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Deep Ocean CO_2 Hydration Kinetics

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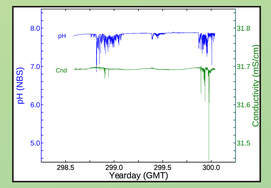
ABSTRACT

The slow hydration / de-hydration kinetics of carbon dioxide at ambient temperatures and pressures are well known to ocean chemists. Johnson (1982) reported the rate constant for the hydration reaction in seawater as a function of temperature. More recently, Zeebe and Wolf-Gladrow (2001), have compiled a comprehensive model of these kinetics, which illustrate the strong impact of pH on reaction rate in addition to the temperature effects. In our recent studies of CO_2 dissolution in seawater as part of an ocean CO_2 sequestration scenario, we have observed a significant under-estimation of the total CO_2 concentrations when pH alone is used in close proximity to the CO_2 source. We attribute this under-estimation of total CO_2 to slow CO_2 hydration kinetics which allows a major fraction of the dissolved CO_2 to remain un-reacted until long after it has passed by the pH electrode and hence was undetectable. For similar reasons, we anticipate analogous errors when measuring the total CO_2 concentrations in close proximity to sea-floor CO_2 vents on the flanks of undersea volcanoes. More recently, measurements of CO_2 hydration kinetics at low temperature but elevated pressures (such as would be encountered at liquid CO_2 sequestration sites or CO_2 vents on the flanks of seafloor volcanoes), have suggested that pressure may be inducing enhanced reaction rates which could partially mitigate the problem. In order to test this hypothesis, we began a systematic study of CO_2 hydration rates in the deep ocean using MBARI's advanced ROV technology.

BACKGROUND

Measurements made during the Ocean Abyssal Carbon Experiment (OACE, a joint project with investigators from Japan, Norway, and the USA, sponsored by NEDO, Japan) first revealed the problem with the under-estimation of total CO_2 when determined by pH measurements alone in a flowing seawater environment immediately down-stream from a pool of liquid CO_2. When instruments (recording CTDs with integral pH sensors) were placed at various distances downstream from the benthic flume, negative pH spikes were recorded when the currents were favorable for the plume of CO_2 enriched seawater to pass by the sensors. These low pH excursions were frequently accompanied by negative spikes in conductivity. Normally, one would expect that if sufficient CO_2 dissolved to depress the pH, a proportional increase in the conductivity would occur due to the presence of the additional H^+ and HCO_3^- ions. It was soon realized that the negative spikes in conductivity were due to various quantities of unreacted, dissolved CO_2 "diluting" the seawater, lowering the salinity and hence the conductivity (Brewer et al. 2005). See the figure below for an example of this effect.



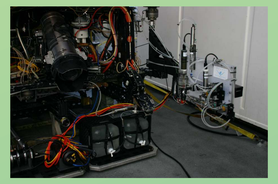
The OACE Benthic flume is visible in the left-hand photograph. It is mounted on an MBARI elevator for deployment to 4000m depth. The trough is about half full of liquid CO_2 and the ROV is maneuvering into position to sample the plume with the snorkel. The figure on the right is a portion of the data collected by the CTD contained in cage #1 (which is visible in the lower right-hand corner of the photograph).

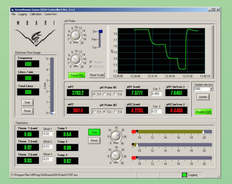
EXPERIMENTAL

In order to test for the existence of unreacted CO_2 dissolved in seawater, we devised a "re-circulating pH cell" for deployment on the ROV swing-arm. A SeaBird CTD pump was used to circulate the seawater within a small loop through a cell containing a SeaBird SBE-18 pH sensor. By use of a series of hydraulically actuated valves, we could continuously re-cycle the seawater within the cell (mixing it thoroughly on time-scales of 3-5 seconds) or open the valves and flush the cell with ambient seawater. When closed, the trapped volume of the system is ~500mL. A sampling wand with a tygon tube attached to the inlet valve allows the ROV pilots to sample seawater anywhere within reach of the ROV manipulator. Pumping rates were 1.2-2.0 L/min.

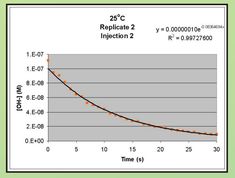
The figure above shows the pH trace from the cell during one of the OACE experiments. The trough was filled with liquid CO_2 and the thruster on the flume was set at a slow speed in order to generate a slow current across the liquid interface. Points A and F show the background seawater pH as water is drawn from a point well above the flume. Points B and D show the slightly lowered pH when seawater from just beyond the lip of the flume is drawn through the pH cell. Because turbulence at the end of the trough caused variable mixing of the CO_2 enriched seawater with ambient seawater, a stable pH is not achieved. However, when the valves are closed and the enriched seawater is re-circulated inside the pH cell, the dissolved CO_2 is allowed to fully react and obtain equilibrium (C & E). The substantially lower pH observed conclusively demonstrates the plume near the end of the flume had not achieved chemical equilibrium.

By adding a small (1mL) hydraulically driven syringe and a mylar reservoir to the apparatus, we could make acid injections into the pH cell and study the kinetics of the CO_2 hydration reaction. At the moment of injection, a very low pH is produced at the tip of the injector, the carbonic acid-bicarbonate-carbonate equilibrium is forced way to the left and dissolved CO_2 is produced consuming most of the acid. As the dissolved CO_2 then mixes throughout the cell, it encounters a much higher pH and slowly reacts with seawater, forming carbonic acid which dissociates and lowers the pH of the cell. Over time, equilibrium of the carbonate system is re-established. One can follow the course of this reaction by monitoring the variation of pH with time (Nakayama et al. 2005).





Re-circulating pH cell with Seabird SBE-18 pH sensor and two hydraulic syringes is mounted on the ROV's swing-arm. Data collection and real-time visualization is accomplished with the Greenhouse Gases DGH Controller GUI.



Following the ROV dive, the pH data can be "re-played" with the pHProbeWorkbench GUI. This graphical interface allows the rapid identification and selection of pH data for further processing to determine the relaxation time for CO_2 equilibration.

HYDRATION KINETICS MODELING

We used the kinetics model of Zeebe & Wolf-Gladrow (2001). Their model is based upon the inter-action of two competing reactions as a function of pH:

$$CO_2 + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HCO_3^- + H^+$$

$$CO_2 + OH^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} HCO_3^-$$

And the following equations for the reaction rates as a function of a perturbation in CO_2 where τ is the relaxation time (also known as the folding time) for the approach to equilibrium:

$$\frac{d(dCO_2)}{dt} = -\frac{1}{\tau} dCO_2 \qquad \frac{1}{\tau} = k_{-1} - k_{-1}(\Pi_b b[H^+] + \Pi_h h[HCO_3^-]) - k_{-4}\Pi_b b + k_{-4}([OH^-] + \Pi_{oh} oh[CO_2])$$

With,

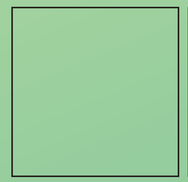
$$\Pi_b b = \frac{\Pi[HCO_3^-]}{\Pi[CO_2]} = -\frac{[H^+] + 2[CO_3^=]}{K_2 + [H+] + [CO_3^=]} / (1+a)$$

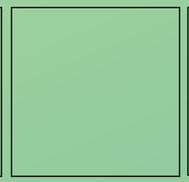
$$\Pi_h h = \frac{\Pi[H^+]}{\Pi[CO_2]} = -\frac{\Pi_b b + 2}{1+a}$$

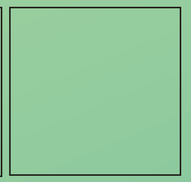
$$\Pi_{oh} oh = \frac{\Pi[OH^-]}{\Pi[CO_2]} = a\frac{\Pi_b b + 2}{1+a}$$

$$a = K_w / ([H^+]) \qquad [CO_3^=] = 1 + [H^+]/K_2 + ([H^+])^2 / K_1 / K_2$$

All of these equilibrium and rate constants are a function of temperature, salinity and pressure. (See: Zeebe and Wolf-Gladrow (2001) for a detailed and thorough presentation of calculations.)

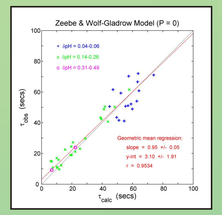




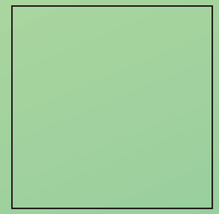


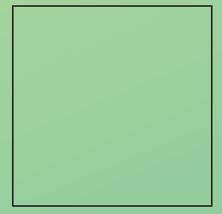
On the left, we see the effect of temperature on τ as a function of pH where S = 35 and TCO_2 = 2mmol/kg. In the middle are two pH profiles calculated with CO2SYS using in situ data. Lastly, we have calculated τ at this same station to show the combined effects of S, T and P.

RESULTS



Comparison of our experimentally determined relaxation times with those calculated using the Zeebe & Wolf-Gladrow model. On the left, τ was calculated at in situ conditions, including a correction for ambient pressure. A slightly better relationship was observed when the pressure correction was omitted suggesting that there maybe a small pressure dependence in the kinetics that is as yet not well characterized – but effect is small.





Recently Schulz et al. (in press) have modified the Zeebe & Wolf-Gladrow model by re-determining k_{-4}. In these figures, we compare our experimentally determined τ with their model predictions. The slope of the regression is not as close to 1 as for the Zeebe & Wolf-Gladrow model suggesting that in this situation the revised model is not as good of a predictor of τ as the original model. As above, a better regression is obtained when the pressure correction to the equilibrium and rate constants is not used – and again the effect is small.

Based upon these comparisons it is clear that experimental measurements on an ROV are in very good agreement with the model of Zeebe and Wolf-Gladrow (2001). Likewise, for future measurements in dynamic environments, this model should be an excellent predictor of the time necessary to achieve equilibrium and give us an advance indication of the spatial and time frames for in situ analyses.

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