

## The effect of pressure on aragonite dissolution rates in seawater

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**Abstract**—Aragonite dissolution in seawater at variable pressure is well described by the equation

$$\text{Rate} = \kappa'([\text{CO}_3^{2-}]_s - [\text{CO}_3^{2-}])^n$$

where  $[\text{CO}_3^{2-}]_s$  is the carbonate ion concentration at saturation,  $[\text{CO}_3^{2-}]$  is the observed carbonate ion concentration, and  $\kappa'$  and  $n$  are empirical constants. Application of the equation

$$\text{Rate} = \kappa(1 - \Omega)^n$$

to descriptions of aragonite dissolution rates (where  $\Omega = [\text{CO}_3^{2-}]/[\text{CO}_3^{2-}]_s$ ) is appropriate at constant pressure, temperature and salinity.

Our measurements in seawater at 5°C are consistent with the estimate  $-\Delta V = 36.5 \text{ cm}^3/\text{mole}$  for the volume change accompanying aragonite dissolution. This result is somewhat higher than laboratory estimates, but lower than estimates based on calcite and the difference between calcite and aragonite molar volumes.

### INTRODUCTION

THE OCEANS PLAY an important role in the absorption and neutralization of atmospheric carbon dioxide (BROECKER and PENG, 1982; WCP, 1981). One of the primary mechanisms by which the neutralization can take place is the dissolution of calcium carbonate (BROECKER and TAKAHASHI, 1977; BROECKER and PENG, 1982). A major area of uncertainty in modeling the neutralization of atmospheric  $\text{CO}_2$  by the oceans is the functional dependence of the  $\text{CaCO}_3$  dissolution rate on the degree of seawater undersaturation (BROECKER, 1977).

Many researchers (MORSE, 1978; MORSE *et al.*, 1979; KEIR, 1980; BYRNE *et al.*, 1984; WALTER and MORSE, 1985) have expressed the dependence of  $\text{CaCO}_3$  dissolution rate on seawater saturation state through an equation of the form

$$\text{Rate} = \kappa(1 - \Omega)^n \quad (1)$$

where  $\Omega$  is defined in terms of the calcium ion concentration  $[\text{Ca}^{2+}]$ , the carbonate ion concentration  $[\text{CO}_3^{2-}]$ , and  $K'_{sp}$ , the apparent solubility product for calcite or aragonite:

$$\Omega = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K'_{sp}} \quad (2)$$

An alternative rate equation for mineral dissolution (CAMPBELL and NANCOLLAS, 1969; SONDEREGGER *et al.*, 1976; LASAGA, 1981) may be expressed in the form

$$\text{Rate} = \kappa'([\text{CO}_3^{2-}]_s - [\text{CO}_3^{2-}])^n \quad (3)$$

where  $[\text{CO}_3^{2-}]_s$  is the carbonate ion concentration at saturation:

$$[\text{CO}_3^{2-}]_s = \frac{K'_{sp}}{[\text{Ca}^{2+}]} \quad (4)$$

The term  $([\text{CO}_3^{2-}]_s - [\text{CO}_3^{2-}])$  is conceptually similar to the term  $\Delta\text{CO}_3^{2-}$  used by TAKAHASHI and BROECKER (1977) to model the dissolution rates of carbonate sediments in the Atlantic. TAKAHASHI and BROECKER (1977) expressed carbonate dissolution rates as a function of  $([\text{CO}_3^{2-}]_{\text{crit}} - [\text{CO}_3^{2-}])$ , where the "critical carbonate ion content",  $[\text{CO}_3^{2-}]_{\text{crit}}$ , is defined empirically, based on indications of dissolution in carbonate sediments. This definition is in contrast to the definition of  $[\text{CO}_3^{2-}]_s$ , which is based on equilibrium solubility considerations.

A simple, fundamental relationship exists between the rate predictions of Eqns. (1) and (3). Using the definitions of  $\Omega$  and  $[\text{CO}_3^{2-}]_s$ , Eqn. (3) can be written as

$$\text{Rate} = \kappa'[\text{CO}_3^{2-}]_s^n(1 - \Omega)^n \quad (5)$$

The quantity  $[\text{CO}_3^{2-}]_s^n$  distinguishes the predictions of Eqn. (3) from the predictions embodied in Eqn. (1). The dependence of  $[\text{CO}_3^{2-}]_s$  on pressure demonstrates that Eqns. (1) and (3) differ substantially in their predictions of  $\text{CaCO}_3$  dissolution in the oceans. In deep oceanic waters which are under-saturated with respect to aragonite, salinity varies only slightly (34‰ to 36‰), the water masses are nearly isothermal ( $3 \pm 2^\circ\text{C}$ ), and pressure is the only important influence on  $[\text{CO}_3^{2-}]_s$ . Over the normal range of oceanic pressures,  $[\text{CO}_3^{2-}]_s$  varies by approximately a factor of two.

If the parameters of Eqns. (1) and (5) are estimated from experimental results at atmospheric pressure,  $\kappa'$  and  $\kappa$  should have the following relationship:

$$\kappa = \kappa'[\text{CO}_3^{2-}]_{s,1}^n \quad (6)$$

Equation (5) indicates that, for a given  $\Omega$ , dissolution rates measured at atmospheric pressure and at a higher pressure  $P$  will have the following relationship

$$\frac{\text{Rate}_p}{\text{Rate}_1} = \left( \frac{[\text{CO}_3^{2-}]_{s,p}}{[\text{CO}_3^{2-}]_{s,1}} \right)^n \quad (7)$$

where estimates of  $n$  based on experiments at constant pressure have ranged between 2.5 and 4.3 (WALTER and MORSE, 1985; KEIR, 1980). The  $[\text{CO}_3^{2-}]_s$  saturation concentration,  $[\text{CO}_3^{2-}]_s$ , increases by approximately a factor of two between the surface ocean and 6000 meter depths. Consequently, using an appropriate lower bound estimate,  $n = 2$ , the dissolution rate at 6000 meters depth would, for a given  $\Omega$ , be approximately four times greater than a corresponding rate measured at atmospheric pressure. Higher values of  $n$  would, of course, indicate even greater enhancement of dissolution rates under pressure.

We have performed  $\text{CaCO}_3$  dissolution experiments under low-temperature, high-pressure conditions, which simulate the deep-ocean environment. The contrast between the functional dependence of dissolution rates on the quantities  $(1 - \Omega)$  and  $([\text{CO}_3^{2-}]_s - [\text{CO}_3^{2-}])$  for these experiments should indicate whether Eqn. (1) or Eqn. (3) better describes observed dissolution kinetics.

#### EXPERIMENTAL METHODS

In a closed system, dissolution of  $\text{CaCO}_3$  increases the pH of a seawater sample. Consequently, pH measurements provide a means of examining the dissolution rate of calcium carbonate. Our dissolution rate investigations are based on spectrophotometric examination of seawater pH using a pH-sensitive dye, phenol red. At constant temperature, pressure and salinity, the pH of a seawater sample can be determined using the relationship (ROBERT-BALDO *et al.*, 1985):

$$\text{pH} = pK_1 + \log \frac{(A - A_{\min})}{(A_{\max} - A)} \quad (8)$$

In this expression,  $pK_1$  is the logarithm of the phenol red association constant in seawater.  $A$  is the measured absorbance for a given phenol red concentration in seawater.  $A_{\max}$  and  $A_{\min}$  are the upper and lower bound absorbance values, at high and low pH, for the same concentration of phenol red. All of these absorbance measurements are made at 558 nanometers, where the absorbance maximum of the dye's deprotonated form is located. At constant temperature, pressure and salinity, the changes in seawater pH which accompany  $\text{CaCO}_3$  dissolution are written as

$$\Delta\text{pH} = \log \frac{(A_2 - A_{\min})}{(A_{\max} - A_2)} - \log \frac{(A_1 - A_{\min})}{(A_{\max} - A_1)} \quad (9)$$

where  $A_1$  denotes an initial absorbance measurement and  $A_2$  denotes a subsequent absorbance measurement.

Our experiments made use of freshly-collected pteropod shells and natural seawater samples from various depths between 100 and 5000 meters. Pteropod shells were obtained from free-floating sediment traps (BETZER *et al.*, 1984), and seawater samples were obtained by hydrocasts, taken aboard the R/V *Discoverer*. Total alkalinity and total carbon dioxide measurements were obtained using the potentiometric methods described in FEELY *et al.* (1984) with minor modifications: Water samples were collected in 30-L Niskin bottles and immediately transferred into 1-L glass stoppered bottles containing 1.0 mL of a saturated solution of  $\text{HgCl}_2$  to decrease bacterial oxidation of organic matter prior to analysis. The samples were stored in a dark cold storage room at 4°C for no more than 12 hours. Titrimetric analyses were conducted using a Brinkman E636 titroprocessor linked to a Hewlett

Packard 85 computer. The data from the titroprocessor were automatically fed into the computer and processed using the non-linear least squares fitting program of DICKSON (1981) with the modifications suggested by JOHANSSON and WEDBORG (1982). Alkalinity contributions from boric, silicic, and phosphoric acid were computed from equations similar to those presented by TAKAHASHI *et al.* (1982) in the GEOSECS Pacific Expedition report. Total borate concentration was computed using the relation given by CULKIN (1965). The dissociation constants of carbonic acid and boric acid are from the work by ALMGREN *et al.* (1977).

Each of our shipboard dissolution experiments was performed according to the following procedure: Pteropod shells and seawater containing phenol red ( $8 \times 10^{-6}$  M) were placed in a variable pathlength spectrophotometric cell. Our variable pathlength cell consisted of a precision-bore glass cylinder and two plexiglas windows fitted with rubber O-rings. This arrangement allowed the windows to move in response to pressure while isolating the seawater sample within the cylinder. Cells of this design are particularly useful because pathlength changes exactly compensate for pressure-induced changes in a dye's molar concentration (BYRNE, 1984). The variable pathlength cell was placed within an outer pressure housing, which was closed with 3/4-inch thick pressure-bearing plexiglas windows. Following pressurization, absorbance readings were taken with a Varian Instruments DMS-90 spectrophotometer. The pressure housing containing the cell was oscillated at approximately 6 cycles/minute between readings. The spectrophotometric cell and its contents were maintained at  $5 \pm 0.2^\circ\text{C}$  with a Lauda K2-R thermocirculator.

Absorbance measurements were made after an initial 10-minute equilibration period following the pressurization, and at subsequent 20-minute intervals. Each measurement included absorbance readings obtained at 558 and 700 nm. As phenol red absorbance at 700 nm is negligible, readings at this wavelength allowed normalization for slight variations in cell alignment. Measurements of a "blank" seawater sample (seawater without dye) enabled instrumental baseline corrections. All of the absorbance readings were signal-averaged with an Apple IIe computer interfaced with the spectrophotometer, which increased the sensitivity of the technique and compensated for signal variations caused by the motion of the ship.

Each data set incorporated the initial total carbon dioxide ( $\Sigma\text{CO}_2$ )<sub>i</sub>, initial total alkalinity ( $TA$ )<sub>i</sub>, and initial NBS scale pH ( $pa_H$ )<sub>i</sub> for each seawater sample. Our absorbance measurements permitted calculation of  $\Delta\text{pH}$  through time using Eqn. (9). NBS scale pH ( $pa_H = -\log a_H$ ) is then calculated as:

$$pa_H = (pa_H)_i + \Delta\text{pH} \quad (10)$$

Dissolution induced changes in total alkalinity and total  $\text{CO}_2$  are related through the equation

$$\Delta TA = (2 \text{ eq. mol}^{-1}) \cdot \Delta\text{CO}_2 \quad (11)$$

The total alkalinity in our closed system can be written as

$$(TA)_i + \Delta TA = \frac{2K'_1K'_2 + K'_1a_H}{K'_1K'_2 + K'_1a_H + a_H^2} ((\Sigma\text{CO}_2)_i + \Delta\text{CO}_2) + \left( \frac{K'_B}{K'_B + a_H} \right) B_T \quad (12)$$

where  $B_T$  is the total boron concentration and  $K'_1$ ,  $K'_2$ ,  $K'_B$ , are carbonic and boric acid dissociation constants calculated according to the methods of MILLERO (1979). By combining Eqns. (11) and (12),  $\Delta\text{CO}_2$  can be calculated through time as:

$$\Delta\text{CO}_2 = \frac{(TA)_i - R_c(\Sigma\text{CO}_2)_i - R_B \cdot B_T}{R_c - 2} \quad (13)$$

where

$$R_c = \frac{2K'_1K'_2 + K'_1a_H}{K'_1K'_2 + K'_1a_H + a_H^2} \quad \text{and} \quad R_B = \frac{K'_B}{K'_B + a_H} \quad (14)$$

Our  $\Delta\text{CO}_2$  measurements were subsequently converted to a dissolution rate in percent per day using the mass of the pteropod shells, which were dried and weighed to  $\pm 0.1 \mu\text{g}$  after the cruise.

## RESULTS

Dissolution rates for a single *Cavolinia tridentata* shell ( $16.2 \pm .1 \text{ mg}$ ) were determined in North Pacific water column seawater samples taken at  $50^\circ\text{N}$  and  $145^\circ\text{W}$ . All of the determinations were performed at  $5^\circ\text{C}$ , and at pressures which corresponded to the depths from which the seawater samples were obtained. Figure 1 shows a plot of the dissolution rates against depth, with an accompanying plot of saturation state versus depth. Our determinations of  $\Omega$  indicated that the degree of undersaturation was greater at 1,000 meters, 1,500 meters and 2,000 meters depth than at 3,000 meters. However, the dissolution rate at 3,000 meters exceeds the rates measured at the shallower depths. If the dissolution rate varies solely as a function of the saturation state, as in Eqn. (1), the rate at 3,000 meters should be slower.

Only a few measurements in the Fig. 1 dissolution rate profile were determined at pressures sufficient to distinguish the predictions of Eqns. (1) and (3). Examination of a second data set, which includes a larger number of rate determinations under pressure, allows

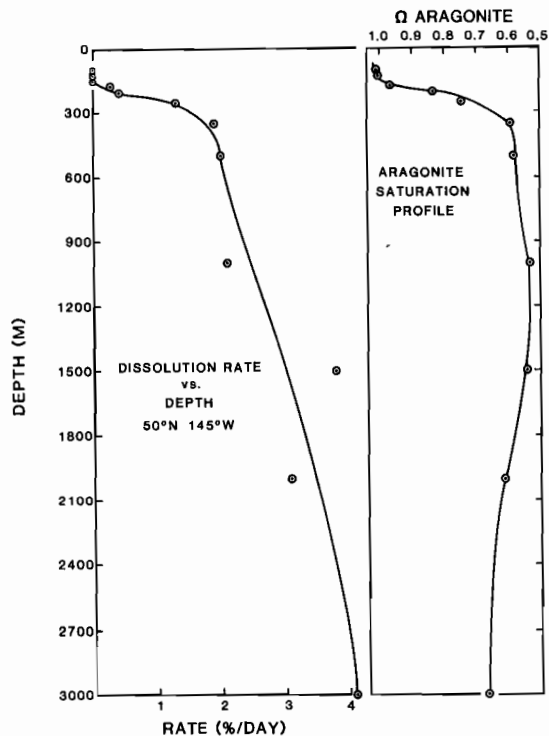


FIG. 1. Dissolution rate and  $\Omega$  profile at  $50^\circ\text{N}$ ,  $145^\circ\text{W}$  in the North Pacific Ocean. Each dissolution rate was obtained using a single *Cavolinia tridentata* shell, mass =  $16.2 \pm .1 \text{ mg}$ . The calculated  $\Omega$  profile corresponds to the saturation state of our shipboard experiments which were performed at  $5^\circ\text{C}$ .

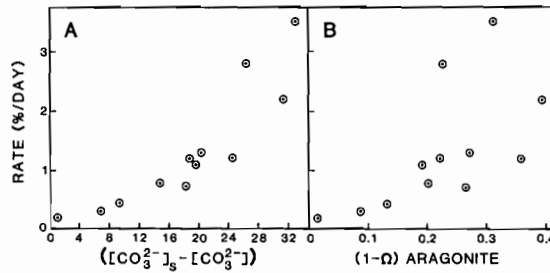


FIG. 2. Dissolution rate versus saturation state for variable pressure experiments using four *Cuvierina columnella* shells, mass  $18.37 \pm .11 \text{ mg}$ : (A) Dissolution rate as a function of  $([\text{CO}_3^{2-}]_s - [\text{CO}_3^{2-}])$ , (B) Dissolution rate as a function of  $(1 - \Omega)$ .  $\Delta V = -31.3 \text{ cm}^3 \text{ mol}^{-1}$ . Note that plots of rate versus  $(1 - \Omega)$  and rate versus  $([\text{CO}_3^{2-}]_s - [\text{CO}_3^{2-}])$  are not equivalent at variable pressure. Equation (5) demonstrates that the predictions of Eqns. (1) and (3) differ at variable pressure due to substantial pressure-induced changes in  $[\text{CO}_3^{2-}]_s$ .

a more definitive comparison of the predictions of Eqns. (1) and (3).

Figure 2 shows data from a set of dissolution rate determinations, in which four *Cuvierina columnella* shells (mass =  $18.37 \pm .11 \text{ mg}$ ) were used over a period of two days. Figure 2 shows that, although there is a definite dependence of dissolution rate on  $(1 - \Omega)$ , the considerable scatter indicates that this term is not sufficient to describe all the features of the data set. Note that in some cases dissolution rates may vary by as much as a factor of 3 for similar values of  $(1 - \Omega)$ . When the same rate data are plotted against  $([\text{CO}_3^{2-}]_s - [\text{CO}_3^{2-}])$ , the data exhibit clear exponential behavior with much reduced scatter. Consequently, this data set indicates that aragonite dissolution rates under variable pressure are better described in the form of Eqns. (3) or (5) than Eqn. (1).

Any assessment of the relationship between aragonite dissolution rates and the saturation state of the water column must be linked to the calculation of aragonite solubility product variation ( $K'_{sp}$ ) with pressure. Our calculation of the pressure dependence of the aragonite solubility product utilizes the following equation (MILLERO, 1979; MUCCI *et al.*, 1982):

$$\ln \frac{K'_{sp}}{K'_{sp}^0} = -(\Delta V/RT)P \quad (15)$$

in which  $\Delta V$  is the partial molal volume change for the dissolution of aragonite, and  $K'_{sp}$  and  $K'_{sp}^0$  represent aragonite solubility products at atmospheric pressure and at a higher pressure  $P$ .  $T$  is the absolute temperature ( $^\circ\text{K}$ ) and  $R$  is the gas constant ( $82.06 \text{ cm}^3 \text{ atm } ^\circ\text{K}^{-1} \text{ mole}^{-1}$ ). Small variations in  $\Delta V$  strongly influence the pressure dependence of  $K'_{sp}$  and calculation of water column saturation state at depth.

Experimentally determined values of  $\Delta V$  for the dissolution of aragonite at  $2^\circ\text{C}$  have ranged from  $-33.1 \pm 2 \text{ cm}^3 \text{ mol}^{-1}$  (HAWLEY and PYTKOWICZ, 1969) to  $-31.8 \pm 2 \text{ cm}^3 \text{ mol}^{-1}$  (INGLE, 1975) and  $-29.0 \pm 3.7 \text{ cm}^3 \text{ mol}^{-1}$  (COOKE and KEPKAY, 1980 and MUCCI *et*

*al.*, 1982). Our Fig. 2 results were calculated using an average  $\Delta V$  value,  $-31.3 \text{ cm}^3 \text{ mol}^{-1}$ .

In an additional set of calculations, a range of  $\Delta V$  values were used in Eqn. (15) to calculate the saturation indices  $(1 - \Omega)$  and  $([\text{CO}_3^{2-}]_s - [\text{CO}_3^{2-}])$  for our second data set. Using our *Cuvierina columnella* data and the methods described above, each choice of  $\Delta V$  generates one set of rate vs.  $(1 - \Omega)$  data pairs and one set of rate vs.  $([\text{CO}_3^{2-}]_s - [\text{CO}_3^{2-}])$  data pairs. Each set of data pairs conjugate to a choice of  $\Delta V$  was fit through non-linear least squares analysis. The quality or "goodness" of fit obtained using Eqns. (1) and (3) can be compared by examining the residual sum of squares (RSS) produced in each case, where

$$\text{RSS} = \sum_i ([\text{rate observed}]_i - [\text{rate predicted}]_i)^2. \quad (16)$$

Figure 3 shows the minimized residual sum of squares obtained using Eqns. (1) and (3) for a series of  $\Delta V$  choices between  $-33 \text{ cm}^3/\text{mole}$  and  $-43 \text{ cm}^3/\text{mole}$ . Figure 3 indicates that within the range of reasonable choices for  $\Delta V$ , Eqn. (3) provides a much better description of our variable pressure dissolution data than descriptions based on  $(1 - \Omega)$ . Using Eqns. (3) and (15), our best fit dissolution rate description (Fig. 4) is obtained with the following parameter estimates:

$$\Delta V = -36.5 \text{ cm}^3/\text{mole} \quad \text{and} \quad n = 1.87 \pm 0.15.$$

The  $\kappa'$  value appropriate to the intact *Cuvierina columnella* shells used in our experiments is  $\kappa' = (3.32 \pm 1.77) \times 10^{-3} \%/ \text{day}$ .

Our best fit estimate of the partial molar volume change for aragonite dissolution is in reasonable accord with the previous upper bound laboratory estimate,  $-33.1 \pm 2.0 \text{ cm}^3/\text{mole}$  at  $2^\circ\text{C}$  (HAWLEY and PYT-

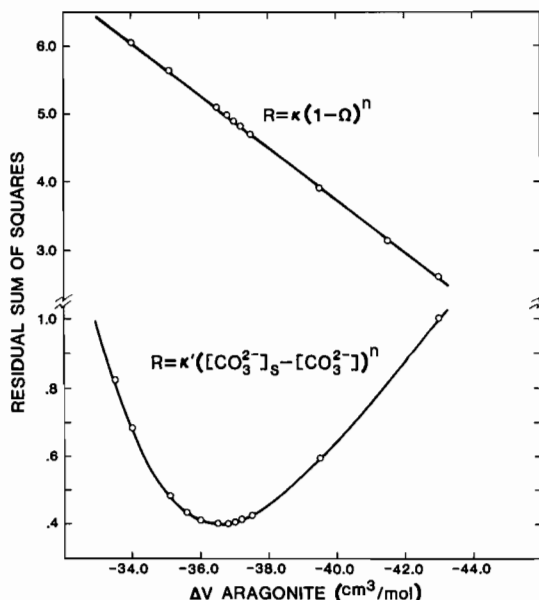


FIG. 3. Our variable pressure aragonite dissolution data are examined using Eqns. (1) and (15), and Eqns. (3) and (15). For each model, the residual sum of squares for our fitted data is shown as a function of  $\Delta V$ .

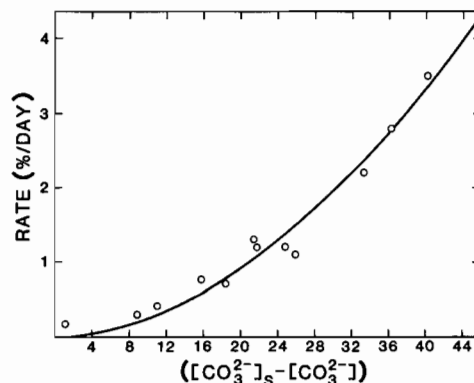


FIG. 4. Our dissolution rate data are shown as a function of  $([\text{CO}_3^{2-}]_s - [\text{CO}_3^{2-}]) \cdot (\text{micromoles}/\text{kg})^{-1}$ , using our best fit estimate,  $\Delta V = -36.5 \text{ cm}^3/\text{mole}$ .

KOWICZ, 1969). Our  $\Delta V$  estimate is also in reasonable accord with the assessment  $\Delta V = -(38.4 \pm 2.7) \text{ cm}^3/\text{mole}$ , based on the partial molar volume change for calcite dissolution,  $\Delta V = -(41.2 \pm 2.7) \text{ cm}^3/\text{mole}$  at  $3^\circ\text{C}$  (SAYLES, 1985) plus the theoretical  $2.8 \text{ cm}^3/\text{mole}$  (MILLERO, 1979) molar volume difference between calcite and aragonite. Since the difference between aragonite and calcite  $\Delta V$  values based on equilibrium measurements (HAWLEY and PYTKOWICZ, 1969; INGLE, 1975; COOKE and KEPKAY, 1980; SAYLES, 1980, 1985) is approximately three times the theoretical difference, our results indicate that kinetic measurements may prove useful in assessing the solubility behavior of carbonates in the deep ocean.

Sea-floor carbonate sediments constitute a reservoir that is sufficient to neutralize the anticipated increase in atmospheric  $\text{CO}_2$  due to anthropogenic input (BROECKER and TAKAHASHI, 1977). The rate at which the neutralization takes place will influence the ocean's rate of atmospheric  $\text{CO}_2$  assimilation. Since the majority of carbonate sediments susceptible to dissolution are found at depth in the ocean, it is important to accurately assess the kinetics of  $\text{CaCO}_3$  dissolution for the global setting in which much of the dissolution will take place. Our results suggest that the parameter  $([\text{CO}_3^{2-}]_s - [\text{CO}_3^{2-}])$  simplifies the assessment of  $\text{CaCO}_3$  dissolution rates under variable saturation conditions.

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