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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 rôle 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 CO_2 in the oceans provide a major control on the chemistry of seawater, and the ultimate fate of excess atmospheric CO_2 lies largely in the oceans (*1*). Fickian transport of CO_2 across the air-sea interface can be accelerated by chemical reaction of aqueous CO_2 with components of the bicarbonate alkalinity system (*2*). At $p\mathrm{H} \leq 8$ the reaction $CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow HCO_3^- + H^+$ (reaction 1) is important, whereas when the pH rises above 8 the reaction $CO_2 + OH^- \rightarrow HCO_3^-$ (reaction 2) increasingly contributes to the removal of CO_2 from solution until it dominates reaction 1 at $p\mathrm{H} > 10$ (*3*). Because a rise in pH leads to both a decrease in the partial pressure of aqueous CO_2 and the direct conversion of CO_2 to HCO_3^- by way of reaction 2, any possible chemical enhancement of CO_2 transport into seawater is strongly dependent on pH. In addition, the relative importance of chemical enhancement of CO_2 transport processes has been shown repeatedly 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, CO_2 chemical reactivity is believed to play a minor role in the exchange of CO_2 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 CO_2 with the oceans. We reexamined this hypothesis in a series of gas transfer experiments under rigid laboratory conditions. To determine whether CO_2 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 CO_2 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 CO_2 concentration was established (*9*), the gas phase was opened to the aqueous phase and the rate of CO_2 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 CO_2 concentration in all experiments was held at 1800 ppm to ensure that absorption of CO_2 into the liquid phase occurred under all our experimental conditions (*11*) and that the reservoir of CO_2 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 CO_2 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 CO_2 and HCO_3^- has no impact on the overall mass transfer of CO_2 into solution when turbulence is high (*5*). Clearly, at 700 rev/min the surface film through which diffusion of CO_2 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.

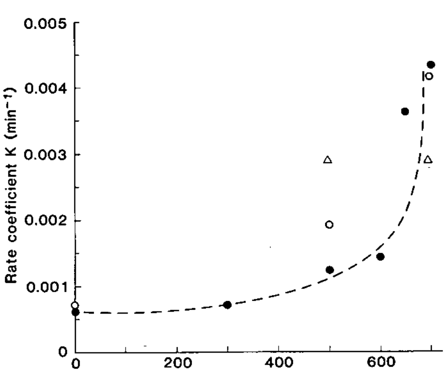

Fig. 1. Gas exchange rate coefficient K as a function of mixing speed for artificial seawater at pH 8.10 and 20°C. Mixing speed of the Teflon-coated magnetic bar was measured with a Strobette stroboscope-tachometer, model K-8221-00. Bubble formation was never observed. Comparisons were made between (●) uncatalyzed rate coefficients and those based on additions of bovine CA (Sigma C-7500) at (○) 0.5 and (△) 20 mg/liter. On the basis of additional experiments at 500 rev/min, we found that enzymatic catalysis was saturated with added CA at 2 mg/liter.

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*).

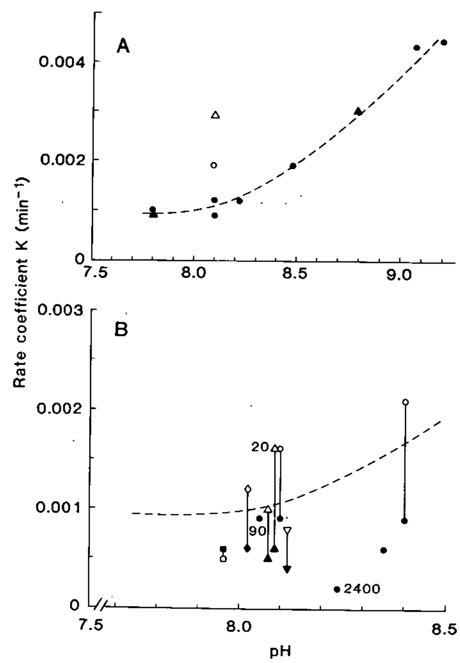

Fig. 2. (A) Gas exchange rate coefficient K as a function of pH in (●) artificial seawater and (▲) filtered surface water from Vineyard Sound, Massachusetts. The pH was adjusted by aeration with CO_2-enriched or CO_2-free air until the desired value was attained. The curve was drawn by eye. Data are included from Fig. 1 for additions of CA at (○) 0.5 and (△) 20 mg/liter. (B) Gas exchange rate coefficient K as a function of pH in various natural seawaters (unfiltered) that include three sets of samples from (●) the Sargasso Sea, obtained between July and November 1981, and one set each from (▲) Vineyard Sound, Massachusetts, (▼) Wild Harbor, Massachusetts, and the outlets of (■) a shellfish tank at the Environmental Systems Laboratory at Woods Hole Oceanographic Institution stocked with the bay scallop *Agropecten irradians* and the hard clam *Mercenaria mercenaria*, and (◆) a fish aquarium at the NOAA Marine Fisheries Service Laboratory in Woods Hole, Massachusetts, stocked with bluefish, *Pomatomus saltatrix*, and striped bass, *Morone saxatilis*, all obtained in February 1982. Data points with numbers represent depth in meters from where the sample was obtained. Data points without numbers represent surface samples. Open symbols represent the effect on K of CA additions (0.5 mg/liter to the Sargasso Sea samples and 2 mg/liter to the other samples). For experiments involving addition of CA, K was determined first without addition of the enzyme, then with addition, followed by addition of the enzyme inhibitor ethoxyzolamide at 2 mg/liter, all during the same experiment. In all cases addition of the inhibitor reduced K to its original value. Dashed line is a portion of the artificial seawater curve from (A).

The close agreement between CO_2 invasion measurements based on naturally occurring and bomb-produced ^{14}C 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 CO_2 into the oceans, given the degree of wind-induced turbulence present.

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

References and Notes

1. W. S. Broecker, T. Takahashi, H. J. Simpson, T.-H. Peng, *Science* **206**, 409 (1979).
2. Mass transport of CO_2 is enhanced chemically because CO_2 may disappear on entering the aqueous phase and the driving force, ΔC, the difference in CO_2 concentration between the gas and liquid phases, will be larger than if CO_2 were nonreactive.
3. D. M. Kern, *J. Chem. Educ.* **37**, 14 (1960).
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); H.-C. Broecker, J. Petermann, W. Siems, *J. Mar. Res.* **136**, 595 (1978).
5. B. Bolin, *Tellus* **12**, 274 (1960); T. E. Hoover and D. C. Berkshire, *J. Geophys. Res.* **74**, 456 (1969); J. A. Quinn and N. C. Otto, *ibid.* **76**, 1539 (1971); S. Emerson, *Limnol. Oceanogr.* **20**, 743 (1975).
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.
7. R. Berger and W. F. Libby, *Science* **164**, 1395 (1969).
8. When equilibrated with atmospheric CO_2 (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 *p*H 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 CO_2 trap consisting of Ascarite (sodium hydroxide–coated asbestos) to remove CO_2 and establish a baseline. The trap was then bypassed and sufficient 100 percent CO_2 gas was injected through a septum on the gas injection bulb to raise the CO_2 partial pressure in the gas phase to the desired concentration.
10. The rate coefficient K (min^{-1}) was calculated from the equation $K = \Delta t^{-1} \ln (C_0 C_t^{-1})$, in which C_0 was the initial CO_2 concentration in the gas phase and C_t was the concentration after the time interval Δt. The liquid phase had a surface area of 18.1 cm^2 and a volume of 450 cm^3.
11. The concentration of CO_2 in our artificial seawater varied from ~ 40 nmole at *p*H 7.8 to ~ 0.5 nmole at *p*H 9.2. The time interval 30 to 45 minutes was chosen to ensure that decreases in *p*H never exceeded 0.1 *p*H unit and that equilibrium between CO_2 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 CO_2 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 CO_2 in seawater (taken to be 2×10^{-5} cm^2/sec), A is the surface area, and V is the volume.
13. Quinn and Otto (*5*) estimated that chemical enhancement of CO_2 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 *p*H 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 *p*H 7.96 to 25.6 mg/liter at *p*H 8.40.
15. Carbonic anhydrase is an essential enzyme in the regulation of CO_2 excretion in marine fish and has been found in numerous shellfish species, even though its function in marine invertebrates is not well understood [T. H. Maren, *Fed. Proc. Fed. Am. Soc. Exp. Biol.* **26**, 1097 (1967); H. F. Bundy, *Comp. Biochem. Physiol. B* **57**, 1 (1977); J. N. Cameron, *Mar. Biol. Lett.* **1**, 3 (1979)].
16. See W. Bascom [*Environ. Sci. Technol.* **16**, 226A (1982)] for a historical review of marine pollution in the waters off the southern California coast.
17. The best estimate for CO_2 invasion rates in the ocean, based on radon measurements, is 16 mole/m^2-year, whereas estimates determined from ^{14}C methods are 19 to 22 mole/m^2-year. Hence, enzymatic catalysis of CO_2 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. Torgensen, *Radiocarbon* **22**, 676 (1980)].
18. Supported by NOAA sea grant NA80AA-D-0077.

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