

Modeling CO₂ in the Ocean: A review

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Introduction

Modeling in the natural sciences plays two roles depending on the maturity of our understanding of the problem. In an initial stage, a conceptual or mathematical model is used to try to differentiate between competing hypotheses by comparing predictions of the model with measured data. Because the aim is to evaluate the natural system by comparison with model predictions, we can call this a "diagnostic" endeavor. An example of this might be the stagnant film versus the boundary layer models for kinetics of gas exchange across an air/water interface, where the controlling mechanisms for gas evaporation from solution are still uncertain. As our understanding of nature progresses, the more mature "prognostic" stage uses an established and successful model to extrapolate data to wider spatial or temporal coverage than is practical to measure in the field. Uptake of fossil fuel CO₂ by dissolution in the oceans is an example of this stage of scientific development. This review presents an overview of the science of modeling CO₂ fluxes in aquatic systems, primarily in the oceans, discussed within the framework of these two stages of scientific development. We begin with the nearly instantaneous molecular scale thermodynamic calculations of CO₂ aqueous chemistry, and conclude with global spatial scale 100,000 year time scale models for CO₂ in the atmosphere and oceans (Figure 1). An underlying motivation for these topics is to understand and predict fossil fuel uptake into the oceans at present and in the coming centuries. While some parts of the discussion are applicable to any gas and any aquatic system, for other parts of this review the focus on CO₂ in the oceans becomes more transparent.

Molecular Scale

On a molecular level, the partitioning of gases between gaseous and aqueous phases is governed by thermodynamics in the form of Henry's law, which states that in ideal (dilute) systems the partial pressure in the gas phase will be proportional to the concentration of the aqueous species in solution. The value of the Henry's law constant for a given gas

depends on temperature (decreasing solubility of CO_2 at higher temperature) and salinity (likewise). In addition, for dissolved CO_2 , there is aqueous phase pH equilibrium chemistry between CO_2 (aqueous), H_2CO_3 (carbonic acid), HCO_3^- (bicarbonate), and $\text{CO}_3^{=}$ (carbonate ion). Partitioning between CO_2 and H_2CO_3 is difficult to detect analytically, so the two species are typically treated as a single species, called H_2CO_3^* , which is taken to be in equilibrium both with gaseous CO_2 and dissolved HCO_3^- . The gas phase equilibrium condition for a water sample is often referred to as the pCO_2 of the solution; note that in disequilibrium the pCO_2 of the solution differs from the pCO_2 of the gas phase. The solubility of CO_2 gas, and the equilibrium dissociation constants for H_2CO_3^* vary as a function of temperature and salinity, such that a 1° increase in sea water temperature leads overall to a 4.23% increase in the equilibrium gas phase partial pressure (pCO_2) of a sea water sample [Chipman et al., 1992], depending on the choice of thermodynamic constants, while a 1 ppt increase in salinity at 25°C generates a 3.2% increase in pCO_2 .

The pH equilibrium model has been first order successful in predicting the behavior of dissolved CO_2 in sea water, while successive studies have improved the consistency of the dissociation [Roy et al., 1993] and solubility [Weiss, 1974] constants for sea water. The carbonate buffer system has two degrees of freedom, so that simultaneous measurements of three or more parameters can be used to test the thermodynamic constants in the field; this also appears to work fairly well [Millero et al., 1993]. The pCO_2 of a water sample can typically be directly measured much more precisely [Chipman et al., 1992] than it can be calculated from other measurements such as the total dissolved CO_2 concentration [Chipman et al., 1992], spectrophotometric pH [Clayton and Byrne, 1993], or the titration alkalinity [Bradshaw et al., 1981]. However pH equilibrium calculations are universally used in numerical models of upper ocean carbon cycling, and they appear to be sufficient for that purpose, because the CO_2 flux is in general limited by circulation rather than by gas exchange, which would be sensitive to the sea surface disequilibrium [Sarmiento et al., 1992].

Microscale

On a spatial scale of millimeters to a meter at the sea surface, the flux of a gas across the air-sea boundary is governed by water and air motions near the surface, and the rate limiting mechanism is usually in the water. Excellent and comprehensive reviews of this topic can be found in [Liss and Duce, 1997]. The conceptual picture begins with a well mixed large reservoir of sea water below the sea surface, and a well mixed atmospheric reservoir in the boundary layer above. Chemical fluxes across the sea surface alter the concentrations of solutes at the sea surface, which generate a chemical boundary layer in the water. Continued air-sea flux is limited by replenishment of this sea surface microlayer, either by molecular diffusion or by fluid flow renewing the sea surface microlayer with bulk fluid from the sea surface mixed layer. The sea surface microlayer is also thought to be cooler than the bulk sea surface mixed layer, because of evaporation, while the air immediately above the sea surface is thought to be more humid than the bulk atmospheric boundary layer. The air-sea flux is driven by these altered microlayer characteristics, rather than by the conditions of the bulk reservoirs above and below the microlayer which can be more easily measured. The sea surface microlayer is distinguished by enrichment in organic matter, and by distinct planktonic communities (the neuston).

The limitation of the gas transfer by stagnation at the sea surface has been described and parameterized by two mechanistically distinct but functionally nearly indistinguishable models, the boundary layer model and the surface renewal model (Figure 2). In the boundary layer model, the transition from turbulent transport to diffusive transport near the sea surface is conceived to occur at a transition depth below the sea surface, demarking a stagnant layer typically 10 - 100 μm thick. Gas exchange rates increase with increasing wind speeds, and this behavior is parameterized as a decreasing thickness of the boundary layer in more turbulent conditions. The surface renewal model imagines that the stagnant layer is replaced with bulk sea water with some frequency which increases with increasing

water turbulence. One potential means of differentiating the two models is in the dependence of the gas fluxes on the diffusion coefficient of the gas; the surface renewal model predicts a square root dependence of flux on D (exponent $1/2$), while the boundary layer models give an exponent of $2/3$ when the sea surface is treated as a smooth rigid wall [Deacon, 1977] or $1/2$ for a free surface [Ledwell, 1984], the difference arising from the effect of the wall on the turbulent flow. In lab experiments, the observed diffusion dependence decreases from $2/3$ order when the surface is calm (low mean square wave slope) to $1/2$ order when the wave slope increases [Jähne, 1985], suggesting that the boundary layer model might be appropriate at low wind speeds, but leaving the question open at high wind speeds. The relationship between exchange rates of different gases is important not only to distinguish between these models, but also because several gas exchange measurement techniques, such as the radon method [Smethie et al., 1985], or the simultaneous deliberate injection of multiple tracers [Watson et al., 1991], depend on being able to relate the gas exchange rates of different gases.

Films of organic molecules at the sea surface have been found to exert a strong influence on the rate of gas exchange [Frew, 1997]. The model of [Davies, 1966] explains this as a result of surface tension exerted by the film, which tends to hold the sea surface molecules together, suppressing the smaller and slower turbulent eddies near the sea surface. Increasing sea surface film concentration in laboratory experiments has been shown to decrease gas exchange velocity by establishing a critical wind speed, below which gas exchange is low and relatively insensitive to winds, and above which gas exchange increases with wind speed, but never to the value which would be expected under clean conditions. The critical wind speed is found to coincide with the onset of capillary waves at the sea surface [Jähne et al., 1987], and laboratory data using a variety of surface films and turbulence conditions collapses to a single line when plotted against mean square wave slope [Frew, 1997].

Another poorly constrained physical process in gas exchange is the effect of bubbles. Here the primary distinction to be drawn is between bubbles that dissolve completely, delivering the original load of gases entirely to solution, and bubbles which survive to rise to the surface again, fractionating the gases according to gas solubility and the kinetics of gas exchange. The effect of bubbles on the gas exchange model is to (1) increase the rate constant for exchange, by increasing the effective area of the sea surface, and (2) increase the average pressure of the atmosphere that the ocean sees, because gases dissolve at greater pressure (depth) than atmospheric [Memery and Merlivat, 1985]. Bubble injection of gases can lead to a steady state supersaturation of the gas at the sea surface, with bubble invasion balanced by surface evasion. The effect of bubbles is greatest for relatively insoluble gases such as oxygen, and less for the more soluble CO₂ (the high solubility can be attributed in part to the aqueous form H₂CO₃), because the concentration of the more soluble gas equilibrates more quickly between the bubble and the liquid phase. The dependence of bubble gas exchange on solubility as well as on diffusion coefficient complicates gas exchange measurements in the field which rely on relating the exchange rates of different gases, because they introduce solubility as a second variable. It is observed that only smaller bubbles (<150µm) are typically mixed below about 1 meter depth (the pressure at which corresponds to a 10% atmospheric supersaturation at the sea surface). Deep bubbles are thought to be most important to the steady state supersaturation at the sea surface, while the more numerous and larger shallow bubbles dominate the bubble-induced increase in the piston velocity [Woolf, 1997].

Another potentially important effect is the temperature gradient at the sea surface, generated by cooling associated with evaporation and surface IR radiation. The deviation of sea surface CO₂ solubility relative to the bulk temperature of the mixed layer has been estimated to contribute 0.7 Gton C yr⁻¹ to the net atmosphere - ocean CO₂ flux [Robertson and Watson, 1992]. Global models of CO₂ uptake are not particularly sensitive to this correction, but global estimates of air-sea CO₂ fluxes based on measured sea surface mixed

layer $p\text{CO}_2$ values [Tans et al., 1990; Takahashi et al., 1997] clearly are. Finally, the reaction of CO_2 with H_2O to form H_2CO_3 , which increases the solubility of CO_2 gas and enables it to participate in the carbonate buffer system of sea water, may play a role in the kinetics of CO_2 transfer. The kinetics of hydration are relatively slow [Johnson, 1982] but if significant concentrations of the enzyme carbonate anhydrase were present in the surface microlayer, the buffer chemistry of sea water might enhance the gas exchange flux by catalytically promoting the hydration of aqueous CO_2 within the surface boundary layer [Wanninkhof, 1992].

Gas exchange rates have been compiled from a variety of field and laboratory sources, using a variety of techniques. These are discussed in detail in another paper in this volume (Lapitan et al.) and will only be summarized here. In general, there is considerable scatter in the data which limits the precision to which the present-day ocean uptake of CO_2 can be estimated from field data [Takahashi et al., 1997]. There may also be a systematic discrepancy between measurement of inert gases (e.g. radon, SF_6 , and He) and ^{14}C [Liss and Merlivat, 1986; Wanninkhof, 1992]. Models for gas exchange on a millimeter to meter scale are therefore still in the diagnostic stage, where research focuses on identifying the relevant mechanisms to encode into the models.

Mixed layer scale

The next spatial scale to consider encompasses the top 10-250 meters of the water column, and a "local" horizontal scale of hundreds of meters to kilometers. On this scale the relevant dynamics are the establishment and destruction of thermal stratification which inhibits mixing of surface waters with subsurface waters below. Photosynthesis is confined to the top zone because only the top 75-150 meters receive enough sunlight to support net photosynthesis. The net effect of biological activity is to capture CO_2 and dissolved nutrients like NO_3^- and PO_4^{3-} and transform them into particulate and dissolved organic matter (reduced carbon). Particulate matter can be removed from its parent water mass by sinking, which results in a net depletion of sea surface water in the nutrients and in

CO₂. In the steady state the downward nutrient flux in sinking particles is regulated by the supply of nutrients to the sea surface, although this is a complicated story. Seasonal excursions in the depth of mixing at the sea surface, with deep mixing in winter and stratification in summer, lead to a seasonal cycle of nutrient entrainment into the euphotic zone. In addition, the shear generated by wind-driven currents leads to turbulent mixing at the base of the well-defined mixed layer.

The physics which describe the dynamics of the mixed layer are therefore thermal (free) convection, both as an adjustment to static stability and with the added possibility of further entrainment derived from the kinetic energy of convection; wind-driven (forced) convection, which appears to generate mixing through shear at the base of the mixed layer; turbulence and Langmuir circulation within the mixed layer; and turbulent mixing below the mixed layer. In many parts of the ocean these processes can be described as a one-dimensional vertical balance driven by surface heat, fresh water, and momentum fluxes. This observation has led to a long history of mixed layer models and their application to modeling of sea surface biological activity and CO₂. These models have been extensively reviewed and compared elsewhere [Price et al., 1978; Martin, 1985; Martin, 1986; Large et al., 1994; Archer, 1995], so we will simply summarize a few salient points here. The models can be divided into several classes. Bulk mixed layer models are based on the assumption that the sea surface mixed layer is completely homogeneous, an assumption which is not bad but not strictly correct either. Often heterogeneity in momentum, turbulence, or even in some short lived chemical species can be observed in the sea surface "mixed layer", especially under conditions of deep convective mixing [Lal and T.Lee, 1988]. Bulk mixed layer models either track the influx and dissipation of turbulent kinetic energy [Kraus and Turner, 1967; Gaspar et al., 1990] or they pay attention to current shear at the mixed layer base [Price et al., 1986]. A second class of models does not predict a priori the degree of mixing in the mixed layer, but rather resolves the statistics of turbulence in the upper water column and allows the model to predict mixing [Mellor and Yamada,

1974; Large et al., 1994]. The challenge here is the tendency to under predict mixed layer homogeneity due to the neglected two or three dimensional structure such as organized convection and Langmuir circulation.

The models are in general reasonably able to reproduce the available pool of ship-based and time series mixed layer physical observations. Discrepancies still exist and discussion continues, but the models are ubiquitously deployed in global ocean circulation and biogeochemistry models. In general, then, we can conclude that the mixed layer physical models have largely reached the prognostic stage of scientific maturity.

In contrast, several chemical issues remain mired in the diagnostic stages. A long-standing issue recently resolved (in my opinion) is the limitation of biological uptake of nutrients in some parts of the upper ocean. The observation is that vast tracts of the upper ocean, in particular the equatorial and North Pacific, and the Southern Ocean, are replete with nutrients and sunlight in surface waters, and yet the rate of biological export of nutrients as sinking particles is relatively low. The residence time of nitrate in surface waters of the equatorial Pacific, for example, is several years while in the North Atlantic the spring bloom consumes and exports the available surface nutrients in a matter of days. This observation has been shown fairly convincingly to be the result of limitation by iron [Martin and Fitzwater, 1988; Coale et al., 1996]. Iron limits production ultimately because of its insolubility. Nitrate and phosphate are present in sea water in roughly the ratio of their utility to phytoplankton, because they tend to travel together through the biological system. Iron, in contrast, is scavenged from sea water by precipitation or adsorption onto particles when its concentration approaches or exceeds its solubility. Therefore a significant or even dominant portion of the source of iron at the sea surface is from wind-blown continental dust. Another source is sediments in coastal areas. In surface waters particulate or dissolved Fe^{3+} can be transformed into the more soluble but oxidatively unstable form Fe^{2+} by reaction with UV light, leading to a diurnal signal in iron speciation [Johnson et al., 1994]. The effect of iron on a planktonic ecosystem appears to be to

promote or encourage the larger diatoms to bloom [Martin and Fitzwater, 1988; Coale et al., 1996]. With size comes the ability to produce particles large enough to escape from the mixed layer by sinking. Therefore modeling the effect of iron on upper ocean carbon cycle requires simulating and predicting (1) atmospheric deposition of dust, (2) dissolution of iron from the particles, (3) upper ocean photochemistry of iron, (4) scavenging and precipitation removal of iron, (5) biological sources and sinks, (6) the global ocean distribution of dissolved iron, to capture the upwelling component, (7) the ecosystem response to changes in the iron supply, and (8) the impact of the ecosystem response on the export of carbon from the mixed layer. Many of these tasks have not yet even begun, leading us to the clear conclusion that a fundamental portion of chemical oceanography is still very much in the diagnostic stage of scientific development.

Another mysterious issue has been revealed at the JGOFS time-series stations in the subtropical oceans, concerning the cycling of nutrients in the upper ocean. In the steady state, the upward flux of nutrients by mixed layer entrainment, turbulent mixing, and mesoscale motions (next section) ought to account for the observed rate of carbon export as sinking particles (measured by a variety of techniques, such as sediment traps, or sea surface oxygen fluxes). In both the time series stations (Hawaii [Karl and Lukas, 1996] and Bermuda [Michaels and Knap, 1996]), this balance cannot be made, as upward nutrient fluxes are inadequate to balance observed carbon export production [Hayward, 1987; Jenkins, 1988]. Possible mechanisms include *in situ* nitrogen fixation, which is clearly diagnosable from nitrate / phosphate data [Gruber and Sarmiento, 1997], atmospheric deposition [Owens et al., 1992], and biological transport of nutrients by active buoyancy regulation among plankton [Villareal et al., 1996]. Given that the mechanisms to account for these observations are still unknown, models of upper ocean nutrient dynamics are clearly still in the diagnostic stage. Our ignorance in this area is a major impediment to predicting future ocean CO₂ uptake in light of changes in global climate.

Mesoscale

The next larger spatial scale to consider ranges from 10-200 kilometers in the horizontal, and to several kilometers in the vertical. This is called the mesoscale, and the physics of circulation at this scale is analogous to storms in the atmosphere. A crucial length scale for ocean flow is the Rossby radius of deformation, which represents the distance which information can be carried by internal gravity waves within the time scale of the rotation of the earth. A spike perturbation in sea surface elevation and subsurface density structure, for example, would excite gravity waves and "run downhill" in all directions, but after a period of time determined by the local vertical rotation rate, the now smeared out hill of sea surface and subsurface anomaly would be confined by rotation and geostrophy. The spatial scale of gravity wave information flow, the Rossby radius of deformation, ranges from ~100 kilometers in low latitudes to ~10 km in higher latitudes, because of the variable projection of the earth's rotation on local vertical. Density and flow structures generated by the mean flow are stretched and distorted by the flow, spawning ever smaller features, until the spatial scale of the Rossby radius is reached; these features are called mesoscale eddies. Features which are generated smaller than the Rossby radius quickly spread out by gravity waves, returning to the mesoscale size scale.

Eddies can affect the internal cycling of the ocean by distorting the depth of the thermocline, bringing nutrient rich subsurface waters within the reach of sunlight from the sea surface. Time series shipboard observations occasionally observe anomalous nutrient injections to the euphotic zone [Jenkins, 1987], large enough that only a few of these events per year could supply the entire nutrient demand. The eddy pumping mechanism is certainly part of the "missing" nutrient flux to the euphotic zone in the subtropics described in the last section [McGillicuddy and Robinson, in press]. However, the story is far from complete, because it not clear that the eddy pumping mechanism, which lifts density surfaces through the ~100 meter depth of sunlight penetration, can generate chemical anomalies at the sea surface such as high sea surface oxygen supersaturation [Spitzer and

Jenkins, 1989] and ^3He data [Jenkins, 1988]. Summarizing material from this, the previous, and the next section, sources of nutrients and carbon at the sea surface include (1) seasonal and faster changes in the depth of the mixed layer, (2) large-scale upwelling in equatorial and subpolar oceans, (3) transient uplift of the thermocline in mesoscale eddies, (4) irreversible mixing required to bring subsurface geochemical signatures such as O_2 and ^3He to the sea surface, and (5) nitrogen fixation. These mechanisms each have distinct signatures on the tracers O_2 and ^3He , but all of the data have yet to be reconciled.

Mesoscale processes are certainly a crucial part of the geochemical cycles of gases and associated biological tracers in the upper ocean, but models of ocean gas chemistry at the mesoscale are still working in the diagnostic stage, attempting to understand which basic processes are important and which are not.

Gyre and Global Scale

On the scale of an entire ocean basin, ocean circulation organizes into wind-driven gyres of cyclic flow. Below the surface mixed layer lie the waters of the thermocline, which communicate with the atmosphere on time scales of years to decades. Contact between the thermocline and the atmosphere occurs mostly in winter, when seasonal cooling extends the reach of surface mixing to its greatest depth. During spring warming, the relict winter mixed layer remains subsurface and now isolated from communication with the atmosphere. The stratification of that water mass determines its potential vorticity, which plays a fundamental role in the physics of thermocline circulation [Luyten et al., 1983]. The constraint that fluid parcels move along lines of constant potential vorticity generates the pathways of fluid flow, including some regions of the thermocline, in theory, called "shadow zones", which are only ventilated by diffusion, not by direct advection.

Below the thermocline, intermediate and deep water masses form primarily at high latitudes and advect through the entire deep ocean. The processes of deep high latitude convection (brine rejection during sea ice formation, convection in ice-free polynias in the Southern Ocean, as examples) are severely underresolved in global models, but the global

deep sea ventilation rate, as indicated by the distributions of tracers such as natural and bomb-produced ^{14}C , freons, and bomb tritium, can be reproduced by clever parameterization. Ocean uptake of anthropogenic CO_2 has been simulated using the global models such as the Princeton model [Sarmiento et al., 1992] or the Hamburg model [Maier-Reimer and Hasselmann, 1987]. In both of these studies the uptake of fossil fuel CO_2 was simulated as an abiotic perturbation to the natural system. An alternative approach has been to prescribe rather than predict the physics of ocean circulation using box models with parameterized physics intended to capture the essence of the real ocean circulation using vertical diffusion, advective formation of deep water, and perhaps a diffusive, outcropping thermocline [Oeschger et al., 1975; Siegenthaler and Oeschger, 1987]. These models, when tuned to reproduce the same transient tracer data as are used to validate the more physical global circulation models, tend to give about the same present-day uptake of fossil fuel as is predicted by the circulation model studies (1.7 - 2.8 Gton C yr⁻¹ [Sarmiento and Sundquist, 1992]).

Still unresolved is the potential for coupling or feedback between ocean circulation and biology, and the effect of biological changes on uptake of fossil fuel CO_2 . Global warming is expected to have at least some impact on the circulation of the ocean, resulting, for example, in a shutdown of deep convection in a 4x CO_2 coupled atmosphere ocean model experiment [Manabe et al., 1994]. Simulations of fossil fuel uptake under these conditions are only beginning to appear [Maier-Reimer et al., 1996; Sarmiento and Quéré, 1996]. The two available model predictions are radically different from each other because of the way that they treat the biological response to the oceanographic changes. Biological uptake and export of nutrients and carbon in the Hamburg model is predicted using a kinetic rate law for nutrient uptake (with a latitude dependence) which has been tuned to reproduce the present day distribution of nutrients at the sea surface under present day flow. The Princeton model restores the sea surface nutrient concentration to the observed value for present day simulation, and for the future, maintains the biological export

production rate even in the face of changing flow and nutrient conditions. In short, biology in the Hamburg model attempts to respond to changes in nutrient supply, although no one, the model least of all, knows what this response will be, while the Princeton model maintains constant biological production in the face of changing circulation and climate. The Hamburg model predicts little effect of changing ocean circulation on fossil CO₂ uptake, while the Princeton model predicts a much larger response. Clearly we need to be able to predict the biological response to changing climate forcing in order to predict future ocean CO₂ uptake.

Geologic scale

On a geological time scale, we must consider the interaction of the chemistry of the ocean with the dissolution of rocks on land (chemical weathering) and sedimentation in the ocean. Here an essential distinction is between weathering of igneous rocks, the calcium component of which can be idealized as CaO, and CaCO₃. The former reacts with two CO₂ molecules from the atmosphere to generate 2 HCO₃⁻ in river water, which is delivered to the ocean. Alkalinity is removed from sea water by burial of CaCO₃, which consumes two alkalinity equivalents, returning one carbon to CO₂. This series of reactions results in the net transfer of one carbon from the atmosphere to the lithosphere as CaCO₃. In contrast, weathering of CaCO₃ consumes one CO₂ from the atmosphere to form 2 HCO₃⁻, but it releases that CO₂ upon recrystallization of CaCO₃ in the ocean, resulting in no net flux from the atmosphere to the lithosphere.

On time scales of thousands to tens of thousands of years, the CaCO₃ weathering reaction buffers or regulates the pCO₂ of the atmosphere as a function of the chemistry of the oceans. Weathering runoff products added to the ocean tend to drive the ocean to higher concentrations of CO₃⁼ (higher pH). CaCO₃ is produced biologically in the ocean, and rains steadily to the sea floor. CaCO₃ shells which land in the abyss of the ocean dissolve because of a pressure effect on CaCO₃ solubility, while CaCO₃ which lands on topographic highs is removed from the ocean by burial in the sediments. An increase in the

ocean $[\text{CO}_3^{=}]$ acts to increase the area on the sea floor where CaCO_3 can be buried, increasing the global burial rate of CaCO_3 . This dynamic sets up a negative feedback which regulates the $[\text{CO}_3^{=}]$ of the ocean, on a global average, to maintain parity between terrestrial weathering and ocean burial of CaCO_3 . This mechanism, called CaCO_3 compensation, regulates the pH of the ocean and thereby the pCO_2 of the atmosphere, on time scales of 5-10 kyr.

Models of this process must resolve the dissolution of CaCO_3 from deep sea sediment, a process which is regulated by the diffusion of carbonate species through the sediment pore water and by the acidification of the pore water by organic carbon diagenesis [Boyle, 1983; Broecker and Peng, 1987; Sundquist, 1990; Archer et al., 1997]. A recent simulation of fossil fuel uptake into an ocean circulation and carbon cycle model [Archer et al., 1997] predicted that 70-80% of the net CO_2 emission (fossil fuel plus whatever eventually happens to the terrestrial biota) will be absorbed by dissolution in the ocean on a time scale of hundreds of years. Chemical neutralization by reaction with CaCO_3 in the oceans and on land will account for another 20% on time scales of 5-8 kyr. 7-8% of the CO_2 release is projected to remain in the atmosphere for hundreds of thousands of years, awaiting neutralization by reaction with igneous rocks on land [Berner et al., 1983].

Another regulation mechanism has been identified associated with the weathering of igneous rocks [Walker et al., 1981]. The CO_2 flux from the atmosphere by igneous rock weathering must be balanced on geologic time by degassing of CO_2 by volcanic and metamorphic decarbonation. The regulation mechanism in this case is the rate of terrestrial weathering, which is limited by the flushing rate of liquid water over the rocks (runoff). Runoff is likely to be positively correlated with global mean temperature, which is in turn driven by atmospheric CO_2 concentration. So the atmospheric CO_2 concentration is controlled by the requirement for balance between the degassing source of CO_2 to the atmosphere and the igneous rock weathering sink. This mechanism is thought to act with

an e-folding time of 100-400 kyr. Models of the igneous rock weathering cycle and atmospheric CO₂ include [Walker et al., 1981; Berner et al., 1983; Berner, 1994].

These two models are not at all in conflict with each other, fundamentally because the pH equilibrium reactions of the carbonate buffer in sea water have two degrees of freedom (according to the phase rule $F = 2 + C - P$, where F is degrees of freedom, C is the number of components, here CO₂, CaCO₃, and H₂O, and P is the number of phases, here gas, solution, and crystalline CaCO₃). The CaCO₃ compensation mechanism in effect specifies the concentration of CO₃⁼ in the ocean, while the igneous rock mechanism specifies the CO₂ concentration in the atmosphere. Both of these demands can be met simultaneously, with no conflict, by varying independently the alkalinity and total CO₂ concentration of the oceans.

Our confidence in predictions of CO₂ uptake on geological time scales is badly marred by our inability to explain the observation that atmospheric CO₂ during glacial time was 30% lower than preanthropogenic Holocene values [Barnola et al., 1987]. The terrestrial biosphere was if anything smaller than today [Shackleton, 1978]; the wrong direction of change to explain the atmospheric data, leaving the ocean as the only conceivable source for the variations. A temperature related increase in CO₂ solubility was nearly offset by a salinity related solubility decrease, as ice sheets withdrew fresh water from the oceans. Candidate mechanisms include an increase in the biological pump which sequesters carbon in the deep sea [Sarmiento and Toggweiler, 1984] or a change in the pH balance of the entire ocean [Archer and Maier-Reimer, 1994; Sanyal et al., 1995]. In either case, changes in the biology and the circulation of the ocean must have been ultimately responsible, and until we understand how this coupling operated in the past, we will be unable to predict with any confidence how atmospheric CO₂ in the future will respond to changes in Earth's climate.

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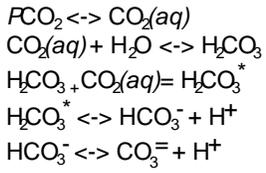
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Molecular Scale



K_0

K_1

K_2

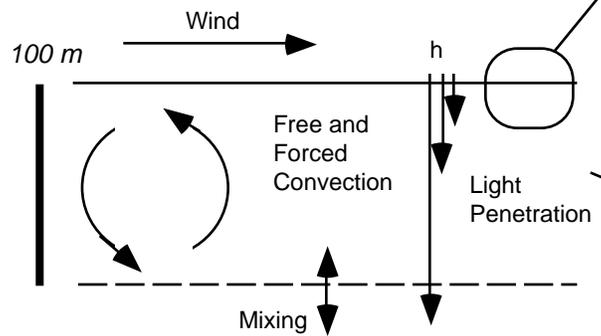
100 μm

CO_2
Gas Exchange

Boundary Layer

Turbulence

Bubbles



100 km

Fe

$\text{CO}_2 \rightarrow \text{Org C}$

$\text{NO}_3 + \text{PO}_4$

Global, 1000 years

CO_2

Water Mass Formation

Mixing

10,000 years

CaCO_3 Weathering

$\text{CO}_3 + \text{CO}_2 \leftrightarrow 2\text{HCO}_3^-$

CaCO_3 Burial

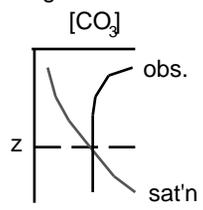


Figure 1

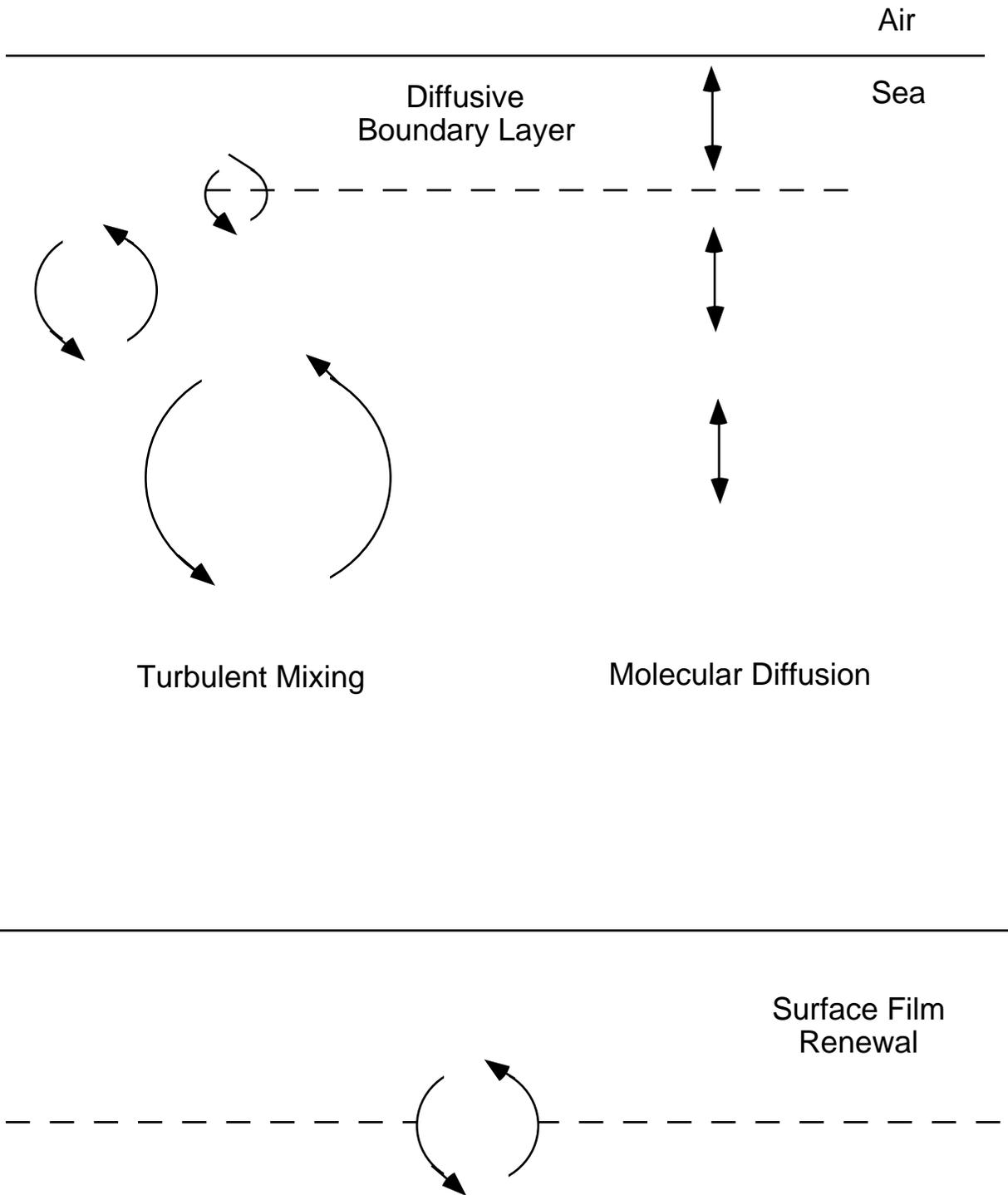


Figure 2