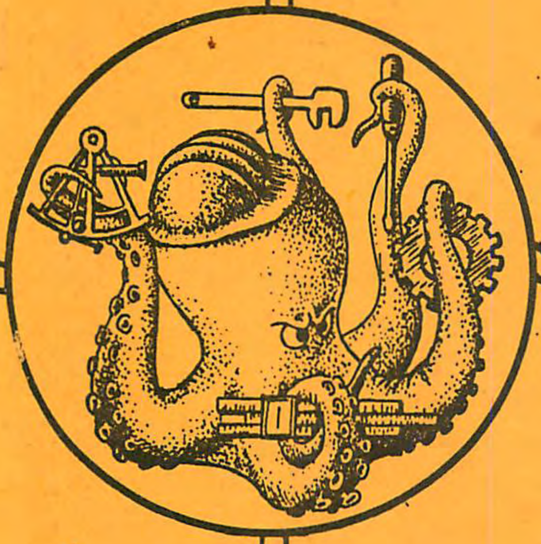
Appendix C

Civil Engineering
201 B

Chemical Oceanology

Pat Wilde - Instructor



COMMITTEE ON OCEAN . ENGINEERING
COLLEGE OF ENGINEERING

UNIVERSITY OF CALIFORNIA
BERKELEY

Winter Quarter

UNIVERSITY OF CALIFORNIA
CE 201B, Winter

Department of Civil Engineering
Instructor: Pat Wilde

CHEMICAL OCEANOLOGY

Chemistry of sea water examined with respect to (1) its relation to the atmosphere, lithosphere, and biosphere; (2) the origin and evolution of sea water; (3) the application of chemistry to problems in related fields of Oceanology. Readings and reports.

Week	Tentative Lecture Schedule
I	Geochemical parameters, concentration, activity, pH, alkalinity , validity of Gibbsian model of sea water.
II	Major constituents of sea water, dissolved solids, dissolved gases, Dittmar"s law of constant ratio, concept of residence time.
III	The oceans as a chemical system - oxygen, nitrogen, phosphorus, carbon dioxide content and variation with latitude and depth.
IV	Origin of sea water - erosional contribution, volcanic and mantle degassing, Rubey volitiles, the geochemical balance.
V	The buffer question - (1) carbonate argument.
VI	The buffer question - (2) silicate argument; mineral equilibria in sea water.
VII	Biological influence on equilibria and content - productivity, organic films.
VIII	Trace elements in sea water - guides to circulation patterns, age of water masses - danger of heavy metals Pb, Hg
IX	Economic chemical products from sea water, salts, magnesium products, bromine, fresh water - chemical processes using sea water.
X	Current research problems - i.e. hot brines, chemical oceanographic instruments.

UNIVERSITY OF CALIFORNIA
CE 201B Winter

Department of Civil Engineering
Division of Hydraulic & Sanitary Engr.
Instructor: Pat Wilde

CHEMICAL OCEANOLOGY

SELECTED REFERENCE BOOKS

Garrels, R. M. and Christ, C. L., 1965, Solutions, Minerals, and Equilibria: New York, Harper and Row, 450 p.

Barnes, H. , 1959, Apparatus and Methods of Oceanography. Part One, Chemical: New York, Interscience, 341 p.

Harvey, H. W., 1963, The Chemistry and Fertility of Sea Waters: Cambridge, Cambridge University Press, 240 p.

Hill, N. H. (ed.), 1963, The Sea. Volume Two, The Composition of Sea Water: New York, Interscience, 864 p.

Martin, D. F., 1968, Marine Chemistry, Volume One, Analytical Methods: New York, Martin Dekker, 280 p.

Riley, J. P. and Skirrow, G., 1965, Chemical Oceanography: London and New York, Academic Press; Vol. I, 712 p. Vol. II, 508 p.

Sverdrup, H. U., Johnson, M. W., and Fleming, R. H., 1942, The Oceans: Englewood Cliffs, N. J., Prentice-Hall, 1087 p.

Horne, R. A., 1969, Marine Chemistry: New York, Wiley, 568 p.

Kalle, K., 1943, Der Stoffhaushalt des Meeres: Leipzig, Akad. Verlag., 263 p.

Klotz, I. M., 1950, Chemical Thermodynamics: Englewood Cliffs, N. J., Prentice-Hall, 369 p.

Stumm, W. (ed.), 1967, Equilibrium Concepts in Natural Water Systems: American Chemical Society, Adv. in Chem., 67, 344 p.

Vetter, R. C. and others, 1959, Conference on Physical and Chemical Properties of Sea Water: Natl. Acad. Sci. - Nat. Res. Council Pub. 600, 202 p.

University of California
CE 201 B

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Problem I

Calculate the ionic strength of sea water using data of

(a) Sverdrup, Johnson, and Fleming (1942, p. 173)
(b) Garrels and Thompson (1962, P. 63)
(c) Lyman and Fleming (1940) (their formula).
(d) Comment on reasons for simularities or differences among answers.

Problem II

Determine the mol fraction for the conservative ions Na, Cl, SO_4, Mg, K, Ca, Sr, Br, and F.

A. As a function of chlorinity and salinity
B. At $35^{o}/oo$ salinity

Show work in tabular form.

Problem III

Using data given in Table II-3 (Week II) calculate for each ion

(a) formality (f)
(b) molarity (M)
(c) molarity (m)

in terms of $\frac{CL}{\text{constant}}$

Hint: Assume these ions are conservative over the range (1) 15.5 - 22% CL, (2) 0° to 30°C temperature. Use the extreme values in calculations of concentration units.

Problem IV

Express the activities of the major species of sea water as negative logarithms (analogy is pH) for:

pO_2	pSO_4
pCO_2	$pHCO_3$
pCl	pCa
pNa	pMg

(continued)

pK pPO_4

For conservative components assume Cl = 19°/oo. For nonconservative components give range. Remember $a = \gamma m$.

Problem V

Using the data of Table I-4 (Week I) of Garrels and Thompson; calculate for sea water of 19°/oo CL

(a) the sum of the equivalents/Kg sea water for the anionic species.
(b) the sum of the equivalents/Kg sea water for the cationic species.

Show your results in tabular form as in Table V-2 (Week V)

(c) discuss in terms of results given in Table V-2.

Problem VI

Using ΔF data from Garrels and Christ (1965, Appendix 2) calculate ΔF at 40°C for the ions Cl, Na, SO_4, Mg, Ca, K, $NaSO_4$, $MgSO_4$, HCO_3, CO_3, $CaHCO_3$, $CaCO_3$, $MgCO_3$, $MgHCO_3$, KSO_4, $NaHCO_3$.

Show work in tabular form.

Problem VII

From Harvey's formulae and tables (1963) (see also Table I-5 in notes) determine:

Titration Alkalinity

Carbonate Alkalinity

Specific Alkalinity

aCO_2

C_{CO_2} as f, M, and m

P_{CO_2}

pCO_2 from $a = \gamma m$

(continued)

for (a) Cl = $15.5^{o}/oo$ T = 20^{o}, pH = 8.0

(b) Cl = $22^{o}/oo$ T = 30^{o}, pH = 8.3

(c) Cl = $22^{o}/oo$ T = 0^{o}. pH = 7.8

Problem VIII

Calculate the theoretical hierarcy of the metal-anion complexes for the anions OH, Cl, SO_4, for two of the following metals Ag^+, Cd^{++}, Hg^{++}, Zn^{++}, Ca^{++}, and Pb^{++} using the technique described by Goldberg (1965, p. 166-171) (see Table VIII-1 of notes)

Discuss the factors in the real ocean which would modify these theoretical answers.

Problem IX

Construct a master variable concentration diagram (Sillen, 1959) assuming the total concentration as found in sea water for one of the following systems

1. carbonate
2. phosphate
3. sulfur

For the conditions

(a) pH = 8.0
Eh = + 400 to - 400 millivolts
(b) pH = 1 to 14
Eh = + 200 millivolts
(c) Discuss what environmental conditions you would use (a) or (b).

University of California
CE 201 B Winter
Chemical Oceanology

Department of Civil Engineering
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TERM PAPER TOPICS - WINTER

There is a growing concern over the possibility that man's activities may be changing the chemistry of the oceans in particular with respect to (1) nutrient stimulating elements, (2) heavy metals, and (3) radioactive elements, to the detriment of marine life and its effects on human health. Accordingly such bodies as the U.N.'s International Oceanographic Commission (I.O.C.), the International Decade of Ocean Exploration (I.D.O.E.), and locally the California State Water Resources Control Board are in the process of making recommendations for standards to govern the composition of allowable wastes that may be discharged into the oceans.

Thus for a term paper topic each student will choose an element from Table 1 given below and examine its chemistry in the marine environment. Such a paper shall contain, but is not limited to the following:

I Natural range of values in sea water
II Natural complexes and ionic states found in sea water
III Natural inputs to the ocean by

  (a) rivers
  (b) wind-dust
  (c) ice
  (d) under sea volcanism
  (e) etc.

IV Man-made inputs to the ocean

  (a) industrial
  (b) domestic

V Pourbaix (Eh-pH) diagrams for dominant species at 25°C and 4°C (Garrels and Christ, 1965, p. 172-266)
VI Bjerrum plots of various species at 25°C for significant master variables (For example, Eh, pH, p5) (Sillen, 1959, p.277-317)
VII Potential dangers from element, if any
VIII Chemical schemes to eliminate dangers
IX Proposed areas of needed research
X Proposed standards for disposal of element.

The format, style, and time table will follow that given in the hand-out "Term papers for oceanology courses".

REFERENCES

Garrels, R. M., and Christ, C. L., 1965, Solutions, minerals and equilibria, Chap. 7, Eh-pH Diagrams: New York, Harpers and Row, p. 172-266.

Schmitt, H. H. (Ed.), 1962, Equilibrium diagrams for minerals: Geological Club Harvard, 199 p.

Sillen, L. G., 1959, Graphic presentation of equilibrium data, in Treatise on analytical chemistry; Kolthoff and Elving (Eds.): New York, Wiley, p. 277-317.

TABLE 1

TOPIC ELEMENTS

Element	Concerned Agency		
	IOC*[1]	IDOE*[2]	CALIF.*[3]
Antimony		X	
Arsenic	X	X	X
Beryllium	X		
Cadmium	X	X	X
Cesium	X		X
Chromium	X	X	X
Cobalt		X	
Copper	X	X	X
Fluorine	X		
Lead	X	X	X
Mercury	X	X	X
Nickel	X	X	X
Nitrogen (ammonia)	X		X
Phosphorus	X		
Plutonium	X		X
Radium	X		X
Selenium		X	
Silver		X	X
Sulfur			
Thallium			
Uranium	X		X
Vanadium	X	X	
Zinc	X	X	X

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*[1] Capurro, L., 1972, Letter on "Convention on the Dumping of Wastes at Sea"

*[2] Goldberg, E. (convener), 1972 Baseline Studies of Pollutants in the Marine Environment and Research Recommendations.

*[3] California State Water Resources Control Agency
Resolution 72-45, 1972, Water Quality Control Plan for Ocean Waters of California.

UNIVERSITY OF CALIFORNIA
CE 201B Winter

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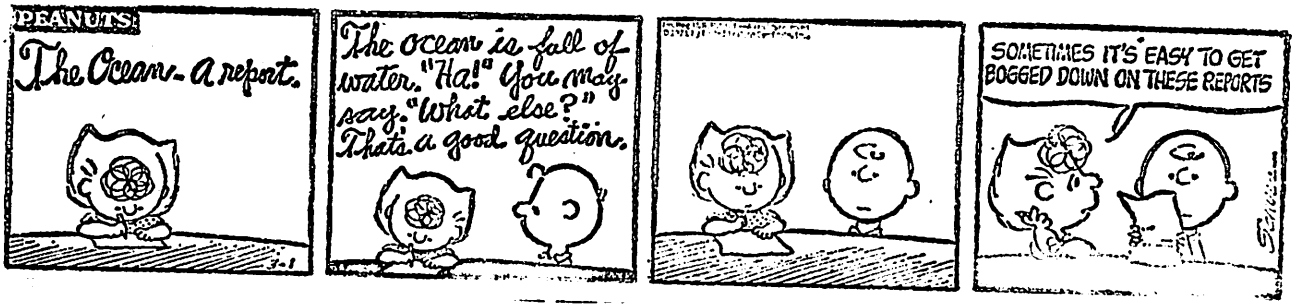
TERM PAPERS FOR OCEANOLOGY COURSES



The purpose of a term paper is three-fold: (1) to acquaint the writer with the problems involved in writing a report; (2) to further the writer's knowledge in some narrow topic in oceanology; (3) to get a better grade. The grade, of course, depends on how skillfully one can write and at the same time demonstrate a command of the subject. One way to impress the grader is to write in simple English, with a minimum of grammatical and spelling mistakes. The easiest way to prevent grammatical errors is to follow the advice given in the U.S. Geological Survey's publication - Suggestions to Authors of the United States Geological Survey, Fourth or Fifth Editions. Copies of this book are available in the Earth Sciences Library and from the discussion instructor. All questions about style; method of reference citation; format of tables, charts, and maps can be answered by Suggestions to Authors.

TOPIC SELECTION:

The subject of a term paper should be chosen with regard to: (1) relevance to oceanology, this should be obvious; (2) the writer's abilities to handle published material on the subject; (3) the requirements of length, make sure the subject can be adequately covered in the space alloted without either padding or stretching; (4) the interest of the writer, do not pick a topic that is boring to you, as a good paper should impart to the reader the author's enthusiasm for his subject. Check reports of previous years for ideas (on file 426 HMB).

REFERENCES:

All allusions to other peoples work whether by direct quotation or borrowed ideas must be adequately cited in at least two places (1) in the body of the text when the idea is expressed; for example: "Culkin and Cox (1966, p. 801) found the mean oceanic Na/chlorinity ratio to be 0.5555."; and (2) in the References Cited section at the end of the paper (see Suggestions to Authors for proper format and abbreviations of journals and so forth).

> Culkin, F. and Cox, R. A., 1966, Sodium Potassium, Magnesium, Calcium and Strontium in Sea Water: Deep-Sea Res., V. 13, p. 789-804.

Do not footnote references! Do not use Latin abbreviations, such as op. cit. or loc. cit., use the author's name, the page or pages from which the quotation or ideas were borrowed, and the year of publication of the article, each time his ideas are used in text!

INCORRECT USAGE:

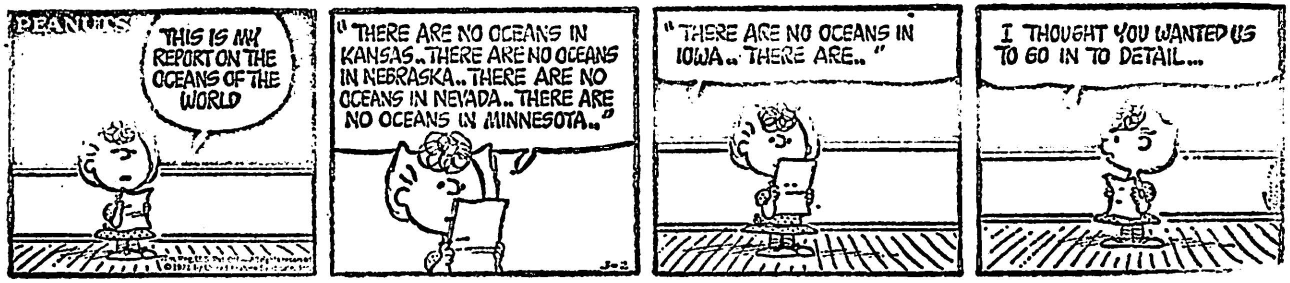
The following words are used incorrectly repeatedly by many writers. You should consult Fowler's Dictionary of Modern English Usage or Suggestions to Authors for discussions of proper usage.

a. While (a time term) for whereas or because
b. Since (a time term) for as or because
c. Height or high for elevation, elevation for altitude
d. Due to for owing to or because of
e. Quite and very (too imprecise, better to omit such words)
f. Strong or high to express concept of intensity
g. Sometimes, usually, frequently, or occasionally (time words for commonly, rarely, or uncommonly)
h. Over and above (words of position) for more than or greater than
i. Roughly (describes surface properties) or around (word of position) for approximately
j. Excessive use of there is or it is construction
k. Improper use of which and that
l. Improper use of it; lack of clarity or double meaning of antecedent of it. Do not be afraid to use nouns.
m. Plus many more

TIPS FOR CLARITY:

a. Avoid the use of the former and the latter unless the concepts involved are too lengthy to repeat. Repetition of the real meanings of former and latter makes for smoother reading and lets the reader follow your ideas without going back to find exactly what the "former" is.

b. Use the present tense and the active voice as much as possible. A sentence in the passive voice is cumbersome. If you did the research, report it in the past tense. However, if you are reporting or discussing a natural process, write about the process in the present tense.



LENGTH:

The text, exclusive of tables, figures, maps and references, should be no more than 20 pages, typewritten, double spaced. However, try to limit the borrowed research part to about one-quarter of the total length. This leaves three fourths for your own views, research and calculations on the subject. The limitation does not include the list of references.

TIME TABLE:

Topic Selection - Title handed in to insturctor by end of third week of quarter.

List of Possible Pertinent References - In suggested format to instructor by end of fifth week of quarter. Remember part of your grade will depend on the throughness of your literature search.

Final Copy - with title page, abstract, text, references and when appropriate appendices, to instructor by Saturday noon of the last week of formal classes.

WARNING:

All papers will be kept for the files, so have an extra copy typed or Xerox a spare for your own use.

UNIVERSITY OF CALIFORNIA
Ocean Engineering
Chemical Oceanology
CE 201B - Winter 1971

Department of Civil Engineering
Division of Hydraulic & Sanitary Engr.
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INTRODUCTION
Chemical Parameters Measured in Sea Water

Sea water shares with air the distinction of being the clcsest thing to a universal substance contemplated by the ancient philosophers exemplified by their division of matter into earth-air-fire or water. Whereas we now know that earth and fire are by no means homogeneous, it is theoretically consistant to refer to sea water as a thermodynamic phase. As sea water covers over 70% of the surface of the globe there can be little doubt of its importance.

The aspect of sea water which we shall concern ourselves primarily is the composition of sea water. Random bulk samples of sea water would show it to be an extremely complex mixture of (1) dissolved solids as ions, (2) suspended organic and inorganic matter as colloids and discrete particles, (3) dissolved gases, and (4) living matter as megascopic as the whale and as microscopic as single celled nano plankton and bacteria. Thus we must redefine and restrict our definition of sea water to the non-living portion of the fluid in the oceans when we speak of homogeneity of sea water. Accordingly this discussion of the composition of sea water will be primarily concerned with the non-living portion of sea water leaving the living segment to the biological oceanographers. However if our total concern was to catalogue just the various constituents that make up sea water the subject could be covered in a hand-out. Our concern is not only with what is sea water but also why does sea water have its particular composition, and also a few guesses on how did sea water attain its present composition. Thus interactions between the various realms in contact with sea water, such as living matter in sea water, the overlying atmosphere, the bottom sediments, erosion products dumped into the oceans from the land, gases, liquids, and solids erupted into the oceans from depth, and particulate matter from various sources such as extraterrestrial. All must be considered with respect to their

TABLE I-1

SOME BASIC FACTS ON THE OCEANS AND SEA WATER

Area of Earth	510,100,934 km^2	
Area of Land	148,847,000 km^2	29%
Area of Oceans	361,254,000 km^2	71%

Volume of Oceans	1,369,000,000	km^3
Volume of Continental Crust	5×10^9	km^3
Volume of Oceanic Crust	2×10^9	km^3

Mean Depth of Oceans	3.790	km
Average Thickness of Continental Crust	3.3×10^1	km
Average Thickness of Oceanic Crust	5×10^0	km

- SEA WATER -

Characteristic Density	1.025 gm/cm^3
Maximum Surface Temperature	32° C
Minimum Surface Temperature	- 2° C
Median Surface Temperature	~~30° C~~ 20°C
Average Temperature	3.8° C

% of Ocean Volume Colder than 10° C	93%
% of Ocean Volume Colder than 4° C	76%

From Von Arx
p. 398-399, 1962

influence on the composition of sea water.

Obviously the first step is to describe sea water so its attributes can be examined in detail.

CHEMICAL PARAMETERS

Concentration units: the quantity of a particular substance is, of course, of fundamental significance. As sea water is a complex solution, it is advisable to know (1) the total amount of dissolved matter and (2) the particular distribution of each dissolved species. The concentration unit must be chosen with care (see Table I-2.) As sea water has a specific gravity significantly greater than one that of pure water. Generally weight comparisons are used in reporting the chemical composition of sea water such as parts per thousand $^{o}/oo$ or grams per kilogram. The common concentration units with the proper conversion among them for use in sea water are listed in Table I-2.

Actually for geochemical purposes the actual amount of a particular substance is of secondary importance to the amount available for reaction with other ions. Thus

$$M_s(\text{individual species}) = \frac{As}{\gamma s}$$

or $A_s = \gamma_s M_s$ where A = Activity or effective concentration
γ = Activity co-efficient
M = Actual concentration in appropriate units.

In many cases it is possible to measure only the activity (for example with glass electrodes). In dilute solutions γ is essentially one; however sea water is not dilute so the activity co-efficient has a value other than one.

TABLE I-2

Common Concentration Units in Sea Water

$$\text{Formality} = f = \frac{\text{Moles of Solute}}{\text{1000 gm. solution}}\ \text{(sea water)}$$

$$= \frac{{}^{o}/oo}{\text{Gram (atomic or formula) weight}}$$

$$= \frac{\text{equivalents}}{\text{kilogram of sea water x Z of solute}}$$

or

$$fz = \frac{\text{equivalents}}{\text{kilogram of sea water}}$$

$$\text{Molarity} = M = \frac{\text{moles of solute}}{\text{liter (1000 cm}^3\text{) solution (sea water)}}$$

$$= f \times \rho\ \text{(DENSITY OF SEA WATER)}$$

$$= \text{gm atoms/liter}$$

M also reported as mg atoms/liter or gm atoms/liter x 10^3

$$\text{Molality} = m = \frac{\text{moles of solute}}{\text{1000 gm of water }(H_2O)}$$

$$= f\frac{\text{(weight of solute)}}{\text{(weight of water)}}$$

$$= f\frac{\text{(weight of solution)}}{\text{(weight of solution - total weight solutes)}}$$

For Sea Water $\rho > 1$

$f < M < m$

Example: $Cl^- = 18.97\ {}^{o}/oo$ $\rho_{SW} = 1.024$

Gram atomic weight Cl = 35.457 gm

$$f(Cl^-) = \frac{18.97}{35.457} = .5353$$

.5353

$$M_{(Cl^-)} = .[illegible] \times 1.024$$

$= .55$

$= 550$ mgm atoms/liter

$$m_{(Cl^-)} = .5353\ \frac{(1000\text{ gms})}{(1000\text{ gms} - 34.38\text{ gms*})}$$

$= .5353 \times 1.036$

$= .554$

Basic Definitions from Garrels and Christ (1965, p. 3-5)

*Total Dissolved Solids = 0.073 + 1.811 CL (Lyman and Fleming, 1940)
where [redacted] (Sverdrup and Others, 1942, p. 173)

$Cl^- = 0.99894$ CL

TABLE I-3

Activity Coefficients of Individual Species in Sea Water*
(Ionic Strength, 0.7; Chlorinity, 19 °/oo, 25°C)

Dissolved Species	Activity Coefficient	Method Used
$NaHCO_3^0$	1.13	Analogy with H_2CO_3
$MgCO_3^0$	1.13	Same
$CaCO_3^0$	1.13	Same
$MgSO_4^0$	1.13	Same
$CaSO_4^0$	1.13	Same
HCO_3^-	0.68	Figure 4.5, A
$NaCO_3^-$	0.68	Analogy with HCO_3^-
$NaSO_4^-$	0.68	Same
KSO_4^-	0.68	Same
$MgHCO_3^+$	0.68	Same
$CaHCO_3^+$	0.68	Same
Na^+	0.76	Meas. glass electrode
K^+	0.64	$\gamma K^+ = \gamma \pm KCl$
Mg^{++}	0.36	$\gamma Mg^{++} = (\gamma^3 \pm MgCl_2)/(\gamma^2 \pm KCl)$
Ca^{++}	0.28	$\gamma Ca^{++} = (\gamma^3 \pm CaCl_2)/(\gamma^2 \pm KCl)$
Cl^-	0.64	$\gamma Cl^- = \gamma \pm KCl$
CO_3^{--}	0.20	Figure 4.5, D
SO_4^{--}	0.12	See text

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*The values of the activity coefficients listed in Table I-3 are taken from the paper of Garrels and Thompson, op. cit. However, the values used for both the neutral and charges ion-pair species, as well as the individual ions, are somewhat controversial, because it is not possible to put accurate limits of error on these numbers. Perhaps the best method of indicating the degree of uncertainty is to cite alternate values representing the extreme differences that have been suggested for some of these values. Garrels and Thompson used 1.13 for uncharges species; it has been suggested that the correct value may be 1.0 or a few percent less. They used 0.36 for γMg^{++}, a value derived from a given published set of data for $\gamma \pm MgCl_2$; another set of published data yields $\gamma Mg^{++} = 0.29$. The value of γNa^+ measured with a glass electrode was 0.76; the value calculated from published data on $\gamma \pm NaCl$ is 0.71. These differemces are probably representative of the maximum errors to be expected.

From Garrels and Christ (1965, p. 103)

(Refer to Table I-3) A useful concept in consideration of the effect of the interaction of various species in a complex solution like sea water is IONIC STRENGTH (I) or

$$I = \frac{1}{2} \Sigma \; m_i \; Z_i^2$$

WHERE:

m_i = molality of individual ion

Z_i = charge of ith ion in solution

Lyman and Fleming (1940) list the emperical relationship between chlorinity and ionic strength as

$$I = 0.00147 + 0.03592 \, CL + 0.000068 \, CL^2$$

WHERE CL = chlorinity in parts per thousand (g/kg).

Experimental plots of γ verses ionic strength (Figure I-1) show the relationship is not simple. Thus in geochemical calculations involving sea water knowledge of the concentration is not sufficient.

Complexing: Another difficulty in making geochemical calculations in sea water is the tendency of ions to complex in solutions of high ionic strength. This is especially true of the anions. Table I-4 shows the distribution of the major dissolved species in surface sea water as determined by Garrels and Thompson (1961). For example a total analysis of $[SO_4^=]$ is really indicative of

$$m \, SO_4^= \text{ TOTAL} = m \, Na \, SO_4^- +$$

$$m \, KSO_4^- + m \, CaSO_4^\circ + m \, MgSO_4^\circ +$$

$$m \, SO_4^= \text{ FREE} + \ldots\ldots$$

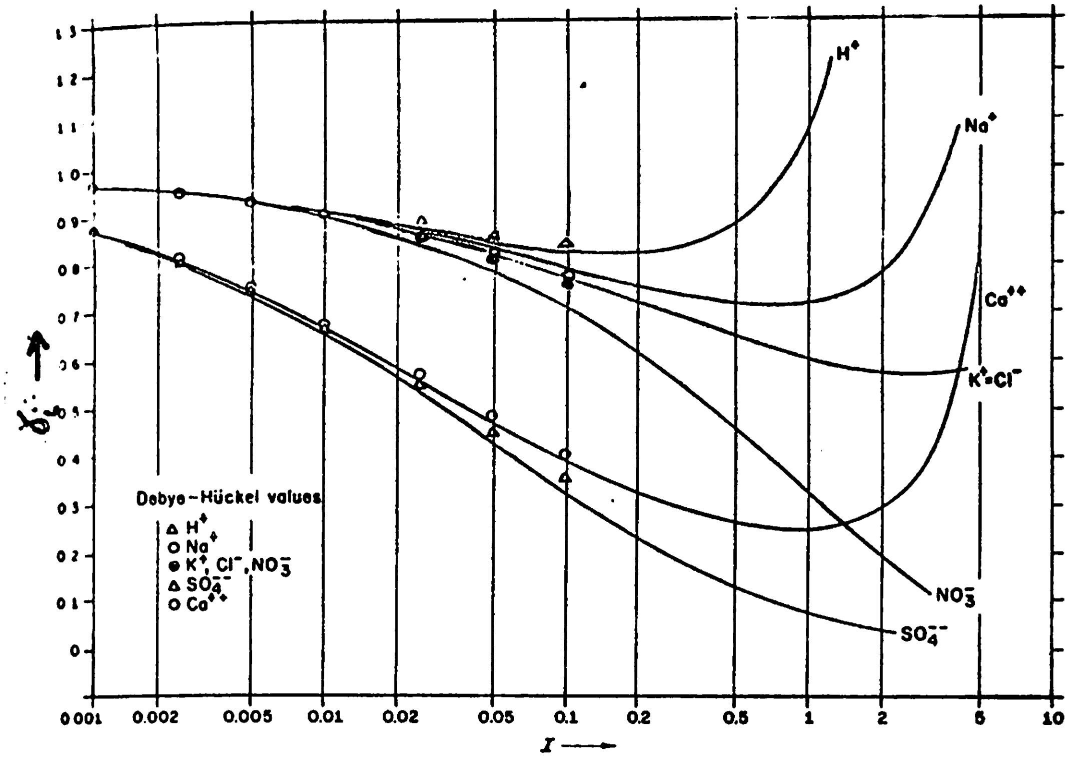

FIG. 2.15. Single ion activity coefficients vs. ionic strength for some common ions. Solid lines represent the values calculated by the mean salt method. Debye-Hückel values were calculated using equation (2.76), with $10^8/\mathring{a}_i = 9$ for H^+; 4 for Na^+; 3 for K^+, Cl^-, NO_3^-; 6 for Ca^{++}; and 4 for SO_4^{--}. The Debye-Hückel γ_i values for the monovalent ions converge, within experimental error, for $I < 0.01$.

Some Ionic Activity Coefficients Determined by Mean Salt and Debye-Hückel Methods

In Figure 2.15 are plotted the individual activity coefficients for some common ions, as determined by the mean salt method and by the Debye-Hückel method. For the calculations by the mean salt procedure, the methods outlined previously were used. It was assumed that $\gamma_{K^+} = \gamma_{Cl^-} = \gamma_{\pm KCl}$; values of γ_{H^+}, γ_{Na^+}, and $\gamma_{Ca^{++}}$ were then calculated, using values of the mean activity coefficients of the respective chlorides in equation (2.71) or in equation (2.72). Values of $\gamma_{NO_3^-}$ were calculated from the relation

$$\gamma_{NO_3^-} = \frac{\gamma^2_{\pm KNO_3}}{\gamma_{\pm KCl}}, \qquad (2.79)$$

and values of $\gamma_{SO_4^{--}}$ by using equation (2.73).

FROM GARRELS AND CHRIST (1965, p.63)

TABLE I-4

DISSOCIATION OF THE MAJOR IONS IN SEA WATER

1 atm. Cl=19% pH=8.1 +25°C

Ion	molality	% Free	% $MeSO_4$	% $MeHCO_3$	% $MeCO_3$
Ca^{++}	0.0104	91	8	1	0.2
Mg^{++}	0.0540	87	11	1	0.3
Na^{+}	0.4752	99	1.0	----	---
K^{+}	0.0100	99	1	----	---

Ion	Molality	% Free	% Ca Anion	% Mg Anion	%Na Anion	%K Anion
$SO_4^{=}$	0.0284	54(39)	3(4)	21.5(19)	21(38)	0.5
HCO_3^{-}	0.00238	69	4	19	8	---
$CO_3^{=}$	0.000269	9	7	67	17	---

Reference: Garrels and Thompson (p. 63, 1962)
Values in parentheses ( ) Kester and Pytkowicz (1970, p. 1047)

Hydrogen Ion: As sea water, with all its dissolved solids is still essentially water the concentration and activity of the hydrogen ion is of extreme importance and enters into practically all geochemical reactions in sea water. The most useful parameter is operational pH or the negative log of the activity of the hydrogen ion. With suitable buffers as standards the pH in sea water may be measured relatively easily and rapidly with glass electrodes. The pH of surface sea water is remarkable constant at a value of between 8.1 to 8.3 with a minimum value of about 7.6 at the oxygen minimum (see Figure I-2); which in itself is indicative of the buffer capacity of sea water. Later we will discuss the buffer question and try to ascertain what factors produce this ability in sea water and what determines the value of the sea water buffer.

Alkalinity: The unfortunate fact that sea water is a good pH buffer detracts from the usefulness of pH as a measurement of variables in sea water. The surface ocean is slightly alkaline pH $\sim$ 8 so there is an excess of anions over cations. The excess base is thought by some (see Harvey, 1963, p. 153) to be equivalent to the bicarbonate, carbonate, and borate ions in sea water. This alkali reserve or titration alkalinity is determined by titration with a strong acid usually HCl. Table I-5 shows how the determination of alkalinity can be useful in estimating other parameters in sea water. Various methods used to determine alkalinity are given by Thompson and Anderson (1940), Park and Others (1963), Dyrssen and Sillen (1967), and Edmonds (1970).

FIGURE I-2

Distribution of pH with depth at 10°12' N., 26°36' W. (Data from *Meteor* Expedition, 1925-7) (Harvey, 1966, p. 37).

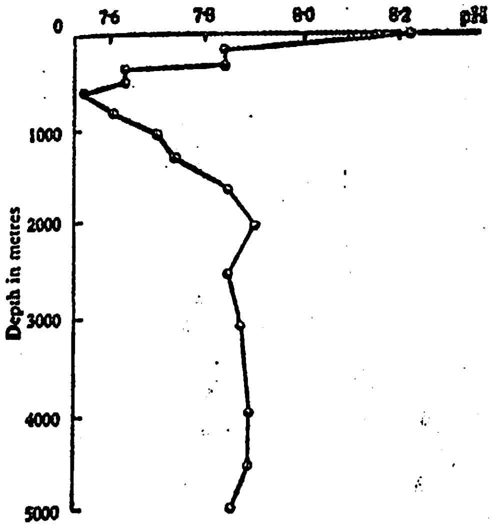

TABLE I-5

FUNDAMENTAL ALKALINITY EQUATIONS

(1) Titration Alkalinity

$$(TA) = M_{HCO_3^-} + 2\ M_{CO_3^=} + M_{H_2BO_3^-} + (M_{OH^-} - M_{H^+})$$

(2) Carbonate Alkalinity (CA) $= M_{HCO_3^-} + 2\ M_{CO_3^=}$

(3) $$M_{H_2BO_3^-} = \frac{K_{zB}' \times 2.2 \times Cl\ ^o/oo \times 10^{-5}}{M_{H^+} + K_B'}$$ (Values given in Harvey, p. 164..Table 20)

where:

$$K_B' = \frac{M_{H^+} \times M_{H_2BO_3^-}}{M_{H_3BO_3}}$$

$$\text{Total Boron} = 2.2 \times Cl\ ^o/oo \times 10^{-5}$$

(4) $$CA = TA - M_{H_2BO_3^-} - (M_{OH^-} - M_{H^+})$$

(for pH 5.5 - 8.5 $(M_{OH^-} - M_{H^+})$ is negligible)

(5a) $$K_1' = \frac{a_{H^+} \times M_{HCO_3^-}}{a_{H_2CO_3}}$$

(5b) $$K_2' = \frac{a_{H^+} \times M_{CO_3^=}}{M_{HCO_3^-}}$$

(6) $$M_{HCO_3^-} = CA \times \frac{1}{1 + 2K_2'}$$

(7) $$M_{CO_3^=} = CA \times \frac{K_2'}{2\ K_2' + a_{H^+}}$$

Fundamental Alkalinity Equations (continued) Table I-5

(8) $a_{CO_2} = P_{CO_2} \times \alpha_o$

where: α_o = CO_2 Solubility (mils/liter) in H_2O (Values in Harvey, p. 168, Table 23)

(9) $a_{H_2CO_3} \equiv a_{CO_2} \times a_{H_2O}$ (Values in Harvey, p. 169, Table 24)

where: a_{H_2O} = Activity of Water

(10) $P_{CO_2} = CA \times \dfrac{a_{H^+}}{K_1'\ \alpha_o\ \left(1 + \dfrac{2K_2'}{a_{H^+}}\right)\ a_{H_2O}}$ (Final Term Values in Harvey, p. 170, Table 25)

(11) $M_{CO_2} = \alpha_s\ P_{CO_2}$ (Values in Harvey, p. 168, Table 23)

where: α_s = Concentration Mols/Liter of CO_2 in Sea Water at Stated Conditions

(12) Total CO_2 = $M_{HCO_3^-} + M_{CO_3^=} + M_{CO_2}$ (in Solution)

$$= CA \left\{ \frac{1 + \dfrac{K_2'}{a_{H^+}} + \dfrac{\alpha_s \times a_{H^+}}{K_1' \times \alpha_o \times \alpha_{H_2O}} \ldots}{1 + \dfrac{2\ K_2'}{a_{H^+}}} \right\}$$

(Values of Last Term in Harvey, p. 174, Table 26)

SEA WATER - GIBBSIAN OR NON-GIBBSIAN?

In chemical oceanology we are forced obviously, to try to utilize the simplest chemical concepts. As shown above simplifications justified for "ideal" or dilute solutions, such as unit activity co-efficients, are not justified and would lead to misleading results in sea water calculations. Although sea water is complex, the fact that it is so uniform spatially today and probably has been so for the past 600 million years as indicated by the fossil record leads one intuitively to feel the mechanisms controlling the composition of sea water are straight forward. In Gibbsian terms there are a finite number of equilibrium reactions governing the composition of sea water. Garrels and Thompson (1962) used this equilibrium approach in their ocean model. Weyl (1966), however has pointed out that the equilibrium concept, although apparently valid for reactions in sea water among dissolved ions and gasses, is unrealistic for sea water - solid reactions and for biological contributions to the composition of sea water. The problem essentially is kinetic, that is the reactions (1) among sea water and solids occur too slowly and (2) among sea water and living organisms should not occur at all according to Gibssian equilibria. Thus finding and solving n equations with n unknowns apparently will not solve the problem of the relative constancy of oceanic composition if very slow or non-equilibrium reactions play a significant role in determining sea water composition. Weyl (1966) proposes three stabilizing mechanisms (1) size, (2) chemical equilibria (Gibbsian) and (3) negative feed-back.

Accordingly in this study of the chemistry of the oceans; although emphasis will be placed on reproducible equilibria in sea water other factors both geological and biological will have an effect on composition. In other words, sea water is not an "ideal" fluid which can be studied in isolation in a chemistry laboratory, but is a "real" fluid which must be examined in terms of its environment and history as well as its chemistry.

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Master

UNIVERSITY OF CALIFORNIA
CE 201 B,
Composition of Sea Water

Department of Civil Engineering
Div., Hydraulic and Sanitary Eng.
Instructor: Pat Wilde

Composition of Sea Water

The first thing to be learned in any systematic treatment of the chemistry of sea water is its composition. This implies investigations into (1) sampling methods, (2) analytical techniques, and (3) the variability of composition. Areas (1) and (2) will be discussed only in passing. A more comprehensive treatment of them is given in the various articles in the reading list. The individual components and their variability will be the primary topic of discussion.

The salinity (^{o}/oo) is approximately equivalent to the total salt content and varies in the open ocean between 33^{o}/oo to 38^{o}/oo. Ions of only nine elements (chlorine, sodium, magnesium, sulfur, calcium, potassium, strontium, bromine, and fluorine) comprise 99 1/2% of the salts in solution. These ions, because of their approximate constant proportion to each other are called the <u>conservative constituents</u> of sea water. Other elements and the dissolved gases occur in varying proportions to each other and are grouped as the <u>non-conservative constituents</u>. The variations in the proportions of the non-conservative constituents are functions of biological activity and changes in temperature and pressure. Table II-I lists the elements present in solution and Table II-2 lists the major constituents of sea water. Appendix II-1 gives several recipes for artifical sea water.

Conservative Constituents

Systematic analytical study of the composition of sea water began with the pioneering work of Forschammer and Dittmar (see Riley's (1965, p. 1-41 excellent historical summary in volume one of <u>Chemical</u>

TABLE II - 1

Table 36

ELEMENTS PRESENT IN SOLUTION IN SEA WATER

(Dissolved gases not included)

Element	mg/kg Cl = 19.00 ‰	mg-atoms/L Cl = 19.00 ‰	Atomic weight (1940)	1/atomic weight	Authority
Chlorine	18980	548.30	35.457	0.02820	
Sodium	10561	470.15	22.997	0.04348	
Magnesium	1272	53.57	24.32	0.04112	
Sulphur	884	28.24	32.06	0.03119	
Calcium	400	10.24	40.08	0.02495	
Potassium	380	9.96	39.096	0.02558	
Bromine	65	0.83	79.916	0.01251	
Carbon	28	2.34	12.01	0.08326	
Strontium	13	0.15	87.63	0.01141	
Boron	4.6	0.43	10.82	0.09242	
Silicon	0.02 –4.0	0.0007 –0.14	28.06	0.03564	
Fluorine	1.4	0.07	19.00	0.05263	
Nitrogen (comp.)	0.01 –0.7	0.001 –0.05	14.008	0.07139	
Aluminum	0.5	0.02	26.97	0.03708	
Rubidium	0.2	0.002	85.48	0.01170	
Lithium	0.1	0.014	6.940	0.14409	
Phosphorus	0.001–0.10	0.00003–0.003	30.98	0.03228	
Barium	0.05	0.0004	137.36	0.00728	
Iodine	0.05	0.0004	126.92	0.00788	
Arsenic	0.01 –0.02	0.00015–0.0003	74.91	0.01335	
Iron	0.002–0.02	0.00003–0.0003	55.85	0.01791	
Manganese	0.001–0.01	0.00002–0.0002	54.93	0.01820	
Copper	0.001–0.01	0.00002–0.0002	63.57	0.01573	
Zinc	0.005	0.00008	65.38	0.01530	Atkins (1936)
Lead	0.004	0.00002	207.21	0.00483	Boury (1938)
Selenium	0.004	0.00005	78.96	0.01266	Goldschmidt and Strock (1935)

Table 36 (*Continued*)

Element	mg/kg Cl = 19.00 ‰	mg-atoms/L Cl = 19.00 ‰	Atomic weight (1940)	1/atomic weight	Authority
Cesium	0.002	0.00002	132.91	0.00752	Wattenberg (1938)
Uranium	0.0015	0.00001	238.07	0.00420	Föyn *et al* (1939)
Molybdenum	0.0005	0.000005	95.95	0.01042	Ernst and Hoermann (1936)
Thorium	<0.0005	<0.000002	232.12	0.00431	Föyn *et al* (1939)
Cerium	0.0004	0.000003	140.13	0.00714	Goldschmidt (1937)
Silver	0.0003	0.000003	107.880	0.00927	Haber (1928)
Vanadium	0.0003	0.000006	50.95	0.01963	Ernst and Hoermann (1936)
Lanthanum	0.0003	0.000002	138.92	0.00720	Goldschmidt (1937)
Yttrium	0.0003	0.000003	88.92	0.01125	Goldschmidt (1937)
Nickel	0.0001	0.000002	58.69	0.01704	Ernst and Hoermann (1936)
Scandium	0.00004	0.0000009	45.10	0.02217	Goldschmidt (1937)
Mercury	0.00003	0.0000001	200.61	0.00498	Goldschmidt (1937)
Gold	0.000006	0.00000002	197.2	0.00507	Haber (1928)
Radium	$0.2 - 3 \times 10^{-10}$	$0.8 - 12 \times 10^{-13}$	226.05	0.00442	Evans, Kip, and Moberg (1938)
Cadmium					Fox and Ramage (1931)
Chromium					Webb (1937)
Cobalt					Thompson and Robinson (1932)
Tin					Thompson and Robinson (1932)

TABLE II-2

TABLE 35

MAJOR CONSTITUENTS OF SEA WATER

($Cl = 19.00$ ‰, $\rho_{20} = 1.0243$)

Ion	‰	Cl-ratio, g per unit Cl	Equivalent per kg of sea water	mg-atoms per liter	Chlorosity factor, mg-atoms per unit *Cl*	Authority
Chloride, Cl^-	18.9799	0.99894	0.5353	548.30	28.17_3	Dittmar (1884), Jacobsen and Knudsen (1940)
Sulphate, SO_4^-	2.6486	0.1394	0.0551	(SO_4-S) 38.24	1.45_1	Thompson, Johnston, and Wirth (1931)
Bicarbonate, HCO_3^-	0.1397	0.00735[a]	0.0023	(HCO_3-C) 2.34	0.12_0	Revelle (1936)
Bromide, Br^-	0.0646	0.00340	0.0008	0.83	0.042_6	Dittmar (1884)
Fluoride, F^-	0.0013	0.00007	0.0001	0.07	0.003_6	Thompson and Taylor (1933)
Boric acid,[c] H_3BO_3	0.0260	0.00137[b]	[c]	(H_3BO_3-B) 0.43	0.022_1	Harding and Moberg (1934), Igelsrud, Thompson, and Zwicker (1938)
Total			0.5936			
Sodium,[d] Na^+	10.5561	0.5556	0.4590	470.15	24.15_8	By difference, and Robinson and Knapman (1941)
Magnesium, Mg^{++}	1.2720	0.06695	0.1046	53.57	2.75_3	Thompson and Wright (1930)
Calcium, Ca^{++}	0.4001	0.02106	0.0200	10.24	0.526_2	Kirk and Moberg (1933); Thompson and Wright (1930)
Potassium, K^+	0.3800	0.02000	0.0097	9.96	0.511_8	Thompson and Robinson (1932)
Strontium, Sr^{++}	0.0133	0.00070	0.0003	0.15	0.007_7	Webb (1938)
Total			0.5936			

Total dissolved solids = 34.4816 ‰

Sum of constituents (HCO_3^- as $O^=$, and Br^- as Cl^-) = 34.324 ‰

Salinity (S ‰ = 0.030 + 1.805 Cl ‰) = 34.325 ‰

[a] Ratio for millival/kg = 0.1205

[b] Ratio for boron/Cl = 0.000240

[c] Boric acid undissociated

[d] Sodium calculated by difference in sums of equivalents

Oceanography). Dittmar (1884) on the basis of 77 relatively complete chemical analyses, mostly from the Challenger Expedition, was first able to establish critically that the major dissolved salts were in approximate constant ratio to one another. Dittmar however did not state the ratio was constant and in fact his data showed a statisfically significant difference in the various ratios between surface and deep waters particularily for calcium.

Local deviations from conservancy have been reported by Bein and others (1935); in particular Billings and others (1969) for the alkaline earths; Greenhalgh and Riley (1961) and Brewer and others for fluoride; and Andersen and others (1970) for strontium. However the nine major elements or conservative elements do show a more constant ratio to each other than the remaining constituents of sea water. Unfortunately Dittmar's discovery lead to an abandonment of complete chemical analyses of sea water as most scientists assumed a constant ratio for the conservative elements thus just measured one, usually chlorine actually chlorinity, and calculated the rest.

Re-examination of the validity of Dittmar's constant ratio concept is now underway at the National Oceanographic Institute of Great Britian where many complete analyses of sea water are being made. Many more analyses on non-surface waters must be made to truly justify the concept. Table II-3 shows some of the recent ratios.

However for most research it is sufficient to recognize two classes of dissolved inorganic material in sea water, (1) the nine major conservative elements in their various ionic forms, whose ratios among themselves is approximately constant and (2) the remaining trace elements and dissolved gases whose concentrations are highly variable.

TABLE II-3

Summary

Ocean etc.	$\frac{\text{Na (g/kg)}}{\text{Cl ‰}}$	$\frac{\text{K (g/kg)}}{\text{Cl ‰}}$	$\frac{\text{Mg (g/kg)}}{\text{Cl ‰}}$	$\frac{\text{Ca (g/kg)}}{\text{Cl ‰}}$	$\frac{\text{Sr (mg/kg)}}{\text{Cl ‰}}$
N. Pacific Ocean	0·5556 (5)	0·0206 (8)	0·06670 (10)	0·02128 (10)	0·40 (10)
S. Pacific Ocean	0·5554 (6)	0·0206 (6)	0·06691 (8)	0·02128 (8)	0·40 (6)
N. Atlantic Ocean	0·5552 (7)	0·0206 (7)	0·06691 (9)	0·02128 (9)	0·40 (6)
S. Atlantic Ocean	—	—	0·06692 (1)	0·02120 (1)	0·38 (1)
Northern Seas	0·5553 (5)	0·0205 (5)	0·06690 (7)	0·02121 (7)	0·39 (6)
Southern Ocean	0·5567 (2)	0·0206 (2)	0·06691 (3)	0·02130 (3)	0·40 (3)
Indian Ocean	0·5554 (6)	0·0207 (6)	0·06696 (10)	0·02124 (10)	0·40 (10)
Mediterranean Sea	0·5557 (11)	0·0206 (11)	0·06685 (11)	0·02131 (11)	0·39 (9)
Red Sea	0·5563 (3)	0·0206 (3)	0·06685 (3)	0·02115 (3)	0·38 (3)
Persian Gulf	0·5557 (1)	0·0208 (1)	0·06695 (1)	0·02123 (1)	0·38 (1)
North Sea	0·5541 (2)	0·0206 (2)	0·06703 (2)	0·02118 (2)	0·40 (2)
Baltic Sea	0·5554 (1)	0·0205 (1)	0·06694 (1)	0·02127 (1)	0·38 (1)
All	0·5555 (49)	0·0206 (54)	0·06692 (66)	0·02126 (66)	0·40 (58)
Standard Sea Water (Batch P33)	0·5562	0·0205	0·06690	0·02122	0·39

(Number of samples in brackets)

Table 1. *Principal determinations of bromine in sea water*

Reference	*Ocean or Sea etc.*	Br (g/kg) *for* S = 35‰	$\frac{\text{Br (g/kg)}}{\text{Cl‰}}$
BERGLUND (1885)	North	0·0638–0·0665	0·00330–0·00334
	Atlantic	0·0652–0·0660	0·00337–0·00341
	Gulf of Mexico	0·0660	0·00341
	Mediterranean	0·0663	0·00343
	Adriatic	0·0660	0·00341
MAKIN (1898)	Atlantic	0·0628	0·00325
WINKLER (1916)	Adriatic	0·0670	0·00347
CAMERON (1922)	Departure Bay	0·0693	0·00358
VASIL'EV (1937)	Japan	0·0643	0·00333
RATMANOFF (1937)	Bering	0·0668	0·00345
MIYAKE (1939)	W. Pacific	0·0640	0·0033
THOMPSON and KORPI (1942)	N.E. Pacific	0·0673	0·00348
	Antarctic	0·0667	0·00345
	Bering	0·0670	0·00347
MATIDA and YAMAUCHI (1951)	Japan	0·0670	0·00347
HASLAM and GIBSON (1950)	British Coastal Waters	0·0667	0·00345

Table 4. *Principal determinations of sulphate in sea water*

Reference	*Ocean, Sea etc.*	SO_4^{2-} (g/kg) *for* S = 35‰	$\frac{SO_4^{2}\text{ (g/kg)}}{\text{Cl‰}}$
DITTMAR (1884)	Various	2·689	0·1388
THOMPSON, LANG and ANDERSON (1927)	N. Pacific	2·701	0·1396
THOMPSON, JOHNSTON and WIRTH (1931)	Various	2·699–2·710	0·1393–0·1399
MIYAKE (1939)	W. Pacific	2·707	0·1397
NISHIKAWA, OKUNA, MAEDA and OGATA (1939)	Pacific and Atlantic	2·751	0·1420
MATIDA (1951)	Tokyo Bay	2·701	0·1394
BATHER and RILEY (1953)	Irish	2·710	0·1399
FUKAI and SHIOKAWA (1955)	W. Pacific	2·710	0·1399
	N. Pacific	2·707	0·1397

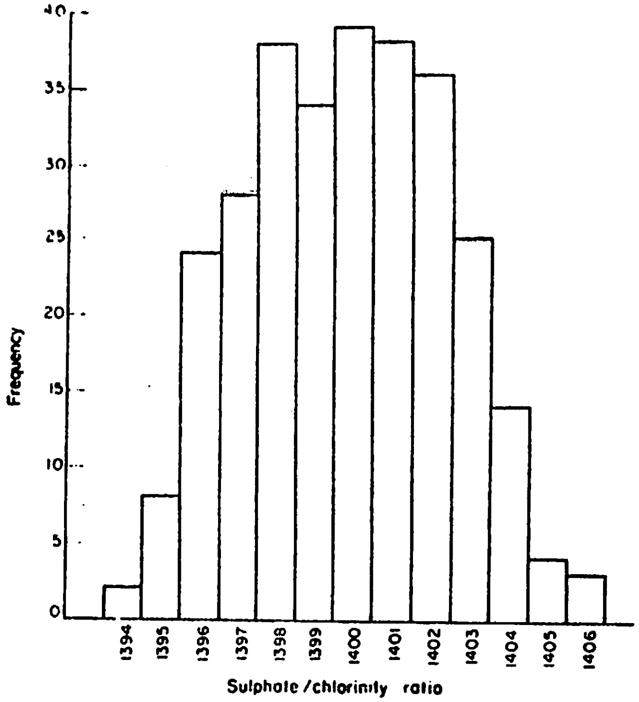

Fig. 2. Histogram of sulphate/chlorinity ratio results.

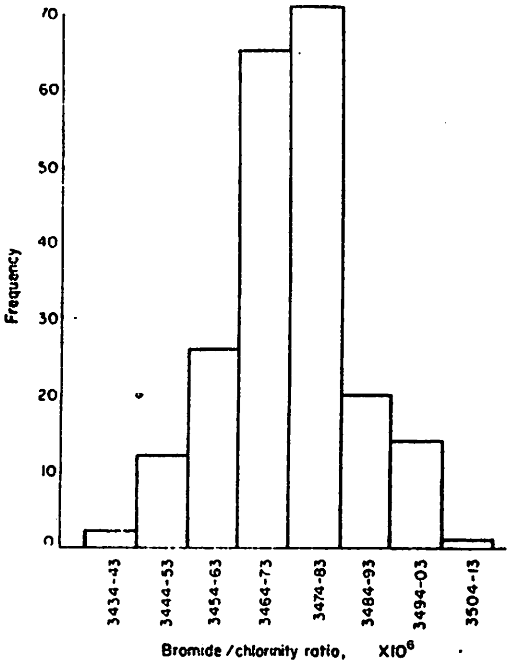

Fig. 1. Histogram of bromide/chlorinity ratio results.

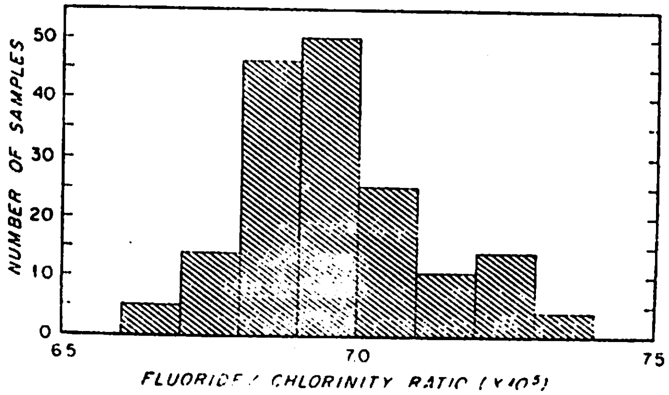

Table II-3

Ion/Chlorinity Relationshios For Conservative Ions

	Mean Ion/CL	Number of Samples	Standard Deviation	Comments
K	0.0206	54	±.0002	
Na	0.5555	49	±.0007	
Mg	0.06692	66	± 0.00004	
Ca	0.02126	66	± 0.00004	Deep values higher than shallow
Sr	0.0004	58	± 0.0002	
Br	0.003473	219	± 0.000012	
SO_4	0.1400	345	± 0.00023	
F	0.000067			Some Anomalously High Deep Value

Values for K, Na, Mg, Ca, Sr from Culkin and Cox (1966),
for Br and SO_4 from MOrris and Riley (1966),
for F from Greenhalgh and Riley (1961) and Brewer and others (1970).

Dissociation in the Conservative Constituents

As analytical techniques improve it becomes easier to know exactly what are the various components of sea water. One fact must be reintegrated when one examines chemical analyses of sea water - the form the results are reported are a function of the analytical methods, and may have little bearing on the form actually in sea water. For example, chemical results in the early 20th century generally were reported as oxides. This does not mean the material analyzed was composed entirely of oxides, but that the final compound of the analyzed element was an oxide. There is a tendancy, which should be resisted strongly to read into chemical analyses information that is simply not there. Most chemical analyses of sea water give only the bulk elemental composition (see Table II-1). The various ionic species of a particular element or ion pair generally can be determined only by equilibrium studies or by analogy with well known ionic reactions. The ionic species must be known before any reasonable ocean models are constructed or any critical investigations into chemical reactions in sea water are undertaken. Garrels and Thompson (1962) gave an excellent survey of the problem in their paper on a surface sea water model. Table II-4 gives a summary on the dissociation of the major ions in sea water.

Non-Conservative Constituents

Trace dissolved solids: The analytical problems for trace dissolved solids are similar ot those encountered for the conservative constituents so do not justify a separate treatment. Other problems concerning the trace dissolved solids will be treated later.

Table II-4

Ionic Complexes of the Conservative Elements of Sea Water

Species

Free	Complexed	Percent
Cl^-		99.5(a) 100(b)
	$C\ell O_4$	0.5(a)
Na^+		99(b)
	$NaSO_4^-$	1(b)
	$NaHCO_3^o$	--
	$NaCO_3^-$	--
K^+		99(b)
	KSO_4^-	1(b)
	$KHCO_3^o$	--
	KCO_3^-	--
Mg^{++}		87(b), 90(c), 90(d), 90(e)
	$MgSO_4^o$	11
	$MgHCO_3^+$	1
	$MgCO_3^o$	0.3
Ca^{++}		91(b), 84(c)
	$CaSO_4^o$	8
	$CaHCO_3^+$	0.8
	$CaCO_3^o$	0.2
SO_4^-		54(b), 39(e)
	$CaSO_4^o$	3(b), 4(e)
	$MgSO_4^o$	21.5(b), 19(e)
	$NaSO_4^-$	21(b), 38(e)
	KSO_4^-	0.5(b)

Table II-4 cont.

Free	Complexed	Percent
HCO_3^-		69(b)
	$CaHCO_3^+$	4(b)
	$MgHCO_3^+$	19(b)
	$NaHCO_3^-$	8(b)
	$KHCO_3^-$	--
$CO_3^{=}$		9(b)
	$CaCO_3^o$	7(b)
	$MgCO_3^o$	67(b)
	$NaCO_3^-$	17(b)
	KCO_3^-	--

References - Table II-4

a Baas-Becking and others
b Garrels and Thompson
c Thompson
d Thompson and Ross
e Kester and Pytkowicz

Dissolved Gases: However the other group on non-conservative elements the dissolved gases because of their difference physical properties must be discussed separately. The factors controlling the gas content of sea water are chiefly functions of (1) the composition of the atmosphere, (2) the partial pressure of the gas in solution, and (3) the solubility of atmospheric gas in sea water Table II-5 shows the composition of the atmosphere which indicates the major gases have a relatively constant composition. Thus the partial pressures of the major gases is a function of the barometric pressure and temperature assuming 100% water saturation at the air-sea interface.

For Henry's Law gases, that is, those gases that do not enter into appreciable chemical reactions in the solution (this excludes CO_2 which has significant dissociation see Table I-5) or

$p \propto P$ where p = partial pressure in the gas phase
P = partial pressure in solution

At equilibrium with the atmosphere

$c = \alpha p$ where

c = concentration of gas in solution
α = solubility co-efficient characteristic of the gas
p = partial pressure in the gas phase

From this discussion it should be apparent why the dissolved gases are non-conservative in the ocean although the ocean is adjacent to the atmosphere with a reasonably constant gas content. For example:

(1) the equilibrium exchange surface is limited to the air-sea interface.

(2) the depth of surface mixing is shallow generally to the depth of the thermocline 50 to 100 meters, where as the average depth of the ocean

25

Table II-5

Composition of Atmosphere

	%	ppm	atm
N_2	78.084 ± 0.004		0.7808
O_2	20.946 ± 0.002		0.2095
CO_2	0.033 ± 0.001		0.0003
Ar	0.934 ± 0.001		0.0093
Ne		18.18 ± 0.04	1.82×10^{-5}
He		5.24 ± 0.004	5.24×10^{-6}
Kr		1.14 ± 0.01	1.14×10^{-6}
Xe		0.087 ± 0.001	8.7×10^{-8}
H_2		0.5	5×10^{-7}
CH_4		2.0	2×10^{-6}
N_2O		0.5 ± 0.1	5×10^{-7}

From Glueckl

auf, E. (1951)

is 3700 meters. (3) several of the important gases particularily CO_2 and O_2 are not ideal Henry's Law gases as they enter into both inorganic and organic chemical reactions such as photosynthesis, oxidation and reduction, and various dissociations.

This implies that internal chemical reactions which determine local gas contents operate at rates faster than the rate of mixing which would tend to make the oceans have homogeneous dissolved gas contents. Also apparently the oceans are buffering the composition of the atmosphere and not the reverse.

The ocean buffer system for the atmosphere must have some lag time as Figure II-1 shows that the CO_2 content of the atmosphere has risen in historic time presumably due to the industrial revolution.

Residence Time

A useful concept relating the reactivities of various elements in sea water is that of residence time.

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

where: τ = residence time

A = total amount of an element in dissolved and particulate state in the ocean

dA/dt = Amount of an element introduced or precipitating per unit time (Barth, 1952)

the quantity "A" can be determined from knowledge of the volume of sea water and from chenical analyses of a particular element in sea water. However, dA.dt is a much more difficult quantity to compute as knowledge is required of (1) the composition and volumes of streams, volcanic gases, and aerosols that empty into the ocean and (2) the chemical reactions in sea water that the various elements participate in.

Order of magnitude calculations of such values have been made by

FIGURE II-1

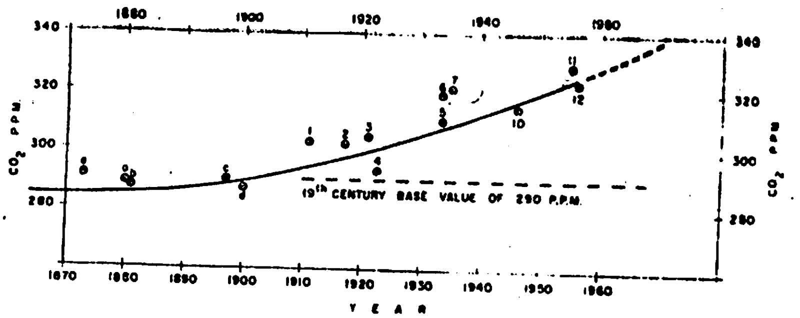

Fig. 1. Amount of CO_2 in the free air of the N. Atlantic region. 1870—1956. Full curve, amount from fossil fuel (See Appx. Table B. for numbered obs. points, and text Table 1 for the 19th century obs. points.)

4. Discussion of Figure 1

It will be seen that the observed points show a decided rising tendency in the later decades, but they appear rather scattered on the scale used for the figure. This scatter is, however, less disturbing when it is realized that both seasonal mean values, and those taken in different parts of Europe during the same season, may differ on occasion by over 5 %. This has been demonstrated by the valuable and extensive new series from Scandinavia, (FONSELIUS et al. 1956). Similar differences are also seen in the 19th century sets covering several seasons, and must result from the interaction of meteorological, biological, and oceanic factors. Certain of these factors have been suggested, (CALLENDAR 1957), to account for the relatively high CO_2 values in the 1930's reported by some observers.

Coming to the present time. It happens that the average of all the new Scandinavian measurements from Dec. 1954 to Dec. 1956, (326 p.p.m. from about 1,000 readings in 25 months at 15 stations. Lat. 56°—68°N. Long. 10°—28°E), lies almost on the fuel line, 12 % above the 1900 base value of 290 p.p.m. Although such very close agreement may be a coincidenc, the general upward trend of the observations since the turn of the century, and especially the manner in which most of them keep near the fuel line, seems very significant. It is, however, most difficult to account for such a large increase of atmospheric CO_2 from the fuel addition only, because radio-carbon methods have recently shown it is in active exchange with very large CO_2 reservoirs in the oceans and biosphere. (CRAIG, l. c. & others). Thus, if the increase shown by the measurements discussed here is even approximately representative of the whole atmosphere, it means that the oceans have not been accepting additional CO_2 on anything like the expected scale. However, this important and interesting problem awaits further observational data, in particular from the Southern hemisphere.

From: Callendar (1958, p. 246)

Livingstone (1963) for river contributions and are summarized by Mackenzie and Garrels (1966) in Table II-5.

Table II-6 lists the residence times for the elements as estimated by Goldberg (1963). Elements with long residence times are characterized by the lack of reactivity with the marine environment or the tendancy to stay in solution. Conversly elements with short residence times are characterized by great reactivity with sea water. Reactivity is controlled by both chemical and biological processes. In general elements which are insoluble have short residence times in sea water, for example aluminium. The reactivity of elements utilized by living matter however is not related directly to solubility constants. Iron, for example, is very soluble but as iron is biologically important, the residence time is much less than would be predicted by its solubility.

Another chemical influence on residence time and reactivity is the degree of undersaturation. The principle here is that the upper limit of concentration that a cation may attain is regulated by the anionic species present. "As a first approximation...Elements with the highest degree of undersaturation would be the most reactive while those at or near saturation would be essentially inert in the marine environment"(Goldberg, 1963).

In short, residence time is primarily a function of (1) the solubility of an element's least soluble compound, (2) degree of saturation, and (3) amount of utilization by the biosphere.

TABLE II-5

Major Constituents of River Water and Sea Water

	River Water			Sea Water		
Constituent	ppm	millimoles/liter	Amount Delivered by Rivers to Ocean Annually	ppm	millimoles/liter	Amount in Ocean
Cl^-	7.8	0.220	25.4 x 10^{10} kg	19,000	535.2	26.1 x 10^{18} kg
Na^+	6.3	0.274	20.7 x 10^{10} kg	10,500	456.5	14.4 x 10^{18} kg
Mg^{++}	4.1	0.171	13.3 x 10^{10} kg	1,300	54.2	1.9 x 10^{18} kg
$SO_4^=$	11.2	0.117	36.7 x 10^{10} kg	2,650	27.6	3.7 x 10^{18} kg
K^+	2.3	0.059	7.4 x 10^{10} kg	380	10.0	0.5 x 10^{18} kg
Ca^{++}	15.0	0.275	48.8 x 10^{10} kg	400	9.7	0.6 x 10^{18} kg
HCO_3^-	58.4	0.958	190.2 x 10^{10} kg	140	2.3	0.19 x 10^{18} kg
SiO_2	13.1	0.218	42.6 x 10^{10} kg	6	0.1	0.008 x 10^{18} kg
H_2O	--	--	3,333,000.0 x 10^{10} kg	--	--	1,370.000 x 10^{18} kg

**After Mackenzie and Garrels,
1966, Tables 1 and 2.**

TABLE II-6

RESIDENCE TIMES IN OCEANS

A. Element	IN YEARS Residence Time	mgm Atoms/Liter Cl = 19 °/oo
Al	1.0×10^2	0.02
Fe	1.4×10^2	0.0003-0.0003
Be	1.5×10^2	
Ti	1.6×10^2	
Nb	3.0×10^2	
Th	3.5×10^2	
Cr	3.5×10^2	
W	1.0×10^3	
Mn	1.4×10^3	0.00002-0.0002
Ga	1.4×10^3	
Pb	2.0×10^3	0.00002
Sc	5.6×10^3	
Ce	6.1×10^3	
Ge	7.0×10^3	
Y	7.5×10^3	
Si	8.0×10^3	0.0007-0.14
V	1.0×10^4	
La	1.1×10^4	
Co	1.8×10^4	
Ni	1.8×10^4	
Cs	4.0×10^4	
Hg	4.2×10^4	
Cu	5.0×10^4	0.00002-0.0002
Ba	8.4×10^4	0.0004
Zn	1.8×10^5	
Rb	2.7×10^5	0.002
Sb	3.5×10^5	
Bi	4.5×10^5	
Mo	5.0×10^5	
Cd	5.0×10^5	
Sn	5.0×10^5	
U	5.0×10^5	
Au	5.6×10^5	3×10^{-6}
Ag	2.1×10^6	2×10^{-8}
Ca	8.0×10^6	10.24
K	1.1×10^7	9.96
Sr	1.9×10^7	0.15
Li	2.0×10^7	0.014
Mg	4.5×10^7	53.57
Na	2.6×10^8	470.15

(after Goldberg, 1963)

Table II-7 Residence Times.

B. Group I - Alkali Earths

Elements	A No.	Ionic Radius	Residence Time
Li	3	0.68	2.0×10^{7}
Na	11	0.97	2.6×10^{8}
K	19	1.33	1.1×10^{7}
Rb	37	1.47	2.7×10^{5}
Cs	55	1.67	4.0×10^{4}

C. Residence Times and Clay Substitutions

Element	Charge	Ionic Radius	Residence Time
	(A) Substitution in Tetrahedral Sheets		
Si	4^+	0.42	8×10^{3}
Al	3^+	0.51	1×10^{2}
	(B) Substitution in Octahedral Sheets		
Al	3^+	0.51	1×10^{2}
Mg	2^+	0.66	4.5×10^{7}
Fe	3^+	0.64	1.4×10^{2}
	(C) Substitution in Interlayer Positions		
Na	1^+	0.97	2.6×10^{8}
Ca	2^+	0.99	8.0×10^{6}
K	1^+	1.33	1.1×10^{7}

D. Residence Times and Carbonate Substitutions

	(A) Calcite Structure		
Mg	2^+	0.66	4.5×10^{7}
Fe	2^+	0.74	1.4×10^{2}
Zn	2^+	0.74	1.8×10^{5}
Mn	2^+	0.80	1.4×10^{3}
Ca	2^+	0.99	8.0×10^{6}
	(B) Aragonite Structure		
Ca	2^+	0.99	8.0×10^{6}
Sr	2^+	1.12	1.9×10^{7}
Pb	2^+	1.20	2.0×10^{3}
Ba	2^+	1.34	8.4×10^{4}

APPENDIX II-1 ARTIFICIAL SEA WATER FORMULAE

Solution A	
NaCl	239.0g
$MgCl_2 \cdot 6H_2O$	108.3g
$CaCl_2$ anhydrous	11.5g
$SrCl_2 \cdot 6H_2O$	0.040g
KCl	6.82
KCr	0.99
Distilled water	8,560.0 cm^3

Solution B	
$NaSO_4 \cdot 10H_2)$	90.6g
$NaHCO_3$	0.20g
NaF	0.003g
H_3BO_3	0.027g
Distilled water	1,000cm^3

Add B to A in a thin jet stirring constantly. Filter after standing one day giving 35°/oo

---

From Dietrich (1963, p. 51)

Solution A	
KCl	10g
KBr	45g
$MgCl_2$	550g
$CaCl_2$	110g
Distilled water to 1 liter	

Solution B	
NaCl	23g
$Na_2SO_4 \cdot 10H_2O$	8g
Soltuion 20 ml	
Distilled water to 1 liter	

For corrosion testing - from Bialek, 1966, p. 379.

NaCl	26.726g
$MgCl_2$	2.260
$MgSO_4$	3.248
$CaCl_2$	1.153
$NaHCO_3$	0.198
NaBr	0.058
H_3BO_3	0.058
Na_2SiO_3	0.0024
$Na_2Si_4O_9$	0.0015
H_3PO_4	0.0002
Al_2Cl_2	0.013
NH_3	0.002
$LiNO_3$ [illegible]	0.0013
KCl	0.721.

Add distilled water to 1 Kg total weight giving 34.4406°/oo TDS

From McClendon and others (1917)

Appendix II-1 Sea Water Formulae

NaCl	26.518g
$MgCl_2$	2.447
$MgSO_4$	3.305
$CaCl_2$	1.141
KCl	0.725
$NaHCO_3$	0.202
NaBr	0.083

From Sublow (1931)

Add distilled water to 1 Kg total weight giving 34.421 °/oo TDS

NaCl	23.476
$MgCl_2$	4.981
Na_2SO_4	3.917
$CaCl_2$	1.102
KCl	0.664
$NaHCO_3$	0.192
KBr	0.096
H_3BO_3	0.026
$SrCl_2$	0.024
NaF	0.003

Add distilled water to 1Kg total weight giving 34.481 °/oo TDS

Lyman and Flemming (1940, p. 143)

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UNIVERSITY OF CALIFORNIA
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THE OCEANS AS A CHEMICAL SYSTEM

The elements in sea water may be divided into two convenient groups (1) those with an approximate constant ratio to each other - conservative elements and (2) those whose concentration varies non-conservative. For chemical analyses sea water may be considered as a simple solution of 11 inorganic ions (Curkin, 1965, p. 122) Cl^-, Na^+, $SO_4^{=}$, Mg^+, Ca^{++}, K^+, HCO_3^-, Br^-, Sr^{++}, B^-, and F^-. Although this arrangement may be justified for analytical purposes it is a simplification of the actual ionic state of the elements. Garrels and Thompson (1962) have shown in their model of surface sea water that although most of the major ions are found chiefly in the uncomplexed form there are significant amounts of complexed ions and ion pairs particularily for the anions (see Table II-4). Thus the specific complex or ion pair is available for chemical reaction not only to the extent of its activity at the ionic strength but also to its degree of complexing. So chemical reactions in sea water can be written using chemical data from analyses only with caution and proper understanding of complexing.

Two of the most complexed ions HCO_3^-, (33%) and $CO_3^{=}$, (90%) initially are produced from dissolved gases (carbonate ions also are produced from solution of the various carbonate solids but as carbonate minerals are formed organically at the surface using complexed dissolved CO_2 gas, the initial source of carbonate ions is still gaseous CO_2). Therefore knowledge of the factors controlling the gaseous content of sea water are important to an understanding of (1) variations in the composition of sea water and (2) what reactions are permitted.

Composition of the Atmosphere

Just above the sea surface is the huge gaseous reservior of the atmosphere. Except in high latitudes where there is a significant cover of ice the lower atmosphere and the upper ocean can exchange freely. The composition of the lower atmosphere is approximately constant except for CO_2 so the partial pressure of the major gases is a function of (1) the barometric pressure and (2) the temperature, assuming 100% saturation at the air-sea interface.

The actual partial pressures in the upper layers of sea water can not be estimated assuming surface pressure = 1 atmosphere. As the oceans may not be precisely in equilibrium with the atmosphere. One needs to know (1) the actual concentration and (2) the solubilities at the given conditions. Both of these factors, especially solubility, are difficult to determine. At equilibrium the partial pressure of the gas phase is proportional to the partial pressure of the gas insolution if the gas obeys Henry's Law or

$p \propto P$ $\quad$ p = partial pressure of gas phase

P = partial pressure in solution

and $c = \propto p$ $\quad$ c = concentration of gas in solution

$\propto$ = solubility coefficient of gas

in practice $\propto$ is calculated empirically by shaking pure gas with sea water. The solubilities of the various gases have been determined historically by equilibrating sea water with air at various temperatures and salinities and measuring the amount of gas assuming Henry's Law.

Weiss (1970) has worked out equations relating the Bunsen solubility coefficient and air solubility for nitrogen, oxygen and argon with respect to temperature and salinity. These relationships, which may be used in place of the Henry's Law coefficient, are as follows:

Bunsen coefficient β:

$$\ln\beta = A_1 + A_2\,(100/T) + A_3 \ln\,(T/100) + S\,^{o}/oo\,[B_1 + B_2\,(T/100) + B_3\,(T/100)^2]$$

Air Solubility C*:

$$\ln C^* = A_1 + A_2\,(100/T) + A_3 \ln\,(T/100) + A_4\,(T/100) + S\,^{o}/oo\,[B_1 + B_2\,(T/100) + B_3 (T/100)^2]$$

Where: S^{o}/oo = Salinity in parts per thousand
T = Temperature in degrees absolute
A, B = Coefficients (see Table III - 1)

Units used in oceanographic work (example given here for oxygen) are

(1) % saturation

% saturation = $100\, O_2/O'_2$ where

O_2 = observed oxygen content
O'_2 = solubility at in situ temperature and salinity

or (2) apparent oxygen utilization: A.O.U. (Redfield, 1942)

$$\text{A.O.U.} = O'_2 - O_2$$

Oxygen

Values calculated by Fox (1909) were questioned by Truesdale and others (1955) (see Figure III - 1) although recent work appears to substantiate Fox's original estimates. Using Fox's values the maximum oxygen in sea water is about 97% saturation. Using Truesdale's figure the maximum is about 100%. Greatly undersaturated values are associated with

Table III-1

Table 1. Constants for the calculation of the Bunsen solubility coefficient according to equation (3).

Gas	A_1	A_2	A_3	B_1	B_2	B_3
N_2	− 59·6274	85·7661	24·3696	− 0·051580	0·026329	− 0·0037252
O_2	− 58·3877	85·8079	23·8439	− 0·034892	0·015568	− 0·0019387
Ar	− 55·6578	82·0262	22·5929	− 0·036267	0·016241	− 0·0020114

Table 2. Volumetric solubility constants for the calculation of solubilities in ml/l. *from moist air at one atmosphere total pressure, according to equation* (4).

Gas	A_1	A_2	A_3	A_4	B_1	B_2	B_3
N_2	− 172·4965	248·4262	143·0738	− 21·7120	− 0·049781	0·025018	− 0·0034861
O_2	− 173·4292	249·6339	143·3483	− 21·8492	− 0·033096	0·014259	− 0·0017000
Ar	− 173·5146	245·4510	141·8222	− 21·8020	− 0·034474	0·014934	− 0·0017729

Table 3. Gravimetric solubility constants for the calculation of solubilities in ml/kg *from moist air at one atmosphere total pressure, according to equation* (4).

Gas	A_1	A_2	A_3	A_4	B_1	B_2	B_3
N_2	− 177·0212	254·6078	146·3611	− 22·0933	− 0·054052	0·027266	− 0·0038430
O_2	− 177·7888	255·5907	146·4813	− 22·2040	− 0·037362	0·016504	− 0·0020564
Ar	− 178·1725	251·8139	145·2337	− 22·2046	− 0·038729	0·017171	− 0·0021281

From: Weiss (1970, p. 727-728)

areas of divergences (upwelling) and over saturation with regions of convergence (sinking) or high winds.

Most of the uncertainty about oxygen saturation stems from the fact that O_2 is not an ideal Henry's Law gas as it is both utilized and given off in photosynthetic reactions. Values as high as 110% to 120% of saturation have been reported which may be due to production of O_2 by marine plants by the breakdown of CO_2

$$CO_2 + H_2O = CH_2O + O_2 \uparrow$$

as this process is light controlled the reaction will reverse at night. Or O_2 will be added during the day at the expense of CO_2 and CO_2 will be added at night or during very cloudy weather or low angles of sunlight - both processes essentially independant of the inorganic exchange between the atmosphere and the oceans.

Values of oxygen solubilities in (mℓ/ℓ)and (mℓ/kg) for surface (one atmosphere) conditions are given in Table III - 2.

Vertical Distribution of Oxygen

The oxygen content of sea water shows the following features (Figure III-2) (Richards, 1965, p. 218-219).

1. A surface layer - essentially in equilibrium with the atmosphere well mixed with a uniform oxygen content down to the thermocline. This usually corresponds to the depth of the wind-mixed layer and has a uniform temperature.

2. A subsurface maximum instable water columns corresponding to the photosynthetic maximum - usually in the upper 50 meters.

3. A gradual decline in oxygen values below surface layers caused by

Figure III-1

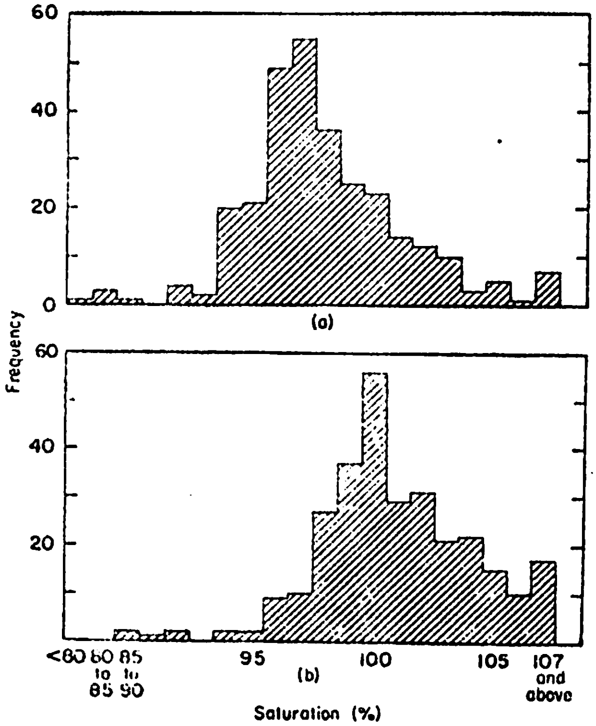

FIG. 1. The apparent percent saturation of oxygen in surface samples taken during the *Meteor* expedition. The solubilities were corrected for the barometric pressure observed at the time of sample collection. (a) Solubility data of Fox (1909); (b) solubility data of Truesdale *et al.* (1955).

From: Richards (1966, p. 209)

Table III-2

Table 8. Solubility of oxygen from moist air at one atmosphere total pressure in (ml/l.).

	SALINITY IN PERMIL								
T(°C)	0	10	20	30	34	35	36	38	40
-1	—	—	9.162	8.553	8.321	8.264	8.207	8.095	7.984
0	10.218	9.543	8.913	8.325	8.100	8.045	7.990	7.882	7.775
1	9.936	9.284	8.676	8.107	7.890	7.836	7.783	7.679	7.575
2	9.666	9.037	8.449	7.898	7.689	7.637	7.586	7.484	7.384
3	9.409	8.801	8.232	7.699	7.496	7.446	7.397	7.298	7.202
4	9.163	8.574	8.024	7.509	7.312	7.264	7.216	7.121	7.027
5	8.927	8.358	7.825	7.327	7.136	7.089	7.043	6.950	6.860
6	8.702	8.151	7.635	7.152	6.967	6.922	6.877	6.787	6.699
8	8.280	7.763	7.278	6.824	6.650	6.608	6.565	6.481	6.398
10	7.891	7.406	6.950	6.522	6.359	6.319	6.279	6.199	6.121
12	7.534	7.077	6.647	6.244	6.090	6.052	6.014	5.939	5.865
14	7.204	6.773	6.367	5.987	5.841	5.805	5.769	5.698	5.628
16	6.898	6.491	6.108	5.748	5.610	5.576	5.542	5.475	5.409
18	6.615	6.230	5.868	5.527	5.396	5.363	5.331	5.268	5.205
20	6.352	5.987	5.644	5.320	5.196	5.166	5.135	5.075	5.015
22	6.106	5.761	5.435	5.128	5.010	4.981	4.952	4.895	4.838
24	5.878	5.550	5.241	4.949	4.836	4.809	4.781	4.727	4.673
26	5.664	5.353	5.058	4.780	4.673	4.647	4.621	4.569	4.518
28	5.464	5.168	4.887	4.623	4.521	4.496	4.471	4.421	4.372
30	5.276	4.994	4.727	4.474	4.377	4.353	4.329	4.282	4.235
32	5.099	4.830	4.576	4.335	4.242	4.219	4.196	4.151	4.106
34	4.932	4.676	4.433	4.203	4.114	4.092	4.070	4.027	3.984
36	4.775	4.530	4.298	4.078	3.993	3.972	3.951	3.910	3.869
38	4.627	4.393	4.171	3.960	3.878	3.858	3.838	3.799	3.760
40	4.486	4.262	4.050	3.848	3.770	3.750	3.731	3.693	3.656

Table 9. Solubility of oxygen from moist air at one atmosphere total pressure in (ml/kg).

	SALINITY IN PERMIL								
T(°C)	0	10	20	30	34	35	36	38	40
-1	—	—	9.020	8.354	8.101	8.039	7.978	7.856	7.736
0	10.221	9.470	8.775	8.131	7.887	7.827	7.767	7.650	7.534
1	9.938	9.213	8.541	7.918	7.682	7.624	7.567	7.453	7.341
2	9.668	8.967	8.318	7.715	7.487	7.431	7.375	7.265	7.156
3	9.410	8.733	8.104	7.521	7.300	7.246	7.192	7.085	6.980
4	9.164	8.509	7.901	7.336	7.121	7.069	7.016	6.913	6.811
5	8.929	8.294	7.705	7.158	6.950	6.899	6.849	6.749	6.650
6	8.703	8.089	7.519	6.988	6.787	6.737	6.688	6.591	6.495
8	8.282	7.705	7.169	6.670	6.480	6.433	6.387	6.296	6.205
10	7.895	7.352	6.847	6.377	6.198	6.154	6.110	6.024	5.938
12	7.538	7.027	6.551	6.106	5.937	5.896	5.855	5.773	5.692
14	7.210	6.727	6.277	5.857	5.697	5.657	5.618	5.541	5.465
16	6.906	6.450	6.024	5.626	5.474	5.437	5.400	5.327	5.254
18	6.625	6.193	5.789	5.411	5.268	5.232	5.197	5.127	5.059
20	6.364	5.954	5.571	5.212	5.075	5.042	5.008	4.942	4.877
22	6.121	5.732	5.368	5.027	4.896	4.864	4.832	4.769	4.707
24	5.894	5.525	5.178	4.853	4.729	4.699	4.668	4.608	4.549
26	5.683	5.331	5.001	4.691	4.573	4.543	4.514	4.457	4.401
28	5.485	5.150	4.835	4.539	4.426	4.398	4.370	4.316	4.261
30	5.299	4.979	4.679	4.396	4.288	4.261	4.235	4.183	4.131
32	5.125	4.819	4.532	4.262	4.158	4.133	4.107	4.057	4.008
34	4.961	4.669	4.394	4.135	4.036	4.011	3.987	3.939	3.891
36	4.806	4.527	4.263	4.015	3.920	3.897	3.873	3.827	3.782
38	4.660	4.392	4.140	3.902	3.810	3.788	3.766	3.721	3.678
40	4.521	4.265	4.022	3.794	3.706	3.685	3.663	3.621	3.579

From: Weiss (1970, p. 731-732)

Figure III-2

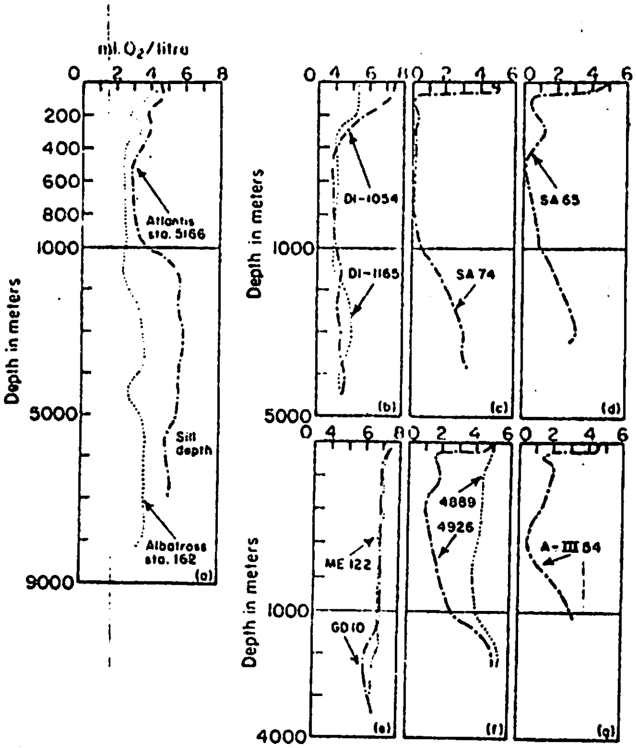

FIG. 2. Representative vertical distributions of oxygen. (a) *Albatross* station 162 in Mindanao deep. 23 January, 1948. 5°23′ N., 127°48′ E., and *Atlantis* station 5166 in the Brownson Deep, 24 February, 1954. 19°55′ N., 64°51′ W., (b) *Discovery* station 1054 in Antarctic Convergence. 3 December, 1932. 50°07·8′ S., 35°48·6′ W. *Discovery* station 1165 in Subantarctic Convergence, 24 February, 1932. 41°00′ S., 09°30′ E. (c) *Albatross* station 74, in eastern tropical Pacific. 22 September, 1947. 11°39′ N., 114°15′ W. (d) *Albatross* station 65 in eastern tropical Pacific, showing two minima. 16 September, 1947, 6°21′ N., 103°42′ W. (e) *Godthaab* station 10, 3 June, 1928, 56°56′ N., 51°17′ W., and *Meteor* station 122, 55°03′ N., 44°46′ W., 9 March, 1935, in North Polar Front. (f) *Atlantis* stations 4926 in tropical eastern Atlantic 28 February, 1952, 12°53′ N., 22°59′ W., and 4889 in south-eastern North Atlantic, 4 February, 1952, 29°52′ N., 30°12′ W. (g) *Albatross* III station 54, showing two minima and lowest concentrations observed in tropical eastern Atlantic. 16 February, 1952, 17°00·5′ N., 30°03′ W., from Richards (1957).

From: Richards (1966, p. 219)

(a) decline in photosynthetic reactions,

(b) reduction of organic matter raining down from upper productive layers. The decrease is small in regions of convergence where oxygen is replentished by the sinking of well oxygenated surface waters. In regions of stable water the decrease may be sharp as in the Eastern Tropical North Pacific where the oxygen concentration decreases from 5 mℓ/ℓ to a few hundreds of a mℓ/ℓ in only 100 meters.

4. An oxygen minimum between 700 and 1000 meters except in regions of convergences.

5. Gradual increase of concentration beneath the minimum caused by venilation of deep waters by oxygen rich water that have sunk from the surface at high latitudes.

The remarkable feature of the oxygen distribution system - the oxygen minimum - is of great interest to both the physical and biological oceanographer as well as the chemical oceanographer. Wyrtki (1962) has determined the depth of the oxygen minimum is a function of the balance between in situ consumption of oxygen and the advective and diffusive renewal of oxygen. He concludes the minimum is in the upper layers of smallest advection, as the rates of oxygen consumption decrease exponentially with depth. The important fact concerning the oxygen minimum is that the amount of oxygen removed from water is the stoichiometric equilivant of the oxidation of organic matter. Thus the relative decline at the minimum is primarily a function of the amount of organic material available and the absolute value is a function of the rate of circulation supplying the oxygen and the amount of organic matter or productivity of overlying water.

As a consequence of this, the Atlantic which (1) has more intense circulation but (2) less productivity in the photic zone, generally has higher absolute oxygen values in the oxygen minimum than the Pacific which (1) has less intense circulation but (2) more organic productivity.

Nitrogen

Nitrogen gas makes up 78% of the lower atmosphere but because it is relatively inert nitrogen has not been investigated with the same intensity as oxygen. Only recently Dugdale and others (1961) have shown the ability of the blue-green algae *Trichodesmium thiebautii* to fix nitrogen thus to modify its concentration beyond that derived from inorganic interchange between the atmosphere and the oceans. The process occurs in the tropical and semitropical waters during periods of thermal stability when nutrients are reduced to low values in the surface layers. At present there is not a significant backlog of nitrogen determinations in sea water to substaniate the effectiveness of bacterial nitrogen fixing to modify nitrogen concentration in sea water. Preliminary studies in the North and South Atlantic show nitrogen concentrations deviate at the most only 1% from values expected from Henry's Law solution of atmospheric nitrogen in sea water. Table III-3 lists nitrogen solubilities for surface (one atmosphere) conditions.

Phosphorus

Phosphorus shows the widest variation in concentration of the non-gaseous components of sea water. This is caused by (1) its numerous complexes and (2) its utilization by phytoplankton in the upper layers of the ocean. Phosphorus occurs in sea water as (1) dissolved phosphates: $H_2PO_4^-$, $HPO_4^=$, and small amount of $PO_4^{\equiv}$; (2) dissolved organic phosphorous

Table III-3

Table 5. Solubility of nitrogen from moist air at one atmosphere total pressure in (ml/l).

SALINITY IN PERMIL

T(°C)	0	10	20	30	34	35	36	38	40
-1	—	—	16.28	15.10	14.65	14.54	14.44	14.22	14.01
0	18.42	17.10	15.87	14.73	14.30	14.19	14.09	13.88	13.67
1	17.95	16.67	15.48	14.38	13.96	13.86	13.75	13.55	13.35
2	17.50	16.26	15.11	14.04	13.64	13.54	13.44	13.24	13.05
3	17.07	15.87	14.75	13.72	13.32	13.23	13.13	12.94	12.76
4	16.65	15.49	14.41	13.41	13.03	12.93	12.84	12.66	12.47
5	16.26	15.13	14.09	13.11	12.74	12.65	12.56	12.38	12.21
6	15.88	14.79	13.77	12.83	12.47	12.38	12.29	12.12	11.95
8	15.16	14.14	13.18	12.29	11.95	11.87	11.79	11.62	11.46
10	14.51	13.54	12.64	11.80	11.48	11.40	11.32	11.17	11.01
12	13.90	12.99	12.14	11.34	11.04	10.96	10.89	10.74	10.60
14	13.34	12.48	11.67	10.92	10.63	10.56	10.49	10.35	10.21
16	12.83	12.01	11.24	10.53	10.25	10.19	10.12	[illegible]	9.86
18	12.35	11.57	10.84	10.16	9.90	9.84	9.77	9.65	9.52
20	11.90	11.16	10.47	9.82	9.57	9.51	9.45	9.33	9.21
22	11.48	10.78	10.12	9.50	9.26	9.21	9.15	9.03	8.92
24	11.09	10.42	9.79	9.20	8.98	8.92	8.87	8.76	8.65
26	10.73	10.09	9.49	8.92	8.71	8.65	8.60	8.50	8.39
28	10.38	9.77	9.20	8.66	8.45	8.40	8.35	8.25	8.15
30	10.06	9.48	8.93	8.41	8.21	8.16	8.12	8.02	7.92
32	9.76	9.20	8.67	8.18	7.99	7.94	7.89	7.80	7.71
34	9.48	8.94	8.43	7.96	7.77	7.73	7.68	7.59	7.51
36	9.21	8.69	8.20	7.75	7.57	7.53	7.48	7.40	7.31
38	8.95	8.46	7.99	7.55	7.38	7.33	7.29	7.21	7.13
40	8.71	8.23	7.78	7.36	7.19	7.15	7.11	7.03	6.95

Table 6. Solubility of nitrogen from moist air at one atmosphere total pressure in (ml/kg).

SALINITY IN PERMIL

T(°C)	0	10	20	30	34	35	36	38	40
-1	—	—	16.03	14.75	14.26	14.15	14.03	13.80	13.57
0	18.43	16.97	15.62	14.39	13.92	13.81	13.69	13.47	13.25
1	17.95	16.54	15.24	14.04	13.59	13.48	13.37	13.15	12.94
2	17.50	16.13	14.87	13.71	13.28	13.17	13.06	12.85	12.64
3	17.07	15.74	14.52	13.40	12.97	12.87	12.77	12.56	12.36
4	16.65	15.37	14.19	13.10	12.68	12.58	12.48	12.28	12.09
5	16.26	15.01	13.87	12.81	12.41	12.31	12.21	12.02	11.83
6	15.88	14.67	13.56	12.53	12.14	12.05	11.95	11.77	11.58
8	15.17	14.03	12.98	12.01	11.64	11.55	11.46	11.29	11.11
10	14.51	13.44	12.45	11.53	11.18	11.10	11.01	10.85	10.68
12	13.91	12.90	11.96	11.09	10.76	10.68	10.60	10.44	10.28
14	13.35	12.40	11.51	10.68	10.37	10.29	10.21	10.06	9.91
16	12.84	11.93	11.09	10.30	10.00	9.93	9.86	9.71	9.57
18	12.36	11.50	10.70	9.95	9.66	9.59	9.52	9.39	9.25
20	11.92	11.10	10.33	9.62	9.35	9.28	9.21	9.08	8.96
22	11.51	10.72	9.99	9.31	9.05	8.99	8.93	8.80	8.68
24	11.12	10.37	9.68	9.02	8.78	8.72	8.65	8.54	8.42
26	10.76	10.05	9.38	8.75	8.52	8.46	8.40	8.29	8.17
28	10.42	9.74	9.10	8.50	8.27	8.22	8.16	8.05	7.94
30	10.11	9.45	8.84	8.26	8.04	7.99	7.94	7.83	7.73
32	9.81	9.18	8.59	8.04	7.83	7.78	7.73	7.62	7.52
34	9.53	8.92	8.36	7.83	7.62	7.57	7.52	7.43	7.33
36	9.26	8.68	8.14	7.63	7.43	7.38	7.33	7.24	7.15
38	9.01	8.45	7.93	7.43	7.25	7.20	7.15	7.06	6.97
40	8.78	8.24	7.73	7.25	7.07	7.03	6.98	6.89	6.81

From: Weiss (1970, p. 730)

compounds of various structures probably phospho- and nucleo proteins, phospholipids, and sugar phosphates; (3) suspended phosphates of calcium (apatite group) and ferric iron, (4) detrital organic phosphates such as bones, teeth, etc. essentially insoluble.

In general the phosphorous content in sea water increases from a minimum value at the surface. The surface minimum is produced by the extraction of phosphorous by phytoplankton living at or near the sea surface in the photic zone. The phytoplankton concentrate phosphorous by a factor of $10^7 - 10^8$ so that their tissues contain 2-3% phosphorous by dry weight. The phytoplankton are eaten by other organisms in a food-chain which practically insures the eventual transfer of phosphorous back into sea water at some place other than where phosphorous was initially extracted.

The average phosphorous concentration in sea water is about 70-75 μgms/liter; although surface values are much lower. (Phosphorus values are reported in various forms see Table III-4.) The interchange between bottom muds and sea water is probably an important feature of the phosphorous cycle. Carrit and Goodgal (1954) found that the uptake of phosphate by suspended sediment was reversible and that desorption was favored by increased pH. The process would increase the dissolved P content of sea water (1) when near neutral fresh water encounters slightly alkaline sea water and (2) during upwelling as the pH of sea water is a maximum at the surface. The absorptive capacity of muds is at a maximum between pH 3 and 9 and increases with Fe to organic matter ratio. Take up rates ranged up to 3mgmP/gm mud. Diurnal changes in phosphorous content are marked. For example in Cheasapeake Bay P content decreases from a maximum of 13 μgmP/ℓ just after sunrise to a minimum of 3 μgmP/ℓ at 5:00 P.M.

Figure III-3

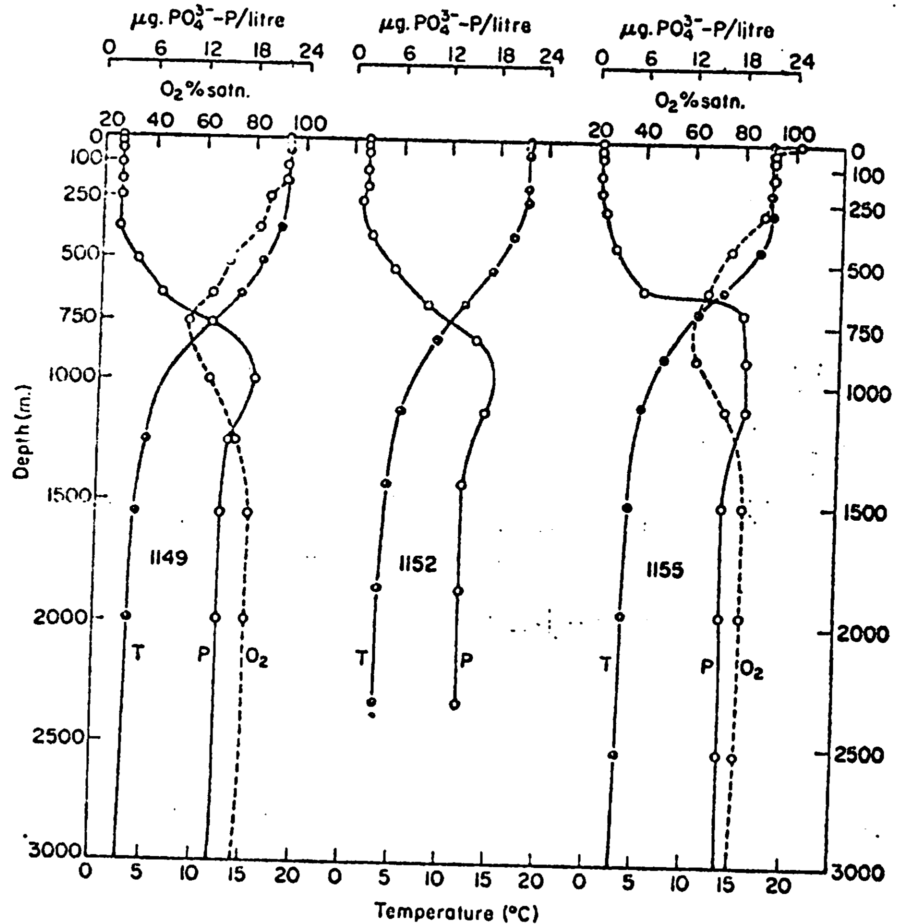

FIG. 11. Vertical distribution of phosphate, oxygen (percentage saturation) and temperature in the North-East Sargasso Sea, February to March, 1932. From Seiwell (1935).

From: Armstrong (1966, p. 342)

Table III-4

The concentration of dissolved phosphate is expressed in different units, in the extensive literature concerning its distribution.

mg. P per m.^{3}	2	4	6	8	10	12	14	16
mg.-atoms P per m.^{3}	0·06	0·13	0·19	0·26	0·32	0·39	0·45	0·52
mg. P_2O_5 per m.^{3}	5	9	14	18	23	28	32	37
mg. PO_4 per m.^{3}	6	12	18	24	31	37	43	49
mg. P per m.^{3}	18	20	22	24	26	28	30	32
mg.-atoms P per m.^{3}	0·58	0·64	0·71	0·77	0·84	0·90	0·97	1·06
mg. P_2O_5 per m.^{3}	41	46	50	55	60	64	69	73
mg. PO_4 per m.^{3}	55	61	67	73	80	86	92	98

Caution. The concentrations, obtained by visual comparison, given in the older literature have in many cases not been corrected for 'salt error', the 'corrected' values are then about 1·3 times the uncorrected values (Cooper, 1938).

From: Harvey (1966, p. 234)

Also see Bialek (ed) (1966, p. 370-371) for more complete tables of conversion of (1) μgP to μg-Atoms P and

$$(2)\ \frac{\mu g/PO_4}{\ell} \text{ to } \frac{\mu g\text{-Atoms.}}{\ell} \quad PO_4\text{-}P$$

CO_2 In Sea Water

As noted by Garrels and Thompson (1962) and as predicted by theoretical calculations, CO_2 in sea water exists as both dissolved gas and in several ionic species. The following reactions govern the reaction of CO_2 with aqueous solutions

$$CO_2 \text{ (gas)} \rightleftarrows CO_2 \text{ (solution)}$$

$$CO_2 \text{ (solution)} + H_2O \rightleftarrows H_2CO_3$$

$$H_2CO_3 \rightleftarrows HCO_3^- + H^+$$

$$HCO_3^- \rightleftarrows CO_3^= + H^+$$

the reaction:

$$CO_2 + OH^- \rightleftarrows HCO_3^-$$

is important only at pH greater than 9 so is relatively insignificant for sea water with a pH 8.3 or less.

Approximate Carbonate Equilibrium Constants in Sea water

Reaction	Temperature	
	5°C	25°C
	K	
1. $CaCO_3 \text{ (solid)} \rightleftarrows Ca^{++} + CO_3^=$		
$\frac{[Ca^{++}][CO_3^=]}{[CaCO_3]} =$	$10^{-5.67}$	$10^{-6.19}$
2. $HCO_3^- \rightleftarrows CO_3^= + H^+$		
$\frac{[CO_3^=][H^+]}{[HCO_3^-]} =$	$10^{-9.18}$	$10^{-8.96}$

Figure III-4

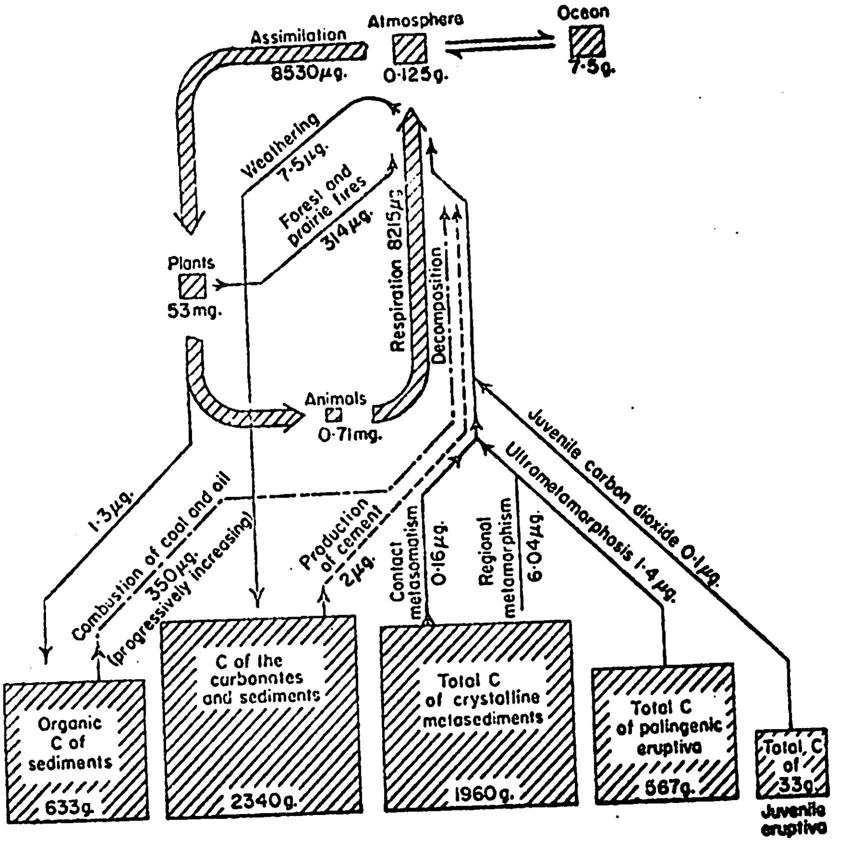

Fig. 1. Geochemical carbon cycle in nature (after Dietrich, 1957).

From: Skirrow (1966, p. 320)

Reaction	Temperature K	
	5°C	25°C
3. $H_2CO_3 \rightleftarrows HCO_3^- + H^+$		
$\frac{[HCO_3^-]\ [H^+]}{[H_2CO_3]} =$	$10^{-6.15}$	$10^{-5.99}$
4. CO_2 (gas) $+ H_2O \rightleftarrows H_2CO_3$		
$\frac{[H_2CO_3]}{[pCO_2]\ [H_2O]} =$	$10^{-1.27}$	$10^{-1.53}$
5. $Ca^{++} + HCO_3^- \rightleftarrows CaCO_3 + H^+$		
$\frac{[CaCO_3]\ [H^+]}{[Ca^{++}]\ [HCO_3^-]} =$	$10^{-3.51}$	$10^{-2.77}$

Modified from: Sillen (1961, p. 560)

At surface conditions ~25°C, pH = 8.1 and $[Ca^{++}] = 10^{-1.99}$

Equation 1. $[CO_3^{=}] = \frac{10^{-6.19}}{10^{-1.99}} = 10^{-4.20}$

Equation 2. $[HCO_3^-] = \frac{[CO_3^{=}]\ [H^+]}{K} = \frac{(10^{-4.20})(10^{-8.1})}{10^{-8.96}} = 10^{-3.34}$

at depth ~5°C, pH 7.8 (sea water pH less than 8 in cold deep waters) and $[Ca^{++}] = 10^{-1.99}$ (questionable as carbonates dissolve at depth $[Ca^{++}]$)

From equation 1. $[CO_3^{=}] = \frac{10^{-5.67}}{10^{-1.99}} = 10^{-3.68}$

From equation 2. $[HCO_3^-] = \frac{(10^{-3.68})\ (10^{-7.8})}{10^{-9.18}} = \frac{10^{-11.48}}{10^{-9.18}} = 10^{-2.30}$

For oceanic conditions from equation 3.

$$\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{10^{-6.15}}{10^{-7.8}} = 10^{1.65}$$ 5°C at depth

$$\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{10^{-5.99}}{10^{-8.1}} = 10^{2.11}$$ 25°C

Thus $[HCO_3^-]$ is about 10^2 or 100X that of $[H_2CO_3]$, so $[H_2CO_3]$ may be ignored in these approximate calculations.

In summary at equilibrium -

Surface Conditions:	At Depth:
$[HCO_3^-] = 10^{-3.34}$	$[HCO_3^-] = 10^{-2.30}$

the measured value of $[HCO_3^-] = 10^{-2.63}$ which implies (1) at the surface $[HCO_3^-]$ is much greater than equilibrium ($10^{-2.63} > 10^{-3.34}$) which would enhance production of $CO_3^{=}$ and suggest $CaCO_3$ would precipitate and (2) at depth, for the bulk of the ocean $[HCO_3^-]$ is less than equilibrium ($10^{-2.63} < 10^{-2.30}$) which indicates $CaCO_3$ would dissolve.

The use of concentration units in calculations of equilibrium in sea water is questionable on both theoretical and experimental grounds as thermodynamically one must use activities rather than concentrations. In dilute waters where (1) the activity coefficient is 1, (2) or where the Debye-Huckel theory is valid, that is ionic strength less than 0.1 good estimations can be made. However the ionic strength of sea water is much higher than 0.1 so that the activity coefficients for the various ions in sea water is not unity. Experimental work by Garrels and Christ (1965) (Figure III-5) show the Debye-Huckel extrapolations are not valid for the δ's for carbonates. Berner (1965) has calculated δ's for carbnnates in sea water as follows:

$\delta HCO_3^- = 0.561 \pm 0.006$

$\delta CO_3^= = 0.024 \pm 0.004$

$\delta Ca^{++} = 0.223 \pm 0.020$

The greatest disrupting factor in trying to determine equilibrium relationships for carbonates in sea water, of course, is biological activity. The relationship between O_2 and CO_2 during life process is important. Removal of CO_2 from sea water is accompanied biologically with the removal of nutrients particularily phosphorous. CO_2 is added to sea water with nutrients (phosphorous) during the oxidation of organic matter. For example in the Pacific, the ratio of phosphate to carbon dioxide liberated during oxidation of organic matter is -

$$0.33 = \frac{\Delta\ PO_4^{\equiv}\ (\mu g\text{Atm/liter})}{\Delta\ CO_2\ (\text{m}\ell/\ \text{liter})}$$

and the ratio of phosphate liberated to oxygen consumed is -

$$0.27 = \frac{\Delta\ PO_4^{\equiv}\ (\mu g\text{-Atm/liter})}{\Delta\ O_2\ (\text{m}\ell/\text{liter})}$$

Figure III-5

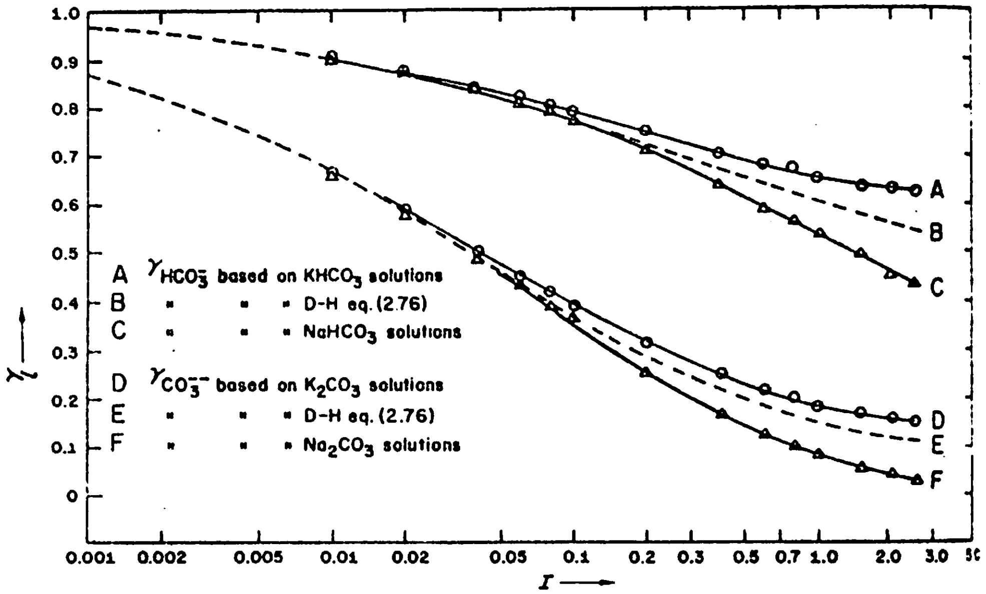

FIG. 4.5. Activity coefficients for bicarbonate and carbonate ions. [Curves A, C, D, F plotted from the experimental data of A. C. Walker, U. B. Bray, and John Johnston, *J. Am. Chem. Soc.*, 49, 1255 (1927). B and E are the Debye-Hückel plots of equation (2.76).]

From: Garrels and Christ (1965, p. 104)

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UNIVERSITY OF CALIFORNIA
CE 201 B Revised 1/1971

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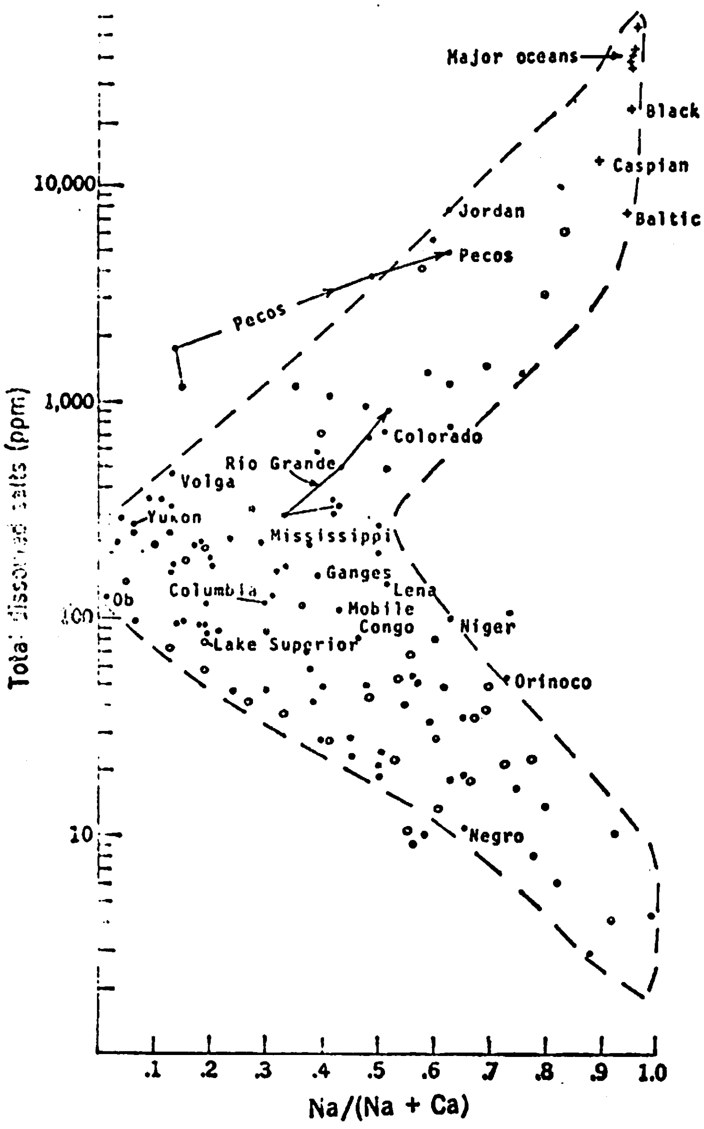
HISTORY OF SEA WATER

Thus far we have concerned ourselves with sea water as it is or at least as we think it is. However, some of the questions concerning sea water really relate to its history. Also many problems conceivably may be solved with a knowledge of both the past and present state of sea water.

Gibbs (1970) has proposed that the chemistry of surface waters (essentially rivers, lakes and the oceans and seas) is a function of I atmospheric precipitation, II drainage area rock composition, and III chemical equilibrium environment. Gibbs has plotted data for various surface waters on a dissolved solids vs chemical parameter diagram (Figures IV-1 and IV-2) which show the interrelation of domains of dominance for the three end member mechanisms. Accordingly, the following discussion of the history of sea water and inter-relationship of the three mechanisms must be kept in mind.

Hypotheses on the history of sea water fall into two broad categories (1) the origin of the volume of sea water (essentially the water) and (2) the time history and origin of the dissolved content. Unfortunately such theories must have a starting point at some time zero or in this case a primordial ocean of given volume and composition. The problem of a primordial ocean obviously is so related to the origin of the earth and atmosphere that inquiry becomes more philosophy and metaphysics than reproducible science. A way out of this dilemna is to search the geologic record (including both rocks and fossils) for events that possibly either influence or reflect the composition of sea water. Extrapolation both forwards and backwards in time from such fixed points

FIGURE IV-1



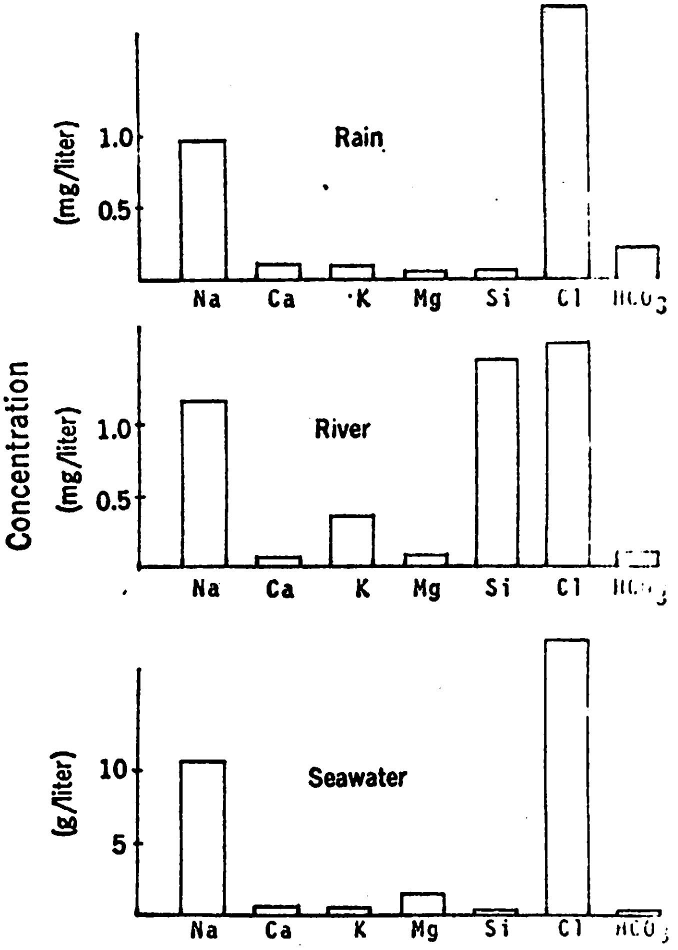
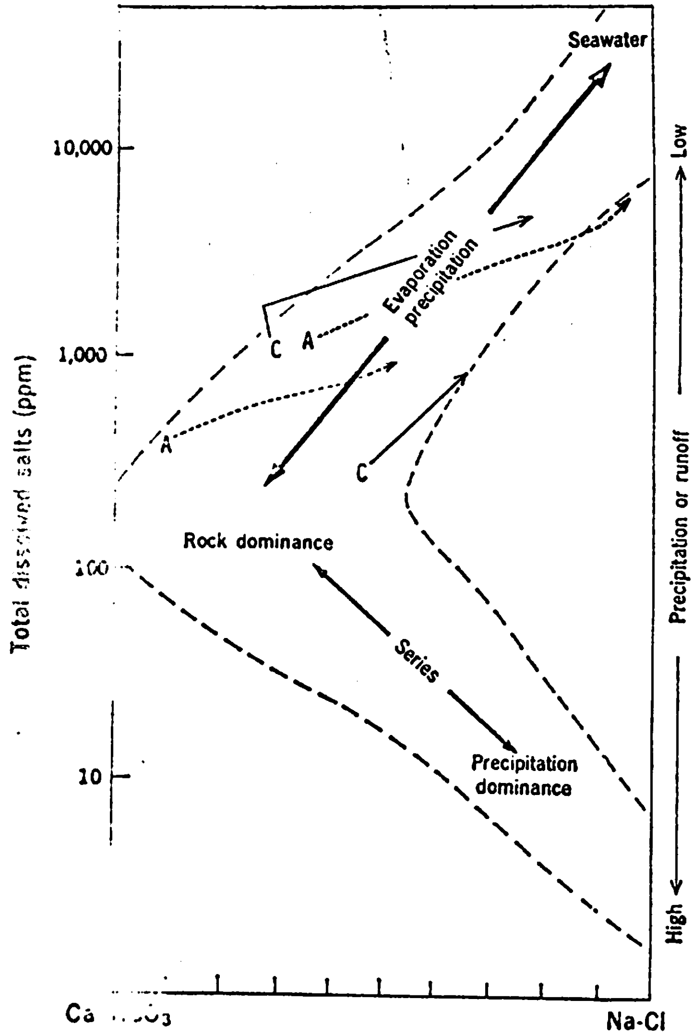


Fig. 1 (left). Variation of the weight ratio Na/(Na + Ca) as a function of the total dissolved salts of world surface waters. ●, Rivers; ○, lakes; +, oceans. Fig. 2 (right). Compositions of Rio Tefé basin (5), Tefé basin rain (5), and seawater (9).

From: Gibbs (1970, p. 1088)

FIGURE IV-2



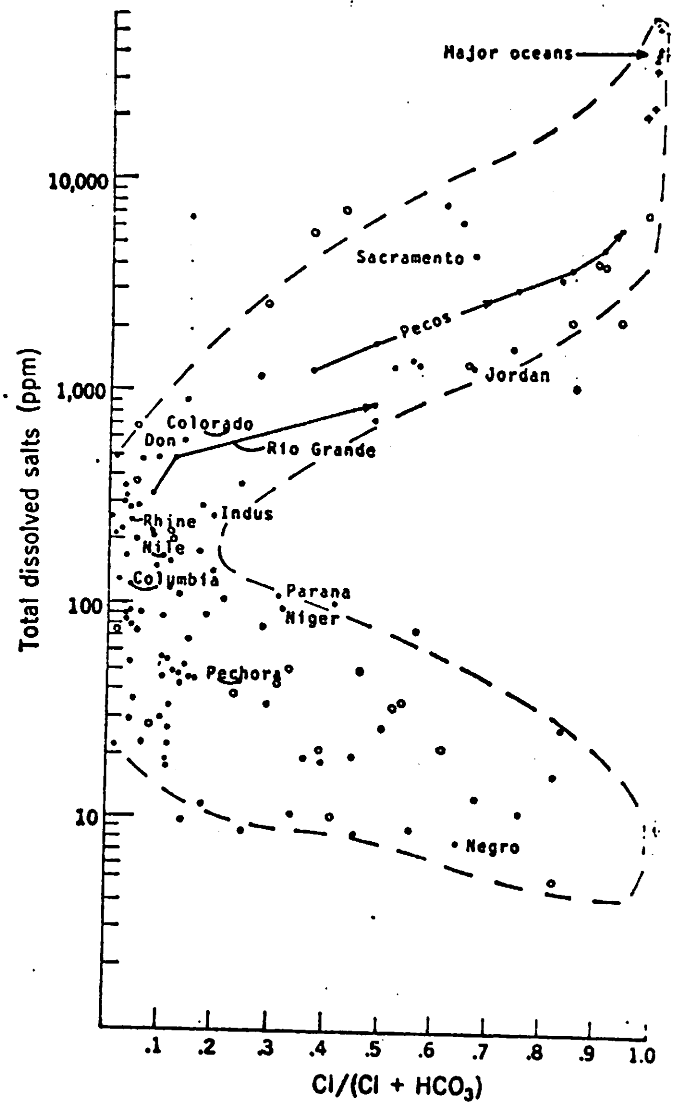


Fig. 3 (left). Diagrammatic representation of processes controlling the chemistry of world surface waters. Fig. 4 (right). Variation of $Cl/(Cl + HCO_3)$ as a function of the total dissolved salts of world surface waters. ●, Rivers; ○, lakes; +, oceans.

From: Gibbs (1970, p. 1089)

hopefully will permit the compilation of the chemical history of sea water. The ability to extrapolate in turn is derived from knowledge of the geochemical balance (Goldschmidt, 1933) or the flux of elements on the earth. The concept of the geochemical balance is simple -- measure all the significant chemical processes occurring on the earth and relate them to the contents of various reserviors or sinks such as the oceans and the atmosphere. As most elements are non-gaseous at earth temperatures and pressures the atmospheric elements will be ignored intially. A further simplification is to consider the source material to be igneous rocks whose elements are to be partioned between sediments and sea water or at any time t.

$$x_i X = y_i Y + z_i Z$$

where: X = mass of weathered igneous rock

Y = mass of sedimentary rocks and sediments

Z = total dissolved content of sea water derived from erosion products

x_i = weight fraction or average concentration of element i in igneous rocks

y_i = weight fraction or average concentration of element i in sedimentary rocks and sediments

z_i = weight fraction or average concentration of element i in sea water

it is apparent that the X and Y (igneous and sedimentary) terms are difficult to measure and must be subdivided into many terms which are evaluated separately. Horn and Adams (1966) with the help of computers have searched the literature and attempted to evaluate the geochemical mass balance equation for the present. Table IV-1 shows their compilation of mass components for the right side (sediments plus the oceans) of the balance equation. Table IV-2 lists the balance, here given as a

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difference in Column 8, for the 65 elements, listed below in order of decreasing surplus, could not be balanced.

As all of the anomalous elements in Table IV-3 are surpluses rather than deficits the cause of the particular anomaly could be either (1) a non weathered igneous rock source, (2) excessive input values for sediments or (3) deficient input values for weathered igneous rocks - the values for sea water are assumed to be good.

Table IV-1

Table 1. Mass estimates

					COMPUTED		
Category	Area, million km²	Thickness km	Volume million km³	Porosity, per cent	Solid phase mass, geograms[1]	Liquid phase mass, geograms[1]	Total mass, geograms[1]
Continent-shield	105	1·2	127	25·3	2560	330	2890 = *C*
Mobile belt-shelf	72	5·5	395	28·1	7670	1150	8820 = *M*
Hemipelagic	63	5	315	20·0	6800	650	7450 = *H*
Pelagic	268	0·9	241	48·1	3380	1200	4580 = *P*
Oceans	—	—	1370	—	—	14250	14250 = *O*

[1] 1 geogram = 10^{20} grams.

Table 2. Lithologic percentage estimates

Category	Shale	Sand and greywacke	Carbonate	Evaporite	Oceanic clay	Oceanic carbonate
Continent-shield	53%	28%	16%	3%	—	—
Mobile belt-shelf	59%	36%	2%	3%	—	—
Hemipelagic	—	—	—	—	90%	10%
Pelagic	—	—	—	—	86%	14%

From: Horn and Adams (1966, p. 282)

Table IV-2

Table 5. Mass distributions of the 65 elements within the various domains specified in the model. In the following table, the masses are given in geograms. 1 geogram = 10^{20} grams = 10^{14} metric tons

		Continent-shield (1)	Mobile-belt shelf (2)	Hemi-pelagic (3)	Pelagic (4)	Connate water (5)	Sea water (6)	Weathered igneous (7)	Difference† (8)	
3	Li	0·0770	0·258	0·200	0·118	0·000293	0·00281	0·657	000	Li
4	Be	0·00315	0·0104	0·0384	0·0225	0·00147*	0·01400*	0·0745	000	Be
5	B	0·130	0·429	0·346	0·206	0·00703	0·0673	0·245	0·940	B
9	F	0·965	3·16	6·54	3·91	0·00191	0·0182	14·6	000	F
11	Na	33·3	104	170	102	15·4	147	572	000	Na
12	Mg	46·9	104	117	69·5	1·91	18·2	358	000	Mg
13	Al	135	452	650	384	0·0000147	0·00014	1620	000	Al
14	Si	624	2170	1900	1120	0·0044	0·0421	5820	000	Si
15	P	1·50	4·85	10·1	5·99	0·000103	0·000982	22·4	000	P
16	S	3·17	8·96	9·20	5·52	1·32	12·6	10·6	30·2	S
17	Cl	38·7	116	74·5	45·6	27·8	267	9·70	559·0	Cl
19	K	44·6	151	203	120	0·557	5·33	524	000	K
20	Ca	159	208	210	155	0·586	5·61	739	000	Ca
21	Sc	0·0145	0·0476	0·155	0·0910	0·0586*	0·561*	0·308	000	Sc
22	Ti	7·58	25·5	41·1	24·3	1·47*	14·0*	98·6	000	Ti
23	V	0·156	0·513	1·48	0·888	1·47*	14·0*	3·04	000	V
24	Cr	0·664	2·25	0·700	0·420	0·0733*	0·701*	4·04	000	Cr
25	Mn	0·573	1·44	27·2	16·1	2·93*	28·1*	22·4	22·0	Mn
26	Fe	69·3	228	355	210	0·0000147	0·00014	862	000	Fe
27	Co	0·0113	0·0378	0·264	0·156	0·733*	7·01*	0·469	000	Co
28	Ni	0·0471	0·143	1·08	0·643	0·0733*	0·701*	1·91	000	Ni
29	Cu	0·0738	0·246	1·05	0·621	4·40*	42·1*	1·99	000	Cu
30	Zn	0·195	0·636	0·503	0·299	1·47*	14·0*	1·63	000	Zn
31	Ga	0·0363	0·120	0·138	0·0833	0·044*	0·421*	0·378	000	Ga
32	Ge	0·00244	0·0084	0·011	0·00648	0·0733*	0·701*	0·0283	000	Ge
33	As	0·00756	0·0242	0·0473	0·0278	4·40*	42·1*	0·0347	0·0722	As
34	Se	0·000495	0·00157	0·000596	0·000365	5·86*	56·1*	0·00153	0·00155	Se
35	Br	0·00571	0·0108	0·200	0·124	0·0953	0·912	0·0639	1·28	Br
37	Rb	0·490	1·65	0·789	0·464	0·000176	0·00168	3·39	000	Rb
38	Sr	0·685	1·54	3·05	2·11	0·0117	0·112	7·51	000	Sr
39	Y	0·0455	0·140	0·411	0·248	4·40*	42·1*	0·844	000	Y
40	Zr	0·347	1·21	1·07	0·642	5·86*	56·1*	3·27	000	Zr
41	Nb	0·0268	0·0889	0·186	0·11	0·00733*	0·0701*	0·412	000	Nb
42	Mo	0·00192	0·00594	0·0223	0·0137	0·0000147	0·00014	0·0306	0·0134	Mo
47	Ag	0·000532	0·00159	0·000593	0·000355	0·440*	4·21*	0·00307	000	Ag
48	Cd	0·000282	0·00089	0·00173	0·00102	0·161*	1·54*	0·00392	000	Cd
49	In	0·000423	0·00137	0·00111	0·000658	0·0000293	0·000281	0·00387	000	In
50	Sn	0·00574	0·0190	0·0164	0·00969	4·40*	42·1*	0·0508	000	Sn
51	Sb	0·00119	0·00373	0·00343	0·00203	0·733*	7·01*	0·0104	000	Sb
53	I	0·00444	0·0149	0·000186	0·000114	0·0000733	0·000701	0·0102	0·00102	I
55	Cs	0·0103	0·0341	0·0272	0·0160	0·733*	7·01*	0·0876	000	Cs
56	Ba	0·504	1·71	6·22	3·70	9·09*	87·0*	12·1	000	Ba
57	La	0·0553	0·180	0·469	0·278	0·00425*	0·0407*	0·982	000	La
58	Ce	0·105	0·356	1·38	0·818	0·00188*	0·0180	2·66	000	Ce
59	Pr	0·0130	0·0445	0·178	0·105	0·000935*	0·00895*	0·341	000	Pr
60	Nd	0·0448	0·149	0·602	0·357	0·00336*	0·0321*	1·15	000	Nd
62	Sm	0·0119	0·0409	0·166	0·098	0·000638*	0·0061*	0·317	000	Sm
63	Eu	0·00221	0·00747	0·0231	0·0137	0·000166*	0·00159*	0·0464	000	Eu
64	Gd	0·00906	0·0309	0·102	0·0604	0·000893*	0·00854*	0·202	000	Gd
65	Tb	0·00133	0·00452	0·0191	0·0113			0·0363	000	Tb
66	Dy	0·00805	0·0273	0·104	0·0615	0·00106*	0·0102*	0·200	000	Dy
67	Ho	0·00199	0·00682	0·0253	0·0150	0·000322*	0·00309*	0·0491	000	Ho
68	Er	0·00319	0·0104	0·0377	0·0224	0·000893*	0·00854*	0·0738	000	Er
69	Tm	0·000635	0·00214	0·0102	0·00619	0·000191*	0·00182*	0·0192	000	Tm
70	Yb	0·00339	0·0116	0·0516	0·0305	0·000765*	0·00742*	0·0972	000	Yb
71	Lu	0·000644	0·00212	0·0127	0·00762	0·000170*	0·00163*	0·0231	000	Lu
72	Hf	0·00650	0·0225	0·0319	0·189			0·0798	000	Hf
73	Ta	0·00486	0·0161	0·00678	0·00399			0·0408	000	Ta
74	W	0·00396	0·0131	0·00753	0·00444	0·147*	1·40*	0·0290	000	W
79	Au	8·70*	28·5*	22·2*	13·4*	0·000586*	0·00561*	72·8*	000	Au
80	Hg	0·000429	0·00140	0·00306	0·00180	0·044*	0·4210*	0·00669	000	Hg
81	Tl	0·00324	0·0113	0 00513	0·00304	0·0147*	0·140*	0·0227	00	Tl
82	Pb	0·0347	0·111	0·308	0·182	4·40*	42·1*	0·367	0·269	Pb
90	Th	0·0211	0·0704	0·0885	0·0520	0·0000733*	0·000701*	0·232	000	Th
92	U	0·00774	0·0235	0·0153	0·00912	0·0000440	0·000421	0·0561	000	U

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* $\times 10^{-6}$ geograms.

† '000' denotes a material balance between the sum of the first six entries and the seventh entry. If the element does not balance, the "surplus" mass in the sedimentary and oceanic domains (first six entries) is given. For example, the sum of the first six entries for chlorine is 559 geograms greater than the weathered igneous mass for chlorine of 9·79 geograms.

The three significant figures of the above table reflect the computer output from which the data were taken.

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From: Horn and Adams (1966, p. 287-288)

TABLE IV-3

Element	Geochemical Balance Surplus in Geograms = 10^{20} Grams = 10^{14} metric tons
Chlorine	559.0
Sulfur	30.2
Manganese	22.9
Bromine	1.28
Boron	0.94
Lead	0.269
Arsenic	0.0722
Molybdenum	0.0134
Selenium	0.00155
Iodine	0.00102

From: Horn and Adams, 1966

Chlorine, sulfur, bromine, boron, arsenic, selenium and iodine are volitile elements which may likely not be derived from weathered igneous rocks. The balance of the other metals suggests that the values for manganese, lead, and molybdenum in sediments are high.

In summary Horn and Adams (1966) have shown that igneous rocks are a reasonable source of 55 elements in the earth's surface environment. Seven elements have abundances in excess of that produced from weathering of igneous rocks indicating an additional source. As these 7 elements are volitile it might be useful to look at the previously ignored volitiles which occur in significant proportion in the atmosphere to see if they also are in excess.

Rubey (1951) and Poldervaart (1955) have calculated geochemical balances for such common volitiles given below in Table IV-4. For the common volitiles Cℓ and S calculated by both Rubey is low by a factor of 2 for Cℓ and in reasonable agreement for S indicating at least an order of magnitude match. The volitiles in excess calculated from the igneous source geochemical balance have been called aptly the Rubey Volitiles in honor of his shrewd initial elucidation of the problem. Rubey considered the possible sources of the excess volitiles to be (1) residuals from the primitive atmosphere and ocean or (2) out gassed volitiles from the gradual differentiation of the earth throughout geologic time.

Table IV-4

Geochemical Balance of Volitile
Elements in Geograms = 10^{20} Grams

	H_2O	Total [illegible] (C) as CO_2	Cℓ	N	S	H, Br, B, A, F
In present atmosphere, Hydrosphere and biosphere	14,600	1.5	267	39	13	1.7
Buried in ancient sedimentary rocks	2,100	920	30	4.0	15	15
Total present budget yiY + ziZ of Horn and Adams (1966)	16,700	921	306	43	28	16.7
Weathered igneous rock source	130	11	5	0.6	6	3.5
Excess unaccounted for by weathering	+16,600	+910	+300	+42	+22	+13

From: Rubey (1951 p. 1116)

Rubey investigated various primitive earth models with respect to their ability to produce the present volume of the ocean as a residual. Using

Goranson's (1932) data on the solubility of water in rock melts Rubey found that at the temperatures of a molten earth and the pressure exerted by placing all present fluid H_2O in the primitive atmosphere eventually most of the water would dissolve in the silicious rock melt. Thus the primitive atmosphere would lose most of its water and when the temperature cooled sufficiently for liquid water to form on earth the atmosphere could not produce the present volume of the oceans. Table IV-5 shows the calculations. Therefore Rubey concluded that the principle source of the excess volitiles was by out gassing of the earth's interior as evidenced today by emanations from volcanoes and fumeroles.

Table IV-5

Primitive Earth Models Assuming All Present Fluid Water in Initial Atmosphere

---

Assumptions:

1. Amount present fluid water in oceans, atmosphere and in sediments

   16.7×10^{20} Kg H_2O

2. Producing a surface pressure over the earth (area $5.1 \times 10^{18} cm^2$)

   $325\ Kg/cm^2$ = ~ 325 atmospheres

3. Water content of crystalline rock to 40 Km

   1.15%

4. Water content of crystalline rock 40-2900 Km (depth of mantle)

   0.5%

Model	WTR content of X' taline RK	Total H_2O	% Total H_2O Diss. in melt	Equil. H_2O atm partial pressure	% H_2O in rock at pressure	Amount H_2O at equilibrium
		$\times 10^{20}$ Kg		Kg/cm^2		$\times 10^{20}$ Kg
I Earth molten to 40 Km	$6.6 \times 1020_{Kg}$	23.3	46	244	1.9	12.5
II Earth molten to 300 Km			85	175	1.3	8.9
III Earth molten to 2900 Km (base of silicious mantle)	207	224	98	76	0.54	3.9
IV Earth molten to center			99	52	0.37	2.7

From: Rubey (1951, p. 1117-1120)

Rubey's explanation of the source of the excess volitiles generally has been accepted by most workers (see Holland, 1963; Hess, 1962; and Nicholls, 1965); although Conway (1943), predating Rubey, argues for an essentially constant ocean volume with the addition of the other volitiles throughout geologic time. Kramer (1965) tentatively modified Conway's (1943) idea of an initial "fresh" ocean but did not get into the philosophical abyss of describing primitive atmospheric models.

Unfortunately direct estimates of the amount of degassing volitiles and juvenile waters are very tenuous as volcanic pipes and fumeroles do not debouch directly into the atmosphere but are contaminated by recycled crustal ground and pore waters. Table IV-6 shows the discrepancy between excess volitile ratios and various natural sources. Happily the best agreement is between excess volitiles and gases trapped in silica rich rocks (as one might expect) Table IV-7 shows a recent compilation of the composition of gases from barious rock types. As shown in Table IV-8 assuming present day partition of H_2O and $C\ell$; juvenile waters would produce a sea water with a close approximatation to present chlorinity. This suggests that an ocean produced simply by addition of juvenile waters would have a reasonably constant composition of H_2O and $C\ell$ (or 98.5% of sea water by weight) throughout geologic time.

Table IV-6

Compositions of "excess" volatiles and gases from various natural sources expressed as weight percentages

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
H_2O	92·8	99·4	85·6	69·1	64·3	90·8	84·9
Total C as CO_2	5·1	0·33	5·7	16·8	23·9	5·0	13·0
S	0·13	0·03	0·7	3·3	10·0	0·4	0·1
N	0·24	0·05	1·7	2·6	1·6	0·7	0·2
Cl	1·7	0·12	1·9	1·5	0·1	1·8	1·7
Ar	0·07	tr.	tr.	tr.	0·1	—	tr.
F		0·03	4·4	6·6	—	0·4	
H, B, Br, etc.		0·05	0·04	0·1	tr.	0·7	

(1) Composition of "excess" volatiles following Rubey (1951).

(2) Median composition of gases from fumaroles and hot springs (Rubey, 1951, Table 6).

(3) Median composition of gases occluded in obsidians and other silica-rich igneous rocks (Rubey, 1951, Table 6).

(4) Median composition of gases occluded in basalts and similar igneous rocks (Rubey, 1951, Table 6).

(5) Typical composition of Hawaiian volcanic gas; recalculated from volume percentage composition given by Eaton and Murata (1960).

(6) Composition of newly emergent gases from fumaroles and hot springs, assuming that 94% of the water recorded in column (2) is re-cycled (6% newly emergent).

(7) Composition of "excess" volatiles based on data given by Poldervaart (1955).

From: Nicholls (1965, p. 282)

Table IV-7

TABLE 7.—*Selected analyses of gases in rocks*

[Recalculated excluding H_2O. After Shepherd, 1938, p. 326-337]

No.	Gases, including H_2O, volume per gram of rock (cc/g)	H_2O (percent of total gases)	Gases, excluding H_2O		Gases (H_2O excluded) recalculated to 100 percent							
			Percent of total gases	Volume per gram of rock (cc/g)	CO_2	CO	H_2	N_2	Ar	S_2	Cl_2	F_2
					Obsidians							
1	1.19	88.380	11.60	0.138	12.00	6.08	0.87	24.07	0.00	3.16	25.56	27.27
2	27.10	96.299	4.253	1.15	37.50	.82	4.00	33.30	.00	.33	11.73	12.13
3	1.45	89.246	14.267	.207	1.25	.51	3.51	27.31	.01	.00	12.76	54.64
4	4.89	94.434	7.230	.354	1.04	.11	31.16	15.95	.00	.54	20.72	30.50
5	55.3	92.761	7.236	4.01	9.20	.10	5.21	1.01	.00	.00	23.67	59.63
6	214.8	98.551	1.447	3.11	5.32	2.21	5.53	3.66	Undet.	.00	4.77	78.51
					Andesitic lavas							
7	4.8	82.525	17.356	0.835	58.24	11.56	1.45	4.92	0.05	2.43	2.23	19.11
8	5.0	70.812	29.186	1.72	25.50	4.30	1.49	8.12	.02	9.91	35.95	14.70
9	26.5	96.227	3.760	.098	21.91	5.69	11.36	5.60	Trace	1.41	26.36	27.61
10	9.5	93.658	6.358	.606	32.40	9.75	6.45	9.03	.05	13.81	4.65	23.86
					Basaltic lavas							
11	6.0	80.834	19.166	1.32	61.34	0.77	1.06	1.46	0.00	8.67	6.96	18.83
12	7.3	78.100	21.893	1.60	51.03	.21	2.12	5.96	Trace	7.65	4.70	26.33
13	5.0	74.953	25.040	1.25	25.01	.15	1.74	8.18	.01	3.95	4.60	56.37
14	4.2	74.402	25.590	1.07	30.84	7.33	2.03	10.02	.02	1.77	2.13	45.65
15	6.6	75.914	24.084	1.59	9.71	.20	13.00	10.45	.01	8.13	3.07	33.35
16	6.2	73.199	26.707	1.66	57.11	5.32	16.46	19.38	.06	.68	.79	.00
17	2.9	79.892	20.155	.585	64.41	4.89	19.21	8.68	.18	2.36	.27	.00
18	3.9	71.322	28.675	1.12	36.12	28.86	3.86	25.13	.06	4.46	1.50	.00
					Granites							
19	34.2	90.512	9.455	3.23	20.78	0.86	51.01	3.53	0.07	2.83	0.07	20.84
20	19.4	79.599	20.400	6.00	20.76	2.62	56.88	6.02	.12	.78	.25	12.56

EXPLANATION OF SAMPLES 1–20

1. Dense black obsidian, Big Glass Mountain, Calif.; Shepherd No. 1.
2. Pumiceous phase of No. 1. Shepherd 2; poor summation, 100.552 percent.
3. Dense black obsidian, Coso Mountains, Calif. Shepherd 3; very poor summation, 103.513 percent.
4. Coarsely vesiculated part of No. 3. Shepherd 4; poor summation, 101.664 percent.
5. Dense black obsidian, Cerro Noagua, N. Mex. Shepherd 5.
6. Pitchstone, Cerro Noagua, N. Mex. Shepherd 6.
7. Spine, 1902-03, Mount Pelée, some glass; Shepherd 8.
8. Pumice, nuée ardente, July 1902, Mount Pelée; Shepherd 10.
9. Glassy shell, bomb from Mount Pelée; Shepherd 11.
10. Surface of 1915 breadcrust bomb, Lassen Peak; Shepherd 12.
11. Kilauea lava dipped from lava lake; Shepherd 16.
12. Kilauea lava, same time and conditions as No. 11; Shepherd 17.
13. Kilauea, pahoehoe, 1923 Makaopuhi flow; Shepherd 18.
14. Kilauea, aa, same flow as No. 13; Shepherd 19.
15. Kilauea, lava brought up on sounding rod; Shepherd 22.
16. Mauna Loa, pumice, 1926 summit eruption; Shepherd 23.
17. Mauna Loa, 1926 aa flow (Murata, oral communication, 1961) from 1,100-foot altitude; Shepherd 24.
18. Niuafoua Island, 1929 eruption; Shepherd 25.
19. Stone Mountain granite; Shepherd 26.
20. North Jay granite; Shepherd 27.

From: White and Waring (1963, p. K27)

Table IV-8

Partition of H_2O and Cℓ

Present ocean volume = 1.4×10^{9} Km^3

Total weight H_2O = 1.4×10^{24} grams

Average oceanic Cℓ content = 1.9%

Total crustal H_2O = 1.7×10^{24} grams

Total crustal Cℓ = 3.1×10^{22} grams

Partition H_2O: $\frac{1.4 \times 10^{24}}{1.7 \times 10^{24}}$ = 82.5% H_2O in oceans

Partition Cℓ: $\frac{2.7 \times 10^{22}}{3.1 \times 10^{22}}$ = 87% Cℓ in oceans

Taking values from Column 3 Table IV-6 as composition of juvenile waters, assuming ocean water is derived from juvenile water following above partitions.

H_2O: 82.5% of 85.6 = 70.6 weight units

Cℓ: 87% of 1.9 = 1.7 weight units

allowing for other dissolved solids as Cℓ = $\frac{1.9}{3.5}$ of total ocean salts = 54% Cℓ or $\frac{1.4}{73.7}$ weight units

$H_2O = \frac{70.6}{73.7}$ = 96% compared to 96.5% oceanic

Cℓ = $\frac{1.7}{73.7}$ = 2.3% compared to 1.9% oceanic

Thus the relative proportions of the two major constituents of sea water H_2O and Cℓ apparently have remained constant throughout geologic time. The next question to be examined is: has there been any change in the proportions of the other major elements of sea water, particularily among the Dittmar conservative elements - Na, Mg, S, Ca, K, Sr, F, and Br? S and Br are Rubey volitiles presumably being added from depth, but the rest are derived apparently from weathered igneous rocks. Thus any evidence for changes throughout geologic time for elements derived from igneous sources must be indicated in sediments or in changes affected chemical processes in the weathering cycle. A further division of the elements derived from igneous source rocks would be into (1) elements whose concentration may be significantly effected by the biological world - Ca and K; and (2) elements whose concentrations are determined chiefly by inorganic reactions - Na, Mg, Sr, and F. The concentrations in sea water of the biologically active elements would be effected by evolutionary changes which could be determined by examination of the fossil record. However the inorganically active elements should be added to sea water in constant proportions assuming a fixed partition of these elements in the geochemical balance. Thus examination of unmetamorphosed marine sediments of various geologic ages for the ratios of

$$\frac{[\text{Biologically active element}]}{[\text{Inorganically active element}]}$$

for element pairs chemically similar such as $\frac{Ca}{Mg}$ (in carbonate rocks) or $\frac{K}{Na}$)(in marine shales) may reflect changes in the oceanic composition of these pairs. The couple between the ratios in sediments to that is sea water would be inverse. Thus an increasing $\frac{Ca}{Mg}$ ratio in sediments implies a decreasing $\frac{Ca}{Mg}$ ratio in sea water.

Any sudden change in the ratios indicates some biological events such as the evolution of an organism which abstracts a biologically active element from sea water thus disturbing the inorganic equilibrium. Gradual changes.

in time, of a ratio suggest adjustments toward equilibrium giving some idea of the rates of reactions. Finally no significant change indicates equilibrium conditions.

A word of caution here -- the concentration of carbonate cations Ca, Mg, and Sr are a function of $[CO_2^{=}]$ and thus a function of both pCO_2 in the atmosphere and the total carbon partition. For a high pCO_2 in the atmosphere and low pH, as postulated by many workers (see Rubey, 1951; Holland, 1962; and Kramer, 1965), before the evolution of plants, there would be little or no carbonate deposition and a higher concentration of Ca, Mg, and Sr in the primitive ocean than in the present ocean. A certain amount of Ca, Mg, and Sr might be sorbed by clay minerals under conditions of no carbonate deposition, but probably not enough to reduce these cations to their present concentrations. However, once the pCO_2 in the atmosphere became reasonably fixed or a new inorganic equilibrium reached, it would be possible utilize the

$$\frac{\text{Biologically Active Element}}{\text{Inorganically Active Element}}$$

ratio as then only the biologically active element may be varying due to evolutionary change. Figure IV-1 shows the variations in the major carbonate elements for the past 600 x 10^6 years. The graph of $\frac{Ca}{Mg}$ for Russian limestones suggests equilibrium values for Ca and Mg in sea water from 600 to 125 x 10^6 years. Then a biological event occurred, presumably the evolution of calcium carbonate secreting pelagic foraminifera in the mesozoic which increased the amount of calcium carbonate deposition and reduced the amount of calcium in sea water. The wide variations in the $\frac{Ca}{Mg}$ ratio in the past 100 x 10^6 years equilibrium has not be reached most likely due to variations in the amount of Ca abstractions. These variations gives further reasons for not including Ca as one of the conservative elements in Sea water (see Week II).

Figure IV-3

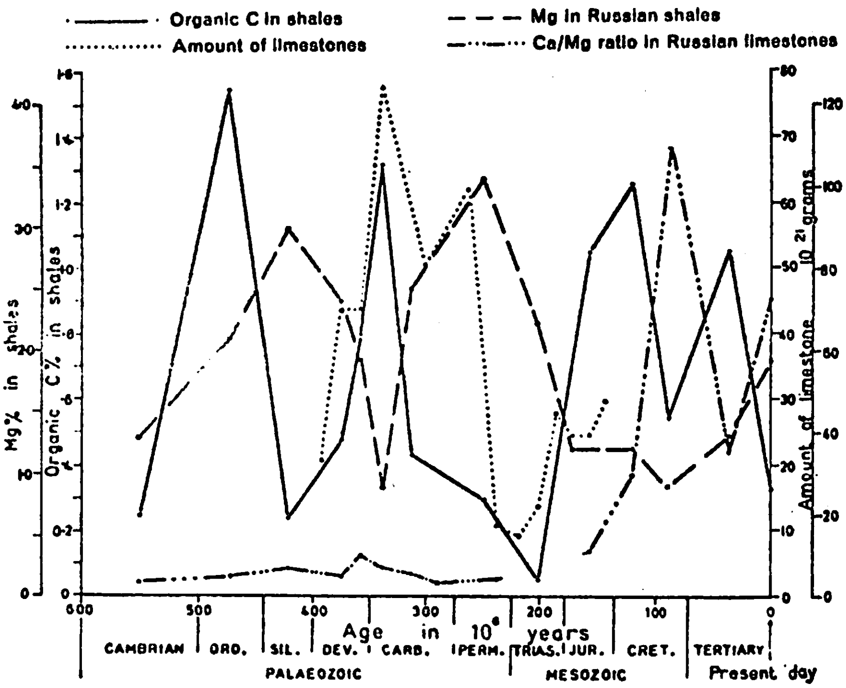

FIG. 1. Variation of various geochemical characters of sedimentary rocks formed during the last 600 × 10^6 years of geological time (data from Ronov (1959) and Green (1959)).

From: Nicholls (1965, p. 286)

Conway (1943, 1945) first amassed evidence that the $\frac{K}{Na}$ ratio in sea water is decreasing since the late precambrian caused by both depletion of K and build-up of Na. Here again the biologically active element K is being preferentially added to sediments while the inorganically active element Na is being concentrated in solution. The geochemical partition is shown in Table IV-9. Nicholls (1965, p. 288-290) using data cited in Table Iv-10 and including values for metamorphosed Precambrian rocks agreed with Conway's idea that during most of the Precambrian the partition of Na and K in sediments was different from today's partition. Nicholls felt that the $\frac{K}{Na}$ ratio in the Precambrian ocean was about .88 or about that in the parent igneous rock. At present the major cites for K and Na in sediments are in the interlayer positions in clay minerals. Nicholls thinks that the evolution of silica secreting organisms (Diatoms-plants, and radiolarians - animals) in the late Precambrian may have reduced the silica content of sea water so that feldspars, the major Na and K bearing minerals in igneous rocks (orthoclase for K and albite for Na), were no longer stable in sea water and Na and K would have to be partitioned among the clay minerals. As K is much more prefered by clays K would be abstracted from sea water whereas Na with no stable forms in equilibrium with sea water would begin to build up lowering the $\frac{K}{Na}$ ratio in sea water.

This would be reflected as an increase in the $\frac{K}{Na}$ ratio in sediments which is shown in Table IV-10 as a decrease in the $\frac{Na}{K}$ ratio in Paleozoic sediments compared to the Precambrian. The rapid decrease in the $\frac{K}{Na}$ ratio in sediments at the beginning of the Mesozoic (220 x 10^6 years ago) suggest (1) a change in the major variety of clay sorbing potassium (Nicholls, 1965, p. 291) montmorillonite instead of illite or 1Md muscouite which would

Table IV-10

TABLE III

Average contents of sodium and potassium and average values of Na/K ratio in argillaceous rocks of various ages

Time scale in 10^6 years	*Period*	*No. of analyses*	*Na%*	*K%*	*(Na+K)%*	*Na/K*	*Source of data*
1	Quaternary	5	0·55	2·6	3·15	0·21	Green (1959, Table I*)
	Tertiary	12	0·88	1·9	2·78	0·46	
70	Cretaceous, upper	4	0·85	1·6	2·45	0·53	
		17	0·81	2·07	2·88	0·39	Tourtelot (1962)
	Cretaceous, lower	8	0·99	2·2	3·19	0·45	Green (1959, Table I)
135	Jurassic	16	1·04	2·6	3·64	0·40	
180	Triassic	4	0·76	1·9	2·66	0·40	
225							
	Permian	28	0·96	2·2	3·16	0·44	
270	Carboniferous, upper	9	0·36	2·51	2·87	0·14	Nicholls and Loring (1962)
	Carboniferous, middle	19	0·54	4·2	4·74	0·13	Green (1959, Table I)
	Carboniferous, lower	17	0·39	2·2	2·59	0·18	
350							
	Devonian	18	0·86	3·07	3·93	0·28	Shaw (1956)
	Devonian, top upper	9	0·47	3·4	3·87	0·14	Green (1959, Table I)
	Devonian, bottom upper	41	0·43	2·9	3·33	0·15	
	Devonian, middle	41	0·45	2·9	3·35	0·16	
400							
	Silurian	6	0·51	3·7	4·21	0·14	
440							
	Ordovician	8	0·59	3·3	3·89	0·18	
500							
	Cambrian	14	0·36	4·0	4·36	0·09	
600		7	0·84	2·86	3·70	0·29	Mohr (1959)
	Keweenawen	4	1·68	2·38	4·06	0·71	Nanz (1953), Macpherson (1958)
1900							
	Upper Huronian	10	1·10	3·38	4·48	0·32	Nanz (1953)
	Lower Huronian	15	0·26	3·54	3·80	0·07	
	Pre-Huronian	4	2·07	2·45	4·52	0·88	Nanz (1953), Macpherson (1958)

* Table I in Green (1959) is compiled from various Russian sources quoted in the paper.

From: Nicholls (1965, p. 289)

Table IV-9

Partition of Sodium and Potassium
(in kilograms)

	K	Na	$\frac{K}{Na}$	$\frac{Na}{K}$
Igneous rocks (1)	524×10^{18}	572×10^{18}	.92	1.1
River waters (2)	7.4×10^{10}	20.7×10^{10}	.35	3
Oceans (2)	0.5×10^{18}	14.4×10^{18}	.035	29

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(1) From: Horn and Adams (1966) - see Table IV-2

(2) From: MacKenzie and Garrels (1966) - see Table II-6

mean a rise in [K] in sea water (Comment: hard to imagine the reason for this change!) or (2) possibly increased competition for the interlayer position by some other cation such as Mg (not likely as Figure IV-1 shows a decrease in Mg content of shales) or NH_4^+ (interesting but little data to back this assumption, see Bada and Miller (1968).

Another way to predict the composition of the oceanic salts is to look at the compositional variation of sedimentary rocks with time (see Figure IV-4. Ronov (1968) studying this and other interrelationships (Figure IV - 5) believed that continental igneous rocks evolved from a more mafic to the present granitic composition. Thus the composition of the average igneous rock would change with time. Thus more alkalines would be introduced with time such that the dominant cation pair would shift from Ca and Mg to Na and potassium (Table IV-11). Ronov's model also implies an increase with time in the amount of juvenile water added as granitic rocks have more water than mafic rocks.

SUMMARY

The chemical history of sea water may be divided into two problems: (1) the development of the volume of sea water and (2) the variations in the major constituents throughout time. The volume of sea water has been increasing throughout geologic time by sweating out of volatiles from a differentiating earth. The salinity of sea water, however, has remained essentially constant with the volume increase as the two major constituents H_2O and $C\ell$ have remained in constant proportion of the non-volatile conservative elements has varied (10 gradually due to changes in composition of land source rocks as well as (2) in discrete steps caused by the evolution of organisms that upset the inorganic equilibrium and cause establishment of new equilibrium concentrations. The three major evolutionary changes in sequence that produced major changes in the chemistry of the oceans were I. evolution of photosynthetic plants that

Table IV-11

RELATIVE ABUNDANCE OF CATIONS IN THE WATERS OF THE AZOIC AND MODERN OCEANS (SUM OF CATIONS = 100%)

No. in seq.	Note	Percent of the sum of cations				
		Mg	*Ca*	*Na*	*K*	*Total*
1	Probable relative abundance of cations in the Azoic ocean (author's data)	24	29	40	7	100
2	Probable relative abundance of cations in the Azoic ocean (CONWAY's data, 1942)	13	23	47	17	100
3	Relative abundance of cations in the Modern ocean (recalculated data from E. Goldberg)	10.7	3.2	83.1	3.0	100.0

From: Ronov (1968, p. 37)

Figure IV-4

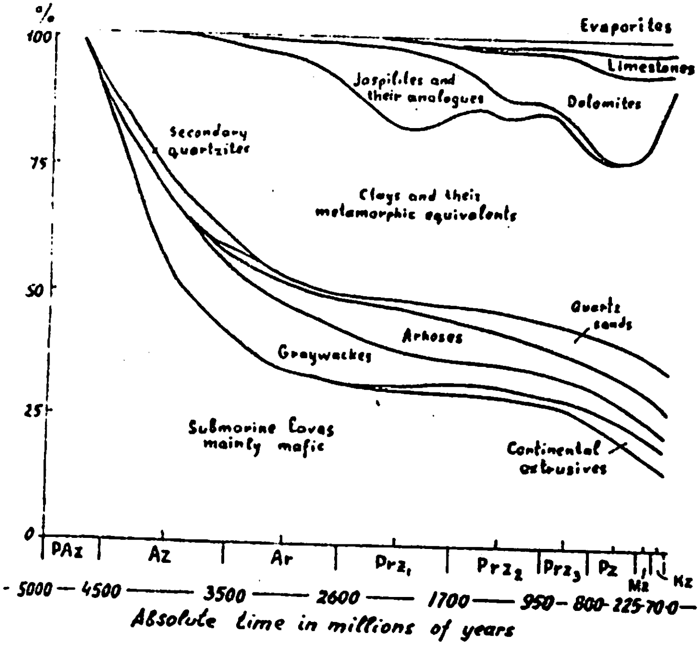
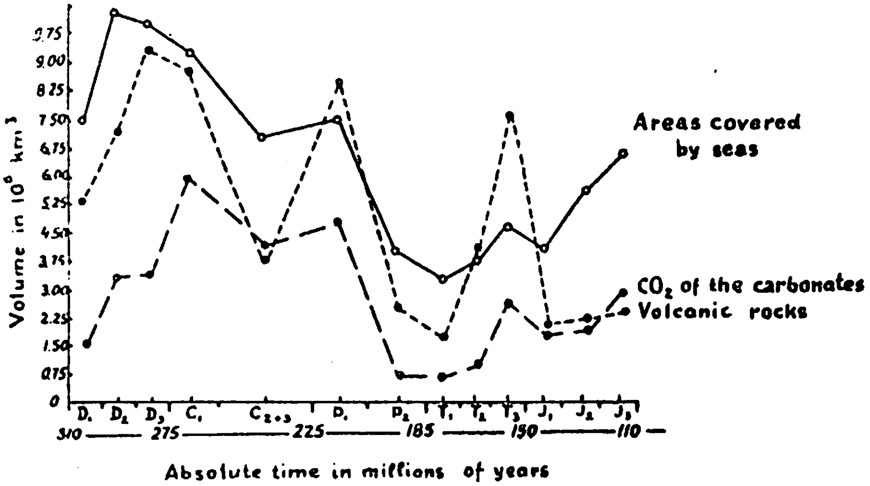


Fig.4. Outline of the compositional evolution of sedimentary rocks. (After RONOV, 1964).

From: Ronov (1968, p. 38)

Figure IV-5



From: Ronov (1968, p. 3

Fig.6. Relation between the volume of volcanic rocks, volume of CO_2 locked in the carbonate rocks an areas covered by seas within present-day continents. (After RONOV, 1959).

reduced the CO_2 content of the atmosphere permitting carbonate deposition and lowering the amounts of Ca, Mg and Sr in sea water.

II Evolution of siliceous plants (diatoms) and animals (radiolarians) which reduced S_1O_2 below saturation and established clays rather than feldspars as the stable reservior of Na and K and reduced the $\frac{K}{Na}$ ratio.

III Evolution of planktonic calcium carbonate secreting organisms (foraminifera) which further reduced the Ca content of sea water.

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THE OCEANIC BUFFER SYSTEM

The problem of the constancy of the composition of the major ions in sea water (Dittmar elements plus pH) resolves itself into a buffer question. These elements maintain a reasonably constant proportion to each other regardless of variations (within limits) of (1) inputs to the ocean via rivers, volcanoes, ice bergs, aerosols, extraterrestrial dust, etc. or (2) geographic location. This implies a buffer system monitoring these elements. Historically the buffer problem has concerned only pH. However since Sillen's (1961) classic discussion of the physical chemistry of sea water the other major elements have been included in the buffer problem.

The discussion, given in Week IV, on the history of sea water indicates that the absolute values of the proportionality, for example $\frac{K}{CL}$, probably has not remained constant throughout geologic time for some of the Dittmar elements. Thus a buffer model must be flexible enough to allow for variations in time for such ratios. Also a buffer model is not likely to be simple because of the diversity in the chemical properties of the major elements in sea water. A final problem to be investigated is whether the buffer mechanism is (1) internal -- reactions totally within sea water; (2) external -- reactions permitted with the oceanic boundaries as the sea floor or the atmosphere; or (3) some combination of (1) and (2).

Essentially two chemical buffer systems have been proposed that have significant support in the scientific community: A carbonate-borate internal buffer system and (2) a silicate external buffer system. The carbonate-borate system is chiefly a pH buffer; although this system has some ability to buffer carbonate cations such as Ca, Mg, and Sr. The silicate system has been proposed as the major buffer system in the oceans not only for pH but also for the Dittmar elements in sea water.

Carbonate-Borate Buffer System

The slight alkalinity of sea water (surface pH ~8.3) has been known since 1779 when Bergman noted that sea water turned indicator paper blue (see Riley, 1965, for a summary of early sea water analytical work). Fornöe (1880) and Dittmar (1884) first noted the presence of carbon dioxide in dissociated species chiefly HCO_3^- in sea water. Dittmar's analyses also showed "the amounts of cations derived from strong acids were not equivalent to the amounts of anions present" but were accounted for by the combined amounts of HCO_3^- and $CO_3^=$ (Spencer, 1965). Rakestraw (1949) using modern acid-base conventions explained the alkalinity of sea water as the relative surplus of strong bases (proton acceptors) over strong acids (proton donors) noting that in sea water none of the major cations present are strong acids while among the anions only the anionic species of carbonic and boric acid (HCO_3^-, $CO_3^=$, and $H_2BO_3^-$) are strong bases whereas $C\ell^-$, $SO_4^=$, and Br^- are weak bases. Table V-1 lists the relatively strong bases and their concentrations in sea water. The excess of proton acceptors over proton donors has been called "excess base", "the buffer capacity" or simply the alkalinity of sea water. Table V-2 shows a calculation of the excess base for standard sea water.

Notice in Table V-2 that if all carbonate species were (1) $H_2CO_3^-$ there would be an excess of cations or (2) $CO_3^=$ there would be an even greater excess equivalents of anions. This is graphically shown in Figure V-1 as variations of the concentrations of carbonate and borate species with pH. At the pH of surface sea water (Ca. 8.1-8.3) only HCO_3^-, $CO_3^=$, and $H_2BO_3^-$ are in sufficient concentrations. To enter into any acid-base reactions or to exhibit "buffer capacity".

Table V-1

Approximate Concentrations of Relatively Strong Bases (Proton Acceptors) in Sea Water @pH 8.3

Ion	g/moles/liter	equivalents/L
HCO_3^-	1.8×10^{-3}	1.8×10^{-3}
$CO_3^=$	$.35 \times 10^{-3}$	$.7 \times 10^{-3}$
total carbonate	2.15×10^{-3}	2.5×10^{-3}
$H_2BO_3^-$	4.5×10^{-4}	4.5×10^{-4}
$PO_4^{\equiv}$	1×10^{-6}	3×10^{-6}
AsO_2	4×10^{-8}	4×10^{-8}
S^- *	$0 - 2.0 \times 10^{-5}$	$0 - 2.0 \times 10^{-5}$

---

* found in euxinic environments only.

From: Skirrow, 1965, p. 241.

Table V-2

"Excess Base" in Sea Water*

Ion	f	z	Equivalents
$C\ell^-$	.54588	1	.54588
$SO_4^=$	.02820	2	.05640
HCO_3^-	.0024	1	.0024
Br^-	.00083	1	.00083
Total anion			.60551
Na^+	.46804	1	.46804
Mg^{++}	.05327	2	.10654
Ca^{++}	.01033	2	.02066
K^+	.01000	1	.01000
Sr^{++}	.00010	2	.00020
Total cation			.60544

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* Based on Copenhagen Standard Sea Water SAL = 35 °/oo

Figure V-1

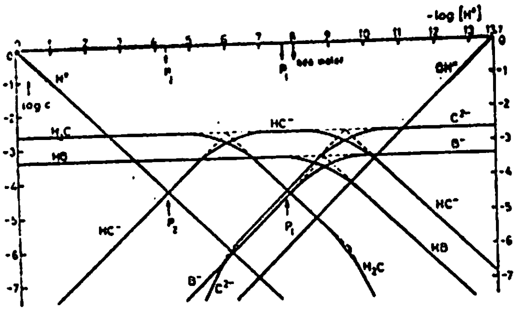


FIG. 1. Logarithmic diagram for protolytes in sea water, assuming log B_t = −3.37, log C_t = −2.62 and pK_a values: H_2C −6.0, HC^- −0.4, HB −8.8. The diagram gives log C for various species, as functions of −log $[H^+]$. P_1 and P_2 are the two equivalence points in titration with acid.

From: Dryssen and Sillen (1967, p. 116)

The stability of $[HCO_3^-]$ in the pH range of sea water indicates (1) why pH is such a poor parameter to measure the actual amount of hydrogen ion present in sea water and (2) why pH in sea water will resist change with the addition of relatively large amount of strong acids or bases.

A measurement of this ability of the strong bases to buffer sea water is made by titrating sea water with a strong acid converting all carbonate and borate species to carbonic and boric acid. The quantity of acid used (in equivalents) is called the titration alkalinity

$$\text{where T.A.} = [HCO_3^-] + 2\,[CO_3^=] + [H_2BO_3^-]$$

An analogous term would be the carbonate alkalinity or that part of the T.A. due to the carbonate species or

$$\text{C.A.} = [HCO_3^-] + 2\,[CO_3^=]$$

the complete neutrality equation for sea water would be:

$$\Sigma\, c_i\, [C_i^{+c_i}] + [H^+] + 2[Ca^{++}] =$$

$$\Sigma\, b_j\, [B_j^{-bj}] + [OH^-] + [HCO_3^-] + 2[CO_3^=] + [H_2BO_3^-]$$

where C_i = other Dittmar cations

B_j = other Dittmar anions

As $[C_i]$ and $[B_j]$ are proportional to chlorinity or chlorosity and $[H^+]$ and $[OH^-]$ are small compared to the carbonate-borate concentrations a simplified neutrality equation may be written

$$[Ca^{++}] = \frac{\text{T.A. *}}{2} \quad -0.465 \text{ Chlorosity (Wattenberg, 1936)}$$

However, as Spencer (1965, p. 42-43) noted Wattenberg's equation is only valid if the system is open to solid calcium carbonate, which would be true if the water contained carbonate particulate matter or shells or if the water was in contact

---

* Actually C.A. for borate concentrations should be considered

with solid carbonate, for example in high latitudes or below the depth of compensation.

Another measure of alkalinity is the specific alkalinity or

$$S.A. = \frac{T.A.}{CL\ ^{o}/oo} \times 10^{3}$$

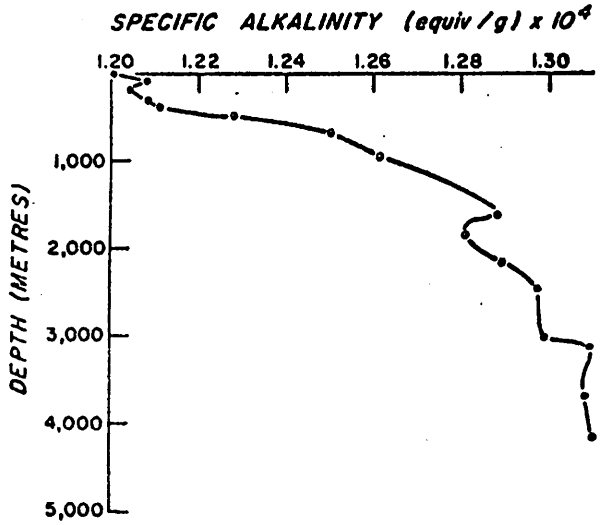
the definition of this unit is an attempt to make the concept of alkalinity independant of salinity changes so that if carbonate and borate contents were truly proportional to C_L then the specific alkalinity would be a constant S.A. = 0.123. However S.A. would vary if (1) solid carbonate is out of equilibrium (either precipitating or dissolving) upsetting the Dittmar proportionality or (2) in near shore environments where the proportionality would be upset by dilution by fresh water or by concentration by evaporation. Thus for open ocean conditions the variations of S.A. from 0.123 could be indicative of the state of saturation of solid carbonate (if available) in sea water.

Measurements of specific alkalinity indicate (1) surface waters of the atlantic averaged 0.122 while those of the Pacific and Indian Ocean averaged 0.120, (see Figure V-2, V-3). Deeper waters of the Atlantic had lower specific alkalinity than those of the Pacific and Indian Oceans although in all oceans the deep waters had higher S.A. than surface waters. (Spencer, 1965, p. 43) Koczy (1956) believed that the higher S.A.'s of deep waters was caused by the increase in solubility of calcium carbonate as a result of lower temperatures which in turn would produce a higher carbonate alkalinity.

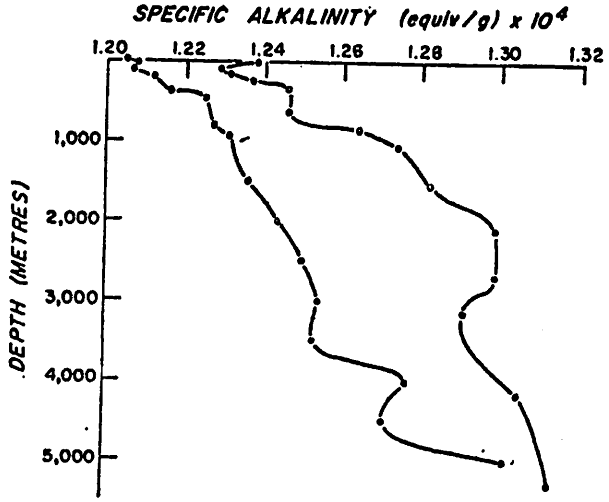
As would be expected near shore specific alkalinities show great variations and in general high values in regions of ocean water - fresh water mixing as the lower C_L content has a greater effect on the specific alkalinity than the reduction of carbonate alkalinity.

Figure V-2

Typical Pacific Specific Alkalinities



—Profile of specific alkalinity at Vityaz station 4329, 19° 58′ N. 169° 59′ W.



.—Profiles of specific alkalinity at Ob station 409, 64° 38·8′ S. 108° 55·9′ W, and Vityaz station 4066, 47° 19′ N. 175° 57′ W.

From: Pytkowicz (1969, p. 119-120)

Figure V-3

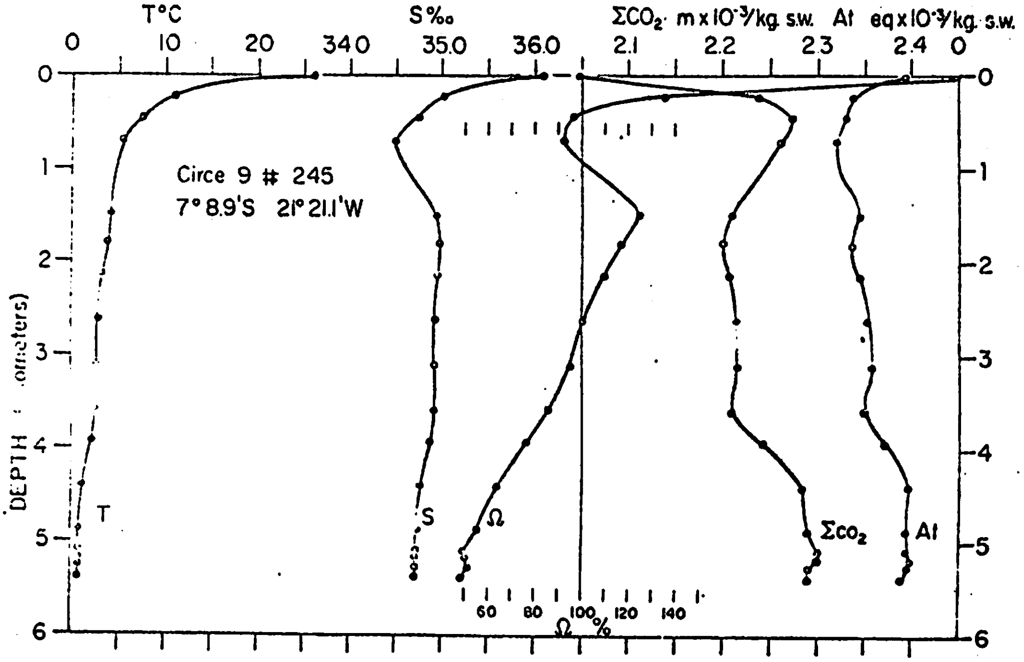


Fig. 12. Depth profiles of temperature, salinity, A_t and ΣCO_2 with the computed value for Ω (calcite) for a station in the Brazil Basin in the south Atlantic. (Data in Table 8.)

Table 8. Circe 9, Station 245, 7°8·9′, 21°21·1′W

Depth (m)	T (°C)	S‰	ΣCO_2 (m. 10^{-3}/kg s.w.)	A_t (eq. 10^{-3}/kg s.w.)	Ω_c%	Ω_a%
1	25·95	36·039	2·047	2·279	448·8	277·1
220	10·91	35·019	2·238	2·293	135·6	88·0
450	7·51	34·741	2·273	2·290	96·1	63·1
700	5·33	34·497	2·261	2·287	92·1	60·9
1500	4·09	34·935	2·209	2·290	124·4	83·7
1800	3·74	34·962	2·200	2·279	116·7	78·9
2165	3·22	34·938	2·207	2·286	109·8	74·6
2630	2·82	34·913	2·216	2·294	100·2	68·5
3110	2·65	34·910	2·215	2·296	95·0	65·4
3585	2·49	34·909	2·209	2·287	85·7	59·3
3925	2·11	34·869	2·242	2·313	76·6	53·3
4400	1·04	34·759	2·283	2·342	63·4	44·5
4875	0·77	34·749	2·289	2·341	55·1	38·8
5090	0·73	34·719	2·301	2·345	49·6	35·1
5185	0·74	34·716	2·300	2·348	50·3	35·6
5275	0·74	34·717	2·291	2·343	51·3	36·3
5385	0·74	34·719	2·290	2·338	48·4	34·4

From: Edmond and Gieskes (1970, p. 1286-1287)

Weyl and Pytkowicz (in Pytkowicz, 1969, p. 128-129) give the following general equation for the variation of specific alkalinity

$$\frac{\partial S.A.}{\partial \tau} = \frac{s}{C_L} - \bar{V} \cdot \nabla S.A. + \nabla D \cdot \nabla S.A. + \frac{2}{C_L} \nabla C \cdot D \cdot \nabla S.A.$$

where:

S.A. = specific alkalinity
s = rate of solution
C_L = chlorinity
V = advective velocity
D = diffusion = $D_x \bar{i}\bar{i} + D_y \bar{j}\bar{j} + D_z \bar{k}\,\bar{k}$
for D_x, D_y, D_z = eddy diffusion coefficients
∇ = LaPlacian operator

Weyl (1961) developed another method to examine the state of saturation of carbonate in sea water. The fundamental assumption is that the total carbon dioxide system in sea water may be represented as

$$[CO_2] + [H_2CO_3] + [HCO_3^-] + [CO_3^=] = y_o - y$$

Where y_o = total carbon dioxide

y = carbonate ion removed by precipitation

this may be expressed in terms of C.A.:

$$C.A. = (yo - y)\left\{ \frac{\dfrac{1 + 2K'2}{aH^+}}{1 + \dfrac{aH^+}{K'1} + \dfrac{K'2}{aH^+}} \right\}$$

(see Harvey (1963) or Table I-5 for derivation of carbonate equilibrium constants)

Further defining F as a function of pH or

$$F = \left\{ \frac{\dfrac{1 + aK'2}{aH^+}}{1 + \dfrac{aH^+}{K'1} + \dfrac{K'2}{aH^+}} - 1 \right\}$$

or C.A. = (yo - y) (F + 1)

95

for neutrality:

$$C.A. + N = P$$

Where: N = equivalents of ionic species other than carbonate

P = equivalents of positive ions

after precipitation of y moles of calcium carbonate

$$C.A. + N = P - 2y$$

if strong acid is added where $Z = 2y$ $C.A. + N = P - Z$

and $$(yo - y)(F + 1) + N = P - 2y$$

$$(yo - y)(F + 1) + N = P - Z$$

or

$$yo\ (F + 1) + N = P - y\ (1 + F)$$

$$yo\ (F + 1) + N = P + ZF$$

thus at a given pH $-y = Z \frac{F}{1 + F}$

Weyl's method is to (1) measure the pH of a given sea water then (2) place near the pH electrode powdered calcite and monitor the resultant pH change. In undersaturated solutions the pH in the saturometer (Weyl's name for the method) will rise with respect to the first case due to the addition of carbonate ions from the dissolving powder. In saturated solutions the pH will fall due to the subtraction of carbonate ions by precipitation or growth on the powder nuclei Weyl found a change of 1 ppm calcite reflects a change of approximately .02pH units. Unfortunately the saturometer can not be used in place in the water column at present. Pytkowicz (1967) using Wattenberg's equation calculated the apparent saturation for a station in the North Pacific at 44° N (see Table V-3). He found that only the upper 150 meters were saturated with respect to $CaCO_3$.

A sophisticated examination of the carbonate saturation problem in sea water has been done by Edmond and Gieskes (1970). Their Data (Figure V-3) essentially affirm that calcite and aragonite, at low latitudes, are (1) super saturated at the surface, and (2) undersaturated at depth. In addition they have developed the following useful relationships.

For

$$pK'_1 = -\log\left[\frac{[a_H{}^+]\,[HCO_3{}^-]}{\left[\,[CO_2] + [H_2CO_3]\,\right]}\right]$$

$$= 3404.71/\tau + 0.032786\cdot\tau$$
$$-14.7122 - 0.19178\ C_L{}^{1/3}$$

$$pK'_2 = -\log\left[\frac{[a_H{}^+]\,[CO_3{}^=]}{[HCO_3{}^-]}\right]$$

$$= 2902.39/\tau + 0.02379 \cdot \tau$$
$$-6.4710 - 0.4693\ C_L{}^{1/3}$$

$p\alpha s$ = -log solubility of CO_2 in sea water

$$= -2385.73/\tau + 14.0184$$
$$-0.0152642 \cdot \tau$$
$$+\mu(0.28596 - 6.167 \times 10^{-4}\tau)$$

$$Ksp' = [Ca^{++}][CO_3{}^=]$$

$$Ksp'\ (\text{calcite}) = (0.1614 + 0.02892 CL - 0.0063\tau)\ 10^{-6}$$
$$Ksp'\ (\text{aragonite}) = (0.5115 + 0.02892\ CL - 0.0063\tau)\ 10^{-6}$$

$$pK_B' = -\log\left[\frac{[a_H{}^+]\,[H_2BO_3{}^-]}{[B(OH)_3]}\right]$$

Figure V-4

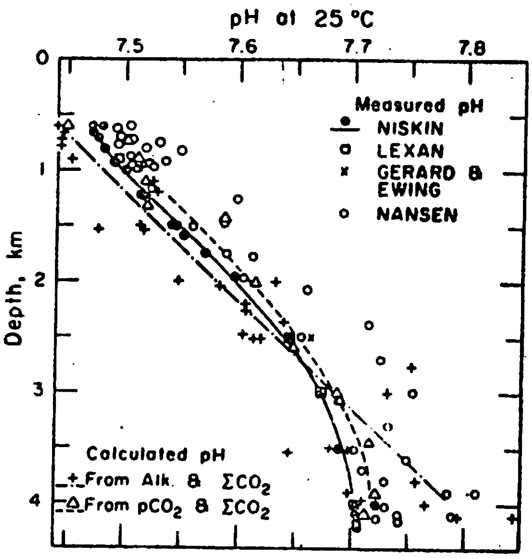


Fig. 1. The measured and calculated *p*H values as a function of depth at the Geosecs station. The *p*H values measured for the samples collected by the Nansen bottles (open circles) are compared with those collected by the Lexan (open squares), Niskin (filled circles) and Gerard-Ewing (crosses) samplers. The *p*H values calculated from the pCO_2 and ΣCO_2 data (triangles) and from the alkalinity and ΣCO_2 data (plus signs) are also compared with the measured values. The general trend of the measured *p*H values for the Niskin and Lexan bottle samples is shown by a solid curve, and the general trend for the *p*H values calculated from the pCO_2 and ΣCO_2 data and from the alkalinity and ΣCO_2 data is, respectively, shown by dashed and dotted curves.

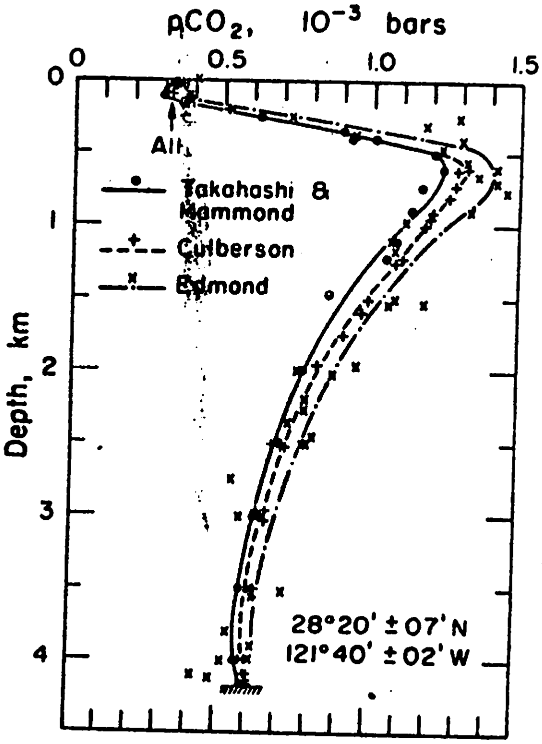


Fig. 2. The pCO_2 depth profile at the Geosecs station. The pCO_2 values measured by the equilibrator-infrared method are compared with the values calculated from the *p*H and alkalinity data of Culberson and from the alkalinity and ΣCO_2 data of Edmond. General trends of each set of the pCO_2 values are indicated by three curves. The pCO_2 in the air at the station is also shown.

From: Takahashi and others (1970, p. 7657, 7659)

Figure V-5

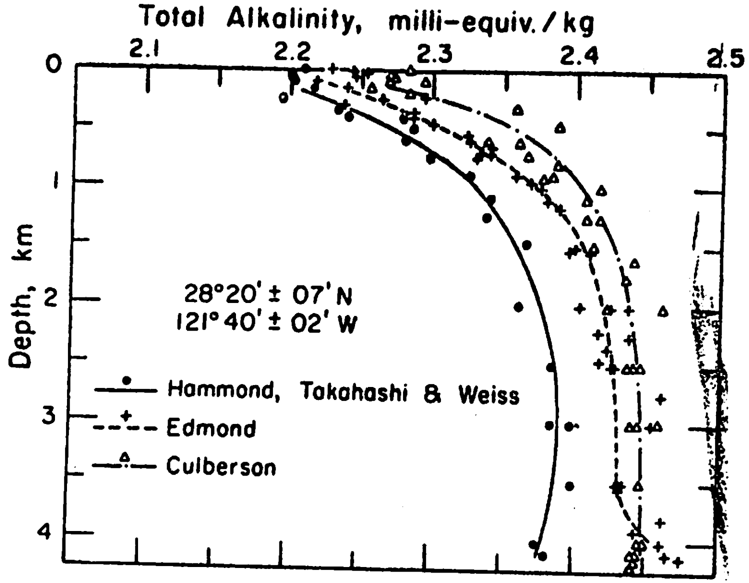


Fig. 3. The total alkalinity depth profile at the Geosecs station. The total alkalinity values were measured by Edmond by using the potentiometric acid titration method and by Culberson by using the *p*H method. The alkalinity values calculated from the pCO_2 and ΣCO_2 values are compared with the measured values. The trends of each set of the values are indicated by three curves.

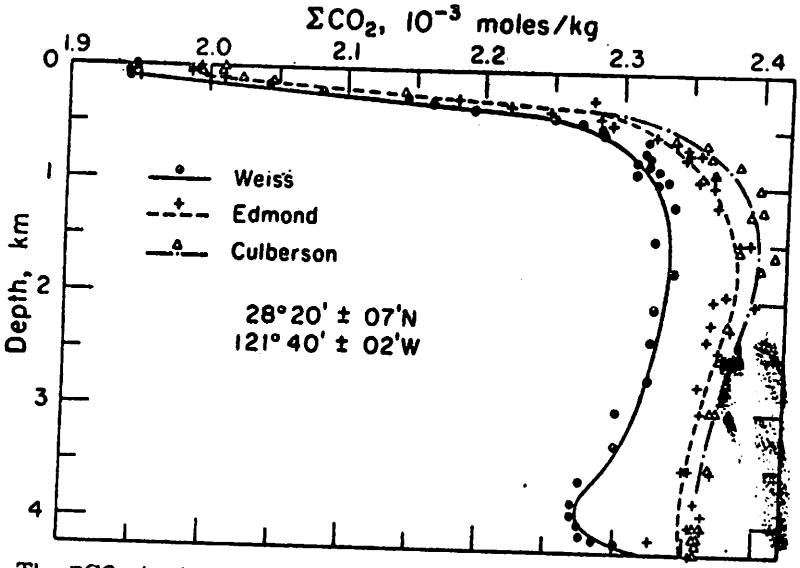


Fig. 4. The ΣCO_2 depth profile at the Geosecs station. The ΣCO_2 values were measured by Weiss by using the gas chromatographic method and by Edmond by using the potentiometric acid titration method. The ΣCO_2 values calculated from the *p*H and alkalinity data of Culberson using the first and second dissociation constants of *Lyman* [1956] for carbonic acid are compared with the measured ones. General trends of each set of the ΣCO_2 values are indicated by three curves.

From: Takahashi and others, (1970, p. 7649 and 7654) a buoy to a depth of approximately 5000 meters on which calcite spheres were set about every 70 meters. Peterson reported that after four months exposure to natural sea water in place only the spheres below 3500 M showed evidence of solution (Figure V-6).

Thus, at this time there seems to be some difficulty relating the equilibrium data with the practical experiments, for example compare Ω calcite of Figure V-3 with Figure V-6. Unquestionably part of the problem is kinetic, as Chave and Schmaltz (1966) noted the variation in solubility with the grain size of carbonates. Also organic masking of protection of carbonate grains from solution apparently occurs in the real ocean (Chave and Suess, 1970). This partially would explain why the calcite spheres in the Peterson experiment did not dissolve as would be predicted from equilibrium studies. On the other hand the calcite spheres did not grow in the near surface ocean where equilibrium calculations would predict carbonate supersaturation. This may be due to organic metabolites inhibition precipitation as noted by Simkiss(1964).

The study of the interference of the organic world with carbonate chemistry certainly appears to be an area of fruitful research particularily as the equilibrium chemistry of the carbonates in sea water is now reasonabily well understood.

$$= 2291.90/\tau + 0.01756\tau$$
$$-3.3850 - 0.32051 CL^{1/3}$$

Where: τ = temperature ° centrigrade

CL = chlorinity in parts per thousand

μ = ionic strength (see Chapter I, p. 6)

The variations of these solubility constants with pressure have been given by (1) Culberson and Pytkowicz (1968) as

$$\Delta pK'_1 = 0.013 + 1.319 \times 10^{-3} P - 3.061 \times 10^{-6} P\tau - 0.161 \times 10^{-6} P^2$$

$$\Delta pK'_2 = 0.015 + 0.839 \times 10^{-3} P - 1.908 \times 10^{-6} P\tau + 0.182 \times 10^{-6} \tau^2$$

$$\Delta pK'_B = 1.909 \times 10^{-3} P - 4.515 \times 10^{-6} P\tau - 0.169 \times 10^{-6} P^2 + 1.759 \times 10^{-12} P^2 \tau^2$$

and (2) Li (in Edmond and Gieskes, 1970, p. 1275) as $\Delta pK'_i = \Delta V'_i/2.303R\tau$

for:

$$\Delta V'_1 = -(24.2 - 0.085\tau) cm^3/mole$$

$$\Delta V'_2 = -(16.4 - 0.040\tau)\ cm^3/mole$$

$$\Delta V_B' = -(27.5 - 0.095\tau) cm^3/mole$$

Because various workers not only use different techniques but also different sampling procedures there has been confusion on how to inter-relate data from different cources. The first attempt at inter-calibration was made in September 1969 in the Pacific at 28°29'N, 121°38'W as the GEOSECS (Geochemical Ocean Sections Study). Figures V-4 and V-5 shows the results of this test with respect to carbonate studies.

A direct method for measuring the state of saturation of carbonate in sea water was used by Peterson (1966) in the Central Pacific. Peterson set

Figure V-6

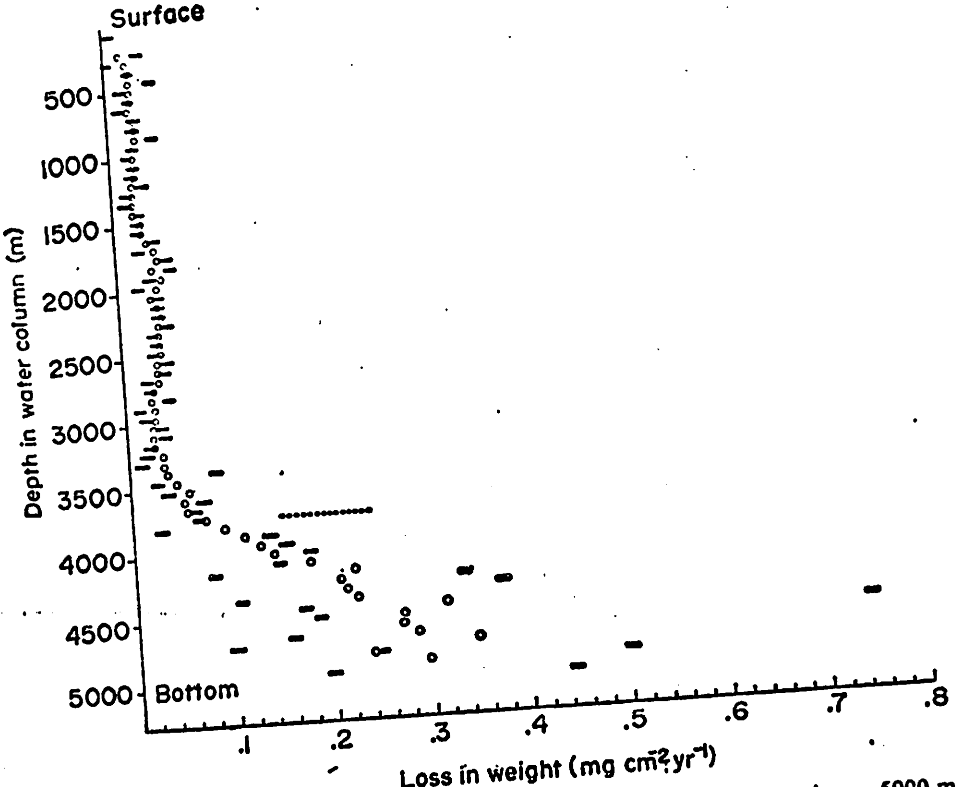


Fig. 2. Vertical profile of rate of dissolution of calcium carbonate in a 5000-m water column. Bars show rates of dissolution for individual calcite spheres (length of bars represents uncertainty due to assigned weighing errors). Circles show rates of dissolution averaged over five adjacent spheres. Dashed line shows the level of abrupt increase in rate.

From: Peterson (1966, p. 1543)

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UNIVERSITY OF CALIFORNIA
CE 201 B

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SILICATE BUFFER MECHANISM

Sillen (1961) first logically expounded the view that the various silicate minerals (chiefly clays) introduced into the ocean as weathering products buffer the composition of sea water. His argument simply stated, as although the carbonate ionic species are more reactively kinectically than silicates, the volume of carbonates and hence their total buffer capacity is much less than the volume of silicates in contact with sea water. In short carbonate reactions are just indicators for the silicate buffer mechanism. Sillen's original hypothesis was based on an equilibrium atmosphere - ocean - sediment model in the proportions 3:1:0.6 based on Goldschmidt's (1933) geochemical balance. Later Sillen used a refined model based on the geochemical balance of Horn and Adams (1966):

igneous rocks +	volatiles →	sea water +	sediments +	atoms.
1.2 Kg	1 Kg	1 liter	1.2 Kg	3 liters

As Sillen's model includes sediments and thus implies at least partial external control of the sea water buffer, equilibrium constants and reactions must be known not only for dissolved species in sea water but also for minerals in contact with sea water.

Table VI-1 lists a compilation of such reactions by Kramer (1965) for 5°C and 1 atmosphere. An idea of the stability fields of abundant silicate minerals is shown in Figure VI-1. Table VI-2 lists the mineral equilibria reactions used by Hess (1966) to develop the diagrams are calculated from free energy data extrapolated to 25°C and 1 atmosphere.

Table VI-1

Table 3. Thermochemical data used in calculations (constants are for 5°C and 1 atm total pressure unless otherwise noted. ( ) ref to activities. [ ] refer to concentrations).

Species or reaction	Constant	Reference	Remark
H-Mont(*C* site) = Na-Mont(C site)	$10^{-3.3} = \frac{[NaC](H^+)}{[HC](Na^+)}$	Blackmon (1958)	1
H-Mont (*E* site) = Na-Mont (E site)	$10^{-7.6} = \frac{[NaE](H)}{[HE](Na)}$	Blackmon (1958)	1
H-Illite(*C* site) = K-Illite (C site)	$10^{-3.4} = \frac{[KC](H)}{[HC](K)}$	Blackmon (1958)	1
H-Illite (*E* site) = K-Illite (E site)	$10^{-6.7} = \frac{[KE](H)}{[HE](K)}$	Blackmon (1958)	1
$CaSO_4.2H_2O = Ca^{+2} + SO_4^{-2} + 2\,H_2O(l)$	$10^{-4.60} = (Ca^{+2})(SO_4^{-2})$	Latimer (1952)	1
Ca^{+2} + H-illite = Ca-illite + $2H^+$	$10^{-3.8} = (Ca^{+2})(H^+)^{0.08}$	Chatterjee and Marshall (1950)	3
$Ca_2Al_4Si_8O_{24}.9H_2O$(phillipsite) + $4\,H^+ = 4\,SiO_2$(qtz) + $2\,Al_2Si_2O_7.2H_2O$(kaol) + $2\,Ca^{+2} + 7\,H_2O(l)$	$10^{13} = (Ca^{+2})/(H^+)^2$	Barany and Kelley (1961)	4
Mg^{+2} + H-illite = Mg-illite + $2H^+$	$10^{-4.4} = (Mg^{+2})(H^+)^{-0.1}$	Chatterjee and Marshall (1950)	3
$Mg_5Al_2Si_3O_{14}.4H_2O$(Chlorite) + $10\,H^+ = SiO_2$(qtz) $Al_2Si_2O_7.2H_2O$(kaol) + $7H_2O + 5\,Mg^{+2}$	$10^{14.2} = (Mg^{+2})/(H^+)^2$		
$Ca_{10}(PO_4)_6(OH)_2 = 10\,Ca^{+2} + 6\,PO_4^{-3} + 2\,OH^-$	$10^{-118} = (Ca^{+2})^{10}(PO_4^{-3})^6(OH^-)^2$		6
Solubility of:			
$Na_{0.56}Ca_{9.56}][(PO_4)_{5.35}(SO_4)_{0.30}(CO_3)_{0.32}][F_{2.04}]$	equilibrium constant = 10^{-103}		
$CaCO_3$(calcite) = $Ca^{+2} + CO_3^{-2}$	$10^{-8.09} = (Ca^{+2})(CO_3^{-2})$	Harned and Scholes (1941)	
$CaCO_3$(aragonite) = $Ca^{+2} + CO_3^{-2}$	$10^{-7.92} = (Ca^{+2})(CO_3^{-2})$	Harned and Scholes (1941)	8
$CaMg(CO_3)_2 = Ca^{+2} + Mg^{+2} + 2\,CO_3^{-2}$	$10^{-16.21} = (Ca^{+2})(Mg^{+2})(CO_3^{-2})^2$	Robie (1958)	
$MgCO_3.3H_2O = Mg^{+2} + CO_3^{-2} + 3\,H_2O(l)$	$10^{-5} = (Mg^{+2})(CO_3^{-2})$	Latimer (1952)	9
$H_2CO_3 = H^+ + HCO_3^-$	$10^{-6.52} = (H^+)(HCO_3^-)/(H_2CO_3)$	Harned and Davis (1943)	
$HCO_3^- = H^+ + CO_3^{-2}$	$10^{-10.6} = (H^+)(CO_3^{-2})/(HCO_3^-)$	Harned and Scholes (1941)	
$CO_2(g) + H_2O(l) = H_2CO_3$	$10^{+1.19} = P_{CO_2}/(H_2CO_3)$	Harvey (1960)	
$CaHCO_3^+ = Ca^{+2} + HCO_3^-$	$10^{-1.26} = (Ca^{+2})(HCO_3^-)/(CaHCO_3^+)$	Garrels and Thompson (1962)	9
$NaCO_3^- = Na^+ + CO_3^{-2}$	$10^{-1.27} = (Na^+)(CO_3^{-2})(/NaCO_3^-)$	Garrels and Thompson (1962)	9
$CaCO_3^0 = Ca^{+2} + CO_3^{-2}$	$10^{-3.2} = (Ca^{+2})(CO_3^{-2})/(CaCO_3^0$	Garrels and Thompson (1962)	9
$NaHCO_3^0 = Na^+ + HCO_3^-$	$10^{+0.25} = (Na^+)(HCO_3^-)/(NaHCO_3^0)$	Garrels and Thompson (1962)	9
$CaSO_4^0 = Ca^{+2} + SO_4^{-2}$	$10^{-2.31} = (Ca^{+2})(SO_4^{-2})/(CaSO_4^0)$	Garrels and Thompson (1962)	9
$KSO_4^- = K^+ + SO_4^{-2}$	$10^{-0.96} = (K^+)(SO_4^{-2})/(KSO_4^-)$	Garrels and Thompson (1962)	9
$NaSO_4^- = Na^+ + SO_4^{-2}$	$10^{-0.72} = (Ha^+)(SO_4^{-2})/(NaSO_4^-)$	Garrels and Thompson (1962)	9
$MgHCO_3^+ = Mg^{+2} + HCO_3^-$	$10^{-1.16} = (Mg^{+2})(HCO_3^-)/(MgHCO_3^+)$	Garrels and Thompson (1962)	9
$MgCO_3^0 = Mg^{+2} + CO_3^{-2}$	$10^{-3.4} = (Mg^{+2})(CO_3^{-2})/(MgCO_3^0)$	Garrels and Thompson (1962)	9
$MgSO_4^0 = Mg^{+2} + SO_4^{-2}$	$10^{-2.36} = (Mg^{+2})(SO_4^{-2})/(MgSO_4^0)$	Garrels and Thompson (1962)	9
$MgF^+ = Mg^{+2} + F^-$	$10^{-1.80} = (Mg^{+2})(F^-)/(MgF^+)$	Connick and Tsao (1954)	10
$NaPO_4^{-2} = Na^+ + PO_4^{-3}$	$10^{-0.25} = (Na^+)(PO_4^{-3})/(NaPO_4^{-2})$	Smith and Alberty (1956)	10
$NaHPO_4^- = Na^+ + HPO_4^{-2}$	$10^{-0.21} = (Na^+)(HPO_4^{-2})/(NaHPO_4^-)$	Smith and Alberty (1956)	10
$KPO_4^{-2} = K^+ + PO_4^{-3}$	$10^{-0.20} = (K^+)(PO_4^{-3})/(KPO_4^{-2})$	Smith and Alberty (1956)	10
$KHPO_4^- = K^+ + HPO_4^{-2}$	$10^{-0.20} = (K^+)(HPO_4^{-2})/(KHPO_4^-)$	Smith and Alberty (1956)	10
$CaHPO_4^0 = Ca^{+2} + HPO_4^{-2}$	$10^{-2.20} = (Ca^{+2})(HPO_4^{-2})/(CaHPO_4^0)$	Davies and Hoyle (1953)	9
$MgHPO_4^0 = Mg^{+2} + HPO_4^{-2}$	$10^{-1.80} = (Mg^{+2})(HPO_4^{-2})/(MgHPO_4^0)$	Greenwald (1940, 1945)	9
$H_2PO_4^- = H^+ + HPO_4^{-2}$	$10^{-7.28} = (H^+)(HPO_4^{-2})/(H_2PO_4^-)$	Van Wazer (1958)	
$HPO_4^{-2} = H^+ + PO_4^{-3}$	$10^{-12.66} = (H^+)(PO_4^{-3})/(HPO_4^{-2})$	Vanderzee and Quist (1961)	
$Ca_2HPO_4.CO_3^0 + H^+ = 2Ca^{+2} + HPO_4^{-2} + HCO_3^-$	$10^{-1.33} = \frac{(Ca^{+2})^2(HPO_4^{-2})(HCO_3^-)}{(Ca_2.HPO_4.CO_3^0)(H^+)}$	Greenwald (1945)	9
$Ca_2.HPO_4.CO_3^0 = H^+ + Ca_2.PO_4.CO_3^-$	$10^{-8.3} = \frac{(H^+)(Ca_2.PO_4.CO_3^-)}{(Ca_2.HPO_4.CO_3^0)}$	Greenwald (1945)	9
$H_2O(l) = H^+ + OH^-$	$10^{-14.73} = (H^+)(OH^-)$	Harned and Hammer (1933)	
$SrSO_4 = Sr^{+2} + SO_4^{-2}$	$10^{-6.55} = (Sr^{+2})(SO_4^{-2})$	Bjerrum *et al.* (1958) Latimer (1952)	
$SrCO_3 = Sr^{+2} + CO_3^{-2}$	$10^{-9.15} = (Sr^{+2})(CO_3^{-2})$	Bjerrum *et al.* (1958) Latimer (1952)	

(1) The cationic clay complex is assumed equal to the protonated clay complex so that the equilibrium constants reduce to: (H)/(cation) constant. The constants listed are for room temperature.

(2) ΔH^0 and ΔS^0 are assumed constant over small temperatures ranges. Hence, $\Delta F^0 = a + bt$ from which the equilibrium constant at 5°C is de

(3) Relationship is derived from an empirical fit to data.

(4) Free energy data for kaolinite from Barany and Kelly (1961); phillipsite estimated from data for leonhardite (Barany, 1962) and relative stabilities of zeolites (Coombs *et al.*, 1959). Free energy of formation from elements for quartz at 25°C taken as −197·33 kcal/mol (Wise *et al.*, 1962; Cochran and Foster, 1962). Rest of data from Latimer (1952).

(5) Free energy of formation value for chlorite estimated. (See 4) for other details.

(6) Heat capacity and entropy data from Egan *et al.* (1951a, b). Heats of formation from elements at 25°C are −3215 kcal/mol for $Ca_{10}(PO_4)_6$(OH and −3260 kcal/mol for $Ca_{10}(PO_4)_6F_2$ (personal communication, Egan). See also Clark (1955), Sillen (1961), and Gottschal (1959) regarding OH-apatite.

(7) Solubility of CO_2–F-apatite from equilibrium studies of a phosphate from Phosphoria formation (Kramer, 1963).

(8) Aragonite constant determined from ratio of aragonite and calcite constants at 25°C and calcite constant at 25°C.

(9) Value is for room temperature or 25°C rather than 5°C.

(10) Data for two temperatures given. Assumed: log $K = a + bt$.

From: Kramer (1965, p. 932-933)

Figure V1-1a

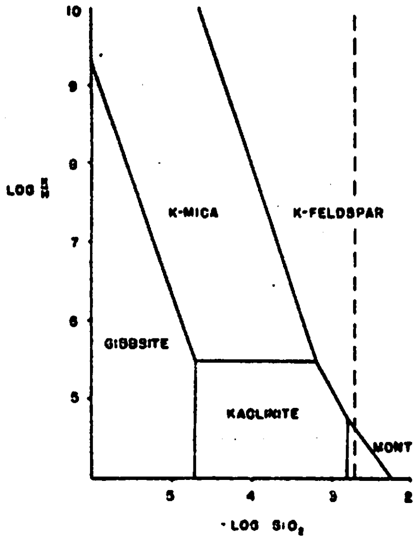

Fig. 2

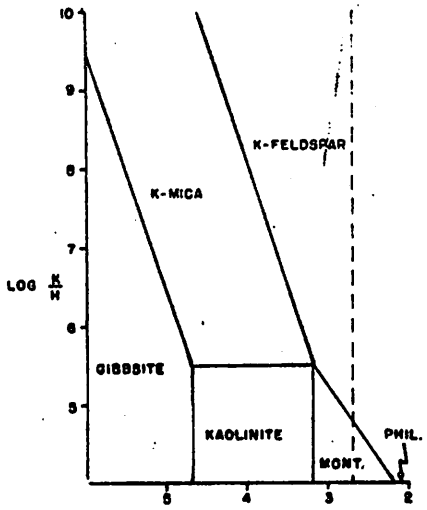

Fig. 3

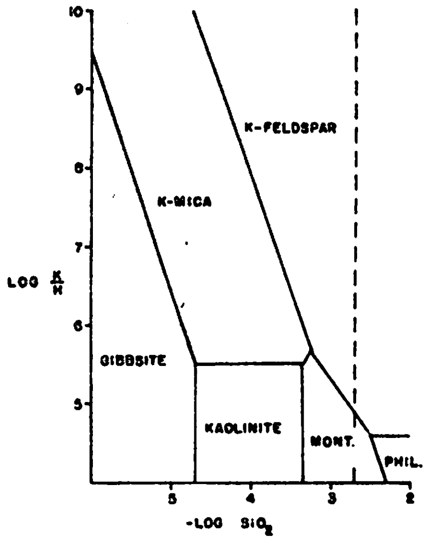

Fig. 4

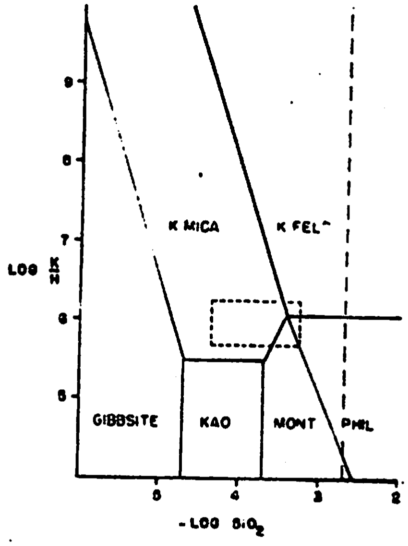

Fig. 5

Fig. 2. Isoplethic section at log Na/H = 4. Dotted line equals solubility of amorphous silica at 25°C. MONT = montmorillonite.

Fig. 3. Isoplethic section at log Na/H = 5.4. Dotted line equals solubility of amorphous silica at 25°C. MONT = montmorillonite, PHIL = phillipsite.

Fig. 4. Isoplethic section at log Na/H = 6.9. Dotted line equals solubility of amorphous silica at 25°C. MONT = montmorillonite, PHIL = phillipsite.

Fig. 5. Isoplethic section at log Na/H = 7.5. Dotted line equals solubility of amorphous silica at 25°C. Dotted box corresponds to oceanic environment. KAOL = kaolinite, MONT = montmorillonite, PHIL = phillipsite.

From: Hess (1966, p. 302)

Figure VI-1b

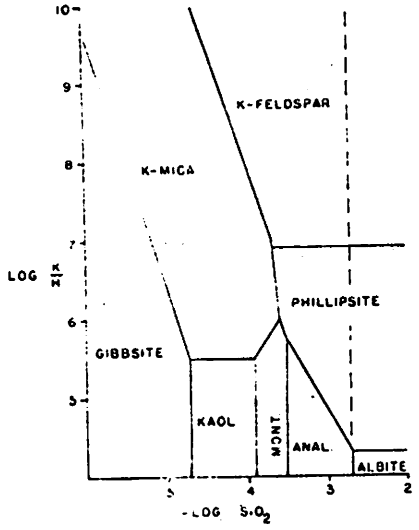

Fig. 6

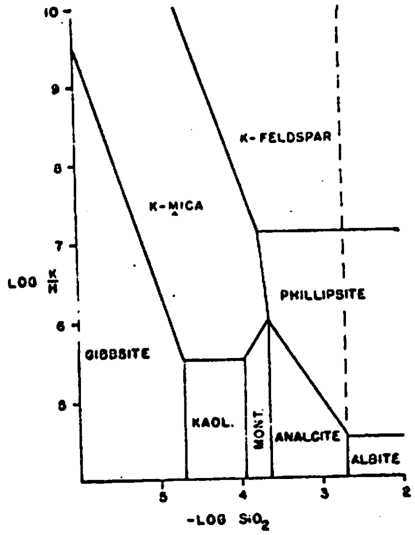

Fig. 7

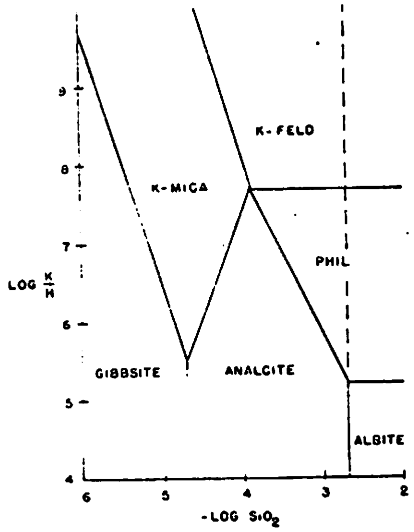

Fig. 8

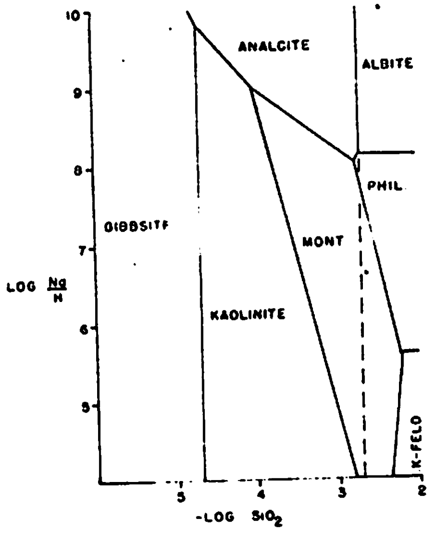

Fig. 9

Fig. 6. Isoplethic section at log Na/H = 8.5. Dotted line equals solubility of amorphous silica at 25°C. KAOL = kaolinite, ANAL = analcite.

Fig. 7. Isoplethic section at log Na/H = 8.7. Dotted line equals solubility of amorphous silica at 25°C. KAOL = kaolinite, MONT = montmorillonite.

Fig. 8. Isoplethic section at log Na/H = 9.5. Dotted line equals solubility of amorphous silica at 25°C. K-FELD = k-feldspar, PHIL = phillipsite.

Fig. 9. Isoplethic section at log K/H = 4. Dotted line equals solubility of amorphous silica at 25°C. MONT = montmorillonite, PHIL = phillipsite, K-FELD = k-feldspar.

From: Hess (1966, p. 303)

Table VI-2a

Representive Mineral Equilibria In The Ocean Environment

1. Gibbsite - Kaolinite

$$Al_2(OH)_6 + 2SiO_2 = Al_2(Si_2O_5)(OH)_4 + H_2O$$

or $\log k = -2 \log SiO_2$

2. Gibbsite - K-mica (illite)

$$3Al_2(OH)_6 + 2K^+ + 6SiO_2 = 2KAl_2(AlSi_3O_{10})(OH)_2 + 2H^+ + 6H_2O$$

or $\log k = -2\log \frac{K^+}{H^+} - 6\log SiO_2$

3. K-mica (illite) - Kaolinite

$$2KAl_2(AlSi_3O_{10})(OH)_2 + 2H^+ + 3H_2O = 3Al_2(Si_2O_5)(OH)_4 + 2K^+$$

or $\log k = 2 \log \frac{K^+}{H^+}$

4. K-feldspar - Kaolinite

$$2KAlSi_3O_8 + 2H^+ + H_2O = Al_2(Si_2O_5)(OH)_4 + 2K^+ + 4\ SiO_2$$

or $\log k = 2 \log \frac{K^+}{H^+} + 4 \log SiO_2$

5. Na-montmorillonite - Kaolinite

$$2Na_{0.33}Al_2(Si_{3.67}Al_{0.33}O_{10})\ (OH)_2 + H^+ + 3.5H_2O =$$
$$3.5Al_2(Si_2O_5)(OH)_4 + 4\ SiO_2 + Na^+$$

or $\log k = \log \frac{Na^+}{H^+} + 4 \log SiO_2$

6. Na-montmorillonite - Phillipsite

$$3Na_{0.33}Al_2(Si_{3.67}Al_{0.33}O_{10})(OH)_2 + 2.5\ Na^+ + 3.5K^+ + 10SiO_2 + 7H_2O =$$
$$7Na_{0.5}K_{0.5}AlSi_3O_8 \cdot H_2O + 6H^+$$

or $\log k = -2.5 \log \frac{Na^+}{H^+} - 3.5 \log \frac{K^+}{H^+} - 10 \log SiO_2$

7. K-mica (illite) - Na-montmorillonite

$$7KAl(Si_3Al0_{10})(OH)_2 + 3Na + 7H^+ + 12SiO_2 =$$

$$9Na_{0.33}Al_2(Si_{3.67}Al_{0.33}O_{10})(OH)_2 + 7K^+ + 3H^+$$

$$\text{or } \log K = 7 \log \frac{K^+}{H^+} - 3 \log \frac{Na^+}{H^+} - 12 \log SiO_2$$

8. K-Feldspar - Na-montmorillonite

$$7KAlSi_3O_8 + Na^+ + 6H^+ = 3Na_{0.33}Al_2(Si_{3.67}Al_{0.33}O_{10})(OH)_2 + 7K^+ + 10\ SiO_2$$

$$\text{or } \log k = 7 \log \frac{K^+}{H^+} - \log \frac{Na^+}{H^+} + 10 \log SiO_2$$

9. K-feldspar - K-mica(illite)

$$3KAlSi_3O_8 + 2H^+ = KAl_2(Si_3Al_{10}O)(OH)_2 + 2K^+ + 6SiO_2$$

$$\text{or } \log k = 0.5 \log \frac{K^+}{H^+} + 3/2 \log SiO_2$$

For Oceans: $H^+ = 10^{-8.1}$

$K^+ = 10^{-2}$

$Na^+ = 10^{-0.33}$

so $\log \frac{K^+}{H^+}$ = approx 6 and $\log \frac{Na^+}{H^+}$ = approx 7.5

Modified from Hess (1966)

or: $\Delta Fr,^{o}t = -RT \ln Qp$

where Qp = equilibrium constant

$$= \frac{[C]^c\ [D]^d}{[A]^a\ [B]^b}$$

for the reaction: $aA + bB \rightleftarrows cC + dD$ (see Garrels and Christ, 1965, p. 10 or p. 352-377)

The Oceanic environment range used by Hess assumes open ocean surface conditions $[H^+] = 10^{-8.1}$; $[K^+] = 10^{-2}$ $[Na^+] = 10^{-.33}$

or: $\log \frac{[K^+]}{[H^+]} \cong 6$ and $\log \frac{[Na^+]}{[H^+]} \cong 7.5$

or the environment of a particle sinking through sea water. Work by Wilde (1966) (See Table VI-3) indicates that the pH of intersitial waters of deep-sea sediments is lower than surface waters or even bottom waters at the sediment sea water interface. Thus the values of $\log \frac{[K^+]}{[H^+]} \cong 5$ and $\log \frac{[Na^+]}{[H^+]} \cong 6.5$ probably are more realistic for sediment reactions. This suggests two stability fields in the marine environment (1) in the water column where sea water is in excess and (2) in the bottom where sediments are in excess. The stability field for the bottom environment is shifted (see Figure VI-1 Figure 5 and 9) more towards the kaolinite-Montmorillonite-Phillipsite fields and definitely out of the feldspar field. Thus for a silicate buffer mechanism the resultant products in any equilibrium equation are restricted to kaolinite or mica, montmorillonite, phillipsite in order of increasing SiO_2 content. In the fluid ocean mica is probably stable with respect to mica so clays stripped of their scavange K from sea water while settling to the bottom.

However, once a mineral particle was incorporated into bottom sediments where the interstitial pH was lower kaolinite and montmorillonite would be stable, the considerable uncertainties of the stability field boundaries are

Table VI-3

Sediment pH

Sediment Type	Glacio-Marine	Green Mud	Diatom Ooze	Foram Ooze	Red Clay
Natural Conditions	7.1-7.8 (Lisitzin, 1960)	7.2-7.7	6.8-7.5 (Lisitzin)	7.4-7.5 (Lisitzin)	7.1-7.2
Laboratory Conditions*	------	7.0-7.3	7.6	7.7-7.6	7.3-7.4
Percentage of Sea Floor	>1	18	9	35	28

* pH of starting water 7.9-8.3 25°C 1 atm

shown in Figure VI-2.

Clay mineral reactivities in sea water was first studied in a comprehensive manner by Carroll and Starkey (1959). They examined not only the pH effect (Table VI-4a) but also the cation exchange capacities (Table VI-5) and the release of silica, alumina, and ferric iron (Table VI-4b) into sea water. Figure VI-3 shows their data on titration of 2% clay suspensions with sea water to a pH of 7.6. This gives the order of pH clay buffer capacity as kaolin, illite, halloysite, mixed layer, and montmontmorillonite; and demonstrates the acid capacity of the clays. The cation-exchange abilities in sea water as shown in Figure VI-4. The removal quality of silica and alumina was nontnorillonite > mixed layer > illite > kaolinite > halloysite.

Figure VI-5 shows some experimental values obtained by MacKenzie and others (1967) by reacting various land derived sediments with sea water (1) undersaturated with respect to silica (0.03 ppm). They found that clay minerals release silica in the silica deficient water and abstract silica in the form of alumino-silicates in enriched waters. The silica abstraction process involved cations as the same experiment was run using distilled water plus silica instead of sea water, with little uptake of silica from solution.

Proposed Silicate Buffer Models

Garrels (1965) investigated a simplified silicate-carbonate weathering model and its ability to buffer the ocean. The reactions used by Garrels were:

a. Carbonate weathering $CaCO_3\text{(calcite)} + H_2O_{liq} + CO_{2\ gas} \rightleftarrows Ca^{++}_{(aq)} + 2HCO_3^{-}{}_{(aq)}$

b. Silicate weathering

Figure VI-2

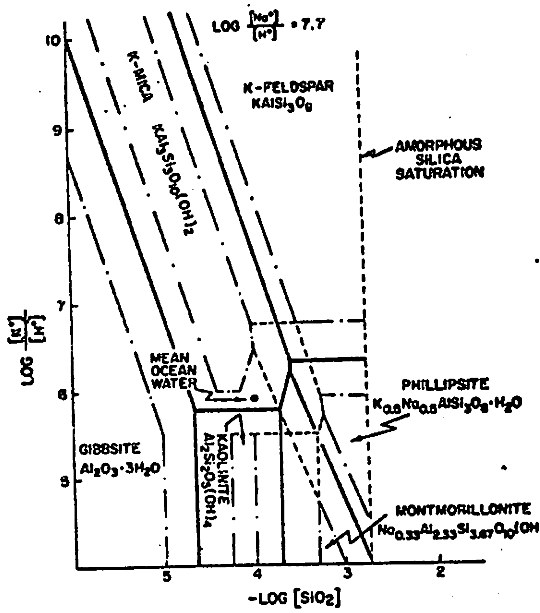

FIG. 2.—Preliminary stability relations in the system $K_2O-N_2O-Al_2O_3-SiO_2-H_2O$ at 25°C. as a function of K^+, Na^+, and H^+, and dissolved silica. Diagram drawn for log Na^+/H^+ equal to that of average ocean water (7.7). Note that stability of phillipsite with respect to K-mica requires higher SiO_2 concentration, or cation ratio. Solid lines, phase boundaries as determined from thermochemical, solubility, or natural association data; dash—dot lines, maximum deviation of boundaries due to uncertainty of presently available data.

From: MacKenzie and Garrels (1965, p. 1082)

Table VI-4

Table 1.—pH of the Experimental Clay Minerals under Various Conditions (1 : 5 clay : water suspensions)

Mineral	Natural Conditions	After Soaking in 50 ml. Sea-water for 10 days	H-form (a)[1]	H-form (a) after Soaking in 50 ml. Sea-water for 10 days
Montmorillonite (A)	8.70	9.22	2.90	5.88
Mixed-layer Mineral (B)	4.50	9.18	3.25	5.87
" Illite " (C)[2]	8.50	9.18	6.80	9.00
Kaolinite (D)	5.18	8.32	5.05	8.35
Halloysite (E)	4.65	8.01	4.70	2.71

[1] Prepared by treatment with H-ion exchange resin.

[2] Contains about 2 percent calcite as impurity.

Table 2.—Silica, Alumina and Ferric Iron Yielded by 10 Samples of Clay Minerals on Soaking in 50 ml Sea-water for 10 and 150 Days[1]

Mineral	SiO_2 (mg)	Al_2O_3 (mg)	Fe_2O_3 (mg)	Total (mg)	Percentage of Mineral
Montmorillonite (A)					
10 days	4.0	<1.0	0.3	5.3	0.53
150 days[2]	5.2	2.5	1.4	9.1	0.91
Mixed-layer Mineral (B)					
10 days	1.0	1.0	0.2	2.2	0.22
150 days[2]	3.6	1.4	0.1	5.1	0.51
" Illite " (C)					
10 days	2.0	6.0	0.3	8.3	0.83
150 days[2]	0.5	0.1	<0.002	0.602	0.06
Kaolinite (D)					
10 days	1.0	4.0	0.1	5.1	0.51
Halloysite (E)					
10 days	1.0	1.0	—	2.0	0.20

(Analyst : Leonard Shapiro)

[1] The sea-water was removed from the clay minerals by centrifugation.

[2] The H-form (a) of the mineral was used except for "illite" (C), 150 days where H-form (b) was used.

(These figures are the amounts in the solutions after deduction of the amounts in a sea-water blank. The blank contained SiO_2, 1 mg, Al_2O_3, <1 mg, Fe_2O_3, 0.06mg.)

From: Carroll and Starkey (1959, p. 85)

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Table VI-5

TABLE 3.—EXCHANGEABLE Ca^{2+}, Mg^{2+} AND Na^{+}, TOTAL CATION EXCHANGE CAPACITY AND PERCENT OF EXCHANGE CAPACITY COMPLETED WITH CATIONS OTHER THAN H^{+} OF THE EXPERIMENTAL CLAY MINERALS UNDER VARIOUS CONDITIONS IN SEA-WATER

Mineral	Exchangeable Cations (meq/100 g)				Cation Exchange capacity (determined)	Percentage Exchange Positions Filled
	Ca^{2+}	Mg^{2+}	Na^{+}	Sum		
Montmorillonite (A)						
Natural	11	15	54	80	89	90
Sea-water, 10 days[1]	7	34	16	57	93	61
H-form (a)	8	14	—	22	66	33
Sea-water 10 days[2]	7	27	21	55	91	60
Sea-water 150 days[3]	8	32	21	61	76	80
Mixed-layer Mineral (B)						
Natural	26	7	—	33	33	100
Sea-water 10 days[1]	3	12	2	17	31	55
H-form (a)	3	1	—	4	34	11
Sea-water 10 days[2]	9	8	2	19	21	90
Sea-water 150 days[3]	5	7	5	17	28	61
"Illite" (C)						
Natural	17	3	—	20	20	100
Sea-water 10 days[1]	12	8	—	20	20	100
H-form (a)	10	2	—	12	24	50
Sea-water 10 days[2]	9	8	2	19	21	90
Sea-water 150 days[3]	8	8	—	16	28	57
Kaolinite (D)						
Natural	0.5	0.4	—	0.9	5	18
Sea-water 10 days[1]	0.9	1.7	—	2.6	8	32
H-form (a)	0.9	—	—	0.9	13	7
Sea-water 10 days[3]	1.4	1.7	—	3.1	16	19
Halloysite (E)						
Natural	1.8	1.7	0.6	4.1	11	37
Sea-water 10 days[1]	2.7	7.1	0.5	10.3	47	22
H-form (a)	1.8	0.8	—	2.6	42	6
Sea-water 10 days[2]	4.1	5.4	0.6	10.1	31	32

[1] Natural mineral soaked in 50 ml sea-water.
[2] H-form (a) soaked in 50 ml sea-water.
[3] H-form (b) soaked in 50 ml sea-water.
"Illite" (C) contained about 2 percent calcite as impurity; the figures given above have been corrected for Ca due to calcite.

From: Carroll and Starkey (1959, p. 87)

Figure VI-3

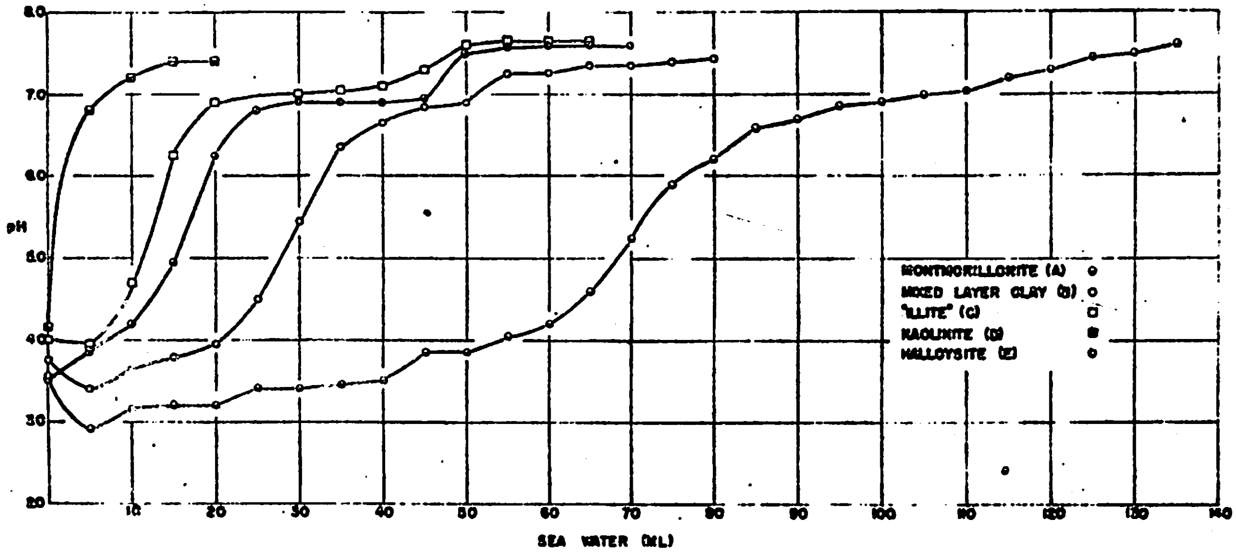


FIGURE 7.—Titration of 2 percent suspensions in distilled water of the H-form (a) of montmorillonite (A), mixed-layer mineral (B), "illite" (C), kaolinite (D), and halloysite (E) with natural sea-water (salinity 35.5‰; chlorinity, 21.5‰; titratable alkalinity, 0.0016; and pH 7.6).

From: Carroll and Starkey (1959, p. 95)

Figure VI-4a

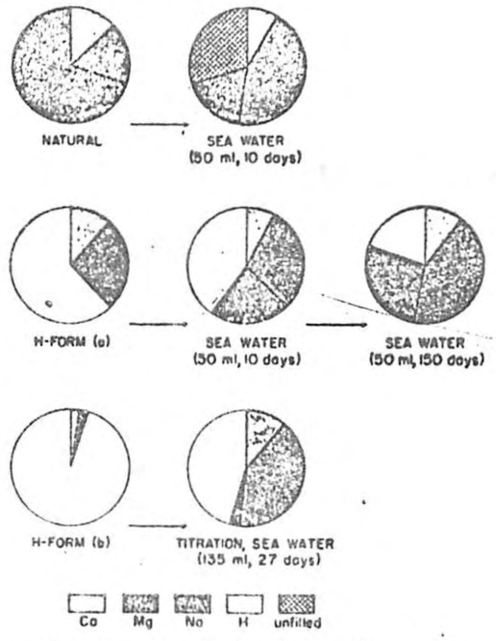


FIGURE 1.—Exchangeable cations in montmorillonite (A) on treatment with sea-water. The diagrams represent the percentage of exchangeable Ca^{2+}, Mg^{2+}, and Na^+ ions as determined (Tables 3 and 4). H^+ ions are assumed to difference from the total exchange capacity of the H-form montmorillonite. The notation " unfilled " for montmorillonite in sea-water indicates that cations did not completely fill the available positions. H-form (a), montmorillonite treated with H-ion exchange resin; H-form (b), montmorillonite treated with HCl (1 + 3) at 25°C.

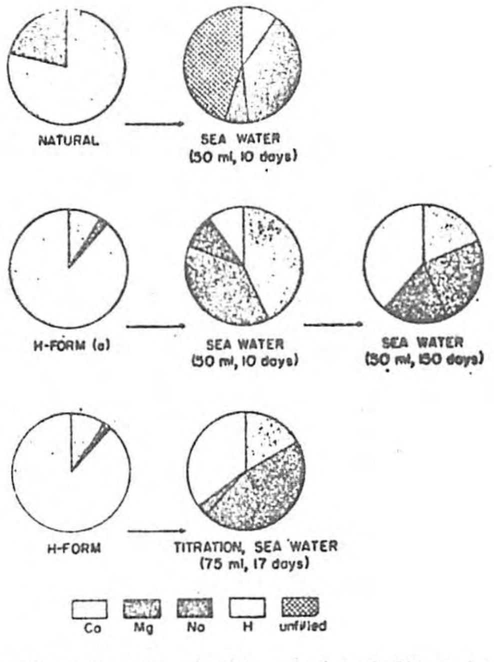


FIGURE 2.—Exchangeable cations in mixed-layer mineral (B) on treatment with sea-water. The diagrams represent the percentage of exchangeable Ca^{2+}, Mg^{2+} and Na^+ ions as determined (Tables 3 and 4). H^+ ions are assumed by difference from the total exchange capacity of the H-form mixed-layer mineral. The notation " unfilled " for mixed-layer mineral in sea-water indicates that cations did not completely fill the available exchange positions. H-form (a), mixed-layer mineral treated with H-ion exchange resin; H-form (b), mixed-layer mineral treated with HCl (1 + 3) at 25°C.

From: Carroll and Starkey (1959, p. 88-89)

Figure VI-4b

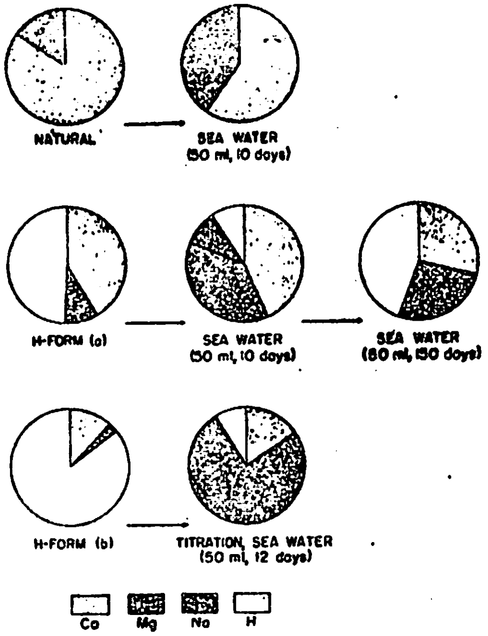


FIGURE 3.—Exchangeable cations in "illite" (C) on treatment with sea-water. The diagrams represent the percentage of exchangeable Ca^{2+}, Mg^{2+} and Na^{+} ions as determined (Tables 3 and 4). H^{+} ions are assumed by difference from the total exchange capacity of the H-form "illite". H-form (a), "illite" treated with H-ion exchange resin; H-form (b), "illite" treated with HCl (1 + 3) at 25°C.

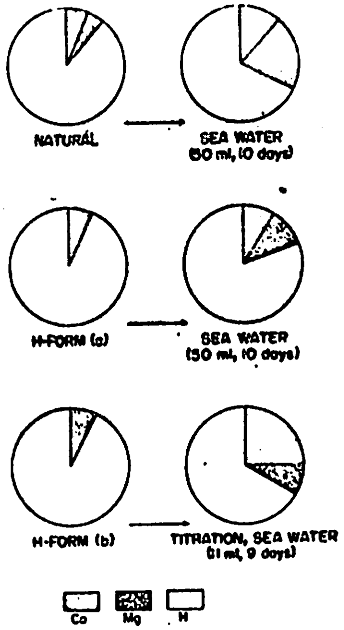
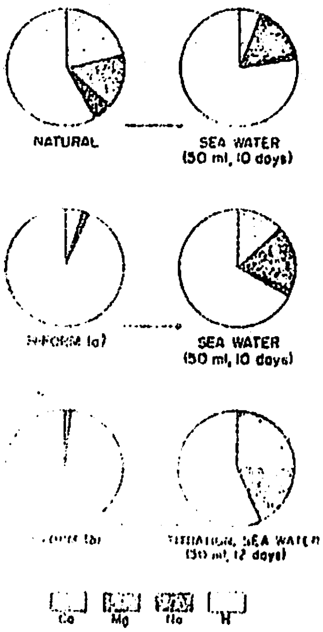


FIGURE 4.—Exchangeable cations in kaolinite (D) on treatment with sea-water. The diagrams represent the percentage of exchangeable Ca^{2+} and Mg^{2+} ions as determined (Tables 3 and 4). It is assumed that H^{+} ions are present in the natural mineral as the pH is low. H-form (a), kaolinite treated with H-ion exchange resin; H-form (b), kaolinite treated with HCl (1 + 3) at 25°C.

From: Carroll and Starkey (1959, p. 90-91)

Figure VI-4c



[illegible] in halloysite (E) on treatment with sea-water. The [illegible] the percentage of exchangeable Ca^{2+}, Mg^{2+} and Na^+ as deter- [illegible] It is assumed that H^+ ions are present in the natural [illegible] H form (a), halloysite treated with H-ion exchange resin; H form (b), halloysite treated with HCl (1 + 3) at 25°C.

From Carroll and Starkey (1959, p. 92)

Figure VI-5

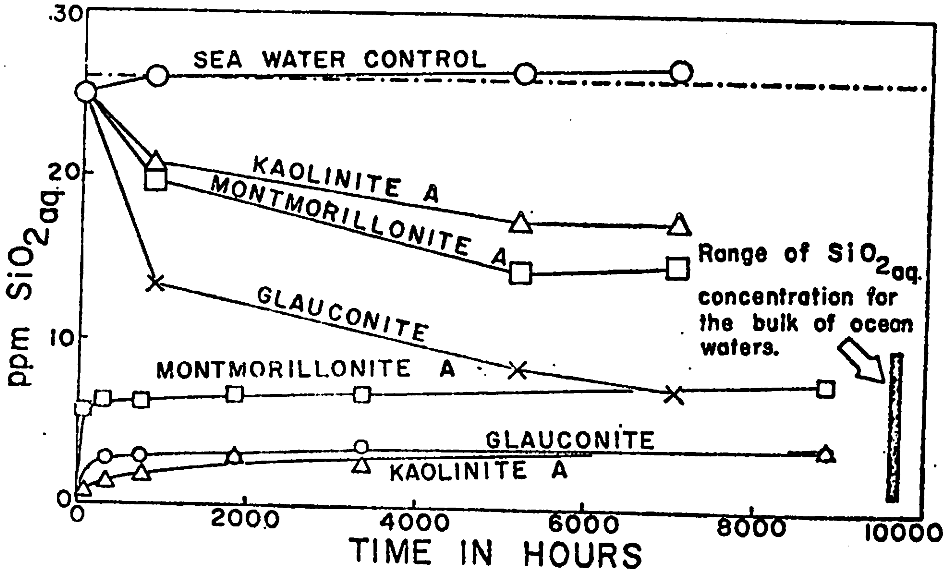


Fig. 1. Concentration of dissolved silica as a function of time for suspensions of silicate minerals in sea water. Curves are for 1-g (< 62 μ) mineral samples in 200 ml of silica-deficient (SiO_2 in water was initially 0.03 ppm) and silica-enriched (SiO_2 was initially 25 ppm) sea water at room temperature. Size of symbols indicates precision of SiO_2 determinations. Dash-dot line shows minimum SiO_2 concentration of sea water in equilibrium with a hydroxylated magnesium silicate at the pH's of our experiments.

From: Garrels and MacKenzie (1967, p. 1404)

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$$2NaAlSi_3O_8 \text{ (albite feldspar)} + 3H_2O_{\,liq} + 2\ CO_{2\ gas} \rightleftarrows$$

$$2Na^{++}_{(aq)} + 2HCO_3^{-}{}_{(aq)} + Al_2Si_2O_5(OH)_4 \text{ Kaolinite} + 4\ SiO_{2\ (aq)}$$

the complete silicate weathering may be subdivided further by addition of intermediate phases between feldspar and kaolinite.

I. $3\ KAlSi_3O_8 \text{ (K-spar)} + 2H^+ \rightleftarrows \underset{\text{illite-mica}}{KAl_2(Si_3AlO_{10})(OH)_2} + 2K^+ + 6SiO_2$

IIa. $2KAl_2(Si_3AlO_{10})(OH)_4 + 2H^+ + 3H_2O \rightleftarrows \underset{\text{Kaolinite}}{3Al_2(Si_2O_5)(OH)_4} + 2K^+$

Reactions I → IIa shows (1) a rise in pH, (2) addition of SiO_2 to the fluid phase, and (3) an intermediate partition of K in the illite phase.

II b. $\underset{\text{illite}}{7KAl_2}\ (Si_3AlO_{10})(OH)_2 + 3Na^+ + 7H^+ + 12SiO_2 \rightleftarrows$

$$\underset{\text{Na-Montmorillonite}}{9Na_{0.33}Al_2(Si_{3.67}Al_{0.38}O_{10})}\ (OH)_2 + H^+ + 3.5\ H_2O$$

IIIb. $3\ \underset{\text{Na-Montmorillonite}}{Na_{0.33}Al_2(Si_{3.67}Al_{0.33}O_{10})(OH)_2} + H^+ + 3.5H_2O \rightleftarrows$

$$3.5\ \underset{\text{Kaolinite}}{Al_2(Si_2O_5)(OH)_4} + 4SiO_2 + Na^+$$

reactions I → IIb → IIIb also shows (1) a rise in pH, (2) addition of SiO_2, (3) but besides intermediate partition of K^+ in illite, the reaction shows (4) an intermediate abstraction of SiO_2 in the montmorillonite.

Garrels noted that probably the reaction feldspar → kaolinite does not go to completion in the marine environment as (1) the ocean is only slightly alkaline (2) the amount of silica (aq) in sea water is less than saturation with amorphous silica but the amount of chert (solid SiO_2) also is small compared to the amount expected by the weathering of feldspars.

The silicates introduced into the oceans obviously are not just feldspars but consist of various clays and micas in various amounts. In fact feldspars are usually just a small fraction of the total suspended and bed load introduced into sea water. Figure VI-6 shows the distribution of minerals in the suspended load for the tropical Amazon, the largest river in the world. Thus the intermediate phases in Garrels' weathering reactions are already present in sea water. Garrels (1965) concluded that the deficiency of silica both in sea water and as pure silica sediments means that the silica back reacts in sea water with the intermediate silicate phases produced by the weathering process forming or upgrading montmorillonite-illite-phillipsite. The partial completion of the weathering reaction and back reactions would also fix the pH and the amounts of alkali cations in sea water. In summary relatively unweathered silicates introduced into sea water would react producing intermediate silicate phases resulting in the reduction of K^+ and increase in the pH. The weathering silicates introduced into sea water would back react also producing intermediate phases releasing H^+ to sea water lowering the pH. The net effect would be intermediate silicate phases stable monitoring pH, Na, K, Al, and silica in sea water. Also the supply of weathering clays such as kaolinite added to sea water as erosion products which reach the bottom where they are stable represent "fixed acid" which acts as a supply of hydrogen ions for back reactions to keep the oceans from becoming too alkaline.

Pytkowicz (1967) questioned the Garrels weathered silicate model and calculated the equipment capacities of carbonate in the water column. Pytkowicz's fluxes are shown in Figure VI-7 as $mgCO_2/cm^2/1000$ years. He pointed out the discrepancy between equivalents of carbonate (2.3m EQ/liter) versus suspended matter-silicates (0.1m EQ/liter assuming 10 mg clay/liter where 10 mg clay = 0.1 mgH^+) in the sea water column. However potential distrubances of the chemical balance of sea water are added chiefly at the boundaries of the ocean

Figure VI-6

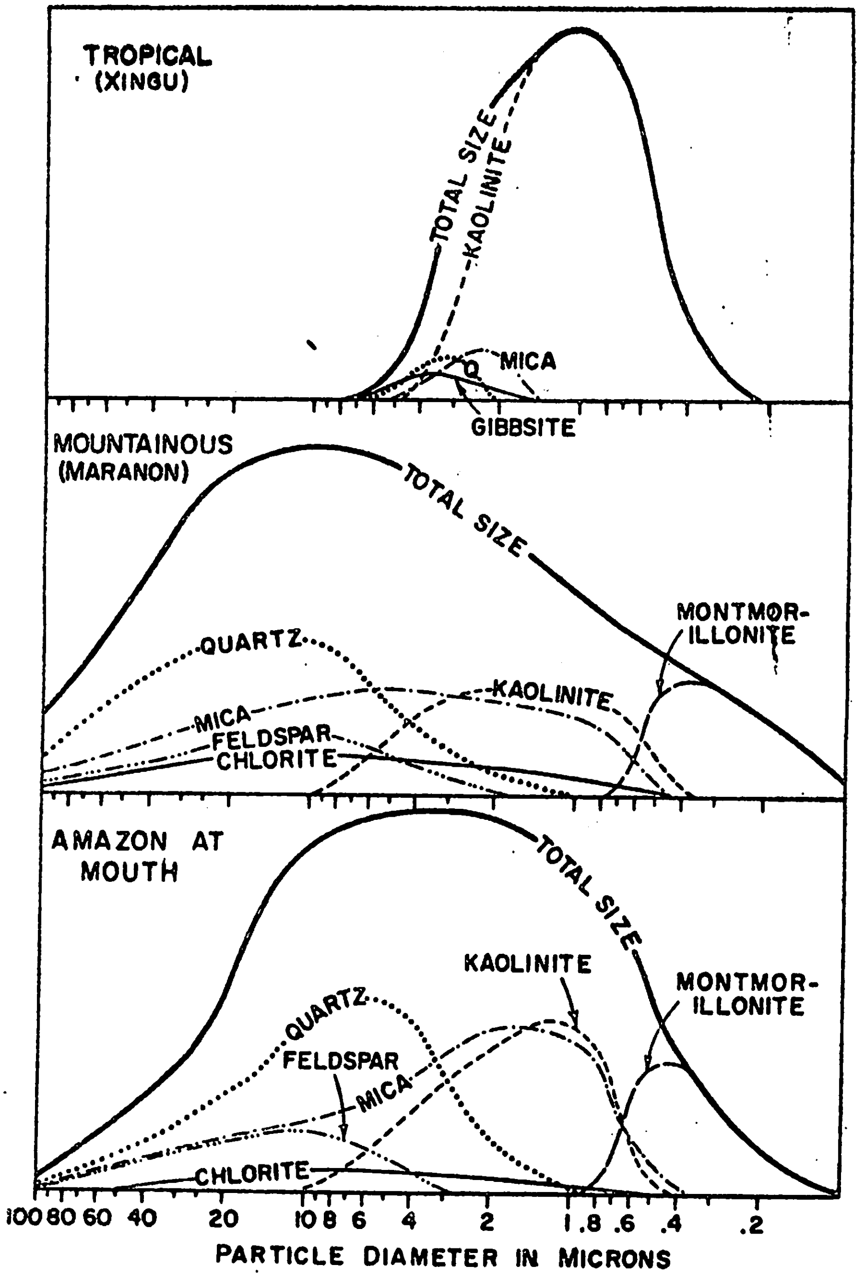

Figure 14. Size and mineralogic frequency distribution of the suspended solids of a tropical and of a mountainous environment tributary and of the Amazon

From: Gibbs (1967, p. 1224)

(the bottom for release of volatiles or the continental margins for erosion products) so reactions at the boundaries probably are more important than in the water column as buffer reactions.

MacKenzie and Garrels (1967) investigated this approach and found (see Figure VI-8) for a steady-state sea water composition that there is a surplus of HCO_3^- to Ca^{++} added by rivers with respect to that in sea water:

$$\frac{\text{Rivers:}}{\text{Year}} \quad \frac{[HCO_3^-]}{[Ca^{++}]} = \frac{3.1 \times 10^{13} M}{1.22 \times 10^{13} M} \sim 3$$

$$\text{Oceans:} \quad \frac{[HCO_3^-]}{[Ca^{++}]} \quad \frac{3.1 \times 10^{18} M}{1.5 \times 10^{19} M} \quad \sim 0.2$$

ignoring volatile contributions of $[Ca^{++}]$ if all Ca^{++} was precipated as $CaCO_3$ (aragonite)

$$\begin{array}{ccccc} [Ca^{++}] + & 2\,[HCO_3^-] \overset{x10^{13}}{\rightleftarrows} & CaCO_3\downarrow & + CO_2\uparrow & + H_2O \\ 1.22M & 2.44M & 1.22M & 1.22M & 1.22M \end{array}$$

$(3.1 \times 10^{13})-(2.44 \times 10^{13})$ or $0.7M \times 10^{13}$ HCO_3^- is still left over.

If all aqueous SiO_2 is in the form of H_4SiO_4 or

$$\begin{array}{cccc} SiO_2 + & 2H_2O & \overset{x10^{13}}{\rightleftarrows} & H_4SiO_4 \\ .7M & 1.4M & \rightleftarrows & .7M \end{array}$$

the $.7M \times 10^{13}$ excess HCO_3^- may be reacted with H_4SiO_4 to eliminate the excess carbonate by converting it to CO_2 so it may be recycled through the atmosphere.

$$\begin{array}{cccccc} H_4SiO_4 + & HCO_3^- & \overset{x10^{13}}{\rightleftarrows} & H_3SiO_4^- & + CO_2\uparrow & + H_2O \\ .7M & .7M & & .7M & .7M & .7M \end{array}$$

The erosion products from the land are not exclusively in the form of dissolved solids as 3.25×10^{16} grams of suspended matter chiefly x-ray amorphous aluminosilicates are added annually (Kuenan, 1950) this would be equivalent to $3.25 \times 10^{14} M\ H^+$.

Mac Kenzie and Garrels (1966) think that the combination of $H_3SiO_4^-$, produced

Figure VI-7

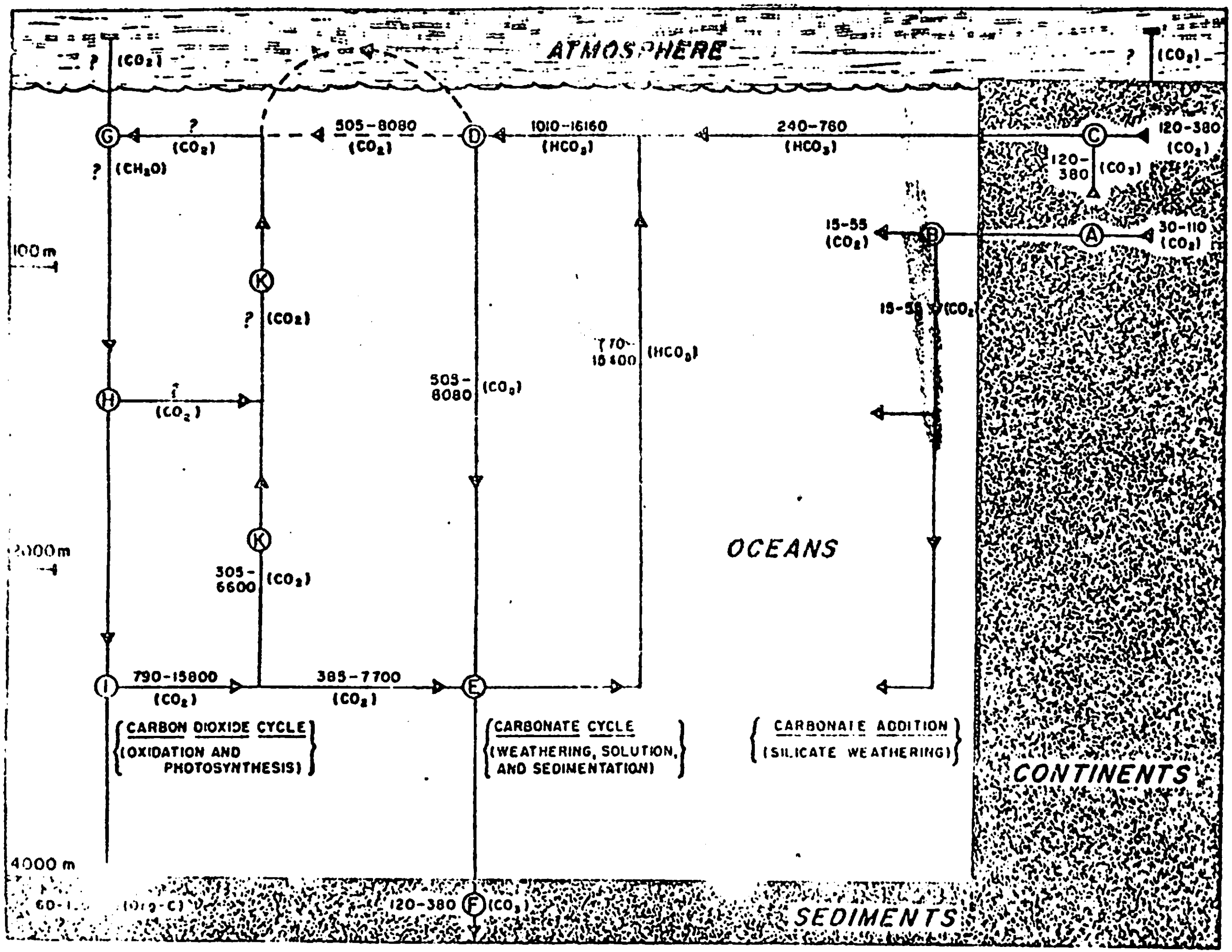

Fig. 1. Carbonate and carbon dioxide cycles in the recent oceans. The fluxes of the actual constituents, which are indicated in parenthesis, are presented as mg $CO_2/cm^2/1000$ yr. Ranges in weathering and sedimentation fluxes indicate uncertainties in rates. Ranges elsewhere result from different values assumed for the residence times of the waters. The number of significant figures used is necessary for material balance and does not represent a degree of certainty for the fluxes.

From: Pytkowicz (1966, p. 64)

Figure VI-8

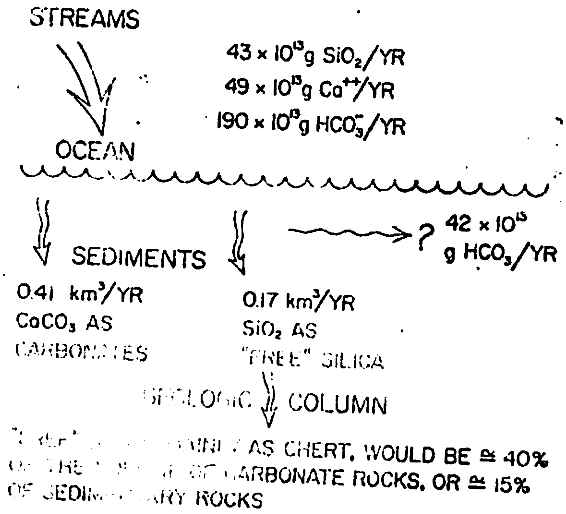

FIG. 1.—Silica—bicarbonate balance assuming present stream discharge and content, and all Ca^{++} deposited as carbonate minerals.

TABLE 3.—*Number of times river constituents have "passed through" the ocean in 10^8 years assuming present annual world-wide river discharge, mean dissolved constituent concentration of rivers and ocean, and ocean volume of 1.37×10^{21} liters*

Constituent	Amount delivered by rivers to the ocean annually	Amount in ocean	Amount delivered by rivers to ocean in 10^8 years	Number of times constituents have been "renewed" in 10^8 years
SiO_2	42.6×10^{10} kg	0.008×10^{18} kg	42.6×10^{18} kg	5300
HCO_3^-	190.2×10^{10} kg	0.19×10^{18} kg	190.2×10^{18} kg	1000
Ca^{++}	48.8×10^{10} kg	0.6×10^{18} kg	48.8×10^{18} kg	81
K^+	7.4×10^{10} kg	0.5×10^{18} kg	7.4×10^{18} kg	15
SO_4^-	36.7×10^{10} kg	3.7×10^{18} kg	36.7×10^{18} kg	10
Mg^{++}	13.3×10^{10} kg	1.9×10^{18} kg	13.3×10^{18} kg	7
Na^+	20.7×10^{10} kg	14.4×10^{18} kg	20.7×10^{18} kg	1.4
Cl^-	25.4×10^{10} kg	26.1×10^{18} kg	25.4×10^{18} kg	1
H_2O	$3,333,000 \times 10^{10}$ kg	1370×10^{18} kg	$3,333,000 \times 10^{18}$ kg	2430

From: MacKenzie and Garrels (1966, p. 1077) by elimination of excess carbonate ions from rivers, and the aluminosilicates from suspended river load plus cations would produce

A. plus $K^+ \rightarrow$ illite

B. plus $Na^+ \rightarrow$ sodium montmorillonite

C. plus $Mg^{++} \rightarrow$ chlorite

It is unlikely that pure phases would result from these reactions as the cations occur simutaneously in sea water but that mixed layer clays would form. This view is born out by the occurrence of mixed layer clays as the major portion of recent marine sediments.

Thus although the dissolved content of Si and Al do not have the equipment capacity of dissolved carbonates, if the suspended load of rivers is included in the mass balance then the alumino silicates have 100 x the capacity of carbonates plus the additional mineralogical ability to buffer the cations of sea water.

NOTE: The following is copied directly from notes used by Prof. Sillen at the 1966 Gordon Conference and are given unedited.

EQUILIBRIUM MODEL

Components in sediments, ocean, plus air are allowed to reach equilibrium (except N_2)

1. System HCl-H_2O-SiO_2-$Al(OH)_3$-KOH-: C = 5 (simplified ocean model K & pH stat.

Four Phases P = 4: Aqueous solution + $SiO_2(s)$ + Kaolinite ($Al_2Si_2O_5(OH)_4$ +

K-mica ($KAl_2Si_3AlO_{10}(OH)_2$

Variables p, T, $[K^+]$, $[H^+]$, $[Cl^-]$, $[Al_{aq}]$, $[SiOH_4]_{aq}$

F = 5 + 2-4 = 3 = p.T, $[Cl^-]$ after the values for these have been chosen, then the concentrations of K^+, H^+, etc. are fixed by the equilibrium conditions.

This can also be seen as follows.

The equilibrium law given for the reaction:

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$$1.5\ Al_2Si_2O_5(OH)_{4(s)} + K^+ \rightleftarrows KAl_2Si_3AlO_{10}(OH)_{2(s)} + 1.5\ H_2O + H^+ \qquad (A)$$

$$K = [H^+] / [K^+] \approx 10^{-6.4}\ (25^o) \qquad (B)$$

and the charge condition is

$$[K^+] + [H^+] = [Cl^-] + K_w/[H^+] \qquad (C)$$

The equilibrium constants, K and K_w are uniquely determined by p and T. There are then two equations (B) and (C) between the three unknown variables, $[H^+]$, $[K^+]$, and $[Cl^-]$ hence two are fixed after the third has been chosen. $[Si(OH)_4]$ is fixed by the presence of $SiO_{2(s)}$. The equilibrium composition of the solution is independant of the amounts of components present in solids, as long as all three solids phases exist.

2. Eight components: $HCl-H_2O-SiO_2-Al(OH)_2-$ NaOH-KOH- MgO-CaO

(intermediate ocean model)

Assume large excess of solids, and search maximum number of phases, with three degrees of freedom (F = 3): p, T, and $[Cl^-]$; only for singular values of these variables, still more phases might exist at equilibrium. For all other variables to be fixed, we would have P = C + 2-F = 8 + 2-3 = 7

<u>Working Hypothesis</u>: In the intermediate ocean model, the seven stable phases are: 1. Aqueous solution (composition close to sea water), 2. Quartz (SiO_2), 3. Kaolinite ($Al_2Si_2O_5(OH)_4$, 4. Chlorite (mostly Mg), 5. Illite K and some Mg, 6. Montmorillonite (Na, Mg, some Ca and K, composition ≈ Si), 7. Phillipsite (Ca and other cations).

Desirable: Analyses of single phases. Equilibrium studies in mixed systems. Note that detrital minerals may be better defined than such particles as are more or less equilibrated with the solution.

3. "Complete Ocean Model"

Add CO_2 and two new phases: A gas phase, and $CaCO_{3(s)}$. We now have

C = 9, P = 9, F = 2: T and [Cl^-], whereas $p(CO_2)$ is determined by equilibria. If a new component is added to the mixture (to make it approach to a "complete" ocean model) we get either a new degree of freedom (concentration variable to be chosen arbitarily), or a new phase. Add N_2: $p(N_2)$ is a new variable. Add SO_3: [$SO_2^=$] is the new variable. Add BaO: $BaSO_{4(s)}$ is new phase. Add FeO and Fe_2O_3: two new solid phases, tentatively FeOoH and glauconite.

Helegeson and MacKenzie (1970) have proposed an expanded Sillen model but noted the following exceptions:

1. The chemical potential of SiO_2 in sea water is not fixed
2. $CaCO_3$ and the atmosphere are not in equilibrium
3. The various silicates phases probably are not in equilibrium
4. Temperature and pressure in the ocean should be independent variables.

The components of their model is given in Table VI-6. The phase diagrams for 0°C and 25°C at one atmosphere are given in Figure 9 and 10 respectively. According to their model microcline (potassium feldspar - K $AlSi_3O_8$) and mixed layer illite-montmorillonite or kaolinite would be stable in sea water. The clay phase data seems reasonable as mixed layer clays are common on the sea floor. However, feldspars are not common minerals in the true ocean. Possibly their rate of formation is so slow that available ions are taken up by clay structures before completion of the microcline reactions.

Table VI-6

Table 1. Alternate sets of thermodynamic components for models of the ocean system.

Set No.	*Oxides*	*Hydroxides*	*Chlorides*
1 (Sillén, 1961)	MgO, CaO, H_2O, CO_2, SiO_2	KOH, $NaOH$, $Al(OH)_3$	HCl
2	K_2O, Na_2O, CaO, MgO, Al_2O_3, SiO_2, H_2O, CO_2		HCl
3	SiO_2, H_2O, CO_2	KOH, $NaOH$, $Ca(OH)_2$, $Mg(OH)_2$, $Al(OH)_3$	HCl
4	Al_2O_3, SiO_2, H_2O, CO_2		HCl, $NaCl$, KCl, $MgCl_2$, $CaCl_2$

*Table 2. Computed molalities and activities of the more abundant ions in sea water.**

Ion	0°C *and* 1000 *atm.* (pH = 7·7)		25°C *and* 1 *atm.* (pH = 8·15)	
	Log activity	*Log molality*	*Log activity*	*Log molality*
Cl^-	− 0·46	− 0·26	− 0·46	− 0·26
Na^+	− 0·49	− 0·33	− 0·50	− 0·33
Mg^{2+}	− 1·77	− 1·27	− 1·79	− 1·29
K^+	− 2·20	− 2·00	− 2·21	− 2·00
Ca^{2+}	− 2·62	− 2·01	− 2·63	− 2·02

*Calculated from dissociation constants and activity coefficients by LAFON (1969) using analytical concentrations reported by GOLDBERG (1965). The calculations include provision for the effects of temperature, pressure, and the following complexes in sea water: $CaSO_4$, $NaSO_4^-$, KSO_4^-, $CaCO_3$, $CaHCO_3^+$, $NaHCO_3$, $MgCO_3$, $MgHCO_3^+$.

From: Helegon and MacKenzie (1970, p. 886)

Figure VI-9

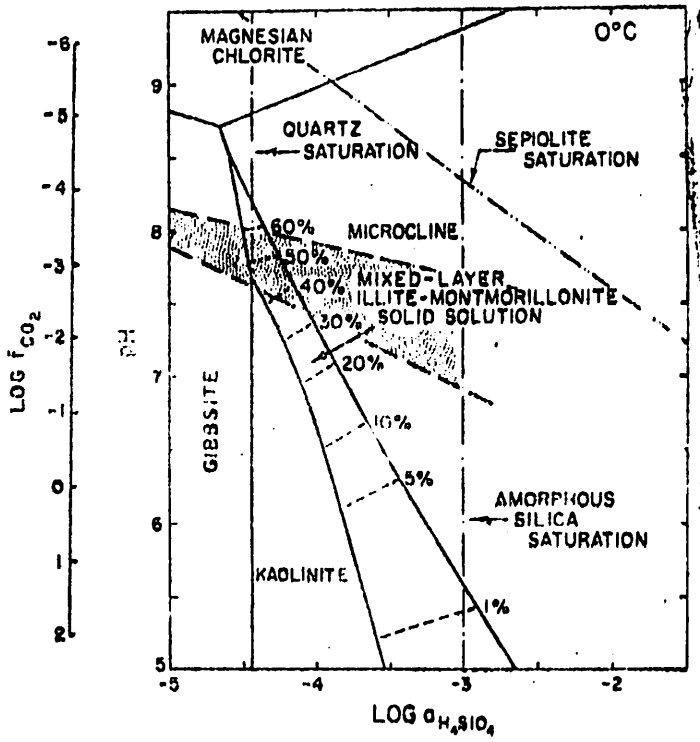

Fig. 3. Logarithmic activity diagram depicting equilibrium phase relations among aluminosilicates and sea water in an idealized nine component model (Table 1) of the ocean system at 0°C, one atmosphere, and unit activity of H_2O—see text. The activities of Na^+, K^+, Ca^{2+}, and Mg^{2+} used in constructing the diagrams are shown in Table 2. The stippled area represents the compositional range of sea water at this temperature, and the dot-dash lines indicate the composition of sea water saturated with quartz, amorphous silica, and sepiolite, respectively. The scale to the left of the diagram refers to calcite saturation for different fugacities of CO_2. The dashed contours designate the composition (in per cent illite) of the mixed-layer illite-montmorillonite solid solution in equilibrium with sea water. The data and methods used in calculating the positions of the field boundaries in the diagram are discussed in the text.

From: Helegeson and MacKenzie (1970, 888)

Figure VI-10

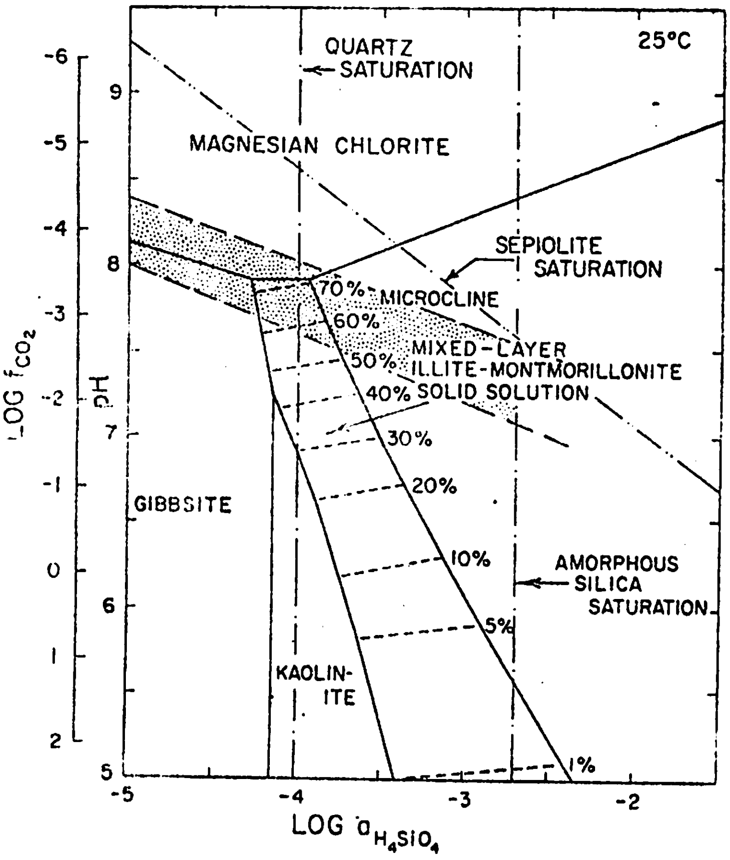

Fig. 2. Logarithmic activity diagram depicting equilibrium phase relations among aluminosilicates and sea water in an idealized nine component model (Table [illegible]) of the ocean system at 25°C, one atmosphere, and unit activity of H_2O—see text. The activities of Na^+, K^+, Ca^{2+}, and Mg^{2+} used in constructing the diagrams are shown in Table 2. The stippled area represents the compositional range of sea water at this temperature, and the dot-dash lines indicate the composition of sea water saturated with quartz, amorphous silica, and sepiolite, respectively. The scale to the left of the diagram refers to calcite saturation for different fugacities of CO_2. The dashed contours designate the composition (in per cent illite) of a mixed-layer illite-montmorillonite solid solution phase in equilibrium with sea water. The data and methods used in calculating the positions of the field boundaries in the diagram are discussed in the text.

From: Helegeson and MacKenzie (1970, p. 886)

Summary

The sophistication of the silicate inorganic buffer models has reached a high level. However, as noted in the disucssion of the carbonate-borate buffer systems, the actual test of the validity of the silicate buffer is still sometime off because of the problems of (1) rates of reactions and (2) how to quantify the biological-inorganic interactions.

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Organic Modification of Sea Water Chemistry

The variety of life in the sea ranges widely in both size and complexity to tiny simple bacteria to gigantic whales the largest living thing. However, unicellular organisms make up the bulk of the living matter of the sea. The plant kingdom, unlike the animal kingdom is restricted to simple organism on the evolutionary scale and away from shallow water where multicellular algae grow only unicellular phytoplankton exist. Phytoplankton, contrasted with land plants which are chiefly carbohydrates are enriched in protein (see Table VII-1) and thus are an attractive source of food.

Living phytoplankton are restricted to the zone of light which varies from a maximum of about 100 meters in clear tropical waters to nearly zero in turbid waters. If the phytoplankton escape being eaten by other organisms and the plant dies because of the lack of nutrients or some other change in the environment the dead organic matter is usually extracted before the dead organism settles to the bottom.

Table VII-1

Organic Composition of Unicellular Algae

Protein	41-53%
Carbohydrate	26-38%
Lipid	20-27%

From: Ketchum and Redfield (1949)

The bulk of organic matter is continually cycled through various organisms in what is called the food chain or food web. Figure VII-1 depicts the food web as conceived by Strickland (1965). As this matter essentially remains in the living world it has little direct effect on the long term composition of sea water and thus is more the concern of biological oceanology than chemical oceanology per se.

Certain seasonal links in the food web however do distrub the short term and regional chemistry of sea water. Figure VII-2 shows the lag in growth of zooplankton to that of phytoplankton in the English Channel. In seasons of plankton blooms the zooplankton to the extent that most of the organic matter is only partially digested by the zooplankton and passes through their bodies and released to sea water as faecal pellets (Harvey, 1963, p. 24) eventually the organic matter in the pellets is utilized by bottom dwelling organisms such as bacteria and worms but during periods of zooplankton blooms much organic matter is withdrawn from sea water and placed in the bottom short circuiting the normal food chain.

Of primary concern to chemical oceanology, however, is the non-living organic fraction which includes organic Detritus-tripton, and dissolved organically derived decay products.

By convention organic matter in sea water which passes a 0.4μ filter is designated dissolved or free organic matter. Extractable organic matter trapped by a 0.4μ filter is considered particulate organic matter.

It can be calculated from Duursma (1960) that ocean water contains about 2.4 kg/m^2 dissolved organic material, and according to Parsons and Strickland (1962) sea water contains 500 g/m^2 of particulate organic material, of which considerably less than one-tenth is living. Thus, the total non-living organic content of sea water if fifty times larger than the living portion. That such large quantities of dissolved organic matter exist in a state seemingly no longer available to many of the living forms inhabiting this environment has long puzzled marine researchers.

Four principal types of organic material are recognized in sea water:

1. Non-nitrogenous - carbohydrates and sugars
2. Nitrogenous - proteins and amino acids
3. Fatty acids - lipids
4. "Gelbstoffe" - humic acids?

Table VII-2 lists analyses of organic matter in sea water.

Table VII-3 shows the partition of suspended matter into organic and inorganic fractions.

In general the amount of particulate organic matter decreases with depth probably due to the ability of bacteria to accumulate on a particle in sufficient numbers to reduce it given enough time as the particle slowly sinks to the bottom.

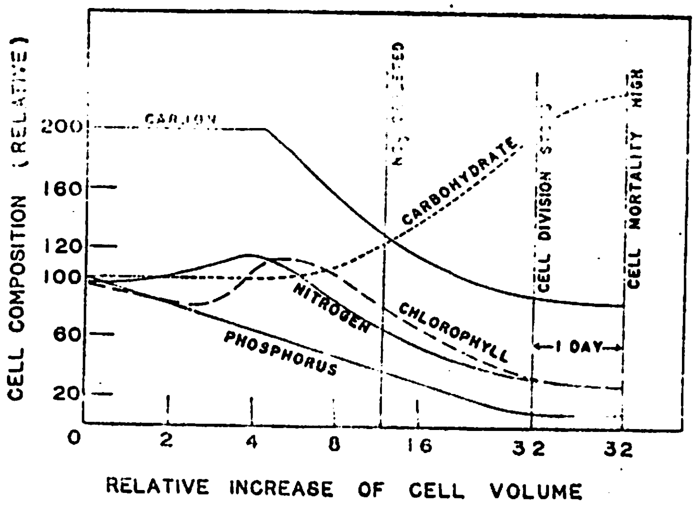


FIG. 3. Relative changes of cell composition of phytoplankton owing to nitrate and phosphorus depletion in sea water.

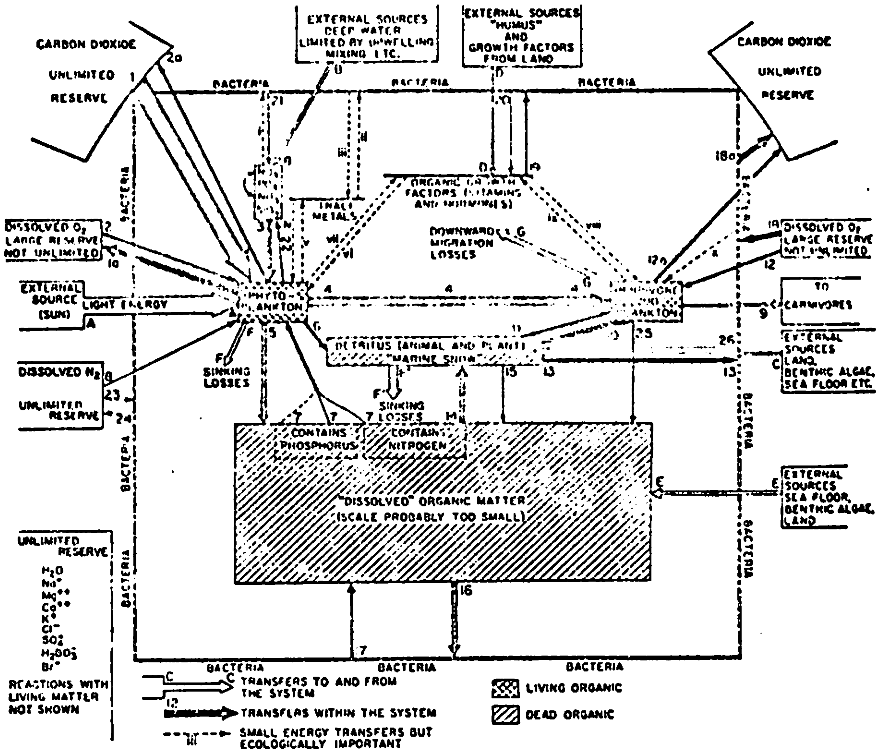


FIG. 5. Chart of idealized food-web in the early stages.

From: Strickland (1965, p. 550 top and 594 bottom)

Figure VII-2

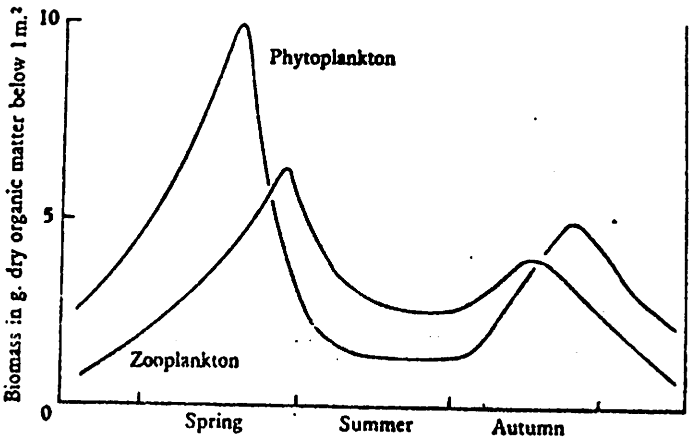


FIG. 12. Change in biomass of phytoplankton and zooplankton below unit area, throughout the seasons, derived from observations in the English Channel, 4 miles offshore.

From: Harvey, (1966, p. 26)

Table VII-2

Specific dissolved organic compounds identified in sea water

Name of compound and chemical formula	*Concentration*				*Author(s)*	*Locality*
	I. Carbohydrates					
Pentoses $C_5H_{10}O_5$	0–8 mg./l.				Collier *et al.* (1950, 1956)	Gulf of Mexico
Pentoses $C_5H_{10}O_5$	0·5 µg./l.				Degens *et al.* (1961)	Pacific off California
Hexoses	14–36 µg./l.				Degens *et al.* (1964)	Pacific off California
Rhamnosides $C_6H_{12}O_5$	0·1–0·4 mg./l.				Lewis and Rakestraw (1955)	Pacific Ocean coast U.S.A.
Rhamnosides						
Dehydroascorbic acid  $\overset{\frown O \frown}{COCOCO}CHCH(OH)CH_2OH$	0·1 mg./l.				Wangersky (1952)	Gulf of Mexico inshore water
	II. Proteins and their derivatives					
Peptides C/N ratio = 13·8:1					Jeffrey and Hood (1958)	Gulf of Mexico
Polypeptides and polycondensates of:	(*a*) µg./l.	(*b*) µg./l.	(*c*) µg./l.	(*d*) µg./l.		
Glutamic acid $COOH(CH_2)_2CH(NH_2)COOH$	< 1	8–13	8–13	0·1–1·8	(*a*) Park *et al.* (1962) (by ion-exchange) (*b*) Tatsumoto *et al.* (1961) (by paper chromatography) (*c*) Tatsumoto *et al.* (1961) (by ion-exchange) (*d*) Degens *et al.* (1964)	Gulf of Mexico Gulf of Mexico Gulf of Mexico Pacific off California
Lysine $NH_2(CH_2)_4CH(NH_2)COOH$		?	trace–3	0·1–0·9		
Glycine NH_2CH_2COOH		—	trace–3	1·2–3·7		
Aspartic acid $COOHCH_2CH(NH_2)COOH$		3–8	trace–3	0·1–1·0		
Serine $CH_2OHCH(NH_2)COOH$	0·5–1	?	trace–3	1·8–5·6	(*a*) Park *et al.* (1962) (by ion-exchange) (*b*) Tatsumoto *et al.* (1961) (by paper chromatography) (*c*) Tatsumoto *et al.* (1961) (by ion-exchange) (*d*) Degens *et al.* (1964)	Gulf of Mexico Gulf of Mexico Gulf of Mexico Pacific off California
Alanine $CH_3CH(NH_2)COOH$		3–8	trace–3	0·7–3·1		
Leucine $(CH_3)_2CHCH_2CH(NH_2)COOH$		8–13	trace–3	0·9–3·8		
Valine $(CH_3)_2CHCH(NH_2)COOH$		trace–3	trace–3	0·1–1·7		
Cystine $[SCH_2CH(NH_2)COOH]_2$		trace–3	—	0·0–3·8		
Iso-leucine $CH_3CH_2CH(CH_3)CH(NH_2)COOH$		8–13	trace–3	—		
Leucine $CH_3CH_2CH_2CH_2CH(NH_2)COOH$		—	—	0·9–3·8		
Ornithine $NH_2(CH_2)_3CH(NH_2)COOH$	< 0·5	—	trace–3	0·2–2·4		
Methionine sulphoxide $CH_3S(:O)CH_2CH_2CH(NH_2)COOH$				—		
Threonine $CH_3CHOHCH(NH_2)COOH$		—	3–8	0·3–1·3		
Tyrosine $HOC_6H_4CH_2CH(NH_2)COOH$		—	trace–3	tr.–0·5		
Phenylalanine $C_6H_5CH_2CH(NH_2)COOH$		—	—	0·1–0·9		
Histidine $C_3H_3N_2CH_2CH(NH_2)COOH$		?	trace–3	tr.–2·4		
Arginine $NH_2C(:NH)NH(CH_2)_3CH(NH_2)COOH$		?	trace–3	0·1–0·6		
Proline C_4H_8NCOOH		?	—	0·3–1·4		
Methionine $CH_3SCH_2CH_2CH(NH_2)COOH$		—	trace–3	tr.–0·4		
Tryptophan $C_8H_6NCH_2CH(NH_2)COOH$		—	trace–3	—		
Glucosamine $C_6H_{13}NO_5$		—	trace–3	—		

From: Duursma (1965, p. 450-451)

Table VII-2 cont.

Name of compound and chemical formula	*Concentration* (e)	*Concentration* (f) µg./l.	*Author(s)*	*Locality*
Free amino acids				
Cystine $[SCH_2CH(NH_2)COOH]_2$	det	—	(e) Palmork (1963a), b	Norwegian coastal water
Lysine $NH_2(CH_2)_4CH(NH_2)COOH$	det.	0·2– 3·1	(f) Degens *et al.* (1964)	Pacific off California
Histidine $C_3H_3N_2CH_2CH(NH_2)COOH$	det.	0·5– 1·7		
Arginine $NH_2C(:NH)NH(CH_2)_3CH(NH_2)COOH$	det.	0·0		
Serine $CH_2OHCH(NH_2)COOH$	det.	2·3–23·4		
Aspartic acid $COOHCH_2CH(NH_2)COOH$	det.	tr.–9·6		
Glycine NH_2CH_2COOH	det.	tr. –37·6		
Hydroxyproline $C_4H_7N(OH)COOH$	det.	tr. – 2·8		
Glutamic acid $COOH(CH_2)_2CH(NH_2)COOH$	det.	1·4– 6·8		
Threonine $CH_3CHOHCH(NH_2)COOH$	det.	2·8–11·8		
α-Alanine $CH_3CH(NH_2)COOH$	det.			
Proline C_4H_8NCOOH	det.	0·0		
Tyrosine $HOC_6H_4CH_2CH(NH_2)COOH$	det.	tr. –5·0		
Tryptophan $C_8H_6NCH_2CH(NH_2)COOH$	det.	—		
Methionine $CH_3SCH_2CH_2CH(NH_2)COOH$	det.	—		
Valine $(CH_3)_2CHCH(NH_2)COOH$	det.	0·3– 2·7		
Phenylalanine $C_6H_5CH_2CH(NH_2)COOH$	det.	tr. 2·4		
Iso-leucine $CH_3CH_2CH(CH_3)CH(NH_2)COOH$	det.	—		
Leucine $(CH_3)_2CHCH_2CH(NH_2)COOH$	det.	0·5– 5·5		
Free compounds				
Uracil $\overline{NHCONHCOCH:CH}$	det.		Belser (1959, 1963)	Pacific coast near La Jolla
Iso-leucine $CH_3CH_2CH(CH_3)CH(NH_2)COOH$	det.			
Methionine $CH_3SCH_2CH_2CH(NH_2)COOH$	det.			
Histidine $C_3H_3N_2CH_2CH(NH_2)COOH$	det.			
Adenine $C_5H_3N_4NH_2$	det.			
Peptone	det.			
Threonine $CH_3CHOHCH(NH_2)COOH$	det.			
Tryptophan $C_8H_6NCH_2CH(NH_2)COOH$	det.			
Glycine NH_2CH_2COOH	det.			
Purine $C_5H_4N_4$	det.			
Urea CH_4ON_2	det.		Degens *et al.* (1964)	Pacific off California

III. Aliphatic Carboxylic and Hydroxy-carboxylic acids

	mg./l. (0–200 m.)	mg./l. (200–600 m.)	mg./l. (>600 m.)		
Lauric acid $CH_3(CH_2)_{10}COOH$	0·01–0·32	0·01–0·28	0–0·28	Slowey *et al.* (1962)	Coastal waters of Gulf of Mexico
Myristic acid $CH_3(CH_2)_{12}COOH$	0·01–0·10	0·01–0·05	0–0·07		
Myristoleic acid $CH_3(CH_2)_3CH:CH(CH_2)_7COOH$	traces–0·02	0·01–0·03	0–0·05		

From: Duursma (1965, p. 452-453)

Table VII-2 cont

Name of compound and chemical formula	*Concentration*	*Author(s)*	*Locality*
Palmitic acid $CH_3(CH_2)_{14}COOH$	0·01–0·17 0·03–0·42 0–0·38		
Palmitoleic acid $CH_3(CH_2)_5CH{:}CH(CH_2)_7COOH$	0·02–0·16 0·02–0·16 0–0·21		
Stearic acid $CH_3(CH_2)_{16}COOH$	0·04–0·09 0·02–0·13 0–0·10		
Oleic acid $CH_3(CH_2)_7CH{:}CH(CH_2)_7COOH$	0·01 0·02 0		
Linoleic acid $CH_3(CH_2)_4CH{:}CHCH_2CH{:}CH(CH_2)_7COOH$	0·01 0·01 0		
	mg./l. (1000–2500 m.)		
Fatty acids with:			
12 C-atoms	0·0003–0·02	Williams (1961)	Pacific Ocean coastal water
14 C ,,	0·0004–0·013		
16 C ,,	0·0027–0·0200		
16 C ,, + 1 double bond	0·0003–0·003		
18 C ,,	0·0037–0·0222		
18 C ,, + 1 double bond	0·0053		
18 C ,, + 2 double bonds	0·0000–0·0029		
20 C ,,	traces–0·0031		
22 C ,,	traces–0·0014		
	mg./l.		
Acetic acid CH_3COOH Lactic acid $CH_3CH(OH)COOH$ Glycollic acid $HOCH_2COOH$	<1·0	Koyama and Thompson (1959)	Pacific Ocean
Malic acid $HOOCCH(OH)CH_2COOH$	0·28	Creac'h (1955)	Atlantic coastal water
Citric acid $HOOCCH_2C(OH)(COOH)CH_2COOH$	0·14		
Carotenoids and brownish waxy or fatty matter	2·5	Johnston (1955) Wilson and Armstrong (1955)	North Sea English Channel
IV. Biologically active compounds (see also Provasoli, 1963)			
Organic Fe compound(s)		Harvey (1925)	Deep sea water
Vitamin B_{12} (Cobalamine) $C_{63}H_{88}O_{14}N_{14}PCo$	3·4–1·6 mμg./l.	Vishniak and Riley (1961)	Long Island Sound
Vitamin B_{12}	0·2 mμg./l. (summer) 2·0 mμg./l. (winter)	Cowey (1956)	Oceanic surface-water
Vitamin B_{12}	0·2–5·0 mμg./l.	Daisley and Fisher (1958)	
Vitamin B_{12}	0–2·6 mμg./l.	Kashiwada *et al.* (1957)	North Pacific Ocean
Vitamin B_{12}	0–0·03 mμg./l.	Menzel and Spaeth (1962)	Sargasso Sea 0–05 m.
Thiamine (Vit. B_1) $C_{12}H_{18}ON_4SCl_2$	0–20 mμg./l.	Cowey (1956)	Surface water, possibly from land drainage
Plant hormones (auxins)	3·41 mμg./l.	Bentley (1960)	North Sea near Scotland
V. Humic acids			
"Gelbstoffe" (Yellow substances) Melanoidin-like		Kalle (1949, 1962) Jerlov (1955) Armstrong and Boalch (1961a,b)	Coastal waters
VI. Phenolic compounds			
p-Hydroxy-benzoic acid HOC_6H_4COOH	1–3 μg./l.	Degens *et al.* (1964)	Pacific off California
Vanillic acid $CH_3(HO)C_6H_3COOH$	1–3 μg./l.		
Syringic acid $(CH_3O)_2(HO)C_6H_2COOH$	1–3 μg./l.		
VII. Hydrocarbons			
Pristane; (2, 6, 10, 14-tetramethylpentadecane)	tr.	Blumer *et al.* (1963)	Cape Cod Bay

tr. = trace
det. = detected
– = not detected
? = possibly present

From: Duursma (1965, p. 454-455)

Table VII-3

Distribution of Organic and Inorganic Fractions in Suspended Particulate Matter

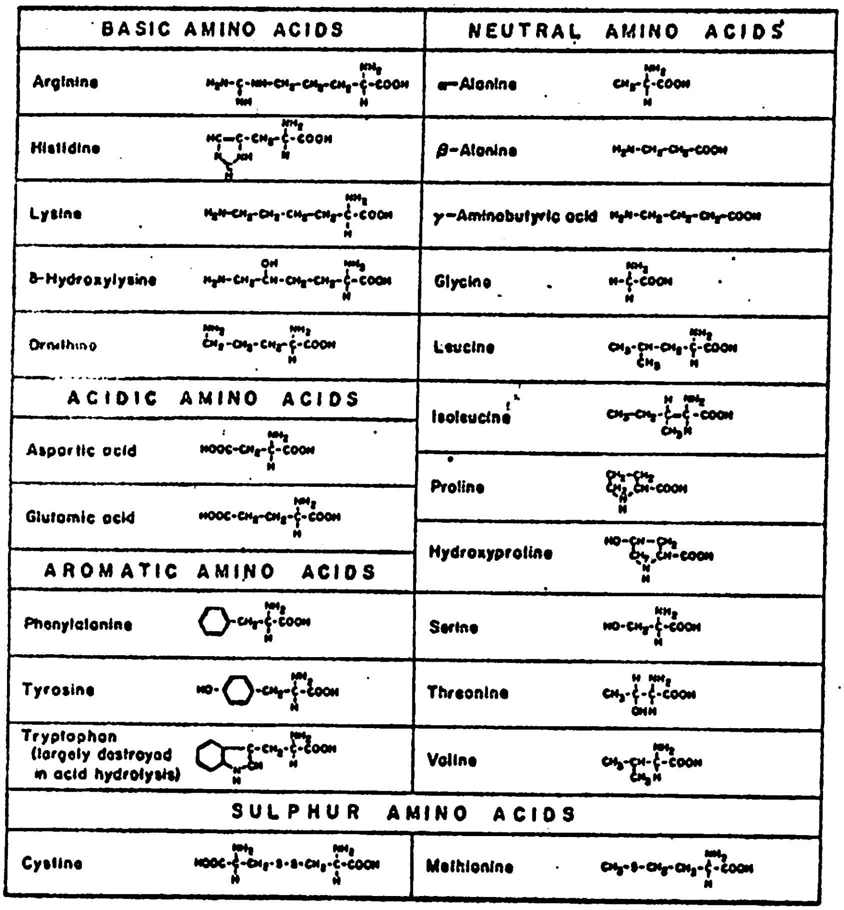
Area	Total Suspended Matter mg/ℓ	% Organic Matter	Reference
Offshore Pacific	10.5	62	Fox (1953)
Offshore Pacific	3.8	29	Fox (1953)
North Sea	6.0	27	Postma (1964)
Wadden Sea	18.0	14	Postma (1954)
Oceanic Average	0.8-2.5	20-60 *	Lisitzen (1959)
Bering Sea	2-4	--	Lisitzen (1959)
Indian Ocean	--	6-36 *	Lisitzen (1959)
Long Island Sound	2-7	20-45	Riley (1959)
Wilmington Canyon-East Coast U.S.A.	0.13-1.11	10-68	Lyall and others (1971)

* cx2 = dry organic matter

From: Parsons, 1963, p. 220.

Fig ~~Table~~ VII-3

Table 14 AMINO ACIDS COMMONLY FOUND IN SEDIMENT AND SOIL HYDROLYSATES.



BASIC AMINO ACIDS		NEUTRAL AMINO ACIDS	
Arginine	$\mathrm{H_2N-\underset{NH}{C}-NH-CH_2-CH_2-CH_2-\overset{NH_2}{\underset{H}{C}}-COOH}$	α-Alanine	$\mathrm{CH_3-\overset{NH_2}{\underset{H}{C}}-COOH}$
Histidine		β-Alanine	$\mathrm{H_2N-CH_2-CH_2-COOH}$
Lysine	$\mathrm{H_2N-CH_2-CH_2-CH_2-CH_2-\overset{NH_2}{\underset{H}{C}}-COOH}$	γ-Aminobutyric acid	$\mathrm{H_2N-CH_2-CH_2-CH_2-COOH}$
δ-Hydroxylysine	$\mathrm{H_2N-CH_2-\overset{OH}{C}H-CH_2-CH_2-\overset{NH_2}{\underset{H}{C}}-COOH}$	Glycine	$\mathrm{H-\overset{NH_2}{\underset{H}{C}}-COOH}$
Ornithine	$\mathrm{\overset{NH_2}{CH_2}-CH_2-CH_2-\overset{NH_2}{\underset{H}{C}}-COOH}$	Leucine	$\mathrm{CH_3-\underset{CH_3}{CH}-CH_2-\overset{NH_2}{\underset{H}{C}}-COOH}$
ACIDIC AMINO ACIDS		Isoleucine	$\mathrm{CH_3-CH_2-\overset{H}{\underset{CH_3}{C}}-\overset{NH_2}{\underset{H}{C}}-COOH}$
Aspartic acid	$\mathrm{HOOC-CH_2-\overset{NH_2}{\underset{H}{C}}-COOH}$		
Glutamic acid	$\mathrm{HOOC-CH_2-CH_2-\overset{NH_2}{\underset{H}{C}}-COOH}$	Proline	
AROMATIC AMINO ACIDS		Hydroxyproline	
Phenylalanine		Serine	$\mathrm{HO-CH_2-\overset{NH_2}{\underset{H}{C}}-COOH}$
Tyrosine		Threonine	$\mathrm{CH_3-\overset{H}{\underset{OH}{C}}-\overset{NH_2}{\underset{H}{C}}-COOH}$
Tryptophan (largely destroyed in acid hydrolysis)		Valine	$\mathrm{CH_3-\underset{CH_3}{CH}-\overset{NH_2}{\underset{H}{C}}-COOH}$
SULPHUR AMINO ACIDS			
Cystine	$\mathrm{HOOC-\overset{NH_2}{\underset{H}{C}}-CH_2-S-S-CH_2-\overset{NH_2}{\underset{H}{C}}-COOH}$	Methionine	$\mathrm{CH_3-S-CH_2-CH_2-\overset{NH_2}{\underset{H}{C}}-COOH}$

From: Degens (1965, p. 214)

A brief summary of organic partition in sea water is given below mainly from Degens (1965).

Carbohydrates:		
Chiefly sugars glucose, galactose, mannose	evenly distributed throughout water column	Total 15µg/ℓ
Nitrogenous Compounds:		
free-serine, ornithine, glycine	total evenly distributed (see Figure VII-3)	Total 10-100µg/ℓ
Lipids:		
Palmitic acid-Stearic acid, near surface related to plankton-with depth increase in saturation decrease in chain length	total apparently uniform with depth	total 10-100µg/ℓ
Gelbstoffe:		
Apparently melanodines produced from carbohydrates and proteins released by decomposition and not land derived phenol humic acid	decreases with increase in salinity	

From: Kalle, 1966.

Man's Contribution (From Carter, 1970)

The discharge of treated wastewater, primarily of sewage origin, constitutes a major contribution of organic matter to the marine environment. Representative concentrations of various organics in raw, primary and secondary treated sewage effluent are given later. The values shown indicate that some 27,000 lbs of grease are discharged to the ocean each day from both San Diego and Los Angeles County. San Francisco Bay area sewage contains 0.036 lb/cap/day grease and 0.0024 lb/cap/day floatables.

ORGANIC MATTER IN WASTE WATER

Characteristic	Tema Raw	L. A. Primary	A. D. Primary	L. A. Secondary
Flow, MGD	1.46	216	80	107
BOD, mg/	280	157	201	13
TSS, mg/	219	936	146	-
Volatile, mg/	142	-	117	-
Grease, mg/	110	15	41	.04
Floatables, mg/	26.5	1.7	-	-

Over the past half century some 5 million tons of petroleum oil are reported spilled to the sea (Pilpel, 1968). Some of this oil dissolves into the sea water. Folowing the Torrey Canyon spill the hydrocarbon levels in the English Channel rose from the usual level of 0.003 ppm to 0.007 - 0.014 ppm at the end of April 1967 and 0.004 - 0.009 ppm at the end of May 1967 (Smith, 1968). The soluability of petroleum in water is increased by the presence of higher weight organic acids (Baker, 1958) and possibly other compounds.

According to (Dzyuben 1958) the microbial oxidation of oil at sea may proceed 10 times faster than auto-oxidation. The rate of oxidation of floating oil under aerobic conditions may be as high as 0.5 g/day per m^2 of oil surface exposed to the particular organism. The addition of nitrogen and phosphorus may increase this rate (Chemical and Engineering News, 7 September 1970).

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Organic Mineralization and Organic Extraction of Trace Elements from Sea Water

The principal elements in organic matter are carbon, nitrogen, and phosphorous. In general these elements are recycled through sea water in various links of the food web. However, organisms also have the ability to abstract carbon and phosphorous and other elements from sea water for use as hard parts as bones, teeth, spicules, etc. or in the life process in coelomic fluid, blood, enzymes, etc. The first process, by which organisms cause precipitation of mineral matter, has a pronounced effect on the chemistry of sea water as the constituent elements of the biologically produced mineral are often abstracted from sea water which is thermodynamically undersaturated with respect to that mineral. As the organically produced mineral is of various composition due to solid solution, and various sizes and shapes its behavior and solubility as a dead particle varies. For example Chave and Schmaltz (1966) noted (a) magnesium calcites have four times the activity of pure calcite, and (b) calcite 10^{-6}cm in diameter has eight times the activity of 1cm particles. Such features make equilibrium calculations extremely difficult if not impossible. The effect of organic mineralization is to give the utilized elements shorter residence times in sea water than would be predicted by equilibrium calculations.

Organisms produce precipitation by the interaction of the surrounding fluid, in this case sea water, with an organic template. As the organic chains have numerous positions for side radicals (see Figure VII-4, 5). By appropiate arrangement along the chain it is possible to have both negative and positive charge deficiencies so that cations and anions from sea water may be attracted. The organic chain may be contourted such that cations and anions of appropiate size can be attracted to produce the required mineral within the tissue. Table VII-4 lists the major minerals utilized by marine organisms and the corresponding template tissue.

For mineralized hard parts in direct contact with sea water the organism often secretes an organic film as a protection against solution in undersaturated waters. For example the outer layer of periostracum of mollusk shells is a nitrogenous-chitin like compound overlaying the carbonate layers.

The second process, by which organisms abstract elements, is for inclusion in organic radicals useful in the life process. Usually these organic compounds

Figure VII-4

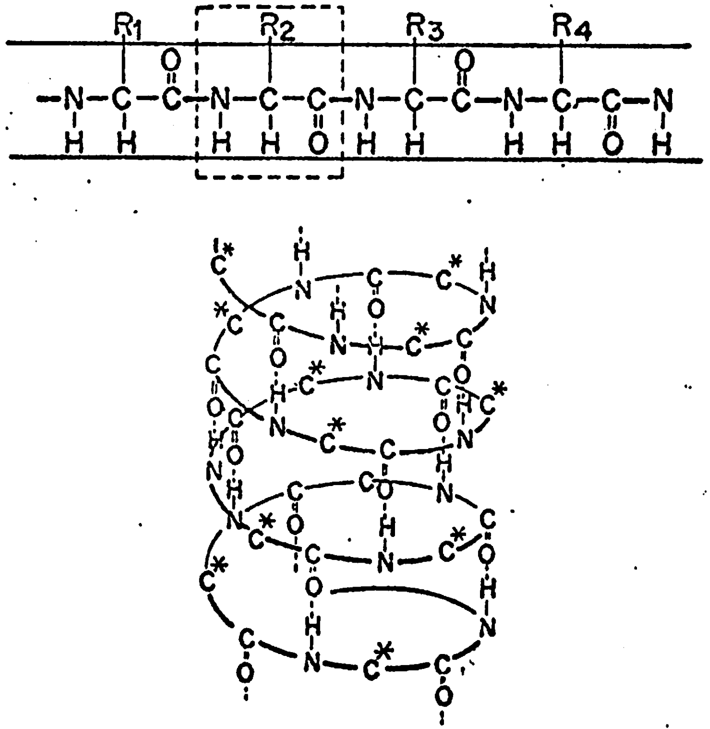

Fig. 45 Protein structure. Simple structural principles; variety of chemical reactivity (after Calvin, 1961)

From: Degens (1965, p. 214)

Table VII-4

Table 15 EXAMPLES OF BIOLOGICALLY MINERALIZED TISSUES (AFTER GLIMCHER, 1960).

Species	*Tissue Mineralized*	*Mineral Form*	*Major Organic-Matrix Components*
Plants	Cell wall	Calcite	Carbohydrates (Cellulose, Pectins), Lignins
Microorganisms	Exoskeleton	Amorphous Silica	Carbohydrates (Pectins)
		Calcite, Aragonite	(?)
		Celestite	(?)
Mollusks	Exoskeleton	Calcite, Aragonite	Protein (Conchiolin)
Arthropods	Exoskeleton	Calcite	Carbohydrate (Chitin), Protein
Vertebrates	Exoskeleton		
	Bone	OH-Apatite	Protein (Collagen)
	Cartilage	OH-Apatite	Protein (Collagen) Carbohydrates (Mucopolysaccharides)
	Tooth		
	Dentin	OH-Apatite	Protein (Collagen)
	Cementum	OH-Apatite	Protein (Collagen)
	Enamel	OH-Apatite	Protein (Eukeratin)

Figure VII-5

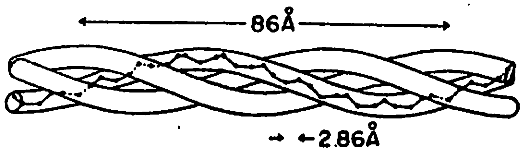

Fig. 51 A segment of the collagen structure. The tubes represent the space filled by polypeptide chains each of which extends about 3000 A. The amino acid residues are 2.86A apart and lie along a minor helix with a pitch of 8.6 A (three residues per turn). Each chain is coiled into a major helix with a pitch of 86 A. (after Piez, 1963)

From: Degens (1965, p.220- table and p. 221 - figure) are in fluids or soft parts so elements utilized return repidly to sea water as the organism dies or is eaten. Thus this process has little effect on the residence time in sea water of the metabolic elements.

Truly marine organisms, that is phyla that always have been marine have a salt composition of their body fluids very similar to that of present sea water. However, marine organisms that have land dwelling or air breathing precursors as the marine fishes and marine mammals have a modified body fluid chemistry generally shown by a much lower sodium content. Table VII-5 shows Vinogradov's compilation of the salt content of body fluids.

Specilized organisms also take up trace elements metabolically. For example, many species of crustacea use copper in haemocyamin, tunicate body fluids are rich in vanadium, and _Cyanea_ contains 1.5g zinc per kilogram dry weight. (Harvey, 1963, p. 29-30). Sea weed shows enrichment of Zn, Mo, Co, Ni, Pb, V, Ti, and Cr with respect to sea water as well as enrichment in iodine. As most of these elements are in soft parts there is little effect on their long term chemistry in sea water. However, Harvey (1963, p. 28) noted seasonal changes in copper concentration in the English Channel which could be related to uptake by animals grazing during plankton blooms or to uptake by phytoplankton themselves.

Table VII-5

COMPARATIVE SALT COMPOSITION OF BLOOD, COELOMIC FLUID, AND SO FORTH (IN G PER L)

ORGANISM	Comments	−Δ°c	Organic matter	Inorganic matter	Na	K	Ca	Mg	Cl	SO$_4$	Author
Brachiopoda*											
Vermes											
Sipunculus nudus		—	—	—	—	0.49	0.47	1.007	23.60	—	Bethe and Berger, 1931
" "		—	—	—	—	0.578	0.496	1.922	22.91	—	Bialaszewicz, 1933
Arenicola claparedii		—	—	—	—	0.676	0.601	1.491	22.27	—	" "
Aphrodite aculeata		—	—	—	—	0.492	0.453	1.396	20.07	—	" "
Echinodermata											
Paracentrotus lividus	♂: haemolymph	2.01	8.94	32.08	—	0.488	1.156	—	20.26	—	Pora, 1936-c
Paracentrotus lividus	♀	2.02	10.29	29.19	—	0.497	0.914	—	20.0	—	" "
Paracentrotus lividus		—	—	—	—	0.496	0.52	1.267	21.98	—	Bialaszewicz, 1933
Astropecten aurantiacus		—	—	—	—	0.566	0.570	1.313	23.40	—	" "
Sphaerechinus granularis		—	—	—	—	0.496	0.512	1.298	21.95	—	" "
Holothuria tubulosa		—	—	—	—	0.534	0.558	1.456	23.08	—	" "
Echinus esculentus		—	—	—	10.22	0.374	0.399	1.223	18.59	2.601	Robertson, 1939
" "	Coelomic fluid	—	—	—	12.20	0.522	0.513	1.23	19.40	—	Bethe and Berger, 1931
" "	Ambulacral fluid	—	—	—	12.00	0.753	0.606	1.21	19.61	—	" "
Mollusca											
Doris tuberculata		—	—	—	11.80	0.588	0.505	1.39	18.75	—	" "
Aplysia punctata		—	—	—	13.50	0.471	0.535	1.30	22.17	—	" "
Helix pomatia	Terrestrial	—	—	—	1.37	0.184	0.166	0.019	1.98	—	Lustig, Ernst and Reuss, 1937
" "	Winter	—	—	—	1.58	0.182	0.262	0.049	2.77	—	" "
Mytilus edulis		—	—	—	10.35	0.35	0.46	—	19.20	—	Bethe and Berger, 1931
Pinna nobilis		—	—	—	—	0.643	0.608	1.44	22.59	—	Bialaszewicz, 1933
Sepia officinalis		2.04	—	—	—	—	—	—	—	—	Pora, 1936-c
Enteropneusta*											
Arthropoda											
Palinurus vulgaris		—	—	—	14.20	1.078	1.11	0.369	21.60	—	Bethe and Berger, 1931
Palinurus interruptus		2.19	—	—	12.21	0.470	0.78	0.25	—	—	Schlatter, 1941
Carcinus moenas		—	—	—	13.27	0.293	0.498	0.646	19.28	—	Bethe and Berger, 1931
" "		—	—	—	—	—	0.611	1.19	22.98	—	Bialaszewicz, 1933
Hyas araneus		—	—	—	11.72	0.507	0.467	0.91	18.40	—	Bethe and Berger, 1931
Portunus depurator		—	—	—	9.80	1.15	0.476	—	18.00	—	" "

* Data are lacking. See also Table 267.

From: Vinogradov (1953, p. 584)

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Table VII-5 cont.

	Comments	−Δ°c	Organic matter	Inorganic matter	Na	K	Ca	Mg	Cl	SO_4	Author
Eriocheir sinensis . .	Fresh .	—	—	—	11.30	0.39	0.565	—	15.50	—	Bethe and Berger, 1931
„ „ . . .	„ .	1.21	—	—	7.56	—	0.722	—	19.05	—	Drilhon-Courtois and Portier, 1939
Eriphia spinifrons		—	—	—	—	0.69	0.566	0.475	22.0	—	Bethe and Berger, 1931
Cambarus clarkii . .	Fresh	0.68	—	—	3.69	0.225	0.49	0.049	—	—	Schlatter, 1941
Pachygrapsus crassipes		1.83	—	—	10.60	0.355	0.54	0.24	—	—	„ „
Homarus vulgaris		—	—	—	11.46	0.778	0.71	0.10	18.45	—	Bethe and Berger, 1931
„ „		—	—	—	11.71	0.555	0.587	0.173	18.26	0.762	Robertson, 1939
Cancer pagurus		—	—	—	11.55	0.468	0.552	0.658	18.08	2.306	„ „
„ „		—	—	—	12.45	0.715	0.49	0.661	18.35	—	Bethe and Berger, 1931
Maja squinada		2.028	—	—	—	0.768	0.83	—	19.3	—	Pora, 1936-e
„ „		—	—	—	13.55	1.365	1.086	1.068	22.0	—	Bethe and Berger, 1931
„ „		—	—	—	—	0.523	0.493	1.49	22.26	—	Bialaszewicz, 1933
Maja verrucosa		—	—	—	—	—	0.490	1.351	22.90	—	Bethe and Berger, 1931
Potamobius fluviatilis .	Fresh	0.81	—	—	—	0.240	0.342	0.062	6.84	—	Scholles, 1933
„ „ .	„	—	—	—	3.00	0.141	0.42	—	7.00	—	——
Telphusa fluviatilis		1.16	—	—	7.75	0.330	0.723	—	17.5	—	Drilhon-Courtois and Portier, 1939
Tunicata											
Phallusia mammillata		—	—	—	—	0.854	0.570	1.45	24.47	—	Bialaszewicz, 1933
Ciona intestinalis		—	—	—	—	0.504	0.52	1.316	23.54	—	„ „
Cyclostomata*											
Pisces											
Raja erinacea . . .	Marine elasmobranch	—	—	—	5.84	0.312	0.480	0.120	9.45	—	Hartman, Lewis, Shelden and Walther, 1941
Pristis microdon . .	Freshwater elasmobranch	1.02	—	—	—	—	—	—	6.03	None	Smith, 1931
Lophius piscatorius .	Marine teleost	—	—	—	4.62	0.273	0.14	0.024	6.73	0.11	Smith, 1929-b
Cyprinus carpio . . .	♂; Freshwater teleost	—	—	—	3.09	0.18	0.09	—	5.65	—	Pora, 1935-b
Mammalia											
Balaenoptera physalus .	4; marine	—	—	—	3.30	0.227	0.06	0.057	4.97	—	Okahara, 1925
Homo sapiens		—	—	—	3.00	0.25	0.09	0.03	3.80	—	——
Sea water		—	—	35.00	10.7	0.38	0.45	1.40	19.0	2.65	——
Fresh water		—	—	0.20	0.016	0.003	0.04	0.007	0.01	0.024	——

* Data are lacking. See also Table 267.

From: Vinogradov (1953, p. 585)

Bacteria Influence on The Composition of Sea Water

Three types of specific element fixing bacteria have been reported for the marine environment: (1) nitrogen fixing, (2) sulfur reducing, and (3) manganese fixing. Except for nitrogen fixing most of these bacterial processes occur in the bottom. Sulfur reducing bacteria are restricted to anoxic basins thus would not influence the sulfur composition in the well ventilated open ocean. Manganese fixing bacteria may have an important role in the formation of ferromanganese nodules and thus aid in the shortening of the residence time for Fe and Mn. However, the major role of bacteria is not removal of elements from sea water but decomposition of organic matter to simple compounds thus returning elements to sea water.

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UNIVERSITY OF CALIFORNIA
CE 201 B

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TRACE IONS IN SEA WATER

I. Metallic Ions - As discussed in Goldberg (1965) the metallic complexing in sea water can be based on the classification of Schwarzenbach (1961):

- (a) Metal ions with a rare gas configuration (d^o cations): - the alkali metals, alkaline earths, Al, Sc, lanthanides, Ti, Th, and Nb.
- (b) 18 electron outer shell cations (d^{10}): - Ag^{+}, Zn^{++}, Ga^{+++}, and Sn^{++++}.
- (c) Transition metals where d electrons are greater than zero but less than 10: Mn^{++}, Fe^{++}, Co^{++}, and Ni^{++}.

To determine the dominant anion for any metal cation M consider: -

$$K_i = \frac{A_{Mi}}{A_M A_i} \qquad \text{for anion } i$$

$$K_j = \frac{A_{Mj}}{A_M A_j} \qquad \text{for anion } j$$

for

$$\text{then } \frac{K_i}{K_j} = \frac{A_{Mi}\ A_M\ A_j}{A_{Mj}\ A_M A_i} \qquad \text{if } \frac{K_i}{K_j} > \frac{A_j}{A_i} \text{ then } M_i \text{ dominant}$$

also for $\log K_i - \log K_j > \log A_j - \log A_i$

but if $\frac{K_i}{K_j} < \frac{A_j}{A_i}$ then M_j dominant

also for $\log K_i - \log K_j < \log A_j - \log A_i$

Table VIII-1 gives log K anion constants for various cations. For conservative anions in sea water such as Cl^-, $SO_4^{=}$, Br^-, F^-, and OH^- their ratios also would be constant and easily calculated from concentration data if δ_i were known. Goldberg (1965, p. 170) uses the assumption:

$$\delta^o = 1$$
$$\delta^{\pm} = 0.7$$
$$\delta^{\pm\pm} = 0.1$$

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Organic Modification of Sea Water Chemistry

The variety of life in the sea ranges widely in both size and complexity to tiny simple bacteria to gigantic whales the largest living thing. However, unicellular organisms make up the bulk of the living matter of the sea. The plant kingdom, unlike the animal kingdom is restricted to simple organism on the evolutionary scale and away from shallow water where multicellular algae grow only unicellular phytoplankton exist. Phytoplankton, contrasted with land plants which are chiefly carbohydrates are enriched in protein (see Table VII-1) and thus are an attractive source of food.

Living phytoplankton are restricted to the zone of light which varies from a maximum of about 100 meters in clear tropical waters to nearly zero in turbid waters. If the phytoplankton escape being eaten by other organisms and the plant dies because of the lack of nutrients or some other change in the environment the dead organic matter is usually extracted before the dead organism settles to the bottom.

Table VII-1

Organic Composition of Unicellular Algae

Protein	41-53%
Carbohydrate	26-38%
Lipid	20-27%

From: Ketchum and Redfield (1949)

The bulk of organic matter is continually cycled through various organisms in what is called the food chain or food web. Figure VII-1 depicts the food web as conceived by Strickland (1965). As this matter essentially remains in the living world it has little direct effect on the long term composition of sea water and thus is more the concern of biological oceanology than chemical oceanology per se.

Certain seasonal links in the food web however do distrub the short term and regional chemistry of sea water. Figure VII-2 shows the lag in growth of zooplankton to that of phytoplankton in the English Channel. In seasons of plankton blooms the zooplankton to the extent that most of the organic matter is only partially digested by the zooplankton and passes through their bodies and released to sea water as faecal pellets (Harvey, 1963, p. 24) eventually the organic matter in the pellets is utilized by bottom dwelling organisms such as bacteria and worms but during periods of zooplankton blooms much organic matter is withdrawn from sea water and placed in the bottom short circuiting the normal food chain.

Of primary concern to chemical oceanology, however, is the non-living organic fraction which includes organic Detritus-tripton, and dissolved organically derived decay products.

By convention organic matter in sea water which passes a 0.4μ filter is designated dissolved or free organic matter. Extractable organic matter trapped by a 0.4μ filter is considered particulate organic matter.

It can be calculated from Duursma (1960) that ocean water contains about 2.4 kg/m^2 dissolved organic material, and according to Parsons and Strickland (1962) sea water contains 500 g/m^2 of particulate organic material, of which considerably less than one-tenth is living. Thus, the total non-living organic content of sea water if fifty times larger than the living portion. That such large quantities of dissolved organic matter exist in a state seemingly no longer available to many of the living forms inhabiting this environment has long puzzled marine researchers.

Four principal types of organic material are recognized in sea water:

1. Non-nitrogenous - carbohydrates and sugars
2. Nitrogenous - proteins and amino acids
3. Fatty acids - lipids
4. "Gelbstoffe" - humic acids?

Table VII-2 lists analyses of organic matter in sea water.

Table VII-3 shows the partition of suspended matter into organic and inorganic fractions.

In general the amount of particulate organic matter decreases with depth probably due to the ability of bacteria to accumulate on a particle in sufficient numbers to reduce it given enough time as the particle slowly sinks to the bottom.

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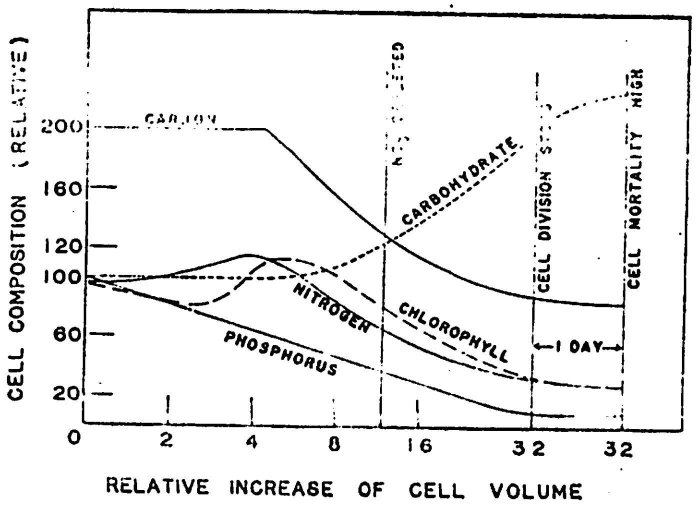


FIG. 3. Relative changes of cell composition of phytoplankton owing to nitrate and phosphorus depletion in sea water.

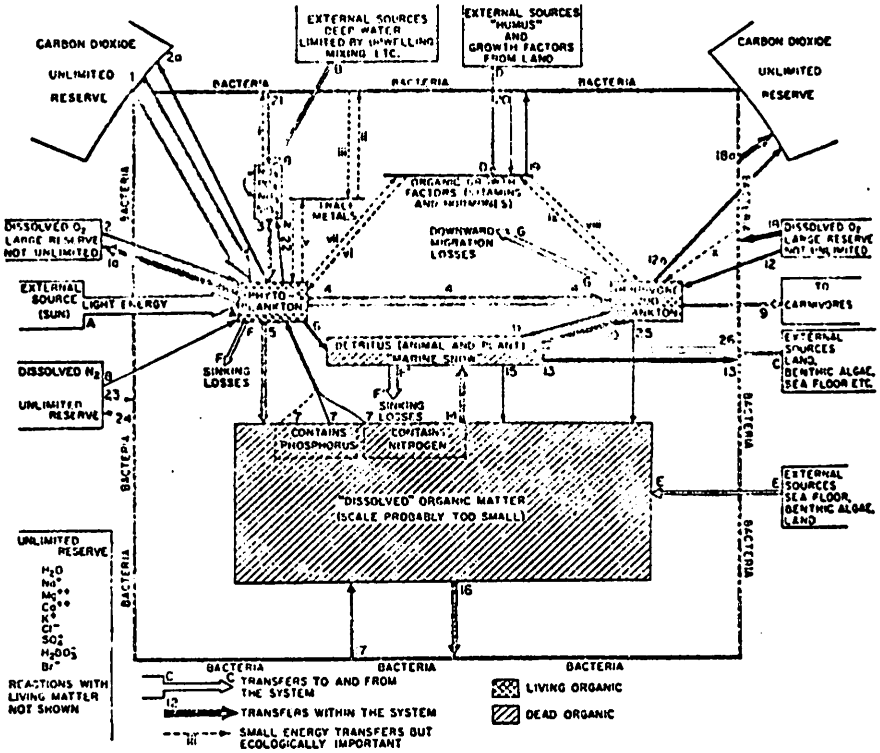


FIG. 5. Chart of idealized food-web in the early stages.

From: Strickland (1965, p. 550 top and 594 bottom)

Figure VII-2

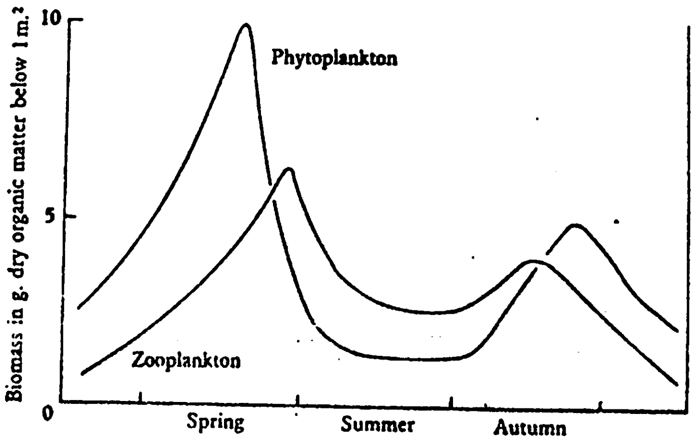


Fig. 12. Change in biomass of phytoplankton and zooplankton below unit area, throughout the seasons, derived from observations in the English Channel, 4 miles offshore.

From: Harvey, (1966, p. 26)

Table VII-2

Specific dissolved organic compounds identified in sea water

Name of compound and chemical formula	*Concentration*				*Author(s)*	*Locality*
	I. Carbohydrates					
Pentoses $C_5H_{10}O_5$	0–8 mg./l.				Collier *et al.* (1950, 1956)	Gulf of Mexico
Pentoses $C_6H_{10}O_5$	0·5 μg./l.				Degens *et al.* (1961)	Pacific off California
Hexoses	14–36 μg./l.				Degens *et al.* (1964)	Pacific off California
Rhamnosides $C_6H_{12}O_5$	0·1–0·4 mg./l.				Lewis and Rakestraw (1955)	Pacific Ocean coast U.S.A.
Rhamnosides						
Dehydroascorbic acid  $\overset{\ulcorner\!-\!O\!-\!\urcorner}{\mathrm{COCOCOCHCH(OH)CH_2OH}}$	0·1 mg./l.				Wangersky (1952)	Gulf of Mexico inshore water
	II. Proteins and their derivatives					
Peptides C/N ratio = 13·8:1					Jeffrey and Hood (1958)	Gulf of Mexico
Polypeptides and polycondensates of:	(a) μg./l.	(b) μg./l.	(c) μg./l.	(d) μg./l.		
Glutamic acid $COOH(CH_2)_2CH(NH_2)COOH$	<1	8–13	8–13	0·1–1·8	(a) Park *et al.* (1962) (by ion-exchange) (b) Tatsumoto *et al.* (1961) (by paper chromatography) (c) Tatsumoto *et al.* (1961) (by ion-exchange) (d) Degens *et al.* (1964)	Gulf of Mexico Gulf of Mexico Gulf of Mexico Pacific off California
Lysine $NH_2(CH_2)_4CH(NH_2)COOH$		?	trace–3	0·1–0·9		
Glycine NH_2CH_2COOH		—	trace–3	1·2–3·7		
Aspartic acid $COOHCH_2CH(NH_2)COOH$		3–8	trace–3	0·1–1·0		
Serine $CH_2OHCH(NH_2)COOH$	0·5–1	?	trace–3	1·8–5·6	(a) Park *et al.* (1962) (by ion-exchange) (b) Tatsumoto *et al.* (1961) (by paper chromatography) (c) Tatsumoto *et al.* (1961) (by ion-exchange) (d) Degens *et al.* (1964)	Gulf of Mexico Gulf of Mexico Gulf of Mexico Pacific off California
Alanine $CH_3CH(NH_2)COOH$		3–8	trace–3	0·7–3·1		
Leucine $(CH_3)_2CHCH_2CH(NH_2)COOH$		8–13	trace–3	0·9–3·8		
Valine $(CH_3)_2CHCH(NH_2)COOH$		trace–3	trace–3	0·1–1·7		
Cystine $[SCH_2CH(NH_2)COOH]_2$		trace–3	—	0·0–3·8		
Iso-leucine $CH_3CH_2CH(CH_3)CH(NH_2)COOH$		8–13	trace–3	—		
Leucine $CH_3CH_2CH_2CH_2CH(NH_2)COOH$		—	—	0·9–3·8		
Ornithine $NH_2(CH_2)_3CH(NH_2)COOH$	<0·5	—	trace–3	0·2–2·4		
Methionine sulphoxide $CH_3S(:O)CH_2CH_2CH(NH_2)COOH$				—		
Threonine $CH_3CHOHCH(NH_2)COOH$		—	3–8	0·3–1·3		
Tyrosine $HOC_6H_4CH_2CH(NH_2)COOH$		—	trace–3	tr.–0·5		
Phenylalanine $C_6H_5CH_2CH(NH_2)COOH$		—	—	0·1–0·9		
Histidine $C_3H_3N_2CH_2CH(NH_2)COOH$		?	trace–3	tr.–2·4		
Arginine $NH_2C(:NH)NH(CH_2)_3CH(NH_2)COOH$		?	trace–3	0·1–0·6		
Proline C_4H_8NCOOH		?	—	0·3–1·4		
Methionine $CH_3SCH_2CH_2CH(NH_2)COOH$		—	trace–3	tr.–0·4		
Tryptophan $C_8H_6NCH_2CH(NH_2)COOH$		—	trace–3	—		
Glucosamine $C_6H_{13}NO_5$		—	trace–3	—		

From: Duursma (1965, p. 450-451)

Table VII-2 cont.

Name of compound and chemical formula	*Concentration* (e)	(f) μg./l.	*Author(s)*	*Locality*
Free amino acids				
Cystine $[SCH_2CH(NH_2)COOH]_2$	det	—	(e) Palmork (1963a), b	Norwegian coastal water
Lysine $NH_2(CH_2)_4CH(NH_2)COOH$	det.	0·2– 3·1	(f) Degens *et al.* (1964)	Pacific off California
Histidine $C_3H_3N_2CH_2CH(NH_2)COOH$	det.	0·5– 1·7		
Arginine $NH_2C(:NH)NH(CH_2)_3CH(NH_2)COOH$	det.	0·0		
Serine $CH_2OHCH(NH_2)COOH$	det.	2·3–23·4		
Aspartic acid $COOHCH_2CH(NH_2)COOH$	det.	tr.–0·6		
Glycine NH_2CH_2COOH	det.	tr. –37·6		
Hydroxyproline $C_4H_7N(OH)COOH$	det.	tr. – 2·8		
Glutamic acid $COOH(CH_2)_2CH(NH_2)COOH$	det.	1·4– 6·8		
Threonine $CH_3CHOHCH(NH_2)COOH$	det.	2·8–11·8		
α-Alanine $CH_3CH(NH_2)COOH$	det.			
Proline C_4H_8NCOOH	det.	0·0		
Tyrosine $HOC_6H_4CH_2CH(NH_2)COOH$	det.	tr. –5·0		
Tryptophan $C_8H_6NCH_2CH(NH_2)COOH$	det.	—		
Methionine $CH_3SCH_2CH_2CH(NH_2)COOH$	det.	—		
Valine $(CH_3)_2CHCH(NH_2)COOH$	det.	0·3– 2·7		
Phenylalanine $C_6H_5CH_2CH(NH_2)COOH$	det.	tr. 2·4		
Iso-leucine $CH_3CH_2CH(CH_3)CH(NH_2)COOH$	det.	—		
Leucine $(CH_3)_2CHCH_2CH(NH_2)COOH$	det.	0·5– 5·5		
Free compounds				
Uracil $\overline{NHCONHCOCH{:}CH}$	det.		Belser (1959, 1963)	Pacific coast near La Jolla
Iso-leucine $CH_3CH_2CH(CH_3)CH(NH_2)COOH$	det.			
Methionine $CH_3SCH_2CH_2CH(NH_2)COOH$	det.			
Histidine $C_3H_3N_2CH_2CH(NH_2)COOH$	det.			
Adenine $C_5H_3N_4NH_2$	det.			
Peptone	det.			
Threonine $CH_3CHOHCH(NH_2)COOH$	det.			
Tryptophan $C_8H_6NCH_2CH(NH_2)COOH$	det.			
Glycine NH_2CH_2COOH	det.			
Purine $C_5H_4N_4$	det.			
Urea CH_4ON_2	det.		Degens *et al.* (1964)	Pacific off California

III. Aliphatic Carboxylic and Hydroxy-carboxylic acids

	mg./l. (0–200 m.)	mg./l. (200–600 m.)	mg./l. (>600 m.)		
Lauric acid $CH_3(CH_2)_{10}COOH$	0·01–0·32	0·01–0·28	0–0·28	Slowey *et al.* (1962)	Coastal waters of Gulf of Mexico
Myristic acid $CH_3(CH_2)_{12}COOH$	0·01–0·10	0·01–0·05	0–0·07		
Myristoleic acid $CH_3(CH_2)_3CH:CH(CH_2)_7COOH$	traces–0·02	0·01–0·03	0–0·05		

From: Duursma (1965, p. 452-453)

Table VII-2 cont

Name of compound and chemical formula	*Concentration*			*Author(s)*	*Locality*
Palmitic acid $CH_3(CH_2)_{14}COOH$	0·01–0·17	0·03–0·42	0–0·38		
Palmitoleic acid $CH_3(CH_2)_5CH{:}CH(CH_2)_7COOH$	0·02–0·16	0·02–0·16	0–0·21		
Stearic acid $CH_3(CH_2)_{16}COOH$	0·04–0·09	0·02–0·13	0–0·10		
Oleic acid $CH_3(CH_2)_7CH{:}CH(CH_2)_7COOH$	0·01	0·02	0		
Linoleic acid $CH_3(CH_2)_4CH{:}CHCH_2CH{:}CH(CH_2)_7COOH$	0·01	0·01	0		
	mg./l. (1000–2500 m.)				
Fatty acids with:					
12 C-atoms	0·0003–0·02			Williams (1961)	Pacific Ocean coastal water
14 C ,,	0·0004–0·013				
16 C ,,	0·0027–0·0200				
16 C ,, + 1 double bond	0·0003–0·003				
18 C ,,	0·0037–0·0222				
18 C ,, + 1 double bond	0·0053				
18 C ,, + 2 double bonds	0·0000–0·0029				
20 C ,,	traces–0·0031				
22 C ,,	traces–0·0014				
Acetic acid CH_3COOH Lactic acid $CH_3CH(OH)COOH$ Glycollic acid $HOCH_2COOH$	mg./l. < 1·0			Koyama and Thompson (1959)	Pacific Ocean
Malic acid $HOOCCH(OH)CH_2COOH$	0·28			Creac'h (1955)	Atlantic coastal water
Citric acid $HOOCCH_2C(OH)(COOH)CH_2COOH$	0·14				
Carotenoids and brownish waxy or fatty matter	2·5			Johnston (1955) Wilson and Armstrong (1955)	North Sea English Channel
IV. Biologically active compounds (see also Provasoli, 1963)					
Organic Fe compound(s)				Harvey (1925)	Deep sea water
Vitamin B_{12} (Cobalamine) $C_{63}H_{88}O_{14}N_{14}PCo$	3·4–1·6 mµg./l.			Vishniak and Riley (1961)	Long Island Sound
Vitamin B_{12}	0·2 mµg./l. (summer) 2·0 mµg./l. (winter)			Cowey (1956)	Oceanic surface-water
Vitamin B_{12}	0·2–5·0 mµg./l.			Daisley and Fisher (1958)	
Vitamin B_{12}	0–2·6 mµg./l.			Kashiwada *et al.* (1957)	North Pacific Ocean
Vitamin B_{12}	0–0·03 mµg./l.			Menzel and Spaeth (1962)	Sargasso Sea 0–05 m.
Thiamine (Vit. B_1) $C_{12}H_{18}ON_4SCl_2$	0–20 mµg./l.			Cowey (1956)	Surface water, possibly from land drainage
Plant hormones (auxins)	3·41 mµg./l.			Bentley (1960)	North Sea near Scotland
V. Humic acids					
"Gelbstoffe" (Yellow substances) Melanoidin-like				Kalle (1949, 1962) Jerlov (1955) Armstrong and Boalch (1961a,b)	Coastal waters
VI. Phenolic compounds					
p-Hydroxy-benzoic acid HOC_6H_4COOH	1–3 µg./l.			Degens *et al.* (1964)	Pacific off California
Vanillic acid $CH_3(HO)C_6H_3COOH$	1–3 µg./l.				
Syringic acid $(CH_3O)_2(HO)C_6H_2COOH$	1–3 µg./l.				
VII. Hydrocarbons					
Pristane; (2, 6, 10, 14-tetramethylpentadecane)	tr.			Blumer *et al.* (1963)	Cape Cod Bay

tr. = trace
det. = detected
– = not detected
? = possibly present

From: Duursma (1965, p. 454–455)

Table VII-3

Distribution of Organic and Inorganic Fractions in Suspended Particulate Matter

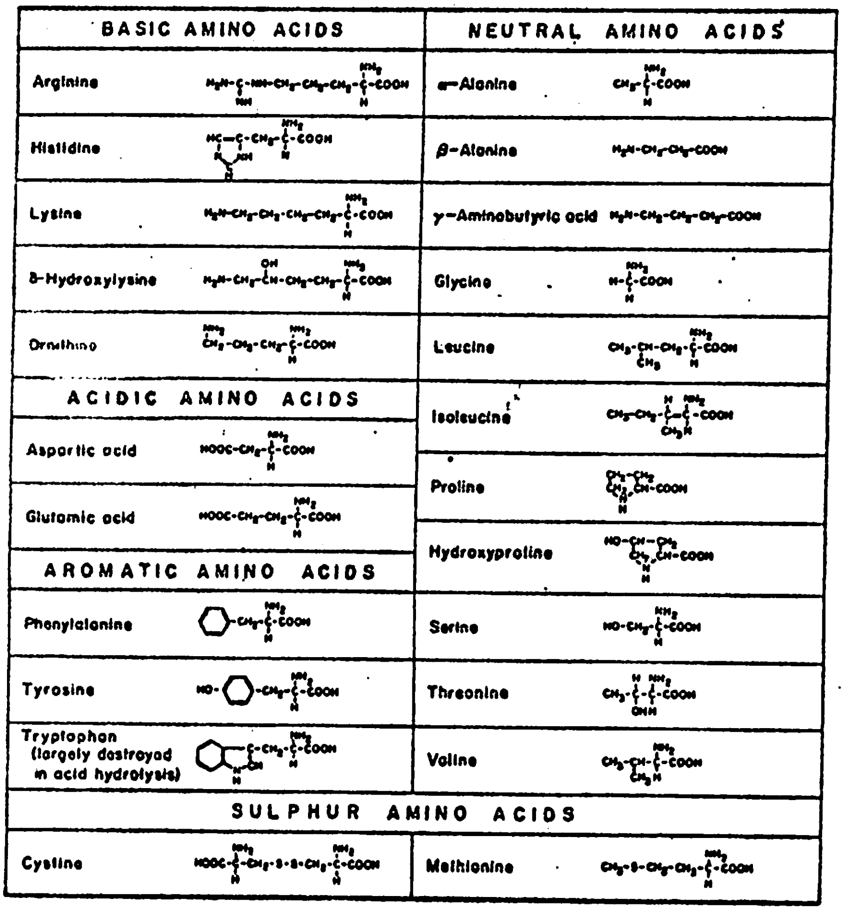
Area	Total Suspended Matter mg/ℓ	% Organic Matter	Reference
Offshore Pacific	10.5	62	Fox (1953)
Offshore Pacific	3.8	29	Fox (1953)
North Sea	6.0	27	Postma (1964)
Wadden Sea	18.0	14	Postma (1954)
Oceanic Average	0.8-2.5	20-60 *	Lisitzen (1959)
Bering Sea	2-4	--	Lisitzen (1959)
Indian Ocean	--	6-36 *	Lisitzen (1959)
Long Island Sound	2-7	20-45	Riley (1959)
Wilmington Canyon-East Coast U.S.A.	0.13-1.11	10-68	Lyall and others (1971)

* cx2 = dry organic matter

From: Parsons, 1963, p. 220.

~~Table~~ Fig VII-3

Table 14 AMINO ACIDS COMMONLY FOUND IN SEDIMENT AND SOIL HYDROLYSATES.



BASIC AMINO ACIDS		NEUTRAL AMINO ACIDS	
Arginine	$H_2N-\underset{NH}{C}-NH-CH_2-CH_2-CH_2-\overset{NH_2}{\underset{H}{C}}-COOH$	α-Alanine	$CH_3-\overset{NH_2}{\underset{H}{C}}-COOH$
Histidine	$HC=C-CH_2-\overset{NH_2}{\underset{H}{C}}-COOH$	β-Alanine	$H_2N-CH_2-CH_2-COOH$
Lysine	$H_2N-CH_2-CH_2-CH_2-CH_2-\overset{NH_2}{\underset{H}{C}}-COOH$	γ-Aminobutyric acid	$H_2N-CH_2-CH_2-CH_2-COOH$
δ-Hydroxylysine	$H_2N-CH_2-\overset{OH}{C}H-CH_2-CH_2-\overset{NH_2}{\underset{H}{C}}-COOH$	Glycine	$H-\overset{NH_2}{\underset{H}{C}}-COOH$
Ornithine	$\overset{NH_2}{C}H_2-CH_2-CH_2-\overset{NH_2}{\underset{H}{C}}-COOH$	Leucine	$CH_3-\underset{CH_3}{CH}-CH_2-\overset{NH_2}{\underset{H}{C}}-COOH$
ACIDIC AMINO ACIDS		Isoleucine	$CH_3-CH_2-\overset{H}{\underset{CH_3}{C}}-\overset{NH_2}{\underset{H}{C}}-COOH$
Aspartic acid	$HOOC-CH_2-\overset{NH_2}{\underset{H}{C}}-COOH$	Proline	$CH-COOH$
Glutamic acid	$HOOC-CH_2-CH_2-\overset{NH_2}{\underset{H}{C}}-COOH$	Hydroxyproline	$HO-CH-CH_2$ $CH-COOH$
AROMATIC AMINO ACIDS			
Phenylalanine	$-CH_2-\overset{NH_2}{\underset{H}{C}}-COOH$	Serine	$HO-CH_2-\overset{NH_2}{\underset{H}{C}}-COOH$
Tyrosine	$HO-\quad-CH_2-\overset{NH_2}{\underset{H}{C}}-COOH$	Threonine	$CH_3-\overset{H}{\underset{OH}{C}}-\overset{NH_2}{\underset{H}{C}}-COOH$
Tryptophan (largely destroyed in acid hydrolysis)	$C-CH_2-\overset{NH_2}{\underset{H}{C}}-COOH$	Valine	$CH_3-\underset{CH_3}{CH}-\overset{NH_2}{\underset{H}{C}}-COOH$
SULPHUR AMINO ACIDS			
Cystine	$HOOC-\overset{NH_2}{\underset{H}{C}}-CH_2-S-S-CH_2-\overset{NH_2}{\underset{H}{C}}-COOH$	Methionine	$CH_3-S-CH_2-CH_2-\overset{NH_2}{\underset{H}{C}}-COOH$

From: Degens (1965, p. 214)

A brief summary of organic partition in sea water is given below mainly from Degens (1965).

Carbohydrates:		
Chiefly sugars glucose, galactose, mannose	evenly distributed throughout water column	Total 15µg/ℓ
Nitrogenous Compounds:		
free-serine, ornithine, glycine	total evenly distributed (see Figure VII-3)	Total 10-100µg/ℓ
Lipids:		
Palmitic acid-Stearic acid, near surface related to plankton-with depth increase in saturation decrease in chain length	total apparently uniform with depth	total 10-100µg/ℓ
Gelbstoffe:		
Apparently melanodines produced from carbohydrates and proteins released by decomposition and not land derived phenol humic acid	decreases with increase in salinity	

From: Kalle, 1966.

Man's Contribution (From Carter, 1970)

The discharge of treated wastewater, primarily of sewage origin, constitutes a major contribution of organic matter to the marine environment. Representative concentrations of various organics in raw, primary and secondary treated sewage effluent are given later. The values shown indicate that some 27,000 lbs of grease are discharged to the ocean each day from both San Diego and Los Angeles County. San Francisco Bay area sewage contains 0.036 lb/cap/day grease and 0.0024 lb/cap/day floatables.

ORGANIC MATTER IN WASTE WATER

Characteristic	Tema Raw	L. A. Primary	A. D. Primary	L. A. Secondary
Flow, MGD	1.46	216	80	107
BOD, mg/	280	157	201	13
TSS, mg/	219	936	146	-
Volatile, mg/	142	-	117	-
Grease, mg/	110	15	41	.04
Floatables, mg/	26.5	1.7	-	-

Over the past half century some 5 million tons of petroleum oil are reported spilled to the sea (Pilpel, 1968). Some of this oil dissolves into the sea water. Folowing the Torrey Canyon spill the hydrocarbon levels in the English Channel rose from the usual level of 0.003 ppm to 0.007 - 0.014 ppm at the end of April 1967 and 0.004 - 0.009 ppm at the end of May 1967 (Smith, 1968). The soluability of petroleum in water is increased by the presence of higher weight organic acids (Baker, 1958) and possibly other compounds.

According to (Dzyuben 1958) the microbial oxidation of oil at sea may proceed 10 times faster than auto-oxidation. The rate of oxidation of floating oil under aerobic conditions may be as high as 0.5 g/day per m^2 of oil surface exposed to the particular organism. The addition of nitrogen and phosphorus may increase this rate (Chemical and Engineering News, 7 September 1970).

Organic Mineralization and Organic Extraction of Trace Elements from Sea Water

The principal elements in organic matter are carbon, nitrogen, and phosphorous. In general these elements are recycled through sea water in various links of the food web. However, organisms also have the ability to abstract carbon and phosphorous and other elements from sea water for use as hard parts as bones, teeth, spicules, etc. or in the life process in coelomic fluid, blood, enzymes, etc. The first process, by which organisms cause precipitation of mineral matter, has a pronounced effect on the chemistry of sea water as the constituent elements of the biologically produced mineral are often abstracted from sea water which is thermodynamically undersaturated with respect to that mineral. As the organically produced mineral is of various composition due to solid solution, and various sizes and shapes its behavior and solubility as a dead particle varies. For example Chave and Schmaltz (1966) noted (a) magnesium calcites have four times the activity of pure calcite, and (b) calcite 10^{-6}cm in diameter has eight times the activity of 1cm particles. Such features make equilibrium calculations extremely difficult if not impossible. The effect of organic mineralization is to give the utilized elements shorter residence times in sea water than would be predicted by equilibrium calculations.

Organisms produce precipitation by the interaction of the surrounding fluid, in this case sea water, with an organic template. As the organic chains have numerous positions for side radicals (see Figure VII-4, 5). By appropiate arrangement along the chain it is possible to have both negative and positive charge deficiencies so that cations and anions from sea water may be attracted. The organic chain may be contourted such that cations and anions of appropiate size can be attracted to produce the required mineral within the tissue. Table VII-4 lists the major minerals utilized by marine organisms and the corresponding template tissue.

For mineralized hard parts in direct contact with sea water the organism often secretes an organic film as a protection against solution in undersaturated waters. For example the outer layer of periostracum of mollusk shells is a nitrogenous-chitin like compound overlaying the carbonate layers.

The second process, by which organisms abstract elements, is for inclusion in organic radicals useful in the life process. Usually these organic compounds

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Figure VII-4

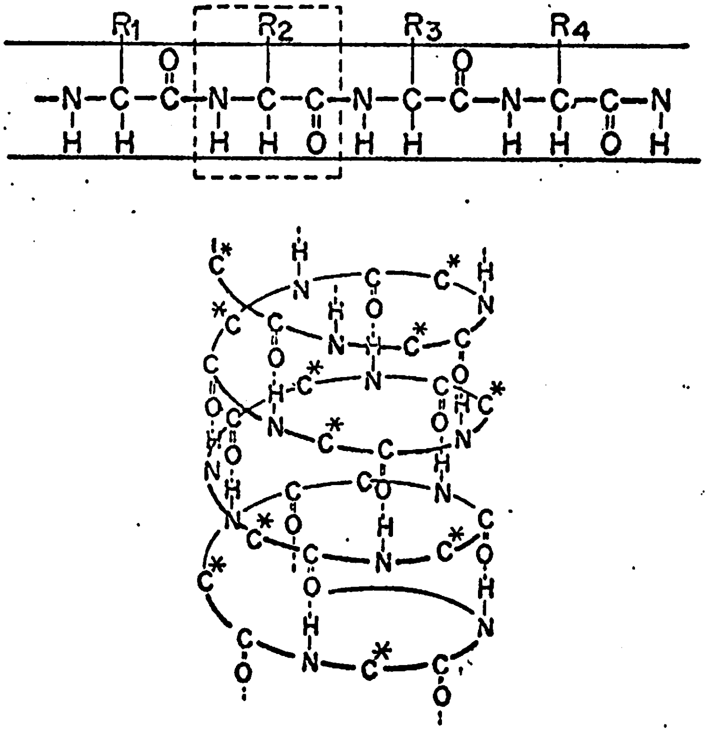

Fig. 45 Protein structure. Simple structural principles; variety of chemical reactivity (after Calvin, 1961)

From: Degens (1965, p. 214)

Table VII-4

Table 15 EXAMPLES OF BIOLOGICALLY MINERALIZED TISSUES (AFTER GLIMCHER, 1960).

Species	*Tissue Mineralized*	*Mineral Form*	*Major Organic-Matrix Components*
Plants	Cell wall	Calcite	Carbohydrates (Cellulose, Pectins), Lignins
Microorganisms	Exoskeleton	Amorphous Silica	Carbohydrates (Pectins)
		Calcite, Aragonite	(?)
		Celestite	(?)
Mollusks	Exoskeleton	Calcite, Aragonite	Protein (Conchiolin)
Arthropods	Exoskeleton	Calcite	Carbohydrate (Chitin), Protein
Vertebrates	Exoskeleton		
	Bone	OH-Apatite	Protein (Collagen)
	Cartilage	OH-Apatite	Protein (Collagen) Carbohydrates (Mucopolysaccharides)
	Tooth		
	Dentin	OH-Apatite	Protein (Collagen)
	Cementum	OH-Apatite	Protein (Collagen)
	Enamel	OH-Apatite	Protein (Eukeratin)

Figure VII-5

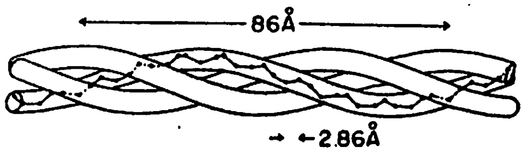

Fig. 51 A segment of the collagen structure. The tubes represent the space filled by polypeptide chains each of which extends about 3000 A. The amino acid residues are 2.86A apart and lie along a minor helix with a pitch of 8.6 A (three residues per turn). Each chain is coiled into a major helix with a pitch of 86 A. (after Piez, 1963)

From: Degens (1965, p.220- table and p. 221 - figure) are in fluids or soft parts so elements utilized return repidly to sea water as the organism dies or is eaten. Thus this process has little effect on the residence time in sea water of the metabolic elements.

Truly marine organisms, that is phyla that always have been marine have a salt composition of their body fluids very similar to that of present sea water. However, marine organisms that have land dwelling or air breathing precursors as the marine fishes and marine mammals have a modified body fluid chemistry generally shown by a much lower sodium content. Table VII-5 shows Vinogradov's compilation of the salt content of body fluids.

Specilized organisms also take up trace elements metabolically. For example, many species of crustacea use copper in haemocyamin, tunicate body fluids are rich in vanadium, and _Cyanea_ contains 1.5g zinc per kilogram dry weight. (Harvey, 1963, p. 29-30). Sea weed shows enrichment of Zn, Mo, Co, Ni, Pb, V, Ti, and Cr with respect to sea water as well as enrichment in iodine. As most of these elements are in soft parts there is little effect on their long term chemistry in sea water. However, Harvey (1963, p. 28) noted seasonal changes in copper concentration in the English Channel which could be related to uptake by animals grazing during plankton blooms or to uptake by phytoplankton themselves.

Table VII-5

COMPARATIVE SALT COMPOSITION OF BLOOD, COELOMIC FLUID, AND SO FORTH (IN G PER L)

ORGANISM	Comments	−Δ°c	Organic matter	Inorganic matter	Na	K	Ca	Mg	Cl	SO_4	Author
Brachiopoda*											
Vermes											
Sipunculus nudus		—	—	—	—	0.49	0.47	1.007	23.60	—	Bethe and Berger, 1931
″ ″		—	—	—	—	0.578	0.496	1.922	22.91	—	Bialaszewicz, 1933
Arenicola claparedii		—	—	—	—	0.676	0.601	1.491	22.27	—	″ ″
Aphrodite aculeata		—	—	—	—	0.492	0.453	1.396	20.07	—	″ ″
Echinodermata											
Paracentrotus lividus	♂; haemolymph	2.01	8.94	32.08	—	0.488	1.156	—	20.26	—	Pora, 1936-c
Paracentrotus lividus	♀	2.02	10.29	29.19	—	0.497	0.914	—	20.0	—	″ ″
Paracentrotus lividus		—	—	—	—	0.496	0.52	1.267	21.98	—	Bialaszewicz, 1933
Astropecten aurantiacus		—	—	—	—	0.566	0.570	1.313	23.40	—	″ ″
Sphaerechinus granularis		—	—	—	—	0.496	0.512	1.298	21.95	—	″ ″
Holothuria tubulosa		—	—	—	—	0.534	0.558	1.456	23.08	—	″ ″
Echinus esculentus		—	—	—	10.22	0.374	0.399	1.223	18.59	2.601	Robertson, 1939
″ ″	Coelomic fluid	—	—	—	12.20	0.522	0.513	1.23	19.40	—	Bethe and Berger, 1931
″ ″	Ambulacral fluid	—	—	—	12.00	0.753	0.606	1.21	19.61	—	″ ″
Mollusca											
Doris tuberculata		—	—	—	11.80	0.588	0.505	1.39	18.75	—	″ ″
Aplysia punctata		—	—	—	13.50	0.471	0.535	1.30	22.17	—	″ ″
Helix pomatia	Terrestrial	—	—	—	1.37	0.184	0.166	0.019	1.98	—	Lustig, Ernst and Reuss, 1937
″ ″	Winter	—	—	—	1.58	0.182	0.262	0.049	2.77	—	″ ″
Mytilus edulis		—	—	—	10.35	0.35	0.46	—	19.20	—	Bethe and Berger, 1931
Pinna nobilis		—	—	—	—	0.643	0.608	1.44	22.59	—	Bialaszewicz, 1933
Sepia officinalis		2.04	—	—	—	—	—	—	—	—	Pora, 1936-c
Enteropneusta*											
Arthropoda											
Palinurus vulgaris		—	—	—	14.20	1.078	1.11	0.369	21.60	—	Bethe and Berger, 1931
Palinurus interruptus		2.19	—	—	12.21	0.470	0.78	0.25	—	—	Schlatter, 1941
Carcinus moenas		—	—	—	13.27	0.293	0.498	0.646	19.28	—	Bethe and Berger, 1931
″ ″		—	—	—	—	—	0.611	1.19	22.98	—	Bialaszewicz, 1933
Hyas araneus		—	—	—	11.72	0.507	0.467	0.91	18.40	—	Bethe and Berger, 1931
Portunus depurator		—	—	—	9.80	1.15	0.476	—	18.00	—	″ ″

* Data are lacking. See also Table 267.

From: Vinogradov (1953, p. 584)

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Table VII-5 cont.

	Comments	−Δ°c	Organic matter	Inorganic matter	Na	K	Ca	Mg	Cl	SO_4	Author
Eriocheir sinensis . .	Fresh .	—	—	—	11.30	0.39	0.565	—	15.50	—	Bethe and Berger, 1931
„ „ . . .	„ .	1.21	—	—	7.56	—	0.722	—	19.05	—	Drilhon-Courtois and Portier, 1939
Eriphia spinifrons		—	—	—	—	0.69	0.566	0.475	22.0	—	Bethe and Berger, 1931
Cambarus clarkii . .	Fresh	0.68	—	—	3.69	0.225	0.49	0.049	—	—	Schlatter, 1941
Pachygrapsus crassipes		1.83	—	—	10.60	0.355	0.54	0.24	—	—	„ „
Homarus vulgaris		—	—	—	11.46	0.778	0.71	0.10	18.45	—	Bethe and Berger, 1931
„ „		—	—	—	11.71	0.555	0.587	0.173	18.26	0.762	Robertson, 1939
Cancer pagurus		—	—	—	11.55	0.468	0.552	0.658	18.08	2.306	„ „
„ „		—	—	—	12.45	0.715	0.49	0.661	18.35	—	Bethe and Berger, 1931
Maja squinada		2.028	—	—	—	0.768	0.83	—	19.3	—	Pora, 1936-e
„ „		—	—	—	13.55	1.365	1.086	1.068	22.0	—	Bethe and Berger, 1931
„ „		—	—	—	—	0.523	0.493	1.49	22.26	—	Bialaszewicz, 1933
Maja verrucosa		—	—	—	—	—	0.490	1.351	22.90	—	Bethe and Berger, 1931
Potamobius fluviatilis .	Fresh	0.81	—	—	—	0.240	0.342	0.062	6.84	—	Scholles, 1933
„ „ .	„	—	—	—	3.00	0.141	0.42	—	7.00	—	——
Telphusa fluviatilis		1.16	—	—	7.75	0.330	0.723	—	17.5	—	Drilhon-Courtois and Portier, 1939
Tunicata											
Phallusia mammillata		—	—	—	—	0.854	0.570	1.45	24.47	—	Bialaszewicz, 1933
Ciona intestinalis		—	—	—	—	0.504	0.52	1.316	23.54	—	„ „
Cyclostomata*											
Pisces											
Raja erinacea . . .	Marine elasmobranch	—	—	—	5.84	0.312	0.480	0.120	9.45	—	Hartman, Lewis, Shelden and Walther, 1941
Pristis microdon . .	Freshwater elasmobranch	1.02	—	—	—	—	—	—	6.03	None	Smith, 1931
Lophius piscatorius .	Marine teleost	—	—	—	4.62	0.273	0.14	0.024	6.73	0.11	Smith, 1929-b
Cyprinus carpio . . .	♂; Freshwater teleost	—	—	—	3.09	0.18	0.09	—	5.65	—	Pora, 1935-b
Mammalia											
Balaenoptera physalus .	4; marine	—	—	—	3.30	0.227	0.06	0.057	4.97	—	Okahara, 1925
Homo sapiens		—	—	—	3.00	0.25	0.09	0.03	3.80	—	——
Sea water		—	—	35.00	10.7	0.38	0.45	1.40	19.0	2.65	——
Fresh water		—	—	0.20	0.016	0.003	0.04	0.007	0.01	0.024	——

* Data are lacking. See also Table 267.

From: Vinogradov (1953, p. 585)

Bacteria Influence on The Composition of Sea Water

Three types of specific element fixing bacteria have been reported for the marine environment: (1) nitrogen fixing, (2) sulfur reducing, and (3) manganese fixing. Except for nitrogen fixing most of these bacterial processes occur in the bottom. Sulfur reducing bacteria are restricted to anoxic basins thus would not influence the sulfur composition in the well ventilated open ocean. Manganese fixing bacteria may have an important role in the formation of ferromanganese nodules and thus aid in the shortening of the residence time for Fe and Mn. However, the major role of bacteria is not removal of elements from sea water but decomposition of organic matter to simple compounds thus returning elements to sea water.

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CE 201 B

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TRACE IONS IN SEA WATER

I. Metallic Ions - As discussed in Goldberg (1965) the metallic complexing in sea water can be based on the classification of Schwarzenbach (1961):

(a) Metal ions with a rare gas configuration (d^o cations): - the alkali metals, alkaline earths, Al, Sc, lanthanides, Ti, Th, and Nb.

(b) 18 electron outer shell cations (d^{10}): - Ag^+, Zn^{++}, Ga^{+++}, and Sn^{++++}.

(c) Transition metals where d electrons are greater than zero but less than 10: Mn^{++}, Fe^{++}, Co^{++}, and Ni^{++}.

To determine the dominant anion for any metal cation M consider: -

$$K_i = \frac{A_{Mi}}{A_M A_i} \qquad \text{for anion } i$$

$$K_j = \frac{A_{Mj}}{A_M A_j} \qquad \text{for anion } j$$

for

$$\text{then } \frac{K_i}{K_j} = \frac{A_{Mi}\ A_M\ A_j}{A_{Mj}\ A_M A_i} \qquad \text{if } \frac{K_i}{K_j} > \frac{A_j}{A_i} \text{ then } M_i \text{ dominant}$$

also for $\log K_i - \log K_j > \log A_j - \log A_i$

but if $\frac{K_i}{K_j} < \frac{A_j}{A_i}$ then M_j dominant

also for $\log K_i - \log K_j < \log A_j - \log A_i$

Table VIII-1 gives log K anion constants for various cations. For conservative anions in sea water such as Cl^-, $SO_4^=$, Br^-, F^-, and OH^- their ratios also would be constant and easily calculated from concentration data if δ_i were known. Goldberg (1965, p. 170) uses the assumption:

$$\delta^o = 1$$
$$\delta^{\pm} = 0.7$$
$$\delta^{\pm\pm} = 0.1$$

Table VIII-1

Stability constants for complexes of the alkaline earth metals with fluoride and hydroxyl ions (Bjerrum et al., *1958). Temperatures between 18 and 25°C. Values at zero ionic strength, except for Be*

	log K_F	*log* K_{OH}
Be	4·29	10·28
Mg	1·82	2·1–2·6
Ca	<1·04	1·29–1·51
Sr	—	0·82–0·96
Ba	<0·45	0·64 0·85

Values of log K_{OH}, K_{SO_4} *and* K_{Cl} *for some* d^{10} *ions (from Bjerrum* et al., *1958). Corrected to zero ionic strength where the data are available*

Species	*log* K_{OH}	*log* K_{Cl}	*log* K_{SO_4}	*log* $K_{Cl}-$ $-$*log* K_{OH}	*log* $K_{Cl}-$ $-$*log* K_{SO_4}	*log* $K_{SO_4^-}$ $-$*log* K_{Cl}
Ag^+	2·3	3·1	1·3	0·8	1·8	0·5
Cd^{2+}	5·5	2·0	2·3	−3·5	−0·3	5·8
Hg^{2+}	11·5	7·3	1·4	−4·2	5·9	5·6
Zn^{2+}	4·4	−0·5	2·3	−4·9	2·8	7·2
Cu^{2+}	6·3	0·4	2·3	−5·9	1·9	8·2
Pb^{2+}	7·8	1·5	—	−6·3	—	—

Log stability constants for the "Irving-Williams" order

Chelating agent	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
EDTA	14	14	16	18	19	16
Malonic acid	3·3	—	3·7	4·0	5·8	3·5
Ethylenediamine	2·7	4·3	5·9	7·9	10·5	6·0
Nitrilotriacetic acid	7·4	8·3	10·5	11·4	12·8	10·5
Cystine	4·1	6·2	9·3	—	—	8·84
8-Hydroxyquinoline	6·8	8·0	9·1	9·9	12·2	8·5

From: Goldberg (1965, p. 168, p. 17)

for example for Hg^{++}

$$[Hg] \cong 10^{-10}M \text{ (chapter II- p. 2)}$$

$$\log A_{OH} = (-.16) + (-5.9) \approx -6.0$$

$$\log A_{C\ell} = (-.16) + (-.5) \approx -0.7$$

$$\log A_{SO_4} = (-.1) + (-1.5) \approx -2.5$$

$$\log A_{OH} - \log A_{C\ell} = -6.0 + 0.7 = -5.3$$

$$\log A_{SO_4} - \log A_{C\ell} = -2.5 + 0.7 = -1.8$$

$$\log A_{OH} - \log A_{SO_4} = -6.0 + 2.5 = -3.5$$

From Table VIII-1 for Hg

$$\log K_{C\ell} - \log K_{OH} > \log A_{OH} - \log A_{C\ell} \quad \text{as} \quad -4.2 > -5.3$$

so $HgCl^-$ species dominant over $HgOH^-$

$$\log K_{C\ell} - \log K_{SO_4} > \log A_{SO_4} - \log A_{CL} \quad \text{as } 5.9 > -1.8$$

so $HgCl^-$ species dominant over $HgSO_4^o$ but:

$$\log K_{SO_4} - \log K_{OH} < \log A_{OH} - \log A_{SO_4} \quad \text{as} -10.1 < -3.5$$

so $HgOH^-$ dominant over $HgSO_4^o$

Krauskopf (1956) looked at the metals in sea water from the viewpoint of undersaturation, that is amount of a metal added to sea water to form a precipitate with the amount found in sea water (Table VIII-2). There are many non-representative features in this approach for example (1) the temperature and pressure were surface values, (2) no organisms or particulate phases were present which would give uncertainties to the results. However, the values should show the orders of magnitude of undersaturation.

A possible explanation of the high degree of undersaturation is suggested in Table VIII-3 which shows the concentration by organisms of various ions. The organisms with the variations in their life cycle would not buffer the system uniformily thus this could be a partial explanation of the non-conservancy of this cations.

Table VIII-2

Comparison of calculated and observed concentrations of metals at saturation with the observed concentrations in sea water. Adapted from Krauskopf (1956)

Metal	*Insoluble compound*	*Solubility product*	*Concentration of element in saturated solution (mg./l.)*		*Concentration of element in ocean water (mg./l.)*	*Ratio of measured saturated concentration of element to that in ocean water*	*Residence time (years)*
			Calculated	*Measured*			
Pb	$PbCO_3$	$1 \cdot 5 \times 10^{-13}$	0·01	0·3–0·7	0·00003	10,000–20,000	$2 \cdot 0 \times 10^{3}$
Ni	$Ni(OH)_2$	$1 \cdot 6 \times 10^{-16}$	150	20–450	0·002	10,000–225,000	$1 \cdot 8 \times 10^{4}$
Co	$CoCO_3$	$8 \cdot 0 \times 10^{-13}$	0·02	25–200	0·0005	50,000–400,000	$1 \cdot 8 \times 10^{4}$
Cu	$CuCO_3$	$2 \cdot 5 \times 10^{-10}$	5·7	0·4–0·8	0·003	133–266	$5 \cdot 0 \times 10^{4}$
Ba	$BaSO_4$	$1 \cdot 0 \times 10^{-10}$	0·03	0·11	0·03	3·7	$8 \cdot 4 \times 10^{4}$
Zn	$ZnCO_3$	$2 \cdot 0 \times 10^{-10}$	4·6	1·2–2·5	0·01	120–250	$1 \cdot 8 \times 10^{5}$
Cd	$Cd(OH)Cl$	$3 \cdot 2 \times 10^{-11}$	105	4–1000	0·0001	40,000–10,000,000	$5 \cdot 0 \times 10^{5}$
Ca	$CaCO_3$	$5 \cdot 0 \times 10^{-9}$	70	100–480	400·0	0·25–1·2	$8 \cdot 0 \times 10^{6}$
Sr	$SrCO_3$	$3 \cdot 16 \times 10^{-10}$	9–44	22	8·0	2·75	$1 \cdot 9 \times 10^{7}$
Mg	$MgCO_3$	$1 \cdot 0 \times 10^{-5}$	84,000	36,000	350·0	27	$4 \cdot 5 \times 10^{7}$

From: Goldberg (1965, p. 179)

Table VIII-3

Concentration factors of elements in marine organisms in relation to the stability of complexes formed by metal ions with a variety of ligands. The only intercomparisons which are valid are along horizontal lines (see text). Elements arranged in "Irving Williams" order, see p. 171.

	Metal									
Organisms	*Cu*	*Ni*	*Pb*	*Co*	*Zn*	*Mn*	*Mg*	*Ca*	*Sr*	*Ba*
Seaweeds (Black and Mitchell, 1952)	—	550	—	—	900	—	—	—	23	—
Benthic algae (Lowman, 1964)	—	2000–40,000	—	—	—	1000–30,000	—	—	—	—
Plankton (Nicholls *et al.*, 1960)	400–90,000	<20–3000	30–12,000	<100–16,000	—	—	—	—	—	—
Marine animals (F. G. Lowan, personal communication)	—	3000–70,000	—	—	—	2000–10,000	—	—	—	—
Anchovetta (Goldberg, 1962)	80	—	10,000	—	400	1000	0·1	7	8	20
Yellow fin tuna (Goldberg, 1962)	200	—	—	—	700	80	0·2	6	7	2
Skipjack tuna (Goldberg, 1962)	100	50	—	—	500	40	0·3	5	5	3
Sponges (Bowen and Sutton, 1951)	1400	420	—	50	—	—	—	0·07	3·5	—

From: Goldberg (1965, p. 185)

FROM PRINGLE AND OTHERS
(1969 p. 460)

TABLE 5.—TRACE METAL ACCUMULATION STUDIES IN A SIMULATED NATURAL ENVIRONMENTAL SYSTEM

Metal	Environmental Level, in parts per million	Values, in milligrams per kilogram		Total Accumulation, in milligrams per kilogram	Accumulation Time, in days	Accumulation Rates, in milligrams per kilogram per day	Species	Sea Water Temperature, in degrees Celsius
		Initial	Final					
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Copper	0.1	23	79	56	10	5.60	Soft Shell	20
Copper	0.2	15	85	70	25	3.00	Soft Shell (Toxic-poor condition)	20
Copper	0.05	35	200	165	8	20	Soft Shell	No Control (25-26)
Copper	0.5	6.5	8	1.5	25	0.06	Quahaug	No Control (10)
Zinc	0.2	10	27	17	50	0.36	Soft Shell	20
Cadmium	0.05	0	8 (3.8 in 4 weeks)	8	70	0.10	Soft Shell	20
Cadmium	0.1	0	9 (6.5 in 4 weeks)	9	56	0.16	Soft Shell	20
Lead	0.1	0	112	112	70	1.60	Soft Shell	20
Lead	0.2	0	235	235	40	5.80	Soft Shell	20
Lead	0.2	0	260 (220 in 70 days)	260	84	3.10	Soft Shell	20
Lead	0.2	0	35	35	56	0.63	Quahaug	20
Lead	0.025	0	17	17	49	0.35	Eastern Oyster	20
Lead	0.05	0	35	35	49	0.71	Eastern Oyster	20
Lead	0.1	0	75	75	49	1.50	Eastern Oyster	20
Lead	0.2	0	200	200	49	4.00	Eastern Oyster	20

FROM PRINGLE AND OTHERS, 1968, P. 460

From Pringle and others (1968, p. 458 & 469)

TABLE 2.—AVERAGE TRACE METAL LEVELS IN SHELLFISH TAKEN FROM ATLANTIC COAST WATERS, IN PARTS PER MILLION OF WET WEIGHT

Element	Eastern Oyster	Soft Shell Clam	Northern Quahaug
Zinc	1428	17	20.6
Copper	91.50	5.80	2.6
Manganese	4.30	6.70	5.8
Iron	67.00	405	30
Lead	0.47	0.70	0.52
Cobalt	0.10	0.10	0.20
Nickel	0.19	0.27	0.24
Chromium	0.40	0.52	0.31
Cadmium	3.10	0.27	0.19

TABLE 3.—RANGE OF TRACE METAL VALUES IN SHELLFISH HARVESTED FROM ATLANTIC AND PACIFIC WATERS, IN PARTS PER MILLION OF WET WEIGHT

Element	Oysters		Soft Shell Clam	Northern Quahaug
	East Coast, U.S.	West Coast, U.S.		
Zinc	180 - 4120	86 - 344	9.0 - 28	11.50 - 40.20
Copper	7.0 - 517	7.80 - 37.50	1.20 - 90	1.0 - 16.50
Manganese	0.14 - 15.0	0.90 - 16	0.10 - 29.90	0.7 - 29.70
Iron	31 - 238	15.30 - 91.40	49.70 - 1710	9.0 - 83.0
Lead	0.10 - 2.30	0.10 - 4.50	0.10 - 10.20	0.10 - 7.50
Chromium	0.04 - 3.40	0.10 - 0.30	0.10 - 5.0	0.19 - 5.80
Nickel	0.08 - 1.80	0.10 - 0.20	0.10 - 2.30	0.10 - 2.40
Cobalt	0.06 - 0.20	0.10 - 0.20	0.10 - 0.20	0.10 - 0.20
Cadmium	0.10 - 7.80	0.20 - 2.10	0.10 - 0.90	0.10 - 0.73

TABLE 8.—TRACE METAL ENRICHMENT FACTORS FOR SHELLFISH COMPARED WITH THAT OF THE MARINE ENVIRONMENT

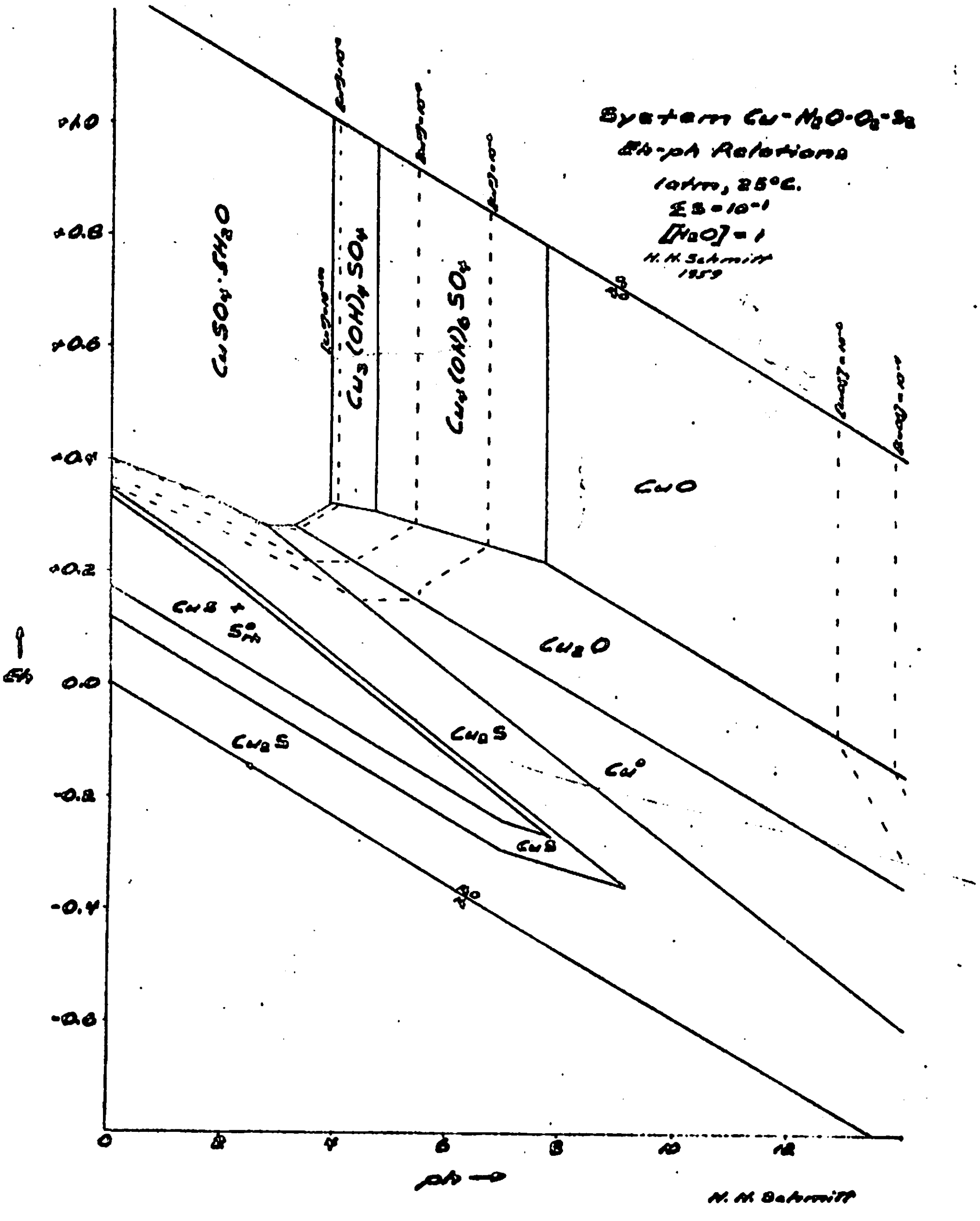
Element (1)	Oyster (2)	Quahaug (3)	Soft Shell Clam (4)	Surf Clam (5)	Mussel (6)	Whelk (7)
admium	318,000[a] 226,000	750	800	—	100,000[a] 800(2)	6,300
Chromium	60,000[a] 31,600	23,400	10,400	—	—	—
opper	13,700[a] 14,800	900	2,000	450	3,000[a] 1,150	3,800
ron	68,200[a] 6,700	3,000	41,000	18,400	196,000[a] 2,900	—
anganese	4,000[a] 2,900	2,900	3,350	1,100	13,500[a] 1,500	2,100
ickel	4,000[a] 3,250(1)	4,500	4,250	—	—	—
Lead	4,000[a] 4,100	5,800	3,400	—	—	—
inc	110,300[a] 148,000	2,100	1,700	1,525	9,100[a] 2,200	8,200

[a] Values from work of Brooks and Rumsby (5).

FROM PRINGLE AND OTHERS, 1968, p. 458 & 469

Another variable which would effect the presence of a particular ion in sea water is the oxidation-reduction state or Eh. Although the water column is reasonably well oxygenated near shore; locally in areas of high organic productivity reducting conditions exist. As shown in Figure VIII 1, 2, 2 a variable Eh with the buffered pH of sea water determines the metallic species in sea water and would be an inorganic control on solution or precipitation of particular ions.

Figure VIII-1



From: Schmitt (1962, p. 110)

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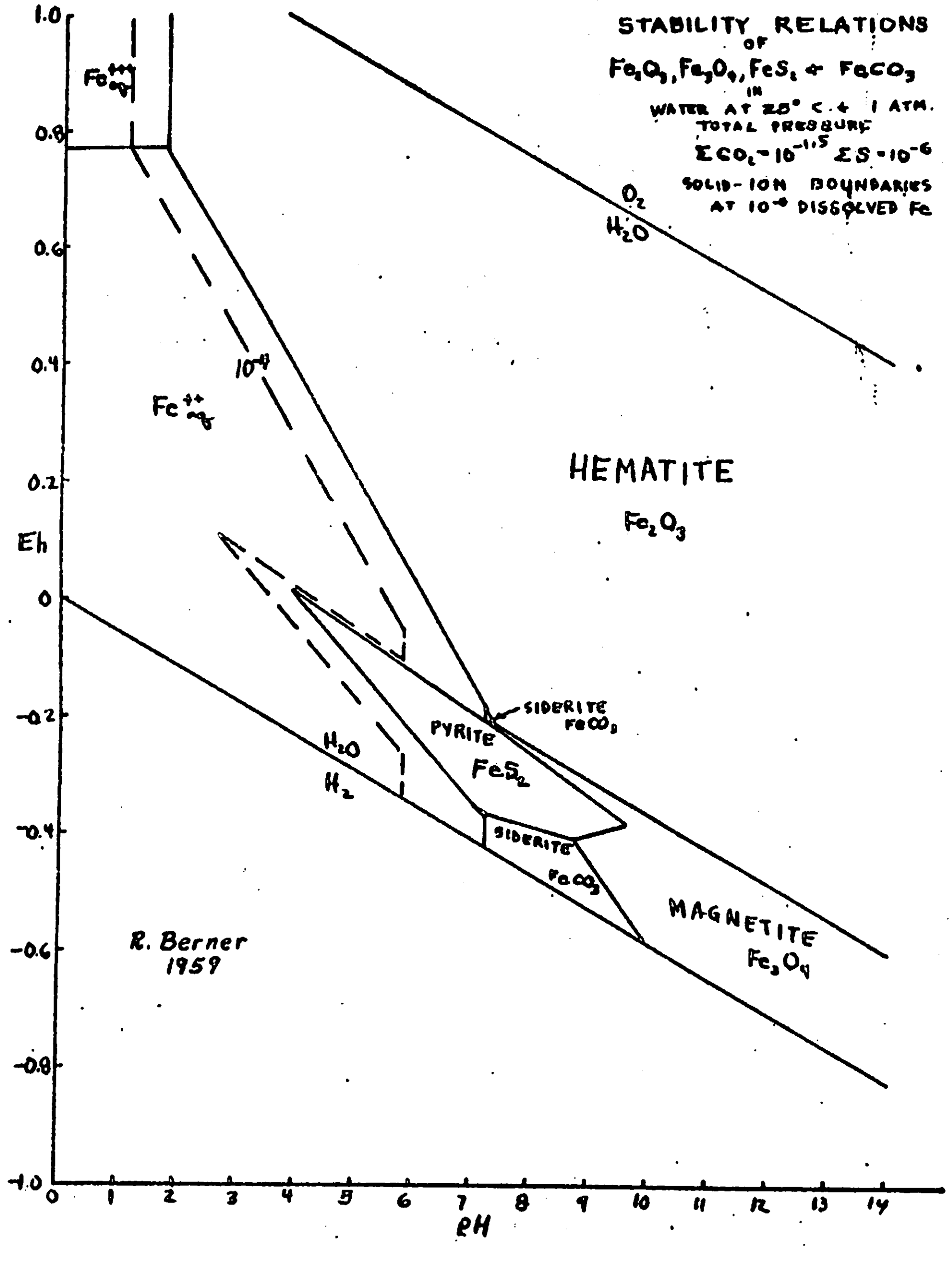
Figure VIII-2



From: Schmitt (1962, p. 76)

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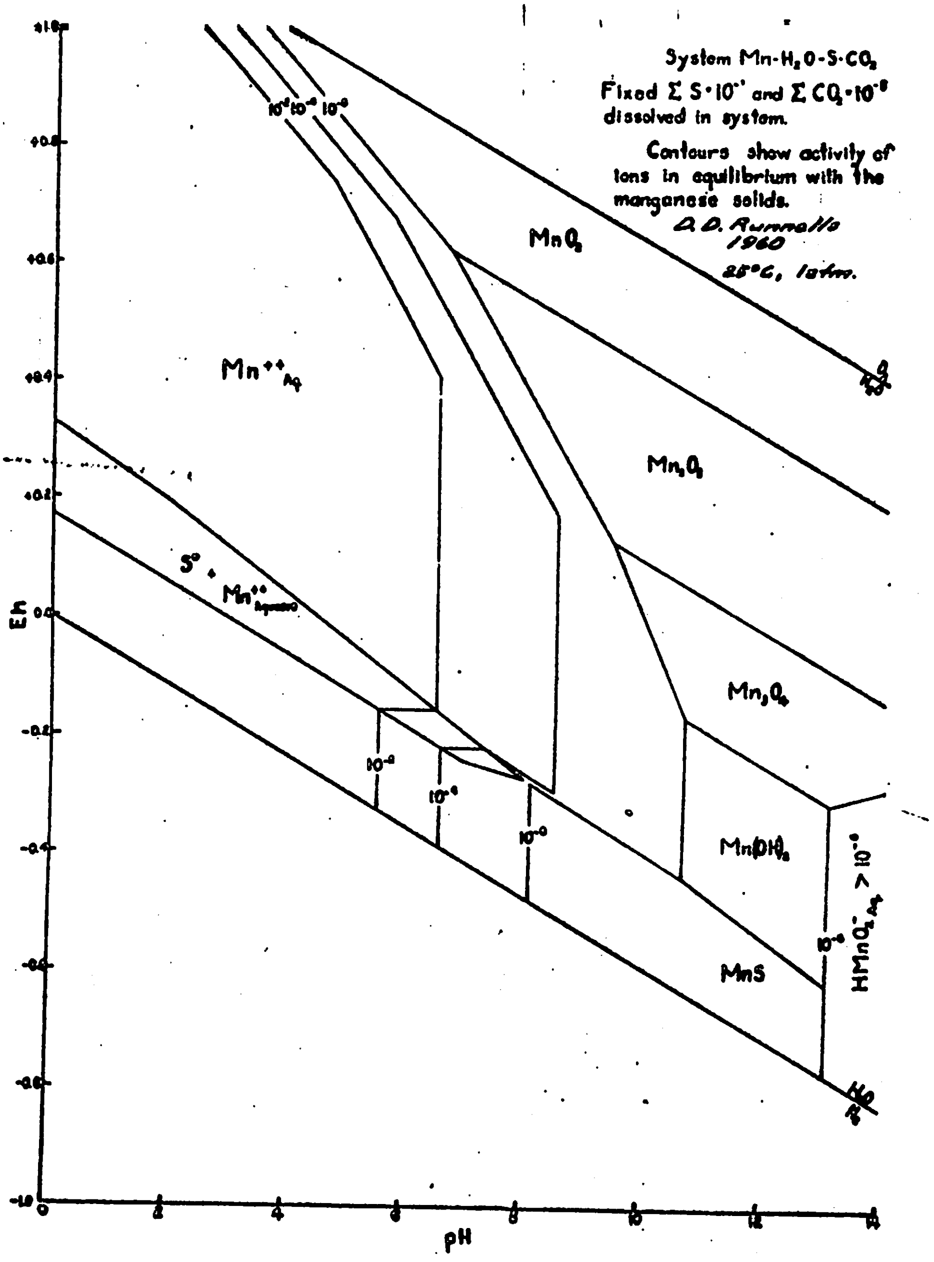
Figure VIII-3



From Schmitt (1962, p. 71)

Radioactive Isotopes in Sea Water

One group of trace elements in sea water, whose value is now being recognized, are the radioactive isotopes. Because of their ability to decay at a constant rate so that the amount present is a function of time, under favorable circumstances certain radioactive isotopes in sea water can be used as (1) tracers in vectorial ocean processes such as mixing or (2) as absolute daters of oceanic sediments and discrete water masses.

The characteristics an isotope must have to be useful in oceanographic work are (1) the half-life of the isotope must be in the same order of magnitude as the time constant of the process investigated. For example if the residence time of a water particle in a mixing process is on the order of 10^3 years an isotope with a half-life measured in days would be useless in following the mixing. (2) the amount of the isotope in sea water must be measurable. (3) the geochemistry of the element in sea water must be known adequately. Obviously if an isotope is precipitated or absorbed on solid particles it would be of little value in tracing water masses. (4) the biochemical cycle of the isotope must be known. Many organisms fractionate isotopes in their life processes such as oxygen as a function of te-perature. (5) the various decay series that produce the isotope and their productivity must be known. Ideally the most useful isotope is one which has only one parent. (6) the initial sources (atmosphere, erosion products from the land, etc.) and if possible the location of where the isotope was introduced into sea water must be known.

Two major types of isotopes are utilized in chemical oceanology: one - naturally occurring isotopes consisting of (a) long lived isotopes initially present at the formation of the earth (see Table VIII-4) and (b) short-lived isotopes that are continually being generated by natural processes (Table VIII-5-6). Two-artificial nuclides introduced indirectly by man through bomb tests or by nuclear wastes from atomic reactors or purposefully in tracer studies (Table VIII-7). Unfortunately the bomb test isotopes also include some such as ^{14}C and ^{3}H which were naturally occurring. This detracts from the usefullness of such isotopes as the natural equilibrium amounts have been augmented from the atomic tests.

Table VIII-4

Useful Naturally Occurring Nuclides

Long Half Lives

Parents Isotope	Half-Life (years)	% of Total Element	Radioactivity in Sea Water	Concentraction in Sea Water ($\mu g/\ell$)
K^{40}	$1.27x10^{9}$	0.0118%	324 pc/ℓ	4600
Rb^{87}	$4.7x10^{10}$	27.85	2.9 pc/ℓ	33
U^{238}	$4.51x10^{9}$	99.27	2.2 pc/ℓ	3.3
U^{235}	$7.1x10^{8}$	0.72		0.05
Daughters				surface
Ra^{226*}	$1.62x10^{3}$			$1x10^{-7}$
th^{230*}	$8.0x10^{4}$			$1x10^{7}$

*From U^{238} series

$$U^{238} \xrightarrow{\alpha} th^{234} \xrightarrow{\beta-} Pa^{234} \xrightarrow{\beta-} U^{234} \xrightarrow{\alpha}$$

$$th^{230} \xrightarrow{\alpha} Ra^{226} \xrightarrow{\alpha} Rn^{222} \xrightarrow{\alpha} Po^{218} \xrightarrow[\text{daughters}]{\text{short lived}} Pb^{210}$$

Table VIII-5

Steady-state fractional inventories and specific activities in sea water for nuclides produced by cosmic radiation

Nuclide	*Tritium*	*Silicon-32*	*Carbon-14*	*Beryllium-10*
Half-life	12·3 years	500 years[b]	5568 years[c]	2·5 × 10^6 years
Fraction of total inventory[a] in				
Stratosphere	0·068	0·0019	0·003	3·7 × 10^{-7}
Troposphere	0·004	0·00011	0·06[e]	2·3 × 10^{-6}
Mixed oceanic layer	0·50[d]	0·005	0·023	8 × 10^{-6}
Deep oceanic layer	0·43	0·95	0·91	1·4 × 10^{-4}
Oceanic sediments	0	0·04	0·01	0·999
Average specific activity in oceans[a] (d.p.m./g.)	3·3 × 10^{-4}	8 × 10^{-9}	10	1·6 × 10^{-9}

[a] The data on fractional inventories and specific activities are taken from Lal (1963a) who emphasizes their approximate nature.

[b] Value cited by Lal (1963a); Sullivan (1957) gives c. 700 years.

[c] The Fifth Radiocarbon Dating Conference at Cambridge (1962) considered that the best value for the half-life of ^{14}C is 5730 ± 40 years, but that "as a temporary expedient" ages should continue to be reported on the basis of the value given here (Godwin, 1962).

[d] Includes tritium in continental hydrosphere.

[e] Includes ^{14}C in biosphere and humus.

From: Burton (1965, p. 448)

Table VIII-6

Nuclides Produced in Atmosphere by Cosmic Radiation

		Half-life
Be^{10}:	${}_7N^{14}$ + cosmic rays $\longrightarrow {}_4Be^{10} + 3\,{}_1H^1 + {}_0n^1$	2.7×10^6 years
Si^{32}:	${}_{18}Ar^{40}$ + cosmic rays $\longrightarrow {}_{14}Si^{32} + 4\,{}_1H^1 + 4\,{}_0n^1$	7×10^2
C^{14}:	${}_7N^{14} + {}_0n^1 \longrightarrow 6C^{14} + {}_1H^1$	5.7×10^3
	${}_6C^{14} \xrightarrow{\beta-} {}_7N^{14}$	
H^3:		1.25×10^0

Table VIII-7

Principal artificial nuclides

(a) *Fission products*

Nuclide	*Half-life*	*Fission yield from fission of ^{235}U by thermal neutrons* (%)	*Radioactive daughter product*	*Half-life of daughter*
Strontium-89	50·4 days	4·8	—	—
Strontium-90	28 years	5·8	Yttrium-90	64·4 hours
Yttrium-91	58·0 days	5·8	—	—
Zirconium-95	63·3 days	6·3	Niobium-95	35 days
Ruthenium-103	41·0 days	3·0	Rhodium-103m	54 minutes
Ruthenium-106	1·0 years	0·4	Rhodium-106	30 seconds
Tellurium-129m	33·0 days	0·9	Tellurium-129	74 minutes
			Iodine-120	1·6 × 10^7 years
Caesium-137	30 years	6·0	Barium-137m	2·6 minutes
Cerium-141	32·5 days	6·0	—	—
Cerium-144	290 days	5·7	Praseodymium-144	17·5 minutes
			Neodymium-144	2 × 10^{15} years
Promethium-147	2·52 years	2·4	Samarium-147	1·3 × 10^{11} years

(b) *Induced activities*

Nuclide	*Half-life*	*Nuclide*	*Half-life*
Tritium	12·3 years	Iron-59	45·1 days
Carbon-14	5568 years*	Cobalt-57	270 days
Phosphorus-32	14·3 days	Cobalt-58	72·0 days
Sulphur-35	87·1 days	Cobalt-60	5·27 years
Chromium-51	27·8 days	Zinc-65	245 days
Manganese-54	300 days	Cadmium-113m	14 years
Iron-55	2·94 years		

From: Burton (1965, p. 459)

Ia Use of Long-Lived Natural Nuclides

As shown in Table VIII-4 most of the background radioactivity in sea water is due to K^{40} and to a lesser extent Rb^{87}. At present these nuclides are not used in the analyses of any sea water process. However, K^{40} and Rb^{87} decay processes have been used to date glauconite type clays (Hurley and others, 1960) as both K and Rb would be concentrated in clay interlayers. Other dating methods using the decay products of U^{235}, U^{238}, th^{232} have been proposed with limited success. Most of these methods are based in part on the fact that Th^{230} (ionium) has a very short half-life in sea water (35 years ± 35 years, Moore and Sackett, 1964) thus is very much depleted in sea water but enriched in sediments. Initially Ra^{226} was used to measure its parent Th^{232} but this method was abandoned because the high mobility of Ra^{226} in sediments gave spurious results. Also the Th^{230}: Th^{232} ratio was thought to be a potential dating method, however, there apparently is no simple sedimentary relation between natural Th^{232} and ionium Th^{230} which is a daughter product of U^{238} decay. Sackett (1964) demonstrated that the Th^{230}, Th^{232}, method measures the diffusion of Th^{230} in sediments and given too low ages as compared with C^{14}, Pa^{231}, Th^{230} has been proposed as a sedimentaty dating method (Rosholt and others, 1961) as the parents of these isotopes U^{235}, and U^{238} respectively have a constant ratio in sea water. As both the daughter isotopes have short residence times in sea water (140 ± 70 years: Pa^{231}) and (35 ± years: Th^{230}) they would be concentrated in sediments. However, at noted above Th^{230} migrates in sediments thus adding uncertainty to Pa^{231}: Th^{230} dates.

The fickleness of Th^{230} may prove an asset for dating sea water processes. The very short residence time of Th^{230} means its very soluble daughter product Ra^{226} is introduced into sea water almost exclusively at the bottom whereas most nuclides presently used in examining sea water processes are added at the surface such as C^{14}. Koczy (1956) proposed that Ra^{226} be used to investigate the eddy diffusivity of sea water. However not enough measurements have been made to test this idea.

Ib Atmospheric Natural Nuclides

Table VIII 5 and 6 list pertinent data on nuclides produced by cosmic bombardment of elements in the upper atmosphere. Presently only C^{14} is used extensively in (1) tracing water movements and (2) dating marine sediments.

C^{14} ages of deep water masses average about 650 years for the North Atlantic; 300 years for Atlantic water originating in the Antarctic; and 1000 years for the oldest water in the Pacific. As Table VIII-5 shows the activity of C^{14} is much higher than the other atmospherically produced nuclides. Thus counting C^{14} is simplier and yields more relaible results with a relatively small volume of water.

H^3 and Si^{32} methods to trace circulation suffer because of their low specific activity. Thus much more sea water is utilized in the counting process for these isotopes. Obtaining the large volumes necessary to count these isotopes becomes an almost insuperable problem for other than surface measurements.

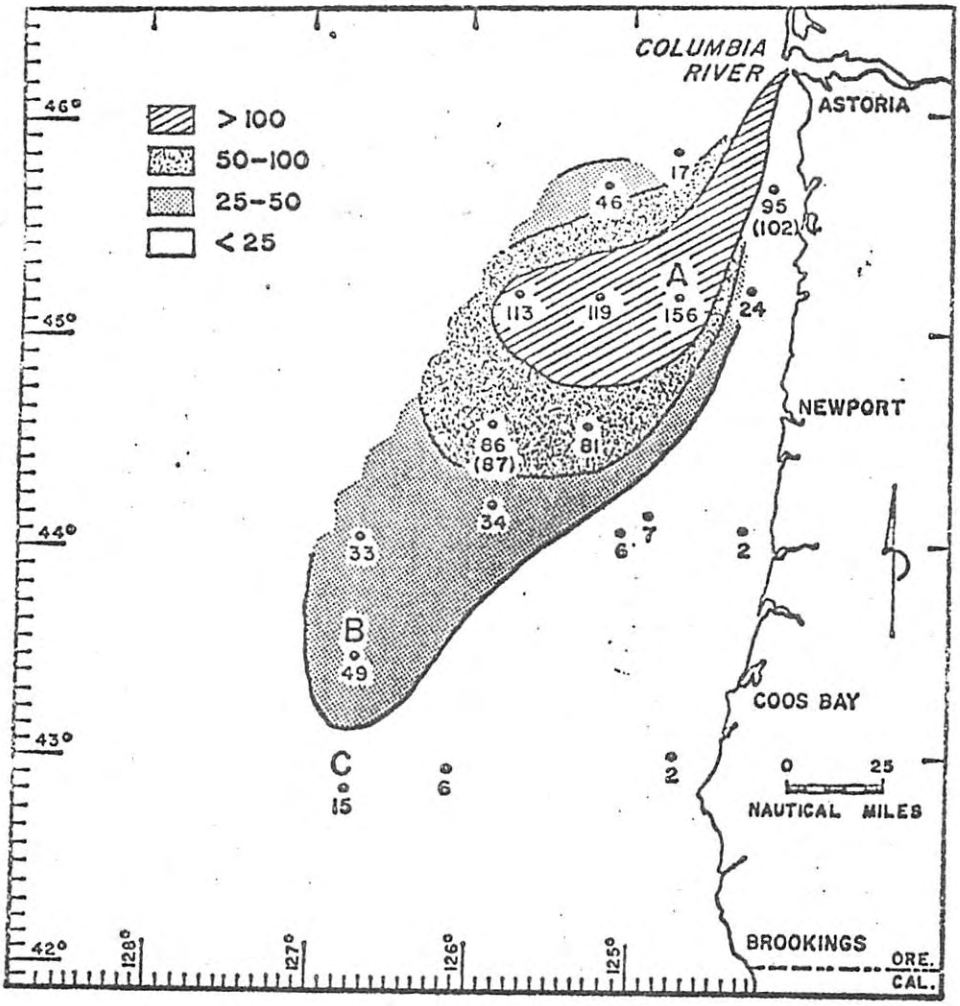
Be^{10} has a short residence time in sea water of about 150 years and has been used by Amin and others (1966) to date marine clays as Be has a similar geochemistry as Al. Their results, for two samples, show agreement of the Be^{10} ages with C^{14} and Pa^{231}: th^{230} ages.

II Artificial Nuclides

With the advent of the atomic age and particularily nuclear bomb tests, several radioactive isotopes not naturally present have been introduced into the marine environment, along with increasing amounts of such natural nuclides as C^{14} and H^3 (Table VIII-6). Most of the artificial nuclides have such small (1) activities and/or (2) half-lives that they are useless for examining any reasonably large scale oceanic process. Osterberg and others (1965), however, have taken advantage of the unique situation by which the Columbia River is contaminated with short half live wastes from the Hanford Atomic Plant to use these isotopes to trace the fresh water plume of the Columbia in the Pacific. Initially they used Zn^{65} as a tracer. However Zn^{65} is biologically active so the exact amount of Zn^{65} in the plume is not known. Satisfactory results were obtained with Cr^{51} which apparently is not abstracted by organisms. Figure VIII-4 shows surface movement of the Columbia River plume as detected by Cr^{51}.

Use of such isotopes as Cr^{51} (half-life 28 days) may be of increasing value to oceanographers investigating seasonal mixing processes and the development of the thermocline.

Figure VIII-4



Chromium-51 (counts per minute per 100 liters of surface sea water), corrected to date of collection, 26 June to 1 July 1965. Parentheses indicate duplicate samples. The number of counts per minute per 100 liters can be converted to picocuries per liter by multiplying by 0.861. The greatest velocity of water movement was between points *A* and *B*.

From: Osterberg, C. and others (1965) p. 1585-1587.

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Economic Chemical Products
From Sea Water

Obtaining useful chemicals from the sea is probably one of man's oldest industrial occupations as shown by the century's old but still producting evaporating salt pans along the Indian Coast. The technological advances of civilization have increased the list of chemicals derived from the sea from simple salt ($NaCl$) needed for the diet of man and animals and for the curing of hides to the list given in Appendix I. The various methods used to obtain such chemicals is shown in Table IX-1 from Tallmadge and other's (1964), excellent summary article. Details of such processes are given below grouped by chemical similarity as (1) halogens (Table IX-2, Figure IX-1) (2) Alkali metals (Table IX-3, Figures IX-2, 3, 4, 5,) (3) Alkali earths (Table IX-4, Figures IX-6, 7) (4) Precious metal plus boron removal (Table IX-5) and (5) mixed salt and multi-product processes (Table IX-6, 7).

In the 20th Century interest in the use of sea water as a source of valuable metals was triggered by the attempt of Fritz Haber in the 20's to pay Germany's World War I debts by extracting gold from sea water. Although his attempts eventually failed (Dow Chemical processed 15 tons of sea water to produce 0.09 mg of gold; Levine, 1968, p. X) the prospect so intrigued the Weimar government that they sponsored the famous <u>Meteor</u> Oceanographic Expedition to the Atlantic, which opened the era of Modern Oceanography. Also of oceanographic interest is the operation of the 4200 ton deep-sea bromine processing ship <u>S.S. Ethyl</u>, in the late 20's. At that time bromine was to be used in an anti-knock gasoline compound tribromoaniline in place of ethylene dibromide. The shipboard process was to add aniline sulfate and bubble chlorine gas through the sea water. The aniline sulfate dissociates into aniline and sulfuric acid. The sea water must be acidified to prevent hydrolysis of the chlorine. Chlorine gas is used to strip the bromide:

$$2\ Br^{-} + Cl_2 \rightleftarrows Br_2 + 2Cl^{+}$$

finally the bromine and aniline combine to form tribromoaniline which is filtered out. The generalized complete reaction is:

$$3\ Br^{-}\ (\text{sea water}) + C_6H_5NH_2 \cdot H_2SO_4 + 3Cl_2\ (\text{gas}) \rightarrow C_6H_2Br_3NH_2 + 5H^{+} + SO_4^{=} + 6Cl^{-}$$

However, the <u>S.S. Ethyl</u> only made one trip as shore produced ethylene dibromide

Table IX-1

TABLE IV. SEPARATION METHODS

Separation Method	Subsequent References	
	Table Number	*Process Number*
1. Precipitation[a]	9–17, 19	10, 13, 17–19, 21, 22, 27, 31–43
2. Electrolysis	6–10, 18, 19	1, 4, 8, 11, 16, 44
3. Electrodialysis	9	11
4. Adsorption	13, 14	24, 28–30
5. Ion Exchange	6, 9, 10, 12, 13	1, 12, 15, 23, 25
6. Chelation[b]	12, 19	20
7. Oxidation	6, 8	2, 7
8. Chlorination	7, 8.19	3, 5, 6
9. Solvent Extraction	13	26
10. Solar Evaporation	9, 10, 15, 19	9, 14, 32

[a] *Precipitation or crystallization is usually followed by filtration. There are three major ways of causing precipitation: by addition of chemicals; by cooling or freezing; by heating or evaporation.* [b] *Use of selective sequestering agents.*

From: Tallmadge and others (1964, p. 48)

Table numbers in subsequent references column refer to tables below listed as from Tallmadge and others 1964.

Table IX-2

Halogen Processes

TABLE VI. CHLORINE RECOVERY PROCESSES

Process No.	*1*	*2*
Location	Japan	U.S.S.R.
Process	Electrolysis, ion exchange	Oxidation
References	(*H1*, *H2*)	(*H3*)
Materials	Sea water, anion resin	Brine, oxidizing agent
Size	Pilot plant	Lab

Ref.	*Chemical Abstracts*	*Original Citation*
(*H1*)	43, 5317g	Nakahara, S., Sueta, H., Kawamura, T., Japan. Patent 175,044 (1958).
(*H2*)	49, 1637[illegible]	Nakahara, M., Aoki, H., Japan. Patent 5014 (1954).
(*H3*)	50, 11570	Matusevich, V. F., Zinc[illegible], *Veterinariya* 34, 69 (1956).

TABLE VII. BROMINE RECOVERY PROCESSES

Process No.	*3*	*4*
Location	U.S.A., Japan	Japan, Israel
Process	Chlorine displacement	Electrolysis
References	(*H4* to *H31*)	(*H32*, *H33*)
Materials	Chlorine, sea water, or brine	Brine
Size	Commercial	Lab

Reference	*Chemical Abstracts*	*Original Citation*
(*H4*)	...	Sconce, J. S. (ed.), ACS Monograph No. 154, Reinhold, New York, 1962. Shreve, R. N., "Chemical Process Industries," 2nd ed., p. 426, McGraw-Hill, New York, 1956. Kirk, R. E., Othmer, D. F., "Encyclopedia of Chemical Technology," Vol. 1, Interscience, New York, 1954.
(*H5*)	28, 3189-9	Stewart, L. C., Ind. Eng. Chem. 26, 361 (1934).
(*H6*)	23, 5014-7	Stine, M. A., *Ibid.*, 21, 434 (1929).
(*H7*)	27, 1999-9	Grebe, J. J., U. S. Patent 1,891,888 (1932).
(*H8*)	...	Robertson, G. R., Ind. Eng. Chem. 34, 133 (1942).
(*H9*)	27, 4636-7	Grebe, J. J., Boundy, R. H., Chamberlain, L. C., U. S. Patent 1,917,762 (1933).
(*H10*)	27, 1110-2	*Ibid.*, 1,885,255 (1932).
(*H11*)	31, 3222-3	Grebe, J. J., Boundy, R. H., Can. Patent 364,742 (1937).
(*H12*)	33, 822-1	Grebe, J. J., Chamberlain, L. C., U. S. Patent 2,133,616 (1938).
(*H13*)	27, 4636-8	Curtin, L. P., Thordarson, W., *Ibid.*, 1,916,094 (1933).
(*H14*)	30, 7789-9	Hanne, M., *Genie Civil* 108, 347 (1936).
(*H15*)	43, 5515e	Spada, A., *Atti Soc. Nat. Mat. Modena* 78, 44 (1947).
(*H16*)	35, 6074-5	Williamson, A. T., U. S. Patent 2,245,314 (1941).
(*H17*)	51, 6962e	Matsushima, Y., Japan. Patent 1121 (1956).
(*H18*)	42, 6068f	Kaltenbach, M., French Patent 861,183 (1941).
(*H19*)	50 16053f	German, F. F., *Khim. Prom.* 1956, p.171.
(*H20*)	47, 7741g	Bock, R., Hackstein, K. G., *Chem. Ing. Tech.* 25, 245 (1953).
(*H21*)	40, 4184-7	Chamagne, G., *Genie Civil* 120, 221 (1943).
(*H22*)	32, 9409-6	Stewart, L. C., *Trans. Can. Inst. Mining Met.* 41, 443 (1938).
(*H23*)	30, 5002-2	Schmidt, E., *La Nature* 1936, 292.
(*H24*)	...	Ind. Eng. Chem. Sup. 27A (1957).
(*H25*)	...	Hart, P., *Chem. Eng.* 54, 102 (1947). Oct.
(*H26*)	...	Heath, S. B., U. S. Patent 2,143,224 (1939).
(*H27*)	...	Hooker, G. W., *Ibid.*, 2,143,224 (1939).
(*H28*)	...	Tennant, W. J., Brit. Patent 523,607 (1940).
(*H29*)	52, 17638a	Stasinevich, D. S., *Zh. Prikl. Khim.* 31, 701, 844 (1958).
(*H30*)	42, 6996f	Nagi, R., *Kogyo. Kagaku Zasshi* 46, 858 (1943).
(*H31*)	43, 8622g	Ishikawa, F., Kobata, Y., *Bull. Inst. Phys. Chem. Res.* (*Tokyo*) 23, 57 (1944).
(*H32*)	45, 5047d	Inoue, S., Japan. Patent 177,354 (1949).
(*H33*)	53, 8895f	Reznik, S., Israel Patent 10,390 (1958).
(*H34*)	35, 6074-8	Urbain, O. M., Stemen, W. R., U. S. Patent 2,246,645 (1941).

TABLE VIII. IODINE RECOVERY PROCESSES

Process No.	*5*	*6*	*7*	*8*
Location	U.S.A., Japan	U.S.A.	U.S.S.R., France	Japan, France
Process	Chlorine displacement	Chlorine displacement	Oxidation	Electroly
References	(*H36* to *H38*)	(*H34*)	(*H39* to *H42*)	(*H43* to *H45*)
Materials	Chlorine, sea water, or brine	Chlorine, activated carbon	HNO_3, O_3	...
Scale	Lab	Lab	Lab	Lab

Ref. No.	*Chemical Abstracts*	*Original Citation*
(*H35*)	..	Dyson, G. M., *Chem. Age* 22, 362 (1930).
(*H36*)	41, 1072g	Cranston, J., U. S. Patent 2,412,390 (1946).
(*H37*)	44, 8086	Sakamoto, Y., Japan. Patent 174,103 (1946).
(*H38*)	...	Sawyer, F. G., Ohman, F. G., Lush, F. E., Ind. En Chem. 41, 1547 (1949).
(*H39*)	33, 4750-6	Denisovitch, B. P., Stetsenk, A. A., U.S.S.R. Pat 49,059 (1936).
(*H40*)	33, 4750-6	Ter-Oganesyan, S. N., *Ibid.*, 51,126 (1937).
(*H41*)	41, 1818c	Gogorishvili, P. V., *Ibid.*, 66,684 (1946).
(*H42*)	49, 12792d	Gloess, M. P. P., French Patent 984,500 (1951).
(*H43*)	51, 4178i	Kawanami, T., Japan. Patent 418 (1956).
(*H44*)	48, 6295h	Obara, U., *Ibid.*, 2626 (1953).
(*H45*)	50, 2860-2	Viel, E., French Patent 790,396 (1935).

From: Tallmadge and others (1964, p. 51 and 52)

Figure IX-1

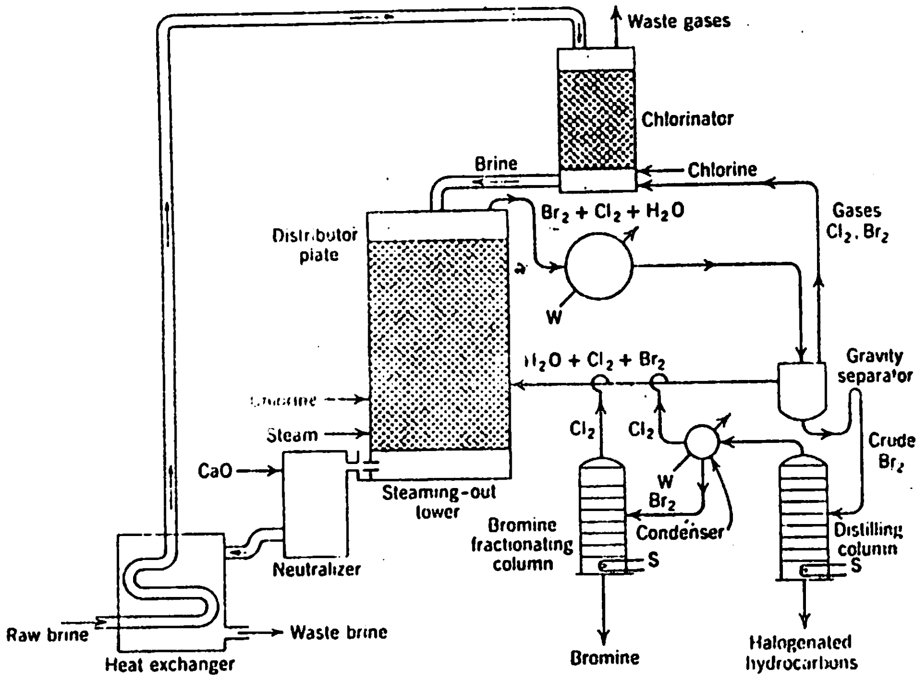

Fig. 2. Steaming-out process for bromine.

From: Standen (1964)

Table IX-3

Table IX-3 Alkali Metal Processes

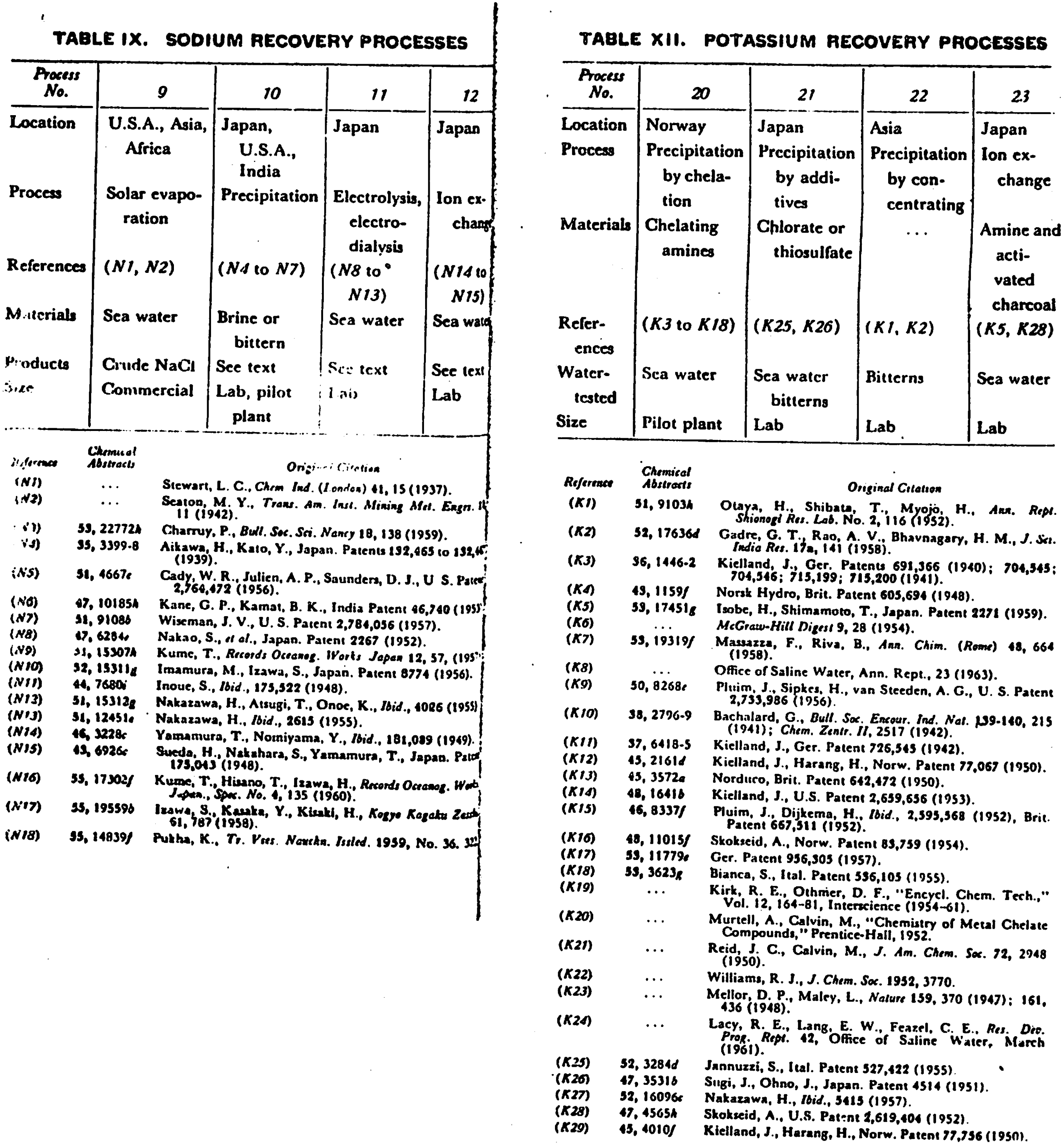

TABLE IX. SODIUM RECOVERY PROCESSES

Process No.	*9*	*10*	*11*	*12*
Location	U.S.A., Asia, Africa	Japan, U.S.A., India	Japan	Japan
Process	Solar evaporation	Precipitation	Electrolysis, electrodialysis	Ion ex-chang
References	(*N1*, *N2*)	(*N4* to *N7*)	(*N8* to *N13*)	(*N14* to *N15*)
Materials	Sea water	Brine or bittern	Sea water	Sea wat
Products	Crude NaCl	See text	See text	See text
Size	Commercial	Lab, pilot plant	Lab	Lab

Reference	*Chemical Abstracts*	*Original Citation*
(*N1*)	. . .	Stewart, L. C., *Chem Ind.* (*London*) 41, 15 (1937).
(*N2*)	. . .	Seaton, M. Y., *Trans. Am. Inst. Mining Met. Engrs.* 1 11 (1942).
(*N3*)	53, 22772*h*	Charruy, P., *Bull. Soc. Sci. Nancy* 18, 138 (1959).
(*N4*)	35, 3399-8	Aikawa, H., Kato, Y., Japan. Patents 132,465 to 132,4 (1939).
(*N5*)	51, 4667*e*	Cady, W. R., Julien, A. P., Saunders, D. J., U S. Pate 2,764,472 (1956).
(*N6*)	47, 10185*h*	Kane, G. P., Kamat, B. K., India Patent 46,740 (195
(*N7*)	51, 9108*b*	Wiseman, J. V., U. S. Patent 2,784,056 (1957).
(*N8*)	47, 6284*e*	Nakao, S., *et al.*, Japan. Patent 2267 (1952).
(*N9*)	51, 15307*h*	Kume, T., *Records Oceanog. Works Japan* 12, 57, (195
(*N10*)	52, 15311*g*	Imamura, M., Izawa, S., Japan. Patent 8774 (1956).
(*N11*)	44, 7680*i*	Inoue, S., *Ibid.*, 175,522 (1948).
(*N13*)	51, 15312*g*	Nakazawa, H., Atsugi, T., Onoe, K., *Ibid.*, 4026 (1955)
(*N13*)	51, 12451*e*	Nakazawa, H., *Ibid.*, 2615 (1955).
(*N14*)	46, 3228*c*	Yamamura, T., Nomiyama, Y., *Ibid.*, 181,089 (1949).
(*N15*)	43, 6926*c*	Sueda, H., Nakahara, S., Yamamura, T., Japan. Pate 175,043 (1948).
(*N16*)	55, 17302*f*	Kume, T., Hisano, T., Izawa, H., *Records Oceanog. Wo Japan., Spec. No.* 4, 135 (1960).
(*N17*)	55, 19559*b*	Izawa, S., Kasaka, Y., Kisaki, H., *Kogyo Kagaku Zas* 61, 787 (1958).
(*N18*)	55, 14839*f*	Pukha, K., *Tr. Vses. Nauchn. Issled.* 1959, No. 36. 3

TABLE XII. POTASSIUM RECOVERY PROCESSES

Process No.	*20*	*21*	*22*	*23*
Location	Norway	Japan	Asia	Japan
Process	Precipitation by chelation	Precipitation by additives	Precipitation by concentrating	Ion exchange
Materials	Chelating amines	Chlorate or thiosulfate	. . .	Amine and activated charcoal
References	(*K3* to *K18*)	(*K25*, *K26*)	(*K1*, *K2*)	(*K5*, *K28*)
Water-tested	Sea water	Sea water bitterns	Bitterns	Sea water
Size	Pilot plant	Lab	Lab	Lab

Reference	*Chemical Abstracts*	*Original Citation*
(*K1*)	51, 9103*h*	Otaya, H., Shibata, T., Myojo, H., *Ann. Rept. Shionogi Res. Lab.* No. 2, 116 (1952).
(*K2*)	52, 17636*d*	Gadre, G. T., Rao, A. V., Bhavnagary, H. M., *J. Sci. India Res.* 17a, 141 (1958).
(*K3*)	36, 1446-2	Kielland, J., Ger. Patents 691,366 (1940); 704,545; 704,546; 715,199; 715,200 (1941).
(*K4*)	43, 1159*f*	Norsk Hydro, Brit. Patent 605,694 (1948).
(*K5*)	53, 17451*g*	Isobe, H., Shimamoto, T., Japan. Patent 2271 (1959).
(*K6*)	. . .	*McGraw-Hill Digest* 9, 28 (1954).
(*K7*)	53, 19319*f*	Massazza, F., Riva, B., *Ann. Chim.* (*Rome*) 48, 664 (1958).
(*K8*)	. . .	Office of Saline Water, Ann. Rept., 23 (1963).
(*K9*)	50, 8268*e*	Pluim, J., Sipkes, H., van Steeden, A. G., U. S. Patent 2,733,986 (1956).
(*K10*)	38, 2796-9	Bachalard, G., *Bull. Soc. Encour. Ind. Nat.* 139-140, 215 (1941); *Chem. Zentr. II*, 2517 (1942).
(*K11*)	37, 6418-5	Kielland, J., Ger. Patent 726,545 (1942).
(*K12*)	45, 2161*d*	Kielland, J., Harang, H., Norw. Patent 77,067 (1950).
(*K13*)	45, 3572*a*	Norduco, Brit. Patent 642,472 (1950).
(*K14*)	48, 1641*b*	Kielland, J., U.S. Patent 2,659,656 (1953).
(*K15*)	46, 8337*f*	Pluim, J., Dijkema, H., *Ibid.*, 2,595,568 (1952), Brit. Patent 667,511 (1952).
(*K16*)	48, 11015*f*	Skokseid, A., Norw. Patent 83,759 (1954).
(*K17*)	53, 11779*e*	Ger. Patent 956,305 (1957).
(*K18*)	53, 3623*g*	Bianca, S., Ital. Patent 536,105 (1955).
(*K19*)	. . .	Kirk, R. E., Othmer, D. F., "Encycl. Chem. Tech.," Vol. 12, 164–81, Interscience (1954–61).
(*K20*)	. . .	Murtell, A., Calvin, M., "Chemistry of Metal Chelate Compounds," Prentice-Hall, 1952.
(*K21*)	. . .	Reid, J. C., Calvin, M., *J. Am. Chem. Soc.* 72, 2948 (1950).
(*K22*)	. . .	Williams, R. J., *J. Chem. Soc.* 1952, 3770.
(*K23*)	. . .	Mellor, D. P., Maley, L., *Nature* 159, 370 (1947); 161, 436 (1948).
(*K24*)	. . .	Lacy, R. E., Lang, E. W., Feazel, C. E., *Res. Dev. Prog. Rept.* 42, Office of Saline Water, March (1961).
(*K25*)	52, 3284*d*	Jannuzzi, S., Ital. Patent 527,422 (1955).
(*K26*)	47, 3531*b*	Sugi, J., Ohno, J., Japan. Patent 4514 (1951).
(*K27*)	52, 16096*c*	Nakazawa, H., *Ibid.*, 5415 (1957).
(*K28*)	47, 4565*h*	Skokseid, A., U.S. Patent 2,619,404 (1952).
(*K29*)	45, 4010*f*	Kielland, J., Harang, H., Norw. Patent 77,756 (1950).

From: Tallmadge and others (1964, p. 52 and 57)

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Figure IX-2

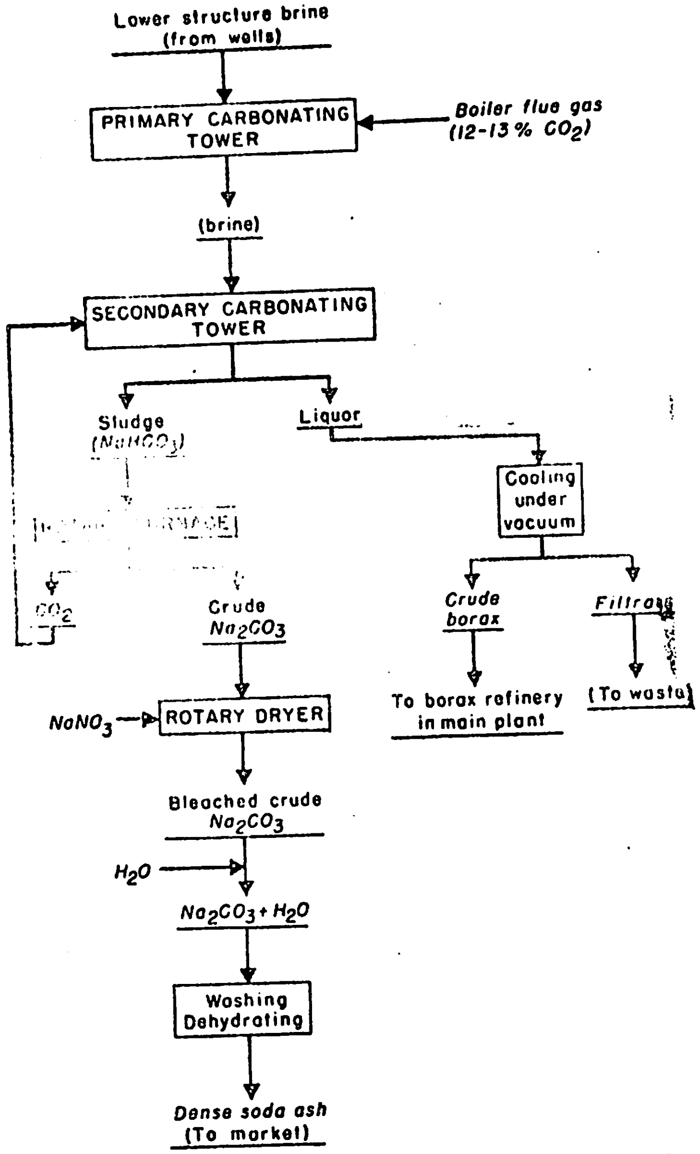


FIGURE 2. Flow sheet, carbonation plant process, American Potash & Chemical Corporation.

From: Van Planck in Wright (1957, p. 478)

Figure IX-3

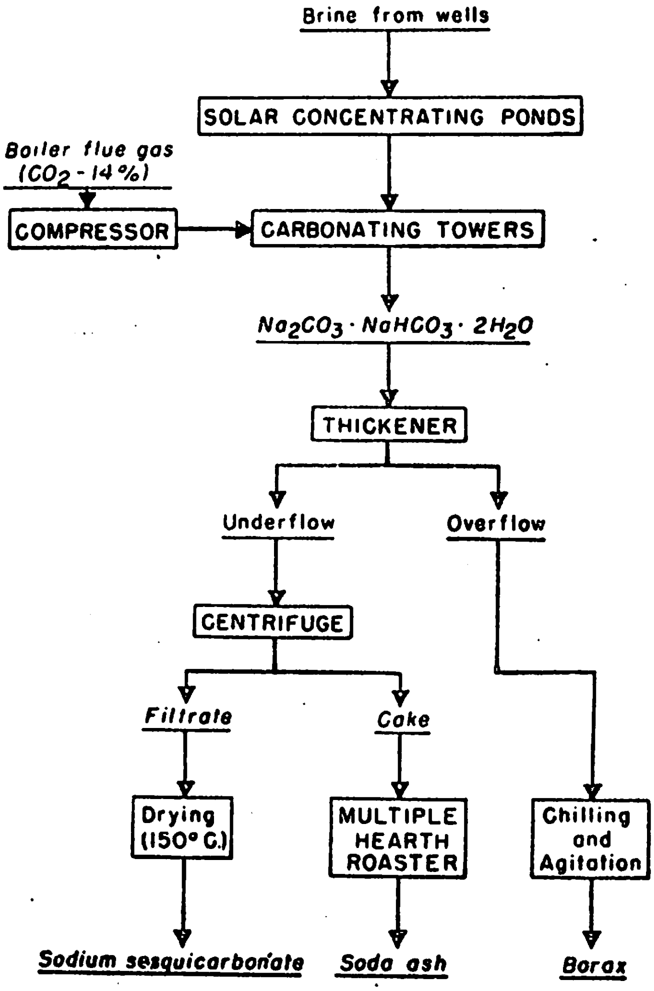


FIGURE 4. Flow sheet, Columbia Chemical Division.

From: Van Planck in Wright (1957, p. 481)

Figure IX-4

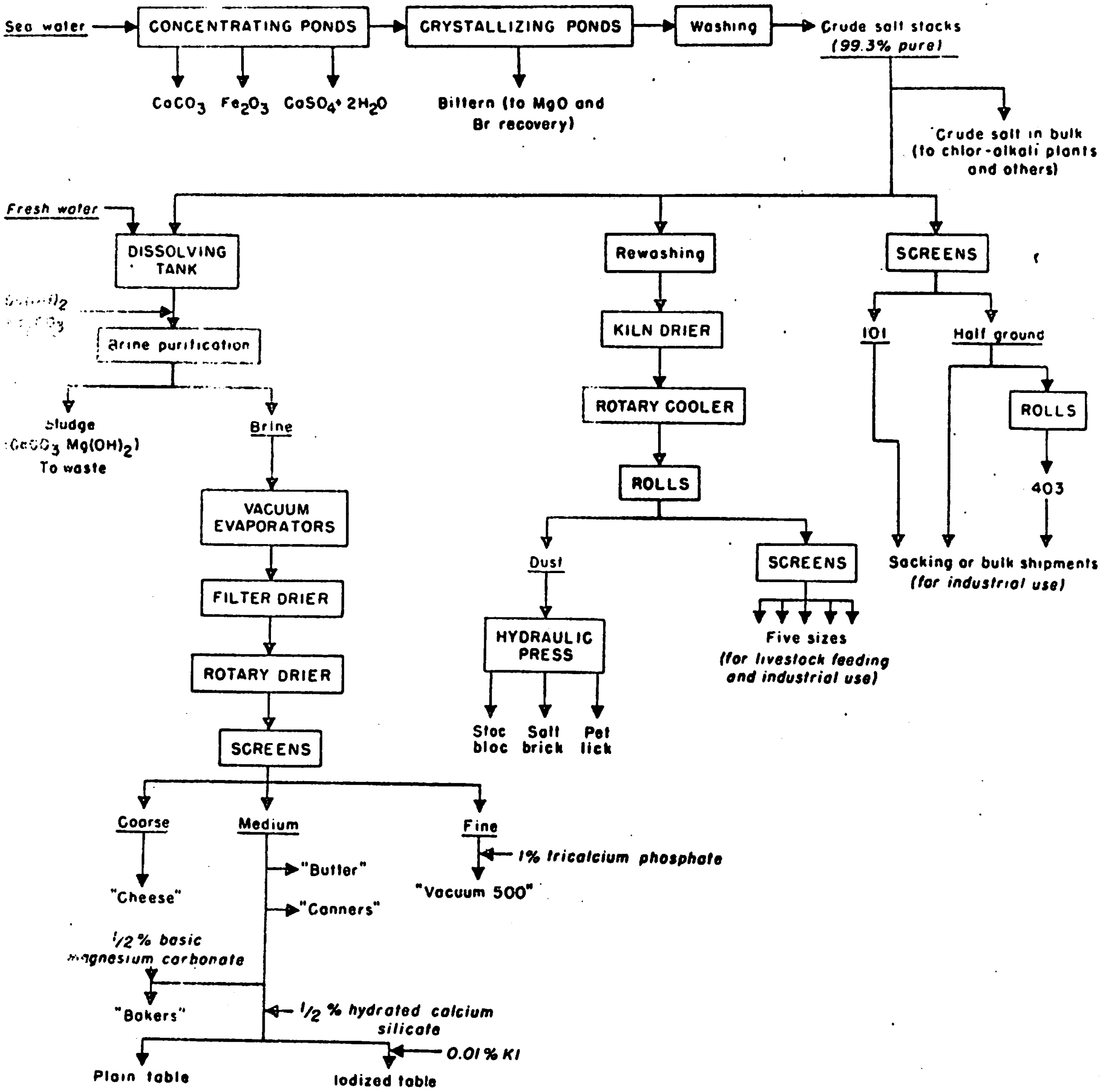


FIGURE 15. Chart showing the making of salt from sea water.

From: Van Planck in Wright (1957, p. 493)

Figure IX-5

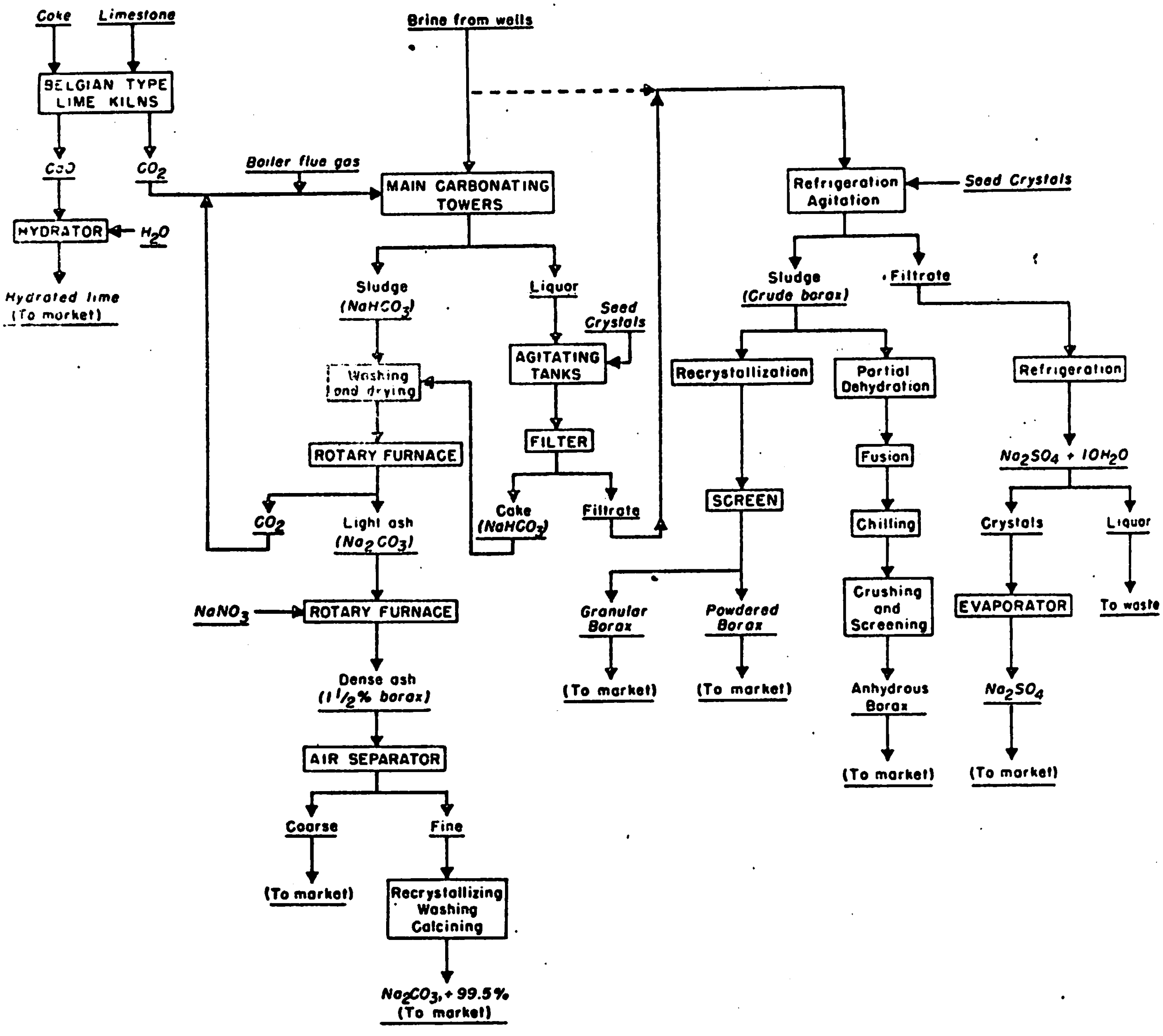


FIGURE 3. Flow sheet, West End Chemical Company.

From: Van Planck in Wright (1957, p. 480)

Table IX-4

Alkaline Earth Processes

TABLE XI. CALCIUM RECOVERY PROCESSES

Process No.	17	18	19
Location	Japan	U.S.A.	Japan
Process	Precipitation	Precipitation	Precipitation
References	(*C5*)	(*C2, C3*)	(*C4*)
Materials	Bittern, $Ca(OH)_2$	Sea water or brine, shells	Sea water, CaO, Na_2SO_4
Products	Gypsum	Gypsum	Gypsum
Scale	Lab	Commercial	Lab

Reference	*Chemical Abstracts*	*Original Citation*
(*C1*)		Staab, W. A., *The Compass* 24, 5 (1946).
(*C2*)	33, 1451-6	Trauffer, W. E., *Pit and Quarry* 30, 43 (1938).
(*C3*)	47, 5648*d*	Naucler, J. O., Swed. Patent 136,600 (1952).
(*C4*)	52, 20937*f*	Munakata, B., Suzuki, A., Japan. Patent 7,566 (1956).
(*C5*)	46, 11,599*b*	Eto, S., *Ibid.*, 274 (1951).
(*C6*)	50, 4470*b*	Span. Patent 220,899 (1955), to Union Salinera, S.A.
(*C7*)	52, 20937*g*	Ishizaka, S., Japan. Patent 7567 (1956).
(*C8*)	33, 4851-2	Repa, A. G., Legkova, T. K., *Bull. Far East Branch Acad. Sci. (USSR)* 32, 59 (1938).
(*C9*)	51, 8394*a*	Myers, C. B., Brit. Patent 755,948 (1956).
(*C10*)	. . .	Office of Saline Water, Res. and Dev. Prog 66 (1962).

TABLE X. MAGNESIUM RECOVERY PROCESSES

Process No.	13	14	15	16
Location	USA, England, Germany, U.S.S.R.	Italy	Japan	Israel
Process	Precipitation	Solar evaporation	Ion exchange	Electrolysis
References	(*M1* to *M5*, *M16*, *M17*)	(*M58*)	(*M59*, *M60*)	(*M61*)
Materials	Dolomite, etc.	. . .	CO_2 and lime, or waste liquor	Bitterns
Products	Salts, metal	$MgCl_2$	$MgHCO_3$ or $MgCl_2$	$Mg(OH)_2$
Size	Commercial	. . .	Lab	Lab

Reference	*Chemical Abstracts*	*Original Citations*
(*M1*)		Shreve, R. N., "Chemical Process Industries," 2nd ed., p. 224, McGraw-Hill (1955).
(*M2*)		*Chem. Met. Eng.* 48, No. 11, 130 (1941).
(*M3*)		Murphy, W., *Chem. Ind.* 49, 618 (1942).
(*M4*)		Schambra, W. P., *Trans. A.I.Ch.E.* 41, 35 (1945).
(*M5*)	37, 5559-5	Spiro, N. S., *Tr. Akad. Nauk Ukr. SSR* 38, 79 (1940).
(*M6*)	34, 860-6	Spiro, N. S., *Bull. Inst. Hallurgii* 3,21 (1938).
(*M7*)	38, 1612-7	Spiro, N. S., *Trudy Inst. Hallurgii* 8, 5 (1940); and *Khim. Referat. Zhur.* 4, No. 9, 106 (1941).
(*M8*)	55, 23949	Spiro, N. S., *Tr. Vses. Nauchn. Issled. Inst. Galurgii* 36, 281 (1959).
(*M9*)	46, 7724*f*	Vettel, A. W., Israel, R. D., U. S. Patent 2,595,314 (1952).
(*M10*)	49, 2909*b*	Aravamuthan, V., *Bull. India Sect. Electrochem. Soc.* 3, 45 (1954).
(*M11*)	46, 11597*e*	Gilpin, W. C., Heasman, N., *Refractories J.* 28, 302 (1952).
(*M12*)	46, 6799*c*	Atoda, T., *Repts. Sci. Police Res. Inst. (Tokyo)* 27, 324, 471 (1951).
(*M13*)	50, 17357*e*	Sugi, J., Shimizu, K., Japan. Patent 1065 (1955).
(*M14*)	55, 10808*j*	Ishizaha, S., Wada, Y., *Rept. Gov. Chem. Ind. Res. Inst. Tokyo* 52, 90 (1957).
(*M15*)	. . .	Chesny, H. H., Ind. Eng. Chem. 28, 383 (1936).
(*M16*)	. . .	Manning, P. D. V., *Chem. Met. Eng.* 45, 478 (1938).
(*M17*)	. . .	*Chem. Met. Eng.* 54, No. 8, 132 (1947).
(*M18*)	50, 14193*d*	Alentiev, A. A., *et al.*, *Ukr. Khim. Zh.* 21, 778 (1955).
(*M19*)	33, 7497-9	Alentiev, A. A., *J. Chem. Ind. (USSR)* 16, no. 4-5, 46 (1939).
(*M20*)	48, 13177*d*	Nagai, S., Yoshizaki, K., Komatsu, S., *J. Ceram. As* *Japan* 62, 325 (1954).
(*M21*)	55, 5881*h*	Takeshima, S., *Records Oceanog. Works Japan, Spec.* 3, 45 (1959).
(*M22*)	55, 25175*c*	Terada, M., *Tokyo Kogyo Shikensho Hokoku* 54, (1959).
(*M23*)	52, 6735*d*	Fujii, H., Isabe, K., Japan. Patent 1317 1957).
(*M24*)	47, 1346*b*	Nakatomi, K., Sakatani, Y., *Ibid.*, 2711 and 2662 (195
(*M25*)	43, 6795*i*	Niwa, S., *Ibid.*, 172,596 (1946).
(*M26*)	47, 8950*e*	Seailles, J. C., French Patent 980,707 (1951).
(*M27*)	49, 5797*d*	Seailles, J. C., U. S. Patent 2,587,001 (1952).
(*M28*)	42, 6068*h*	Seailles, J. C., French Patent 862,074 (1941).
(*M29*)	44, 292*f*	Scoles, L. W., U. S. Patent 2,479,138 (1949).
(*M30*)	43, 2798*h*	Green, W. H., McBride, G. A., Hertzing, G. A., *Ib* 2, 458, 261 (1949).
(*M31*)	41, 841*a*	Clark, L. M., Robinson, J. G., Brit. Patent 571, (1945).
(*M32*)	38, 5372-5	Prytherch, W. E., *Ibid.*, 553,731 (1943).
(*M33*)	48. 7858*f*	Sugi, J., *et al.*, Japan. Patent 2281 (1953).
(*M34*)	43, 6374*d*	Skogseid, A., Norway Patent 74,138 (1948).
(*M35*)	52, 8479*c*	Forbath, T. P., *Chem. Eng.* 65, No. 6, 112 (1958).
(*M36*)	49, 2695*h*	Woodward, T., U. S. Patent 2,695,242 (1954), 2,571, (1951).
(*M37*)	49, 9894*a*	Clarke, R. E., Collings, N. R., *Ibid.*, 2,703,748 (1955)
(*M38*)	48, 11021*c*	Dodd, A. E., *Ceramics*, 474 (1953).
(*M39*)	47, 5643*g*	Britton, H. T. S., Gregg, S. J., Willing, E. G. J., *Appl. Chem.* 2, 701 (1952).
(*M40*)	47, 2444*d*	Seailles, J. C., French Patents 975,099 and 971, (1951).
(*M41*)	47, 4568*d*	Kuhlmann, *E. T.*, *Ibid.*, 884,976 (1943).
(*M42*)	46, 7724*f*	Vettel, A. W., Israel, R. D., U.S. Patent 2,595, (1952).
(*M43*)	44, 2711*f*	Thorp, H. W., Gilpin, W. C., *Soc. Chem. Ind., Chem. E* *Group*, Oct. 25 (1949).
(*M44*)	47, 10821*f*	Nagai, S., Fukumori, Y., *J. Ceram. Assoc. Japan* 61, 266 (1953).
(*M45*)	51, 18502*a*	Goldberg, A., *Bull. Res. Council Israel* 50, 122 (1955).
(*M46*)	50, 11863*g*	Rohm & Haas Co., Brit. Patent 738,520 (1955).
(*M47*)	49, 4953*d*	Dancy, W. B., MacDonald, R. A., U.S. Pat 2,687,339 (1954).
(*M48*)	41, 575*i*	Hunter, M. J., Bauman, W. C., *Ibid.*, 2,409, (1946).
(*M49*)	39, 5417-1	Douglas, M., *Refractories J.* 21, 11 (1945).
(*M50*)	31, 3641-7	Manning, P. D. V., *Chem. Met. Eng.* 43, 116 (1936).
(*M51*)	52, 8922*d*	Nishikawa, Y., Japan. Patent 5504 (1956).
(*M52*)	55, 14838*i*	Takahima, S., Akiyama, R., Okamoto, K., *Nipp* *Shio Gakkaishi* 10, 117 (1956).
(*M53*)	46, 8337*d*	Société des Prod. mar. du Pouliguen, French Pat 971,919 (1951).
(*M54*)	45, 10153*d*	Axt, M., *Przemysl Chem.* (28), 482 (1949).
(*M55*)	45, 5375*c*	Galimberti, L., Spinedi, P., Stein, A. M., *Ann. chi* *applicata* 39, 572 (1949).
(*M56*)	50, 14188*g*	Davidenko, N. K., *Ukrain. Khim. Zhur.* 21, 773 (1955).
(*M57*)	55, 15850*e*	Babachiev, G. N., Popov, M. A., *Khim. Ind. (Sofia)* No. 6, 167 (1960).
(*M58*)	46, 224*c*	Piromallo, A., Ital. Patent 460,207 (1950).
(*M59*)	45, 10522*i*	Akabori, S., *et al.*, Japan. Patent 179,562 (1949).
(*M60*)	47, 12775*b*	Shirakabe, S., *Ibid.*, 4468 (1952).
(*M61*)	51, 18500*d*	Schacher, O., *Bull. Res. Council Israel* 5C, 100 (1955).
(*M62*)	43, 4819*c*	Antonena, C. M., *Bol. Inform. Petrol* 25, No. 285, (1948).
(*M63*)	38, 1611-8	Mandel, R. A., *Tr. Inst. Halurgii* 1940, No. 18, 4

From: Tallmadge and others (1964, p. 54 and 56).

Figure IX-6

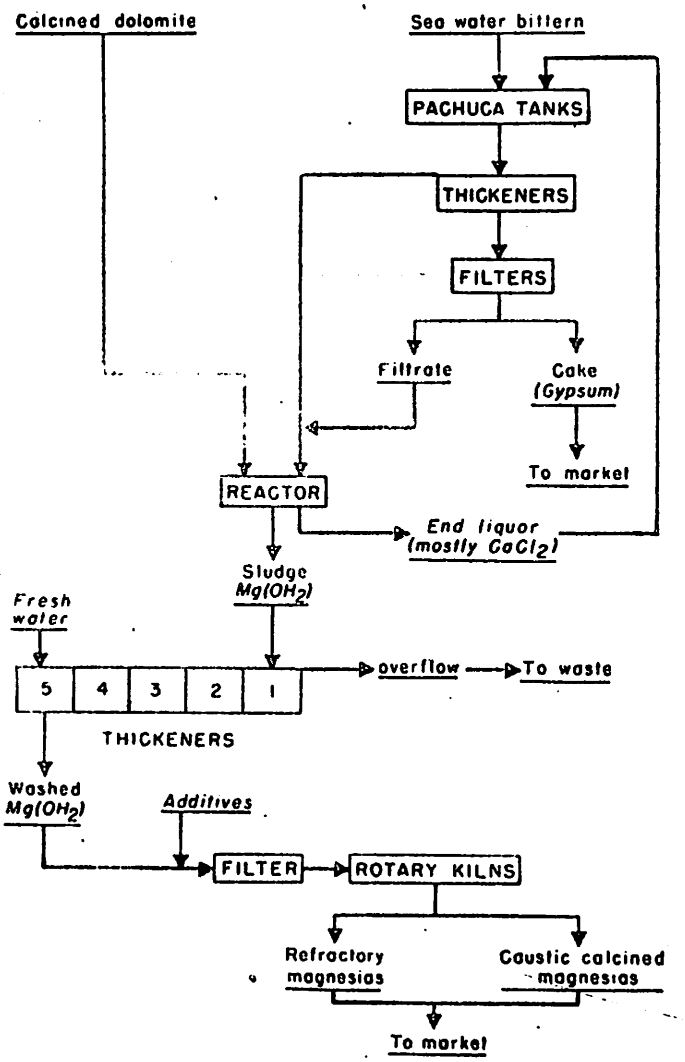


FIGURE 6. Flow sheet of Newark plant, Westvaco Chemical Division, Alameda County.

From: Van Planck in Wright (1957, p. 319)

Figure IX-7

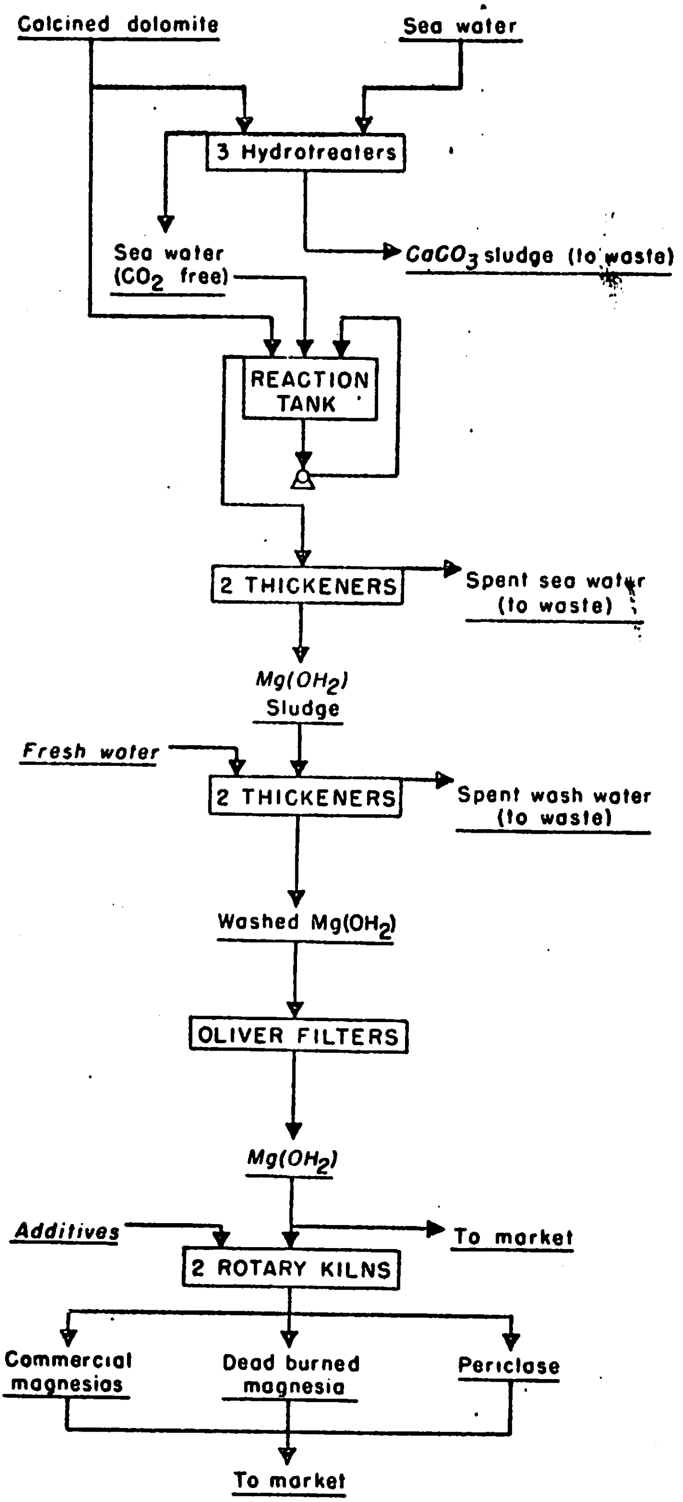


FIGURE 5. Flow sheet of Moss Landing plant, Kaiser Aluminum & Chemical Corporation, Monterey County.

From: Van Planck in Wright (1957, p. 318)

Table IX-5

TABLE XIV. PRECIOUS METAL RECOVERY PROCESSES

Process No.	*28*	*29*	*30*	*31*
Location	France	Japan	U.S.A.	Great Britain
Method	Adsorption	Adsorption	Adsorption	Precipitation
Materials used	Tannin rags; pyrites	Activated carbon	Zeolites	Sulfides
Solution tested	Sea water	Bitterns	Saline solutions	...
Metal sought	Gold	Gold	Silver	Uranium
References	(*R12*, *R13*)	(*R17*)	(*R18*)	(*R19*)

Reference	*Chemical Abstracts*	*Original Citation*
(*R8*)	37, 6505-3	Stark, W., *Helv. Chim. Acta* 26, 424 (1943).
(*R9*)	48, 5569e	Putnam, C. L., *J. Chem. Ed.* 30, 576 (1953).
(*R10*)	21, 1787	Haber, F., *Z. Angew. Chem.* 40, 303 (1927).
(*R11*)	41, 1899b	Baur, E., *Helv. Chim. Acta* 25, 1202 (1942).
(*R12*)	23, 4656-7	Glazunov, A., *Chem. Listy* 23, 188, 215 (1929), *Chim. Ind.* (*Paris*) *Spec.* No. 426-7, Feb. (1929).
(*R13*)	27, 2356-5	Gurevich, A., *Chim. Ind.* (*Paris*) 29, 284 (1933).
(*R14*)	43, 5238e	Thurston, J. T., U.S. Patent 2,455,282; and 2,468,471 (1949).
(*R15*)	44, 4607b	Day, H. M., *Ibid.*, 2,497,054 (1950).
(*R16*)	23, 1861-4	Bardt, H., Brit. Patent 294,655 (1927).
(*R17*)	48, 12637i	Suzuki, H., Orihata, S., Nakamura, S., *Nippon Engaku Kaishi* 5, 144 (1951).
(*R18*)	48, 535d	Brooks, J. M., U.S. Patent 2,653,089 (1953).
(*R19*)	50, 14194b	Bader, H. E. R., Bader, D. E., Waringuet, M. Y., Brit. Patent 748,593 (1956).

TABLE XIII. BORON REMOVAL PROCESSES

Process No.	24	25	26	27
Location	Japan, U.S.A.	U.S.A.	Japan	U.S.S.R.
Process	Adsorption	Ion exchange	Solvent extraction	Precipitation
Solution tested	Brine	Synthetic solution	Acidified brine	Concentrated sea water
Materials	Oxide gels	Resins	Alcohols	...
Reference	(*R3*, *R4*)	(*R2*)	(*R1*)	(*R6*, *R7*)

From: Tallmadge and others (1964, p. 58 and 59)

Reference	*Chemical Abstracts*	*Original Citation*
(*R1*)	44, 4212f	Nakamura, S., Suzuki, K., Japan. Patent 174,696 (1947
(*R2*)	52, 3203e	Lyman, R. W., Preuss, A. F., U.S. Patent 2,813,83 (1957).
(*R3*)	40, 6228-6	Gustafson, H., Kominek, E., *Ibid.*, 2,402,959 (1946).
(*R4*)	51, 17714b	Tadenuma, H., Japan. Patent 6661 (1955).
(*R5*)	...	Murphy, N. F., Tinsley, R. S., Meenaghan, G. F., *Bull. Virginia Poly. Inst. Eng. Expt. Sta.* 115, Feb. (1957).
(*R6*)	38, 935-4	Selivanova, N. M., *Tr. Mosk. Khim.-Tekhnol. Inst. Mendeleeva* 133 (1940); *Khim. Referat. Zur.* 4, No. 9, 45 (1941).
(*R7*)	32, 1529-3	Igelsrud I., Thompson, T., Zwicker, B., *Am. J. Sci.* 35, 47 (1938).

Table IX-6

Mixed Salt Processes

TABLE XVI. MIXED SALT PRECIPITATION BY EVAPORATION

Process No.	*32*	*33*	*34*	*35*	*36*
Location	India, France	France	Japan, Spain	India	U.S.A.
Heat source	Solar	Steam	Steam	Steam	Combustion
Water used	Sea water	Bitterns	Bitterns	Bitterns	Sea water
Major compd. in mixed salt	NaCl	K_2SO_4	NaCl	Carnallite	NaCl
References	(*S16, S17*)	(*S16*)	(*S21, S24*)	(*S18*)	(*S19*)

[illegible]	*Chemical Abstracts*	*Original Citation*
[illegible]		Myers, D. M., Bonython, C. W., *J. Appl. Chem.* (*London*) 8, 207 (195[illegible])
(*S16*)	27, 2258·6	Galimberti, L., French Patent [illegible]3.394 (1932).
[illegible]	53, 207[illegible]	Sitaraman, R., Srinivasan, M. [illegible] *[illegible]tech.* (*Univ. Madras*) 8, 21 (1958–59).
(*S18*)	53, 9587*e*	Gadre, G. T., Rao, A. V., Bhavnagary, H. M., *J. Sci. Ind. Res.* (*India*) 17A, 141, 376 (1958).
(*S19*)	50, 15980*a*	Lee, J. A., *Food Eng.* 27, 90 (1955).
(*S20*)	52, 20804*f*	Ishizuka, S., Japan. Patent 6075 (1956).
(*S21*)	50, 4770*b*	Un. Sal. d'Esp. S.A., Span. Patent 22,089 (1955).
(*S22*)	51, 13331*f*	Clarke, R. E. (Merck), U.S. Patent 2,793,099 (1957).
(*S23*)	42, 6999*b*	Casti, S., Ital. Patent 413,511 (1946).
(*S24*)	48, 7268*b*	Suginohara, K., Japan. Patent 2282 (1953).
(*S25*)	32, 3102-5	Il'inskii, V. I., Chertok, A. I., Bekker, V. E., U.S.S.R. Patent 44,244 (1935).
(*S26*)	34, 4530-9	Farnsworth, W. H., Martin, C. H., U.S. Patent 2,191,561 (1940).
(*S27*)	50, 4470*c*	Sekiguchi, S., Japan. Patent 7175 (1954).
(*S28*)	53, 2702*a*	Frantz, J. F., La. State Univ. Dissertation, Univ. Microfilms, *Dissertation Abstr.* 19, 495 (1958).
(*S29*)	. . .	Office of Saline Water, *Ann. Rept.* (1958–62).
(*S30*)	49, 1290*h*	Sugimoto, K., Yawataya, T., Japan. Patent 1266 (1954).

TABLE XVIII. MIXED SALT PRECIPITATION WITH CHEMICALS

Process No.	*40*	*41*	*42*	*43*
Location	Japan, U.S.A.	India	India	Several
Process	Ammonium phosphate	Ammonia	Phosphate	Recycled silver and copper salts
Products	Fertilizer	Fertilizer	Fertilizer	Chlorides
Size	Pilot plant	Lab	Lab	Lab
References	(*S35, S39*)	(*S37*)	(*S38*)	(*S40–S44*)

Reference	*Chemical Abstracts*	*Original Citation*
(*S35*)	53, 5572*c*	Ishizaka, S., Iwata, S., Japan. Patents 1861 and 3769 (1958).
(*S36*)	49, 6524*d*	Kashiwagi, S., *et al.*, Japan. Patent 3226 (1954).
(*S37*)	48, 11702*d*	Seshadri, K., Gupta, J., *J. Sci. Ind. Res.* (*India*) 13B, 204 (1954).
(*S38*)	48, 14077*i*	Gadre, G. T., *Ibid.*, 12B, 171 (1953); 13B, 46 (1954).
(*S39*)	. . .	Office of Saline Water, *Ann. Rept.*, 1960–62, Spec. Rept. PB 181406.
(*S40*)	53, 13523*b*	Zarchin, A., Israeli Patent 10,737 (1958).
(*S41*)	41, 5267*a*	Ocean Products Ltd., Brit. Patent 575,339 (1946).
(*S42*)	30, 554-6	Mutosel, French Patent 784,767 (1935).
(*S43*)	51, 2240*e*	Ugo, S., Japan. Patent 7014 (1954).
(*S44*)	50, 6758*d*	Ugo, S., Japan. Patent 1870 (1955).

TABLE XVII. MIXED SALT PRECIPITATION BY FREEZING

Process No.	*37*	*38*	*39*
Location	U.S.A.	Sweden	Japan
Temperature	−20° C. and lower	−10° C.	20° C., −10° C
Water used	Sea water	Sea water	Brines
Mixed products	Many	Sodium sulfate	NaCl
References	(*S12–S14*)	(*S31*)	(*S34*)

Reference	*Chemical Abstracts*	*Original Citation*
(*S31*)	33, 7054-4	Oman, E., Swed. Patent 96,638 (1939).
(*S32*)	48, 7268*a*	Sakaguchi, T., Japan. Patent 2278 (1953).
(*S33*)	55, 8712	*Advan. Chem. Ser.* 27, pages 56, 75, 82, 90 (1960).
(*S34*)	52, 5765*d*	Yada, H., Japan. Patent 183 (1957).

From: Tallmadge and others (1964, p. 62 and 63)

Table IX-7

TABLE XXI. SOME MULTIPRODUCT PROCESSES

Year Reported	*Author or Company*	*Ref. No.*	*Other References*	*Major Aspect*	*Step 1*	*Step 2*	*Step 3*	*Notes*
1938	Spiro (U.S.S.R.)	(*M6*)	(*M63*) (*S25*)	Ppt.	$Mg(OH)_2$; $CaSO_4$	NaCl, Na_2SO_4	Fe, Ca salts, bromine	Not necessarily in order
1956	Tanaka (Japan)	(*S45*)	(*S46, 47*)	Elect.	Mg and Ca removal	Water by evap.; saturation	NaOH, Cl_2 electrol.	Step 4—removal of NaCl
1932	Galimberti (France)	(*S16*)	. . .	Evap.	Solar evap.; NaCl; $MgSO_4$	Evap. to mixed fertilizer (Mg, K, Na)	$MgCl_2$, bromine	Patent
1939	Oman (Sweden)	(*S31*)	. . .	Freezing	$Mg(OH)_2$ Ppt.	Freeze Na_2SO_4; then NaCl	Evap. to Mg, K chlorides	Patent
1940	Farnsworth (U.S.A.)	(*S26*)	. . .	Heating	Evap. NaCl	Evap. Mg and Ca	Roasting HCl, MgO	Patent with brines
1950	Norsk (Norway)	(*K29*)		Chelation	KCl, KNO_3 chelation	Bromine		Patent
1953	Raymond (U.K.)	(*S11*)	(*S10*)	Evap.	$CaCO_3$; $MgCO_3$; $CaSO_4$	Na_2SO_4	Mg and K salts	Batch study
1954	Nelson (U.S.A.)	(*S14*)	(*S12, S13*)	Freezing	$CaCO_3$; Na_2SO_4	NaCl	KCl; $MgCl_2$	Low temp. batch study
1954	Uno (Japan)	(*S43*)	(*S44*)	NH_4Cl recycle	Evap. centrifug. $MgCl_2$	$MgSO_4$ KCl, NaOH	. . .	Or carnallite, patent
1954	Seshadri (India)	(*S37*)	. . .	Ammonia CO_2	$MgCO_3$	$CaCO_3$	Evap. to fertilizer	. . .
1955	Lee (U.S.A.)	(*S19*)	. . .	Evap.	Remove Mg and Ca	Roast to mixed salt	. . .	Table salt
1957	Clarke (U.S.A.)	(*S22*)	. . .	Evap.	$Mg(OH)_2$	Add SO_2, evap. $CaSO_4$	Evap. NaCl	Step 4—bromine patent
1958	Zarchin (Israel)	(*S40*)	. . .	Recycle four components	Add Ag_2SO_4 AgCl	$Mg(OH)_2$; $CaSO_4$	$NaHCO_3$	Step 4—$MgCO_3$ patent
1958	Madras (India)	(*S17*)	. . .	Solar and steam evap.	$CaSO_4$, $MgSO_4$	NaCl, KCl, $MgCl_2$	Bromine	Not necessarily in order
1958	Gadre (India)	(*S18*)	. . .	Evap. and cooling	$MgSO_4$, KCl (add HCl)	Evap. cool carnallite	. . .	From solar evap. bitterns
1958	Ishizaka (Japan)	(*S35*)	. . .	Ammonia phosphate	Fertilizer Mg, Ca, N, P	Add HCl; NaCl	Cool NH_4Cl KCl	Patent or step 1—$Mg(OH)_2$ and step 2—fertilizer
1960	Grace Co. (U.S.A.)	. . .	. . .	Phosphate	Fertilizer Mg, Ca, N, P	Fresh water evap.	. . .	Pilot plant

From: Tallmadge and others (1964, p. 65) still was cheaper. Eventually tetraethyl lead was used as an anti-knock compound. However with the environmental pressure to "get the lead out" of gasoline the successor of the S. S. Ethyl may soon set sail.

Recent impetus to the development of sea water processes has been the expansion of research into desalination or the extraction of fresh water from brackish and sea water funded chiefly by the Department of Interior Office of Saline Water. Any successful desalination scheme would produce large quantities of brine as a waste product. Thus it was thought at least partial reclamation of the salts and metals of the brine might reduce the over-all cost of desalination (see Figure IX-8, 9, 10, and 11) and help to eliminate the pollution problem of disposal of brine. Unfortunately as shown in Table IX-8 and 9 so much sea water is used in even a small desalination operation (6.6×10^{11} gallons of sea water per year) that the market for such salts would be glutted and produce unknown economic havoc on existing producers.

Figure IX-8

Table 1. Value of minerals in sea water.

Assuming: 50% of present bulk sale price, no recovery cost.

Recoverable mineral	Value in sea water
Sodium chloride,	$0.21/1,000 gal. (as crude)
Refined	0.81
Magnesium oxide	0.34
Bromine	0.06
Potassium chloride	0.05
Calcium oxide	0.02
Borax	0.004
Strontium sulfate	0.003

Table 2. Output of by-product minerals. From a single ten million gallon per day sea water conversion plant.

Mineral	By-product mineral output (maximum), ton/yr.	Total U.S. production, ton/yr.
Salt (NaCl)	740,000	25,500,000
Magnesia (MgO)	58,000	572,000
Potassium chloride	19,500	4,500,000 (equivalent)
Quicklime (CaO)	15,400	8,300,000
Bromine	1,800	87,500
Strontium salts	740	6,200
Boron (as B_2O_3)	580	324,000

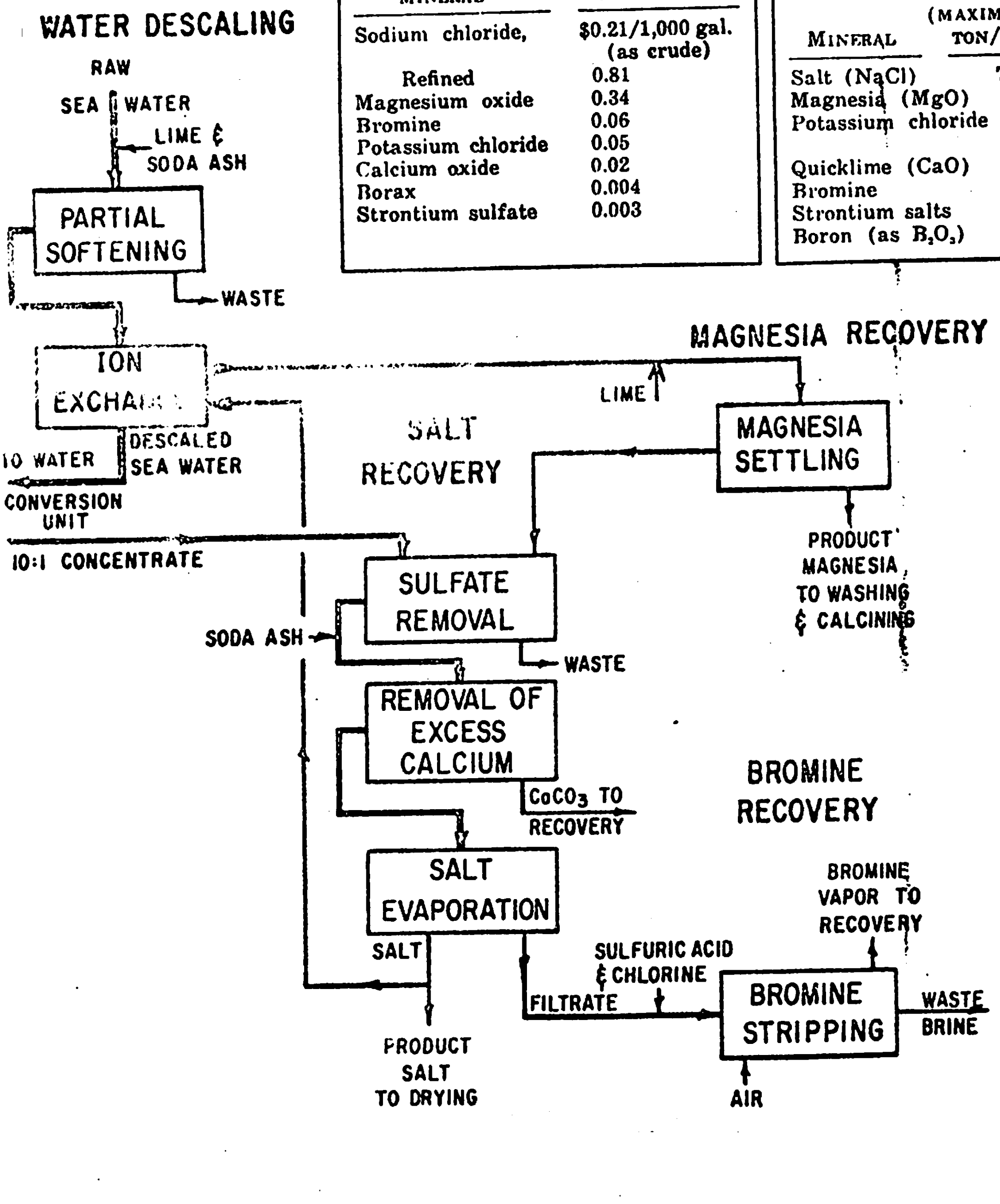
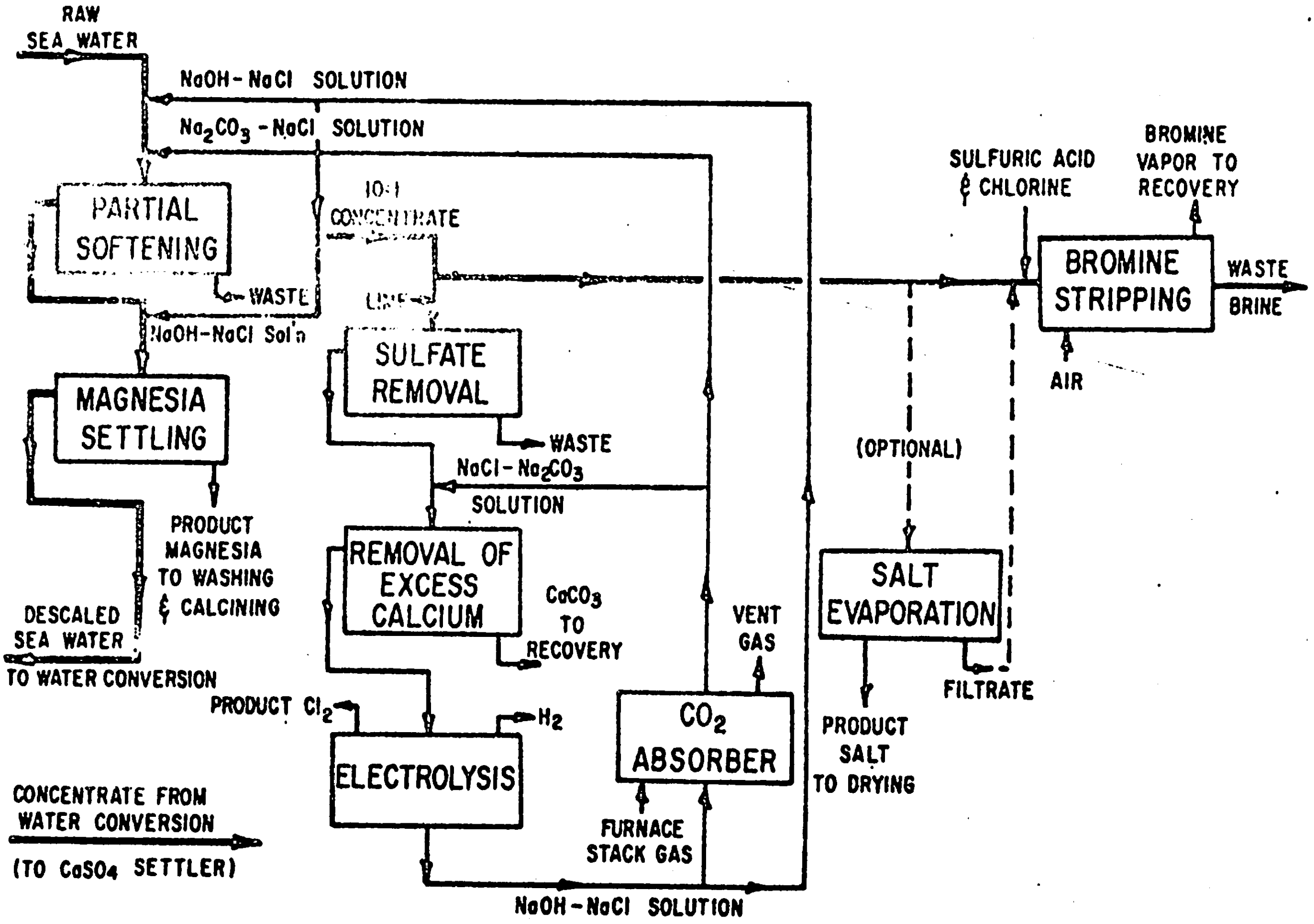


Figure 1. Process 1 for descaling and recovery of minerals from sea water.

From: Weinberger and DeLapp in Levine (1968, p. 17)

Figure IX-9

Figure 2. Schematic flow sheet of process 2 for descaling and recovery of minerals from sea water.



From: Weinberger and DeLapp in Levine (1968, p. 18)

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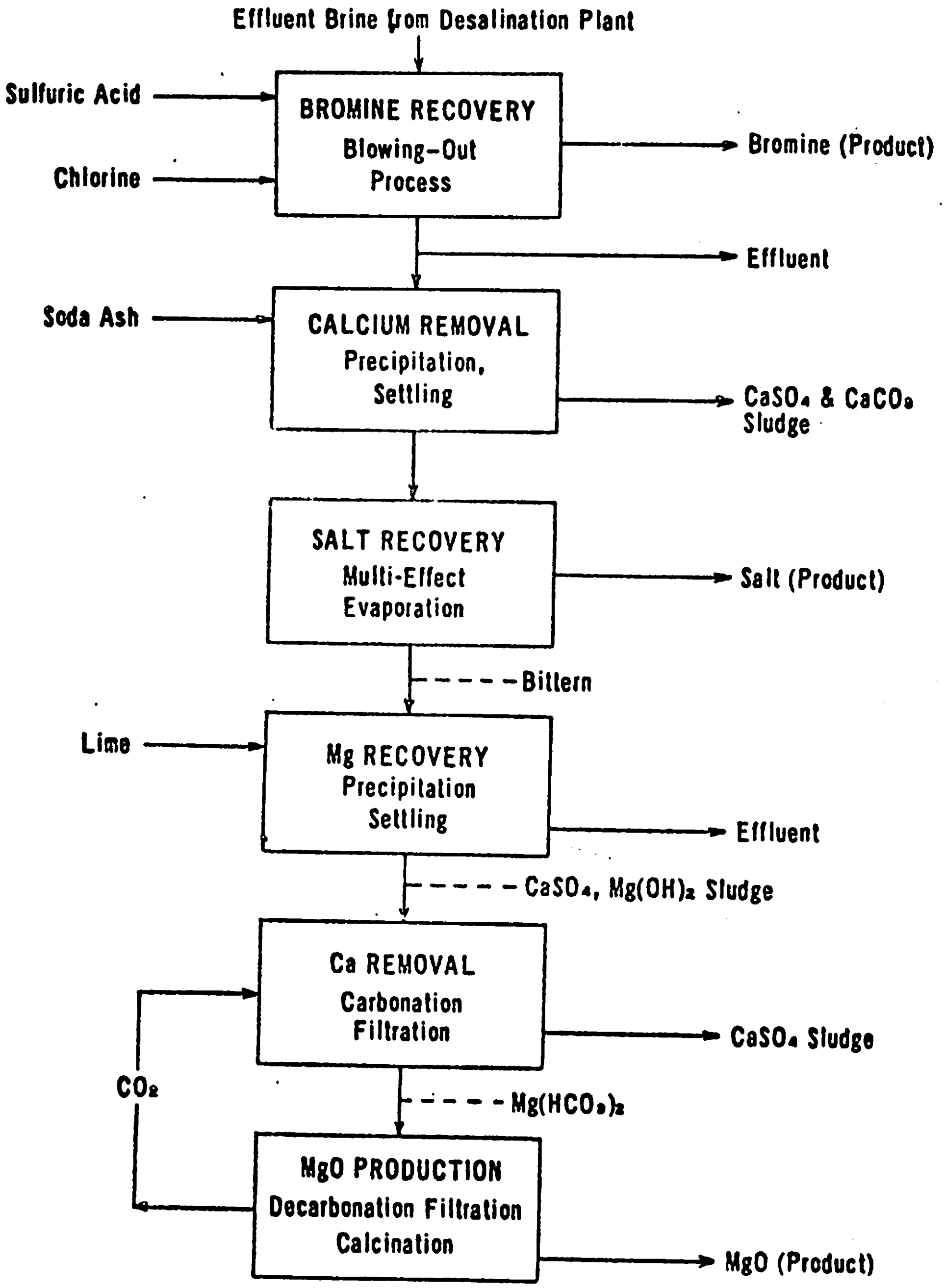
Figure IX-10

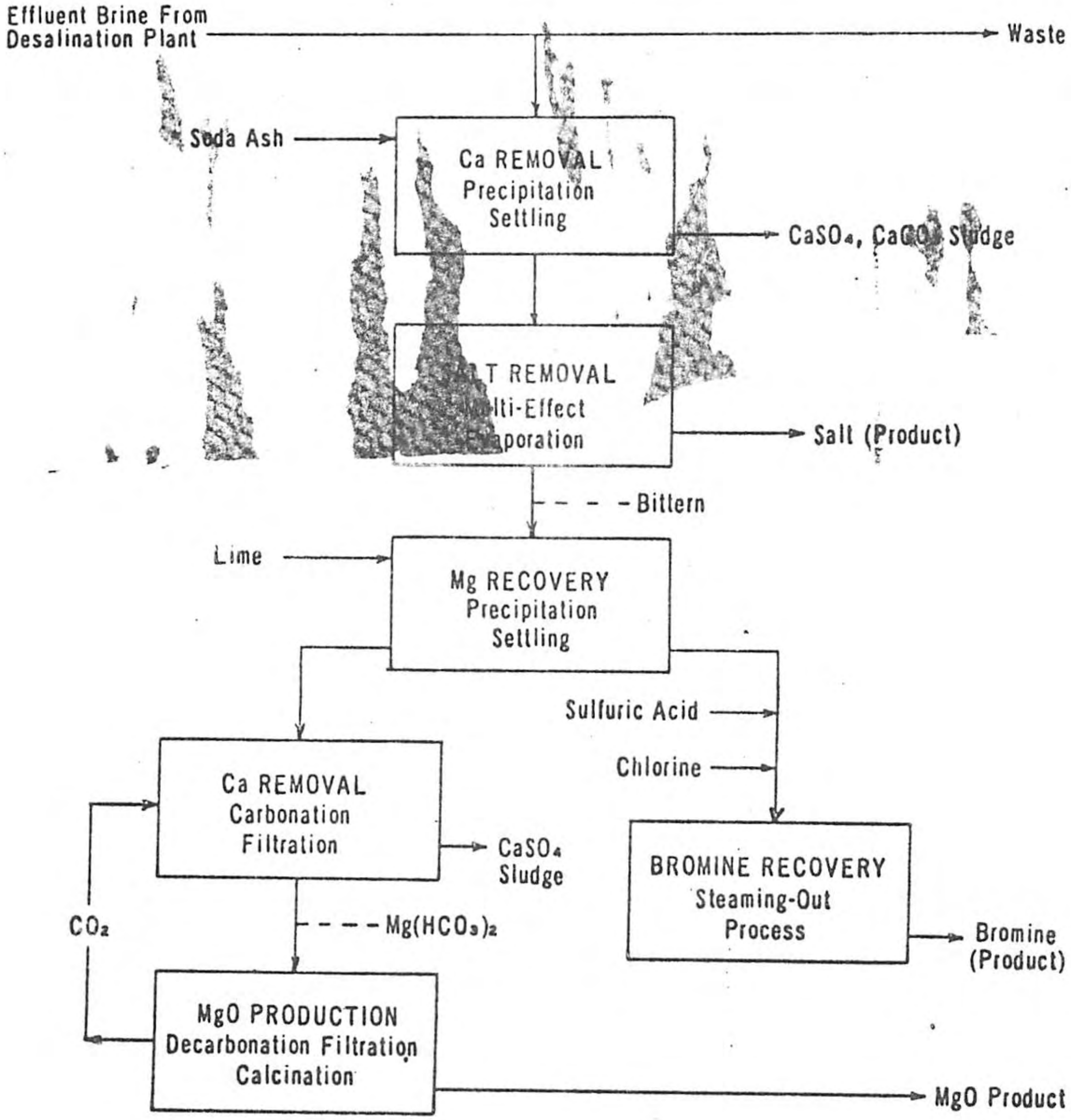
FIG. VI – C – 1
RECOVERY OF THREE PRODUCTS FROM
EFFLUENT OF SEA-WATER DESALINATION PLANT



From: Christensen and others (1967, p. 138)

Figure IX-11

FIG. VI – C – 2
ALTERNATE RECOVERY OF THREE PRODUCTS
FROM EFFLUENT OF SEA-WATER DESALINATION PLANT



From: Christensen and others (1967, p. 139)

Table IX-8

Elements in Sea Water	Sea Water Concent. ppm	T/yr.* to Fact.	Production 1961 1,000 ST U.S.	World	Consumpt. 1961 1,000 ST U.S.	Reserves 1,000,000 ST Estimated U.S.	1958 World
Chlorine	19,361	53,959,107	25,700	96,400	26,100	Unlimited	
Sodium	10,768	30,010,416					
Magnesium	1,298	3,617,526	41	115	45		
Compounds of MG			604	8,600	880	Unlimited	
Sulfur	880	2,452,560	14,000	21,800	6,[illegible]0	150	NI
Calcium	408	1,137,096					
Potassium	388	1,081,356	2,270	8,720	1,880	315	44,800
Bromine	66	183,942	90	NI	85	Unlimited	
Carbon	28	78,036	-	-	-	-	-
Strontium	13	36,231	NI	5	6.7	1.5	NI
Boron	4.6	12,820	187	190	100	20	NI
Silicon	4.0	11,148	-	-	-	-	-
Fluorine	1.3	3,623	100	1,120	430	11	50
Nitrogen	1.0	2,787	-	-	-	-	-
Aluminum	1.0	2,787	1,900	5,200	2,3[illegible]	14	635
Rubidium	0.2	557	Small	Small	Small	NI	NI
Lithium	0.1	279	NI	42	NI	6	NI
Phosphorous	0.07	195	3,490	19,100	6,100	5,900	20,400
Barium	0.05	139	430	1,760	820	66	NI
Iodine	0.05	139	NI	NI	1.5	NI	1
Arsenic	0.02	56	5	59	26	2.5	NI
Manganese	0.01	28	16	4,900	600	27	350
Zinc	0.009	25	1,210	3,550	460	14	84
Lead	0.004	11	261	2,660	1,030	3	48
Selenium	0.004	11	0.5	1.0	0.5	0.2	NI
Tin	0.003	8.4	NI	190	49	0.3	0.5
Cesium	0.002	5.6	Small	Small	Small	NI	NI
Uranium	0.002	5.6	15	30	2[illegible]	0.25	1.0
Iron	0.002	5.6	40,500	283,900	56,500	500	1,500
Copper	0.001	2.8	1,170	5,000	1,230	33	170
Chromium	0.001	2.8	56	3,220	820	2.7	450
Titanium	0.001	2.8	470	1,440	570	25	160
Molybdenum	0.0005	1.4	21	29	15	1,[illegible]	3,000
Gallium	0.0005	1.4	Small	Small	Small	NI	NI
Thorium	0.0005	1.4	0.1	NI	0.1	0.10	NI
Cerium	0.0004	1.1	NI	NI	2.1	NI	0.4
Cadmium	0.0003	0.8	4.9	10	5	0.03	0.4
Lanthanum	0.0003	0.8	NI	NI	NI	NI	[illegible]
Silver	0.0003	0.8	1.2	7.9	5.5	0.03	0.1[illegible]
Vanadium	0.0003	0.8	5.3	8.7	6.7	NI	NI
Yttrium	0.0003	0.8	Small	Small	Small	NI	NI
Antimony	0.0002	0.6	0.7	60	13	0.03	7.7
Bismuth	0.0002	0.6	0.4	2.7	0.7	0.03	NI
Nickel	0.0001	0.3	13	400	18	0.6	15
Cobalt	0.0001	0.3	NI	16	5	0.04	1.8
Mercury	0.00003	0.08	1.3	9.1	2.1	0.01	0.15
Gold	0.000006	0.02	0.5	1.6	0.9	0.002	0.04

ST = Short Ton
NI = No Information
PPM = Parts Per Million

* Assuming a treatment plant handling 6.6 x 10^{11} Gallons per year

Concentration, production, consumption and availability of elements present in sea water (McIlhenny and Ballard, 1963)

Table IX-9

Element in Sea Water	Selling Form	Converted T/Yr.*	1962 Price $/Ton	Value of Compound $/Yr.	Factory Production U.S. Consumption
Chlorine	NaCL	76,295,000	10	762,950,000	2.9
Sodium					
Magnesium	Mg	45,000	705	31,725,000	1.0
Compounds	MgO	5,923,248	53	313,932,144	5.25
Sulfur	S	2,452.560	23.5	57,635,160	0.41
Calcium	$CaSO_4$	6,105,068	4.2	25,641,286	0.56
Potassium	KCL	2,062,146	31	63,926,526	0.58
Bromine	Br	183,942	430	79,095,060	2.16
Carbon	-	-	-	-	-
Strontium	$SrSO_4$	75,940	66.2	5,023,431	7.7
Boron	$Na_2B_4O_7 \cdot 10\ H_2O$	112,903	43.5	4,914,761	0.12
Silicon	-	-	-	-	-
Fluorine	HF	3,815	320	1,220,800	1×10^{-2}
Nitrogen	-	-	-	-	-
Aluminum	Al	2,787	450	1,254,150	1×10^{-3}
Rubidium	-	-	-	-	-
Lithium	$LiOH \cdot H_2O$	3,368	1,080	3,637,440	6×10^{-3}
Phosphorous	Super Phosphate	223	70	15,610	3×10^{-5}
Barium	$BaSO_4$	236	160	37,760	1×10^{-4}
Iodine	I	139	2,200	305,800	0.11
Arsenic	As_2O_3	74	100	7,400	2×10^{-3}
Manganese	Mn	28	700	19,600	4×10^{-5}
Zinc	Zn	25	230	5,570	5×10^{-5}
Lead	Pb	11	200	2,200	1×10^{-5}
Selenium	Se	11	11,500	126,500	4×10^{-5}
Tin	Sn	8.4	2,240	18,816	2×10^{-4}
Cesium	-	-	-	-	
Uranium	U_3O_8	6.6	16,000	105,600	2×10^{-4}
Iron	Fe	5.6	59	332	1×10^{-7}
Copper	Cu	2.8	620	1,736	2×10^{-6}
Chromium	Cr_2O_3	4.1	70	287	3×10^{-7}
Titanium	TiO_2	4.7	540	2,538	5×10^{-6}
Molybdenum	MoO_3	2.1	3,200	6,720	9×10^{-5}
Gallium	-	-	-	-	
Thorium	ThO_2	1.6	11,000	17,600	1×10^{-2}
Cerium	Mischmetal	1.1	6,000	7,800	2×10^{-4}
Lanthanum	Mischmetal	0.8	6,000	5,400	
Cadmium	Cd	0.8	3,600	2,880	2×10^{-4}
Silver	Ag	0.8	35,146	28,333	1×10^{-4}
Vanadium	V_2O_5	1.4	2,760	3,864	1×10^{-4}
Yttrium	Y_2O_3	1.0	120,000	120,000	
Antimony	Sb	0.6	650	390	5×10^{-5}
Bismuth	Bi	0.6	4,500	2,700	9×10^{-4}
Nickel	Ni	0.3	1,580	474	2×10^{-5}
Cobalt	Co	0.3	3,040	912	6×10^{-5}
Mercury	Hg	0.08	4,810	385	4×10^{-5}
Gold	Au	0.02	1,020,835	20,417	2×10^{-5}

* Assuming a treatment plant handling 6.6 x 10" Gallons per year.

Values of Elements and Compounds of Elements in Sea Water (McIlhenny and Ballard, 1963)

Appendix I

PRODUCTS CURRENTLY RECOVERED COMMERCIALLY FROM BRINES

A List of Abbreviations of Company Names Appears
in Table V-A-III

An Asterisk (*) appearing Before a Product Name
Indicates a Second-Generation Product

Product: Borax ($Na_2B_4O_7 \cdot 10H_2O$).

Company	Location	Ref.
Am. Pot.	Trona, Calif. (Searles Lake)	80
West End	Westend, Calif. (Searles Lake)	21

Product: Bromine (Br_2).

Company	Location	Ref.
Am. Pot.	Trona, Calif. (Searles Lake)	80
Dead Sea Br.		135
Dow	Midland, Mich.	80
Dow	Ludington, Mich.	80
Ethyl-Dow	Freeport, Tex.	80
FMC	Newark, Calif.	135
Gr. Lakes	Filer City, Mich.	80
Mich. Chem.	Eastlake, Mich.	80
Mich. Chem.	El Dorado, Ark.	80
Mich. Chem.	St. Louis, Mich.	80
Morton	Manistee, Mich.	80
Pomeroy	Minersville, O.	80
Seshasayee	Madras, India	135
Tata	Mitrapur, India	152
Westvaco Chlorine	California	152
Westvaco Mineral	South Charleston, W. Va.	80
	Anglesea, Gr. Britain	152
	Alsace, France	152
	Cornwall, Gr. Britain	152
	Jacob's Bay, Union of South Africa	152
	Port-de-Bouc, France	152
	Stassfurt Area, Germany	152

Product: Calcium Chloride ($CaCl_2$).

Company	Location	Ref.
Cal. Rock Salt	Amboy, Calif.	80
Desert	Amboy, Calif.	80
Dow	Midland, Mich.	80
Hill	Amboy, Calif.	80
Liverpool	Hartford, W. Va.	80

(Continued)

Product: Calcium Chloride ($CaCl_2$). (Continued)

Company	Location	Ref.
L. A. Chem.	Los Angeles, Calif.	80
Mich. Chem.	Eastlake, Mich.	80
Mich. Chem.	El Dorado, Ark.	80
Mich. Chem.	St. Louis, Mich.	80
Pomeroy	Minersville, O.	80
Westvaco Mineral	South Charleston, W. Va.	80

Product: Iodine (I_2).

Company	Location	Ref.
Deepwater	Compton, Calif.	80
Dow	Inglewood, Calif.	80
Dow	Midland, Mich.	80
Dow	Seal Beach, Calif.	80
Dow	Venice, Calif.	
	Chile	135
	Indonesia	135
	Italy	135

Product: Lithium Sodium Phosphate (Li_2NaPO_4).

Company	Location	Ref.
Am. Pot.	Trona, Calif. (Searles Lake)	357

Product: * Magnesium (Mg).

Company	Location	Ref.
Dow	Freeport, Tex.	357
Norsk Hydro	Heroya, Norway	357
	Japan	357

Product: * Magnesium Carbonate ($MgCO_3$).

Company	Location	Ref.
Fibreboard	Emeryville, California	357
Mar. Mag.	South San Francisco, Calif.	357
Mich. Chem.	St. Louis, Mich.	357
Morton	Manistee, Mich.	357

Product: Magnesium Chloride ($MgCl_2$).

(Continued)

Product: Magnesium Chloride ($MgCl_2$). (Continued)

Company	Location	Ref.
Dow	Ludington, Mich.	357
FMC	Newark, Calif.	357

Product: Magnesium Hydroxide ($Mg(OH)_2$).

Company	Location	Ref.
Dow	Freeport, Tex.	357
Dow	Ludington, Mich.	357
Dow	Midland, Mich.	357
FMC	Newark, Calif.	357
Kaiser	Moss Landing, Calif.	357
Mar. Mag.	South San Francisco, Calif.	15
Mich. Chem.	St. Louis, Mich.	357

Product: * Magnesium Oxide (MgO).

Company	Location	Ref.
Dow	Freeport, Tex.	357
Dow	Midland, Mich.	357
FMC	Newark, Calif.	357
Intor. Min.	Carlsbad, N. Mex.	357
Kaiser	Moss Landing, Calif.	357
Mich. Chem.	Port St. Joe, Fla.	357
Mich. Chem.	St. Louis, Mich.	357
Morton	Manistee, Mich.	357
N. W. Mag.	Cape May, N. J.	357
Porter	Pascagoula, Miss.	357
Std. Lime	Manistee, Mich.	357

Product: Magnesium Sulfate Heptahydrate ($MgSO_4 \cdot 7H_2O$).

Company	Location	Ref.
Agro Min.	Tonasket Wash.	357
Dow	Midland, Mich.	357

Product: * Magnesium Silicate (Mg_2SiO_4).

Company	Location	Ref.
Mar. Mag.	South San Francisco, Calif.	357

Product: Potassium Chloride (KCl).

(Continued)

Product: Potassium Chloride (KCl).

Company	Location	Ref.
Am. Pot.	Trona, Calif. (Searles Lake)	80
Arab Pot. (Jor.)	Jordan	135
Blumer	Davenport, Calif.	80
Bonneville	Wendover, Utah	80
Dead Sea	Near Sodom	135
Dow	Midland, Mich.	80
Leprechaun	Nevada	135
State	Tuticorin, India	135

Product: Potassium Sulfate (K_2SO_4).

Company	Location	Ref.
Am. Pot.	Trona, Calif. (Searles Lake)	267

Product: Sodium Carbonate (Na_2CO_3).

Company	Location	Ref.
Am. Pot.	Trona, Calif. (Searles Lake)	80; 357
F.P.G.	Bartlett, Calif.	357
West End	Westend, Calif.	80; 357

Product: Sodium Chloride (NaCl).

Company	Location	Ref.
Am. Salt	Mt. Eden, Calif.	80
Cal. Salt	Bristol Lake, Calif.	80
Chem. Salt	Grantsville, Utah	80
Crys. Wh.	Grantsville, Utah	80
Dia. Crys.	Bahama Islands	80; 135
Dow	Midland, Mich.	80
Leslie	Alvarado, Calif.	80
Leslie	Newark, Calif.	80
Mich. Alk.	Wyandotte, Mich.	80
[illegible] Bay	Moss Landing, Calif.	80
[illegible]	Newark, Calif.	80
Morton	Saltair, Utah	80
Penn. Salt	Wyandotk, Mich.	80
Solvay	Delray, Mich.	80
Stansbury	Stansbury, Utah	80
Stauffer	Redwood City, Calif.	80
Surprise Valley	Cedarville, Calif.	80
Western	Tustin, Calif.	80

(Concluded)

Product: Sodium Sulfate (Na_2SO_4).

Company	Location	Ref.
Am. Ag.	Detroit, Mich.	357
Am. Pot.	Trona, Calif. (Searles Lake)	357
Ariz. Chem.	Brownfield, Tex.	357
Ariz. Chem.	O'Donnell, Tex.	357
Con. Chem.	Houston, Tex.	357
Con. Chem.	Fort Worth, Tex.	357
Dale	Amboy, Calif.	357
Ozark-Mahoning	Brownfield, Tex.	357
Ozark-Mahoning	Monahans, Tex.	357
Pratt	Wyo.	357
U. S. Borax	Calif.	357
West End	Westend, Calif. (Searles Lake)	357

References - Week IX

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