Reports

Calcite Dissolution: An in situ Study in the Panama Basin

Abstract. *The results of an in situ study of calcite dissolution in the Panama Basin indicate that the rate of dissolution in the water column increases suddenly below a water depth of about 2800 meters. This coincides with the depth at which the calcium carbonate content of surface sediments begins to decrease rapidly or the sedimentary lysocline. Since this level of increased dissolution both in the water column and on the sea floor does not appear to be related to the transition from supersaturation to undersaturation with respect to carbonate, there may be a kinetic origin for the lysocline in this region.*

Carbonate dissolution is a process that not only is responsible for the systematic distribution of calcite in the world ocean (*1*) but may also play an important role in neutralizing the CO_2 generated by fossil-fuel combustion (*2*). Direct measurement of the dissolution rates of various types of carbonate particles (*3*) suspended on deep-sea moorings have been made in both the Atlantic (*4, 5*) and the Pacific (*6–8*). In general, these experiments show similar trends, although the magnitudes of the dissolution rates and the depths at which critical changes in these rates take place do vary between the oceans. Both Peterson (*6*) and Berger (*7*) observed in the Pacific minimal dissolution above a water depth of 3000 m and then a rapid increase in the rate of dissolution between 3000 and 3700 m. Within the North Atlantic, this level of rapid acceleration in dissolution or the hydrographic lysocline (*9*) occurs substantially deeper, below 4500 m (*4, 5*).

Observations from sediment-based studies (*10*) have also been used to map the level at which there is a sharp decrease in the carbonate content of sediments [termed the sedimentary lysocline by Berger (*9*)] or a marked decrease in the preservation of foraminiferal assemblages [the foraminiferal lysocline (*9*)]. All of these studies have been used to support various hypotheses dealing with both the mechanism of calcite dissolution and its relationship to the carbonate chemistry of seawater (*11, 12*); however, there has been a noticeable lack of agreement in these studies.

Broecker and Takahashi (*12*) have argued that the sedimentary lysocline in both the Atlantic and the Pacific is associated with a critical CO_3^{2-} concentration that is depth-related, and as a result dissolution is a thermodynamic process. The hydrographic lysocline determined from Peterson's experiment in the Pacific (*6*) does not coincide with this critical level of CO_3^{2-} concentration, and it has been suggested that the lysocline is related to current velocity (*13*). On the basis of the results of an Atlantic mooring study, Honjo and Erez (*5*) concluded that dissolution is more of a kinetic phenomenon as proposed by Morse and Berner (*11*). In the present study, we have attempted to reconcile the relationship between calcite dissolution rates measured from an in situ experiment in the Panama Basin with the carbonate chemistry of the water column and calcite dissolution patterns in deep-sea sediments from this region.

As part of the Particulate Flux Experiment Phase 1, a mooring line was deployed in the Panama Basin (4°N, 82°W; water depth 3855 m) for a period of 123 days beginning on 1 July 1979. To this mooring line, 14 preweighed samples of foraminiferal calcite were attached at six different levels (665, 1268, 2265, 2869, 3769, and 3791 m). The foraminiferal samples were obtained from surface sediments collected in a box core (TR 148-3) from the Caribbean (15°51.2′N, 74°34.3′W; water depth 4140 m). Approximately 20 to 30 mg of foraminiferal calcite larger than 250 μm was placed in each of the sample containers. These specimen cages are approximately 4 cm in diameter and 6 cm in length and are covered with a 100-μm polyester mesh (*14*). They are designed to allow water to flow freely through them and to prevent an increase in the in situ carbonate concentration which might inhibit dissolu-

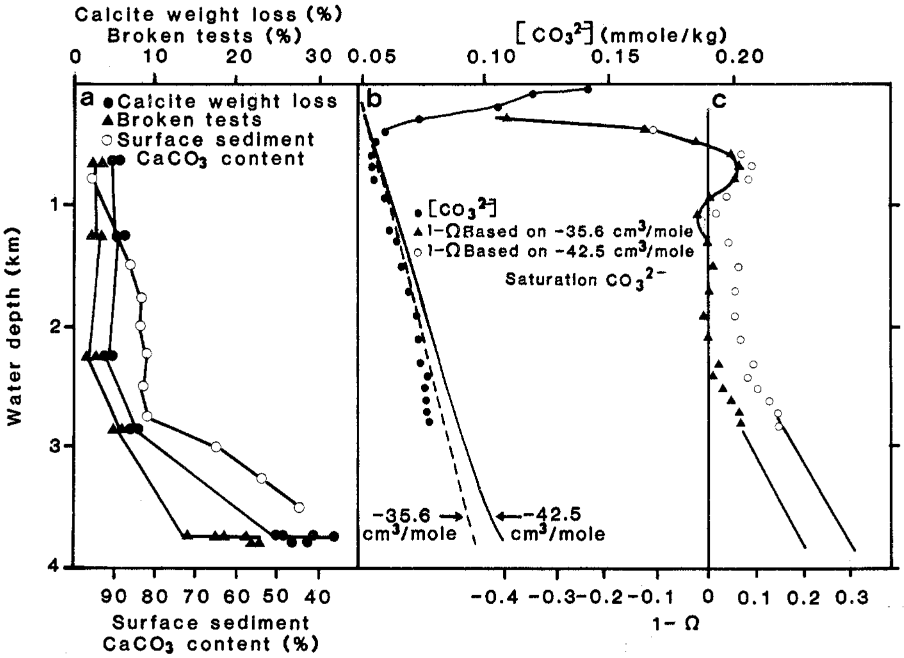

Fig. 1. (a) Comparison of calculated calcite weight loss (solid circles) and the percentage of broken foraminiferal tests (solid triangles) from the in situ study, with the percentage of $CaCO_3$ (open circles) from Panama Basin surface sediments (*16*). (b) Calculated in situ [CO_3^{2-}] from *p*H and titration alkalinity and estimated $CaCO_3$ saturation with respect to calcite based on pressure coefficients of −35.6 cm³/mole and −42.5 cm³/mole at 2°C. (c) A plot of (1 − Ω) versus depth based on pressure coefficients of −35.6 and −42.5 cm³/mole. The extrapolated values of (1 − Ω) were estimated on the basis of a uniform [CO_3^{2-}] of 0.077 mole/kg. Carbonate ion concentration and saturation state versus depth for the Panama Basin.

tion. After recovery, all samples were reweighed and the percentages of broken foraminiferal tests, which increase with enhanced dissolution, were determined.

The carbonate chemistry of the water column was determined from *p*H and titration alkalinity measurements made during July 1979 at a hydrographic station close to the mooring site. The degree of saturation with respect to calcite is expressed as $(1 - \Omega)$ (*15*), with values less than zero indicating supersaturation and values greater than zero indicating undersaturation. The percentages of $CaCO_3$ reported here for surface sediments from the Panama Basin were determined by Moore *et al* (*16*).

The percentage calcite weight loss determined from the mooring experiment, the percentage of broken foraminiferal tests, which is a measure of preservational quality, and the percentage of $CaCO_3$ in surface sediments are plotted versus depth in Fig. 1a. Both weight loss and the percentage of broken foraminiferal tests show that very little dissolution is occurring above 2265 m. The average weight loss for the six samples suspended above 2265 m is only 4 percent, with an average of less than 2.5 percent of the tests being broken.

A slight increase in dissolution at 2869 m is reflected in both the calcite weight loss and the number of broken foraminiferal tests. At this depth, weight loss due to dissolution and the percentage of broken tests are almost double the averages calculated for the three shallower stations.

Six samples were placed at the two deepest stations (four at 3769 m and two at 3791 m), all of which showed substantial dissolution. The maximum calculated weight loss was 32 percent, with the average for both stations being 28 percent. The number of broken foraminiferal tests also increased dramatically between 2869 m and the two deepest stations. An average of almost 20 percent of the foraminiferal tests were broken at 3769 and 3791 m, in comparison to approximately 5 percent at 2869 m.

From these results, it appears that the level of rapid dissolution in the water column, or the hydrographic lysocline, occurs slightly below 2869 m. Although dissolution begins to become noticeable between 2265 and 2869 m, below 2869 m the rate of dissolution increases rapidly.

The dissolution trends determined from the mooring study are also compared with the $CaCO_3$ content of surface sediments from this region (Fig. 1a). After a slight decrease in the $CaCO_3$ content in surface sediments between 750 and 1500 m, the concentration of $CaCO_3$ remains fairly constant down to 2750 m. The observed decrease in the $CaCO_3$ content between 750 and 1500 m is most likely due to a number of factors including some calcite dissolution on the sea floor, the loss of aragonite which is much more susceptible to dissolution than calcite (*17*), and the removal of $CaCO_3$ from topographic highs in this region by winnowing (*16*). An overall pattern of only slight dissolution is therefore observed in both the mooring study and the sediment-based study down to depths of 2869 and 2750 m, respectively.

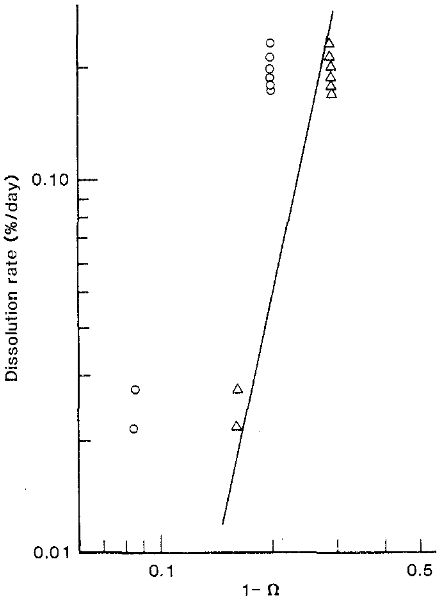

Fig. 2. Dissolution rate based on the weight loss from Fig. 1 and corrected by 4 percent versus $(1 - \Omega)$ estimated from pressure coefficients of -35.6 cm^3/mole (circles) and -42.5 cm^3/mole (triangles). The solid line represents the laboratory-derived dissolution rate of planktonic foraminifera (*26*).

Below 2750 m, there is an almost linear decrease in the $CaCO_3$ content of surface sediments. This rapid increase in dissolution indicates that the sedimentary lysocline (*9*) in this region lies between 2750 and 3000 m. These results are consistent with those of the mooring study, which suggest that the hydrographic lysocline (*9*) is slightly below 2869 m. This correlation between levels of accelerated dissolution in the water column and on the sea floor suggests that both may be expressions of the same feature. That is, the sedimentary lysocline is simply the level at which the hydrographic lysocline impinges on the sea floor.

The results of the $CaCO_3$ chemistry work are shown in Fig. 1, b and c, in terms of CO_3^{2-} concentration and calcite saturation $(1 - \Omega)$. After an initial decrease in the upper 500 m, the CO_3^{2-} concentration displays a rather systematic increase down to 2300 m. From this point it remains relatively constant with depth at approximately 77 μmole/kg. This is precisely the CO_3^{2-} concentration that one calculates from the *p*H and alkalinity data of Culberson (*18*) at a station 700 km to the west. However, our calculated CO_3^{2-} concentration is systematically higher by 13 μmole/kg than that calculated from the *p*H and alkalinity reported at station YTP 108 (4°N, 75°W) of the *Yaloc* 69 cruise (*19*).

We calculated two carbonate saturation profiles $(1 - \Omega)$ (*15*), using pressure coefficients of -35.6 cm^3/mole (*12, 20*) and -42.5 cm^3/mole (*21*) at 2°C (Fig. 1c). The result indicates that the water column from 1 to 2.3 km is saturated or slightly undersaturated. Below this level, there is a fairly linear increase in the degree of undersaturation. This result agrees with that of Bishop *et al.* (*22*) at 0°45′N, 86°10′W but is contrary to that of Swift and Wenkam (*23*), who proposed that the interval from 1 to 2.3 km was uniformly undersaturated at $\Delta p\mathrm{H} = 0.15$ $(1 - \Omega = 0.5)$. We believe that this result is erroneous as it was obtained from the suspect *Yaloc* data and calculated according to the technique of Berner and Wilde (*24*), whose estimated apparent solubility for calcite is now widely regarded as too high by about 35 percent (*25*).

If the apparent weight loss of 4 percent in the planktonic foraminiferal samples placed above 2300 m represents a systematic error in the weighing due to transfer or other causes, one can calculate the rate of dissolution (in percent per day) for the samples placed at 2869, 3769, and 3791 m by correcting the weight loss by 4 percent. The calculated rates for these samples are plotted versus corresponding values for $(1 - \Omega)$ (Fig. 2); also shown is the result of laboratory dissolution rate measurements on planktonic foraminifera at 1 atm and 20°C (*22*). Although there is no a priori reason why the laboratory and in situ rates should agree, this appears to be the case if the pressure coefficient of -42.5 cm^3/mole is correct.

For both the CO_3^{2-} concentration and $(1 - \Omega)$, 2300 m appears to be a critical depth. Below this depth, the CO_3^{2-} concentration ceases to increase and $(1 - \Omega)$ increases in a linear fashion (Fig. 1, b and c). However, this does not appear to be a critical depth for carbonate dissolution based on the trends observed in both the mooring and sediment-based studies (Fig. 1a). The $CaCO_3$

content of surface sediments is fairly uniform between 1750 and 2750 m, with accelerated dissolution beginning below that depth. For the mooring experiment, there was a slight increase in dissolution between 2256 and 2869 m, with the level of rapid increase in dissolution in the water column occurring below that depth. These results indicate that within the Panama Basin neither the sedimentary lysocline nor the hydrographic lysocline can be directly related to a transition from saturation to undersaturation. Earlier mooring studies in both the Atlantic (*4*, *5*) and the Pacific (*6*–*8*) also demonstrated a lack of correlation between the hydrographic lysocline and this critical level of carbonate saturation. If the pressure coefficient of -42.5 cm^3/mole is correct, the results of this study indicate that the dissolution kinetics of biogenic calcite in the laboratory and the deep sea may be similar.

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3. In his Atlantic experiments, Milliman (*4*) used magnesian calcite ooids, planktonic foraminifera, and aragonitic ooids. Honjo and Erez (*5*) used reagent calcite, calcite crystals, synthetic aragonite, planktonic foraminifera, coccoliths, and pteropods. In his Pacific experiment Peterson (*6*) used only spheres of optical calcite, whereas Berger (*7*) used planktonic foraminifera at the same location. In the most recent work of Milliman *et al.* (*8*) in the Pacific, they used planktonic foraminifera, pteropods, and aragonitic ooids.
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15. $\Omega = [Ca^{2+}]\,[CO_3{}^{2-}]/K_{sp}'$, where $[CO_3{}^{2-}]$ and $[Ca^{2+}]$ are the in situ dissolved total $CO_3{}^{2-}$ and Ca^{2+} concentrations, and K_{sp}' is the in situ apparent solubility product for calcite. This index is calculated in the following way (i) Total CO_2 is calculated from the *p*H and alkalinity measurement at 1 atm and 35°C and the in situ $[CO_3{}^{2-}]$ is determined from the total CO_2 and titration alkalinity [R. S. Keir, *Mar. Chem.* **8**, 95 (1979)]. (ii) The value of K_{sp}' at 1 atm is calculated from the *p*H and alkalinity measurements of S. E. Ingle, C. Culberson, J. Hawley, and R. Pytkowicz [*Mar. Chem.* **1**, 295 (1973)]. (iii) Lyman's [thesis, University of California, Los Angeles (1956)] K_1', K_2', and K_B' (K_1' and K_2' are the first and second dissociation constants for carbonic acid and K_B' is the first dissociation constant for boric acid) are used to calculate total CO_2 and K_{sp}' at 1 atm, and the pressure corrections of C. H. Culberson and R. Pytkowicz [*Limnol. Oceanogr.* **13**, 403 (1968)] are applied to K_1', K_2', and K_B' in order to calculate in situ $[CO_3{}^{2-}]$. Two pressure coefficients, -36.0 cm^3/mole (*12*, *20*) and -42.5 cm^3/mole (*21*), at 0°C are used to correct the 1-atm K_{sp}' to in situ pressure.
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27. We thank J. Erez for discussions and suggestions. P. G. Brewer, chief scientist of R.V. *Knorr* leg 73, kindly let R.S.K. acquire carbonate hydrographic data during his Panama Basin cruise. This study was supported in part by NSF contracts OCE77-27080 and OCE80-23959. Contribution 371 from the Belle W. Baruch Institute for Marine Biology and Coastal Research. Contribution 4638 from the Woods Hole Oceanographic Institution.

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Method for Estimation of Ocean Current Velocity from Satellite Images

Abstract. *Barotropic instability waves on a shear interface propagate at the average speed of the water on the two sides. Assuming the instability to be excited by tidal oscillations, the phase speed is the wavelength divided by the tidal period. If the water is at rest on one side of the shear layer the current speed on the other side can be calculated. This method, applied to the Gulf Stream beyond Cape Hatteras as seen in satellite images, gives estimates of current speed in general agreement with in situ observations.*

Infrared satellite images show the sharp thermal boundaries formed where ocean currents separate from topographic boundaries. These thermal interfaces are also velocity interfaces (free shear layers), which in turn are unstable to perturbations caused by disturbances originating elsewhere in the ocean. A clear example of such a free shear layer is that formed by the inshore edge of the Gulf Stream as it passes Cape Hatteras, North Carolina, as shown in Fig. 1. The image is a Tiros-N infrared image with resolution ~ 1 km, obtained on digital tape from the Environmental Data and Information Service of the National Oceanic and Atmospheric Administration and processed further in our facilities at Massachusetts Institute of Technology for navigational reference and contrast enhancement.

The undulations in the free shear layer beyond Cape Hatteras contain a strongly periodic component. The apparently periodic waves upstream of Cape Hatteras we attribute to a local topographic disturbance. Figure 1 shows the inshore and offshore maxima in shear layer excursion marked with short line segments. The nearly periodic structure of the shear instability suggests that its excitation is periodic. Laboratory experiments by Browand (*1*) and Miksad (*2*) showed that periodic excitation of a free shear layer organized the instability fluctuations in a nearly periodic structure, while random excitation gave a random structure. Figure 2 shows the power spectral densities of velocity fluctuations near a free shear layer that is unstable; the spectra are shown for a series of distances from the origin of the shear layer (*2*). The upper part of Fig. 2 shows spectra with random, nearly white-noise excitation, while the lower part shows the result for periodic excitation.