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THE SOLUBILITY OF CALCITE AND ARAGONITE IN SEAWATER AT ATMOSPHERIC PRESSURE AND 34.5‰ SALINITY

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ABSTRACT. Direct measurement of the solubility of calcite in seawater is difficult and irreproducible because of kinetic factors that inhibit the attainment of true, reversible equilibrium. To avoid this problem, the solubility product constant for calcite in seawater was determined in the present study by calculation from new measurements of the aragonite solubility product constant in seawater and the differential solubility of calcite and aragonite in carbonated distilled water. All measured equilibria were reversed, and redundant measurement of pH, P_{CO_2}, calcium concentration, and carbonate alkalinity was used as a check on the results. The resultant calculated values of $K_c' = [Ca^{++}]\,[CO_3^{--}]$ for 34.5‰ seawater at 1 atm total pressure are:

$$K_c' = 5.94 \pm 0.39 \times 10^{-7} \quad \text{at } 25°C.$$
$$K_c' = 7.98 \pm 0.43 \times 10^{-7} \quad \text{at } 5°C$$

where c refers to calcite, and units of K_c' are $mol^2\ l^{-2}$. The analogous measured values for aragonite in seawater are:

$$K_a' = 8.76 \pm 0.40 \times 10^{-7} \quad \text{at } 25°C$$
$$K_a' = 11.4 \pm 0.50 \times 10^{-7} \quad \text{at } 5°C.$$

Whereas the aragonite values are in reasonably good agreement with the results of MacIntyre (1965), the calculated K_c' values are consistently higher than either those of MacIntyre or of Ingle and others (1973). The difference in solubility between calcite and aragonite determined in the present study is in good agreement with thermodynamic measurements of others, whereas the results of MacIntyre are not.

Recalculation, using the new K_c' data, of the state of saturation of the Atlantic and Pacific Oceans from the data of Takahashi (1975) shows that the lysocline, north of 30°S, in both oceans is found well below the saturation depth for calcite and occurs near where accelerated dissolution, based on similarly recalculated laboratory results, is to be expected. However, additional indirect determinations of calcite solubility, especially for elevated pressures, are needed to check these conclusions.

INTRODUCTION

It is a well known fact that calcium carbonate, which is secreted by unicellular organisms in shallow waters of the oceans, is dissolved upon falling into the deep sea. Many hypotheses have been offered to explain this dissolution and its sudden occurrence with water depth (Murray and Renard, 1891; Revelle and Fairbridge, 1957; Bramlette, 1961; Turekian, 1964; Pytkowicz, 1965; Berner, 1965; Peterson, 1966; Berger, 1967, 1968; Li, Takahashi, and Broecker, 1969; Hawley and Pytkowicz, 1969; Heath and Culberson, 1970; Edmond and Gieskes, 1970; Morse and Berner, 1972; Broecker and Broecker, 1974; Edmond, 1974; Ben-Yaakov, Ruth, and Kaplan, 1974; Takahashi, 1975). A major question, which has arisen in recent years, is whether the depth where removal due to dissolution occurs, often referred to as the carbonate compensation depth, represents a change from overlying supersaturated water to underlying undersaturated water (for example, Li, Takahashi, and Broecker, 1967; Ben-Yaakov, Ruth, and Kaplan, 1974) or whether this depth falls wholly within a wide undersaturation depth zone and sudden dissolution is brought about by oceanographic (see Edmond, 1974) or surface chemical kinetic (see Berner and Morse, 1974) phenomena. Thus, it is critical for

the various dissolution hypotheses to be able to determine with some assurance the state of saturation of seawater with respect to calcium carbonate.

To be able to determine the state of saturation of a given seawater sample the following shipboard measurements need to be made: temperature; pressure (depth); salinity; the concentration of calcium ion (which can be calculated from salinity); and any two of the four parameters pH, P_{CO_2} (partial pressure of carbon dioxide), ΣCO_2 (sum of the concentrations of dissolved CO_2, H_2CO_3, HCO_3^-, and CO_3^{--}) and A_c (carbonate alkalinity equal to the concentration of HCO_3^- plus twice the concentration of CO_3^{--}). From these measurements, saturation state(s) can be calculated using equilibrium constants for: the solubility of CO_2 (if P_{CO_2} is measured), the dissociation of H_2CO_3 to HCO_3^- and CO_3^{---}, and the solubility of calcium carbonate. (For methods of calculation consult Li, Takahashi, and Broecker, 1967; Edmond and Gieskes, 1970; or Takahashi, 1975). A device for direct measurement of in situ saturation state, the carbonate saturometer (Ben-Yaakov, Ruth, and Kaplan, 1974), has been used to avoid these calculations, but, as discussed below and in later sections, it is believed by the writer that such direct measurement can lead to serious errors due to kinetic problems.

There is general agreement at present that shipboard measurement techniques and the dissociation constants of H_2CO_3 are not the major problems in calculating saturation states. Rather, the chief source of disagreement lies in the value for the solubility product constant for calcite and its variation with temperature and pressure (for example, see Takahashi, 1975). Since the majority of calcareous organic remains falling into the deep ocean consists of calcite (low in magnesium), it is important that the in situ solubility product for this mineral be known accurately.

One of the major reasons for disagreement in previous work on the solubility of calcite is that calcite does not easily equilibrate with seawater. If the seawater used in the laboratory is initially supersaturated, during equilibration the precipitation of supersoluble highly magnesian calcite on low-Mg calcite seeds may occur (Weyl, 1965; Berner, 1975), and an incorrectly high value for calcite solubility may, thereby, be measured. On the other hand, if saturation is approached from undersaturation, the rate of approach may drop severely at an appreciable degree of undersaturation (Berner and Morse, 1974) due to the adsorption of dissolution-inhibiting trace species (poisons) such as orthophosphate anions. This can give rise to an apparent equilibrium and an incorrectly low value for the solubility product. Calcite behaves in seawater in a manner analogous to that of an irreversible electrode of low exchange current. Near equilibrium in both cases, there is a "flat" region of very slow reaction which renders exceedingly difficult the determination of equilibrium solubility (in the case of calcite) and equilibrium potential (in the case of an irreversible electrode).

One way out of the calcite dilemma is to measure the solubility of aragonite in seawater, which behaves more reversibly than calcite (Mg does not inhibit aragonite precipitation), and *calculate* the solubility of calcite from a knowledge of the solubility difference between calcite and aragonite in other Mg-free solutions where calcite behaves reversibly. This approach is used in the present paper. It is hoped that further studies using similar indirect methods will be pursued by others to check the results of the present study and to enable more accurate solubility determinations at elevated pressures. Only in this way will unavoidable kinetic problems, posed when calcite is added directly to seawater, be avoided.

METHODS

General principles.—Solubility product constants (in terms of Ca^{++} and CO_3^{--}) for aragonite in seawater and calcite and aragonite in carbonated distilled water were determined by measurement of the equilibrium values of pH, calcium concentration, and carbonate alkalinity. During reaction each solution was also equilibrated with a gas mixture of known CO_2 content by continuous bubbling of the gas through the solution. This provided a redundant check on solubility product calculations. Once equilibrium was achieved, the solubility product was calculated as follows:

For seawater:

$$K_a' = \frac{[Ca^{++}]\, A_c}{2 + a_{H^+}/K_2'} \tag{1}$$

where

K'_a = apparent solubility product constant of aragonite in seawater (a function of temperature, pressure, and salinity)

$[Ca^{++}]$ = concentration of total calcium (free ion plus ion pairs) in mols per l

A_c = carbonate alkalinity in mols per l ($[HCO_3^-] + 2[CO_3^{--}]$)

a_{H^+} = activity of hydrogen ion measured relative to standard N.B.S. buffers

K_2' = second dissociation constant of carbonic acid in seawater

For distilled water:

$$K_{c,a} = \frac{\gamma_{Ca^{++}}\, \gamma_{HCO_3^-}\, m_{Ca^{++}}\, A_c}{2(\gamma_{HCO_3^-}/\gamma_{CO_3^{--}}) + a_{H^+}/K_2} \tag{2}$$

where:

$K_{c,a}$ = solubility (activity) product of calcite or aragonite at infinite dilution (a function of temperature and pressure only)

γ = activity coefficient

K_2 = second dissociation constant of carbonic acid at infinite dilution (in terms of activities)

$m_{Ca^{++}}$ = molality of total calcium ion

Since ionic strengths encountered in the distilled water runs were all less than 0.05, molality and molarity were assumed identical, and γ values were calculated using the extended Debye-Huckel expression. In addition, $CaHCO_3^+$ ion pair formation was ignored (see discussion of results section).

The value of K_c', the apparent solubility product constant of calcite in seawater, was calculated, for a given temperature, by:

$$K_c' = K_a'(K_c/K_a) \tag{3}$$

This equation rests upon the thermodynamic assumption that the free energy difference between pure calcite and aragonite is a constant (at a given temperature and pressure) for all reactions in which they are involved.

Apparatus and materials.—All solubility determinations were made using the apparatus described by Morse (1974) with the modification that the pH was allowed to drift freely and not kept constant (as is the usual case for kinetic studies). A glass plus saturated calomel electrode pair (L. and N. with dual glass liquid junction) was used to measure pH, and temperature was held constant to ± 0.1°C using a constant temperature bath.

Gases bubbled through the solution were N_2–CO_2 mixtures containing 100, 10, or 0.32 percent CO_2 by volume. Percentages reported by the manufacturer were checked by measuring the pH of a dilute $NaHCO_3$ solution (of known HCO_3^- activity) equilibrated with each gas and/or by gas chromatography. Reported values were found to be correct within the limits of accuracy of the bubbling-equilibration and gas-chromatographic techniques (±4 percent).

Seawater used in all studies came from a single batch of artificial seawater of 34.5‰ salinity made up to include all species of abundance equal to or greater than fluoride ion as given by Turekian (1968) (HCO_3^- and CO_3^{--}, however, were generally somewhat lower). A double check was provided by measurement of chloride, sulfate, magnesium, and calcium, by standard volumetric or gravimetric techniques. Distilled water was prepared from doubly deionized water using all-glass apparatus.

Solids used were Fisher reagent calcite with average crystal size of 5 to 10 μm and a hand ground aragonite stalactite. In one run synthetic aragonite prepared according to the method of Katz (1973) was used. The stalactite was found to consist of pure aragonite, within the limits of X-ray diffraction and optical petrographic measurement, and to contain less than 1 mol percent $SrCO_3$ in solid solution. It is likely that grinding of the aragonite produced grains of excess solubility (Chave and Schmalz, 1966), but that the excess solubility was relieved during equilibration. This could be seen by the addition of extra aragonite to saturated or very slowly precipitating supersaturated seawater. The pH would immediately rise but then return within 2 to 8 hrs to its original value indicating relief of surface strain, recrystallization, et cetera of the added material. Moreover, the results of the seawater run using unground synthetic ara-

gonite are in good agreement with those for the ground stalactitic material. This agreement has also been found for seawater by MacIntyre (1965) using synthetic and ground shell aragonite. Relief of excess solubility in distilled water runs was demonstrated by the attainment, in sufficiently long runs, of solubilities predictable from calcite solubilities using the known difference in free energy.

Procedure.—All runs were conducted at either 5° or 25°C. The glass-calomel electrode pair was standardized against fresh N.B.S. 4.01, 6.86, and 7.41 buffers at the beginning and end of every run. Occasionally pH 9.18 buffers were also used. No electrode slope correction was needed at 25°C (measured pH values of buffers were within 0.01 of their stated value); at 5°C a constant 98 percent slope correction was necessary. Electrode drift during runs was checked with a single buffer and found to be less than 0.02 pH for periods as long as 30 hrs.

Seawater runs were conducted using only 0.32 percent CO_2. The reason for this is that higher CO_2 concentrations would cause excessive concentrations of Ca^{++} and HCO_3^- to appear during dissolution and, thus, appreciably alter the composition of seawater (Ben-Yaakov and Goldhaber, 1973). Equilibrium was approached from undersaturation by presaturating the seawater with 0.32 percent CO_2. Aragonite was then added, and the pH continually monitored during dissolution. In many runs additional aragonite was later added to check for true equilibrium (see below). From time to time alkalinity and calcium concentration measurements were made. Once saturation with aragonite was achieved by dissolution, 0.5 or 1.0 ml of 1.00 m $NaHCO_3$ solution was added to the seawater (300-400 ml), and equilibrium, thereby, approached by precipitation. (In two additional runs $NaHCO_3$ was added, and equilibrium approached by precipitation at the start of the run.) In this way reversed equilibrium values were determined. Individual run length (dissolution or precipitation) ranged from about 15 to 120 hrs. Longer equilibration times were necessary at lower temperature and for precipitation.

The criterion for equilibrium in seawater runs was no observable change in pH defined as less than 0.0005 pH units per hr. It was found that when initially employing smaller amounts of aragonite, the "equilibrium pH" could usually be shifted upward for dissolution runs and downward for precipitation runs by the addition of more aragonite (after allowing for relief of surface strain). The probable reason for this is that due to adsorption of trace impurities, initial false equilibrium pH values were attained analogous to the situation for calcite (see introductory section). Addition of more aragonite caused further adsorption and removal of the impurities, thus enabling a closer approach to equilibrium. At the end of each run a total of at least 10 g of aragonite had been added to 5°C runs and about 5 g to 25°C runs. Seawater volume was 300 to 400 ml. Without this procedure a large gap between minimum undersaturation-approached and maximum supersaturation-approached solubilities can result. An example are the values $K_a' = 7.7 \times 10^{-7}$ (under) versus 13.8×10^{-7} (super) for 5°C using 2 g of synthetic ara-

gonite (per 400 ml of seawater) without subsequent aragonite addition. Large gaps like this were found to be associated with high (>2μ m/l) contaminant phosphate concentrations suggesting that phosphate hinders the equilibration of both aragonite and calcite with seawater.

In distilled water runs various CO_2 gas percentages were employed. This enabled approach to saturation via precipitation which is otherwise impossible at a fixed temperature using carbonated distilled water. The procedure for accomplishing this was to equilibrate, via dissolution, with calcite or aragonite at a given percent CO_2 and then change to a gas mixture of lower CO_2 content using the same solution. As in seawater runs, pH was continually monitored, and extra solid was occasionally added to check for equilibrium. Individual equilibration times (dissolution or precipitation) averaged 3 to 10 hrs for calcite and 15 to 30 hrs for aragonite. Longer aragonite runs were required because of the necessity for relief of surface strain, recrystallization, et cetera of the ground aragonite.

When saturation with $CaCO_3$ had been attained in either seawater or distilled water runs, the pH was recorded, and determinations of dissolved calcium, dissolved chloride, and total alkalinity were made. Chloride was measured in order to check for dilution or evaporative concentration in seawater runs (none was found) and to measure small concentrations of KCl given off to solution by the calomel electrode in long distilled water runs. The KCl was taken into consideration in calculating ionic strength but was actually negligible except in runs using 0.32 percent CO_2, where it contributed up to 10 percent of the ionic strength. Chloride was determined by $AgNO_3$ titration using dichromate as indicator. Use of standards and blanks indicate ± 1 percent total range in accuracy for seawater and ± 25 percent accuracy for dilute KCl in distilled water runs. Calcium was determined in all runs by EDTA titration using cal-red as indicator. Replicate analyses of standards showed a total range of accuracy of ± 2 percent.

Total alkalinity was determined on all samples via potentiometric titration using a glass-calomel electrode pair and 0.01 molar HCl. The whole titration curve was recorded, and the inflection point identified visually. Use of $NaHCO_3$ standards indicate a total range of accuracy of ± 2 percent. To determine carbonate alkalinity in the seawater runs, correction for borate alkalinity using the equilibrium constants of Lyman (ms) were made. This correction was always less than 1 percent of the total alkalinity.

RESULTS

Measured equilibrium values of pH, calcium concentration, and carbonate alkalinity and calculated solubility product constants for calcite and aragonite are summarized in tables 1 and 2. Average values of solubility product constants for calcite and aragonite in distilled water, and for aragonite in seawater, and calculated values for calcite in seawater are shown in table 3. Errors stated for K_a, K_c, and K_a' in table 3

TABLE 1

Equilibrium values of calcium concentration, carbonate alkalinity (A_c), and pH and values of K_a' and P_{CO_2} calculated from them using the K_1' and K_2' values of Lyman (ms) and α_s values of Weiss (1974). Aragonite in 34.5‰ seawater under 99.68 percent N_2 + 0.32 percent CO_2, at 1.00 atm total pressure. (und = approach to equilibrium by dissolution; sup = approach by precipitation.)

Temp °C	$[Ca^{++}]$ mol/l $\times 10^2$	A_c mol/l $\times 10^3$	pH	Approach	K_a' mol^2/l^2 $\times 10^7$	$P_{CO_2} \times 10^2$
25	1.065	3.22	7.512	und	8.38	0.322
25	1.05	3.40	7.515	sup	8.80	0.337
25	1.105	3.24	7.523	und	9.01	0.317
25	1.015	3.46	7.535	sup	9.05	0.329
25	1.00	3.31	7.535	sup	8.55*	0.314
5	1.18	5.56	7.600	und	11.5	0.324
5	1.08	5.65	7.616	sup	11.1	0.316
5	1.005	5.73	7.644	sup	11.1	0.302
5	1.20	5.67	7.602	und	11.9	0.328

* Synthetic aragonite; all other runs with ground stalactitic aragonite.

represent total ranges of the measurements, whereas the error assigned to K_c' represents the standard deviation of values derived from all possible combinations of K_a, K_c, K_a' values using equation (3). Solubility products of tables 1 to 3 are based on K_2' of Lyman (ms) and K_2 of Harned and Scholes (1941).

Besides solubility products, values of P_{CO_2} were also calculated for each run from carbonate alkalinity and pH via the expressions:
For seawater:

$$P_{CO_2} = \frac{a_{H^+} A_c}{\alpha_s K_1' (1 + 2 K_2'/a_{H^+})} \tag{4}$$

where:

α_s = solubility (Henry's Law) coefficient of CO_2 gas in seawater (present as CO_2 plus H_2CO_3)
K_1' = first dissociation constant of carbonic acid in seawater.

For distilled water:

$$P_{CO_2} = \frac{a_{H^+} \gamma_{HCO_3^-} A_c}{\alpha_0 K_1} \tag{5}$$

where:

α_0 = solubility coefficient of CO_2 in pure water (infinite dilution)
K_1 = first dissociation constant of carbonic acid at infinite dilution (in terms of activities)
γ_{HCO_3} = molal activity coefficient calculated via the extended Debye-Hückel expression.

(Note—a small correction for CO_3^{--} in A_c was made for 0.32 percent CO_2 runs.) Values of equilibrium constants used in calculating P_{CO_2} are taken from the results of Lyman (ms) for K_1' and K_2', Weiss (1974) for α_s, Harned and Scholes (1941) for K_2, and Harned and Davis (1943) for K_1 and α_0.

TABLE 2

Equilibrium values of calcium concentration, carbonate alkalinity (A_c), and pH and values of K_c or K_a and P_{CO_2} calculated from them ignoring $CaHCO_3^+$ ion pairs and using the α_0 and K_1 values of Harned and Davis (1943), the K_2 values of Harned and Scholes (1941), and the extended Debye-Hückel equation for activity coefficients. Calcite or aragonite in carbonated distilled water at 1.00 atm total pressure of $N_2 + CO_2$. (und = approach to equilibrium by dissolution; sup = approach by precipitation.)

Mineral	T°C	% CO_2	$[Ca^{++}]$ mol/l $\times 10^3$	A_c mol/l $\times 10^3$	pH	Approach	$K_{c,a}$ mol^2/kg$^2 \times 10^9$	$P_{CO_2} \times 10^2$
calcite	25	100	8.85	17.70	6.011	und	3.62	96
calcite	25	10	3.72	7.55	6.657	und	3.56	9.7
calcite	25	10	3.67	7.55	6.654	sup	3.47	9.8
calcite	25	0.32	1.11	2.22	7.632	sup	3.59	0.31
aragonite	25	100	10.25	20.8	6.079	und	5.47	96
aragonite	25	100	10.35	20.7	6.086	und	5.63	95
aragonite	25	10	4.40	8.82	6.715	und	5.37	9.8
aragonite	25	10	4.25	8.62	6.703	sup	5.03	9.9
aragonite	25	10	4.20	8.45	6.705	sup	4.90	9.7
aragonite	25	0.32	1.26	2.55	7.680	sup	5.15	0.32
calcite	5	100	12.45	25.3	6.052	und	4.35	97
calcite	5	100	12.5	25.0	6.032	und	4.09	100
calcite	5	100	12.5	25.2	6.037	und	4.18	100
calcite	5	10	5.45	10.9	6.672	sup	4.25	10.2
calcite	5	0.32	1.53	3.08	7.683	und	4.40	0.31
aragonite	5	100	15.05	30.3	6.090	und	6.45	104
aragonite	5	100	14.9	29.8	6.083	und	6.18	104
aragonite	5	10	6.07	12.1	6.732	und	5.89	10.1
aragonite	5	10	6.10	12.2	6.736	sup	5.82	10.1

TABLE 3

Average values for K_a, K_c, and K_a' measured in the present study and values of K_c' calculated via equation (3) from them. Errors assigned to K_a, K_c, and K_a' represent total range of measured values. Error for K_c' is the standard deviation of values calculated from all individual values of K_a, K_c, and K_a' (120 numbers for 25°C; 80 numbers for 5°C). Data are for 34.5‰ salinity and 1 atm total pressure.

	$mol^2/kg^2 \times 10^9$		$mol^2/l^2 \times 10^7$	
T°C	K_a	K_c	K_a'	K_c'
25	5.26 ± 0.35	3.56 ± 0.10	8.76 ± 0.40	5.94 ± 0.39
5	6.09 ± 0.35	4.25 ± 0.15	11.4 ± 0.50	7.98 ± 0.43

DISCUSSION

CO_2 solubility.—Good agreement between measured percent CO_2 and calculated P_{CO_2} is shown in tables 1 and 2. This indicates the internal consistency of our pH and alkalinity measurements as well as the overall validity of the equilibrium constants used to calculate P_{CO_2}. Use of the seawater equilibrium constants of Mehrbach and others (1973), instead of those of Lyman (ms), gave essentially identical values, within the measurement error of the present study, at 25°C. However, at 5°C the Mehrbach-based values were somewhat too high averaging 0.34 to 0.35 $\times 10^{-2}$ atm. Actually, calculated P_{CO_2} values should be slightly lower (not higher) than nominal percent values, because the N_2–CO_2 gas pressure includes the equilibrium vapor pressure of water (0.03 atm at 25°C; 0.01 atm at 5°C). Since the total pressure of the laboratory was 1.00 atm, the value of P_{CO_2} should be about 1 to 3 percent lower than the nominal 0.32, 10, or 100 percent CO_2. Calculated values in tables 1 and 2 agree in general with this correction, but the experimental scatter of ±4 percent for some runs inhibits one from overextending this argument.

Christ, Hostetler, and Siebert (1974) have suggested that while bubbling CO_2-containing gases through aqueous solutions the effective value of P_{CO_2} may average as low as 90 percent of the nominal percentage. This was not found to be the case in the present study either for seawater, dilute $Ca(HCO_3)_2$ solutions (table 2), or for dilute $NaHCO_3$ solutions used as P_{CO_2} calibration checks.

Jacobson and Langmuir (1974) and Langmuir (1968) point out that internal consistency between calcium ion concentration, pH, and P_{CO_2} exists for distilled water solutions saturated with 100 percent CO_2 and calcite, but only if ion pairing between calcium and bicarbonate ions is ignored. The good agreement between calculated and measured P_{CO_2} shown in table 2 further corroborates this hypothesis. Values of P_{CO_2} were calculated using only the Debye-Hückel equation and ignoring ion pairing. Since there appears to be good evidence for the existence of $CaHCO_3^+$ with an infinite dilution association constant of about 17 (Christ, Hostetler, and Siebert, 1974; Jacobson and Langmuir, 1974; Nakayama,

1968), and since effective P_{CO_2} is not appreciably less than expected, as discussed above, no ready explanation can be given for this discrepancy.

$CaCO_3$ solubility.—At present the most commonly used solubility product constants for calcite in seawater are those of MacIntyre (1965) and Ingle and others (1973). (The older literature is discussed in detail by MacIntyre.) Comparison of the results of the present study with the results of MacIntyre and Ingle and others are shown in table 4. In order to compare results with those of Ingle and others, Ingle's solubility products were recalculated using the K_2' values of Lyman (ms) and the concentration scale changed from mol/kg of seawater to mol/l. Also, as pointed out by Ben-Yaakov and Goldhaber (1973) and Ingle and others (1973), MacIntyre measured K_c' and K_a' in "seawater" of 18‰ chlorinity with twice the Ca concentration and ten times the alkalinity of normal 19‰ Cl^- seawater. To compare his results with those of the present study, values for 25°C have been lowered by 2 percent so as to apply to normal seawater (Ingle and others, 1973).

Note in table 4 that there is fairly good agreement between the corrected aragonite values of MacIntyre and the present study, but that agreement for calcite between all three studies is poor. Arguments will now be presented to try to convince the reader that the values of the present study are the most accurate.

TABLE 4

Comparison of solubility product constants for calcite and aragonite in seawater of 34.5‰ salinity at 1 atm total pressure. All values based on K_2' values of Lyman (ms). MacIntyre results for 25°C corrected according to the method of Ingle.

Mineral	Temp °C	K_a', $K_c' \times 10^7$ (mol^2/l^2) Ingle and others (1973)	MacIntyre (1965)	Present study
aragonite	25	—	8.9	8.8
aragonite	5	—	10.6	11.4
calcite	25	5.0	5.4	5.9
calcite	5	5.8	6.7	8.0
K_a'/K_c'	25	—	1.67	1.48
K_a'/K_c'	5	—	1.58	1.43

First, the free energy difference between calcite and aragonite at 25°C and 1 atm has received exhaustive study by Langmuir (ms) who came to the conclusion that the best value was -230 ± 30 cal/mol. The work of Christ, Hostetler, and Siebert (1974) suggests a value of -218 cal/mol. These values correspond to K_a/K_c ratios of 1.48 and 1.45 respectively .The ratio of K_a'/K_c' should be the same. The value for K_a'/K_c' used in the present study is 1.48. That of MacIntyre is 1.67. Therefore, the K_a'/K_c' ratio of the present study is in much better agreement with the results of others than is MacIntyre's.

Secondly, the ratio K_c/K_c' is equal to the total activity coefficient of dissolved $CaCO_3$ in seawater $\gamma_{T_{CaCO_3}} = \gamma_{T_{Ca^{++}}} \gamma_{T_{CO_3^{--}}}$. From the data of table 3, $\gamma_{T_{CaCO_3}} = 0.060$ at 25°C. This is in good agreement with the

value $\gamma_{T_{CaCO_3}} = 0.061$ derived independently from CO_2 solubility plus H_2CO_3 dissociation equilibria, for $\gamma_{T_{CO_3^{--}}}$ (Pytkowicz, 1975), and experimental measurements and the Brønsted-Guggenheim model, for $\gamma_{T_{Ca^{++}}}$ (Whitfield, 1973). By contrast the K_c' value of Ingle and others (1973) when divided into the K_c value of the present study gives the value $\gamma_{T_{CaCO_3}} = 0.071$.

Thirdly, those results of MacIntyre that are in greatest disagreement with the present study, the low temperature (0°C; 5°C) calcite and aragonite values, were obtained only by approach to equilibrium from undersaturation. They are, thus, minimum values. As a result, MacIntyre's findings are in better qualitative agreement with the 5°C values of the present study, which are all greater than those of MacIntyre, than with the low temperature results of Ingle and others which are all less than those of MacIntyre. (The finding by Takahashi, 1975, of probable disequilibrium between CO_2 gas and seawater in some of MacIntyre's runs does not affect this argument.)

Finally, as pointed out in the introduction, many kinetic difficulties are encountered when trying to equilibrate calcite directly with seawater. Several workers have demonstrated this problem (Weyl, 1965; Chave and Suess, 1970; Berner and Morse, 1974; W. S. Broecker, personal commun.). It is likely that much of the disagreement between directly measured K_c' values (for a recent summary of values, see Ingle and others, 1973) is due to each worker encountering false equilibria due to kinetic inhibition. The writer has personally found that, even if a 10 percent suspension of fine-grained calcite in seawater is used, a factor of 1.5 to 2 difference in solubility is obtained depending upon whether equilibrium is approached from undersaturation or supersaturation. The value given in the present study was *not* measured directly but calculated from less kinetically complicated measurements. In this way it is felt to be more accurate.

Average values for pK_c (where p refers to the negative logarithm to the base ten) are compared to the results of two recent studies in table 5. (Earlier work is discussed in detail by Jacobson and Langmuir, 1974.) All results are based on Debye-Hückel activity coefficients without correction for ion pairing. There is excellent agreement with the results of

TABLE 5

Solubility product constants for calcite (expressed as the negative log, pK_c) at infinite dilution and 1 atm total pressure. Calcium-bicarbonate ion pairing not considered (Nakayama raw data recalculated to remove ion-pair correction).

Reference	pK_c (25°C)	pK_c (5°C)
Jacobson and Langmuir (1974)	8.42	8.35
Nakayama (1968)	8.45	—
Present study	8.45	8.37

Nakayama (1968) at 25°C and excellent agreement with the temperature coefficient of Jacobson and Langmuir. The consistently lower values of pK_c (0.02-0.03 units) recorded at each temperature by Jacobson and Langmuir, although within experimental reproducibility, suggest a fixed error between their study and the present one. Comparison of raw data for 5°C indicates that the major part of the error resides in the value for equilibrium pH. Although further work is necessary to pin down the reason for the pH disagreement, it it really not critical, for the main purpose of the present study, to know the exact value of pK_c. The critical parameter is pK_c–pK_a which is in excellent agreement with other studies. Apparently, small pH errors, if they exist, are constant for both calcite and aragonite and, therefore, vanish upon taking the difference between pK values. Also, correction for ion pairing for a given P_{CO_2} affects pK_c and pK_a equally, and, therefore, *the value of pK_c–pK_a is constant and independent of whether or not ion pairing is considered.*

APPLICATION OF THE RESULTS

Since new values for the solubility product constant of calcite in seawater are presented in this study, it is instructive to see how much change the new values require in the results of earlier studies which involved attempts to calculate the saturation state of seawater with respect to calcite. Three studies are chosen for examination. They are those of Morse and Berner (1972) (see also Berner and Morse, 1974), Berner and Wilde (1972), and Takahashi (1975). This group was chosen because of their obvious interest to the present writer and because they form an interdependent set: the saturation state calculations of Takahashi are used to test the kinetic hypothesis of Morse and Berner which in turn rest upon rate versus saturation state measurements in the laboratory and calculations by Berner and Wilde of saturation state at a locality in the central Pacific Ocean.

In the studies of Morse and Berner it was concluded that at a critical degree of undersaturation the rate of calcite dissolution in seawater suddenly accelerates. The degree of undersaturation was expressed as ΔpH:

$$\Delta pH = p\bar{H} - pH \tag{6}$$

where:

pH = pH of the seawater sample under study
$p\bar{H}$ = pH for saturation with calcite at the same calcium concentration and P_{CO_2}.

The value of $p\bar{H}$ was calculated from the relation:

$$p\bar{H}_{MB} = -\frac{1}{2}\log\left[\frac{\alpha_o K_1 K_2}{K_c}\gamma_{Ca_T^{++}}\, m_{Ca_T^{++}}\, P_{CO_2}\right] \tag{7}$$

where the subscript T refers to total calcium ion (free ion plus ion pairs) and MB refers to Morse and Berner.

Using the data of the present study for K_c', $p\bar{H}$ can be calculated by the alternative expression:

$$p\bar{H}_{PS} = -\frac{1}{2} \log \left[\frac{\alpha_s K_1' K_2'}{K_c'} [Ca^{++}] P_{CO_2} \right] \quad (8)$$

where PS refers to the present study. From (6), (7), and (8) (assuming molality = molarity):

$$\Delta pH_{PS} - \Delta pH_{MB} = \frac{1}{2} \log \left[\left(\frac{\alpha_0 K_1 K_2}{K_c} \gamma_{Ca_T^{++}} \right) \Big/ \left(\frac{\alpha_s K_1' K_2'}{K_c'} \right) \right] \quad (9)$$

The values used by Morse and Berner for 25°C and 1 atm total pressure were: $\alpha_0 K_1 K_2 = 10^{-18.143}$ (Harned and Scholes, 1941; Harned and Davis, 1943), $K_c = 10^{-8.40}$ (Langmuir, 1968), and $\gamma_{Ca_T^{++}} = 0.20$ (Berner, 1965). In the present study values are: $\alpha_s K_1' K_2' = 10^{-16.636}$ (Weiss, 1974, for α_s; Lyman, ms, for K_1' and K_2') and $K_c' = 5.95 \times 10^{-7}$ (table 3). Substitution of these values into equation (9) yields:

$$\Delta pH_{PS} = \Delta pH_{MB} - 0.016 \quad (10)$$

Thus, to be in agreement with the solubility product of the present study and the generally accepted equilibrium constants of Lyman (ms), the results of Morse and Berner (1972) as well as those of Berner and Morse (1974) for 25°C and 1 atm total pressure should be shifted by 0.016. This correction is within the error limits discerned by Morse (1974) who showed by direct kinetic measurements that the true calcite equilibrium pH for a given P_{CO_2} was within a few hundredths of the value calculated by Morse and Berner. Also, the correction of 0.07 applied by Takahashi (1975) to the ΔpH values of Morse and Berner, using the solubility product of Ingle and others (1973), is believed to be too high by 0.05. Takahashi's correction must be somewhat too high because it would place some of Morse and Berner's measured *dissolution* rates into the field of calcite *supersaturation* which is impossible.

In the work of Berner and Wilde (1972) it was shown that:

$$\Delta pH = -\frac{1}{2} \log \Omega \quad (11)$$

where Ω is the degree of saturation expressed as the product of calcium and carbonate ion concentrations divided by their product at equilibrium or, in other words, the solubility product. Berner and Wilde attempted to evaluate Ω and ΔpH for calcite at the site in the central Pacific Ocean where the dissolution experiments of Peterson (1966) and Berger (1967) were undertaken. For this purpose they used the expression:

$$\Omega = \frac{m_{Ca^{++}} A_c}{K_c' (2 + a_{H^+}/K_2')} \quad (12)$$

to calculate Ω versus depth. The values used for K_2' at 1 atm were 26 percent larger, at all temperatures, than those of Lyman (ms) and are now believed by most workers (for example, see Takahashi, 1975) to be less accurate than Lyman's. The values used for K_c' were derived from K_c and activity coefficients for Ca^{++} and CO_3^{--}. For depths below 2000 m, where the temperature ranges from 1.4° to 2.0°C, the value used for K_c' before correcting for the effect of pressure (that is, K_c' at 2°C and 1 atm) was 11.1×10^{-7}. If the results of the present study are linearly extrapolated to 1.7°C (linear extrapolation over small temperature differences as shown by MacIntyre, 1965, appears to be reasonable), the value obtained for K_c' is 8.3×10^{-7}. Thus, the value of K_c' used by Berner and Wilde is believed to have been 34 percent too high. To summarize the above, the following corrections will be used for depths in excess of 2000 m (BW refers to Berner and Wilde; PS to the present study):

$$K_{c\,PS}' = 0.747\ K_{c\,BW}' \tag{13}$$

$$K_{2\,PS}' = 0.795\ K_{2\,BW}' \tag{14}$$

Now, equation (12), for the purpose of correction, can be recast as:

$$\frac{\Omega_{PS}}{\Omega_{BW}} = \frac{K_{c\,BW}'}{K_{c\,PS}'}\left[\frac{2 + a_{H^+}/K_{2\,BW}'}{2 + a_{H^+}/K_{2\,PS}'}\right] \tag{15}$$

Below 2000 m at the Peterson and Berger site, a_{H^+}/K_2' falls in the range 20 to 35 regardless of which value of K_2' is used. This means that the term in parenthesis in equation (15) is closely approximated by 1.015 ($K_{2\,PS}'/K_{2\,BW}'$). Thus, substituting (13) and (14) in (15) and using this approximation:

$$\Omega_{PS} = 1.08\ \Omega_{BW} \tag{16}$$

or:

$$\Delta pH_{PS} = \Delta pH_{BW} - 0.017 \tag{17}$$

This correction indicates that the ΔpH results of Berner and Wilde (1972), to be in agreement with the data of the present study, should be shifted by 0.017, *practically the same shift* as required by the results of Morse and Berner (1972) and Berner and Morse (1974). Therefore, the major conclusion of these studies, that calcite dissolution in the oceans suddenly accelerates upon reaching a critical degree of undersaturation, is not affected by the use of revised equilibrium constants. The laboratory saturation states are corrected by the same amount as in situ saturation states for the ocean. Actually the agreement is not surprising because similar corrections are applied to both laboratory and field results as can be shown by straightforward algebraic manipulation.

In the study of Takahashi (1975) the degree of saturation Ω, with respect to calcite, of seawater at numerous locations in the Atlantic and Pacific Oceans was calculated using the solubility product constants of Ingle and others (1973). His results show that in both oceans the car-

bonate compensation depth falls far below the level where $\Omega = 1$, in other words, the compensation depth does not constitute an equilibrium boundary. Takahashi's data for depths greater than 2000 m can be easily recalculated using the solubility product data of the present study. This is because at these depths the temperature ranges only from about 0° to 2°C. At 2°C the linearly extrapolated value from the results of table 3 for K_c' is 8.3×10^{-7}. At the same temperature K_c' from the results of Ingle and others is 5.8×10^{-7}. Thus, as a good approximation, the results of Takahashi for Ω at any depth below 2000 m can be corrected by the expression:

$$\begin{aligned} \Omega_{PS} &= 5.8/8.3\ \Omega_T \\ \Omega_{PS} &= 0.70\ \Omega_T \end{aligned} \tag{18}$$

where T refers to Takahashi, and PS to the present study. With this correction, the depth separating the compensation depth and the level where $\Omega = 1$ becomes even greater. As a result the conclusion that the compensation depth is a kinetic, and not a thermodynamic, phenomenon receives additional backing.

Takahashi's results show that north of 30°S in both the Atlantic and the Pacific the carbonate compensation depth tends to parallel contours of constant Ω. Takahashi used this observation to back the contention of Morse and Berner (1972) and Berner and Morse (1974) that dissolution of calcite in deep-sea sediments is greatly accelerated upon reaching a critical degree of undersaturation, the value of which depends upon the phosphate concentration in the surrounding water. Actually the hypothesis of Morse and Berner was intended to apply to the lysocline (Berger, 1968) or depth where dissolution of $CaCO_3$ in bottom sediments begins to accelerate, rather than the compensation depth, where $CaCO_3$ disappears. In the Atlantic the lysocline tends to parallel the compensation depth, at a level about 500 m shallower (Berger, 1975), and, thus, it also parallels contours of constant Ω. Revision of Takahashi's results using equation (18) indicates that the lysocline in the Atlantic (north of 30° south) falls at an Ω value of approximately 0.55. At the average phosphate level of deep Atlantic Ocean water ($\sim 1\mu$ mol per l) the results of Berner and Morse (1974), revised via equation (10), indicate that accelerated dissolution should occur at a critical $\Omega \approx 0.60$ ($\Delta pH = 0.11$). This is reasonably good agreement considering all the errors in calculating Ω values.

In the south Pacific Ocean (north of 30°S) the lysocline diverges from the compensation depth upon going north toward the equator (Parker and Berger, 1971). The revised Ω values at the lysocline, using equation (18) vary systematically from about 0.48 to 0.54 indicating that, while there is some crossing of contours, the crossing is not large. The revised results of Morse and Berner (1974) for phosphate levels typical of the deep Pacific (2.0-2.5 μ mol/l) indicate a critical undersaturation level at $\Omega = 0.52$-0.58 ($\Delta pH = 0.12$-0.14). Again there is reasonably good agreement between the laboratory results and Takahashi's revised data.

In fact, if the revised Takahashi Ω values were increased by 10 percent, there would be excellent agreement for both the Atlantic and Pacific (north of 30°S). In other words, the difference between oceans of the average Ω value at the lysocline is predictable, from the laboratory studies, from the difference in average phosphate concentration in deep water.

South of 30°S the compensation depth as mapped by Berger and Winterer (1974) does not occur at a constant Ω value, and, if their data are correct, the hypothesis of Morse and Berner does not work in the southern ocean. Here an alternative hypothesis, such as that of Edmond (1974) which attributes enhanced dissolution at depth to the greater turbulence of bottom water, may be more correct. However, before a firm choice of hypotheses is made in this region or any other part of the ocean, additional measurements of calcium carbonate solubility in seawater, especially as a function of pressure, are needed as well as further mapping of the lysocline, especially in the north Pacific.

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