

## History of sea water. Constant temperature-pressure equilibrium models compared to liquid inclusion analyses

JAMES R. KRAMER\*

The University of Michigan, Ann Arbor

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**Abstract**—An inorganic ocean is derived from the solution equilibrium of clay minerals, calcite, OH-apatite, CO<sub>2</sub>-F-apatite, phillipsite, gypsum, strontianite, celestite and aragonite. The minerals are considered in equilibrium in different combinations with and without chloride.

A "most probable" model for the major ions has concentrations very close to modern sea water; an "upper limit", model has concentrations slightly higher than modern sea water except that Mg and SO<sub>4</sub> are 5 to 6 times higher than modern ocean concentrations. A "lower limit" model is quite similar to "fresh" water. The presence or absence of Cl seems to be the most important factor in determining "fresh" or saline water concentrations. It is suggested that very ancient ocean waters may have been quite similar in composition and concentration to modern "fresh" water environments.

Liquid inclusion analyses from salt and chert from the Silurian Salina and Niagaran Groups of Michigan, Ontario, Ohio and Wisconsin compare very favorably with modern ocean compositions except that Ca and Mg compositions appear to be reversed.

### INTRODUCTION

THE solution of many geological problems depends upon knowledge of the composition of the oceans in geological times. Chemical sedimentary systems, geo-biochemical processes, and basic questions in evolution may be interpreted only if information concerning the composition of the oceans is available. Ocean compositions in geological time may even be excellent indicators of tectonic activity as suggested by KRAMER (1962) and UFFEN (1963).

It has generally been held that the composition of the oceans has been uniform (within an order of magnitude) since the beginning of the Paleozoic with slight increase in total salinity with time (CONWAY, 1943; RUBEY, 1951; LOWENSTAM, 1959; CHAVE, 1960). There has been, however, no agreement on the composition of sea water before the Paleozoic. For example, DALY (1910) suggests a Precambrian ocean virtually void of calcium; RONOY (1959) suggests an ocean in contact with a high carbon dioxide atmosphere; and TUREKIAN (1959) suggests an ocean with abnormal amounts of iron, silica and alumina. The lack of abundant fossils and the presence of abundant iron formations have suggested to many investigators a quite different atmosphere and ocean composition in the Precambrian compared to more recent geological periods.

SILLÉN (1958) outlined the limits of composition for the ocean on a geological time scale, and GARRELS and THOMPSON (1962) developed a more rigorous quantitative model for the ocean at 25°C. The theoretical model developed in this paper is

\* Present address: Department of Geology, Syracuse University, Syracuse, New York.

an outgrowth of Sillén's and Garrel's and Thompson's calculations and HALLEY's (1715) early ideas on the "... cause of the saltness of the ocean".

### CONSTANT TEMPERATURE-PRESSURE EQUILIBRIUM MODEL

#### General

The dynamic hydrologic cycle consisting of carrying constituents in solution to the oceans (runoff), and evaporation and precipitation of nearly pure water always tends towards increasing concentration of all ligands in sea water. The hydrologic

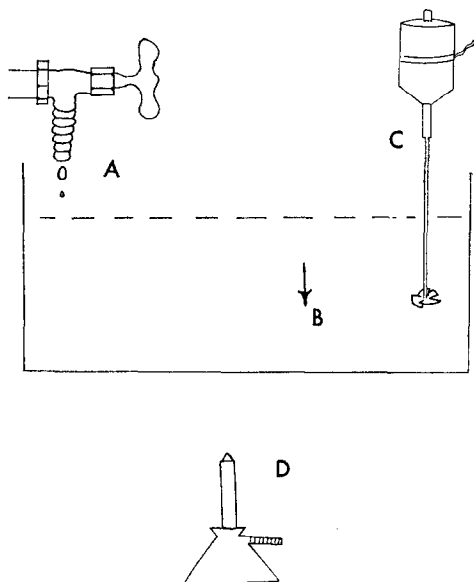


Fig. 1. Control of the composition of sea water. Additions (A) by run-off are balanced by mineral precipitation (B).

cycle, therefore, acts as a circular conveyor belt for dissolved materials. Sedimentational processes, however, tend to maintain the concentrations of ligands at equilibrium with respect to a solid phase and without regard to rate of runoff or composition of runoff waters. High velocity currents (compared to the rate of the above processes) tend to keep the oceans one homogeneous liquid phase. Ligand concentrations in the ocean are, therefore, controlled by equilibrium conditions with respect to a solid, since supersaturation conditions are not permissible without deposition of a solid.

Figure 1 illustrates schematically the principle of the above theory. A represents the net addition of dissolved materials due to the hydrologic cycle; B represents the process of precipitation of substance,  $i$ , when  $i$  is supersaturated in the ocean; C represents the rate of stirring of the ocean; and D represents the heat effects and hence the temperature of the ocean. Note that this model is not effected by changes in volume of the ocean due to changes in ice caps etc., since either process A or B will correct for the volume change. Precipitation of a substance ( $B_i$ ) is dependent upon the chemistry of the substance and the rate of addition ( $A_i$ ); both B and A

represent averages for all the oceans. As long as the rate of mixing,  $C$ , is large compared to  $A$  or  $B$  (and hence a homogeneous liquid is maintained), averages may be considered without introducing error.

The justification of constant temperature, constant pressure, and homogeneity of composition of the ocean with geological time is based upon the nature of the media, observation of the present ocean, and pure assumption because of lack of information.

Table 1. Residence times of constituents in sea water

Constituents	Time	
	This paper	Barth's estimates
Na <sup>+</sup>	480 m.y.	208 m.y.
K <sup>+</sup>	51	—
Cl <sup>-</sup>	870	—
SO <sub>4</sub> <sup>2-</sup>	54	—
Ca <sup>+2</sup>	5	1
Mg <sup>+2</sup>	95	22
CO <sub>3</sub> <sup>2-</sup>	1	—
PO <sub>4</sub> <sup>3-</sup>	28,000 y.	—
F <sup>-</sup>	3 m.y.	—

An estimate of the rate of stirring,  $C$ , may be obtained from radioactive dates of bottom waters. Sr and C ages for ocean currents range from a decade to a few thousand years for one revolution (ROCCO and BROECKER, 1963). If the rate of addition of a constituent compared to sea water concentration of the constituent,  $A_i$ , is much less than the stirring rate, a homogeneous liquid phase should develop. Table 1 depicts the amount of time required to replenish any one ion in sea water by addition from run-off. The calculations are based upon present day run-off rates (CONWAY, 1942, 1943; LIVINGSTONE, 1963) and are probably reasonable for past geological conditions within an order of magnitude. Only phosphate with a replenishing period of  $10^4$  y is nearly as small as the mixing rate of  $10$ – $10^3$  y per revolution.\* Conservatively one per cent of the total phosphate in the oceans is added at the same rate at which the ocean is stirred, but all the rest of the constituents considered are added at a rate so low that mixing would homogeneously disseminate the ions throughout the liquid. Hence the nearly uniform composition of the present ocean!

Approximately 95 per cent of the volume of the ocean lies within  $0$ – $5^\circ\text{C}$  with an overall volume average temperature of  $3.8^\circ\text{C}$ . Figure 2 shows temperature distribution as a function of volume as determined from integrating and averaging temperature profiles in SVERDRUP *et al.* (1942) and HARVEY (1960). Therefore, the temperature of most of the ocean today for all practical purposes is constant with the fringe areas not at constant temperature.

\* This argument assumes that an average of one revolution of a current would mix the liquid phase well. It further assumes that there are many interlocking currents in the ocean to cover the entire volume of the ocean. The development of chemical potentials due to inhomogeneities, however, would tend to aid mixing in developing a homogeneous phase; the rates of most chemical reactions are much less than a decade, and hence these reactions would tend to make current mixing much more efficient.

Changes in temperature of the ocean due to changes in heat input from the atmosphere or from the interior of the Earth are considered negligible due to the large mass and high specific heat of the ocean. On a volume basis, the heat capacity of the ocean is approximately  $3 \times 10^3$  times air. Therefore, quite extreme temperatures should be noted on land in contact with the atmosphere if these temperatures

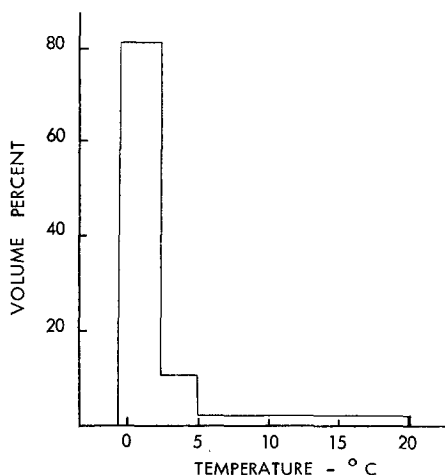


Fig. 2. Temperature distribution in the ocean.

are to develop throughout the sea. Extreme land temperatures in the past should be discernible as world wide distributions of tillite, red-beds etc. Since these deposits have not been noted on a world wide basis, one concludes that extreme temperatures and hence small variations in the oceans did not take place.

BARTH (1952) has summarized the possibility of large heat inflow from the interior of the Earth. Because of the poor thermal conductivity of rocks, Barth estimates that had no heat been generated, the Earth would have cooled  $22^{\circ}\text{C}$  in 1 billion years. Even if rates of heat flow were quite different in the past, the net effect upon heating the surface of the Earth, and particularly the oceans would be negligible compared with solar radiation.

Any changes in heat input would be felt in the ocean as a rate of stirring. If the stirrer ran at approximately 1 revolution per century, any change in heat input or output would be felt as a temperature change on the surface of the Earth before most of the ocean would change in temperature.

The effect of pressure on the model must be considered. Free energy dependency of reactions upon pressure is a function of the specific volume change; hence large changes in density of minerals with pressure may have important effects upon equilibrium. Likewise reactions with large volume changes such as the gypsum-anhydrite relationship may be influenced appreciably at great depths within the ocean. The volume change and hence the pressure effect upon ions is poorly known (OWEN and BRINKLEY, 1941), however, and quantitative calculations are poor at best. The average depth of the ocean is equivalent to approximately 200 atm pressure. In the following calculations, one atmosphere is assumed.

The final consideration is to compare the rate of precipitation of any constituent,  $B_i$  (Fig. 1) with the rate of addition.  $A_i$  generally would be a function of tectonic setting of the continents and would be maximum for maximum size and relief.  $B$  depends only upon the mineral forming. For a solid-liquid equilibrium ocean,  $B$  must be greater than or equal to  $A$ , so that equilibrium may be attained. If rate of addition of a constituent exceeds rate of formation for a particular mineral, supersaturation rather than equilibrium takes place with respect to that particular mineral. However equilibrium may be achieved with another mineral of the same general composition, whose rate of formation is rapid compared to rate of addition due to runoff. We can imagine different sets of minerals representing different ocean equilibria achieved under different rates of addition due to runoff; or in short, different equilibria are a function of tectonic setting.

### *Constituents*

The models developed on the following pages consider only the major inorganic constituents in solution. The ligands considered constitute 99 per cent of the dissolved material in sea water today. Organic constituents are not considered in the model because of their negligible concentration relative to the major ions. Soluble organic materials are at most  $10^{-4}$  times any of the major inorganic constituents. Even if an organic constituent were highly reactive, it would have negligible effect upon any of the major inorganic constituents because of its small abundance. This conclusion does not limit biochemical reactions to negligible importance in certain environments of the ocean (such as the depositional interface) or in influencing elements of the same abundance, but biochemical reactions averaged over the entire ocean are negligible (KRISSE and RUKINA, 1952).

For a unique solution to a constant temperature-pressure model, there must be as many independent relationships as there are independent variables. One relationship (based on electro-neutrality) may always be written; the equilibrium of a solid phase with a liquid phase represents an independent relationship; and each ionic type represents an independent variable. Therefore, the number of solid phases in equilibrium with the aqueous phase must be one less than the number of ionic types considered. I shall consider K, Na, Ca, Mg, P, F, S, H, C and Cl in the model. Therefore, I must consider nine solid phases in equilibrium with the ocean. Fewer phases demand more assumptions for a unique solution (Table 2).

The choice of minerals for the equilibrium model are based upon consideration of abundant occurrence (not amount) in nature, and the ease of formation of the mineral as observed in nature or in laboratory studies. The minerals considered can be divided into the alumino-silicates, carbonates, phosphates, sulfide-sulfates and oxides for ease of consideration. The alumino-silicates considered include the clays (montmorillonite, kaolinite, illite, muscovite, glauconite, chlorite), feldspars (albite, anorthite, K-feldspar) and zeolites (phillipsite). The carbonates include aragonite, calcite, nesquehonite, strontianite and dolomite; the phosphates include OH-apatite and carbonate-F-apatite; the sulfides-sulfates include pyrite celestite, and gypsum; and the oxides include ferric oxide.

1. *Aluminum-silicates*. It is apparent from the field studies of POWERS (1959) on the James River, OINUMA *et al.* (1958) on Pacific Ocean sediments, MURRAY and

LEININGER (1956) and HARRISON and MURRAY (1957) on Illinois tills, GOLDBERG and ARRHENIUS (1958) and ZEN (1959) on Pacific Ocean sediments and from laboratory studies by WHITEHOUSE and McCARTER (1958) and SLAUGHTER and MILNE (1960) that (1) montmorillonite and kaolinite are stable in the weathering zones, (2) chlorite and illite are stable in the marine environment, (3) authigenic feldspars are formed in the marine environment, and (4) zeolites (particularly phillipsite) are formed in the marine environment. Therefore, we should expect chlorite, feldspars,

Table 2. Solid phases in equilibrium with sea water

Liquid Phase	Solids controlling concentrations		
	<i>Lower Limit</i>	<i>Most Probable</i>	<i>Upper Limit</i>
			(a) (b)
Na <sup>+</sup>	Na-mont. (C site)	Na-mont (E site)	Na-mont (E site)
K <sup>+</sup>	K-illite (C site)	K-illite (E site)	K-illite (E site)
Cl <sup>-</sup>	O (assumed)	0.55 (assumed)	0.55 0.77 (assumed)
SO <sub>4</sub> <sup>2-</sup>	O (assumed)	SrCO <sub>3</sub> ; SrSO <sub>4</sub>	gypsum
Ca <sup>+2</sup>	Ca-clay	phillipsite	phillipsite
Mg <sup>+2</sup>	Mg-clay	chlorite	chlorite
PO <sub>4</sub> <sup>3-</sup>	OH-apatite	OH-apatite	OH-apatite
CO <sub>2</sub>	calcite	calcite	aragonite
F <sup>-</sup>	F-CO <sub>2</sub> -apatite	F-CO <sub>2</sub> -apatite	F-CO <sub>2</sub> -apatite
H <sup>+</sup>	electroneutrality	electroneutrality	electroneutrality

illites and phillipsite to be the cation controlling solids in the marine environment, and montmorillonites to be the cation regulating solids in a "fresh-water" low cation activity environment.

MARSHALL and his students (MARSHALL and BERGMAN, 1942; MARSHALL and KRINBILL, 1942; CHATTERJEE and MARSHALL, 1950) have determined the hydrogen and cation activity relationships for Na, K, Ca and Mg montmorillonites, kaolinites and illites. GARRELS and CHRIST (1956) and BLACKMON (1958) interpreted the data of MARSHALL *et al.* as a simple mass action equilibrium involving two discrete exchange sites, C and E. Equilibrium constants that fit the experimental data very closely were determined for "C" sites and "E" sites, for Na and K clays. The two sites may be equivalent to structural and interlayer sites or interlayer and edge sites.\* The C site would be filled with cations before the E site. Figure 3(a) is a plot of the Na and K data and shows the marked discontinuity (suggesting two processes—2 sites) for the Na and K clays. This is not the case, however, for Mg and Ca clays as shown by Fig. 3(b). In fact there is a simple linear relationship between log-hydrogen ion activity and log-cation activity. It is possible that the Mg and Ca curves, given enough time to equilibrate would show a break similar to the Na and K curves. This break would probably represent a transition to chlorite or zeolite.

Combining the field and laboratory analysis, I conclude that in a "fresh" water environment (low ion activities) Na-montmorillonite (C site), K-montmorillonite (C site), Mg-montmorillonite, and Ca-montmorillonite would be the stable and regulating aluminosilicates, whereas in a "marine" environment (high ion activities), Mg-chlorite, phillipsite, Na-montmorillonite (E site) and K-illite (E site) would be the

\* SCHWERTMANN and JACKSON (1963) report three ranges for clays perhaps representing filling of these three sites.

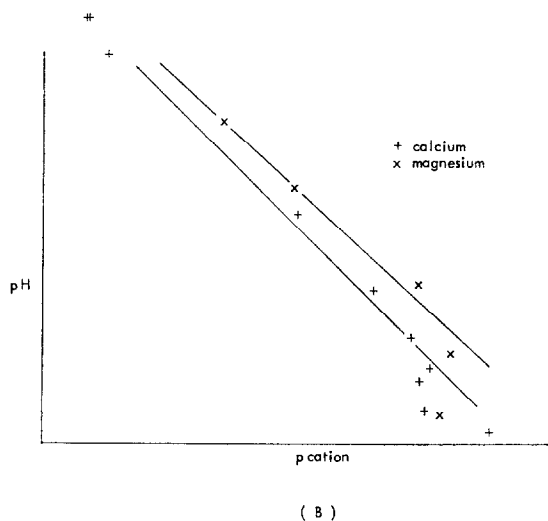
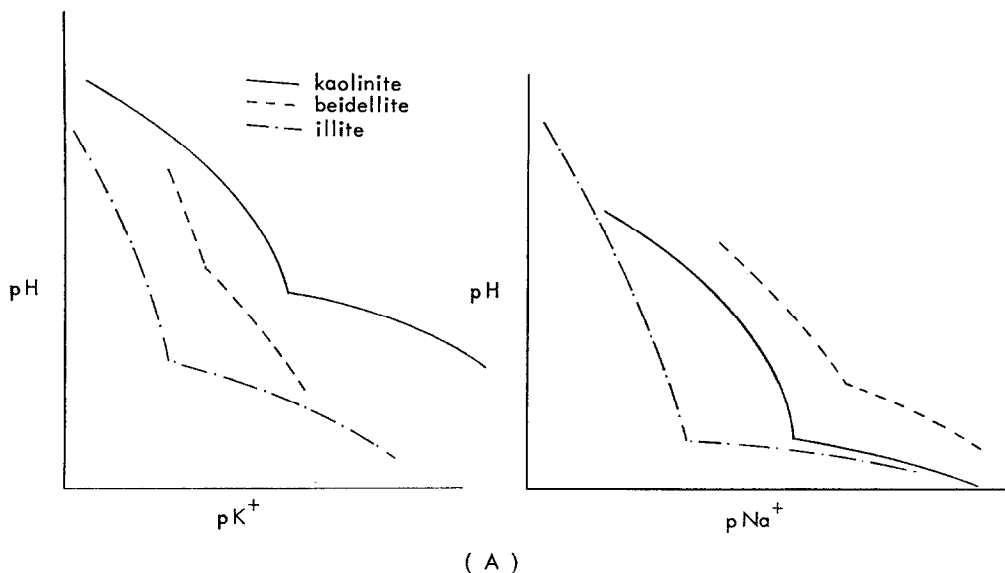


Fig. 3. pH-cation relationships for clays. (A) From data of MARSHALL and BERGMAN (1942), MARSHALL and KRINBILL (1942). Relative positions of curves are not valid, only the shapes. (B) Illite plot for Ca and Mg from data of CHATTERJEE and MARSHALL (1950).

stable and regulating solids. In addition, albite, K-feldspar and kaolinite should be at equilibrium in the marine environment. Muscovite is chemically stable relative to the clays but does not appear to form as an authigenic mineral under sedimentary conditions. No doubt glauconite is saturated with respect to sea water (HOWER, 1961) and may represent an Fe-rich equivalent of K-illite (E site), but not enough data are available to incorporate it in this study.

2. *Carbonates*. Calcite and dolomite are very common and abundant in the stratigraphic record. Both calcite and aragonite are *obviously* forming in the oceans at present; dolomite is not. Calcite and aragonite can be easily synthesized in the laboratory; dolomite can not be formed under sedimentary conditions (MEDLIN, 1959). It seems apparent that (1) calcite has always been in equilibrium with the

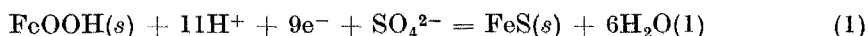
oceans, (2) aragonite may also have always been in equilibrium with the oceans,\* and (3) dolomite may have been in equilibrium only during times of extremely slow additions due to runoff. Nesquehonite may have been in equilibrium with the ocean, but it is very rare in the geologic record and very uncommon in recent marine sediments.

3. *Phosphates*. Both CO<sub>2</sub>-F-apatite and OH-apatite are found in the geologic record and in recent marine sediments. Stoichiometric F-apatite is not found in recent marine sediments, however, and is very uncommon in ancient sediments (JACOB *et al.*, 1933; SMITH and WHITLATCH, 1940; DIETZ *et al.*, 1942; DEISS, 1949; THOMPSON, 1954; MALDE, 1959; GULBRANDSEN, 1960). OH-apatite is easily formed in the laboratory; CO<sub>2</sub>-F-apatite has not been formed at room temperature. CO<sub>2</sub>-F-apatite is metastable relative to F-apatite under the more common Earth surface chemical conditions; therefore, F-apatite should form under severe diagenetic conditions. Both CO<sub>2</sub>-F-apatite and OH-apatite should be the regulating solids in the "fresh" water and "marine" environments. Fluorite is not saturated in the oceans at present.

4. *Sulfides-sulfates-oxides*. It is possible that the sulfate regulation of the oceans has been due to gypsum. Gypsum is very common in the geologic record, but it is not very abundant except in evaporite deposits. It is easily crystallized in the laboratory. The control of sulfate by gypsum is considered an upper limit value for sulfate concentration.

Another possible control of sulfate is the saturation of strontium sulfate and strontium carbonate. The strontium concentration could be stated as a function of the carbonate concentration, and the sulfate concentration in turn could be stated as a function of the strontium concentration. Sr and S-SO<sub>4</sub> are of approximately the same abundance in crustal rocks; therefore there is little chance that one of the constituents (Sr or SO<sub>4</sub>) would be added rapidly enough that the other constituent would be totally exhausted so that the saturation control would be lost. Similarly it is probably true that BaSO<sub>4</sub> and BaCO<sub>3</sub> are saturated in sea water, although BaSO<sub>4</sub> crystallizes very poorly at low temperatures.

A final consideration for the control of sulfate would be by the saturation of FeS (or FeS<sub>2</sub>) and FeOOH (or Fe<sub>2</sub>O<sub>3</sub>). This control is outlined by the following reaction:



and,

$$\log K = 11\text{pH} + 9\text{pE} - \log (a_{\text{SO}_4^{2-}}) = 37$$

The pE is controlled by:



where:

$$\text{pE} = 20.78 + \frac{1}{4} \log P_{\text{O}_2} - \text{pH}$$

Simple calculations show that equation (1) would be valid (FeS and FeOOH in equilibrium) for a sulfate activity of 10<sup>167</sup> (!) at a pH of 8 and a pE of 12.5 (modern ocean

\* There is only a small difference in the solubility chemistry of aragonite and calcite. Hence there would be minor differences in concentration in the aqueous phase.



conditions). Combining equations (1) and (2), I calculate that for FeOOH-FeS equilibrium and a reasonable sulfate activity (assumed  $10^{-2}$ ), the atmospheric value of oxygen must be  $10^{-76}$  atm. It is apparent that the above equilibrium is not the present regulating mechanism for sulfate. It might appeal to those who would wish a deficient oxygen atmosphere sometime in the geological past.

From the above discussion, I conclude that (1) sulfate has not reached a high enough concentration in the "fresh-water" environment to be regulated by a saturation process (therefore, I would assume sulfate concentration is zero in this case) (2) gypsum is the regulator in the upper limit "marine" environment, and (3)  $\text{SrSO}_4$ - $\text{SrCO}_3$  are the most probable regulators of sulfate.

5. *Chloride*. Chloride appears to have no solubility regulation in water. Most of the chloride in the oceans was probably derived from "de-gassing" the crust (RUBEY, 1951), and it is also highly probable that some of the Cl has been recycled between ocean and crust by Earth processes. HOERING and PARKER (1961) have shown that there is no isotopic fractionation of Cl which suggests that either Cl is very rapidly cycled or that Cl is so weakly bonded that it can not be isotopically differentiated by Earth processes. A simple calculation tends to verify the mixing between crust and ocean and the resultant equilibrium of partitioning of Cl in the two "phases".\* Assume the crust was "mantle", at time zero. Cl is degassed from the original crust by tectonic and igneous processes. An equilibrium would develop between the Cl concentration in the crust and the Cl concentration in the ocean. Therefore:

$$(\text{Cl}_{t=0} - \text{Cl}_{\text{today}})_{\text{crust}}(\text{Volume})_{\text{crust}} = \text{Cl in the oceans}$$

KURODA and SANDELL (1953) give an average figure of 0.02 wt per cent for Cl in crustal rocks; I estimate an average of 0.07 wt per cent as an average for Precambrian "crust" from Precambrian ultrabasics (EARLEY, 1958). The Cl in the oceans is  $2.7 \times 10^{22}$  g (SVERDRUP *et al.*, 1942). The density of the crust at present is taken as 2.9 and the density of the crust initially is taken as 4.5. I calculate that all the Cl in the oceans could be accounted for by degassing the crust to an average depth of 19 km. This compares with an average depth of crust of 15 km (70%-6 km for ocean; 30%-35 km for continents). The uncertainties in the values assumed for Cl concentrations in the crust could easily account for the difference in the degassing depth and crust-mantle depth.

One limit on the concentration of Cl in the ocean is zero; the other extreme would be to assume at some time there was no retention of Cl in the crustal rocks. If there were no retention of Cl in the crust, I calculate the oceans may have reached as high as 1.4 times their Cl concentration today, assuming a constant volume ocean.

The time-dependent development of Cl in the oceans may be derived from a constant-volume ocean assumed initially void of Cl. Assume a crust and ocean making up two phases of a system with respect to Cl. Cl is added to the ocean by volcanism, hot spring action and other igneous and metamorphic activity and at a rate proportional to the Cl concentration in the crust. Some Cl is returned to the crust from the ocean by the trapping and burial of sea water in sediments, and

\* If LOVERING's (1958) hypothesis that the crust-mantle boundary does not represent a compositional change is correct, these calculations would be highly suspect.

assimilation by tectonic squeezing and igneous and metamorphic processes. The rate of return would be proportional to the ocean Cl concentration in sea water. This develops into a growth curve equivalent to a first order opposing reaction:

Let  $V_c$  = volume crust;  $V_0$  = volume of ocean;  $A_c$  = initial Cl concentration in the crust.

At time  $t = 0$ ,  $C_0$  (concentration Cl in ocean) = 0;  $C_c$  (Cl conc. in crust) =  $A_c$ .

At time  $t = t$ ,  $C_0 = A$ ;  $C_c = (A_c V_c - A V_0)/V_c = A_c - A(V_0/V_c)$

$$\text{Ocean to crust rate is: } \frac{dA}{dt} = -R_0 A$$

$$\text{Crust to ocean rate is: } \frac{dA}{dt} = R_c(A_c - V_0/V_c),$$

where  $R_c$  and  $R_0$  are proportionality constants for the crust and ocean respectively. Positive direction is taken towards addition of Cl to the ocean. The net addition to the ocean is:

$$\frac{dA}{dt} = R_c \left( A_c - A \frac{V_0}{V_c} \right) - R_0 A \quad (3)$$

At equilibrium, the forward rate equals the reverse rate. The chloride concentration at equilibrium ( $A_{eq}$ ) is represented by the rate equilibrium:

$$R_0 A_{eq} = \frac{R_c(A_c - A_{eq} V_0/V_c)}{A_{eq}} \quad (4)$$

Substituting (4) into (3), and integrating with the limits,  $t = 0$ ,  $t$ ;  $A = 0$ ,  $A$ :

$$A = \frac{A_{eq}[\exp\{(R_0 + R_c V_0/V_c)(t)\} - 1]}{\exp\{(R_0 + R_c V_0/V_c)(t)\}} \quad (5)$$

Figure 4 is a plot of equation (5). The derivation of equation (5) assumes a constant volume ocean and a constant volume crust. It also assumes that the proportionality factors are constant with respect to time. I would assume that the value of  $A_{eq}$  is the concentration of Cl in sea water today.

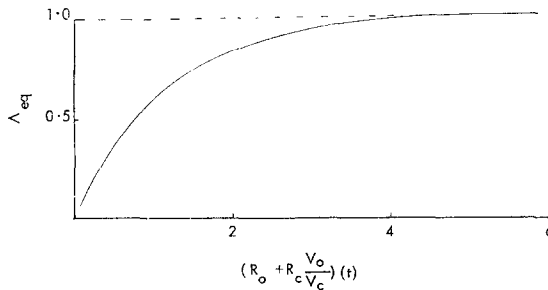


Fig. 4. Plot of equation (5). Curve shows attainment of constant Cl concentration with time.

6. *Carbon dioxide.* In the following models, the carbon dioxide content of the atmosphere and the oceans is controlled by the solid equilibria established in the oceans. A few simple calculations will show that only very large additions or subtractions of carbon dioxide (from the lithosphere) could overwhelm these equilibria. On the other hand, a change in models may have a profound effect on the  $\text{CO}_2$  in the atmosphere. At present almost all of the carbon dioxide from the hydrosphere, biosphere, and atmosphere is distributed in the oceans. There are  $2.5 \times 10^{-2}$  geo-mols\* in the hydrosphere,  $5.7 \times 10^{-4}$  geo-mols in the atmosphere, and a maximum of  $8.3 \times 10^{-4}$  geo-mols in the biosphere.† Relatively large additions of carbon dioxide to the atmosphere, biosphere, or hydrosphere from the lithosphere would be dissolved in the oceans, and only extremely drastic changes in the composition of the oceans would have an important effect upon atmospheric  $\text{CO}_2$  (ERIKSSON, 1963). More specifically, large increases in carbon dioxide to the ocean can come only from the lithosphere, and changes would have to be large before a large change in atmospheric or biospheric carbon dioxide would take place; most of the carbon dioxide added would result in carbonate rocks with little net change in atmospheric or hydrospheric chemistry. This is due to the chemical interchange of carbon dioxide between atmosphere and ocean, the extremely large amount of carbon dioxide stored in the oceans, and the saturation of  $\text{CO}_2$  in the oceans relative to a solid.

It seems reasonable to assume that the  $\text{CO}_2$  required to form the lithosphere (5 geo-mols) could be acquired from a slow degassing of the crust rather than demanding that it represent  $\text{CO}_2$  from an initial atmosphere. It also seems plausible that there exists a steady state of equilibrium between ocean (and atmosphere and biosphere) and crust similar to that described for chlorine. That is the rate of usage of  $\text{CO}_2$  in forming carbonate rocks is equal to the rate of addition of  $\text{CO}_2$  to the ocean (from the lithosphere).

### Calculations

As summarized above, there are quite a few possible combinations of regulatory minerals for the composition of sea water calculations. Table 2 summarizes the various models considered here. I consider a "lower limit" compositional model, an "upper limit" model, and a "most probable" model. The "lower limit" model will, in general, correspond to low rates of runoff and a less concentrated brine ("fresh" water). The "upper limit" model will consider the higher concentration brines ("marine"), and will represent, in general, maximum concentrations for all constituents. In the "lower limit" model, I assume the chloride and sulfate concentrations to be zero; in the "upper limit" model, I shall consider concentrations resulting from a model containing (a) 1.0 and (b) 1.4 times the present chloride concentration in sea water. The "most probable" model compares with modern ocean conditions, and the derived values are between the two other models. The major change in the "most probable" model is the substitution of  $\text{SrCO}_3$ - $\text{SrSO}_4$  for gypsum. The E site clays

\* A geo-mol is defined as  $10^{20}$  mol.

† Calculations are based upon data from RANKAMA and SAHAMA (1950). The mass of the atmosphere is assumed to be 51.3 geograms and composed of  $4.6 \times 10^{-2}$  wt. per cent  $\text{CO}_2$ . Mass of the hydrosphere is  $6.9 \times 10^5$  times the biosphere; the biosphere is assumed to consist of 50 wt. per cent carbon. There are approximately 5 geo-mols in limestone and dolomite deposits.

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

Species or reaction	Constant	Reference	Remarks
H-Mont(C site) = Na-Mont(C site)	$10^{-3.2} = \frac{[NaC](H^+)}{[HC][Na^+]}$	BLACKMON (1958)	1
H-Mont (E site) = Na-Mont (E site)	$10^{-7.4} = \frac{[NaE](H)}{[HE](Na)}$	BLACKMON (1958)	1
H-Ililite(C site) = K-Ililite (C site)	$10^{-3.4} = \frac{[KC](H)}{[HC](K)}$	BLACKMON (1958)	1
H-Ililite (E site) = K-Ililite (E site)	$10^{-5.7} = \frac{[KE](H)}{[KE](K)}$	BLACKMON (1958)	1
CaSO <sub>4</sub> ·2H <sub>2</sub> O = Ca <sup>+2</sup> + SO <sub>4</sub> <sup>-2</sup> + 2 H <sub>2</sub> O(l)	$10^{-4.60} = (Ca^{+2})(SO_4^{-2})$	LATIMER (1952)	1
Ca <sup>+2</sup> + H-Ililite = Ca-Ililite + 2H <sup>+</sup>	$10^{-3.8} = (Ca^{+2})(H^+)^{0.08}$	CHATTERJEE and MARSHALL (1950)	3
Ca <sub>2</sub> Al <sub>2</sub> Si <sub>8</sub> O <sub>24</sub> ·9H <sub>2</sub> O(philipsite) + 4 H <sup>+</sup> = 4 SiO <sub>3</sub> (qtz) + 2 Al <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O(kaol) + 2 Ca <sup>+2</sup> + 7 H <sub>2</sub> O(l)	$10^{13} = (Ca^{+2})(H^+)^2$	BARANY and KELLEY (1961)	4
Mg <sup>+2</sup> + H-Ililite = Mg-Ililite + 2H <sup>+</sup>	$10^{-4.4} = (Mg^{+2})(H^+)^{-0.1}$	CHATTERJEE and MARSHALL (1950)	3
Mg <sub>2</sub> Al <sub>2</sub> Si <sub>8</sub> O <sub>11</sub> ·4H <sub>2</sub> O(Chlorite) + 10 H <sup>+</sup> = SiO <sub>3</sub> (qtz) + Al <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O(kaol) + 7H <sub>2</sub> O + 5 Mg <sup>+2</sup>	$10^{14.2} = (Mg^{+2})(H^+)^2$		
Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub> = 10 Ca <sup>+2</sup> + 6 PO <sub>4</sub> <sup>-3</sup> + 2 OH <sup>-</sup>	$10^{-11.2} = (Ca^{+2})^{10}(PO_4^{-3})^6(OH^-)^2$		6
solubility of:			
[Na <sub>60</sub> Ca <sub>90</sub> Ca <sub>90</sub> 55]((PO <sub>4</sub> ) <sub>5</sub> 35)(SO <sub>4</sub> ) <sub>10</sub> 30(CO <sub>3</sub> ) <sub>10</sub> 33[F <sub>2</sub> -0.1]	equilibrium constant = 10 <sup>10.3</sup>		
CaCO <sub>3</sub> (calcite) = Ca <sup>+2</sup> + CO <sub>3</sub> <sup>-2</sup>	$10^{-8.09} = (Ca^{+2})(CO_3^{-2})$	HARNED and SCHOLES (1941)	8
CaCO <sub>3</sub> (aragonite) = Ca <sup>+2</sup> + CO <sub>3</sub> <sup>-2</sup>	$10^{-7.82} = (Ca^{+2})(CO_3^{-2})$	HARNED and SCHOLES (1941)	8
CaMg(CO <sub>3</sub> ) <sub>2</sub> = Ca <sup>+2</sup> + Mg <sup>+2</sup> + 2 CO <sub>3</sub> <sup>-2</sup>	$10^{-18.81} = (Ca^{+2})(Mg^{+2})(CO_3^{-2})^2$	ROBIE (1958)	9
MgCO <sub>3</sub> ·3H <sub>2</sub> O = Mg <sup>+2</sup> + CO <sub>3</sub> <sup>-2</sup> + 3 H <sub>2</sub> O(l)	$10^{-5} = (Mg^{+2})(CO_3^{-2})$	LATIMER (1952)	9
H <sub>2</sub> CO <sub>3</sub> = H <sup>+</sup> + HCO <sub>3</sub> <sup>-</sup>	$10^{-6.32} = (H^+)(HCO_3^-)/(H_2CO_3)$	HARNED and DAVIS (1943)	9
HCO <sub>3</sub> <sup>-</sup> = H <sup>+</sup> + CO <sub>3</sub> <sup>-2</sup>	$10^{-10.6} = (H^+)(CO_3^{-2})/(HCO_3^-)$	HARNED and SCHOLES (1941)	9
CO <sub>2</sub> (g) + H <sub>2</sub> O(l) = H <sub>2</sub> CO <sub>3</sub>	$10^{-1.19} = P^{CO_2}/(H_2CO_3)$	HARVEY (1960)	9
CaHCO <sub>3</sub> <sup>+</sup> = Ca <sup>+2</sup> + HCO <sub>3</sub> <sup>-</sup>	$10^{-1.26} = (Ca^{+2})(HCO_3^-)/(CaHCO_3^+)$	GARRELS and THOMPSON (1962)	9
NaCO <sub>3</sub> <sup>-</sup> = Na <sup>+</sup> + CO <sub>3</sub> <sup>-2</sup>	$10^{-1.27} = (Na^+)(CO_3^{-2})/(NaCO_3^-)$	GARRELS and THOMPSON (1962)	9
CaCO <sub>3</sub> <sup>0</sup> = Ca <sup>+2</sup> + CO <sub>3</sub> <sup>-2</sup>	$10^{-5.2} = (Ca^{+2})(CO_3^{-2})/(CaCO_3^0)$	GARRELS and THOMPSON (1962)	9
NaHCO <sub>3</sub> <sup>0</sup> = Na <sup>+</sup> + HCO <sub>3</sub> <sup>-</sup>	$10^{-0.25} = (Na^+)(HCO_3^-)/(NaHCO_3^0)$	GARRELS and THOMPSON (1962)	9
CaSO <sub>4</sub> <sup>0</sup> = Ca <sup>+2</sup> + SO <sub>4</sub> <sup>-2</sup>	$10^{-2.31} = (Ca^{+2})(SO_4^{-2})/(CaSO_4^0)$	GARRELS and THOMPSON (1962)	9
KSO <sub>4</sub> <sup>-</sup> = K <sup>+</sup> + SO <sub>4</sub> <sup>-2</sup>	$10^{-0.95} = (K^+)(SO_4^{-2})/(KSO_4^-)$	GARRELS and THOMPSON (1962)	9
NaSO <sub>4</sub> <sup>-</sup> = Na <sup>+</sup> + SO <sub>4</sub> <sup>-2</sup>	$10^{-0.72} = (Na^+)(SO_4^{-2})/(NaSO_4^-)$	GARRELS and THOMPSON (1962)	9
MgHCO <sub>3</sub> <sup>+</sup> = Mg <sup>+2</sup> + HCO <sub>3</sub> <sup>-</sup>	$10^{-1.16} = (Mg^{+2})(HCO_3^-)/(MgHCO_3^+)$	GARRELS and THOMPSON (1962)	9
MgCO <sub>3</sub> <sup>0</sup> = Mg <sup>+2</sup> + CO <sub>3</sub> <sup>-2</sup>	$10^{-3.4} = (Mg^{+2})(CO_3^{-2})/(MgCO_3^0)$	GARRELS and THOMPSON (1962)	9
MgSO <sub>4</sub> <sup>0</sup> = Mg <sup>+2</sup> + SO <sub>4</sub> <sup>-2</sup>	$10^{-2.56} = (Mg^{+2})(SO_4^{-2})/(MgSO_4^0)$	GARRELS and THOMPSON (1962)	9

$\text{MgF}^+ = \text{Mg}^{+2} + \text{F}^-$	$10^{-1.60} = (\text{Mg}^{+2})(\text{F}^-)/(\text{MgF}^+)$	CONNICK and TSAO (1954)	10
$\text{NaPO}_4^{-2} = \text{Na}^+ + \text{PO}_4^{-3}$	$10^{-0.35} = (\text{Na}^+)(\text{PO}_4^{-3})/(\text{NaPO}_4^{-2})$	SMITH and ALBERTY (1956)	10
$\text{NaHPO}_4^- = \text{Na}^+ + \text{HPO}_4^{-2}$	$10^{-0.24} = (\text{Na}^+)(\text{HPO}_4^{-2})/(\text{NaHPO}_4^-)$	SMITH and ALBERTY (1956)	10
$\text{KPO}_4^{-2} = \text{K}^+ + \text{PO}_4^{-3}$	$10^{-0.20} = (\text{K}^+)(\text{PO}_4^{-3})/(\text{KPO}_4^{-2})$	SMITH and ALBERTY (1956)	10
$\text{KHPO}_4^- = \text{K}^+ + \text{HPO}_4^{-2}$	$10^{-0.20} = (\text{K}^+)(\text{HPO}_4^{-2})/(\text{KHPO}_4^-)$	SMITH and ALBERTY (1956)	10
$\text{CaHPO}_4^0 = \text{Ca}^{+2} + \text{HPO}_4^{-2}$	$10^{-2.20} = (\text{Ca}^{+2})(\text{HPO}_4^{-2})/(\text{CaHPO}_4^0)$	DAVIES and HOYLE (1953)	9
$\text{MgHPO}_4^0 = \text{Mg}^{+2} + \text{HPO}_4^{-2}$	$10^{-1.50} = (\text{Mg}^{+2})(\text{HPO}_4^{-2})/(\text{MgHPO}_4^0)$	GREENWALD (1940, 1945)	9
$\text{H}_2\text{PO}_4^- = \text{H}^+ + \text{HPO}_4^{-2}$	$10^{-7.28} = (\text{H}^+)(\text{HPO}_4^{-2})/(\text{H}_2\text{PO}_4^-)$	VAN WAZER (1958)	
$\text{HPO}_4^{-2} = \text{H}^+ + \text{PO}_4^{-3}$	$10^{-12.66} = (\text{H}^+)(\text{PO}_4^{-3})/(\text{HPO}_4^{-2})$	VANDERZEE and QUIST (1961)	
$\text{Ca}_2\text{HPO}_4\text{CO}_3^0 + \text{H}^+ = 2\text{Ca}^{+2} + \text{HPO}_4^{-2} + \text{HCO}_3^-$	$10^{-1.33} = \frac{(\text{Ca}_2\text{HPO}_4\text{CO}_3^0)(\text{H}^+)}{(\text{H}^+)(\text{Ca}_2\text{PO}_4\text{CO}_3^0)}$	GREENWALD (1945)	9
$\text{Ca}_2\text{HPO}_4\text{CO}_3^0 = \text{H}^+ + \text{Ca}_2\text{PO}_4\text{CO}_3^-$	$10^{-8.3} = \frac{(\text{Ca}_2\text{HPO}_4\text{CO}_3^0)}{(\text{Ca}_2\text{PO}_4\text{CO}_3^-)}$	GREENWALD (1945)	9
$\text{H}_2\text{O}(1) = \text{H}^+ + \text{OH}^-$	$10^{-14.78} = (\text{H}^+)(\text{OH}^-)$	HARNED and HAMMER (1933)	
$\text{SrSO}_4 = \text{Sr}^{+2} + \text{SO}_4^{-2}$	$10^{-6.55} = (\text{Sr}^{+2})(\text{SO}_4^{-2})$	BJERRUM <i>et al.</i> (1958)	
$\text{SrCO}_3 = \text{Sr}^{+2} + \text{CO}_3^{-2}$	$10^{-9.15} = (\text{Sr}^{+2})(\text{CO}_3^{-2})$	LATIMER (1952)	
		BJERRUM <i>et al.</i> (1958)	
		LATIMER (1952)	

- (1) The cationic clay complex is assumed equal to the protonated clay complex so that the equilibrium constants reduce to:  $(\text{H})/(\text{cation}) = \text{constant}$ . The constants listed are for room temperature.
- (2)  $\Delta\text{H}^0$  and  $\Delta\text{S}^0$  are assumed constant over small temperature ranges. Hence,  $\Delta\text{F}^0 = a + bT$  from which the equilibrium constant at 5°C is derived.
- (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 leornhardtite (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  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  and  $-3269$  kcal/mol for  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$  (personal communication, EGAN). See also CLARK (1955), SILLEN (1961), and GOTTSCHAL (1959) regarding OII-apatite.
- (7) Solubility of  $\text{CO}_2$ -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:  $\log K = a + bT$ .

rather than the C site clays along with the different chloride assumptions represent the most important change in the "most probable" and "upper limit" model compared to the "lower limit" model.

Concentrations are determined by substituting expressions into the expression for electroneutrality. A few iterations will develop limiting values for activities and ionic strength from which concentrations may be obtained. Activity coefficients are determined using the Debye-Huckel expression. The various ionic constituents are summarized by the following equations\*:

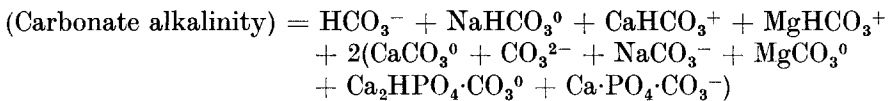
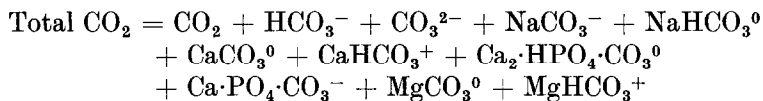
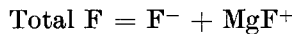
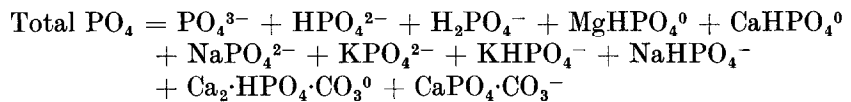
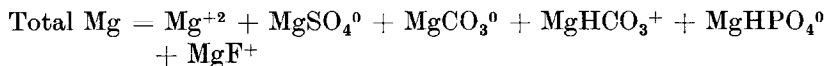
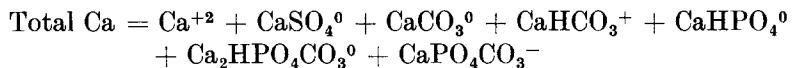
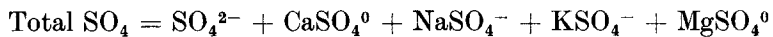
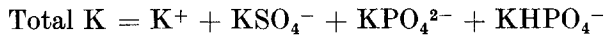
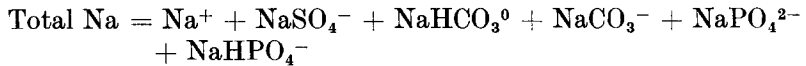


Table 3 is a summary of the constants used in the calculations. The constants substituted in the above equations along with an equation depicting electroneutrality are used to solve for the concentrations in the various ocean water models outlined in Table 2. The derived values are listed in Table 4. Also tabulated in Table 4 is the concentration of present ocean water, the composition of average river water, and the average values for Lake Superior, and Lake Erie.

### *Results and interpretation*

The "most probable" model fits the present ocean values very closely with the following exceptions: (1) Ca concentration in the model is 60 per cent of that in the present oceans; (2) Mg in the model is 120 per cent of that in the oceans; (3) carbonate alkalinity in the model is 190 per cent that of the present ocean; (4) CO<sub>2</sub> in

\* Many of these species will be negligible in the calculations and simplify the arithmetic quite a bit. In addition, species of Br and B will affect the equilibria, particularly of the less concentrated constituents, F, CO<sub>2</sub> and PO<sub>4</sub>.

Table 4. Composition of sea water models. All values are in mol/l. except  $P_{CO_2}$  which is in atmospheres and carbonate alkalinity (equiv./l.). Present ocean values from SVEDDRUP *et al.* (1942); average river values (LIVINGSTONE, 1963); Lake Superior (BEETON and CHANDLER, 1963); Lake Erie (KRAMER, 1961); Fluoride data, Lake Erie (POWERS *et al.*, 1960). Solids and data used in calculating values in models are listed in Tables 2 and 3.

Ion	Lower Limit	Most Probable	Models			Limit	Present ocean	Average river	Lake Superior	Lake Erie
			Upper	Upper	Limit					
$Na^+$	$7.9 \times 10^{-6}$	0.45	(a) 0.70	(b) 0.68		0.47	$2.7 \times 10^{-4}$	$4.8 \times 10^{-5}$	$4.3 \times 10^{-4}$	
$K^+$	$1.4 \times 10^{-6}$	$9.7 \times 10^{-3}$	$1.1 \times 10^{-2}$	$1.5 \times 10^{-3}$		$1.0 \times 10^{-2}$	$5.9 \times 10^{-5}$	$1.5 \times 10^{-5}$	$4.9 \times 10^{-5}$	
$Ca^{+2}$	$7.9 \times 10^{-4}$	$6.1 \times 10^{-3}$	$1.2 \times 10^{-2}$	$1.2 \times 10^{-2}$		$1.0 \times 10^{-2}$	$3.8 \times 10^{-4}$	$3.1 \times 10^{-4}$	$9.6 \times 10^{-4}$	
$Mg^{+2}$	$3.5 \times 10^{-4}$	$6.7 \times 10^{-2}$	0.20	0.23		$5.4 \times 10^{-2}$	$3.4 \times 10^{-4}$	$1.2 \times 10^{-4}$	$3.7 \times 10^{-4}$	
F <sup>-</sup>	$3.4 \times 10^{-6}$	$2.4 \times 10^{-5}$	$9.9 \times 10^{-5}$	$2.1 \times 10^{-5}$		$7 \times 10^{-5}$	$5.3 \times 10^{-6}$	$7 \times 10^{-6}$	$5 \times 10^{-6}$	
$Cl^-$	0 (defined)	0.55(defined)	0.55(defined)	0.77(defined)		0.55	$2.2 \times 10^{-4}$	$3.3 \times 10^{-5}$	$2.5 \times 10^{-4}$	
$SO_4^{2-}$	0 (defined)	$3.4 \times 10^{-2}$ *	0.29	0.21		$3.8 \times 10^{-2}$	$1.2 \times 10^{-4}$	$3.3 \times 10^{-5}$	$2.5 \times 10^{-4}$	
pH	8.33	7.95	7.88	7.81		7.89	—	7.4	7.70	
Carbonate alkalinity	$2.1 \times 10^{-3}$	$4.3 \times 10^{-4}$	$9.0 \times 10^{-3}$	$7.8 \times 10^{-3}$		$2.3 \times 10^{-3}$	$9.6 \times 10^{-4}$	$9.2 \times 10^{-4}$	$1.9 \times 10^{-3}$	
$P_{CO_2}$	$4.9 \times 10^{-4}$	$1.7 \times 10^{-3}$	$1.7 \times 10^3$	$2.5 \times 10^{-3}$		$4 \times 10^{-4}$	$4 \times 10^{-4}$	$4 \times 10^{-4}$	$4 \times 10^{-4}$	
Tot. P.	$1.3 \times 10^{-7}$	$2.7 \times 10^{-6}$	$2.4 \times 10^{-6}$	$2.1 \times 10^{-6}$		$1.5 \times 10^{-6}$	—	$1.6 \times 10^{-7}$	$1.9 \times 10^{-6}$	
Ionic strength	$3.6 \times 10^{-3}$	0.66	0.89	1.2		0.65	—	—	$4.4 \times 10^{-3}$	

\* Strontium value for this determination is  $5.5 \times 10^{-4}$ ; ocean value is  $4 \times 10^{-4}$ .

the model is 400 per cent that of the present atmosphere (reflecting the higher carbonate alkalinity), and (5) F in the model is 35 per cent that of the present ocean. All of these discrepancies may be due to poor estimates of equilibrium constants. I would suspect particularly the chlorite and phillipsite constants.

The "lower limit" model fits lake and river waters very well except for the very low Na and K values of the model. This may be due to poor estimation of equilibrium values or to the invalidity of the assumption: (cation-clay complex) = (H-clay complex). More studies on clays (CHRIST and TRUESDELL, 1963) may develop better data for application to these calculations.

The most important conclusion of these calculations is that changing Cl concentration has the effect of changing from "fresh water" composition to "marine" composition. If the oceans were initially quite low in Cl, it is quite possible that their composition approximated fresh water. With the addition of more Cl and the overwhelming of equilibria governed by "fresh water" solids due to addition of ions by runoff, new equilibria would be set up determining a composition equivalent to present ocean water. This change would represent the separation of the hydrosphere into "fresh" water and "marine" water. In short, "fresh" water compositions today may be excellent representatives of ancient ocean water.

It is impossible to determine when this separation took place, and whether Cl build-up was complete when the shift occurred in the solids governing equilibria. Further there is no evidence to show that the shift in the solids governing equilibria took place all at once, one at a time etc. The limits specified by all the possible combinations for the major constituents would be less than the limits established by the "fresh water" model and the "upper limit" model. For example, a "most probable" ocean model with no Cl would give values of: pH—8.43;  $P_{CO_2}$ — $1.9 \times 10^{-3}$  atm;  $Na^+$ —0.12 mol/l.;  $K^+$ — $2.5 \times 10^{-3}$  mol/l.;  $Ca^{+2}$ — $3.9 \times 10^{-4}$  mol/l.;  $Mg^{+2}$ — $5.4 \times 10^{-3}$  mol/l.;  $SO_4^{2-}$ —0.11 mol/l.; carbonate alkalinity— $1.9 \times 10^{-3}$  equiv./l.

## LIQUID INCLUSIONS

### *Introduction*

The only way of accumulating evidence to check the above models is to assume that there is fossil sea water contained within the geologic record. If this is true, the obvious phenomena to investigate are liquid inclusions. Liquid inclusions are common in almost all crystalline materials, and they are concentrated enough to extract and analyze without too sophisticated methods. It is another matter to interpret the meaning of analytical results of liquid inclusions, particularly in context to fossil sea water.

The approach used in this study was to assume that there are some inclusions of fossil sea water in sedimentary minerals and some inclusions significantly altered by post-depositional processes. To separate the two groups, I assumed that the post-depositional effects would vary from place to place. Therefore, those analyses which showed a great deal of variation would be influenced by secondary effects; those analyses which were consistent throughout would represent fossil sea water.

The procedure is to pick a sequence of rocks of the same age with large geographical extent. The final interpretation, however, depends upon the assumptions: (1)



secondary influences will vary from place to place, and (2) sea water was the same composition from place to place, to start. Any solid must represent a change in the composition of the liquid phase, and therefore the trapped brine can not truly represent "open" sea water. We do observe, however, in modern environments (such as Andros Island with respect to carbonate rocks) negligible change in composition of aqueous phase going from the open sea to the depositional environment. It is only

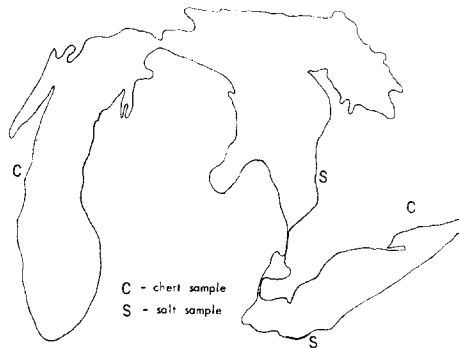


Fig. 5. Sample locations of chert and salt.

in restricted areas, such as evaporite deposits (MORRIS and DICKEY, 1957), that the system is not open enough to maintain constancy of composition of the brine during precipitation. Since halite is one of the solids analyzed, assumption (2) is valid only if I further assume that the rate of addition of "open" sea water was large compared to rate of precipitation at the points sampled, and therefore constancy of composition of brine was maintained.

Salt from the lower units of the Silurian Salina group was sampled from the Michigan Basin along with chert from the very top of the Lockport Group. The Salina rests upon the Lockport group. At each salt sampling locality (Fig. 5), samples of obviously re-crystallized halite were taken to compare their analyses with the analyses of the best examples of salt with primary inclusions. The best examples of primary inclusions were considered small hopper crystals in well-bedded and undeformed deposits. When there were no clear-cut distinctions, the criteria mentioned by ROEDDER (1962, 1963) were used to classify the inclusions. No classification of inclusions in chert could be made because all inclusions were barely discernible under the petrographic microscope.

The Salina-Niagaran was chosen to sample because there were numerous sampling localities, and two different rock types representing quite different environments were included. Halite is advantageous to work with because inclusions are obvious, quite easy to classify, and easy to analyze. Inclusions in chert can not be classified and are not easy to analyze, but chert is non-crystalline and its inclusions probably represent the best example of fossil sea water. As pointed out previously, inclusions in halite may not represent "open" sea brine composition.

#### *Analytical procedure*

*Sampling.* Multiple samples were collected from the four localities. Salt was sampled from the Sifto Salt mine and from cores at Goderich, Ontario, and from the

Morton Salt mine at Fairport, Ohio; chert was sampled from the Ancaster chert just northeast of Ancaster, Ontario on Highway No. 2 and on the Niagaran escarpment. Another chert was sampled near Manitowoc, Wisconsin, in the upper Niagaran group (PROUTY, 1960, stop 4, p. 31). Salt units A<sub>1</sub>, A<sub>2</sub>, and B were analyzed from Goderich; salt from unit F (?) was analyzed from Fairport, Ohio. Additional chert samples were taken from Wisconsin, Northern Michigan, Illinois, and Indiana, and additional salt samples were collected from Windsor, Ontario. They have either been discarded because of obvious contamination or presented nearly impossible analytical problems.

The preparatory procedures for salt and chert were quite different:

1. *Chert*. Approximately 50 lb of chert (when available) was carefully selected at the outcrop site. This sample was further sorted to approximately one kg in the laboratory. Selected pieces were thin-sectioned (approximately 5 slides per sample), and the sections were checked for number of inclusions, size of inclusions, smallest "grain" size, composition of rock, and degree of crystallization.

The sample was then ground and sized so that all particles were greater than inclusion size but less than "grain" size. The samples were washed and clay size particles were separated by decantation. The samples were treated four times for a duration of one day on a steam bath with a mixture of approximately 6 N HCl with HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. After treatment, the sample was leached with tap water for one day and then leached with deionized water for one day. The sample was transferred to a high-alumina ball mill with Burundum grinding media (U.S. Stoneware Co., Akron, Ohio); and triple deionized water (conductance  $0.4 \times 10^{-6}$  ohm<sup>-1</sup> cm<sup>-1</sup>) was added. Platinum electrodes were inserted, and a potential of 90 V d.c. was applied. The water was removed after maximum current was recorded (ROEDDER, 1958)\*. Generally one week of cleansing was required before a maximum current of 0.05 mA at 90 V could be maintained†. The material was then ball-milled for 24–36 hr. The liquid was extracted using ultrafilters (L.K.B. Products, Stockholm). The solution was evaporated to 25 ml, and the separate constituents were determined. Only ratios and not absolute concentrations were determined for chert.

2. *Salt*. All samples of salt were stored in sealed polyethylene bags prior to laboratory handling. Approximately one pound pieces were taken from mines and one-half pound pieces from core. The samples were examined for inclusions with a binocular microscope under dry atmosphere conditions. Approximately 30 mg samples with high inclusion-to-sample ratios were isolated and stored in small vials. An additional sample with no inclusions was also taken and stored in a vial. This sample was run as a blank. Once in the vial, the samples were carefully examined for details of crystal shape and shape and mode of occurrence of inclusions. Blanks were observed to insure there were no inclusions present. The samples were then transferred to a dry box, specially constructed to contain a hot plate and an ultramicro balance sensitive to and with a reproducibility of 2 μg and with a capacity of 20 g. The sample was transferred to a miniature mullite mortar and pestle, and the weight of the sample

\* All materials in contact with the solution besides the platinum electrodes, sample grinding jar, and medium were made of first quality luicite.

† A good deal of wearing in of the mill and grinding media is prerequisite to operation to obtain these low values.

was determined. The sample was then dried to constant weight at 125°C on the hot plate. It was then carefully ground while observing with a small power microscope or magnifying glass. It was again dried to constant weight at 125°C. The loss in weight ( $2-4 \times 10^{-4}$  g) was taken as the loss of inclusion water. All the above operations were done in the dry box and consumed 1-2 weeks per sample. The sample was then dissolved in approximately one-half gram of water and portions were taken for analysis.

### *Chemical analysis*

The methods employed were flame emission for Na and K, chloranilate colorimetry and thorin titration for sulfate, potentiometric titration with  $\text{AgNO}_3$  for Cl, alizarin colorimetry for F, fluorescence titration with calcein and EDTA for Ca, and EBT titration with EDTA for Ca and Mg. Chert was analyzed by the same methods detailed below, but not on a micro scale. All titrations of salt extractions were done with a microtitrator with an accuracy of 0.01  $\mu\text{l}$ . Endpoints (except fluorescence) were viewed within a white environment through a magnifying lens. Unless the solution color is magnified, the operator will introduce serious error by integrating extraneous color into his determinations. Colorimetric measurements were made using a Bekman B spectrophotometer and 1.0 cm light path cells with 0.075 ml. capacity (Pyrocell Manufacturing Co., Westwood, New Jersey). Flame measurements were made using the B spectrophotometer with attachments. In all determinations, small volume, high concentration spikes were added directly to the samples to correct for interferences.

1. *Sodium and potassium.* Five microliters of centrifuged sample was pipetted and diluted one thousand fold. The sample was excited in a hydrogen-oxygen flame, and readings were taken between readings of standards. A small volume spike was added, and readings were taken between readings of standards.

2. *Sulfate.* The sulfate colorimetric procedure is a modification of that of KLIPP and BARNEY (1959). Ten microliters of sample are added to a centrifuge tube containing 40  $\mu\text{l}$ . of water and a few grains of cation exchange resin. After mixing and centrifuging, the solution is transferred to another tube with 40  $\mu\text{l}$ . of water. Ten microliters of buffer (0.1 M NaAc and 0.1 M HAc), 100  $\mu\text{l}$ . of ethyl alcohol and  $6 \times 10^{-4}$  g of Ba-chloranilate are added. The solution is mixed for 30 min, then centrifuged, and read at 332  $\mu$ . Simultaneously a spiked solution is run for comparison.

The chloranilate method is not sensitive to small changes in sulfate. Therefore a modification of the thorin method (RAINWATER and THATCHER, 1960) was tried with success. Five microliters of sample are taken and cations removed with exchange resins. The pH was adjusted to 2.5, and 50  $\mu\text{l}$ . of dioxane and one microliter of thorin were added and titrated to the endpoint. A spiked sample was run to correct for interferences.

3. *Chloride.* Five microliter samples are added to a titration cup containing 0.7 ml of 50 volume per cent HAc solution and equipped with a Ag electrode and a reference electrode filled with saturated  $\text{K}_2\text{SO}_4$ . The solution is titrated with 0.02 N  $\text{AgNO}_3$  to a 100 mV endpoint. Five microliters of NaCl solution are added and titrated to the same end point.

4. *Fluoride.* Ten microliters of sample, 80  $\mu\text{l}$ . of water, and 20  $\mu\text{l}$ . of fluoride

solution [0.25 g of "Amadac F" (Burdick and Jackson Laboratories, Muskegon, Mich) in 2.5 ml. of 40/60 by volume water/isopropyl alcohol] are put in a micro-cuvette. The solution is allowed to stand for one hour in diffuse light and read against standards at 620  $\mu$ . A spiked sample is run simultaneously.

5. *Calcium and Magnesium.* Five microliters of sample are added to 50  $\mu$ l. of

Table 5. Liquid inclusion results. Values are molar ratios

	Ocean	Inclusions				Brine seep
		Salt Ontario	Ohio	Ontario	Chert Wisconsin	
Ca <sup>2+</sup> /Cl <sup>-</sup>	1.8	11	10	15(?)	12	28 × 10 <sup>-2</sup>
Mg <sup>2+</sup> /Cl <sup>-</sup>	9.9	2.2	2.1	4.5	11	11 × 10 <sup>-2</sup>
SO <sub>4</sub> <sup>2-</sup> /Cl <sup>-</sup>	6.9	15	9.7	13	1.2	0.7 × 10 <sup>-2</sup>
Na <sup>+</sup> /Cl <sup>-</sup>	0.84	0.97	0.94	0.78	0.86	0.22
K <sup>+</sup> /Cl <sup>-</sup>	1.8	2.7	2.9	3.0	7.8(?)	2.0 × 10 <sup>-2</sup>
F <sup>-</sup> /Cl <sup>-</sup>	1.3	10	8.1	1.0	6.8	— × 10 <sup>-4</sup>
Ionic strength/Cl <sup>-</sup>	1.3	1.5	1.4	1.5	1.6	

water in a titration cup. Add 10  $\mu$ l. of 1 N KOH and 3 grains of calcein indicator. Titrate with EDTA using a u.v. mineral lamp until fluorescence disappears. The sample is spiked with calcium and run again.

For magnesium plus calcium, 5  $\mu$ l. of sample are added to 50  $\mu$ l. of water. Five microliters of buffer (66 g of NH<sub>4</sub>Cl, 500 ml. of concentrated NH<sub>4</sub>OH and 500 ml. of water) and a small drop of EBT indicator are added, and the solution is titrated to a blue endpoint. A spike is added, and the solution is titrated to a second endpoint.

### Results and interpretations

Compilation of the "best" values are in Table 5. These figures represent compilation of results from 22 separate analyses: 1 Wisconsin chert, 3 Ontario cherts, 8 Ontario salts (and 8 blanks), and 1 Ohio salt (and 1 blank). The Ontario cherts gave consistent results. The hopper salt crystals (4) from Ontario gave consistent results except Mg which showed a variation of 50 per cent of the value stated in Table 5. The obviously secondary salt inclusions from Ontario (B zone) were almost pure NaCl brine. Except for the Mg discrepancies, only one other sample deviated from either pure NaCl in solution or from the values listed in Table 5. The one analysis of Ohio salt was from a hopper crystal in a well-bedded horizon.

The average of concentrations of ions in the salt inclusions other than Na and Cl suggest the brine was saturated between 12–14 times normal sea water. This would represent a rather open system in contrast to the data of HOLSER (1963, p. 90).

The Ontario chert had finely disseminated calcite throughout. It may be in preparation of the chert that not all calcite was removed, and hence the analyses are high in Ca. On the other hand, all three analyses gave almost the same values (Ca/Cl: 14.9, 15.1, 15.9) suggesting that the Ca is representative of the inclusions.

The Wisconsin chert was not a very good sample to analyse, since it contained a high amount of clay material. (This was the best sample of all specimens taken on

the Western side of the Michigan Basin.) No doubt the high potassium value for the Wisconsin chert listed in Table 5 reflects some clay impurities. The high potassium value of the Ontario chert may be due to the same impurity.

The values in the table compare favorably to the composition of sea water except for Ca and Mg. The inclusion values for Ca and Mg are almost exactly reversed from those values for modern sea water. It may be that the Ca and Mg values listed in the table do not represent fossil sea water due to preparatory and analytical error or secondary alteration after deposition. Also included in Table 5 is the analysis of a brine encountered in a seep in the Ontario salt mine. It is believed that this brine does not represent fossil sea water. The similar results for Mg (and Ca) for brine seep and inclusions cast doubt upon the other values in the table.

If the analyses represent open fossil sea water composition, the chlorinity was approximately 10 per cent less during the Salina than it is today.

#### DISCUSSION

The compositions of the liquid inclusions and models do not vary much from the composition of modern sea water, suggesting little change in the composition of sea water in the past. The main discrepancy appears in the reversed Ca/Cl and Mg/Cl ratios for liquid inclusions compared to the models and modern sea water. As mentioned earlier, the ligand inclusion data may reflect secondary effects.

The models support theories for relatively low composition  $\text{CO}_2$  atmospheres in the geological past. High  $P_{\text{CO}_2}$  atmospheres (1 atm) would tend to develop a pH of 6 which in turn would increase total phosphate and decrease the alkalis since the C-site clay would probably be developed in a low pH environment. Hence oceans in a high  $P_{\text{CO}_2}$  environment would be relatively low concentration brines (equivalent to "fresh" water) with a pH near 6.

I propose an evolution of the ocean from pure water and under approximately constant  $P_{\text{CO}_2}$  conditions. Initially the composition would be very similar to "fresh" water ("lower limit" model) and eventually would change (probably discontinuously) to a brine similar in composition to modern sea water ("most probable" model). It would be very difficult to change the "marine" composition once it was achieved. It is very tempting to suggest that the discontinuous change in composition of the oceans took place at the Precambrian-Paleozoic boundary and then tie in all the apparent differences in Precambrian and Paleozoic rocks to this change. It is possible that the Precambrian-Paleozoic boundary coincides with this change, but there is no evidence for or against the idea. Perhaps a detailed study of clay minerals might be helpful, but it is also probable that katamorphic processes have obliterated the original form of the clay in the older rocks. The study of BAILEY and TYLER (1960) suggests little difference between clay assemblages in Precambrian iron formations compared to clay assemblages in more recent sedimentary rocks. DROSTE (1963) emphasizes a change in clay mineral content in Middle Mississippian which might represent the change in composition theorized for the oceans. A great deal more detailed mineralogical and chemical knowledge of the clays will no doubt help ascertain when changes and what sort of changes in composition of the oceans took place. Continued improvements in techniques of analysis of liquid inclusions will allow more

analyses for comparison with the models suggested here for the composition of sea water.

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