

A Kinetic Model for the Chemical Composition of Sea Water¹

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Abstract—The thermodynamic ocean of the Sillen school offers little incentive to those who search the sedimentary record for evidence of changes in ocean chemistry during Cenozoic time. Their models predict a uniform chemical composition. However as the sediments presently accumulating in the ocean show little evidence of equilibration with the overlying water, the possibility that kinetic factors play an important role must be seriously explored. Such a model is presented in this paper. Material balance restrictions are substituted for some of the usual chemical equilibria. The role of organisms is shown to be dominant for at least some of the important components of sea salt (i.e., C, N, P, Si, . . .). If, as proposed here, the chemistry of sea water is dependent on rates of supply of individual components, the rate of vertical mixing in the sea, and the type of material formed by organisms, then substantial changes in the chemical composition have almost certainly taken place. Several means by which such changes might be reconstructed from chemical and isotopic measurements on marine sediments are discussed.

INTRODUCTION

Following Sillen's (1961, 1963, 1967a,b) lead, most discussions of the factors controlling the chemical composition of sea water have centered on thermodynamic equilibria between sea water and mineral phases in marine sediments (Holland, 1965; Mackenzie and Garrels, 1966a,b; Siever, 1968a,b). Although the processes taking place within the sea must tend toward these equilibria, there is a considerable body of evidence indicating that this ideal state may not be achieved. The reactions of interest are notoriously slow and have rarely been carried out reversibly in the laboratory; the isotopic and mineralogic composition of deep

sea sediments is not that which would exist if equilibrium were established with the overlying water; pore waters in sediments show little evidence of modification through interaction with the adjacent silicate phases; organisms create thermodynamically unstable phases which become long term constituents of deep sea sediments. The purpose of this paper is to emphasize the role of kinetic and material balance considerations. Unlike the thermodynamic ocean of Sillen, the model proposed here permits sizable temporal variations in the chemical composition of the sea.

In order to understand the chemistry of the sea, we must consider the factors causing vertical and lateral variations in sea salt composition and the factors fixing its overall composition. We will begin with an analysis of the processes taking place in the present ocean. Then we will turn our attention to

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means of ascertaining changes which may have taken place in the past 100 million years.

FACTORS CONTROLLING THE DISTRIBUTION OF PROPERTIES WITHIN TODAY'S OCEAN

The one process operating in today's ocean that has been demonstrated to yield geographic and depth variations in the chemical composition of sea salt is uptake of dissolved constituents by organisms. The remains of these organisms sink under the influence of gravity and are gradually destroyed by oxidation and corrosion. The superposition of this particulate cycle upon the ordinary mixing cycle in the sea accounts for the present distribution of chemical properties.

The most prominent of the chemical anomalies (excluding those shown by dissolved gases) are as follows: (1) the constancy in composition of the warm surface water realm, (2) the depletion of surface water with respect to deep water in those elements fixed by organisms, and (3) the increase in deep water content from the North Atlantic around through the Indian Ocean to the North Pacific. These distributional characteristics are shown for the element carbon in Fig. 1.

It is not difficult to provide a qualitative explanation for this distribution pattern. Take phosphorus, for example; the deep waters of the ocean have on the average more than ten times greater phosphorus content than those at the surface. As vertical mixing works to smooth out this difference, the phosphorus reaching the surface must be consumed by organisms and sent back to the deeps in particulate form. Deep dwelling organisms consume this falling debris and return the phosphorus to solution, completing the cycle. The net upward flux of phosphorus due to mixing is balanced by the downward flux of particulate debris.

Phosphorus-free water sinking in the North Atlantic sweeps toward the Antarctic. Here after being joined by deep water

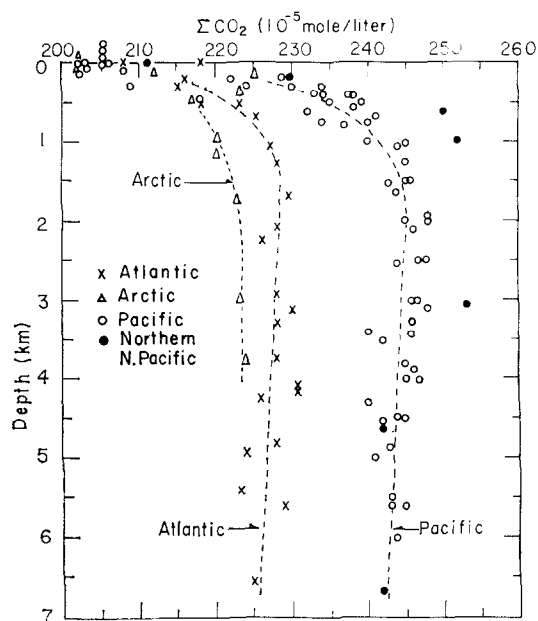


FIG. 1. Distribution of total dissolved inorganic carbon with depth in the Atlantic, Arctic, and Pacific Oceans (Li *et al.*, 1969).

formed in the Weddell Sea, it moves through the Indian Ocean and into the Pacific. As it proceeds toward the Aleutian Arc, this deep current continuously loses water by upwelling to the surface. The return flux of water (necessary to balance the export of Atlantic deep water) occurs at or near the surface. Much of the phosphorus carried by the returning water is "filtered" by plants living in the surface waters and dropped back to the deep current. Thus the mixing regime in the ocean is driving those elements consumed by organisms down from the surface and around toward the North Pacific. "Leaks" in the biologic filter limit the extent to which this process depletes the surface waters (and the waters in the deep Atlantic) leading to the steady-state distribution we now see.

Only three elements are known to show a nearly complete depletion in surface water; phosphorus, nitrogen, and silicon. It appears that the availability of Si limits the productivity of siliceous organisms such as diatoms

and radiolarians and that of P and N, the productivity of the remaining organisms. For some as yet unexplained reason, N and P are present in sea water in almost exactly the same proportions as in marine organisms. Their depletion in surface water occurs simultaneously.

As shown in Table 1, silicon shows a much stronger enrichment in North Pacific relative to North Atlantic deep water than does phosphorus (or nitrogen). This suggests that the biological filtering is more efficient for silicon than phosphorus. This is consistent with the observations that the hard parts of organisms undergo destruction on the average at greater depths than do the soft parts (Edmond, 1970) and that silica-bearing particles fall to the deeps closer to the point of nutrient input to surface water than do phosphorus-bearing particles. The most likely reason for the latter difference is the fact that the oxidation of plant debris by planktonic animals permits a P atom to be recycled several times within the surface ocean before it falls to the deep sea. Such recycling is probably less prevalent for opalline silica.

Three other elements (C, Ba, and Ca) show a similar distribution pattern in the

oceans but of much smaller magnitude. Barium varies in concentration by a maximum of times 3, C by a maximum of times 1.25, and Ca (as measured by alkalinity) by about 1.01. The concentrations of these elements in surface water are nearly uniform. The pattern of deep water excess of C is similar to those of P and N while that of Ba is more similar to the Si pattern. The nearly constant surface values of C, Ca, and Ba reflect the "inert" residuals of these elements remaining after the P (and N) and Si have been consumed. For the C-P-N system, this covariance has been confirmed by direct analyses of plankton tows (see Redfield *et al.*, 1963). The organic tissue indeed contains C, P, and N in the same proportions as in the deep water excesses of these elements (see Li *et al.*, 1969).

In general then the distribution of any element, x , used in constant proportions to phosphorus, P, is given by

$$[x] = a[P] + b$$

where b is the relatively constant surface water concentration of the element (i.e., its concentration in phosphorus-free water) and a the ratio of moles of element x to moles of P found in living organisms.

TABLE 1
CONCENTRATION DISTRIBUTIONS IN THE SEA FOR ELEMENTS USED
IN SIGNIFICANT AMOUNTS BY MARINE ORGANISMS^c

Element	[S]	[D.A.]	[D.P.]	[D.P.]	[D.P.] - [S]	Ref.
				[S]	[D.A.] - [S]	
P ^b	<0.02	0.17	0.25	>10	1.7	<i>d</i>
N ^b	<0.2	2.1	3.3	>10	1.7	<i>d</i>
C ^b	205	227	248	1.25	1.9	<i>d</i>
Ca ^b	1000	1004	1009	1.01	~2	<i>d</i>
Si ^a	<100	1000	5000	>50	5	<i>e</i>
Ba ^a	9	12	27	3	6	<i>e</i>

^a Values are in $\mu\text{g/liter}$.

^b Amount— 10^{-5} moles/liter.

^c [S], [D.A.], [D.P.], represent respectively the concentrations of the given element in warm surface water, deep Atlantic water, and deep Pacific water.

^d Li *et al.*, 1969.

^e Wolgemuth and Broecker, 1970.

There are two rather important consequences of the biologic removal-circulation pattern combination which are reflected by deep sea sediments. First it leads to the relative dearth of diatom productivity in the Atlantic relative to the Pacific Ocean. Second it leads to a tilting of the horizon separating CaCO_3 saturated and under-saturated waters. (As shown by Li *et al.*, 1969, this level is at least 1500 meters deeper in the Atlantic than in the Pacific Ocean.) The first results in a greater abundance of siliceous sediments in the Pacific and the second in a greater abundance of calcareous sediment in the Atlantic.

FACTORS CONTROLLING THE OVERALL COMPOSITION OF SEA SALT

For the purposes of this discussion, the chemical properties of the ocean will be placed in four categories.

- I. ΣCl and ΣS
- II. ΣNa , ΣK , ΣMg , and ΣCa
- III. ΣSi , ΣP , ΣC
- IV. pCO_2 , pH , and pO_2

This list includes only the primary properties. Others which might be added play secondary roles and need not be considered here.

CATEGORY I PROPERTIES

The elements Cl and S form highly soluble salts. They are everywhere in the open ocean in constant proportion to the other elements making up the sea salt matrix. Currently except for a few peripheral lagoons, the sea is well under saturated with respect to the chloride and sulfate salts formed by the major cations present in the sea. Although estimates vary, roughly one-half of all earth surface Cl (see Gregor, 1967) and one-seventh of the S (Holser and Kaplan, 1966) are currently dissolved in the sea. The remainder reside largely in ancient evaporite deposits.

The concentration of these two components in the sea must then depend on two factors:

(1) the ratio of the gases bearing these two elements to water vapor in the volatiles driven to the earth's surface over geologic time by outgassing of the earth's interior, and (2) the fraction of Cl and S retained in sediments at any given time (earth surface H_2O is now and likely has always been almost entirely in the sea). Since outgassing of the mantle during the past hundred million years has contributed only a small fraction of the total volatiles now at the surface, the relative amounts of the three substances on the earth's surface has probably not changed over the time interval of interest. On the other hand, the fractions of the Cl and S held in sediments may well have varied. The rate at which $\text{SO}_4^{=}$ and Cl^- are released from sediments to the sea depends on the chance exposure of old salt beds to weathering. The rate at which these species are removed from the sea and added to the sediment depends mainly on the geometry of the marginal seas. The immense evaporite deposits found scattered through the geologic column bear witness to the existence of large hypersaline arms of the sea capable of removing far more salt per year than is being removed today. The paleogeographic changes required by the ocean floor magnetic record clearly demonstrate that the required changes have indeed occurred. Thus although our present knowledge does not permit either the magnitude or temporal sequence of the variations to be estimated, the likelihood of their occurrence is high. Judging from the present rates of erosion and the present rates of ocean floor spreading, the time scale of any Cl^- and $\text{SO}_4^{=}$ cycles is unlikely to be less than a few tens of millions of years.

CATEGORY II PROPERTIES

Currently more than 98 percent of the anionic charge in the sea comes from Cl^- and $\text{SO}_4^{=}$ ions. The cationic charge comes almost entirely from the four cations Na^+ , Mg^{++} , K^+ , and Ca^{++} . Except for Ca which shows small variations (± 1 percent), these elements

are also in constant proportion to the sea salt matrix. Let us assume for the moment that this has been the case over the last hundred million years. If so, then the tectonic factors which have fixed the fraction of Cl^- and SO_4^{2-} dissolved in the sea have also determined the total amount of Na, K, Mg, and Ca dissolved in the sea. What fixes the ratio of these four cations, one to the other?

One hypothesis which has been put forth is that these ions equilibrate with the silicate debris passing through the ocean and assume the thermodynamic equilibrium ratios dictated by the chemical and mineralogic composition of this debris. This idea derived support from the observation that the observed ratio of Na to K is about that predicted by the extrapolation of high temperature distribution coefficients for aqueous solutions and Na K bearing silicate minerals (Holland, 1965). Very damaging to this argument, however, is the observation that none of the diagnostic chemical properties of this same debris show any evidence of equilibration. Dasch (1969) has shown that the isotopic composition of strontium from the bulk silicate in sediments has not achieved the sea water value. Ku (1965, 1966) has shown the same thing for uranium and Savin and Epstein (1970) for oxygen and hydrogen. Hurley *et al.* (1963) found that recent marine sediments contain much radiogenic argon indicating a detrital origin for the bulk of the K-bearing phases.

Another possibility is that only the superficially exposed ions of the silicate debris exchange with sea water. In this case, the question arises as to whether the available surface ions are adequate in number to influence the sea. It is more likely that the sea dictates the surface chemistry of the silicate debris.

The most reasonable suggestions are those involving precipitation of authigenic silicate minerals (Mackenzie and Garrels, 1966a,b). These new minerals carry away Na, K, and

Mg in the same ratio that they are found in river water. Because Ca is removed mainly as CaCO_3 its situation is more complicated. Unfortunately these newly formed silicates have never been identified in sediments. This may be because they are so poorly crystallized that they do not produce recognizable X-ray spectra. It may be because they are mineralogically identical to detrital phases. It may also, of course, be due to the fact that they do not exist.

Consideration of the element Mg points up the problem. If an amount of Mg equal to that supplied each year by rivers were, for example, being precipitated as MgSiO_3 and spread uniformly over the ocean floor, the amount appearing in the sediments would be 0.1 gm/cm^2 1000 years. On a CaCO_3 -free basis, sedimentation in the deep sea averages only about 0.4 gm/cm^2 1000 years (see Ku *et al.*, 1968). Even if *all* the Mg in these sediments is assumed to be in the form of authigenic MgSiO_3 then the accumulation rate of this mineral is only 0.02 gm/cm^2 1000 years (i.e., one-fifth the required amount). This failure to identify the main sink for Mg represents one of the major problems in marine chemistry.

It is instructive in this connection to compare the ocean with other closed basin water bodies. This is done in Table 2. Whereas the Na/K and Mg/Ca ratios for these lakes are remarkably similar to that for the ocean, the ratio of Na to Ca (or of Na+K to Mg+Ca) varies by four orders of magnitude. The ratio of ions of the same charge shows a considerable coherence while the ratio of those of different charge varies enormously.

The question immediately arises as to why Ca which leaves these water bodies primarily as CaCO_3 and Mg which almost certainly leaves as a silicate mineral should show such coherence. A possible reason for this is shown by the hypothetical situation where Ca is removed as calcite and Mg as pyroxene (or any other magnesium silicate). In this

TABLE 2
CATION CONTENTS ^a OF MAJOR CLOSED BASIN LAKES AND SEAS

Lake or sea	Na	K	Mg	Ca	Na/K	Mg/Ca	Na/Ca	Ref.
1. Dead (Israel)	32,000	8000	28,000	14,000	4	2.0	2	<i>b</i>
2. Caspian (U.S.S.R.)	3,200	70	750	300	46	2.5	11	<i>b</i>
3. Bolac (Australia)	310	7.5	80	27	42	3.0	11	<i>c</i>
4. Desmet (U.S.A.)	1,380	85	425	75	16	5.7	18	<i>b</i>
5. Ocean	10,500	380	1250	400	28	3.1	26	—
6. Murdeduke (Australia)	3,850	38	410	25	100	16.4	38	<i>c</i>
7. Timboram (Australia)	36,000	400	4250	1350	90	3.1	40	<i>d</i>
8. Gnarpurt (Australia)	3,800	40	475	65	95	7.3	40	<i>c</i>
9. Colongulac (Australia)	2,760	80	215	35	34	6.1	80	<i>c</i>
10. Tagar (U.S.S.R.)	6,000	210	860	57	28	15.1	105	<i>b</i>
11. Tekir Ghoi (Rumania)	24,500	1200	1300	190	20	6.8	130	<i>b</i>
12. Corangamite (Australia)	7,000	100	605	35	70	17.3	200	<i>c</i>
13. Bitter (U.S.S.R.)	18,800	810	750	90	23	8.3	210	<i>b</i>
14. Pyramid (U.S.A.)	1,610	100	110	7.2	16	15.3	220	<i>e</i>
15. Walker (U.S.A.)	2,330	95	105	7.0	25	15.0	330	<i>e</i>
16. Great Salt (U.S.A.)	83,600	4070	7200	240	20	30.0	350	<i>e</i>
17. Little Borax (U.S.A.)	3,400	730	24	8.0	5	3.0	430	<i>e</i>
18. Abert (U.S.A.)	3,800	175	12	4.2	22	2.9	900	<i>e</i>
19. Big Borax (U.S.A.)	6,140	295	25	4.0	21	6.3	1500	<i>e</i>
20. Mono (U.S.A.)	21,700	1150	37	4.3	19	8.6	5000	<i>e</i>

^a All cation contents are in ppm.

^b Clarke, 1924.

^c Maddocks, 1967.

^d McLaughlin, 1966.

^e Whitehead and Feth, 1961.

case $\text{Ca}^{++} + \text{CO}_3^{=} \rightarrow \text{CaCO}_3$ and $\text{Mg}^{++} + \text{H}_4\text{SiO}_4 + \text{CO}_3^{=} \rightarrow \text{MgSiO}_3 + \text{CO}_2 + 2\text{H}_2\text{O}$. If saturation for both minerals were achieved

$$K_{\text{sp}}^{\text{CaCO}_3} = [\text{Ca}^{++}] [\text{CO}_3^{=}]$$

and

$$K_{\text{sp}}^{\text{MgSiO}_3} = \frac{[\text{Mg}^{++}] [\text{CO}_3^{=}] [\text{H}_4\text{SiO}_4]}{[\text{CO}_2]}$$

and the ratio of doubly charged ions would be

$$\frac{[\text{Ca}^{++}]}{[\text{Mg}^{++}]} \propto \frac{[\text{H}_4\text{SiO}_4]}{[\text{CO}_2]}.$$

This treatment could be generalized to include any Mg-bearing silicate mineral. In all cases, the Mg/Ca ratio would be expected to vary with the dissolved silica content of the water body (the power of the silica de-

pendence depending on the mineral) and on the partial pressure of CO_2 in the water. Since the silica content and CO_2 partial pressures of these lakes have been observed to be similar to that in the deep sea, the small range of the Mg/Ca ratio is consistent with removal of Mg with an authigenic silicate phase and of Ca as a carbonate.

Until some breakthrough in our knowledge of the fate of these four major cations, any discussion of the temporal variability of the major cation composition of the sea must remain highly speculative.

One might ask at this point whether any other anion or cation ever competed with the six we have just discussed. For cations, the answer is almost certainly no. For anions, there are three possible candidates, HCO_3^- , $\text{CO}_3^{=}$, and HS^- . We know that in certain closed basin lakes as much as one-third of the anionic charge is contributed by HCO_3^-

and $\text{CO}_3^{=}$. Is it possible that the ocean was once highly alkaline? We also know that some lakes and some small arms of the ocean have anaerobic bottom waters. In such situations, reduced sulfur can become great enough in amount so that the species HS^- contributes significantly to the anionic charge. Has the deep sea ever been anaerobic? These possibilities will be discussed in a later section of this paper.

CATEGORY III PROPERTIES

The concentrations of the elements Si, P, and C in sea water are almost certainly influenced by the cycles of particulate debris produced by living organisms. Si is carried to the sea floor bound in the opal produced by diatoms and radiolarians, P bound in the soft tissue and in the bones and teeth of marine organisms, and C in the soft tissue and the CaCO_3 hard parts of coccoliths and foraminifera. Currently about 20 percent of the carbon brought to the euphotic zone by upwelling deep waters becomes incorporated in organic debris which falls to the deep sea (Li *et al.*, 1969). In the case of P and Si, over 95 percent brought to the surface is returned to the deep sea in particulate form. Although a large fraction of these particles is destroyed in the deep sea by oxidation and mineral solution, a portion of the C, Si, and P bound into these particles must become a permanent part of the marine sediments. If this resistant debris carries away a major portion of the Si, P, and C leaving the sea, then the abundances of these three elements must be strongly influenced by the life cycles of marine organisms.

A simple model for marine cycles of any biologically incorporated element is shown in Fig. 2. The ocean is divided into two reservoirs separated by the main oceanic thermocline. The surface water of the ocean participates in two water cycles; one involves exchange of water with the deep sea and the other is the evaporation-continental runoff

cycle. The annual amount of water received by the surface ocean from runoff is designated v_R and that from the deep sea v_D . The concentrations of the element of interest in mean runoff water, surface sea water, and deep sea water are, respectively, designated $[R]$, $[S]$, and $[D]$.

Based on river gauge records, the yearly amount of runoff from the continents is equal in volume to a layer 10 cm thick over the entire ocean surface (Livingstone, 1963). Based on the distribution of natural radio-carbon in the ocean, the mean residence time of water in the deep sea is on the order of 1600 years (Bien *et al.*, 1963; Broecker and Li, 1970). Since the mean thickness of the deep water reservoir is about 3200 meters, the upwelling rate is 200 cm per year. Hence v_D/v_R is about 20.

The amount of a given element entering the surface reservoir each year is then $v_D[D] + v_R[R]$. The return flow of surface water to the deep sea carries away an amount of the element equal to $v_D[S]$. Material balance requires that the remainder, $v_D[D] + v_R[R] - v_D[S]$, be carried by falling particles. Designating the fraction of an element removed from the surface ocean by these particles as g , we have

$$g = \frac{v_D[D] + v_R[R] - v_D[S]}{v_D[D] + v_R[R]}$$

Since v_D/v_R is about 20,

$$g = 1 - \frac{20 ([S]/[R])}{20 ([D]/[R]) + 1}.$$

If the element of interest is to be removed from the sea in the form of debris of organisms at the same rate that rivers bring it to the sea, then the fraction, f , of the particles sinking to the deep sea which are preserved in the sediment is given by

$$f = \frac{v_R R}{v_D[D] + v_R[R] - v_D[S]}.$$

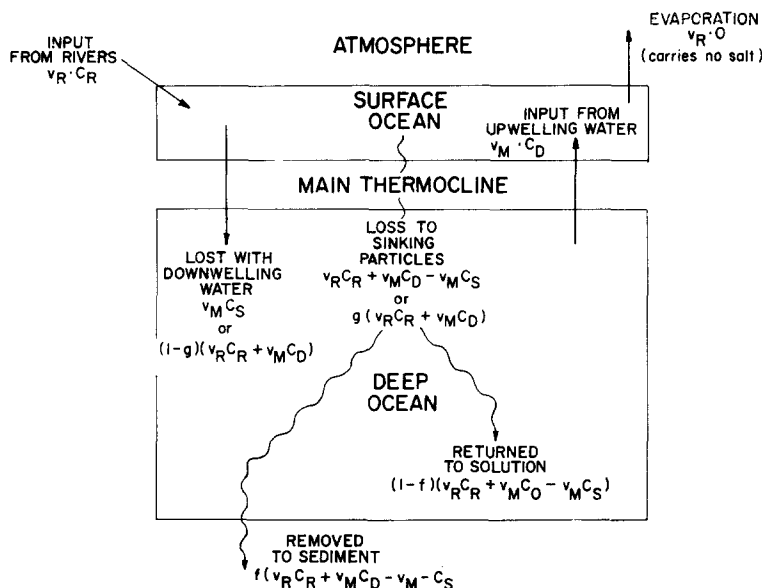


FIG. 2. Idealized model for the marine cycles of biologically fixed elements. See text for definition of symbols.

Again since v_D/v_R is about 20,

$$f = \frac{1}{20 ([D]/[R]) - ([S]/[R]) + 1}.$$

The fraction of the element removed to the sediments per visit to the surface is given by the product $f \times g$.

$$f \times g = \frac{1}{20 ([D]/[R]) + 1}.$$

Table 3 lists the concentration data for the elements Si, P, C, Ca, and Ba, and the corresponding values of the parameters f and g . With this model in mind, let us consider individually the elements in Category III.

Silica. Then entire ocean is one order of magnitude or more undersaturated with respect to opalline silica yet organisms extract silica from sea water and produce opalline hard parts. A fraction of these tests manage to survive solution and become part of the sediments. In areas of high radiolarian and diatom productivity, opal contents of more than 50 percent are not uncommon in sedi-

ments. The numerous chert layers encountered in the JOIDES cores suggest that this silica survives for periods of many tens of millions of years without combining with other constituents in the sediment.

If, as discussed by Gregor (1968), the major part of the Si leaving the sea enters the sediments as organically precipitated opal, then the following control mechanism for silica concentration must operate in the ocean. The silica content of the deep sea seeks that level where upwelling of deep water brings silica to the surface at a rate such that organisms form a quantity of solution-resistant opalline hard parts just balancing the amount of new silica entering the sea. If some perturbation in the oceanic cycle were to leave the ocean with a silica content lower than this ideal value, silica would be fixed into solution-resistant tests at a rate less than silica enters the sea. The silica content of the sea would then rise until the balance between input and loss was reestablished. On the other hand, if the silica content becomes too high, silica will leave

the ocean at a rate faster than it enters and the concentration will fall until the balance is reestablished. If, as proposed here, the removal rate of silica is proportional to its abundance in the sea, then the concentration will seek that level where loss matches input. As we shall see, similar feedback systems operate for other elements. As shown in Table 3, virtually all the silica reaching the surface ocean is currently fixed in opal and falls to the deep sea (i.e., $g \cong 1.0$) and about 1 percent of this opal is being preserved in the sediment (i.e., $f \cong 0.01$).

If this model is valid, then the mean silica content of the sea depends on the rate of vertical mixing in the sea (i.e., v_D), the rate at which silica enters the sea (i.e., $v_R [R]$), and the proportion of the opal produced which manages to survive solution in the deep sea (i.e., f). Certainly these three factors have varied with time. If so, then so has the silica content of sea water.

Mackenzie and Garrels (1965) and Mackenzie *et al.* (1967) have shown that when exposed in the laboratory to clay minerals the silica content of sea water approaches that found in the deep sea. On the basis of this result, they propose that interactions with clay minerals fix the silica content of sea water. It is, of course, possible that the number of diatoms and radiolarians entering the sediment is inadequate to carry away the silica entering the sea (i.e., $f < 0.01$) and that most of the silica leaves via reaction with clay minerals. If the capacity

of the silicates is large enough and the reaction rate fast enough, this silicate control mechanism could well override the biologic control mechanism proposed here. The silica content required to yield enough solution-resistant opal tests might never be reached. Instead the concentration would level off at that value where silica flowed onto silicate minerals as fast as it entered the sea.

Amit (1969) has presented strong evidence in favor of silica control by organisms. He has shown that in the lifeless Dead Sea, the silica content is ten times higher than in sea water and that by contrast to the ocean where sediment pore waters often have far higher silica contents than the overlying sea water (Siever *et al.*, 1965), the sediment pore waters for the Dead Sea have less silica than the overlying water. The implication is that in the absence of life the ocean would have a far higher silica content.

Although there is perhaps not enough information to choose between opal and silicate controls, it is clear that the purely kinetic model for silica discussed here must be given serious consideration. Since the biological mill processes the silica at such a high rate that it dominates the silica distribution within the sea, it may well dominate the through-put of silica as well.

Phosphorus. Although a trace species in sea water, the dominant role of the element phosphorus in the life cycle requires that the control on its abundance be considered.

TABLE 3
PARAMETERS FOR ELEMENT CYCLES WITHIN THE SEA

Element	$[R]/[D]$	$[S]/[D]$	g	f	$f \times g$
N	$\sim 0.20^a$	~ 0.05	0.95	0.01	0.01
P	$\sim 0.20^a$	~ 0.05	0.95	0.01	0.01
C	$\sim 0.10^b$	0.80	0.20	0.02	0.004
Si	~ 0.20	< 0.05	~ 1.0	0.01	0.01
Ba	~ 2	0.30	0.75	0.12	0.09
Ca	0.04	0.99	0.01	0.12	0.001

^a River value poorly known.

^b Corrected for atmospheric recycling.

As for silica, organisms remove virtually all the phosphorus reaching the surface ocean and send it to the deep sea in particulate form (i.e., $g \cong 1.0$). The abundance of phosphorus shows little variation in living organisms (about one P atom for every 106 C atoms). As in the deep Pacific Ocean there are about 640 C atoms for each P atom, when this water is brought to the surface complete depletion of P leads to only a 20 percent removal of the carbon.

Productivity of organisms is limited by the availability of phosphorus. Plants now consume and send to the deeps more than 95 percent of the available P. No matter how efficient they become, the amount of debris falling to the deep sea could rise by no more than 5 percent. The rate at which phosphorus-bearing debris falls to the deep sea depends only on the rate at which phosphorus is exposed to light by the vertical mixing in the sea. Given a rate of vertical mixing, the rate at which debris falls from the surface into the deep sea is fixed by the phosphorus content of the sea.

The fraction of this falling debris which survives to become part of deep sea sediments depends on the oxygen content of deep water. Where oxygen is present, benthic organisms destroy a very high fraction of the arriving organic material. Where oxygen is absent, although anaerobic bacteria using sulfate as an oxidation agent destroy some of the debris, this process is not very effective, (as attested by the high organic content of sediments in anaerobic basins). Were the amount of oxygen dissolved in deep water to drop, the fraction of the ocean floor covered by anaerobic waters would rise, allowing a greater fraction of the organic debris to fall to a safe haven. Also the efficiency with which the debris was oxidized in the remaining aerobic waters would very likely fall.

The oxygen content of deep waters depends on two factors: the amount of oxygen carried by the water descending from the

surface and the amount of organic debris falling into the water while at depth. The former is fixed by the oxygen content of the atmosphere and the latter by the phosphorus content of the deep ocean. If the amounts of atmospheric O_2 and of oceanic P are fixed, then the residual oxygen content of deep water is *independent* of the mixing rate of the ocean. Were, for example, the mixing rate to double, phosphorus would be brought to the surface twice as fast. This would, in turn, double the rate of falling debris. Hence the oxygen demand would double in the deep water masses. However, the renewal rate of oxygen in the deep sea would also double and hence the fraction of the oxygen consumed would remain unchanged (until either the O_2 content of the atmosphere or the P content of the deep sea began to change). The fraction of the organic debris falling into the deep sea surviving to become part of the sediment is thus fixed by the O_2/P ratio in the ocean-atmosphere system.³ If phosphorus leaves the ocean mainly in the form of organic tissue, teeth and bones, then about 1 percent of the phosphorus carried by organic debris falling into the deep sea is currently being preserved ($f \sim 0.01$).

For a given supply rate of phosphorus to the ocean (i.e., $v_R[R]$), a given vertical mixing rate (i.e., v_D), and a given oxygen content of the atmosphere, both the rate of production of phosphorus-bearing particles and the fraction of these particles becoming incorporated into the sediments will rise with phosphorus content of the sea water. In other words, an enhanced P content would *increase* the rate of plant productivity and *reduce* the residual O_2 content of deep water. Negative feedback from both these factors would then drive the phosphorus content of the ocean toward that value where phosphorus loss just balances phosphorus input. As for silica, the system will respond to any

³ More than 95 per cent of the P resides in the deep sea and more than 95 percent of the O_2 in the atmosphere.

perturbation in such a way as to reestablish a balance between loss and gain of the element phosphorus. Also, as for silica, the phosphorus content of the ocean is unlikely to have been constant with time.

Since for each mole of phosphorus consumed by organisms about 130 moles of O_2 are released, any drop in the phosphorus content of the deep ocean will be accompanied by a rise of O_2 content of the atmosphere. The two changes will then work in sympathy toward restoring the balance. However, since atmospheric O_2 and oceanic PO_4 are in the molar proportions of 5000 to 1, the percentage change in P will be about 30 times that for O_2 . On a short time scale, the adjustment will be accomplished by a changing P content.

As in the case of silica, the concentration of phosphorus could be limited by the solubility of some mineral phase, such as apatite. As discussed by Pytkowicz and Kester (1967), the absolute degree of saturation of sea water with calcium phosphates has not yet been determined. It is possible that organic debris does not carry away phosphorus at a sufficiently high rate to dispose of the incoming phosphate and that inorganic precipitation from deep water is the dominant control. Again, the fact that P is so rapidly cycled by organisms requires that the model proposed here be given serious consideration.

Carbon. If the model proposed here is correct, then the amount of carbon leaving the ocean in organic form is fixed by the phosphorus cycle. However, as the ratio of C to P in the residual detritus need not be the same as the 106-to-1 proportion found in marine plankton, it is not possible to estimate the precise fraction removed in this way. The presence of large quantities of $CaCO_3$ in the deep sea sediments proves that the organic removal is by no means adequate to match the incoming carbon.

How then does the ocean manage to dispatch the leftover carbon to the sediments as $CaCO_3$? Although the warm surface ocean

is several-fold supersaturated with respect to both the minerals calcite and aragonite, spontaneous crystallization of $CaCO_3$ is not recognized in the open ocean. Removal seems to be entirely by organisms. Since the productivity of these organisms is limited by phosphorus, they currently precipitate $CaCO_3$ at a rate largely independent of the availability of either Ca or C in the sea.

That this rate of generation greatly exceeds the rate at which $CaCO_3$ is made available to the sea is witnessed by the distribution of $CaCO_3$ in marine sediments. Sediments found at depths below 4500 meters are almost always nearly free of $CaCO_3$ while those on the flanks of ridges at depths less than 3000 meters are usually more than 70 percent by weight $CaCO_3$. That this difference is not due to variations in the rate of accumulation of silicate debris has been shown by absolute dating (see, for example, Ku *et al.*, 1968). Rather it reflects the presence of waters undersaturated with respect to $CaCO_3$ in the abysses of the ocean and of waters supersaturated with respect to $CaCO_3$ at shallower depths (see Fig. 3). The $CaCO_3$ fragments falling into the deepest parts of the ocean basins redissolve while those falling onto shallower parts are preserved. The gradient in degree of saturation is generated by three factors. The solubility of $CaCO_3$ rises with pressure, with decreasing temperature, and with increasing acidity of the water. The CO_2 released in the deep sea by the oxidation of organic tissue raises its acidity. As shown by Li *et al.* (1969), this CO_2 is only in part neutralized by the solution of $CaCO_3$ (roughly 1 mole of $CaCO_3$ is dissolved for each 4 moles of CO_2 released by oxidation of organic debris).

With these facts in mind, it is easy to see how the ocean disposes of the remaining carbon. Organisms are generating more $CaCO_3$ than necessary for carbon removal. This has caused the carbonate ion content of the sea to drop to the level where a sufficiently large area of the sea floor is bathed by

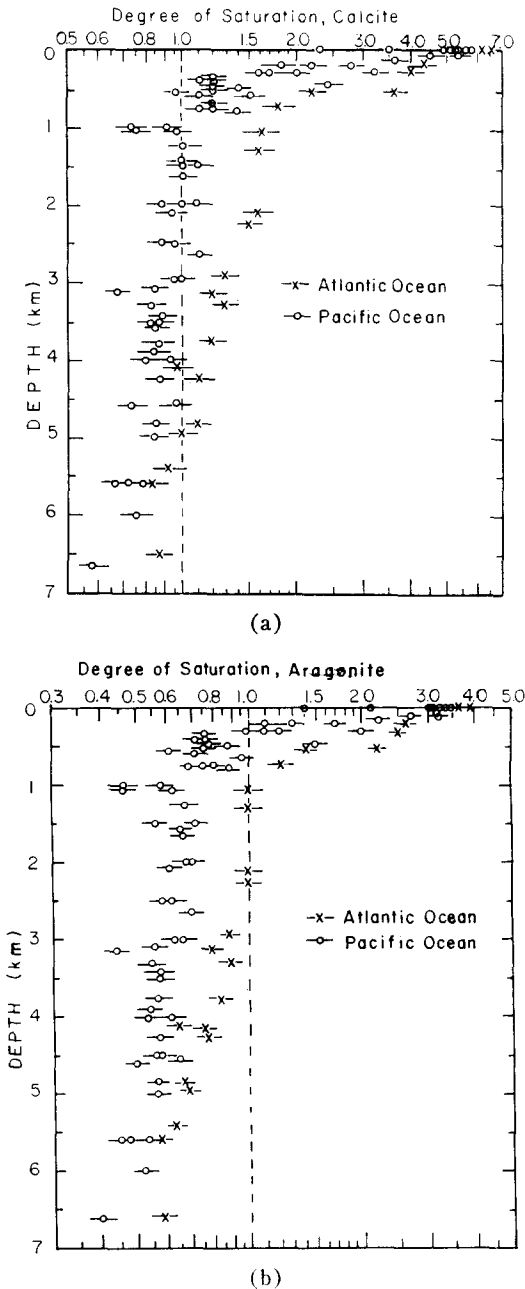


FIG. 3. Degree of saturation for the minerals (a) calcite and (b) aragonite as a function of depth in the Atlantic and Pacific (after Li *et al.*, 1969).

waters corrosive to CaCO_3 that the overproduction of CaCO_3 is just balanced by solution in the deep sea. Were the horizon

separating saturated and undersaturated waters too deep, then the removal of carbon would exceed its supply and the carbonate ion content of the sea would decrease with time. This would force the saturation horizon up until balance was restored between input and loss of C. Thus only at one horizon in the sea is the product of Ca and CO_3 ion concentration at saturation with respect to the mineral calcite. The position of this surface depends on the economics of the element carbon. Thus, like Si, the rate of removal of CaCO_3 depends on the concentration of C in the sea (as the amount of C drops, the $\text{CO}_3^{=}$ ion concentration must rise in order to maintain charge balance). Unlike silica, the control is largely effected through the changing of the rate of destruction rather than of the production of the solid phase. If, for example, at some time in the past the removal rate of calcium carbonate by organisms exceeded the rate at which carbon was made available by an even greater amount than today, the saturation horizons would have moved toward even shallower depths than today. Were at that time the amount of residual carbon to be disposed of the same as today then CaCO_3 must have been accumulating at a higher rate over a smaller area of the sea floor. If silicates were reaching the sea floor at the same rate as today, then the silicate content of carbonate oozes would have been even lower than today. Thus the degree to which the silicate and carbonate components of deep sea sediments are laterally separated depends on the ratio of the rate of carbonate supply (i.e., total carbon minus carbon destined for organic debris) to the rate of carbonate consumption by organisms.

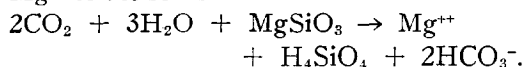
To conclude this section, it can be said that the H_4SiO_4 , H_3PO_4^- , and $\text{CO}_3^{=}$ contents of sea water are fixed by the economic requirements that Si, P, and C flow smoothly through the ocean. The concentrations of the first two components are very likely quite different from that demanded for thermo-

dynamic equilibrium. Although calcite saturation exists at one horizon in the ocean, large gradients toward super- and undersaturation occur above and below this horizon. The fact that the position of the horizon is controlled by economic considerations means that the thermodynamic equilibrium restriction sets only the order of magnitude of the carbonate ion content at any point in the sea. Considerable latitude on either side of this limit is permitted.

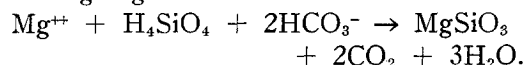
CATEGORY IV PROPERTIES

Carbon Dioxide. Weathering processes on the continents and sea floor continually add more Na + K + Mg + Ca to the sea. Except for a large part of the Ca, all these ions must be leaving the sea in the form of silicate minerals. What balances the removal and addition rates?

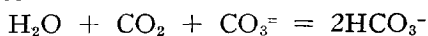
A typical weathering reaction providing Mg^{++} to the sea is



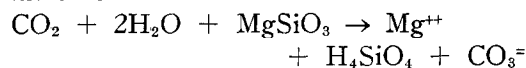
A possible silicate formation reaction removing Mg^{++} is



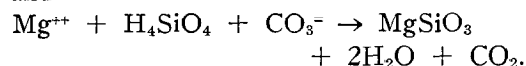
Since



these reactions can be rewritten



and

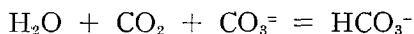


The factors controlling the concentrations of all these species except CO_2 have been discussed above. Hence if these were the only reactions altering the Mg content of the sea, the means of balance would easily be seen. The CO_2 content in the ocean would assume that value which would lead to an exact balance between the forward and reverse reaction.

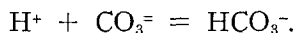
In reality, many such forward and reverse

reactions are taking place. Their identities are largely unknown. However, regardless of the weathering reaction chosen, it will be encouraged by an increased CO_2 content of the atmosphere and regardless of the precipitation reaction chosen it will be impeded by an increased CO_2 content of sea water. Thus without any detailed knowledge of the processes going on, if the model proposed here is valid, then the throughput of major cations must be ultimately controlled by the CO_2 pressure. Since the many other factors influencing erosion and deposition rates have certainly varied with time, so must the equilibrium atmospheric CO_2 pressure.

Thus the $CO_3^{=}$ ion content of the system is fixed at all points by the necessity that carbon flow smoothly through the system and the CO_2 gas content by the requirement that the major cations flow smoothly through the system. Once the concentrations of these two species are fixed, then so also are those of HCO_3^- and H^+ ions. This is clear from the reactions



and



The total dissolved inorganic carbon content of the sea (i.e., $CO_2 + HCO_3^- + CO_3^{=}$) is also everywhere fixed.

Oxygen. Weathering of continental rocks results in the oxidation of reduced S, Fe, and C. Although during and after deposition in sea sediments some of this S, Fe, and C is returned to reduced form, a portion remains oxidized. This net oxidation consumes O_2 . It seems reasonable that the O_2 content of the atmosphere has achieved that level where the oxidation state of the sedimentary products equals that of the weathering source. In other words, there is no net gain or loss of O_2 as the result of the weathering cycle. If the balance is upset and the products entering the sediments have on the average a more reduced character than the material being weathered, then the O_2 content of the

atmosphere will rise. This rise will cause a greater degree of oxidation of sediments. This feedback will seek to restore the balance.

SUMMARY OF CONTROL MECHANISMS

In the model presented here, thirteen properties of the sea were considered (ΣCl , ΣSO_4 , ΣNa , ΣK , ΣCa , ΣMg , ΣP , ΣSi , $\text{CO}_3^{=}$, pCO_2 , HCO_3^- , pH , and pO_2). The thirteen control factors are as follows:

- 1, 2. Tectonic control of the fraction of S and Cl present in the sea at any given time.
3. Charge balance.
- 4, 5, 6. Unknown mechanisms fixing the ratios K/Na , Mg/Ca , and $(\text{Mg} + \text{Ca})/(\text{K} + \text{Na})$.
- 7, 8, 9. H_3PO_4^- , H_4SiO_4 , and $\text{CO}_3^{=}$ fixed by the requirement that organic debris carry the elements P, Si, and C to the sediments at the same rate they are supplied to the sea.
10. pCO_2 fixed so as to maintain a balance between the supply and removal of the elements Na, K, Mg, and Ca.
11. HCO_3^- fixed by the reaction: $\text{CO}_2 + \text{CO}_3^{=} + \text{H}_2\text{O} = 2\text{HCO}_3^-$.
12. pH fixed by the reaction: $\text{CO}_3^{=} + \text{H}^+ = \text{HCO}_3^-$.
13. pO_2 fixed by the requirement that the oxidation state of the material leaving the ocean be on the average equal to that of the material undergoing weathering.

PALEOCHEMISTRY OF THE OCEAN

The type of temporal chemical changes to be expected depends on the time scale of the events responsible for the changes. In considering this time dependence, it is of interest to list seven important time constants.

1. Residence time of water in the surface ocean ($\sim 10^2$ yrs).

2. Residence time of water in the deep ocean ($\sim 10^3$ yrs).

3. Response time of $\text{CO}_3^{=}$ ion content of the sea ($\sim 10^4$ yrs).

4. Response time of C, P, and Si contents of sea water ($\sim 10^5$ yrs).

5. Response time of Ca content and O_2 content of the atmosphere of sea water ($\sim 10^6$ yrs).

6. Response time of K and Mg contents ($\sim 10^7$ yrs).

7. Response time of Na, S, and Cl content of sea water ($\sim 10^8$ yrs).

For an event of duration t the response will be limited to that part of the ocean or to those properties whose response times are less than t . For example, glacial cycles ($\sim 10^4$ years duration) are long enough to be felt throughout the ocean and to cause sizable changes in the $\text{CO}_3^{=}$ ion content. They are too short to produce large changes in the total Si, P, and C contents of the sea and far too short for changes in the Ca content of the sea or the O_2 content of the air. Changes resulting from man-made fossil CO_2 must be confined largely to the surface ocean. During Cenozoic time (6×10^7 yrs), all the properties except Na, Cl, and S may have shown sizable variations.

Are there any means by which the paleocomposition of sea water can be reconstructed from measurements of the properties of marine sediments? Although suggestions have been made as to how this might be done, these attempts have been largely foiled by uncertainties introduced by diagenetic alteration of the initial properties of the authigenic components of these sediments. The older the sediment and the more complex its history, the greater the uncertainty. Lowenstam (1961), for example, has suggested on the basis of simultaneous measurements of the Mg, Sr, and O^{18} contents of fossil brachiopods that the oceanic

composition with regard to O^{18}/O^{16} and Ca/Mg/Sr ratios has been constant since Mississippian time. Turekian and Armstrong (1961) criticize these conclusions, stating that the materials used must certainly have undergone diagenetic changes. Although other claims and counterclaims could be quoted, they are relatively few in number and all highly controversial.

Three of the most promising approaches are outlined below:

The Uranium Content of Corals. Well preserved aragonitic corals appear to preserve their initial trace element and trace isotope compositions. This is demonstrated by the facts that they yield highly consistent Th^{230} and Pa^{231} ages (Broecker *et al.*, 1968; Ku, 1968), and reliable He/U ages (Fanale and Schaeffer, 1965; Bender, 1970). Also their alteration is signaled by solution of the most delicate components of their structure and by partial recrystallization to calcite. As shown in Fig. 4, the U/Ca ratio of

Pleistocene interglacial corals is close to that in present day sea water. The scatter that does occur about this value seems to correlate with the species analyzed. Thus, the measurement of the uranium content of a given species of coral over a range of time should provide a measure of the change in U/Ca ratio in sea water over the corresponding time interval.

Uranium shows an unusually high concentration in sea water compared to its crustal abundance. This is presumably the result of complexes formed with $CO_3^{=}$, HCO_3^{-} , OH^{-} , and $SO_4^{=}$ ions. Closed basin lakes showing higher carbonate ion concentrations than the ocean appear to have correspondingly high U contents. Mono Lake, for example, has a total carbonate ion content (i.e., free and complexed) 100 times higher (Simpson, 1970) and a uranium content 50 times higher than sea water (Thurber, 1965). If the uranium content of sea water is assumed for simplicity to be proportional to the $CO_3^{=}$

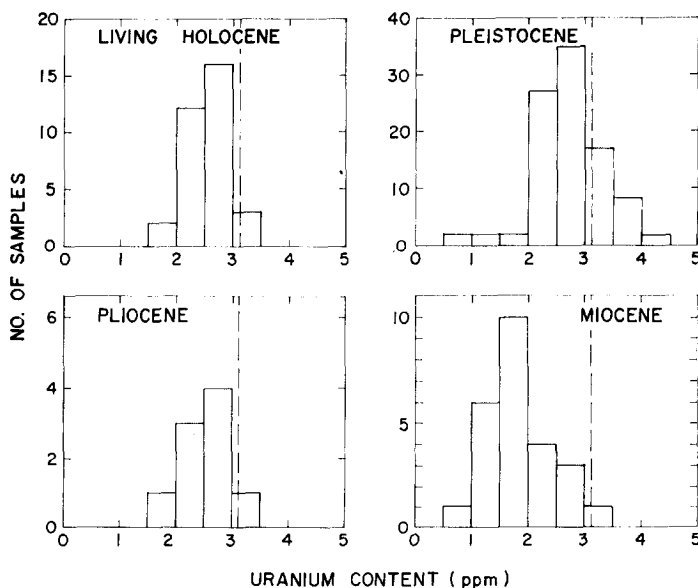


FIG. 4. Histogram of uranium contents of corals in four major age groups. The data are from papers by Sackett and Potratz (1963), Thurber *et al.* (1965), Veeh (1966), Komura and Sakanoue (1967), Veeh and Turekian (1968), Mesolella *et al.* (1969) and Veeh and Chapell (1970), and from the data of Bender (1970). The dotted lines are the U contents which would exist in a coral having the same U/Ca as in present day sea water.

ion content of sea water, then the uranium content of corals is a measure of the $\text{CO}_3^{=}/\text{Ca}^{++}$ ion ratio in sea water. A fossil coral with twice the uranium content of its living descendants would be assumed to have grown in an ocean with twice the $\text{CO}_3^{=}/\text{Ca}^{++}$ ratio.

Since uranium and calcium both have residence times in sea water greater than several hundred thousand years, this method would not be particularly useful for detecting, let us say, interglacial to glacial variations in the chemical composition of the ocean. During the 100,000 years required for a complete climatic cycle, the U and Ca contents of the sea would not have time to respond. Any progressive shift in the $\text{CO}_3^{=}/\text{Ca}^{++}$ ratio over the past several million years should, however, be recorded. Since an alkaline ocean would have a much higher than present $\text{CO}_3^{=}/\text{Ca}^{++}$ ratio, this is a means of determining if such a condition ever existed.

Bender (1970) shows that the uranium content of corals has changed no more than ± 30 percent over the last 4 million years but may have been 50 percent lower during Miocene time (see Fig. 4). This suggests either that there have been no large excursions in the $\text{CO}_3^{=}/\text{Ca}^{++}$ ratio in sea water over this time interval or that the U content of sea water does not respond as postulated here to changes in the $\text{CO}_3^{=}$ ion content of the sea. If the former is the case, we can eliminate the possibility of an alkaline ocean during the last few tens of millions of years.

The $\text{C}^{13}/\text{C}^{12}$ Ratio in Planktonic and Benthic Forams. In today's ocean, the $\text{C}^{13}/\text{C}^{12}$ ratio in the total dissolved inorganic carbon in surface water is about 2.5 per mil enriched over that in deep Pacific water (Craig, 1970; Kroopnick *et al.*, 1970). This enrichment is the result of removal of carbon from surface water in the form of organic particulate debris. Such debris is about 20 per mil depleted in C^{13} relative to the dissolved carbon in surface water (Sackett *et al.*, 1965). As the carbon depletion of surface

water due to this organic uptake is about 15 percent (see Li *et al.*, 1969), the enrichment of C^{13} in the residual water is expected to be about 3 per mil. The expected and observed differences are hence consistent with one another.

Although the $\text{C}^{13}/\text{C}^{12}$ ratio in foraminifera shells forming in these water masses reflects the growth temperature and perhaps a vital effect as well as the isotopic composition of the dissolved carbon in the waters in which they grow, if the temperature remains constant and the vital effect unchanged, then forams living in a given water mass should record the local $\text{C}^{13}/\text{C}^{12}$ variations.

Since deep Pacific water constitutes the main oceanic carbon reservoir, its isotopic composition should reflect the mean for the ocean. Its response time should then be that of the element carbon (i.e., $\sim 10^5$ years).

The $\text{C}^{13}/\text{C}^{12}$ ratio in surface ocean water reflects in addition to the mean isotopic composition of the dissolved carbon in sea water, the ratio of P/C in mean sea salt to that in marine organisms. The fraction of dissolved carbon removed from surface water by marine organisms is currently about 15 percent of that reaching the surface as the result of vertical mixing (the P/C ratio in deep sea water is about 15 percent of that in marine organisms). Were either the ratio of these two elements in the ocean as a whole or in marine organisms to have been different in the past, then the fraction of carbon reaching the surface lost to particulate matter would also have been different. This difference would be recorded by a change in the difference between the $\text{C}^{13}/\text{C}^{12}$ ratios in planktonic and benthic organisms.

Since the residence times of both C and P are thought to be about 10^5 years, the $\text{C}^{13}/\text{C}^{12}$ record in foraminifera shells should show composition induced changes only for times of this magnitude or greater.

As shown in Fig. 5, there have been substantial changes in the $\text{C}^{13}/\text{C}^{12}$ ratios in planktonic forams over the last 2.5 million

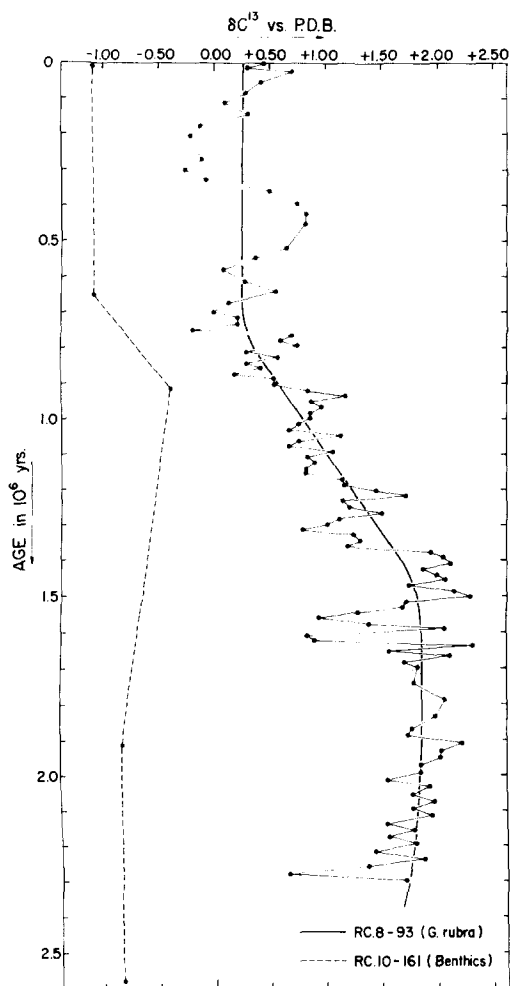


FIG. 5. Variation with time of the C^{13} - C^{12} ratio in benthic and planktonic forams in the Pacific Ocean.

years. The constancy of the C^{13}/C^{12} ratios in Pacific benthics suggests that the ocean as a whole has maintained nearly the same C^{13}/C^{12} ratio over this period. The two-fold increase in the C^{13}/C^{12} ratio difference between benthic and planktonic forams in the Pacific over the last 2.5 million years suggests either a gradual decrease in the P/C ratio in the ocean as a whole or a gradual increase in the P/C ratio in marine organisms. These variations are discussed in detail in a separate paper (van Donk and Broecker, in press).

The higher frequency variations superim-

posed on this long term trend pose a problem. Their duration, although not precisely dated, is about that of a glacial cycle (i.e., 10^5 years). If these variations are also the result of P/C ratio changes (rather than, for example, a change in depth habitat), then the response time of the oceanic carbon or phosphorus content or both must be more rapid than estimated. Clearly much valuable information lies in the C^{13}/C^{12} record preserved in marine carbonates. Already we have positive evidence for important temporal changes in ocean chemistry.

Rates of $CaCO_3$ Accumulation. Four factors control the rate at which $CaCO_3$ accumulates on any region of the sea floor.

1. The phosphorus content of the ocean as a whole.
2. The rate at which oceanic mixing brings this phosphorus to the surface ocean.
3. The ratio of $CaCO_3$ to P in falling particulate debris.
4. The extent to which the $CaCO_3$ falling toward any region of the sea floor is subject to solution.

The extent to which the net $CaCO_3$ accumulation rate has varied can be assessed by absolute dating of the sediment (either by C^{14} or Th^{230} - Pa^{231}). The extent to which solution effects have varied with time on any portion of the sea floor can be roughly estimated by observing the ratios of aragonitic (pteropods) to calcitic (forams + coccoliths) carbonate, planktonic to benthic forams, solution-prone to solution-resistant planktonics, and fragments to whole planktonic forams.

The dependence of the rate of production of $CaCO_3$ on the rate of vertical mixing in the ocean suggests that short term accumulation rate changes largely independent of ocean chemistry could have taken place. Such changes would bring about an imbalance in carbon input and loss. An adjustment of $CO_3^{=}$ ion content (time constant $\sim 10^4$ years) should gradually remedy such an unbalance. This shift in $CO_3^{=}$ ion concentration would make itself felt by changing

the ratio of the sea floor covered by under-saturated and supersaturated water. The sediments would record such changes by variations of the extent of calcium carbonate solution at any given point on the sea floor.

Broecker (1971) has presented evidence indicating that the degree to which marine sediments were attacked by solution was higher during the last interglacial than during the last glacial period. If so, then the carbonate ion content of the ocean must have been generally higher during glacial than during interglacial times. Such a difference suggests that the ratio of CaCO_3 productivity to dissolved CaCO_3 supply from rivers was higher during warm than cold periods. If due to a change in productivity rather than supply rate, then four explanations come to mind.

1. Vertical mixing was more rapid during warm than cold periods.

2. The phosphorus content of the sea was higher during warm than cold periods.

3. Organisms generate more CaCO_3 per unit of phosphorus brought to the surface during warm than cold periods.

4. Shallow water productivity of CaCO_3 is a significant contributor to the total and it was seriously reduced during periods of low sea level (hence glacials).

The first three explanations would call for the same net CaCO_3 deposition rate over the ocean floor as a whole (fluctuations in the carbonate ion content would force the loss rate to equality with the assumed constant input rate). The last explanation would call upon a proportionally higher deep sea accumulation rate during times of lower sea level. If the observed change reflects a decrease in the CaCO_3 input rate to the sea during interglacial times rather than a higher productivity during interglacial times then, of course, sedimentation rates should be lower during interglacial than glacial times. Thus Broecker's finding that the rates changed by less than 20 percent between the interglacial and glacial half cycles would

tend to exclude the shallow water productivity and the variable CaCO_3 input explanations. At present there is no way to choose between the other three possibilities. In any case, studies of temporal changes in CaCO_3 accumulation rates and in degree of solution attack offer considerable promise as paleo-ocean chemistry indicators. The fact that variations in the degree of solution attack on carbonate sediments have been found provides further evidence for the nonconstancy of ocean chemistry.

SUMMARY

Sillen's (1961) model for the controls on the chemical composition of sea water revolutionized thinking in this field. It pointed out the necessity for considering all the important properties of the sea together rather than singly. His implicit assumption that thermodynamic equilibria could be achieved sufficiently rapidly to negate the importance of kinetic factors was, however, unrealistic. The facts that some constituents are used far more rapidly by organisms than they can react inorganically and that the reactivity of other constituents are kinetically inhibited to the point where considerable concentration excesses are necessary to accomplish throughput must be taken into account. Unlike the thermodynamically fixed composition, that fixed by kinetics is likely to show important temporal changes. The record of these changes can hopefully be read from deep sea sediments. As our understanding of these kinetic factors improves, it should also be possible to predict with more certainty man's impact on the system.

ACKNOWLEDGMENTS

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