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DISSOLUTION KINETICS OF CALCIUM CARBONATE IN SEA WATER: II. A KINETIC ORIGIN FOR THE LYSOCLINE

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ABSTRACT. Rates of dissolution for reagent grade calcite and carbonate-rich deep sea sediment have been determined by steady state disequilibrium experiments. The results indicate an abrupt change in dissolution rate at a ΔpH of 0.14 to 0.16 which is independent of P_{CO_2}. This is in agreement with the undersaturation at which a sudden increase in rate of dissolution of polished calcite spheres suspended in the Pacific Ocean was found by Peterson (1966). It is also in general agreement with the level at which a marked change occurs in the percent carbonate removed by dissolution in sediment core tops from the Pacific. These results suggest that the sharp change in dissolution rate represents a critical value of undersaturation in sea water for a change of mechanism in surface-controlled dissolution.

INTRODUCTION

Calcium carbonate of biogenic origin is a major component of open ocean sediments in the bathypelagic zone (1000-4000 m). Below this zone carbonate content decreases with depth due to dissolution. The region where the carbonate content of the sediment drops to less than a few percent is known as the compensation depth. This region represents a level of kinetic equilibrium in which the rate of carbonate supply equals the dissolution rate. Berger (1968) has introduced the term "lysocline" to define a zone, on the order of 1000 m above the compensation depth, where the effects of dissolution of calcitic foraminiferal tests in the sediments become readily apparent. This zone does not correspond to the saturation level which can be higher by up to 4000 m but generally occurs near the lower level of the bathypelagic zone.

The experiments of Peterson (1966) and Berger (1967) dramatically demonstrate that the lysocline is a region where the rate of dissolution with depth radically increases. Figure 1 shows a summary of these results. There is an excellent correlation between the depth at which the calcite spheres start to dissolve at an increasing rate and where the amount of carbonate starts to diminish significantly. However, the results from the suspended foraminiferal sediment show a sharp break at a lower level. The validity of the results obtained from the calcite spheres, as a good test for natural carbonate dissolution rates, is enhanced by the observation that at the lysoclinal level Berger found the dissolution rate for both untreated Foraminifera and those boiled in H_2O_2 was the same. This strongly implies that down to at least 4000 m level the natural organic matrix on the Foraminifera is not a primary control on the dissolution rate. Below the lysocline, Peterson's data show an increasing scatter with depth. Consequently it is possible that the lack of correlation found in Berger's curve may be due to the small number (1) of samples taken in the critical region between 3800 and 5000 m.

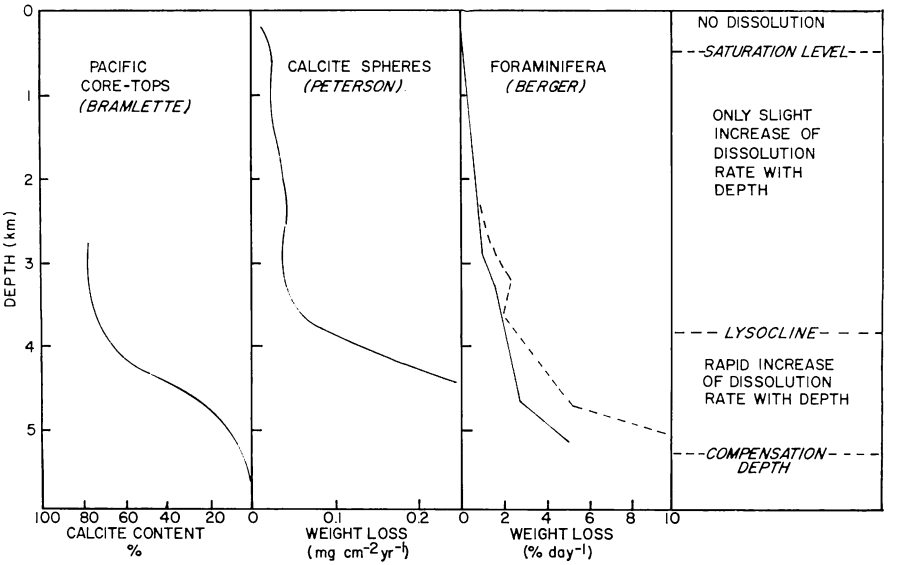

Fig. 1. Calcium carbonate dissolution in the Central Pacific after the general form of Berger (1970).

CARBONATE CONTENT OF SEDIMENTS

Heath and Culberson (1970) have shown that the rate of dissolution divided by the rate of supply, which is equivalent to percent original carbonate dissolved, is a better indicator of dissolution than weight percent carbonate. For a constant rate of supply their method often yields a near linear increase in rate of solution with depth *below the lysocline.* Three relations that are calculated here are: grams carbonate per gram insoluble sediment, grams carbonate lost per gram insoluble deposited, and percent of originally deposited carbonate dissolved.

If the rate of supply and the original deposited ratio of carbonate to insoluble component over an area of varying depth are constant, a calculation of relative rate of carbonate dissolution with depth can be made.

Let W = g $CaCO_3$/g sediment
$1\text{-}W$ = g insoluble/g sediment
W_o = original value
W_d = value at depth d
F = g $CaCO_3$/g insoluble
L = g $CaCO_3$ dissolved/g insoluble deposited
D = percent of $CaCO_3$ dissolved

$$F = \frac{1\text{-}W}{W} \tag{1}$$

$$L_d = F_o - F_d = \frac{W_o - W_d}{(1\text{-}W_o)(1\text{-}W_d)} \tag{2}$$

$$D_d = \frac{L_d}{F_o} \cdot 100 = \frac{1 - \frac{W_d}{W_o}}{1 - W_d} \cdot 100 \qquad (3)$$

Figure 2 shows that the three methods all show an abrupt change at about 3800 m using Bramlette's (1961) data for all Pacific core tops. The abrupt change is believed to represent the lysocline.

Berger (1971) has made a calculation similar to D_d. In applying this to sediments from different regions it was found that in equatorial regions of high productivity the lysocline is much more diffuse. He has suggested that this may be due in part to dissolution at shallow depths caused by a higher CO_2 production within the sediment. It may also be due in part to the rapid burial of calcareous tests and consequent protection from overlying undersaturated water.

EXPERIMENTAL METHOD

Rates of $CaCO_3$ dissolution in sea water were determined in the laboratory at constant undersaturation using a pH-stat technique.[1] This method is based on the reaction:

$$CaCO_3 + 2H^+ \rightarrow Ca^{++} + H_2O + CO_2 \text{ gas} \qquad (4)$$

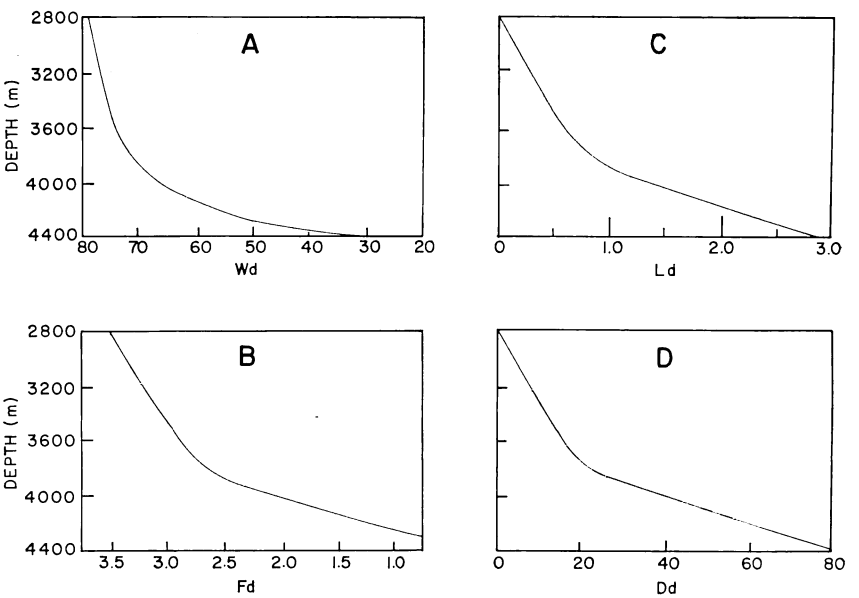

Fig. 2. A. Weight percent $CaCO_3$ versus depth; B. Grams $CaCO_3$ per gram of insoluble versus depth; C. Grams $CaCO_3$ dissolved per gram of insoluble deposited versus depth; D. Percent $CaCO_3$ dissolved versus depth. The lysocline is very apparent in B, C, and D at about 3800 m. Based on data of Bramlette (1961).

[1]A detailed discussion of this technique developed and utilized during more than 300 runs will be discussed in a subsequent paper.

The partial pressure of carbon dioxide is held constant by bubbling CO_2-air mixtures (P_{CO_2} = 0.3 and 0.03 atm) continuously through the solution during reaction. The concentration of calcium, $m_{Ca^{++}}$ is held constant by dissolving negligibly small amounts of $CaCO_3$ relative to the amount of Ca^{++} originally present in the sea water. The activity of hydrogen ions and temperature are held constant using a pH-stat and a thermostat respectively (see below). In this way the ion product $m_{Ca^{++}}\, m_{CO_3^{--}}$ during dissolution is held constant. This can be seen from the expression:

$$m_{Ca^{++}}\, m_{CO_3^{--}} = \frac{m_{Ca^{++}}\, K\, P_{CO_2}}{a^2_{H^+}} \tag{5}$$

where K = the equilibrium constant for the reaction:

$$CO_2 \text{ gas} + H_2O \rightleftarrows 2H^+ + CO_3^{--}$$

a_{H^+} = activity of hydrogen ion

Also since pH is held constant, the parameter, ΔpH (Berner and Wilde, 1972) is also held constant. It is defined as:

$$\Delta pH = \overline{pH} - pH \tag{6}$$

where $\overline{pH}$ = pH for calcite saturation at the same P_{CO_2} and $m_{Ca^{++}}$ as employed in the experiment.

pH = constantly maintained value.

Experimentally, the pH is held constant using a controller in conjunction with a pH meter. Whenever the pH reaches a preset value the controller activates an automatic syringe that feeds hydrochloric acid into the reaction chamber. Both the pH and the volume of acid added are simultaneously recorded as a function of time on a dual pen recorder. The volume of added acid is used as a measure of the degree of dissolution via the stoichiometry of reaction (4). Under the conditions that these experiments were carried out, this method was capable of maintaining the pH within $\pm$ 0.002 units and measuring reaction rates as slow as 0.10 percent per hour. The stirring rate was the same for all runs and fast enough to keep the sample in suspension. A suspended magnetic stirring bar was used to prevent grinding. Temperature was maintained by a constant temperature bath at 25.0 $\pm$ 0.1°C. A constant amount of calcite (225 mg) or sediment (400 mg) and a constant volume of sea water (300 ml) were used within each series of runs. Varying the amount of carbonate has subsequently shown that rates, when normalized for surface area, are independent of the amount used.

Filtered ($< 0.45\ \mu$m) Long Island sea water of 30‰ salinity was used in all runs. The calcite (Fisher low alkali, reagent grade) consisted of rhombs ranging in diameter from 1 to 20 microns. The carbonate sediment (V17-106SBT) came from a biologic trawl at a depth of 3299 to 3358 m at 36° 06′ N, 45° 56′ W. Weight percent carbonate in the sediment was determined by dissolving a small amount of sediment in HCl and then analyzing calcium by atomic absorption spectrophotometry. It

was found to contain 86 weight percent $CaCO_3$. On one occasion the carbonate was dissolved from the sediment using 2 normal acetic acid and the remaining insoluble residue soaked in sea water to remove adsorbed hydrogen ions. This residue was then run as a background blank to determine if the noncarbonate fraction of the sediment was contributing to the reaction rate. No reaction was found.

RESULTS

The results of the dissolution experiments can be found in table 1 and figure 3. Note the presence of a sudden change in dissolution rate, independent of P_{CO_2}, at $\Delta pH = 0.14$ to 0.16. This sudden change has been discovered in a large number of additional runs, not reported here, using artificial sea water, $CaCl_2$–NaCl solutions, and natural and artificial $CaCO_3$. All rates shown in table 1 and figure 3 represent initial reaction rates obtained by dissolving only a small percentage (< 2 percent) of

TABLE 1

ΔpH*	Rate (mg/cm²/yr)	ΔpH**	Rate (%/day)
0.09	0.9	0.06	3.5
0.14	3.2	0.11	5.4
0.17	13.7	0.14	7.8
0.19	22.7	0.15	11.3
0.24	54.3	0.16	15.3
		0.18	24.1
		0.19	34.0
		0.20	46.8

* Reagent calcite powder run at $P_{CO_2} = 10^{-2.5}$ in sea water.
** Sediment run at $P_{CO_2} = 10^{-3.5}$ in sea water.

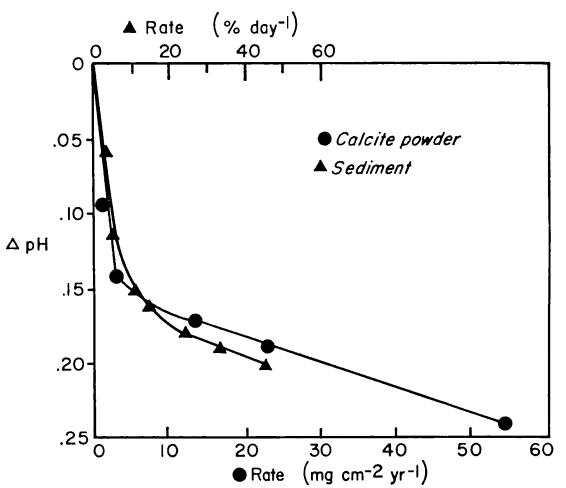

Fig. 3. The rate of reaction for the calcium carbonate rich sediment and the calcite powder as a function of ΔpH. The calcite powder was dissolved at $P_{CO_2} = 10^{-2.5}$ and the sediment at $P_{CO_2} = 10^{-3.5}$.

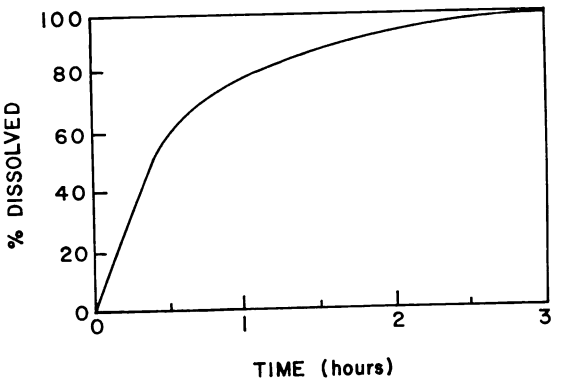

Fig. 4. Percent dissolved versus time. The data for this plot was collected at a $\Delta pH = 3.0$ and matches the computer predicted curve for the grain size distribution in the sample.

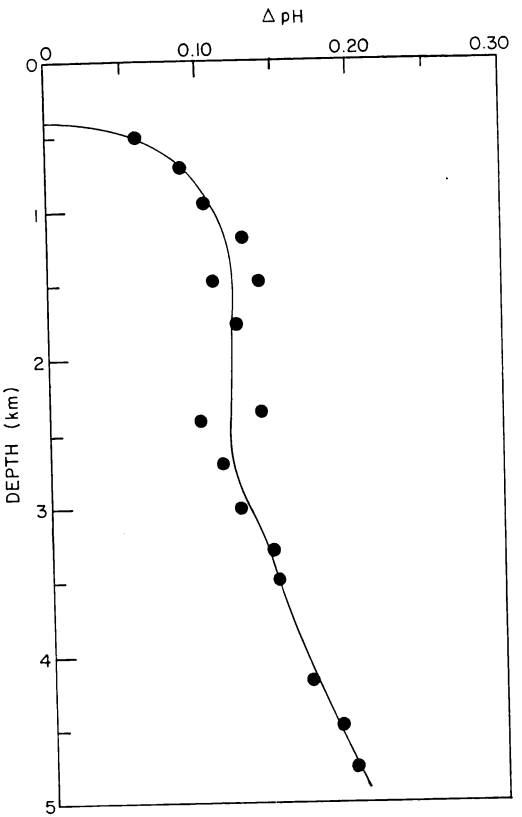

Fig. 5. ΔpH versus depth based on the calculations of Berner and Wilde (1972), for the site of the Petersen sphere experiment.

a given sample. The validity of this method is illustrated in figure 4 where it is shown that a close to constant reaction rate is maintained until over 50 percent of the material has been dissolved. The exact shape of the curve is dependent on the particle size distribution for each sample.

Berner and Wilde (1972) have calculated ΔpH values for sea water at the same site of the Peterson (1966) and Berger (1967) dissolution experiments. Their results are shown in figure 5. From figures 3 and 5 and Peterson's and Berger's data, figure 6 has been constructed. This figure demonstrates that our laboratory experiments expressed in terms of equivalent depth are definitely comparable with and give similar results to those obtained in the ocean experiments. Results from both investigations are in general agreement with the level at which the lysocline is found in this area of the Pacific (Parker and Berger, 1971) and for the "average Pacific lysocline" based on Bramlette's (1961) data shown in figure 2. All these results indicate a pronounced increase in the rate of dissolution with increasing depth at a $\Delta pH = 0.14$ to 0.16.

The results also indicate for a constant ΔpH a significantly faster rate of dissolution for the experiments carried out in the laboratory. The reason for this is that a much finer material was used in the laboratory experiments. It is obvious that this should raise the rate, as expressed in percent per day, because of a larger specific surface area. It is less obvious, however, why the laboratory rates are still higher after normalizing for surface area. One reason for this lies in the nature of the dissolution process. As will be demonstrated later, dissolution in both Peterson's and our experiments was controlled by the rate of detachment of ions from the calcite surface. Since surface reactions are strongly dependent upon the nature and composition (in terms of adsorbed ions) of crystal surfaces, it is quite likely that minor differences in surface configuration and chemistry can account for at least part of the difference in rates. In addition our experiments were conducted at 25°C whereas Peterson's results (below 1000 m) are for about 2°C. This factor, alone, should cause the laboratory rates to be faster.

ORIGIN OF THE LYSOCLINE

The lysocline has been attributed to two possible origins. Edmond (1971) proposed that the sharp increase in dissolution observed by Peterson (1966) was due to an increase in the water velocity and not attributable to carbonate chemistry in the water column since there was no sharp change with depth in the degree of undersaturation Ω where $\Omega = (m_{Ca^{++}}\ m_{CO_3})/(\bar{m}_{Ca^{++}}\ \bar{m}_{CO_3^{--}}$ at calcite saturation). The other possible origin was put forth by Peterson (1966) in the original paper on the calcite spheres. There he stated "there seems no assurance that the rate of solution will be related in a simple way to the degree of undersaturation as the departure becomes small. Masking and coating and exchanging molecules and ions may be important rate determining effects under these conditions."

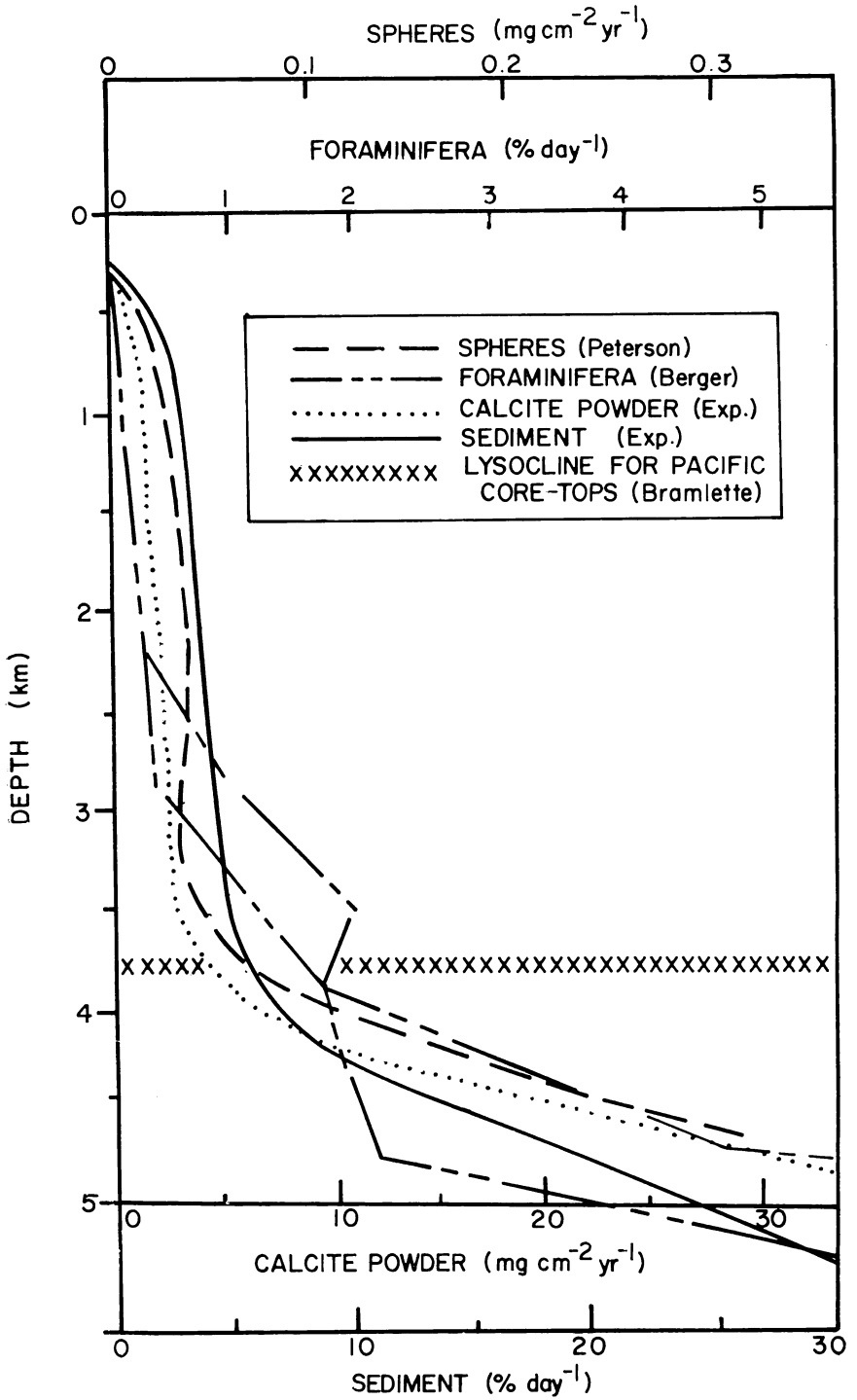

Fig. 6. Plot of the Petersen (1966), Berger (1967) results versus depth and our data as a function of equivalent depth. The depth of the lysocline is based on the calculations shown in figure 2.

Hydrodynamic origin.—The water velocity about a dissolving particle is of primary importance in dissolution only in systems where transport of material from the surface is the rate-controlling step. In such systems the rate of transport depends strongly on the velocity and turbulence of the water. In the absence of turbulence and mass flow (that is stagnant water) transport is by means of molecular diffusion, which is a much slower process. Thus, if measured rates prove to be even less than those predicted for molecular diffusion, dissolution must be limited by surface reaction which is not affected by water velocity and turbulence.

Berner (1971) has shown that the quantity to use in testing molecular diffusion as a rate limiting step is not Ω but rather the chemical gradient $(C_s - C_\infty)$ between an equilibrium solid-solution interface and the bulk solution. This is because the concentration gradient and not the degree of undersaturation is the driving force in diffusion. The degree of undersaturation and the concentration gradient are not linearly related as can be seen in the preceding paper by Berner and Wilde (1972). The following calculation is made to compare the observed and experimental dissolution rates with those theoretically calculated for control by molecular diffusion. For diffusion controlled dissolution (Berner, 1971, p. 65):
where:

$$\overline{\frac{dM}{dt}} = \frac{-D(C_s - C_\infty)}{r} \tag{7}$$

r = spherical radius of dissolving particles

$\frac{dM}{dt}$ = rate of dissolution in mass per unit time

$\overline{\frac{dM}{dt}} = \frac{dM}{dt} / 4\pi r^2$ = rate per unit area

C_s = concentration of Ca^{++} at the surface of the dissolving particle assumed to be the value for saturation equilibrium

C_∞ = concentration of Ca^{++} out in the solution

D = diffusion coefficient

For the purpose of calculation, assume that $r = 1$ cm (corresponding to an 11 g sphere) and that $D = 10^{-5}$ cm^2/sec. From Berner and Wilde (1972) at 4500 m depth, at the site of the Peterson experiment, $(C_s - C_\infty) = 1.55 \times 10^{-7}$ moles/cm^3. Thus, for diffusion controlled dissolution of Peterson's spheres:

$$\overline{\frac{dM}{dt}}_{\text{diffusion}} = 4.4 \text{ mg/cm}^2\text{/yr} \tag{8}$$

By comparison the measured value at 4500 m reported by Peterson (1966) was:

$$\left(\frac{\overline{dM}}{dt}\right)_{\text{Peterson}} = 0.25 \text{ mg/cm}^2\text{/yr} \tag{9}$$

Thus:

$$\frac{\left(\frac{\overline{dM}}{dt}\right)_{\text{diffusion}}}{\left(\frac{\overline{dM}}{dt}\right)_{\text{Peterson}}} \approx 20 \tag{10}$$

Similarly for our experiments with a 225 mg sample of 10 μm diameter calcite particles, at a ΔpH = 0.18 which corresponds to $(C_s - C_\infty) = 1.1 \times 10^{-7}$ moles/cm^3 (at 25°C and 1 atm pressure)

$$\frac{\left(\frac{\overline{dM}}{dt}\right)_{\text{diffusion}}}{\left(\frac{\overline{dM}}{dt}\right)_{\text{experimental}}} = \frac{6600 \text{ mg/cm}^2\text{/yr}}{28 \text{ mg/cm}^2\text{/yr}} \approx 240 \tag{11}$$

Since the measured rates are much slower than those predicted for molecular diffusion, dissolution must be limited by the rate of detachment of ions from the calcite surface, and thus water velocity and turbulence are not rate-controlling factors, at least not for the dissolution of particles suspended in sea water. It is possible that water turbulence may be important in stirring into suspension bottom sediment which is otherwise buried in pore water saturated with $CaCO_3$. In this case the turbulence would act to change the aqueous environment about each particle from saturation to undersaturation but not to change the mechanism of dissolution. However, the exact state of saturation in pore waters is poorly known, and the good correspondence of the depth of increased dissolution rate found by Peterson (1966) with the depth of the lysocline for central Pacific sediments (Parker and Berger, 1971) strongly suggests that changing turbulence with depth is not the predominant factor in bringing about a lysocline. This conclusion is reinforced by the observation of Heath and Culberson (1970) that near continental margins the lysocline does not appear to be associated with the boundary between water masses.

Pond, Pytkowicz, and Hawley (1971) have attempted to use a hydrodynamically controlled diffusion model for the dissolution of sinking foraminiferal tests. Their calculations predict that in the North Pacific Ocean all thin-shelled species should dissolve before reaching a depth of 1000 m and only large thick-shelled types should reach the bottom at depths greater than 3000 m. However, Berger's (1970) results indicate little solution damage for the small thin-shelled species after being suspended at depths shallower than 2500 m for four months. This period

is at least ten times longer than the residence time predicted for complete dissolution of even slower-dissolving types at this depth. Thus, Berger's observations are in agreement with our calculations which strongly suggest that calcareous Foraminifera should dissolve much more slowly than the rate predicted for any diffusion-type model.

Kinetic origin.—If the lysocline cannot be readily explained by a change in water velocity, it must be due to chemical changes in the water column. The results of the experiments indicate that there is a good correlation between the distance from equilibrium in terms of ΔpH and a sharp increase in dissolution rate in both the laboratory and the oceans. As shown in figure 3 and by many additional experiments this increase is independent of P_{CO_2}.

A major concern that arises is why there should be a sharp change in the slope of the rate of dissolution with increasing ΔpH. Such an occurrence is not at all uncommon in the study of kinetic phenomenon and is generally interpreted as representing a change in mechanism. Terjesen and others (1961) have found that various ions are capable of strongly inhibiting the dissolution of calcite at concentrations as low as 10^{-7} molar. It is therefore very probable that in sea water adsorbed ions and/or organic molecules (Chave and Suess, 1970) play an important role in controlling the surface chemistry and hence the dissolution rate. In fact, differences in trace element composition may explain the disagreement in absolute rate, for a given ΔpH, between our results and those of Peterson. We have found PO_4^{-3} to be a particularly strong inhibitor which is capable of greatly slowing the rate of dissolution and that the ΔpH at which the discontinuity occurs that we associate with the lysocline is a function of the PO_4^{-3} content of the sea water. (The phosphate content of the sea water used in the laboratory dissolution experiments was very close to that found at the Peterson and Berger site.) Since from additional studies at high ΔpH we have found that both before and after the break in slope a straight line is obtained in the plot of rate versus ΔpH, the same general reaction mechanism is probably in effect on both sides of the break. Nestaas and Terjesen (1969) have found that "kink" models work very well in explaining the dissolution kinetics of calcite when surface adsorbed ions are present. A good summary of "kink" related phenomena can be found in Ives (1965).

SUMMARY

The lysocline is not necessarily associated with water mass boundaries as has been suggested for the Central Atlantic (Berger, 1968). Rather it results from the attainment of a well defined chemical condition in which the distance from equilibrium expressed as ΔpH reaches a critical value. This causes a change in the surface controlled reaction kinetics. Consequently we believe that the lysocline is an excellent sedimentary marker of sea water (or sediment pore water) with a phosphate content similar to North Pacific deep water at a ΔpH = 0.14 to 0.16.

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