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THE CONTROL OF SEAWATER *pH* BY ION PAIRING¹

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ABSTRACT

The control of *pH* in seawater is effected through the whole set of ion-pairing equilibria, involving all of the major ions in seawater, rather than through the simple reaction series between water and carbon dioxide. The resistance to change of this system is greater than the buffer capacity of the CO₂ system, and the speed of reaction is much faster than that of the silicate system proposed by Sillén.

INTRODUCTION

The mechanism for *pH* control in seawater that is generally believed to operate involves the reactions between atmospheric CO₂ and water, according to the reaction series $\text{CO}_2(\text{gas}) \rightleftharpoons \text{CO}_2(\text{sol.}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \rightleftharpoons 2\text{H}^+ + \text{CO}_3^{2-}$. Once the dissociation constants for the formation of bicarbonate and carbonate ions are known, the results of subsequent addition of any one of the reactants can easily be calculated. The dissociation constants can be measured by adjusting the *pH* of the solution until only one of the ionized carbon species, either HCO₃⁻ or CO₃²⁻, is present and analyzing for the concentrations of the reactants.

This technique is effective in extremely dilute solutions of CO₂ in distilled water; however, the presence of appreciable concentrations of other ions gives rise to changes in the activities of the carbonate and bicarbonate ions and of water. In solutions such as seawater, therefore, only

apparent dissociation constants can be determined in this manner.

A discussion of the classical point of view on carbonate equilibria in seawater is given by Edmond and Gieskes (1970). They emphasize that the various association complexes between carbonate and the cations present in solution must be considered, and that (Edmond and Gieskes 1970, p. 1262) "before it can be determined by calculation whether a given sea water sample is in equilibrium with a calcium carbonate phase all the significant solution equilibria involving calcium and carbonate must be characterised. At present both experimental and theoretical understanding is inadequate for this task." They then proceed to the use of apparent constants as a possible approach to the problem.

These constants are empirically derived in much the same manner as the normal dissociation constants. The *pH* of the seawater sample is adjusted so that only HCO₃ is present, around a *pH* of 5, and *K'*₁, the apparent constant for the reaction $\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$, is determined. This constant is then used in the determination

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of K'_2 , the constant for the reaction $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$, and of K'_B , the apparent dissociation constant for boric acid. In seawater, whether real or artificial, H^+ is a reactant in a web of equilibria, involving all of the major ions; a shift in $p\text{H}$ will result in an extensive rearrangement of the whole ion-pairing system. An apparent constant found in this manner can be applied to the system held at another $p\text{H}$ either gingerly or with great bravado.

It could be predicted that K'_2 would be subject to greater error than K'_1 , since any error in the determination of the first apparent constant would be incorporated into the second. The carbonate ion is also reported to be more subject to ion pairing than is bicarbonate. From the work of Takahashi et al. (1970), this would indeed seem to be the case; they found discrepancies between measured and calculated parameters of the seawater CO_2 system which they felt could only be accounted for by a 30% error in the accepted values of K'_2 .

As Sillén (1961) has noted, the buffering capacity of the water- CO_2 system is very low indeed, of the order of 0.03 meq/ $p\text{H}$ unit. While a buffer of this capacity might be sufficient to handle the diurnal fluctuations in CO_2 resulting from biological activity, major changes in CO_2 content arising from changes in sedimentation occurring over geological time should have been reflected in $p\text{H}$ changes in the seas. Even such changes as the fluctuations in volume of the oceans resulting from glaciations might have occasioned measurable changes in oceanic $p\text{H}$.

The oceans cannot simply be regarded as a homogeneous system; calcium carbonate can be found in suspension at all depths at least to 5,000 m (Wangersky and Gordon 1965; Wangersky 1969). Extensive calcium carbonate deposits are found in contact with seawater in many areas of the ocean. The disappearance of these deposits at depths greater than 5,000 m suggests that a fairly large degree of interaction actually exists between the deposited

calcium carbonate and seawater. Thus the reaction $\text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$ must also be considered as a control on the CO_2 system, and therefore on the $p\text{H}$ of seawater. The addition of this second, heterogeneous reaction to the CO_2 system would raise the buffer capacity of seawater to 5 meq/ $p\text{H}$ unit. However, a response lag equivalent to the circulation time of the deep water would be built into such a system, since the major part of the CaCO_3 is present as bottom sediments and is therefore out of immediate contact with the main body of seawater.

As the concentration of ions in a solution increases, the activity of each ionic species decreases, in part because of the formation of complexes and ion pairs. At high concentrations an appreciable portion of the ions in solution may actually be present as charged and uncharged ion pairs. Garrels and Thompson (1962) calculated that much of the sulfate and carbonate in seawater was present in the form of ion pairs. Kester and Pytkowicz (1969) extended this work and estimated the proportions of the major ions in seawater bound up in this fashion. A similar extension for freshwater was carried out by Wigley (1971).

The existence of ion pairing in such proportions suggests that reactions linking the CO_2 system with each of the major ions in seawater must be considered as taking part in the control of seawater $p\text{H}$. If we ignore the minor and trace ions, we are left with the list of reactions in Table 1. Still other reactions may exist; this list serves merely as an example of the complexity of the situation. Not all of these reactions are of real significance in the control of $p\text{H}$ in seawater; equilibrium constants established under realistic conditions will help to determine how many of them must be taken seriously.

Equilibrium constants for many of these equations are in fact present in the literature; however, the methods of evaluating such constants must be considered carefully. In general, the constants are derived either from solutions of the particular salt

in distilled water, or, when solutions of high ionic strength are required, in a background of sodium chloride or perchlorate—ions usually considered not to form ion pairs.

If the basic assumptions of the Debye-Hückel treatment of ionic solutions were in fact valid, and water could be treated as a featureless medium of constant dielectric, then perhaps ionic strength might be the only important consideration. Water actually contains a large amount of short-range ordering, and the effect of introduced ions on this ordering must be considered. Some ions, such as sodium and lithium, are thought to strengthen the structures already existing in water, or at least to increase the length of time for which such structures persist. Other ions, such as potassium, rubidium, chloride, and the oxygen-containing anions, act as structure-breakers. The divalent alkaline earths magnesium and calcium act as strong structure-makers, and possibly induce the formation of structures of a different kind from those normally found in water.

The ease of pairing between two ions should depend to some extent on the degree and kind of structuring present in the solvent and therefore on the kinds of ions present in the solution. One would expect a different degree of ion pairing to occur in a solution whose ionic strength was derived largely from a structure-maker like sodium than in a solution based on a structure-breaker such as potassium. An equilibrium constant for an ion-pair reaction should thus apply strictly to a solution of a given composition.

If control of pH in seawater occurs through this whole web of equilibria, a change in the proportions of the major elements in seawater should lead to a change in ion pairing and finally to a change in pH. This hypothesis can be tested by preparing artificial seawaters of the same salinity, but of differing major ion composition, and measuring the resultant pH. In the experiments described below, magnesium and sulfate were the

TABLE 1. *Reactions linking the CO₂ system with major ions in seawater*

1.	$\text{CO}_2(\text{gas}) \rightleftharpoons \text{CO}_2(\text{sol.})$
2.	$\text{CO}_2(\text{sol.}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$
3.	$\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$
4.	$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$
5.	$\text{CO}_3^{2-} + \text{Ca}^{2+} \rightleftharpoons \text{CaCO}_3(\text{ppt})$
6.	$\text{CO}_3^{2-} + \text{Ca}^{2+} \rightleftharpoons \text{CaCO}_3^0$
7.	$\text{HCO}_3^- + \text{Ca}^{2+} \rightleftharpoons \text{CaHCO}_3^+$
8.	$\text{CaCO}_3 + 2\text{H}^+ + \text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + 2\text{H}_2\text{O} + \text{CO}_2 \uparrow$
9.	$\text{CaCO}_3 + \text{H}_2\text{CO}_3 \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^-$
10.	$\text{CO}_2(\text{sol.}) + \text{OH}^- \rightleftharpoons \text{HCO}_3^-$
11.	$\text{Na}^+ + \text{Cl}^- \rightleftharpoons \text{NaCl}^0$
12.	$\text{Mg}^{2+} + \text{Cl}^- \rightleftharpoons \text{MgCl}^+$
13.	$\text{Mg}^{2+} + 2\text{Cl}^- \rightleftharpoons \text{MgCl}_2^0$
14.	$\text{Ca}^{2+} + \text{Cl}^- \rightleftharpoons \text{CaCl}^+$
15.	$\text{Ca}^{2+} + 2\text{Cl}^- \rightleftharpoons \text{CaCl}_2^0$
16.	$\text{Na}^+ + \text{HCO}_3^- \rightleftharpoons \text{NaHCO}_3^0$
17.	$\text{Na}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{NaCO}_3^-$
18.	$\text{Mg}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{MgCO}_3^0$
19.	$\text{Na}^+ + \text{SO}_4^{2-} \rightleftharpoons \text{NaSO}_4^-$
20.	$\text{Mg}^{2+} + \text{HCO}_3^- \rightleftharpoons \text{MgHCO}_3^+$
21.	$\text{K}^+ + \text{SO}_4^{2-} \rightleftharpoons \text{KSO}_4^-$
22.	$\text{Mg}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{MgSO}_4^0$
23.	$\text{Ca}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{CaSO}_4^0$

ions varied, with the sodium chloride content adjusted to give a constant salinity. These ions are linked to the $\text{CaCO}_3\text{-CO}_2$ system only through the ion-pair equilibria, and changes in the CO_2 content or in pH must come about by means of these equilibria. In each series of experiments the basic artificial seawater was prepared according to Lyman and Fleming (1940). Calcium chloride and sodium bicarbonate were held constant in all experiments.

In each experiment, an artificial seawater was bubbled with a gas of known CO_2 content. After passing through the solution, the gas flowed through a nondispersive infrared CO_2 analyzer. A steady state was usually achieved in 15–30 min, with the CO_2 downstream from the reaction vessel reaching the upstream concentration. At least 30 min after this steady state had been reached, a sample of seawater was withdrawn from the reaction vessel with a hypodermic syringe and its pH measured. Each experiment was run several times. The reproducibility was very high; repeated measurements of the same solution and measurements of solutions of

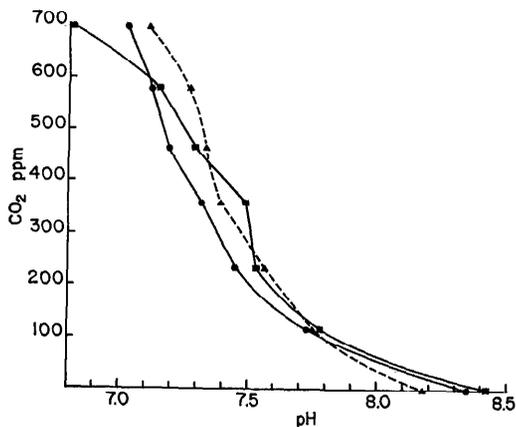


FIG. 1. Effect of variation in magnesium content on pH of artificial seawater. \blacktriangle : $+Mg^{2+}$; \blacksquare : $-Mg^{2+}$; \bullet : artificial seawater.

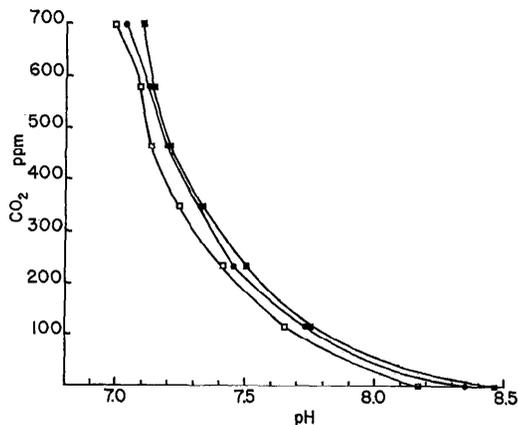


FIG. 2. Effect of variation in sulfate content on pH of artificial seawater. \blacksquare : $+SO_4^{2-}$; \bullet : artificial seawater; \square : $-SO_4^{2-}$.

the same composition prepared and run as much as a week apart gave values within ± 0.01 pH units.

DISCUSSION

It would perhaps have been neater and more satisfying to have measured pH at true equilibrium rather than at steady state. However, such experiments demand an extreme degree of temperature control and a very long period of time for each single experiment. The reproducibility of the pH measurements on separate runs as much as a week apart suggests that in the time allowed (between 1 and 2 hr) the systems being studied had reached a point on the curve of pH change such that any further change would be very slight and would take place very slowly indeed. Continuous monitoring of pH change within the system was not attempted because the combination of streaming potential and instrumental drift produced an error almost as large as the effect being measured.

According to Garrels and Thompson (1962) and Kester and Pytkowicz (1969), magnesium is the element most involved in ion pairing with the carbonate and bicarbonate ions. Therefore, a series of experiments was made with 0.5 times the amount of magnesium normally found in seawater and another with 2 times the

amount. The results of these experiments, along with a series run on normal artificial seawater, are shown in Fig. 1. The progression from high magnesium to low magnesium involves a change in the slope of the pH vs. CO_2 curve, with the low magnesium seawater showing the greatest pH change. This suggests that the stability of seawater pH may in fact be due to a large extent to the ion-pairing ability of the magnesium ion. At half the normal magnesium concentration the control of pH is marginal, and the curve of pH vs. CO_2 begins to resemble that found with 3.5% sodium chloride solution.

The anion most concerned in ion pairing with magnesium is sulfate. According to Garrels and Thompson (1962), some 11% of the magnesium present in seawater is bound up in ion pairs with sulfate. Accordingly, the second series of experiments involved artificial seawaters with 2.5 times the normal sulfate content (Fig. 2). The progression from high sulfate to low sulfate involved a shifting of the entire pH curve to lower values. For a given partial pressure of CO_2 , the more sulfate present the less magnesium and sodium available for ion pairing with bicarbonate and carbonate, and the less H^+ free in solution.

To accentuate the effects of shifting ion ratios, I included in the final series of

experiments a run with 2 times the magnesium and 0.5 times the sulfate content and one with 0.5 times the magnesium and 2 times the sulfate. These results are shown in Fig. 3. The effects of sulfate concentration on the actual positioning of the curve and of magnesium concentration on the shape of the curve are both exhibited. The influence of sulfate seems perhaps to be more important in this series; since three-fourths of the sulfate present in normal seawater is tied up in ion pairs—in competition with carbonate and bicarbonate for cations—a change in sulfate concentration should be directly and strongly reflected in pH change. Magnesium, present to a large extent as the free ion, could fluctuate somewhat more before the ion-pair equilibria would be seriously disarranged. Some of the ions freed by a shortage of magnesium would certainly be absorbed by the tremendous excess of sodium ions.

The effects of fairly large variations in composition are in fact fairly small. This is only to be expected if the entire mass of inorganic solutes in seawater is involved in the equilibria. In an environment subject to periodic fluctuation, a large number of relatively weak restraints can be a more effective control than a single strong restraint. In ecological terms, the difference in stability between a food chain and a food web is a good analogy. The greater the degree of internal connection, the greater the stability of the system.

Control of pH in this fashion is by means of a pH -stat rather than through a buffering system. The capacity of the system is huge; at 348 ppm CO_2 in the gas phase, a concentration reasonably near the normal CO_2 content of the atmosphere, the extreme difference in ionic compositions produced a difference of only 0.25 pH units. Over the extreme range of CO_2 concentrations, 0–696 ppm, the largest pH difference was 1.4 pH units. For seawater with normal ionic ratios, a doubling of the CO_2 content of the air would lead to a change of only 0.30 pH units—an amount

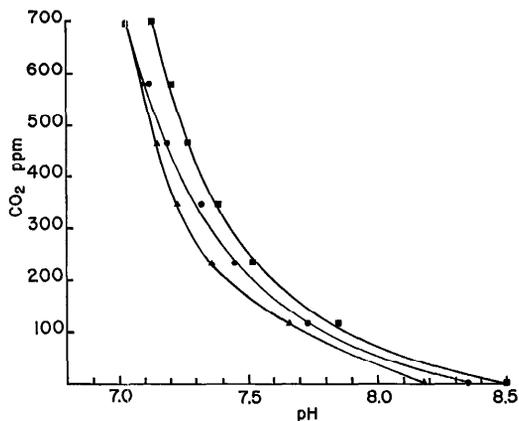


FIG. 3. Effect of variation in both magnesium and sulfate on pH of artificial seawater. ●: artificial seawater; ▲: $2 \times Mg^{2+}$, $0.5 \times SO_4^{2-}$; ■: $2 \times SO_4^{2-}$, $0.5 \times Mg^{2+}$.

about equal to the normal range of variation of seawater pH .

The response of the system to changes in concentration of any of the reactants should also be swift. In surface waters, the slowest reaction may well be the passage of CO_2 across the air-sea interface. The reactions in solution can reflect instantaneous variations in carbonate and calcium due to photosynthesis and to the formation of calcite tests by planktonic organisms, while the air-sea system lags behind, serving as an averager. Time of day may be an important variable in the study of pH and the CO_2 system in surface water.

The CO_2 content of the atmosphere will in fact influence the final pH of surface water just as will any other reactant. This effect is easily seen in all of the experiments shown here. The influence of dissolved CO_2 content is most marked at low CO_2 concentrations. In water deep enough to be effectively out of contact with the atmosphere the dominant influence on pH should be the change in ion pairing induced by pressure. The results of increased pressure are hard to predict, since so many reactions are involved, but in general one would expect increased ion pairing with pressure, due to the stripping

of hydration sheathes, to the breakdown of water structure, and to the compression of the solution, bringing about higher effective concentrations. The most important effect may well be the stripping of the hydration sheath from Na^+ and its concomitant increases in ion pairing with Cl^- , CO_3^{2-} , and SO_4^{2-} . At depth, ion pairing with Na^+ may become more important in the maintenance of $p\text{H}$ than the pairing with Mg^{2+} .

The overall control of $p\text{H}$ in seawater would thus be the same mechanism controlling the ratios of major ions. Sillén's (1961) postulated long-term control of the composition of seawater by means of the heterogeneous silicate system might well also serve to control the $p\text{H}$ almost instantaneously through the mechanism of linked ion-pair equilibria.

CONCLUSIONS

1. The immediate control of $p\text{H}$ in seawater out of contact with the air-sea surface is through extensive interrelated equilibria involving ion pairing between all of the major ions.

2. This control functions as a $p\text{H}$ -stat, rather than as a buffer, and displays great resistance to change.

3. The ultimate $p\text{H}$ control is therefore through regulation of major ion composition, perhaps by the heterogeneous silicate mechanism proposed by Sillén (1961).

4. The use of apparent dissociation constants to calculate the state of the CO_2 system is open to doubt, since the method

of determining such constants involves disturbance of the whole set of ion-pairing equilibria. Extension of such constants to the deep water is even more doubtful a procedure, since the effects of pressure on ion pairing are largely unknown.

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