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A kinetic pressure effect on calcite dissolution in seawater

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Abstract

This study provides laboratory data of calcite dissolution rate as a function of seawater undersaturation state ($1 - \Omega$) under variable pressure. ^{13}C-labeled calcite was dissolved in unlabeled seawater and the evolving δ^{13}C composition of the fluid was monitored over time to evaluate the dissolution rate. Results show that dissolution rates are enhanced by a factor of 2–4 at 700 dbar compared to dissolution at the same Ω under ambient pressure (10 dbar). This dissolution rate enhancement under pressure applies over an Ω range of 0.65–1 between 10 dbar and 700 dbar. Above 700 dbar (up to 2500 dbar), dissolution rates become independent of pressure. The observed enhancement is well beyond the uncertainty associated with the thermodynamic properties of calcite under pressure (partial molar volume ΔV), and thus should be interpreted as a kinetic pressure effect on calcite dissolution. Dissolution at ambient pressure and higher pressures yield non-linear dissolution kinetics, the pressure effect does not significantly change the reaction order n in $Rate = k(1 - \Omega)^n$, which is shown to vary from 3.1 ± 0.3 to 3.8 ± 0.5 from 10 dbar to 700 dbar over $\Omega = 0.65$–0.9. Furthermore, two different dissolution mechanisms are indicated by a discontinuity in the rate-undersaturation relationship, and seen at both ambient and higher pressures. The discontinuity, $\Omega_{critical} = 0.87 \pm 0.05$ and 0.90 ± 0.03 at 10 dbar and 1050 dbar respectively, are similar within error. The reaction order, n, at $\Omega > 0.9$ is 0.47 ± 0.27 and 0.46 ± 0.15 at 10 dbar and 700 dbar respectively. This $\Omega_{critical}$ is considered to be the threshold between step retreat dissolution and defect-assisted dissolution. The kinetic enhancement of dissolution rates at higher pressures is related to a decrease in the interfacial energy barrier at dissolution sites. The impact of pressure on the calcite dissolution kinetics implies that sinking particles would dissolve at shallower depths than previously thought.

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1. INTRODUCTION

The investigation of calcium carbonate dissolution in the ocean is critical in constructing global carbon budgets and understanding the ocean's role in neutralizing atmospheric CO_2 by dissolving $CaCO_3$. Most kinetics studies (Morse, 1978; Morse et al., 1979; Keir, 1980; Byrne et al., 1984; Walter and Morse, 1985; Hales and Emerson, 1997; Gehlen et al., 2005; Subhas et al., 2015) of the dissolution behavior of calcium carbonates in seawater have expressed the dependence of dissolution rate on seawater saturation state through an empirical equation of the form:

$$Rate = k(1 - \Omega)^n \tag{1}$$

where k is a rate constant, n is a positive constant known as the "order" of the reaction, Ω is the saturation state defined as the ion concentration product over the stoichiometric solubility product (K^*_{sp}):

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$$\Omega = \frac{[Ca^{2+}][CO_3{}^{2-}]}{K^*_{sp}} \qquad (2)$$

Ω varies either by changing the numerator – ion concentrations (water chemistry), or by changing the denominator, K^*_{sp}. In deep oceanic waters, which are undersaturated with respect to calcite, salinity varies only slightly (34–36), the water masses are nearly isothermal (3 ± 2 °C) and pressure is the most important influence on K^*_{sp}. At 2 °C and a pressure corresponding to a depth of about 6500 m, K^*_{sp} is about 3.7 times greater than at atmospheric pressure (Ingle, 1975). Another factor that decreases Ω in the deep ocean is that respiration of sinking organic matter releases CO_2, decreases pH and $[CO_3^{2-}]$, and thus Ω. The relative importance of these two factors (pressure and microbial respiration of organic matter) in modulating Ω can be seen in a North Pacific Ocean Section (Fig. 1). Ω_{real} is the actual Ω in the ocean. $\Omega_{chemistry}$ is Ω calculated by Ocean Data View if there is no effect of pressure on K^*_{sp} (Ω affected only by DIC, alkalinity, salinity and temperature). $\Omega_{pressure}$ is Ω afftected by pressure, which is shown as the difference of Ω_{real} and $\Omega_{chemistry}$ here.

Above 1000 m, Fig. 1a (Ω_{real}) generally follows the trend of 1b ($\Omega_{chemistry}$), meaning that water chemistry dominates changes in Ω. $\Omega_{chemistry}$ varies between 6 at the ocean surface (not shown in the figure) and 1. Below 1000 m, Ω_{real} deviates from $\Omega_{chemistry}$ due to the effect of pressure on Ω ($\Omega_{pressure}$). At 5000 m depth, Ω can be up to 1.2 units lower than predicted by $\Omega_{chemistry}$ (Fig. 1c). The impact of $\Omega_{pressure}$ is greater in the South Pacific, somewhat less in the north, which reflects the North Pacific oxygen minimum zone's strong influence on the saturation state.

Oceanographers have assumed that carbonate dissolution under pressure follows the same dissolution rate law (same k and n for Eq. (2)) obtained at atmospheric pressure, with pressure only changing the stoichiometric solubility product (K^*_{sp}). In other words, a change in the denominator in Eq. (1) has the same effect as a change in the numerator in determining dissolution rates (Eq. (2)). This implies that dissolution will be kinetically the same regardless of pressure. Whether this assumption is true is the question we address in this study.

The only study, as far as we know, that examined the effect of pressure on carbonate dissolution rates versus saturation state in seawater was that of Acker et al. (1987). Their shipboard experiments measured pteropod (aragonite) dissolution rates in natural seawater at various depths between 100 and 5000 meters, based on spectrophotometric examination of seawater pH using a pH-sensitive dye, phenol red. They concluded that aragonite dissolution in seawater at variable pressures was well described by the equation $Rate = \kappa' \, ([CO_3^{2-}]_s - [CO_3^{2-}])^n$, where $[CO_3^{2-}]_s$ is the carbonate ion concentration at saturation, $[CO_3^{2-}]$ is the observed carbonate ion concentration, and κ' and n are empirical constants; and that their measurements were consistent with the estimate $\Delta V = -36.5\ cm^3$/mole for the volume change accompanying the dissolution of aragonite. However, two factors limited the measurement precision and thus could change the interpretation of data in their study. First, dissolution rates determined from ΔpH may have a limited precision. The largest amount of dissolution in Acker et al. (1987) was only equivalent to a ΔpH ~ 0.05; at Ω = 0.8–1, ΔpH was <0.01. Even though the error on dissolution rates were not discussed in the paper, pH determination based on the spectrophotometric method has an error on the order of 0.002 (Robert-Baldo et al., 1985), which is greater than 20% of the ΔpH at Ω = 0.8–1. This precision limit also arises in other seawater carbonate dissolution studies in which dissolution rates were estimated from ΔpH (e.g. Byrne et al., 1984; Gehlen et al., 2005), acid additions to keep pH constant (e.g. Walter and Morse, 1985), alkalinity change (e.g. Keir, 1980), or $CaCO_3$ dry weight loss (e.g. Peterson, 1966; Berger, 1967; Honjo and Erez, 1978; Keir, 1980; Thunell et al.,1981; Fukuhara et al., 2008). Second, shipboard experiments performed at pressures which corresponded to the depths from which the seawater samples were obtained lacked control in other key variables. Specifically, dissolution experiments were conducted under different water chemistry (carbonate system parameters) and other factors that may affect dissolution (e.g. microbial activity, soluble reactive phosphate concentrations, carbonic anhydrase activity etc.). The problem of uncontrolled variables also exists in other *in situ* seawater dissolution studies (e.g. Peterson, 1966; Berger, 1967; Milliman, 1978; Honjo and Erez, 1978; Thunell et al., 1981; Metzler et al., 1982; Fukuhara et al., 2008). The value of these earlier studies is unquestionable, yet we sought to conduct more controlled experiments to constrain the effect of pressure on calcite dissolution kinetics, focusing on Ω values closest to those most commonly encountered in the modern ocean (0.65–1).

Our goal is to distinguish the pressure effect on carbonate dissolution kinetics from the effect of water chemistry. We performed dissolution experiments in acidified Dickson standard seawater using ^{13}C labeled inorganic calcite following methodologies described in Subhas et al. (2015). This ^{13}C labeled method, coupled with tight constraints on seawater saturation state (from measurements of dissolved inorganic carbon (DIC) and total alkalinity (TA)), provides much more sensitive determinations of dissolution rates compared to previously employed methods. Desired Ω values were obtained by changing experimental pressure and/or adding HCl to the same standard Dickson seawater, so that the effect of changing pressure versus changing alkalinity on dissolution rates could be distinguished and compared. Much of the work describing $CaCO_3$ dissolution from a mechanistic perspective in this paper has built upon the foundational work of Subhas et al. (2017), and ongoing work by our group in which we investigate dissolution mechanisms as a function of temperature across a wide range of Ω values.

2. METHODS

Synthetic inorganic $Ca^{13}CO_3$ (calcite) purchased from Sigma Aldrich (SKU 492027, ≥99 atom%) was wet-sieved to a grain size of 70–100 μm using 18.2 MΩ Milli-Q water adjusted to a pH of ~8 using ammonium hydroxide. The powders were then dried at 60 °C overnight. The mineral-

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