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Calcium Carbonate Equilibria in the Oceans—Ion Pair Formation

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The preceding paper (1) discussed calcium carbonate saturation in fresh water lakes. The question of calcium carbonate saturation in the oceans is one of long controversy and is still not completely resolved. This paper, using calcium carbonate as an example, will call attention to some chemical problems of the marine environment.

Activity Coefficients and Ion Pairs

The approximate concentrations of the major species in surface sea water at pH 8.15 are given in Table 1 (2). The pH of sea water does not fluctuate as much as in many lakes, but like most lakes is somewhat lower at depth. At depth, the carbonate, bicarbonate, and calcium ion concentrations would be somewhat different than at the surface. At the high ionic strength, 0.70, of sea water, the Debye-Huckel Theory is not satisfactory and mean salt methods are used to calculate activity coefficients (2, 3). Table 1 also gives the calculated and experimentally determined activity coefficients, γ , for some of the ions. It can be seen that mass law calculations for sea water (about 0.6 M total concentration) that ignore activity coefficients are meaningless.

Although some discrepancies exist in the literature regarding the measurement, calculation, and interpretation of activity coefficients for sea water, it is nevertheless apparent that calculated values are con-

siderably higher than experimental values for carbonate, bicarbonate, and probably sulfate; somewhat higher for magnesium and calcium; and about the same for sodium, potassium, and chloride ions. Ion pair formation (2, 3, 10-12) can explain the differences between the calculated and experimental values.¹ Some examples of ion pairs found in sea water are CaCO_3 , MgCO_3 , NaCO_3^- , CaHCO_3^+ , MgHCO_3^+ , CaSO_4 , and MgSO_4 . The carbonate ion will be used as an illustrative example in this paper. The dissociation constants for NaCO_3^- , MgCO_3 , and CaCO_3 as given by Garrels, Thompson, and Siever (10) are listed below.²

$$(\text{Na}^+)(\text{CO}_3^{2-})/(\text{NaCO}_3^-) = 10^{-1.27} \quad (1)$$

$$(\text{Mg}^{2+})(\text{CO}_3^{2-})/(\text{MgCO}_3) = 10^{-3.4} \quad (2)$$

$$(\text{Ca}^{2+})(\text{CO}_3^{2-})/(\text{CaCO}_3) = 10^{-3.2} \quad (3)$$

The total carbonate concentration is given by

$$m_{\text{CO}_3^{2-}(\text{total})} = m_{\text{NaCO}_3^-} + m_{\text{MgCO}_3} + m_{\text{CaCO}_3} + m_{\text{CO}_3^{2-}(\text{free})} \quad (4)$$

The total carbonate concentration is what is normally determined by analytical procedures. If eqns. (1)-(4) are solved,³ it is found that about 67% of the total carbonate is tied up as MgCO_3 , about 17% as NaCO_3^- , about 7% as CaCO_3 , and about 9% is free carbonate ion (2, 3). Table 2 gives the percentages of various

Table 1. Surface Sea Water at pH 8.15

Ion	Molality ^a	γ_{Calc} ^b	γ_{Exptl}
Na^+	0.48	0.71, 0.70 (4)	0.68-0.73 (5)
Mg^{2+}	0.054	0.36	...
Ca^{2+}	0.010	0.28	0.22 (6), 0.24 (7)
K^+	0.010	0.64	0.64 (2)
Cl^-	0.56	0.64, 0.70 (4, 5)	0.68-0.73 (5)
SO_4^{2-}	0.028	Uncertain (2, 3)	0.11 (3, 8)
HCO_3^-	0.0024	0.68	0.47, 0.55 (6), 0.36 (9)
CO_3^{2-}	0.00027	0.20	0.020 (6), 0.019 (9)

^a Total analytically determined concentrations including that in ion pairs.

^b These values are for the free, individual species as listed in the first column.

¹ Some authors, including Bjerrum himself, look upon ion pair formation as only a mathematical way of treating the low values of activity coefficients, and feel that ion pairs do not actually exist as such.

² The reader should understand that these are not solubility products for MgCO_3 and CaCO_3 . The ion pair is not a precipitate but exists in solution as a separate and distinct species.

³ If it is assumed that the percentages of Na^+ , K^+ , Ca^{2+} , and Mg^{2+} in ion pairs are small, the solution is easy (2). Otherwise, additional mass balance equations would have to be written for each species and the problem solved on a computer.

Table 2. Amounts of Various Species in Sea Water From Garrels and Thompson (3)

Ion	Percentage in Ion Pairs	Ion Pair Species
Na ⁺	1	NaSO ₄ ⁻
K ⁺	1	KSO ₄ ⁻
Ca ²⁺	9	8% CaCO ₃ , 1% CaHCO ₃ ⁺ , 0.2% CaCO ₃
Mg ²⁺	13	11% MgSO ₄ , 1% MgHCO ₃ ⁺ , 0.3% MgCO ₃
CO ₃ ²⁻	91	67% MgCO ₃ , 17% NaCO ₃ ⁻ , 7% CaCO ₃
HCO ₃ ⁻	31	19% MgHCO ₃ ⁺ , 8% NaHCO ₃ , 4% CaHCO ₃ ⁺
SO ₄ ²⁻	46	22% MgSO ₄ , 21% NaSO ₄ ⁻ , 3% CaSO ₄
Cl ⁻	0	

species complexed in sea water calculated by methods similar to the above example (2, 3).

It can be seen that magnesium ion is the major ion pair former in sea water. The percentage of Mg²⁺ complexed as ion pairs is low because the magnesium ion concentration is high compared to the complexing anions. Table 2 also shows why the calculated and experimental values for the activity coefficients deviate more for carbonate, bicarbonate, and sulfate than for calcium and magnesium and why they are about the same for sodium, potassium, and chloride ions.

The difference in the carbonate ion activity coefficients can now be explained. If the activity coefficient is for the total carbonate, including that in ion pairs, its value is about 0.019; if it is for the free carbonate ion species only, its value is 0.20. That is, using the conventions in this paper and generally in the references cited,

$$a_{\text{CO}_3^{2-}} = m_{\text{CO}_3^{2-}(\text{total})} \gamma_{\text{experimental}} \\ = m_{\text{CO}_3^{2-}(\text{free})} \gamma_{\text{calculated}}$$

If ion pair formation is ignored, sea water appears to be supersaturated at all depths with respect to calcium carbonate; if ion pair formation is considered, sea water is supersaturated at the surface and undersaturated at depth (10). Kramer (13), using a similar approach, and Berner (6), and Pytkowicz (14), using somewhat different approaches, have also come to this conclusion. Peterson (15) and Berger (16) suspended samples of calcium carbonate at various depths in the oceans and determined the weight gain or loss. They also concluded that the oceans are supersaturated near the surface and undersaturated at depth.

Pytkowicz (17) has shown that supersaturated calcium carbonate solutions are stable for long periods of time and has estimated that inorganic precipitation of calcium carbonate in saturated sea water would take 100,000 years. Chave (18) has shown that calcium carbonate particles in surface sea water may be protected by organic coatings. No satisfactory explanation has been offered for the observed undersaturation. As mentioned in the preceding paper (1), work in this laboratory indicates that lack of sufficient mixing is a very significant factor in the observed undersaturation in fresh water lakes.

Other Problems in the Marine Environment

Another difficulty in systems of high ionic strength, such as sea water, is the determination of pH (19, 20). Reproducible values can very easily be determined by conventional methods but the accuracy appears to be poor as the theoretical foundations are not clear. Spencer (20) has written a critical review and should be

consulted for details. Pytkowicz (21) discusses the roles of silicates and carbonates in controlling the pH of the oceans and concludes that the carbonates are the primary buffering agents.

The very high pressure developed at depth in the seas is a factor which will be briefly discussed here. The solubility product of calcium carbonate is pressure dependent. Pytkowicz and Connors (22) and Berner (6) estimate that it increases by a factor of about 1.6 for an increase in pressure of 400 atmospheres. This corresponds to a depth of 13,600 ft, the approximate average depth of the deep water oceans. Furthermore, the pH of a water solution containing a given amount of the carbonate system is dependent on the hydrostatic pressure since the dissociation constants of carbonic acid are pressure dependent (23). The reader is referred to papers by Berner (6) and Pytkowicz (24) for more detailed discussions of the problem of calculating the calcium carbonate solubility as a function of pressure.

Current methods of obtaining deep-sea data present many problems. The very high pressures make *in situ* measurements difficult with existing equipment and instrumentation. If samples are brought to the surface and analyzed, the pressure will decrease and, in addition, the water will begin to equilibrate with the carbon dioxide in the atmosphere.

It might also be mentioned that the solubilities of gases are only slightly dependent on the hydrostatic pressure of the water as contrasted to the external gaseous pressure in equilibrium with the water (25, 26). Some confusion in the limnology and oceanography literature exists on this point.

Summary

The oceans are a complex chemical, physical, and biological system. A presumably simple problem, such as the determination of calcium carbonate saturation, is still not completely quantitatively resolved and requires much additional research.

Acknowledgment

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Literature Cited

- (1) MORTON, S. D., AND LEE, G. F., *J. Chem. Educ.*, This issue p. 511.
- (2) GARRELS, R. M., AND CHRIST, C. L., "Solutions, Minerals, and Equilibria," Harper & Row Publishers Inc., New York, 1965, Chap. 4.
- (3) GARRELS, R. M., AND THOMPSON, M. E., *Am. J. Sci.*, **260**, 57 (1962).
- (4) PLATFORD, R. F., *J. Fish. Res. Bd. Canada*, **22**, 4 (1965).
- (5) PLATFORD, R. F., *J. Marine Res.*, **23**, 55 (1965).
- (6) BERNER, R. A., *Geochim. Cosmochim. Acta*, **29**, 947 (1965).
- (7) THOMPSON, M. E., AND ROSS, J. W., *Science*, **154**, 1643 (1966).
- (8) PLATFORD, R. F., AND DAFOE, T., *J. Marine Res.*, **23**, 63 (1965).
- (9) SVERDRUP, H. U., JOHNSON, M. W., AND FLEMING, R. H., "The Oceans," Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1942, p. 205.
- (10) GARRELS, R. A., THOMPSON, M. E., AND SIEVER, R., *Am. J. Sci.*, **259**, 24 (1961).
- (11) DAVIES, C. W., "Ion Association," Butterworths, Washington, 1962.

- (12) BJERRUM, N., *Trans. Faraday Soc.*, **23**, 433 (1927).
- (13) KRAMER, J. R., *Science*, **146**, 637 (1964).
- (14) PYTKOWICZ, R. M., *Limnol. Oceanog.*, **10**, 220 (1965).
- (15) PETERSON, M. N. A., *Science*, **154**, 1542 (1966).
- (16) BERGER, W. H., *Science*, **156**, 383 (1967).
- (17) PYTKOWICZ, R. M., *J. Geology*, **73**, 196 (1965).
- (18) CHAVE, K. E., *Science*, **148**, 1723 (1965).
- (19) SKIRROW, G. in "Chemical Oceanography," (Editors: RILEY, J. P., AND SKIRROW, G.) Academic Press Inc., New York, 1965, Volume 1, p. 236.
- (20) SPENCER, C. P. in "Oceanography and Marine Biology," (Editor: BARNES, H.), Hafner, New York, 1965, Volume 3, p. 44.
- (21) PYTKOWICZ, R. M., *Geochim. Cosmochim. Acta*, **31**, 63 (1967).
- (22) PYTKOWICZ, R. M., AND CONNERS, D. N., *Science*, **144**, 840 (1964).
- (23) PARK, K., *Science*, **154**, 1540 (1966).
- (24) PYTKOWICZ, R. M., *Deep-Sea Res.*, **10**, 633 (1963).
- (25) KLOTZ, I. M., *Limnol. Oceanog.*, **8**, 149 (1963).
- (26) KLOTS, C. E., *Limnol. Oceanog.*, **6**, 365 (1961).

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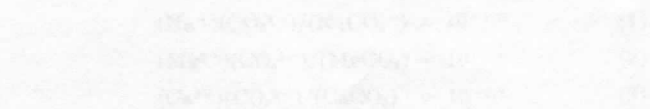
The preceding paper (1) discussed sodium carbonate saturation in fresh water lakes. The question of carbonate equilibrium in the oceans is one of long controversy and is still not completely resolved. The paper dealing calcium carbonate, for example, is still not identical to some chemical equilibria of the ocean environment.

Activity Coefficients and Ion Pairs

The approximate salinities of the major species in seawater at salinity 35 are given in Table 1 (2). About 97% of sea water does not fluctuate as much as it first takes, but the most ions fluctuate lower at depth. At depth, the carbonate, bicarbonate, and other ion concentrations would be somewhat different than at the surface. At the high concentration, 0.70, of seawater, the Debye-Hückel Theory is not satisfactory, so many salt methods are used to calculate activity coefficients (3, 4). Table 1 also gives the calculated and experimentally determined activity coefficients, γ , for most of the ions. It can be seen that many less values exist for sea water (about 0.6 M total concentration) and more activity coefficients are meaningless.

Although some discrepancies exist in the literature regarding the environment, calculation, and interpretation of activity coefficients for sea water, it is nevertheless apparent that calculated values are con-

siderably higher than experimental values for cations are bicarbonate, and probably sulfate, carbonate, higher for magnesium and calcium, and about the same for sodium, potassium, and chloride ions. Ion pair formation (5, 6, 10-12) can explain the differences between the calculated and experimental values. Some examples of ion pairs found in sea water are $\text{Ca}^{2+}\text{CO}_3^{2-}$, $\text{Mg}^{2+}\text{CO}_3^{2-}$, $\text{Na}^{+}\text{CO}_3^{2-}$, $\text{Ca}^{2+}\text{HCO}_3^{-}$, $\text{Mg}^{2+}\text{HCO}_3^{-}$, $\text{Ca}^{2+}\text{SO}_4^{2-}$, and $\text{Mg}^{2+}\text{SO}_4^{2-}$. The carbonate ion will be used as an example in this paper. The ion pairs are constants for $\text{Na}^{+}\text{CO}_3^{2-}$, $\text{Mg}^{2+}\text{CO}_3^{2-}$, and $\text{Ca}^{2+}\text{CO}_3^{2-}$ as given by Thompson, Thompson, and Sauer (10) are listed below:



The total carbonate concentration is given by

$$[\text{CO}_3^{2-}]_{\text{total}} = [\text{CO}_3^{2-}] + [\text{NaCO}_3^{-}] + [\text{MgCO}_3] + [\text{CaCO}_3] \quad (1)$$

The total carbonate concentration is what is normally determined by analytical procedures. If eqn. (1) is solved, it is found that about 67% of the total carbonate is tied up as MgCO_3 , about 17% as NaCO_3 , about 7% as CaCO_3 , and about 1% free carbonate ion (3, 4). Table 2 gives the percentages of carbonate

Table 1. Seawater at Salinity 35

Ion	Molarity	Activity Coefficient	Percentage of Total
Na^{+}	0.47	0.71	10.0
Mg^{2+}	0.054	0.20	1.0
Ca^{2+}	0.010	0.25	0.20
CO_3^{2-}	0.0001	0.44	0.02
HCO_3^{-}	0.001	0.44	0.05
SO_4^{2-}	0.028	0.44	0.10
Cl^{-}	0.56	0.71	10.0
K^{+}	0.010	0.71	0.20
Br^{-}	0.008	0.71	0.10

Total carbonate concentration is calculated from eqn. (1). The activity coefficients are calculated from eqn. (1). The activity coefficients are calculated from eqn. (1).