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THE INFLUENCE OF SURFACE STATE AND SATURATION STATE ON THE DISSOLUTION KINETICS OF BIOGENIC ARAGONITE IN SEAWATER

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ABSTRACT. Laboratory observations of aragonite dissolution in seawater, under temperature and pressure conditions that approximate the natural oceanic environment, indicate that

$$R = k'([CO_3^{2-}]_s - [CO_3^{2-}])^n$$

is an appropriate expression describing the dependence of dissolution rate on seawater saturation state, where R is aragonite dissolution rate in percent per day, $[CO_3^{2-}]_s$ is the carbonate ion concentration at saturation, and $[CO_3^{2-}]$ is the in-situ carbonate ion concentration. Under conditions in which the influence of surface alteration is minimized, plots of dissolution rate, R, versus $([CO_3^{2-}]_s - ([CO_3^{2-}])$ approach linearity. Consequently, in the absence of surface alteration effects, our results suggest that the reaction order, n, in the above expression should be equal to one. Use of single pteropod shells in extended experimental sequences indicates that progressive roughening of the shell surface by dissolution can substantially enhance shell dissolution rates. Surface alteration leads to variable values of the rate "constant", k′, in the expression above. For rate measurements obtained at increasing degrees of both undersaturation and shell roughness, the multiplicative factors k′ and $([CO_3^{2-}]_s - ([CO_3^{2-}])$ give rise to curvature in plots of rate versus $([CO_3^{2-}]_s - ([CO_3^{2-}])$. For models in which variations in k′ are not explicitly acknowledged, dissolution rates are generally described successfully with reaction orders (n) greater than one.

Our experiments, performed at variable pressure, were modeled using several realistic partial molar volume changes (ΔV) for aragonite dissolution in seawater. Our results indicate that the molar volume change for aragonite dissolution is within the bounds -37 cm^3/mole $\leq \Delta V \leq -39.5$ cm^3/mole.

INTRODUCTION

The calcium carbonate minerals calcite and aragonite are integral components of the oceanic carbon dioxide system. Both minerals are produced in the open ocean by several different taxa of planktonic organisms. Sediments resulting from the deposition of these biogenically-produced forms cover large areas of the ocean floor.

Atmospheric CO_2 levels have increased since the middle of the 19th century due to the input of anthropogenic CO_2, caused by the burning of fossil fuels for energy production. Atmospheric CO_2 is absorbed by the oceans and subsequently interacts with the mineral

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components of the oceanic CO_2 system. Because the dissolution of oceanic $CaCO_3$ sediments is a primary mechanism that neutralizes absorbed atmospheric CO_2, the investigation of $CaCO_3$ dissolution kinetics in seawater is a significant area of inquiry.

Due to their differing crystal structures, calcite and aragonite have dissimilar thermodynamic and chemical properties. In seawater, aragonite is more soluble (by an approximate factor of 1.5) than calcite (Morse, Mucci, and Millero, 1980). The greater solubility of aragonite in seawater causes predominantly aragonitic sediments to be confined to limited, shallow regions of the ocean.

Although aragonite is a minor component of marine carbonate sediments compared to calcite, Berner (1977) suggested that aragonite and calcite are produced by planktonic organisms in roughly equal amounts. In the same work, Berner postulated that equal production rates for aragonite and calcite could balance an independent model of the oceanic CO_2 system originally formulated by Broecker (1971). Berner's conjecture of approximately equal aragonite and calcite production rates has been supported by the work of Berner and Honjo (1981), Betzer and others (1984), and Almogi-Labin, Hemleben, and Deuser (1988).

Additional evidence for a significant impact of aragonite on the oceanic CO_2 system may be found in the work of Fiadeiro (1980), where he described a model of the alkalinity distribution in the Pacific Ocean. Fiadeiro indicated that an alkalinity source is necessary in the 2000 to 4000 m depth range of the Pacific. The prediction and demonstration of water column aragonite dissolution in the Pacific (Byrne and others, 1984) provided a possible alkalinity source in this depth region.

In addition to the potential importance of aragonite dissolution in the oceanic water column, the predominance of aragonite in shallow marine carbonate sediments means that shallow water neutralization of anthropogenic CO_2, where it occurs, should generally involve aragonite. For these reasons, our ongoing investigations of $CaCO_3$ dissolution characteristics (Byrne and others, 1984; Betzer and others, 1984; Acker and others, 1987) have focused on the behavior of aragonite, in the form of pteropod shells, under conditions representative of the oceanic environment.

The investigation of $CaCO_3$ dissolution in seawater requires quantification of the saturation state of seawater with respect to carbonate minerals. A common expression of seawater saturation state, widely used in previous research on calcite and aragonite dissolution kinetics, is the quantity Ω (Edmond and Gieskes, 1970) defined for aragonite as

$$\Omega = [Ca^{2+}][CO_3^{2-}]/K'_{spa} \quad (1)$$

In this expression, $[Ca^{2+}]$ and $[CO_3^{2-}]$ are the concentrations of calcium and carbonate ions in moles per kilogram of seawater. In a given parcel of seawater, K'_{spa} is equal to the total calcium ion concentration multi-

plied by the total carbonate ion concentration in solubility equilibrium with aragonite:

$$K'_{spa} = [Ca^{2+}][CO_3^{2-}]_s \tag{2}$$

When examining the saturation state of a parcel of seawater, the solubility product (K'_{spa}) is defined for ambient temperature, pressure, and salinity conditions. The calcium ion concentration for the parcel is calculated by a direct proportionality to salinity. Using the above equations, Ω can be directly expressed as:

$$\Omega = [CO_3^{2-}]/[CO_3^{2-}]_s \tag{3}$$

In previous investigations of the relationship between carbonate mineral dissolution rates and the saturation state of seawater, the following relationship has been usefully employed by a number of researchers (Morse, 1978; Morse, deKanel, and Harris, 1979; Keir, 1980; Byrne and others, 1984; Walter and Morse, 1985):

$$\text{Rate}_{\%} = k(1 - \Omega)^n = k\left(1 - \frac{[CO_3^{2-}]}{[CO_3^{2-}]_s}\right)^n \tag{4}$$

In the above expression, the rate constant k and exponent n are empirically derived, based upon observations of dissolution rate, R, versus seawater saturation state, expressed by Ω.

An alternative measure of seawater saturation state with respect to aragonite or calcite is the difference between the actual carbonate ion concentration and the carbonate ion concentration at saturation: $[CO_3^{2-}] - [CO_3^{2-}]_s$. This quantity was termed DELTA CO_3^{2-} by the GEOSECS expedition (Takahashi and others, 1980).

Lasaga (1981) noted that the difference between equilibrium (C_{eq}) and actual (C) ionic concentrations, that is, ($C_{eq} - C$), is an appropriate general measure of mineral dissolution kinetics. The form of such an expression specific to carbonate minerals is ($[CO_3^{2-}]_s - [CO_3^{2-}]$).

Acker and others (1987) provided quantitative descriptions of aragonite dissolution rates in seawater using the following rate equation:

$$\text{Rate}_{\%} = k'([CO_3^{2-}]_s - [CO_3^{2-}])^n \tag{5}$$

Eq (5) may be rewritten in a form that distinguishes it from eq 4:

$$\text{Rate}_{\%} = k'([CO_3^{2-}]_s - [CO_3^{2-}])^n = k'[CO_3^{2-}]_s^n\left(1 - \frac{[CO_3^{2-}]}{[CO_3^{2-}]_s}\right)^n \tag{6}$$

The presence of the quantity $[CO_3^{2-}]_s$ as a multiplicative factor for the rate constant k′ in eq (6) is a key difference between this expression and eq (4). Because the carbonate ion concentration at saturation varies substantially in the ocean, the predictions of the two rate eqs (4 and 5) under a variety of temperature and pressure conditions are clearly dissimilar.

Eqs (4) and (5) are equivalent when $[CO_3^{2-}]_s$ is constant. As $[CO_3^{2-}]_s$ is a function of temperature (T), salinity (S), and pressure (P), and laboratory experiments are commonly conducted under constant T, S, and P conditions, eq (4) has been employed successfully to describe aragonite dissolution kinetics in a number of studies (Morse, deKanel, and Harris 1979; Keir, 1980; Byrne and others, 1984; Walter and Morse, 1985). Each experimental protocol took place at 1 atm or (Byrne and others, 1984) at nearly constant elevated pressure. Although there are substantial differences in the rate constants (k) and exponents (n) obtained in previous studies, correlations between assumed K'_{spa} values and derived k and n values lead to dissolution rate predictions which are in relatively good agreement, considering the different types of aragonite used in each study. A comparison of the predictions derived from the above works is shown in table 1.

In this work we present results of a large number of at-sea and laboratory dissolution rate determinations. Our dissolution rate data at variable pressure and variable saturation state are examined in terms of the ion concentration difference $[CO_3^{2-}]_s - [CO_3^{2-}]$. Dissolution rate differences attributable to surface effects rather than exclusively solution chemistry are quite evident in our study and are consequently

TABLE 1

Comparison of the predictions of dissolution rate equations from Morse, deKanel, and Harris (1979), Keir (1980), Byrne and others (1984), and Walter and Morse (1985). Dissolution rates (R) are expressed as percent of shell mass dissolved per day. Calculation of $[CO_3^{2-}]_s$ in column 3 assumed 25°C, S = 35, and atmospheric pressure. For all cases $[Ca^{2+}] = 1.028 \times 10^{-2}$ mol/kg sw

Work	K'_{spa} ($\times 10^7$) mol^2 (kg sw)$^{-2}$	$[CO_3^{2-}]_s$($\times 10^5$) mol/kg sw	Rate equation
Morse, deKanel, and Harris (1979)	8.11	7.89	$R = 110(1 - \Omega)^{2.93}$
Keir (1980)	8.21	7.99	$R = 318(1 - \Omega)^{4.2}$
Byrne and others (1984)			
eq (1)	7.81	7.60	$R = 125(1 - \Omega)^{4.1}$
eq (2)	9.0	8.75	$R = 130(1 - \Omega)^{3.1}$
Walter and Morse (1985)	6.65	6.47	$R = 302(1 - \Omega)^{2.54}$

$[CO_3^{2-}]$ ($\times 10^5$)	Morse, deKanel, and Harris (1979)	Keir (1980)	Byrne and others (1984) eq 1	Byrne and others (1984) eq 2	Walter and Morse (1985)
6.144	1.3	0.7	0.77	0.87	0.05
5.820	2.2	1.3	1.4	1.4	0.35
5.497	3.3	2.4	2.4	2.2	1.2
5.174	4.8	4.0	3.8	3.2	5.1
4.850	6.7	6.3	5.6	4.6	9.0
4.527	9.0	9.5	7.8	6.3	14.2
4.204	11.8	13.8	10.6	8.6	21.0
3.880	15.1	19.5	14.1	11.3	29.5
3.557	19.0	26.7	18.4	14.7	39.7
3.233	23.5	36.0	23.2	18.8	51.9

described in some detail. Our characterizations of solution and surface influences on aragonite dissolution rates are used to assess the general nature of aragonite dissolution in the deep ocean.

EXPERIMENTAL METHODS

Our experiments were conducted by monitoring the pH changes that accompany $CaCO_3$ dissolution in isolated seawater samples. Measurements of pH changes were obtained spectrophotometrically, using the sulfonephthalein indicator dye phenol red (Robert-Baldo, Morris, and Byrne, 1985). Spectrophotometric measurements allow resolution of pH differences on the order of 0.0005 pH units (Byrne and Breland, 1989).

The spectrophotometric cell used in this study, which enabled experimentation under elevated pressures, consisted of a precision-bore glass cylinder and two plexiglas windows fitted with rubber O-rings. This arrangement allowed the windows to slide in response to pressure changes while isolating the seawater sample within the cylinder. The internal volume of our cell was approx 8 cm^3.

The seawater used in our at-sea analyses was obtained at depth and was usually undersaturated when returned to *in-situ* temperature and pressure conditions. However, in some cases, hydrochloric acid (HCl) was added to induce or increase the degree of undersaturation. The addition of HCl to available seawater was necessary to induce undersaturation for all laboratory experimentation. Laboratory alkalinity analyses were obtained using a single-step acid addition (Culberson, Pytkowicz, and Hawley, 1970) conducted in a manner such that the final pH of our purged acidified solutions was on the order of 4.5. The precision of our alkalinity analyses was $\pm$ 8 μ eq/kg. Measurements of pH were obtained using a Ross combination electrode calibrated on the NBS scale. Additionally, using TRIS buffer our electrodes were calibrated on the free hydrogen ion concentration scale. The initial total CO_2 (ΣCO_2) and carbonate alkalinity of our laboratory samples were calculated from initial pH, total alkalinity, and borate alkalinity. At-sea determinations of alkalinity and ΣCO_2 were obtained according to the methods of Feely and others (1984, 1988).

Prior to each experiment, undersaturated seawater containing phenol red ($\simeq 8 \times 10^{-6}$ molar), along with pteropod shells (mass range 10–43 mg; species *Cuvierina columnella*, *Cavolinia tridentata*, *Cavolinia gibbosa*, *Clio pyramidata*), was placed within the spectrophotometric cell. The cell was placed within a thermostatted outer pressure housing, which was closed with ¾-inch pressure-bearing plexiglas windows.

The apparatus was pressurized using a hand-operated hydraulic pump. Following pressurization, absorbance readings were taken with a Varian Instruments DMS-90 spectrophotometer. Absorbance measurements were made after an initial 10-min equilibration period, which followed the pressurization, and subsequently at 20-min intervals. The dissolution rate was calculated from the cumulative absorbance change

over a 1-hr period. For experiments conducted within the normal range of seawater saturation states, no systematic changes in dissolution rate were observed over this period of time.

The pressure housing containing the spectrophotometric cell was oscillated at approx 6 cycles/min between readings. The spectrophotometric cell and its contents were maintained at 5 ± 0.2°C during at-sea research. Lower working temperatures at-sea produced condensation on optical surfaces. Laboratory experiments were conducted at 2 ± 0.2°C.

Control experiments were performed to examine the possibility of dye interaction with the shell surface. In experiments conducted with saturated or slightly supersaturated seawater, no change in absorbance with time was observed, indicating negligible absorption of the dye on the shell surface. Also, in another set of experiments performed within the saturation range $30 \leq ([CO_3^{2-}]_s - [CO_3^{2-}]) \leq 36$ μ eq/kg, dissolution rates were observed at 3 dye concentrations: 4×10^{-6} M, 8×10^{-6} M (the normal dye concentration in experiments), and 16×10^{-6} M. These experiments (Acker, ms) provided no indication of dissolution rate inhibition due to dye interaction with the shell surface.

The effects of surface alteration on the dissolution rates of aragonitic shells were evaluated in a series of experiments performed over an extended period using a single set of robust pteropod shells. The dorsal halves of one *Cavolinia tridentata* and one *Cavolinia gibbosa* shell were used in a sequence of 10 experiments over a period of 9 days. Each experiment consisted of rate determinations at three successively elevated pressures. Saturation states at each elevated pressure were calculated using ΔpH measurements to monitor changing saturation state. Between experimental measurements, shells were stored in a large volume of the same seawater used in each rate determination. Thus, the shells were continuously exposed to undersaturated seawater. The entire length of exposure was approx 200 hrs.

Further insights into the consequences of pronounced surface alteration were gained through an additional set of dissolution rate determinations in which shells were stored under very highly undersaturated conditions. In this sequence of experiments which employed a single pair of fresh shells, undersaturation in the storage solution ($([CO_3^{2-}]_s - [CO_3^{2-}]) > 100$ μ eq/kg) was induced by addition of hydrochloric acid (HCl). The degree of undersaturation in this storage solution was considerably greater than any of our other test and storage solutions. This highly-corrosive solution was used for storage of shells between experiments over a five-day period.

CALCULATIONS

The absorbance changes observed in our experiments were used to calculate directly solution pH changes (ΔpH) attributable to $CaCO_3$(s) dissolution and subsequently changes in the total alkalinity (ΔTA) and total CO_2 ($\Delta\Sigma CO_2$) content of the seawater. A detailed description of the

calculation algorithm used to convert absorbance changes to aragonite dissolution rates appears in Acker and others (1987). Our calculations of $\Delta\Sigma CO_2$ in the seawater solution were subsequently used to calculate shell dissolution rates in percent per day, using the mass of the pteropod shells. The shells were rinsed briefly and dried subsequent to the experiments, and the mass of the shells was determined on a Perkin-Elmer microbalance.

Carbonate system characterization requires quantitative descriptions of carbonic and boric acid dissociation constants at in-situ pressure and temperature conditions. Variations in carbonic and boric acid dissociation constants with pressure were calculated using the following equation (Millero, 1979)

$$\ln (K_i^P/K_i^O) = -(\Delta V/RT)P + (0.5\ \Delta K/RT)P^2 \quad (7)$$

where ΔV and ΔK are the molar volume and molar compressibility (the change in the molar volume with pressure) for a reaction, R is the gas constant, and K_i^O and K_i^P are the dissociation constants at 1 atm total pressure (gauge pressure O) and at gauge pressure P. Values of ΔV, ΔK, and K_i^O for boric and carbonic acid equilibria were obtained using the equations of Millero (1979).

The pressure dependence of the aragonite solubility product, K'_{spa}, was calculated directly from the molar volume change (ΔV) for aragonite dissolution using the equation of Mucci, Millero, and Morse (1982):

$$\ln (K'^P_{spa}/K'^O_{spa}) = -(\Delta V/RT)P \quad (8)$$

Our calculations of K'^O_{spa} (the aragonite solubility product at 1 atm total pressure) utilized both the K'^O_{spc} descriptions of Ingle (1975) and the direct K'^O_{spa} measurements of Mucci (1983). Ingle's equation expressing K'^O_{spc} as a function of temperature and salinity was multiplied by a constant to provide K'^O_{spa} ($K'^O_{spa} = \rho \cdot K'^O_{spc}$). All 15 of our aragonite dissolution analyses were conducted at salinities within the range $S = 35 \pm 1.3$. The multiplicative constant used in our analyses was chosen to provide a close concordance with the K'^O_{spa} results of Mucci at $S = 35$. The final equation used to express the variation of K'^O_{spa} with S and T in our work is given as:

$$K'^O_{spa} = [-49.842 - 57.68\ S^{1/3} + 159.42 \log S - 1.096 \times 10^{-5} T^2] \cdot 10^{-7} \quad (9)$$

This equation yields a K'_{spa} value of 6.66×10^{-7} mol^2 (kg sw)$^{-2}$ at $S = 35$ and 25°C and 6.81×10^{-7} mol^2 (kg sw)$^{-2}$ at 5°C. The experimentally determined values of Morse, Mucci, and Millero (1980) and Mucci (1983) at $S = 35$ are 6.65 and 6.82×10^{-7} mol^2 (kg sw)$^{-2}$ at 25° and 5°C respectively.

The datasets generated consist of dissolution rate versus calculated initial values of $(1 - \Omega)$ and dissolution rate versus calculated initial

values of the quantity ($[CO_3^{2-}]_s - [CO_3^{2-}]$). These datasets were examined through non-linear least-squares analysis. The minimized residual sum-of-squares (RSS) values produced by analysis of the rate versus ($[CO_3^{2-}]_s - [CO_3^{2-}]$) datasets and the rate versus ($1 - \Omega$) datasets were compared to indicate the quality or "correctness" of fit to our data. The residual sum-of-squares function in our work was defined as

$$\text{RSS} = \Sigma_i ([\text{rate observed}]_i - [\text{rate predicted}]_i)^2 \quad (10)$$

Analysis of a single experimental dataset in Acker and others (1987) demonstrated that the relationship between aragonite dissolution rates and seawater saturation state, under variable pressure conditions, was better described by eq (5) than by eq (4). To investigate whether this conclusion is supported by a larger body of experimental data, fourteen additional experimental datasets, obtained in the laboratory and at sea, were examined by non-linear least squares analysis. The complete datasets used in our analyses can be found in the work of Acker (ms).

Acker and others (1987) presented arguments for the use of more negative values of the molar volume change for aragonite dissolution (ΔV) than had been determined by previous researchers. Consequently, three values of ΔV were used in our analyses: -31.3, -37.0, and -39.5 cm^3/mol. The initial value of ΔV used in the calculations, -31.3 cm^3/mol, is an average of three values obtained in equilibrium measurements (Hawley and Pytkowicz, 1969; Ingle, 1975; and Cooke and Kepkay, 1980). In contrast, Acker and others (1987) determined a best-fit for their rate versus ($[CO_3^{2-}]_s - [CO_3^{2-}]$) results using $\Delta V = -36.5$ cm^3/mol. Subsequent analysis of the same dataset, using a slightly revised calculation algorithm, yielded a new best estimate for the aragonite dissolution ΔV equal to -37.0 cm^3/mol. In addition, a third "theoretical" value of ΔV was used. Our theoretical estimate was based on the molar volume change for calcite dissolution (-42.3 cm^3/mol (Ingle, 1975) or -41.2 cm^3/mol (Sayles, 1985) and the theoretical 2.8 cm^3/mol difference between calcite and aragonite molar volumes. The more negative of the two estimates, -39.5 cm^3/mol, was used in the analysis of our fifteen experimental datasets.

RESULTS AND DISCUSSION

In thirteen of fifteen cases, eq (5) provided better fits to our rate data than eq (4). This conclusion was obtained using each of the three values of ΔV. In twelve of fifteen experiments, the residual sum of squares (RSS) values obtained in data-fits using eq (5) with $\Delta V = -39.5$ cm^3/mol were less than 84 percent of RSS results obtained using eq (4). In general, the most distinct RSS differences were obtained in experiments that included the widest possible range in pressure (and $[CO_3^{2-}]_s$). Consequently, these results indicate that for variable pressure conditions, aragonite dissolution rates are more closely related to the saturation index ($[CO_3^{2-}]_s - [CO_3^{2-}]$) than ($1 - \Omega$). This result supports the conclusion that the relationship between seawater saturation state and

aragonite dissolution rates is best expressed using eq (5) when rates are determined under variable $[CO_3^{2-}]_s$ conditions (Acker and others, 1987).

In ten of 15 cases, our analyses demonstrated minimized or decreasing RSS values for $\Delta V \leq -37.0$ cm^3/mol. This observation supports the use of ΔV values more negative than those obtained through previous equilibrium observations (Hawley and Pytkowicz, 1969; Ingle, 1975; Cooke and Kepkay, 1980). Based on the aragonite K'_{spa} characterizations of Morse, Mucci, and Millero (1980), we suspect that, for equilibrium determinations, accurate ΔV measurements may require lengthy equilibration periods.

Our best-fit estimates for the exponent (n) in eq (5) were generally lower than the values obtained in previous works using eq (4) (see table 1). Figure 1 shows best-fit values of n for all 15 datasets, obtained using eq (5) and each of our ΔV choices. For the majority of our datasets, the exponent is less than 1.5. In addition, it appears that increasingly negative ΔV values cause the value of n to approach 1.0 in several of the datasets. The average values obtained for n in our fifteen analyses (at $\Delta V = -31.3$, -37.0, and -39.5 cm^3/mol) are 1.41, 1.36, and 1.35. (Without dataset 9, the exponential values are 1.36, 1.27, and 1.22, respectively).

Since eq (4) has been appropriately used in previous studies (at constant pressure), the lower values of n obtained in the present work

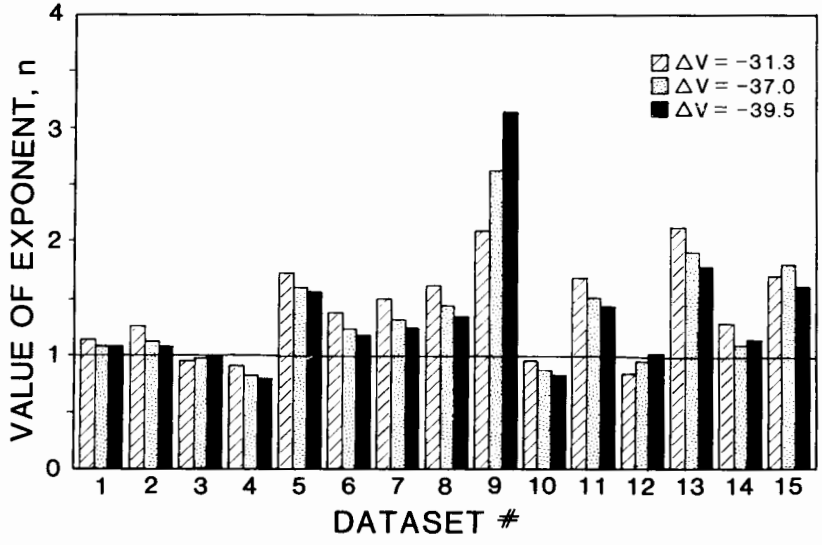


Fig. 1. Values of the exponent, n, in the eq $R = k'([CO_3^{2-}]_s - [CO_3^{2-}])^n$, generated by non-linear least square analysis of fifteen datasets. Note that the form of this equation requires that $R = 0$ at $[CO_3^{2-}]_s = [CO_3^{2-}]$ ($R = 0$ at saturation).

should not be attributed to differences in the data fitting procedures used in previous works. We will subsequently present arguments contending that differences in the curvature of rate versus saturation state plots are a systematic feature of aragonite dissolution measurements attributable to surface alteration effects.

Influence of surface alteration.—During the course of experimentation using single shells, it became evident that for approximately equal values of ($[CO_3^{2-}]_s - [CO_3^{2-}]$), dissolution rates measured near the end of a series of experiments were elevated compared to dissolution rates determined initially. The effect becomes more evident the longer a shell is exposed to undersaturated conditions and is more extreme at higher dissolution rates. These observations suggest that surface-specific processes affect dissolution rates as removal of the shell surface progresses.

In the series of 10 experiments performed with a single set of robust shells, the trend of increasing dissolution rates with increased time of exposure was evident. To elucidate this trend, the ten experiments were subdivided into three groups: determinations performed on the first 3 days, the second 2 days, and the final 4 days of the 9-day sequence. Figure 2A shows a clearly increasing trend in dissolution rates with time. Figure 2B shows least-squares curves fitted to each of the three experimental data groups in figure 2A. Elevated dissolution rates and increasing exponential curvature appeared to be important general features of our experiments in which shells were continuously exposed to undersaturated seawater.

When shells were stored between experiments in a strongly acidified seawater medium, in which the degree of undersaturation was considerably greater than any of our other test or storage solutions, unusual results were obtained. Experiments performed over a 5-day period with a single set of shells and this highly-corrosive storage solution ($([CO_3^{2-}]_s - [CO_3^{2-}]) > 100\ \mu$ eq/kg) provided the results shown in figure 3. For comparable saturation states (note points where $([CO_3^{2-}]_s - [CO_3^{2-}] \simeq 25\ \mu$ eq/kg) dissolution rates obtained near the end of the 5-day period considerably exceeded rates obtained at the beginning of the 5-day period. Additionally, in experiments performed on days 3, 4, and 5, the rate observed at the lowest pressure and minimum degree of undersaturation exceeded the rate observed at our second observation point, which was obtained under more undersaturated conditions. As this sequence progressed, it was also noted that the absorbance change observed in the first 20 min of a rate determination was markedly greater than the change observed over the rest of the hour.

We believe that the above observations result from dissolution-induced alteration of the shell surface. Scanning electron microscopy of shells exposed to corrosive seawater (Adelseck and Berger, 1975; Berner, Berner, and Keir, 1976; Berner, 1979; Byrne and others, 1984) demonstrates progressive transformation of smooth, undissolved shells to ragged, microcrystalline topography: Comparable results have been

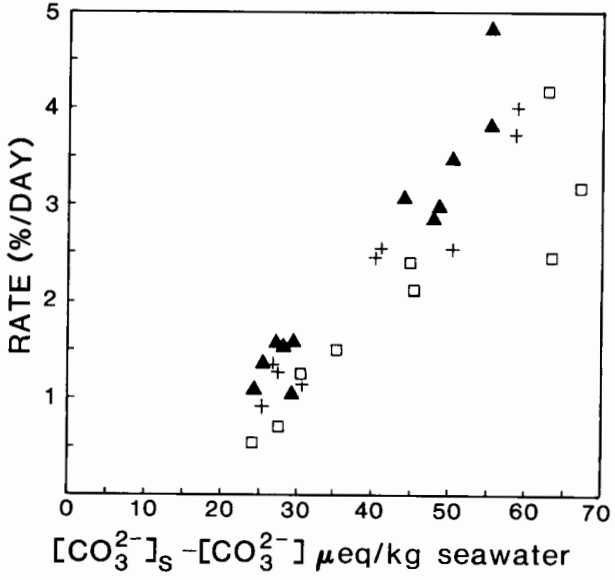
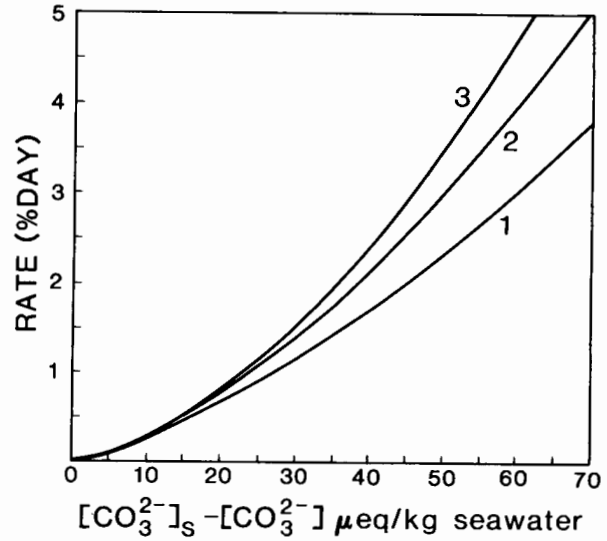


Fig. 2(A) Dissolution rate data plotted as a function of ($[CO_3^{2-}]_s - [CO_3^{2-}]$) from a 9 day, 10 experiment sequence. Each experiment consisted of rate determinations at three successively increased pressures. The data are divided into three groups: □ designates data from the first 3 experiments; + designates data from the subsequent 3 experiments; ▲ designates data from the final 4 experiments. The mass of the two shells used in these experiments totaled 13.50 mg.



(B) Curves fit to the three data groups shown in (A). Each curve was generated by least-squares analysis. Curve 1 was generated by fitting data from the first 3 experiments. Curve 2 is a fit to data from the next 3 experiments. Curve 3 was generated by fitting data from the final four experiments.

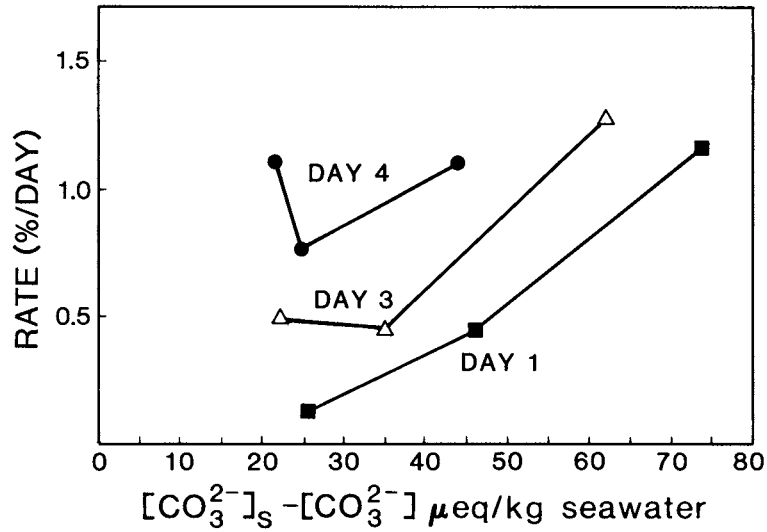


Fig. 3. Experimental sequence during which shells were stored in highly-undersaturated seawater between experiments, showing strong effects of advancing surface dissolution. In each experiment, dissolution rates were determined at low, intermediate, and high pressure. Higher pressures caused the seawater to become increasingly undersaturated. Data from experiments conducted on day 2 and day 5, which also conformed to the observed trend of increasing dissolution rates with time, were omitted for clarity. The mass of the shell used in these experiments was 33.51 mg.

obtained for experimentally dissolved foraminiferal tests (Bé, Morse, and Harrison, 1975).

Calcium carbonate dissolution in the near-equilibrium regime characteristic of seawater has been described (Berner and Morse, 1974) as being dependent on the number of high-energy surface sites where ion detachment is favored. Increased shell roughness increases the specific surface areas of the shells and may also allow the formation of a greater number of high-energy sites. Walter and Morse (1985) demonstrated that the absolute dissolution rates of various carbonates (at a given grain size and saturation state) are controlled by the grain microstructure. Accordingly, increases in the surface roughness of a single dissolving shell can be expected to influence the dissolution rate of the shell. The time-dependent dissolution seen in figure 2 can be attributed to progressive increases in surface area and number of high-energy sites on progressively-dissolving shells. The results shown in figure 3, especially the determinations performed on day 4, suggest that for a given mass of aragonitic shells, surface area and number of high-energy sites are significantly dependent on dissolution rate. Dissolution in highly-undersaturated storage solutions apparently produces larger increases in molar surface area (cm^2/mol $CaCO_3$) and greater surface-site densities (number of sites/mol $CaCO_3$) than are produced by an equivalent extent of dissolution under more saturated storage conditions. In a similar manner, dissolution in more saturated environ-

ments induces smoothing of shell surfaces and a reduction in the number of high-energy ion detachment sites per mole of aragonite. The unusual behavior illustrated in figure 3 is believed to result from ephemeral changes in shell surface-state. Therefore, alteration of the shell surface, as it is transferred between storage and test solutions, provides a plausible mechanism for the observed dependency of dissolution rates on factors other than solution saturation-state.

In addition to the influence of molar surface area (cm^2/mol) on dissolution rate measurements, mineral solubilities are functionally dependent on the molar surface area of a mineral (Stumm and Morgan, 1981). The dependence of solubility on molar surface area becomes evident for measurements involving very small particles (edge lengths less than 0.1 μm), or equivalently, for surfaces having very small radii of curvature (see Lewis and Randall, 1961). SEM observations of partially-dissolved shells (Adelseck and Berger, 1975; Byrne and others, 1984; Acker, ms) reveal the development of microscopic, stalactitic aragonite needles on the shell surface. The tips and edges of these needles with estimated radii of curvature on the order of 0.05 μm can be expected to influence mineral solubility.

It therefore appears that the fundamental relationship between seawater saturation state and the dissolution rate of aragonitic shells can be significantly modified by the influence of shell surface alterations. When our experimental conditions limited the extent of surface alteration, the relationship between dissolution rate and saturation state more nearly approached linearity. In a number of our experiments employing large, fresh pteropod shells, small seawater volumes, and short overall dissolution times, surface roughening was minimized, and we noted an approximately linear relationship between dissolution rate and $([CO_3^{2-}]_s - [CO_3^{2-}])$. Such observations lead us to propose that, in the absence of surface alterations, the relationship between rate and $([CO_3^{2-}]_s - [CO_3^{2-}])$ should, in fact, be linear.

ARAGONITE DISSOLUTION KINETICS—CONCEPTUAL MODELS

As a means of illustrating our hypotheses regarding the influences of seawater saturation state and surface alteration on the dissolution of aragonite, figure 4 provides the results of model experiments, in which the various factors involved in aragonite dissolution are separately examined. Four cases will be described, corresponding to figure 4A through D.

1. In the first model experiment, aragonitic materials are stored in seawater until equilibrium is achieved. Subsequently, instantaneous determinations of aragonite dissolution are made for several degrees of undersaturation. In this "instantaneous" experiment, surface chemical changes are insignificant. The result which we would expect in such an experiment (fig. 4A) is a linear relationship between R and $([CO_3^{2-}]_s - [CO_3^{2-}])$.

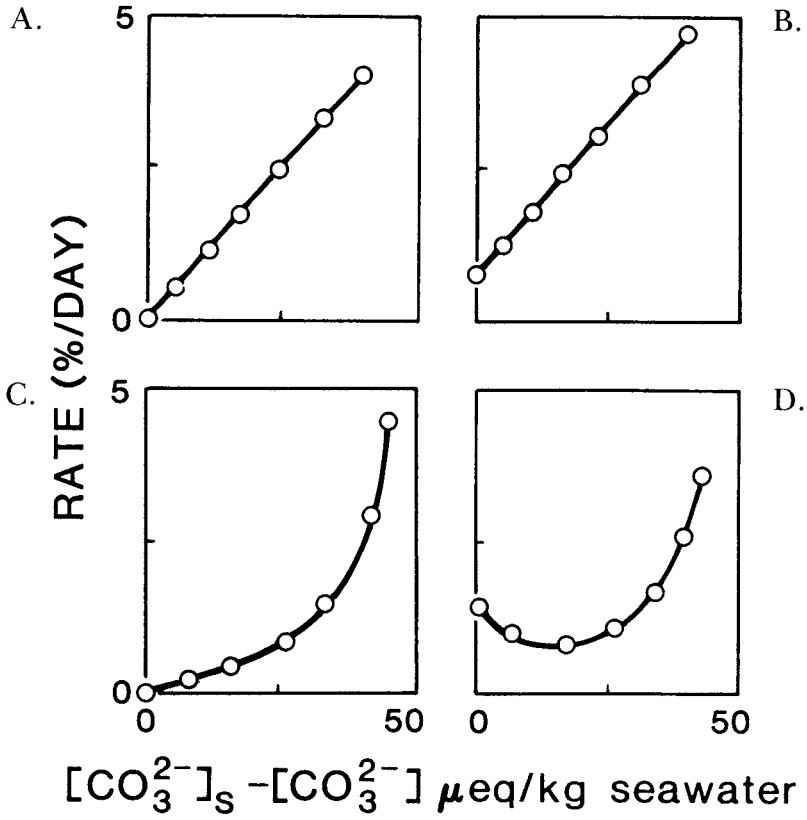


Fig. 4(A) Model experiment in which aragonite dissolution rates are determined instantaneously over a range of saturation states for a shell previously stored at saturation. In the absence of surface chemistry variation we expect that a linear relationship would be observed between dissolution rate and ($[CO_3^{2-}]_s - [CO_3^{2-}]$).

(B) Model experiment in which the dissolution kinetics of kinetics of aragonitic material, previously stored in undersaturated seawater, are determined instantaneously over a range of saturation conditions.

(C) Model experiment illustrating steady-state dissolution at discrete levels of undersaturation beginning at ($[CO_3^{2-}]_s = [CO_3^{2-}]$). Nonlinear dissolution rates versus ($[CO_3^{2-}]_s - [CO_3^{2-}]$) are expected, due to surface area enhancement with increasing dissolution rate and extent of dissolution.

(D) Idealized experiment in which a shell dissolves under nonsteady-state conditions. In this experiment the shell has been stored in a highly undersaturated solution. The initial rate is elevated due to extreme surface roughening. Tendency toward equilibrium initially slows the dissolution rate. The dissolution rate is subsequently increased at increasing degrees of undersaturation.

2. In a second model experiment, the materials used in the first experiment are exposed to highly-undersaturated seawater for an extended period of time. Following this exposure, dissolution rates are again determined instantaneously for several degrees of undersaturation. In principle, with sufficient surface roughness, a solubility product

increase may be observed so that dissolution will occur when ($[CO_3^{2-}]_s - [CO_3^{2-}]$) is calculated as zero. (The type of behavior illustrated in figure 4B was, in fact, observed in several experiments (Acker, ms)). Following exposure to highly-undersaturated seawater, we expect that instantaneous determinations of rate versus ($[CO_3^{2-}]_s - [CO_3^{2-}]$) would produce the observations depicted in figure 4B.

3. In a third model experiment, aragonitic materials are again stored in seawater until solubility equilibrium is achieved. Subsequently, dissolution rates are determined for a series of saturation states, in such a manner as to obtain steady-state dissolution rates at each point. It should be expected that this experimental procedure will generate continual increases in aragonite molar surface area. Consequently, the multiplicative factor k′ (eq 5) will steadily increase with increasingly undersaturated conditions, and a plot of R versus ($[CO_3^{2-}]_s - [CO_3^{2-}]$) will exhibit curvature similar to that depicted in figure 4C.

4. In the fourth model experiment, aragonitic materials are dissolved relatively slowly but are not allowed to approach steady-state dissolution. Storage in highly-undersaturated seawater prior to experimentation induces an initially elevated dissolution rate. The subsequent rate determination intervals are long enough to allow surface alteration but insufficient to allow the surface to reach a steady-state condition. This procedure causes the shell surface to be smoothed initially, and then, at higher degrees of undersaturation, roughened. The rate versus saturation state curve expected in this experiment is shown in figure 4D.

Although total surface area and reactive surface area of biogenic carbonates are not necessarily identical (Walter and Morse, 1985), expression of dissolution rate measurements in terms of area rather than mass can, in principal, eliminate much of the curvature observed in "pH-stat" and other types of dissolution experiments. Previous measurements have, however, only rarely been performed in a manner which is likely to exhibit linear rate versus saturation state behavior. In nearly every case, surface area measurements have been indicative of initial areas. Previous measurements have not quantitatively accounted for the continual surface area variations which occur in the course of each experiment. In order for dissolution rate measurements expressed in terms of area to be truly distinct from measurements expressed on a per gram basis, surface area determinations would have to be performed continuously throughout the course of the rate measurements. If such measurements could be performed successfully, we would expect to observe an approximately linear relationship between dissolution rate and saturation state.

Oceanic aragonite dissolution.—Aragonite dissolution in oceanic sediments takes place over long periods of time under essentially steady-state conditions. As such, the "pH-stat" method, which incorporates the influence of solution chemistry on dissolution rate behavior as well as the influence of steady-state surface chemistry on dissolution

behavior, is ideally suited to descriptions of aragonite dissolution kinetics at the sediment/seawater interface. The dissolution model of Walter and Morse (1985) is based upon solubility data (Morse, Mucci, and Millero, 1980; Mucci, 1983) appropriate to thermodynamic equilibrium. Consequently, we believe that the model of Walter and Morse (1985) is well-suited to descriptions of the progression of aragonite dissolution rates from near-saturation to the considerable degrees of undersaturation encountered in the deep ocean. However, we also contend that the descriptions of Walter and Morse (1985), obtained at 1 atm total pressure, should be modified better to account for the influence of pressure on dissolution kinetics. Our work indicates that, for constant Ω, the ratio of dissolution rates obtained at pressure P and at 1 atm total pressure should be given by

$$R_P/R_O = \left(\frac{[CO_3^{2-}]_{s,P}}{[CO_3^{2-}]_{s,O}}\right)^n \tag{11}$$

where $[CO_3^{2-}]_{s,P}$ and $[CO_3^{2-}]_{s,O}$ are, for a given parcel of seawater, the saturation concentrations at pressure P and at 1 atm. Our work indicates that $n \geq 1$. Consequently, aragonite dissolution rates in the deep ocean will be significantly elevated (that is by a factor $\geq [CO_3^{2-}]_{s,P}/[CO_3^{2-}]_{s,O}$) compared to the rate versus Ω predictions of Walter and Morse (1985), shown in table 1. Further, since our results indicate that -37 cm^3/mol $\geq \Delta V \geq -39$ cm^3/mol for aragonite dissolution in seawater (eq 8), aragonite dissolution may commence at shallower depths than would be deduced from previous ΔV results (Hawley and Pytkowicz, 1969; Ingle, 1975; Cooke and Kepkay, 1980) obtained for aragonite.

Our dissolution rate measurements, obtained in the laboratory and at sea, indicate that even for the exceptionally large shells used in our experiments, dissolution rates appropriate to relatively shallow depths in the North Pacific Ocean are on the order of 3 percent per day. Our research demonstrated that, for two shells of similar dimensions, the shell that was three times less massive (due to shell thickness) had a corresponding rate constant k′ nearly ten times greater than k′ for the more massive shell. Had our experiments been conducted with much smaller, but highly abundant shells (such as *Limacina inflata* or *Limacina helicina*), we would expect that our modeled dissolution rates appropriate to the North Pacific would be elevated to the degree that complete dissolution for small, slowly-sinking shells would be predicted for this water column.

The multi-faceted character of aragonite dissolution depicted in this and previous works may serve to reaffirm the suspicion (Broecker, 1977) that the surfaces of marine carbonate particles "lead a life of their own." In view of the large number of factors that influence aragonite dissolution kinetics in the ocean (solution chemistry, surface chemistry, organic and inorganic inhibitors, et cetera), it appears that laboratory examinations of aragonite dissolution appropriate to the natural envi-

ronment should very strongly emphasize close simulation of natural conditions. We suggest that "pH-stat" experiments conducted under in-situ (high pressure) conditions could significantly improve aragonite dissolution descriptions appropriate to sea-floor sediments. In addition, the substantial complexities inherent in investigations of water column aragonite dissolution should, in future work, be addressed through methodologies that account for the ever-changing surface chemistries of aragonite particles during transit of the deep ocean.

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