the shelves is for oil, and the disappointment here is that once the thrill of discovery is over and the shareholders have been paid, its use represents an irreversible drain on our energy inventory with the added insult of pollution of the environment from oil spills, petrochemical damage, toxic exhausts, and build up of carbon dioxide. Mining of the seas for base and heavy metals is mostly in the future although even now Japan is harvesting some ferromanganese nodules. These fabulous formations have also been overrated insofar as present markets are concerned, but perhaps

not in the future. For example, iron and manganese are in plentiful enough supply in terrestrial deposits that some countries produce more than they can use or sell without going to more expensive submerged supplies. Of more value would seem the other elements such as nickel, copper, cobalt, lead etc., but even nickel is at present an embarrassment to Canada in terms of its present marketability. But the nodules are widespread and available, and contain more than trace amounts of some most interesting elements whose future use is not yet predictable.

On the positive side certain elements are supplied reliably from the sea in world markets. Sulphur formed presumably by reduction of sulphate from the sea and trapped under salt domes constitutes a major supply as recovered by the Frasch process. Magnesium and sodium are obtained by electrolysis of brines which deposits these metals by reduction at a cathode with chlorine a by-product. Common salt itself (NaCl) is harvested in warm regions simply by evaporation of sea water from shallow embayments. Bromine is prepared commercially by the oxidation of bromide from sea water by chlorine. On the east coast of Canada Irish moss is harvested, dried and pressed into bales like hay for commercial sale.

An important nutrient element which winds up at the bottom of the sea with virtually no return path to complete its cycle is phosphorus. Much of this element is misplaced in cemeteries and in waters already suffering from eutrophication. As a means of recovering some of the earth's phosphorus the mining of certain deposits of phosphorites which occur fairly commonly on shelves, particularly off California as nodules, is of understandable interest. The content of P_2O_5 in phosphorites is about 30 percent.

Lastly, there is a strong current interest in obtaining unusual and valuable drugs from the sea flora and fauna, a case of this being the acquisition of the strangely named "prostaglandins", the diverse applications of which are so extensive as to qualify them as "wonder" drugs.

SUGGESTED FURTHER READING

Horne, R.A.: *Marine Chemistry*, Wiley-Interscience, New York, 1969.

Stumm, W. and J.J. Morgan: *Aquatic Chemistry*, Wiley-Interscience, New York, 1971.

Goldberg, E.D., W.S. Broecker, M.G. Gross, K.K. Turekian: "Marine Chemistry" Ch. 5 in *Radioactivity in the Marine Environment*, National Academy of

Sciences, Washington, 1971.

MacIntyre, F.:"Why the Sea is Salt", *Scientific American*, 223 (5), 1970.

Riley, J.P. and G. Skirrow (eds.): *Chemical Oceanography*, Vols. 1 and 2, Academic Press, New York, 1965.

Harvey, H.W.: *The Chemistry and Fertility of Sea Waters*, Cambridge Univ. Press, London, 1960.