Chemical Solution of Calcium Carbonate in Sea Water

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SYNOPSIS. Sea water must be undersaturated for chemical solution of calcium carbonate to occur. A practical criterion for undersaturation is shown to be \((\text{Ca}^{2+}) (\text{CO}_3^{2-}) < K'_{\text{SP}}\), where \(K'_{\text{SP}}\) is the apparent (stoichiometric) solubility product. The calculations used in conjunction with this rule are outlined. The factors which affect \(K'_{\text{SP}}\) are examined. These factors are temperature, salinity, pressure, crystal structure, mineral composition, particle size, adsorption of ions such as magnesium, chelation, and formation of ion pairs. The ion concentration product is affected by temperature, pressure, salinity, solution and precipitation of carbonates, and changes in the partial pressure of carbon dioxide. Oceanic data that reflect the effects of many of these factors are presented. Possible effects of the degree of saturation and of turbulence on the rate of solution of calcium carbonate are examined.

Factors that control the solution of calcite and of aragonite in sea water will be reviewed. Vaterite occurs rarely in calcareous organisms, although Dudich (1931) mentioned finding it in arthropod skeletons, and its solubility will not be examined.

Chemical solution of calcium carbonate in sea water can occur only if the sea water is undersaturated. In the oceans it is the concentrations of calcium ions, \((\text{Ca}^{2+})\), and of carbonate ions, \((\text{CO}_3^{2-})\), which are determined rather than the activities. Therefore, a useful criterion for undersaturation is

\[
IP = (\text{Ca}^{2+}) (\text{CO}_3^{2-}) < K'_{\text{SP}} \quad (1)
\]

\(IP\) is the ion concentration product, \(K'_{\text{SP}}\) is the thermodynamic solubility product \([\text{Ca}^{2+}] [\text{CO}_3^{2-}]\), where brackets indicate activities, \(f_{\text{Ca}}\) and \(f_{\text{CO}_3}\) are the activity coefficients, and \(K'_{\text{SP}}\) is the apparent (stoichiometric) solubility product.

\(K'_{\text{SP}}\) is a function of temperature and pressure while \(K'_{\text{SP}}\) also depends on the salinity. However, the use of \(K'_{\text{SP}}\) requires knowledge of the activity coefficients as functions of temperature, salinity, and pressure. Therefore, the direct determination and use of \(K'_{\text{SP}}\) is preferable in oceanographic practice. Another difficulty in the use of thermodynamic constants in concentrated mixed electrolyte solutions such as sea water is that the activity coefficients, which depend on the forming of ionic pairs, cannot be obtained by extrapolation of the Debye-Huckel equation or from data in simple solutions. The extent to which ionic pairs are formed is not well known over the ranges of temperatures, pressures, and salinities encountered in the oceans. Thus, the use of thermodynamic constants can only be justified when apparent constants are not known.

An alternative criterion for undersaturation is the number of moles of calcium carbonate that must dissolve to achieve saturation. In this criterion it is necessary to take into account the conversion of dissolved carbonate to bicarbonate by the reaction \(\text{CO}_3^{2-} + \text{H}_2\text{CO}_3 \rightarrow 2 \text{HCO}_3^-\). This conversion depends on the partial pressure of carbon dioxide. Its use, illustrated by Pytkowicz (1965), is cumbersome and the application of equation (1) is preferable as a criterion for undersaturation.

DETERMINATION OF \((\text{Ca}^{2+}), (\text{CO}_3^{2-}),\) AND \(K'_{\text{SP}}\)

The quantities of interest; \((\text{Ca}^{2+}), (\text{CO}_3^{2-}),\) and \(K'_{\text{SP}}\) may be determined by the following procedures.

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Calcium. The calcium ion concentration can be determined by an EDTA titration (Carpenter, 1957; Pate and Robinson, 1958). However, the calcium/chlorinity ratio in sea water is relatively constant and \((\text{Ca}^{2+})\) can be estimated within a few percent from the chlorinity. The ratio \(\text{Ca}/\text{Cl}\), where calcium is expressed in g/kg and Cl in parts per thousand, is about 0.021 (Culkin, 1965). A more precise estimate, which takes into account the solution and precipitation of calcium carbonate, is obtainable from the equation (Sverdrup, et al., 1942)

\[
\text{Ca} \text{(mg atoms/liter)} = \frac{\text{CA}}{2} + 0.465 \times \text{chlorosity}
\]

where \(\text{CA}\) is the carbonate alkalinity in meq/liter. The chlorosity is expressed in g/liter at 20°C. The last term in equation (2) can also be expressed as 0.477 \(\times\) chlorinity.

Carbonate. Two measurements are needed to calculate the carbonate ion concentration. These measurements are usually the pH and TA, the titration alkalinity. CA, the carbonate alkalinity, is obtained from the measured quantities. The detailed procedures and tables for the determinations of pH, TA, and CA are available in several books (Harvey, 1960; Barnes, 1959; Skirrow, 1965). Skirrow’s version is the most up-to-date. The correct procedure at high pressures is shown by Culberson and Pytkowicz (1968). An outline of the method follows.

The carbonate ion concentration is obtained from the expression

\[
\text{CO}_3^{2-} = \text{CA} \frac{K_2'}{2K_2' + a_H} \quad (3)
\]

where \(K_2' = a_H \text{ (CO}_3^{2-})/\text{(HCO}_3^-)\) is the second apparent dissociation constant of carbonic acid. \(a_H = -\log_{10} \text{pH}\) is a quantity that is formally related to the hydrogen ion activity.

CA is obtained from the titration alkalinity by the expression

\[
\text{CA} = \text{TA} - \frac{K_B' \text{T}(B)}{K_B' + a_H} \quad (4)
\]

\(\text{T}(B)\) is the total boron, calculated from the \(T(B)/\text{chlorinity}\) ratio, and \(K_B'\) is the first apparent dissociation constant of boric acid. Values of \(K_B'\) at one atmosphere were determined by Lyman (1956).

The best values of \(K_2'\) at atmospheric pressure are those of Lyman (1956) which are also available in Skirrow (1965). Earlier workers did not measure the temperature coefficients of apparent constants but assumed that the thermodynamic coefficients were valid.

The pH does not yield the thermodynamic hydrogen ion activity. However, Pytkowicz, Kester, and Burgener (1966) have shown that the operational definition of the pH is valid in oceanographic practice.

Equations (3) and (4) are also valid at high pressures if the pH, \(K_2'\), and \(K_B'\) are the values of these parameters at the pressure under consideration. Culberson and Pytkowicz (1968) determined the values at pressure, issued tables with the pressure corrections, and illustrated the method with computations of oceanic data.

Now, with the calcium and the carbonate ion concentrations known at the in situ conditions, the ion concentration product can be calculated.

Apparent Solubility Product. The apparent solubility product, \(K_{sp}'\), is the ion concentration product when the sea water is at equilibrium with solid calcium carbonate. There have been several determinations of \(K_{sp}'\) at atmospheric pressure for calcite and for aragonite. The most comprehensive and possibly the most precise set of results is that of MacIntyre (1965). The values of \((K_{sp}')_p\), the apparent solubility product at pressure \(P\), are obtainable by multiplying the value of \(K_{sp}'\) at one atmosphere by the appropriate pressure coefficient. The pressure coefficients were measured by Pytkowicz and Connors (1964), Pytkowicz, Disteche, and Disteche (1967), and by Pytkowicz and Fowler (1967).
Calcium Carbonate in Sea Water

Considerations presented in the next sections will show the advisability, when possible, of determining $K'_{SP}$ for specific calcareous species. The pressure coefficients, however, should be approximately valid for most species because they depend primarily on the specific volume of the solid phase and on the partial molal volumes and ionic interactions in sea water. The specific volume should not vary too much. The partial molal volumes and the ionic interactions are independent of the species under study. Good techniques for measuring $K'_{SP}$ are presented by Weyl (1961) and by MacIntyre (1965).

Factors That Affect $K'_{SP}$

Temperature. The effects of temperature on the solubility products of calcite and of aragonite are presented in Table 1.

Salinity. The combined effects of salinity and temperature on the apparent solubility product of calcite, based on the results of MacIntyre, can be expressed by

$$K'_{SP} = (0.69 - 0.0068 \cdot t^\circ C) \cdot 10^{-6} \cdot S/34.3. \quad (5)$$

$S$ is the salinity, expressed in parts per thousand. Thus, increasing salinity increases the solubility products in a linear manner. The effect of salinity on the solubility of aragonite in sea water has not been studied systematically. The effect of salinity is not only due to the ionic strength but also to the formation of cation-carbonate ion pairs which reduce the concentration of free carbonate ion. Therefore, ion pairing enhances the apparent solubility product. This effect will be discussed in greater detail later.

Pressure. Pressure also increases the solubility products of calcite and of aragonite (Table 2). One thousand atmospheres correspond to a depth of 10,000 meters. The value of $(K'_{SP})_P$, the apparent solubility product at $P$ atmospheres, can be obtained by multiplying $K'_{SP}$, the apparent solubility product at one atmosphere, by the appropriate pressure coefficient from Table 2 (Pytkowicz, Disteche, and Disteche, 1967; Pytkowicz and Fowler, 1967).

Pressure affects calcite more than aragonite. The increase in $K'_{SP}$ with pressure is exponential for both minerals.

Crystal form. Calcite is in the rhombohedral class of the hexagonal system while aragonite is in the orthorhombic system. Aragonite is more soluble than pure calcite (Table 1). The greater effect of pressure on calcite is not enough to make the solubility of calcite greater than that of aragonite even at a depth of 10,000 m.

Mineral composition. Chave, et al. (1962) made a comparative study of the effect of magnesium on the solubility of forms of calcium carbonate. Some of their results are shown in Table 3. It can be seen that calcareous tests containing large amounts of magnesium are much more soluble than pure calcite and are more soluble than aragonite.

Particle size. The activity of the solid phase increases with decreasing radius according to the equation

$$a_{\text{CaCO}_3} = a_{\text{CaCO}_3}^{\infty} \cdot \exp \left( \frac{2t}{R T} \right) \quad (6)$$
TABLE 3. Effect of magnesium content on the apparent solubility product of calcium carbonate (based on Chave, et al., 1962).

<table>
<thead>
<tr>
<th>Crystal form</th>
<th>% magnesium</th>
<th>$K'<em>{SP}/K'</em>{SP}$ (calcite)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>Calcite</td>
<td>5</td>
<td>1.4</td>
</tr>
<tr>
<td>Aragonite</td>
<td>13</td>
<td>1.7</td>
</tr>
<tr>
<td>Calcite</td>
<td>17</td>
<td>2</td>
</tr>
<tr>
<td>Calcite</td>
<td>25</td>
<td>8</td>
</tr>
</tbody>
</table>

$a'_{CaCO_3}$ is the activity for a planar surface with $r = \infty$. $t$ is the interfacial tension, $v$ is the molar volume, $R$ is the gas constant, $T$ is the absolute temperature, and $r$ is the particle radius.

The solubility product should increase with decreasing radius because in reality $K'_{SP} = a_{CaCO_3}/a_{CaCO_3}$. The activity of the solid phase can only be set as one for one crystal form of a pure and relatively large grained compound. Other crystal forms, impure phases, and very fine grains will have values of $a_{CaCO_3}$ which differ from unity.

The effect of particle size on calcium carbonate was studied by Chave and Schmalz (1966) (Table 4). The effect of size is slight over a wide range of particle sizes.

TABLE 4. Effect of particle size on the activity product of calcite (Chave and Schmalz, 1966).

<table>
<thead>
<tr>
<th>Size (cm)</th>
<th>$a_{CaCO_3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>$1\times10^{-4}$</td>
<td>1.09</td>
</tr>
<tr>
<td>$2\times10^{-4}$</td>
<td>1.15</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>8.92</td>
</tr>
</tbody>
</table>

$K'_{SP} = K_{SP}/f_{Ca}f_{CO_3}$

from supersaturation. The importance of this hysteresis effect has not been ascertained. Weyl (1966) considers it very significant but MacIntyre (1965) did not observe it.

Precautions have not been taken in most solubility experiments in the past to eliminate the effects of bacterial activity on the pH. Such activity, which was recently observed by us in calcium phosphate flow experiments, could be misinterpreted as resulting from solution of precipitated carbonates, unless the carbonate alkalinity was also measured. Another possible source of hysteresis could be the formation of very fine calcite particles which could alter the average solubility in the course of experiments.

Maybe a solubility which is reversible in a thermodynamic sense cannot be obtained in sea water, because of changes in the composition of the mineral surface. However, this does not affect the usefulness of $K'_{SP}$ values obtained under conditions that approximate those in the natural system, because the value of $IP/K'_{SP}$ still indicates whether solution occurs or not.

Weyl (1966) speculated that sinking calcareous species in the oceans may adjust their surface composition to the environment in such a way that no solution would occur above about 4,000 m, the so-called compensation depth. This is not likely because Pytkowicz and Fowler (1967) observed that the pH of sea water, exposed to calcitic foraminifera in a pressure bomb, already increased at 100 atmospheres, showing that solution would occur at 1,000 m.

Formation of ion pairs. The apparent solubility product of calcite in sea water of 35% salinity is 193 times larger than the solubility product in distilled water (Wattenberg, 1933, 1956). This can be readily understood by examining the equation

$f_{Ca}$ and $f_{CO_3}$ are the total activity coefficients because total concentrations are used in $K'_{SP}$. Thus, the activity coefficients must reflect not only the effects of ionic
strength but also the results of forming ion pairs. This point was discussed by Pytkowicz, Duedall, and Connors (1966).

The greater ionic strength of sea water depresses the activity coefficients of calcium and carbonate ions. This effect alone causes $f_{Ca}$ to be 0.28 and $f_{CO_3}$ to be 0.20 at 34.5% salinity and 25°C (Garrels and Thompson, 1962). In addition, the pairing of ions further decreases the activity coefficients. This effect is slight on calcium because of its high total concentration; however, it is large for carbonate and causes about a tenfold decrease in $f_{CO_3}$. These two effects combined would lead roughly to a 200-fold increase in $K'_{SP}$ over $K_{SP}$, which is about what was observed by Wattenberg. This increase shows up when $K'_{SP}$ is determined as a function of the salinity and the effects of ionic strength and of ion pairing do not have to be calculated individually in oceanographic practice.

The strong effects of ion pairing on acid dissociations, solubilities, and chemical speciation in sea water were also demonstrated for phosphoric acid and for calcium phosphates by Kester and Pytkowicz (1967) and Pytkowicz and Kester (1967). Chelation. Any species that chelate calcium ions depress $f_{Ca}$ and, therefore, increase the apparent solubility product. Complexing of magnesium ions should release carbonate ions which form ion pairs with magnesium and, therefore, would decrease the solubility product.

FACTORS THAT AFFECT IP, THE ION CONCENTRATION PRODUCT

The value of IP, the ion product, depends primarily upon solution and precipitation of calcium carbonate and upon changes in the pH induced by photosynthesis and oxidation, through removal or formation of carbon dioxide. The interaction of carbon dioxide with carbonate ions can be represented by the reaction $CO_2 + H_2O + CO_3^{2-} = 2HCO_3^-$. The effect of solution or precipitation of calcium carbonate shows up in the $CA$ term in equations 2 and 3. The effect of the pH on the concentration of carbonate ion shows up in the $a_H$ term in equation 3.

The concentration of calcium ion is affected by changes in salinity which may result from river runoff, rain, evaporation, and mixing of water masses. Temperature, salinity, and pressure affect the carbonate ion concentration through the $K'_{SP}$ and the $a_H$ terms in equation 3.

Local gradients in carbon dioxide and gradients in the concentrations of other acids and bases near organisms and in the interstitial waters of sediments may affect the pH and the degree of calcium carbonate saturation. Thus, data in the bulk water may not be representative of conditions in the microenvironment of calcium carbonate solution.

DEGREE OF CALCIUM CARBONATE SATURATION IN THE OCEAN

The degree of calcium carbonate saturation, $IP/K'_{SP}$, obtained for a station in the North Pacific Ocean, relative to the solubility of a mixed foraminiferal sample (Pytkowicz and Fowler, 1967) is presented in Table 5. Other examples have been presented by Pytkowicz (1965a, 1967). It is seen that the waters were supersaturated above 190 m and undersaturated at greater depths. The stability of the supersaturation at shallow depths was explained by Pytkowicz (1965b). The minimum saturation at 753 m is due to the low pH which

<table>
<thead>
<tr>
<th>Depth (meters)</th>
<th>Saturation*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.3</td>
</tr>
<tr>
<td>190</td>
<td>0.61</td>
</tr>
<tr>
<td>468</td>
<td>0.62</td>
</tr>
<tr>
<td>753</td>
<td>0.59</td>
</tr>
<tr>
<td>1,425</td>
<td>0.72</td>
</tr>
<tr>
<td>2,562</td>
<td>0.74</td>
</tr>
<tr>
<td>3,526</td>
<td>0.84</td>
</tr>
<tr>
<td>4,499</td>
<td>0.73</td>
</tr>
<tr>
<td>7,230</td>
<td>0.55</td>
</tr>
</tbody>
</table>

* 1.00 corresponds to saturation, lower values to undersaturation, and higher values to supersaturation.

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results from the high production of carbon dioxide by oxidation of organic matter in the oxygen minimum layer. The low saturation at greater depths is due primarily to the effect of pressure which increases the solubility product exponentially with depth.

Undersaturation indicates solution of carbonates. The effects of solution on the distribution and fluxes of calcium carbonate in the oceans were examined by Pytkowicz (1967, 1968).

RATE OF SOLUTION OF CALCIUM CARBONATE

Probably the water layer next to a calcareous particle is saturated with calcium carbonate. Otherwise, there would be an infinite gradient of chemical potential across the particle surface, which would cause extremely fast solution or precipitation of carbonate. Further solution is therefore limited by the rate of renewal of the saturated layer. In the oceans this would occur by turbulent exchange which, in general, is several orders of magnitude faster than molecular diffusion. It is possible that molecular diffusion is the rate-determining step in stagnant interstitial waters within sediments.

The effect of eddy diffusion may be written as

\[
\frac{d\text{CO}_3^{2-}}{dt} = -E \frac{\partial (\text{CO}_3^{2-})}{\partial r}
\]

\(d\text{CO}_3^{2-}/dt\) is the rate of solution of calcium carbonate. Calcium is not considered because its concentration is high and is hardly affected by solution of calcium carbonate. \(E\) is the eddy diffusion coefficient and \(r\) is the distance from the calcareous test. If the gradient of \(\langle\text{CO}_3^{2-}\rangle\) is assumed to be linear, equation 8 becomes

\[
\frac{d\text{CO}_3^{2-}}{dt} = \frac{E}{r} \left[ (\text{CO}_3^{2-})_s - (\text{CO}_3^{2-}) \right] \quad (8)
\]

\[
= \frac{E(\text{CO}_3^{2-})_s}{r} \left( 1 - \frac{IP}{K'_{sp}} \right) \quad (9)
\]

\(r\) now is the thickness of the layer between the particle surface and a point at which the properties of the bulk water start. \(\text{CO}_3^{2-})_s\) is the carbonate ion concentration at saturation, and \(\text{CO}_3^{2-}\) is the concentration in the bulk water.

\(E = D\), the coefficient of molecular diffusion, if the layer next to the particle is laminar. In this case the turbulence enters only through \(r\), as the thickness of the layer is decreased; and, therefore, the rate of solution is increased by enhanced turbulence. The rate of solution, as is expected, also depends on the degree of undersaturation, \(IP/K'_{sp}\).

The sinking time of calcareous tests is short compared to the exposure time after the tests reach the sediments. However, the turbulence should be much greater during settling than at the bottom. It is not possible at present to evaluate the relative importance of solution during these two phases.

Organic coatings have been shown to inhibit the precipitation of calcium carbonate on carbonate surfaces (Chave and Suess, 1967). Such coatings probably also retard the solution of calcium carbonate particles in undersaturated waters.

CONCLUSION

The many factors that control the solubility and the rate of solution of calcium carbonate were examined. An important conclusion to be drawn from this work is that, when possible, it is worthwhile to make solubility measurements with the particular calcareous species under study at representative values of temperature, salinity, and pressure. Data from the literature may be used, however, if no great accuracy is required. In general, oceanic waters are supersaturated in the upper layers and undersaturated at depth. However, the degree of saturation of bulk waters may not be representative of conditions in body fluids and next to organisms where production of carbon dioxide and of other acids and bases may alter the pH.

REFERENCES

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