Carbon Dioxide Exchange Between Air and Seawater: No Evidence for Rate Catalysis

Joel C. Goldman and Mark R. Dennett
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Abstract. It has been suggested that enzymatic catalysis plays a major role in regulating the mass transport of carbon dioxide from the atmosphere into the oceans. Evidence for this mechanism was not found in a series of gas exchange experiments in which the gas transfer rate coefficients for samples obtained from various natural seawaters, with and without the addition of carbonic anhydrase, were compared with those from artificial seawater. Wind-induced turbulence appears to be the major factor controlling the ocean's response to anthropogenic increases in atmospheric carbon dioxide.

It is well recognized that uptake and regeneration of CO₂ in the oceans provide a major control on the chemistry of seawater, and the ultimate fate of excess atmospheric CO₂ lies largely in the oceans (1). Fickian transport of CO₂ across the air-sea interface can be accelerated by chemical reaction of aqueous CO₂ with components of the bicarbonate alkalinity system (2). At pH ≤ 8 the reaction CO₂ + H₂O → H₂CO₃ → HCO₃⁻ + H⁺ (reaction 1) is important, whereas when the pH rises above 8 the reaction CO₂ + OH⁻ → HCO₃⁻ (reaction 2) increasingly contributes to the removal of CO₂ from solution until it dominates reaction 1 at pH > 10 (3). Because a rise in pH leads to both a decrease in the partial pressure of aqueous CO₂ and the direct conversion of CO₂ to HCO₃⁻ by way of reaction 2, any possible chemical enhancement of CO₂ transport into seawater is strongly dependent on pH. In addition, the relative importance of chemical enhancement of CO₂ transport processes has been shown to be an inverse function of wind-induced turbulence across the liquid surface (4).

At the pH of seawater, which typically is about 8.0 to 8.2, and with the turbulence usually present at the ocean surface, CO₂ chemical reactivity is believed to play a minor role in the exchange of CO₂ between the atmosphere and the oceans (5). However, because reaction 1 is relatively slow (3), chemical enhancement could be important even at the pH of seawater, were catalysis of this reaction possible (6).

Berger and Libby (7), on the basis of experiments performed over a decade ago with samples from southern California coastal waters, concluded that carbonic anhydrase (CA), which is produced and excreted by numerous marine vertebrates and invertebrates, might be present in some oceanic areas in sufficient quantities to play an important role in regulating the exchange of atmospheric CO₂ with the oceans. We reexamined this hypothesis in a series of gas transfer experiments under rigid laboratory conditions. To determine whether CO₂ exchange with natural seawater was enhanced enzymatically, we compared, under a fixed mixing regime and in the presence or absence of commercially prepared bovine CA or ethoxyzolamide (an inhibitor of carbonic anhydrase activity), the pH-dependent gas transfer coefficients for various marine waters with those for an artificial seawater that was known not to have any catalytic properties (8).

Our gas-liquid exchange system consisted of (i) a circulating, closed-loop gas environment coupled through a nondispersing infrared spectrophotometer for continuous CO₂ analysis and (ii) an aqueous phase which was both temperature-controlled and mixed with a magnetic stirring bar to provide moderate turbulent diffusion. Once a steady-state atmospheric CO₂ concentration was established (9), the gas phase was opened to the aqueous phase and the rate of CO₂ transport between the two phases was measured over a period of 30 to 45 minutes to calculate a gas transfer rate coefficient (10). The starting atmospheric CO₂ concentration in all experiments was held at 1800 ppm to ensure that absorption of CO₂ into the liquid phase occurred under all our experimental conditions (11) and that the reservoir of CO₂ in the gas phase remained relatively unchanged during an experiment.

We first established the optimum liquid mixing regime in our gas exchange system to ensure that if catalysis of CO₂ transport took place, it could readily be observed. The gas transfer rate coefficient K (min⁻¹) at pH 8.10 was hardly affected by mixing speeds up to 500 rev/min, but then increased dramatically with further increases in mixing up to 700 rev/min, the maximum speed possible before the magnetic bar became unstable (Fig. 1). Addition of 0.5 to 20 mg of bovine CA per liter had no effect on K at either end of this range of mixing speeds, but at 500 rev/min we found a 60 percent increase in K with addition of CA at 0.5 mg/liter and a twofold increase with addition of the enzyme at ≡ 2 mg/liter. Hence, all subsequent experiments were performed with a constant mixing speed of 500 rev/min.

These results confirm the general conclusion that chemical reactivity between CO₂ and HCO₃⁻ has no impact on the overall mass transfer of CO₂ into solution when turbulence is high (5). Clearly, at 700 rev/min the surface film through which diffusion of CO₂ occurred was so thin, about 100 μm (12), that physical diffusion rather than chemical enhancement was the rate-limiting step, whereas at 500 rev/min the surface film thickness had increased to about 450 μm and chemical enhancement became important in the overall transport process.
Moreover, the catalyzed transfer rates at 500 rev/min were lower than the uncatalyzed rates at 700 rev/min, indicating that enzymatic catalysis can increase the magnitude of $K$, but that this mechanism is not nearly as important in controlling mass transport as is the thickness of the surface film (13).

Addition of CA without mixing (zero stirring speed) likewise had no effect on $K$ (Fig. 1), probably because of the very low ratio of surface area to volume of the reaction vessel combined with the short duration of the experiment; hence, there was little liquid turnover, and chemical reactivity was restricted to a very small fraction of liquid in the chamber.

After establishing the optimum mixing speed, we determined the effect of $pH$ on $K$ for artificial seawater (Fig. 2A). In the $pH$ range 7.8 to 8.2, $K$ remained relatively unchanged at about 0.0010 min$^{-1}$, but at higher $pH$ values we observed a dramatic increase in $K$ to 0.0044 min$^{-1}$ at $pH$ 9.2. We used this curve as a baseline to gauge the potential for enzymatic catalysis of CO$_2$ transport in representative marine waters (Fig. 2B) that included samples from the Sargasso Sea (an oligotrophic water), Vineyard Sound, Massachusetts (a moderately productive coastal water), Wild Harbor, Massachusetts (a productive inlet of Buzzards Bay, Massachusetts), and the outlets of tanks of shellfish and assorted large fish that were flushed continuously with Vineyard Sound seawater. There was little difference between the partial pressures of CO$_2$ in these samples and in the artificial seawater at common $pH$ values (14). Thus any differences in $K$ at a given $pH$ between the natural and artificial seawater samples were due primarily to differences in chemical enhancement potential or other gas transport properties between the two types of seawater.

Overall, we could not find any evidence for the presence of CA in the seawater samples we tested. In all experiments $K$ fell slightly below or close to the baseline curve of $K$ versus $pH$ (Fig. 2B). The depth at which the seawater samples were taken had no discernible effect on $K$ in the Sargasso Sea and Vineyard Sound samples. Moreover, addition of CA at up to 2 mg/liter increased $K$ by a factor of no more than 2 to 3, far less than the $>25$-fold increase in $K$ observed by Berger and Libby (7); and in every case when the addition of enzyme was followed by addition of an equal amount of the enzyme inhibitor ethoxyzolamide, the rate coefficient was reduced to the value measured before the enzyme was added. Were CA originally present in any of the samples, we would have expected $K$ in the presence of the inhibitor to be reduced below these uncatalyzed values. In particular, we could find no evidence of biological production of CA in the waters that were most likely to have catalytic properties, the shellfish or fish tank samples (15).

A major difficulty in interpreting the results of Berger and Libby (7) is that they did not define the conditions necessary for observing catalysis and they had no control experiment. For example, they aerated their samples in 200-liter tanks at a rate of 200 liter/hour for 3 to 68 days and found that the rate of CO$_2$ absorption into two batches of water obtained at Santa Monica beach during the winter of 1965–1966 was lower by a factor of 25 to 50 than the rate in two separate samples obtained about 4 months later from the same location, but with bovine CA added at 0.5 mg/liter (a control experiment without addition of the enzyme was not performed at this time). Seawater samples from 60 m at nearby locations obtained 1 and 2 years later were characterized by the same rate coefficients as the catalyzed surface samples.

A simple explanation for the results of Berger and Libby is possible if the turbulence they used was great enough to negate any catalytic effect of added or naturally occurring CA. Then the observed differences in CO$_2$ exchange between the surface waters and the deep and catalyzed surface waters could have been due to the presence of a surfactant or hydrocarbon pollutant (or some other constituent) that retarded CO$_2$ exchange in the surface water samples obtained in the winter of 1965–1966. The presence of such pollutants in southern California coastal waters was not uncommon during the late 1960’s (16).
The close agreement between CO₂ invasion measurements based on naturally occurring and bomb-produced ¹⁴C methods and those obtained from radon measurements allows us to place limits on the role of catalysis in the oceans (17). These results support our overall conclusion that enzymatic catalysis, even if it does occur, would have little effect on the mass transport of CO₂ into the oceans, given the degree of wind-induced turbulence present.

JOEL C. GOLDMAN
MARK R. DENTENET
Woods Hole Oceanographic Institution,
Woods Hole, Massachusetts 02543

References and Notes

2. Mass transport of CO₂ is enhanced chemically because CO₂ may disappear on entering the aqueous phase and the driving force, Δτ, the difference in CO₂ concentration between the gas and liquid phases, will be larger than if CO₂ were nonreactive.
4. J. Kanwisher, J. Geophys. Res. 68, 3921 (1963);
   P. S. Liss, Deep-Sea Res. 20, 221 (1973); W. S. Broecker and T.-H. Peng, Tellus 26, 21 (1974);
6. Quinn and Otto (5) calculated that in the presence of bovine CA at about 3 mg/liter an effective surface film thickness in seawater of 300 μm could be reduced tenfold.
8. When equilibrated with atmospheric CO₂ (360 ppm) by long-term aeration, the artificial seawater (defined in J. C. Goldman and J. J. McCarthy, Limnol. Oceanogr. 23, 695 (1978)) had a pH of 8.3 and a total inorganic carbon concentration of 26 mg/liter at 20°C.
9. With the valve closed to the liquid phase, air in the gas phase was first circulated through a CO₂ trap consisting of Ascarite (sodium hydroxide-coated asbestos) to remove CO₂ and establish a baseline. The trap was then bypassed and sufficient 100 percent CO₂ gas was injected through a septum on the gas injection bulb to raise the CO₂ partial pressure in the gas phase to the desired concentration.
10. The rate coefficient K (min⁻¹) was calculated from the equation K = Δτ⁻¹ ln (C₀ / Cₜ), in which C₀ was the initial CO₂ concentration in the gas phase and Cₜ was the concentration after the time interval Δτ. The liquid phase had a surface area of 18.1 cm² and a volume of 450 cm³.
11. The concentration of CO₂ in our artificial seawater varied from —40 nmole at pH 7.8 to —0.5 nmole at pH 9.2. The time interval 30 to 45 minutes was chosen to ensure that decreases in pH never exceeded 0.1 pH unit and that equilibrium between CO₂ in the gas and liquid phases was never attained. We expressed the rate coefficient in units of reciprocal minutes rather than in the more conventional CO₂ exchange units of meters per year or moles per square meter per year used by oceanographers because the geometry of our system was so unlike that of the ocean.
12. The estimated film thickness (μm) was calculated from the expression DA/KV, in which D is the diffusion coefficient of CO₂ in seawater (taken to be 2 × 10⁻⁹ cm²/sec), A is the surface area, and V is the volume.
13. Quinn and Otto (5) estimated that chemical enhancement of CO₂ transport into seawater becomes important only for surface film thicknesses ≥ 400 μm, which is consistent with our findings. In contrast, Broecker and Peng (4) estimated a conservative surface film thickness of the oceans to be ≤ 60 μm, far less than is necessary for chemical enhancement to be effective.
14. Over the range of pH in the natural seawater samples (7.96 to 8.40) the concentration of total inorganic carbon varied between 25.5 and 27.1 mg/liter, whereas the concentration of total inorganic carbon in the artificial seawater decreased from 27.5 mg/liter at pH 7.96 to 25.6 mg/liter at pH 8.40.
17. The best estimate for CO₂ invasion rates in the ocean, based on radon measurements, is 16 mole/m²-year, whereas estimates determined from ¹³C methods are 19 to 22 mole/m²-year. Hence, enzymatic catalysis of CO₂ transport could at best account for a 40 percent enhancement effect, assuming the different measurements were essentially error-free [W. S. Broecker, T.-H. Peng, G. Mathieu, R. Hesslein, T. Torgersen, Radiocarbon 22, 676 (1980)].
18. Supported by NOAA sea grant NAR86AA-D-0077.

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