

6.10

Biological Fluxes in the Ocean and Atmospheric p_{CO_2}

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6.10.1 INTRODUCTION

The basic outlines for the carbon cycle in the ocean, as it is represented in ocean carbon cycle models, were summarized by Broecker and Peng (1982). Since then, ongoing field research has revised that picture, unearthing new degrees of freedom and sensitivities in the ocean carbon cycle, which may provide clues to changes in the behavior of the carbon cycle over the glacial cycles and deeper into geological time. These sensitivities include new ideas about the chemistry and cycling of phytoplankton nutrients such

as nitrate and iron, the physics of sinking organic matter, and the production and redissolution of phytoplankton companion minerals CaCO₃ and SiO₂, in the water column and in the sediment.

The carbon cycle is typically broken down into two components, both of which will be summarized here. The first is the biological pump, effecting the redistributing of biologically active elements like carbon, nitrogen, and silicon within the circulating waters of the ocean. The second is the ultimate removal of these elements by burial in sediments. These two components of the carbon cycle together control the mean concentrations of

many chemicals in the ocean, including ocean pH and the $p\text{CO}_2$ of the atmosphere.

This chapter overlaps considerably with the only two others from this Treatise I have had the pleasure to read: Chapters 6.04 and 6.19. My chapter is distinguished, I suppose, by the perspective of a geochemical ocean modeler, attempting to integrate new field observations into the context of the ocean control of the $p\text{CO}_2$ of the atmosphere.

6.10.2 CHEMICAL REARRANGEMENT OF THE WATERS OF THE OCEAN

6.10.2.1 The Organic Carbon Biological Pump

The cycling of dissolved carbon and associated chemicals (such as oxygen, nitrogen, and phosphorus) in the ocean is driven by the lives and deaths of phytoplankton. Sunlight is required as an energy source for photosynthesis, and is available in sufficient intensity only into the top 100 m or so of the ocean; the rest of the ocean is dark, or at least too dark to make a living harvesting energy from light. The net geochemical effect of photosynthesis in the ocean is to convert dissolved constituents into particles, pieces of solid material that can take leave of their parent fluid by sinking. As they do, they strip the surface waters of whichever component locally limits the growth of phytoplankton (typically nitrogen or iron), and carry the entire suite of biologically useful elements to depth.

As the particles sink, they degrade in the water column, or they reach the seafloor, to degrade within the sediments or to exit the ocean by burial. This combination of removal at the sea surface and addition at depth maintains higher concentrations of bioactive elements and compounds at depth in the ocean than at the surface. The shape of a depth profile of dissolved nitrogen in the form of nitrate, a limiting “fertilizer” or nutrient to phytoplankton, resembles those of other bioactive compounds, including C, PO_4 , Si, Fe, and Cd. This process, fundamental to the ocean carbon cycle, has been called the biological pump (Broecker and Peng, 1982; see Chapter 6.04).

6.10.2.1.1 Nutrient limitation and new production

Phytoplankton in surface waters, upon completion of their earthly sojourns, suffer one of two fates. Either they are degraded and consumed within the surface waters of the ocean, or they may sink to the deep sea. On average, the removal of dissolved nutrients from the surface zone to depth must be balanced by mixing up of dissolved nutrients from below, or other sources

such as deposition from the atmosphere (as in the case of iron), or local production (as in nitrogen fixation). Traditionally, oceanographers have distinguished “new” versus “recycled” primary production using the different forms of biologically available nitrogen (Eppley and Peterson, 1979). When phytoplankton degrade, their nitrogen is released in the reduced form, as ammonia, which corresponds to nitrogen’s chemical oxidation state in proteins and DNA. Ammonia released within the euphotic zone is quickly assimilated by the next generation of phytoplankton. Ammonia released below the euphotic zone escapes this fate, because the darkness precludes photosynthesis. Instead, this ammonia gets oxidized by bacteria to nitrate. Therefore, most of the biologically available nitrogen in deep waters of the ocean is in the form of nitrate. Using this dichotomy, oceanographers can distinguish between new production, supported by upwelling from below, as the uptake of isotopically labeled nitrate, versus recycled production as the uptake of isotopically labeled ammonia. The ratio of new production to production has been called the f -ratio by biological oceanographers (Dugdale and Goering, 1967). Values of the f -ratio range from 10% to 20% in warm, oligotrophic, low-nutrient open-ocean conditions, to 50% in blooms and near-shore conditions (Eppley and Peterson, 1979). However, the apparent correlation between f -ratio and primary production may be an artifact of differences in sea-surface temperature (Laws *et al.*, 2000).

6.10.2.1.2 Iron as a limiting micronutrient

Martin and Fitzwater (1988) originally proposed that the availability of the micronutrient iron may be limiting phytoplankton production in remote parts of the world ocean. This proposal was convincingly proven by a series of open-ocean fertilization experiments, in the equatorial Pacific (Coale *et al.*, 1996; Martin *et al.*, 1994) and in the Southern Ocean (Boyd *et al.*, 2000). Although photosynthesis rates and chlorophyll concentrations increased significantly in all cases, the iron fertilization was less effective at stimulating carbon sinking to depth, especially in the Southern Ocean, where the added iron recycled in the euphotic zone until it dispersed by lateral mixing some months later (Abraham *et al.*, 2000). Several attempts have been made to model the iron cycle in the ocean (Archer and Johnson, 2000; Fung *et al.*, 2000; Lefevre and Watson, 1999). Although dust deposition delivers more iron to the surface of the ocean (Fung *et al.*, 2000), uncertainty remains about the availability of that iron to the phytoplankton. It has been argued that dust deposition may play only a minor role in regulating

phytoplankton abundance (Archer and Johnson, 2000; Lefevre and Watson, 1999). The North Pacific Ocean, in particular, appears to be a problem area, with high deposition of dust (Duce and Tindale, 1991) failing to drive depletion of sea-surface nutrients.

6.10.2.1.3 Measuring carbon export

In the steady state (that is to say, on a long enough time average), the uptake of new nutrients, nitrate for example, must be balanced by the removal of nutrients in exported organic matter. Oceanographers have defined a quotient called the *e*-ratio, describing the export efficiency of euphotic zone organic matter, export production/gross production. On long enough timescales, the *e*-ratio must equal the *f*-ratio. In this way, the biological pump acts to limit the productivity of the ocean, pacing it according to the overturning timescale of the ocean circulation.

Sediment traps and sinking particles. The measurement of organic carbon export from the surface ocean has remained problematic over the decades. The workhorse of the oceanographic community for determining sinking particulate fluxes is the moored sediment trap. Sediment traps are plagued by biases from hydrodynamics and from “swimmers,” which actively enter the open collection cups of the traps to feed, either consuming our signal or perhaps perishing in the preservative and adding to it (Hedges *et al.*, 1993). Swimmers are operationally excluded by picking them out individually. Hydrodynamic over- or under-trapping can be detected by comparing the delivery rate of radiogenic thorium with its known source rate in the water column above (Buesseler, 1991). In general, deeper traps (below 1,500 m) are found to be unbiased by hydrodynamic trapping errors, whereas shallower traps may undersample the true sinking flux by a factor of 2 or more, on average (Yu *et al.*, 2001). Thus, historical estimates of euphotic zone carbon export based on sediment traps must be evaluated with caution (Berger, 1989; Martin *et al.*, 1987).

Export of DOC. Another recent revision of our understanding of carbon export has been the generation of dissolved organic matter (DOM). Dissolved matter is unable to physically separate itself from its parent fluid, the way particulate organic matter (POM) does by sinking. However, significant gradients in the concentration of DOC exist in the ocean, so fluid transport through the steady-state DOC concentration field represents the export of significant quantities of organic matter in the dissolved form. Concentrations of DOC in the deep ocean range fall in a relatively low and narrow range, 37–42 μM . DOC reaches higher concentrations in the surface ocean, up to 80–100 μM in oligotrophic surface

waters. Vertical convection thus drives export of sea-surface DOC to depth. Upwelling brings low-DOC water to the sea surface, where photosynthesis begins the production of DOC. This DOC can be exported laterally or back to the ocean interior. On a global mean, DOC export accounts for less than half of the export of organic matter from the surface ocean, and only a tiny fraction to the deep sea (Yamanaka and Tujika, 1997).

Nutrient supply. In spite of the developments of sediment trap calibration by radiogenic isotopes and export of organic matter in the suspended or dissolved states, problems remain in balancing carbon and nutrient export against supply by physical fluid transport. This problem is most acute in the subtropical gyres, intensely sampled in two time-series JGOFS stations: one near Bermuda (BATS) and one near Hawaii (HOT). Net vertical motions in the upper ocean are determined by the divergence of surface currents, driven by friction with the wind. The direction and intensity of the resulting vertical motion is determined by the curl of the wind stress, which leads to net upwelling in the subpolar gyres, carrying nutrients vertically into the euphotic zone, but downward in the subtropical gyres, supplying no nutrients for photosynthesis at all (Peixoto and Oort, 1992). On a smaller spatial scale, eddies and fronts lead to vertical motion and offsets in the depth of the constant-density (isopycnal) surfaces (Mahadevan and Archer, 2000; McGillicuddy and Robinson, 1997; Oschlies and Koeve, 2000). These mesoscale motions may carry nutrients vertically into the euphotic zone, particularly in Bermuda where the proximity to the Gulf Stream generates high levels of mesoscale motions. Sea-surface helium concentrations (Jenkins, 1988) seem to support the idea of vertical transport by physical fluid motions. At Hawaii in particular, nitrogen fixation, the production of biologically available nitrogen in the form of ammonia from the generally inert but ubiquitous N_2 gas, is thought to supply a large fraction of the required nitrogen (Karl *et al.*, 1997). Nutrients may be mined from deeper waters and actively transported into the euphotic zone by diatoms (Villareal *et al.*, 1999).

6.10.2.2 CaCO_3 Production and Export

6.10.2.2.1 Calcite and aragonite

Several mineral phases are produced by phytoplankton and exported to depth in the ocean, associated with and analogous to the production and export of organic matter. First among these is CaCO_3 , comprised of two mineral phases: calcite and the more soluble aragonite (Milliman, 1974; Mucci, 1983). The solubility of calcite depends also on the concentration of magnesium; higher

magnesium leads to higher solubility (Plath *et al.*, 1980). The dominant mineral in deep-sea sediments is low-magnesium calcite, the least soluble form. Calcite is thermodynamically stable in the surface ocean in most parts of the world, and down to several kilometers depth (Broecker and Peng, 1982; Millero, 1982).

6.10.2.2.2 Temperature and $[\text{CO}_3^{2-}]$ regulation of CaCO_3 production

In general, CaCO_3 sinking fluxes in the deep sea tend to correlate with fluxes of organic matter (Dymond and Lyle, 1993; Klaas and Archer, 2002; Milliman, 1993; Tsunogai and Noriki, 1991). However, CaCO_3 production decreases dramatically when sea-surface temperatures drop below $\sim 10^\circ\text{C}$ (Honjo *et al.*, 2000; Wefer *et al.*, 1990). This could be because CO_2 gas solubility increases with decreasing temperature, driving CO_3^{2-} to a lower concentration by pH equilibrium chemistry. Laboratory and controlled system growth experiments have observed a correlation between water $[\text{CO}_3^{2-}]$ and calcification rates in coccolithophorids (Riebesell *et al.*, 2000) and in corals (Langdon *et al.*, 2000). Shells of foraminifera tend to be thicker from higher $[\text{CO}_3^{2-}]$ (warmer) source waters (Barker and Elderfield, 2002). However, in deep traps there is no significant correlation between the rain ratio and sea-surface temperature, once SST rises above the critical 10°C level (Klaas and Archer, 2002).

6.10.2.2.3 Latitudinal distribution discrepancy

A discrepancy exists between satellite observations of calcification by coccolithophorids and geochemical estimates of the spatial distribution of calcification rate. Massive blooms of coccolithophorids are seen from space as the organisms shed their CaCO_3 plates (coccoliths), which scatter light in the water and, therefore, appear light from space. These blooms are found in high latitudes, especially in the North Atlantic (Brown and Yoder, 1994). In contrast, geochemical estimates of calcification, such as the sources of alkalinity in the water column of the ocean (Feely *et al.*, submitted; Sarmiento *et al.*, submitted), and the distribution of CaCO_3 on the seafloor (Archer, 1996a) tend to reveal a world where total calcification is most intense in lower latitudes.

6.10.2.2.4 Organic C/ CaCO_3 production ratio

The classical estimate, 4 mol of organic matter per mole of CaCO_3 , was derived from the relative

deep-surface gradients in alkalinity (mostly from dissolved CaCO_3) and some proxy for organic carbon degradation, such as nitrate or total CO_2 corrected for CaCO_3 (Li *et al.*, 1969). However, this estimate is sensitive to the depth scale of particle degradation in the water column. Organic matter degrades more quickly than CaCO_3 dissolves, and so much of the organic matter produced may degrade in the top few hundred meters of the water column, where its impact on the abyss/surface chemical gradients will be smaller than if it degraded in the abyss itself. A recent analysis of the 100–200 m gradients in phosphate and alkalinity from WOCE data seems to indicate a production ratio of 10 or more (Sarmiento *et al.*, submitted). Reconciling the shallow- and whole-ocean gradients of soft-tissue and CaCO_3 pump products will require some knowledge of the depth to which these components both sink.

6.10.2.3 SiO_2 Production and Export

The second most important mineral phase of the biological pump is biogenic opal, SiO_2 . Opal shells are produced by diatoms, a marine alga, and by radiolarians, a heterotrophic protist. On a large scale, production of SiO_2 is limited by the availability of dissolved silica, in the form of silicic acid, H_4SiO_4 .

In general, diatoms appear to be adapted to turbulent, unstable conditions (Margalef, 1978), and changes in water column turbulence associated with climate may be responsible for decadal-timescale changes in the relative production rates of diatoms and coccolithophorids in the North Atlantic (Antia *et al.*, 2001). The dynamics of diatom growth are documented most clearly in the North Atlantic, where deep wintertime mixing limits the growth of phytoplankton until springtime stratification and the spring bloom. The sequence of events that follows is that diatoms bloom most quickly, stripping the surface ocean of dissolved silica, and partially depleting it of the soft-tissue nutrients nitrate and phosphate (Lochte *et al.*, 1993). The same sequence is seen in the Southern Ocean, where diatoms apparently deplete surface water of H_4SiO_4 before the elimination of dissolved nitrate and phosphate (Levitus, 1982; Levitus *et al.*, 1993). Diatoms are found in coastal waters where nutrients are replete (Nelson *et al.*, 1995), and in the blooming plume of iron fertilization experiments (Coale *et al.*, 1996). Diatom export from the surface ocean has been correlated with organic carbon export, and it has been proposed that a few large diatoms might, in fact, dominate the export of organic carbon (Goldman, 1987). (Iron may play another role in the silica cycle, as it has been shown that

the diatoms that grow in iron-limited Southern Ocean conditions carry more silica per mole of organic carbon or nitrogen (Franck *et al.*, 2000; Hutchins and Bruland, 1998; Takeda, 1998.)

These considerations have led to a model paradigm wherein abundant supply of silica might stimulate the diatoms, depleting available sea-surface nitrate and thus starving out the coccolithophorids who would produce CaCO_3 . Honjo refers to the Atlantic as a “carbonate ocean” and the Pacific as a “silicate” ocean based on a comparison of Atlantic and Pacific CaCO_3 and SiO_2 sinking fluxes (Honjo, 1996). Models of ocean biogeochemistry (Archer *et al.*, 2000b; Heinze *et al.*, 1999; Matsumoto *et al.*, in press) tend to include some silica dependence for CaCO_3 production rates, based on the idea that diatoms outcompete coccolithophorids given sufficient dissolved silica. In deep sediment traps, however, the sinking flux of silica tends to correlate positively with CaCO_3 flux, rather than negatively as one might expect if silica inhibits CaCO_3 production (Figure 1; Klaas and Archer, 2002).

6.10.2.4 Geochemical Signature of the Biological Pump

The intensity of the biological pump signature on the chemistry of the ocean depends, of course, on the total rate at which material is exported from the surface euphotic zone, but it also depends on how deep it sinks before it degrades back to dissolved constituents. This is because shallower

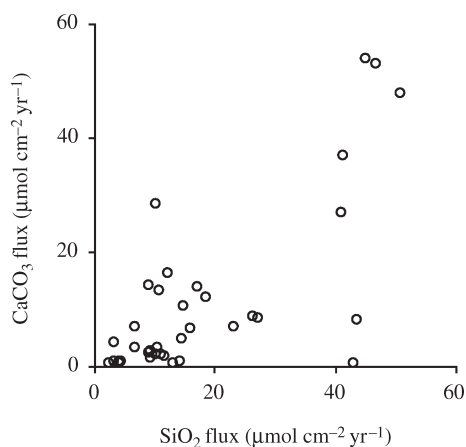


Figure 1 Sediment trap sinking fluxes of CaCO_3 plotted against SiO_2 . The point of this plot is that high fluxes of SiO_2 tend to correlate with high fluxes of CaCO_3 , except in regions of cold SST (sources Brewer *et al.*, 1980; Deuser, 1986; Dymond and Collier, 1988; Dymond and Lyle, 1993; Honjo, 1990; Honjo *et al.*, 1982, 1998; Ittekkot *et al.*, 1991; Martin *et al.*, 1987; Milliman, 1993; Noriki and Tsunogai, 1986; Pilskaln and Honjo, 1987; Tsunogai and Noriki, 1991; Wefer *et al.*, 1982, 1988).

subsurface water masses return to the sea surface more quickly than the deepest waters of the ocean. Carbon and nutrients deposited in the shallow thermocline will, therefore, have a smaller impact on the surface/deep fractionation of the ocean than abyssal redissolution. The mineral phases calcite and opal, and to a lesser extent aragonite, tend to dissolve more deeply in the water column.

6.10.2.4.1 Organic carbon redissolution depth

Martin *et al.* (1987) published an initial formulation of a redissolution curve for organic carbon, which has extremely been influential in the ocean modeling community. Their formulation was based on sediment trap data from the North East Pacific Ocean (the VERTEX program) and described the sinking flux of organic matter as a power law:

$$\text{Flux}(z) = \text{Flux}(100 \text{ m})(z/100)^{-0.858}$$

Subsequent analysis has revealed spatial heterogeneity in the organic carbon sinking flux (Lutz *et al.*, in press). In general, the fluxes in the interior of the ocean are less variable than export fluxes determined from the surface ocean; in other words, more productive regions tend to be relatively less efficient at sinking to depth than less productive regions. Other analyses have focused on the role of heavier materials, such as CaCO_3 , SiO_2 , and lithogenic clays, as ballast, in transporting organic matter to depth (Armstrong *et al.*, 2002; Klaas and Archer, 2002) (see below).

6.10.2.4.2 CaCO_3 water column redissolution

A significant fraction of the CaCO_3 produced in the surface ocean reaches the seafloor, to dissolve or accumulate in the sediments. The traditional view has always been that water column CaCO_3 dissolution is relatively insignificant, consistent with its thermodynamic stability. Sediment trap results suggest that CaCO_3 survives relatively intact its trip through the water column of the ocean. Measured fluxes of CaCO_3 on multiple sediment traps at different depths on a single mooring show no clear trend toward decreasing CaCO_3 flux with depth (Figure 2). In addition, visual examination of CaCO_3 shells captured in sediment traps does not reveal any overwhelmingly obvious signs of dissolution within the water column (Honjo, 1976). However, three lines of evidence suggest that, in spite of sediment trap data, a considerable fraction of the CaCO_3 produced in the upper ocean dissolves as it sinks through the water column.

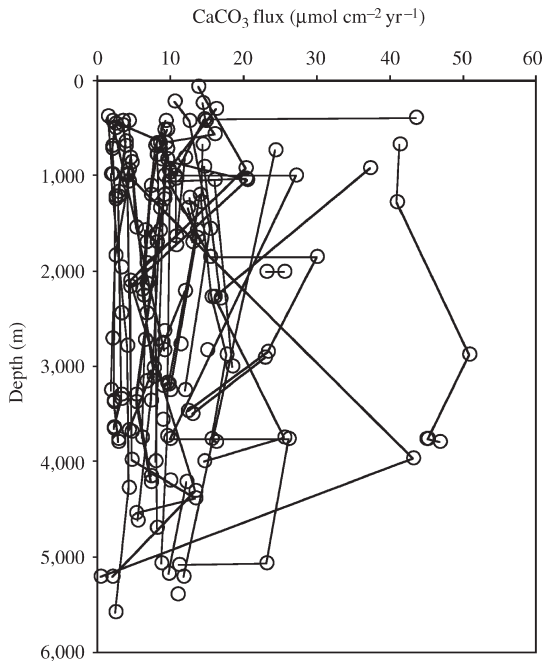


Figure 2 Sediment trap sinking fluxes of CaCO_3 . Multiple traps which share a common mooring are connected with lines. The point of this messy plot is that the sinking flux of CaCO_3 does not appear to decrease with depth in response to water column dissolution (sources Brewer *et al.*, 1980; Deuser, 1986; Dymond and Collier, 1988; Dymond and Lyle, 1993; Honjo, 1990; Honjo *et al.*, 1982, 1998; Ittekkot *et al.*, 1991; Martin *et al.*, 1987; Milliman, 1993; Noriki and Tsunogai, 1986; Pilskaln and Honjo, 1987; Tsunogai and Noriki, 1991; Wefer *et al.*, 1982, 1988).

Chemical signature. One such line of evidence arises from the distribution of alkalinity in the water column. Using Geosecs data, Fiadiero (1980) concluded that the alkalinity distribution in the deep Pacific Ocean could only be explained by water column dissolution of CaCO_3 . More recently, the WOCE program global ocean survey has provided us with a new, much more extensive and higher-quality global survey of ocean chemistry. Feely *et al.* (submitted) have used these data to essentially confirm the Fiadiero findings. In the Pacific Ocean, they conclude that up to 75% of the CaCO_3 production flux could be degrading in the water column of the ocean. They find two hot zones of CaCO_3 dissolution, one correlating with the aragonite saturation horizon in the depth range of 1–2 km, comprising approximately half of the total dissolution flux, and another source in the depth range of 2–5 km. The deep alkalinity source is comparable to calculated rates of sedimentary dissolution (Archer, 1996b), which may be difficult to distinguish from dissolution in the water column. Addressing a different question, that of the location of diapycnal mixing in the

ocean, Munk and Wunsch (1998) showed that boundary mixing, advected into the ocean interior along isopycnal surfaces, is indistinguishable from more diffuse mixing throughout the interior. We may presume that the same reasoning applies to sources of alkalinity.

CaCO_3 budgets. Another argument comes from comparison of measured calcification rates in the surface ocean with rates of CaCO_3 accumulation in sediments. Milliman *et al.* (2000) make a strong case for dissolution in the water column above the saturation horizon for CaCO_3 , based on a comparison of euphotic zone calcification rate estimates (Balch *et al.*, 2000; Balch and Kilpatrick, 1996) and sediment accumulation rates in regions where the overlying water is supersaturated with respect to calcite. Ocean carbon cycle models typically impose a significant water column dissolution fraction of CaCO_3 rain (Archer and Maier-Reimer, 1994; Orr *et al.*, 2001). The mechanism for this dissolution is unclear. The Feely results seem to indicate that the flux of aragonite in the open ocean may be higher than had previously been assumed. However, they also find a significant dissolution flux uncorrelated with the aragonite saturation horizon, which is presumably calcite. It has been proposed that calcite might be dissolving in the guts of zooplankton (Jansen and Wolf-Gladrow, 2001), or within acidic microenvironments inside marine snow.

Planktonic shell thickness. A third indicator of CaCO_3 dissolution within the water column comes from a more subtle examination of the shells of foraminifera, the thickness of their walls in fact. This technique was pioneered by Lohmann (1995) and further pursued by Broecker and Clark (2001). What they find is that the shell thickness of forams increases throughout the first kilometer of the water column, and decreases below ~3 km, representative of dissolution within the water column.

6.10.2.4.3 SiO_2 sinking and redissolution

The dissolution of SiO_2 as it sinks through the water column is another ongoing topic of research and discussion. The Southern Ocean is a crucial depocenter for SiO_2 in deep-sea sediments, in the form of a band of high-opal sediments known as the opal belt. In the view of Nelson *et al.* (1995), the intensity of opal burial in this location is not due to high rates of opal production, but rather a peculiar high efficiency of opal transfer to the seafloor in this region. Gnanadesikan *et al.* (1999) point to extreme temperature sensitivity of opal dissolution kinetics, and find that an ocean circulation/silica cycle model is better able to reproduce the observed distribution of opal when this dependence is included. Opal dissolves faster

in warmer water, in part explaining the seafloor transport efficiency within the cold Southern Ocean waters. An additional factor may be the episodic nature of primary production, which precludes a standing crop of grazers.

6.10.2.4.4 *The ballast model for sinking particles*

One of the more robust features of the sediment trap data set is the constancy of the “organic carbon”: CaCO_3 rain ratio in the deep sea. Although the absolute fluxes vary widely by area and time, the ratio of their fluxes (mol : mol) seems quite stable in the range of 0.5–1.0. One explanation for this observation, which has significant implications for the ability of the ocean to change its pH by changing the rain ratio, is called the ballast model (Armstrong *et al.*, 2002; Klaas and Archer, 2002). The density of organic matter is similar enough to that of water that organic matter, by itself, would not sink at all. Armstrong *et al.* (2002) did a regression of sediment trap from the equatorial Pacific and found that organic carbon sinking fluxes could be described remarkably well by combining a ballasted flux (a simple function of the ballast flux at depth times some uniform “carrying coefficient”) with a “Free POC” component, which degrades over a 600 m depth scale in the surface ocean. Klaas and Archer (2002) extended this analysis to the global sediment trap dataset, and distinguished three forms of ballast: CaCO_3 , biogenic silica, and lithogenic material, mainly terrestrial clays. They found that the carrying coefficient (grams organic carbon per gram ballast) for CaCO_3 was twice as high as for the other phases, a result which is qualitatively consistent with the greater density of CaCO_3 . When the global fluxes of the three ballast phases are multiplied by their carrying coefficients, they found that 80% of the organic matter flux to the seafloor was carried by CaCO_3 . This explains the relative constancy of the rain ratio in the deep sea, and it also seems to limit the ability of the ocean carbon cycle to vary this rain ratio by changing, e.g., the relative productivities of diatoms and coccolithophorids. Some ecological change in the surface ocean, impacting the sinking flux of CaCO_3 , would merely change the flux of organic matter in concert with the changing CaCO_3 flux.

This idea is somewhat at odds with the common observation from near the sea surface, either from shallow sediment traps or from phytoplankton growth studies, that diatoms dominate the export of carbon from the surface ocean (Goldman, 1987). However, there is room in the “Free POC” component of Armstrong *et al.* (2002) for diatoms

and carbon export. Perhaps the particles, produced in the organic carbon to CaCO_3 ratio of 4–10, are unable to sink very quickly until organic matter degradation decreases the organic ratio to the 0.5–1.0 range seen in the deep sea, at which point the express elevator takes them to the seafloor.

6.10.2.5 Direct Atmospheric p_{CO_2} Signature of the Biological Pump

6.10.2.5.1 *Organic carbon pump*

The biological pump has a first-order impact on the CO_2 concentration of the atmosphere, and therefore on the climate of the earth. The removal of dissolved CO_2 from surface water during photosynthesis decreases the equilibrium partial pressure of CO_2 in the overlying atmosphere (this quantity is defined as the p_{CO_2} of the surface water). Changes in the biological pump in some form may be responsible for the glacial/interglacial p_{CO_2} cycles (Petit *et al.*, 1999). The strongest direct impact of the biological pump on p_{CO_2} is driven by the depletion of surface waters of dissolved CO_2 by the production of organic carbon (the “soft-tissue” pump).

Timescale. The timescale for sea-surface depletion of CO_2 to affect atmospheric p_{CO_2} is that of ocean rearrangement and atmosphere/ocean gas exchange equilibration: on the order of hundreds of years. Looking into the past for biological pump-driven changes in the p_{CO_2} of the atmosphere, we would look for changes that occur on this timescale (unless the efficiency of the biological pump itself is changing more slowly than that).

Model sensitivity. One of the more recent surprise was the discovery that the sensitivity of atmospheric p_{CO_2} to the biological pump is quite model specific (Archer *et al.*, 2000a; Bacastow, 1996; Broecker *et al.*, 1999). In particular, box models of ocean chemistry are more sensitive to the efficiency of the biological pump than are ocean models based on a continuum representation of circulation and chemistry, most notably the general circulation models (GCMs) (Figure 3). The horizontal axis of this plot is the inventory of the dissolved nutrient phosphorus, in the form of PO_4^{3-} , within the top 50 m of the world ocean. The sea-surface phosphorus inventory depends on a balance between delivery by upwelling and mixing of phosphorus from below, and removal as sinking biogenic particles.

The reason for the discrepancy is that most of the available sea-surface nutrients (which could be depleted were the phytoplankton more efficient or the circulation less energetic) are to be found in the high latitudes, notably in the Southern Ocean. A startling and seminal finding in the 1980s was

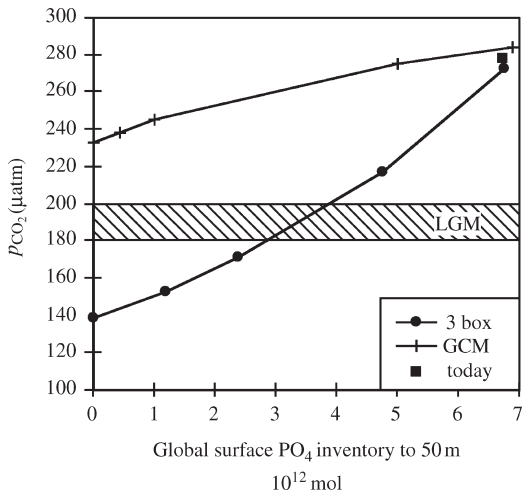


Figure 3 Steady-state model atmospheric p_{CO_2} response to the efficiency of the biological pump, as indicated by the inventory of PO_4^{3-} in the top 50 m of the ocean (source Archer *et al.*, 2000a).

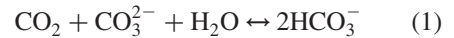
that changes to the nutrient concentration in the high-latitude surface ocean in a simple type of ocean chemistry models called box models have a disproportionately large impact on the steady-state CO_2 concentration of the atmosphere (Knox and McElroy, 1984; Sarmiento and Toggweiler, 1984; Siegenthaler and Wenk, 1984). The low-latitude surface ocean is conversely less effective at determining the p_{CO_2} of the atmosphere.

A box model is comprised of some small number of ocean reservoirs, typically three to a few tens. The chemical characteristics of the seawater with each box is taken to be homogeneous (well mixed). Water flow in the ocean is described as fluxes between the boxes; given in units of Sv (Sverdrups, 10^6 m s^{-1}), these typically range to values less than 100 Sv. A flow between two boxes carries with it the chemical signature of the source box; this numerical technique is called “upstream” differencing. Gas exchange acts to pull sea-surface gas concentrations, such as CO_2 and $^{14}\text{CO}_2$, toward equilibrium values with the atmosphere. The fluxes imposed between boxes are determined by tuning various tracers, usually ^{14}C , toward observed values.

More recently, however, it was found that GCMs have a greater sensitivity to low-latitude forcing (Bacastow, 1996; Broecker *et al.*, 1999), and therefore lower sensitivity to high-latitude forcing (Archer *et al.*, 2000a). A GCM aims to represent the chemical and physical fields of the ocean in a continuous way, sampled on a finite difference grid (discretized). Flows across the grid are determined by balancing the forces of inertia, gravity, stress, friction, and the rotation of the Earth. Because atmospheric p_{CO_2} values above GCMs are less sensitive to the high-latitude sea

surface than it is above box models, atmospheric p_{CO_2} is also less sensitive to the soft-tissue pump, variations in which are focused in the high latitudes by the availability of nutrients. Conversely, the effects of the CaCO_3 pump seem to be stronger in GCMs than in box models (Matsumoto *et al.*, in press), perhaps because CaCO_3 production occurs predominantly in warm surface waters. The reasons for the discrepancy are still unclear. Archer *et al.* (2000a) pointed to vertical diffusion, which dominates the residence time of water in the surface layers of the ocean. Toggweiler (2003) points to the extent of equilibration of surface waters, in particular in the high latitudes. Until the discrepancy between box models and GCMs is resolved, it is difficult to predict the sensitivity of the real ocean to changes in the soft-tissue biological pump.

CaCO₃ pump. The CaCO_3 component of the biological pump also affects the p_{CO_2} of surface waters and therefore of the atmosphere. CaCO_3 production depletes the parent water of dissolved carbonate ion, CO_3^{2-} , which actually drives the dissolved CO_2 concentration up by the reaction



The CaCO_3 pump therefore acts to increase the p_{CO_2} of the atmosphere, counteracting, to a small extent, the effect of the soft-tissue pump. This seeming paradoxical behavior is a result of the pH chemistry of the carbonate buffer system. Dissolved CO_2 , in its hydrated form H_2CO_3 , is an acid, and it exists in buffer chemistry equilibrium with carbonate ion, CO_3^{2-} , the base salt form of H_2CO_3 . The removal of CO_3^{2-} by calcification acidifies the parent seawater, shifting the carbonate buffer system equilibrium toward higher CO_2 concentration. A converse of this process is the dissolution of CaCO_3 on the seafloor or in coral reefs in response to the invasion of fossil fuel CO_2 into the ocean (Archer *et al.*, 1989b, 1997; Walker and Kasting, 1992). One might naively expect coral reefs to grow larger with the increased availability of carbon to build them from, but the pH equilibrium chemistry overrides the absolute abundance of dissolved carbon.

6.10.3 CONTROLS OF MEAN OCEAN CHEMISTRY

The mean concentrations of constituents of seawater are determined not by simple distillation of river water but by their various mechanisms of removal from the ocean. The dominant cation in river water, e.g., is calcium from weathering of carbonate and silicate rocks, whereas the dominant cation in the ocean is sodium, because there are no efficient loss mechanisms for sodium analogous to the formation of CaCO_3 as a loss

mechanism for calcium (Holland, 1978). The cycle of CaCO_3 in the ocean is of particular interest, as it determines the pH of the ocean and the p_{CO_2} of the atmosphere, on timescales of thousands to hundreds of thousands of years. Organic matter burial can be considered a net source of oxygen to the atmosphere, and mechanisms for regulating atmospheric O_2 focus on the mechanics of burying organic matter in sediments (Cappellen and Ingall, 1996; Walker, 1977).

The redissolution or burial of organic matter in sediments is a decision that is made jointly by the physics of diffusion, chemistry of organic matter oxidation, and the biology which mediates the chemical reactions. The concentration profile of a solute in sediment pore water is governed by the diffusion equation, which can be written most simply as

$$\frac{\partial C}{\partial t} = 0 = \frac{\partial}{\partial z} D_M \frac{\partial C}{\partial z} + j_C$$

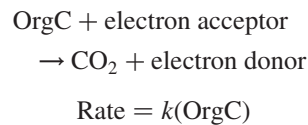
where C is a solute concentration, D_M is a molecular diffusion coefficient, and j_C is a production or consumption rate. When applied to the distribution of dissolved oxygen, this expression results in a generic oxygen profile within the sediments (e.g., Figure 4(a)). At any depth in the sediments, the downward diffusive flux of oxygen is balanced by the integrated consumption below that depth. When applied to the concentration of a dissolution product such as H_4SiO_4 or CO_3^{2-} , the diffusion equation results in a generic profile as illustrated in Figure 4(b). With depth, the pore waters become increasingly isolated from diffusive contact with the overlying water, and the concentration of the solute approaches

equilibrium with the solid phase. The chemistry of the overlying water serves as an upper boundary condition for this equation.

6.10.3.1.1 Controls on organic matter burial

Hypsometry. Globally, the burial of organic matter in sediments is accomplished largely within a relatively small area of the seafloor, in coastal waters of the continental shelf and slope. There are several reasons for this. First, rates of primary production tend to be higher in coastal waters, in part because of coastal upwelling, and in part because of riverine and recycling sources of nutrients such as iron (Johnson *et al.*, 2001). Accumulation rates of abiotic material such as clay minerals are orders of magnitude higher in near-shore sediments than in the abyssal ocean (Middelburg *et al.*, 1997; Tromp *et al.*, 1995). This tends to promote organic carbon burial. Second, the efficiency of organic matter transfer to the sediments is higher in coastal waters. The water column itself is thinner, minimizing degradation of sinking material. Also, coastal phytoplankton themselves tend to be larger than their pelagic cousins, increasing their export efficiency (see Chapter 6.04). The highest rates of primary production tend to be found on continental shelves or just along the shelf/slope break, where coastal upwelling is manifested most strongly. Results of the SEEP program indicate that most of the organic matter produced on the slope respire there (Biscaye *et al.*, 1994). However, organic carbon concentrations in sandy shelf sediments are often rather low. Measured sediment respiration rates often reach a maximum somewhat further offshore, in finer-grained continental slope sediments that deposit in this lower-energy setting (Jahnke *et al.*, 1990). Although carbon export from the shelf to the slope may be a negligible term in the shelf carbon budget, it is by no means trivial to the budget of the slope, analogous to crumbs from the high table.

Degradation rate kinetics. Because most of the chemical and physical processes that control organic matter degradation are determined by biology, most of them are determined for modeling purposes empirically. The first order of business is a rate constant for the degradation reaction itself:



where k is the rate constant, in units of inverse time. It has been found that degradation rates are independent of the concentration of the electron acceptor (e.g., O_2) until the concentration of O_2 reaches some critical low level ($\sim \mu\text{M}$).

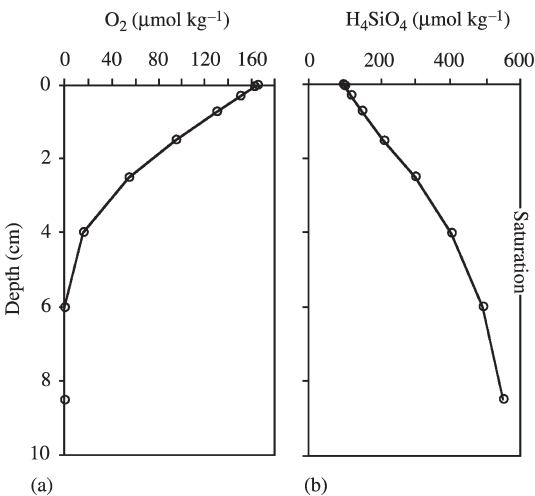


Figure 4 Model profiles of (a) O_2 and (b) H_4SiO_4 in surface sediments. From the Muds model (Archer *et al.*, 2001).

This pseudo-zero-order dependence is called Monod kinetics (Devol, 1978). These kinetic rate formulations become important if the rate constants for organic degradation differ for different electron acceptors. Oxidic degradation, in particular, appears to be faster than sulfate degradation, but it is confined to the upper oxic zone of the sediment (Figure 5).

Rate constants for organic degradation can be estimated in the field from pore-water data (e.g., high-resolution microelectrode oxygen profiles (Hales *et al.* 1993)) or from laboratory incubations (for sulfate respiration in particular, Weber *et al.* (2001)). These rate constants vary widely, with values orders of magnitude higher in shelf and slope than in abyssal sediments. The rate constants have been parametrized as a function of total sediment accumulation rate (Middelburg *et al.*, 1997; Tromp *et al.*, 1995), organic carbon rain (Archer *et al.*, 2001), or the mean age of the sedimentary organic matter (Emerson, 1985). In fact, there is not simply one homogeneous kind of organic matter in sediments, but rather modeling and field studies are able to resolve at least two types of organic matter with degradation kinetics differing by several orders of magnitude (Berner, 1980).

Bioturbation. Other biologically mediated relevant processes include bioturbation, the physical mixing of solid sediment, and pore-water irrigation, an enhancement of solute transport by benthic fauna. Bioturbation is so ubiquitous that its absence in sedimentary deposits (indicated by fine laminae) is taken as strong evidence of anoxia during deposition. In general, the rate of bioturbation scales similarly to that of organic carbon respiration, increasing in shallower water. The depth of bioturbation appears to be much less variable (Boudreau, 1994, 1998). The bioturbation rate appears to decrease smoothly with depth (Archer *et al.*, 2001; Martin and Sayles, 1990), but

can also be treated as a constant within the bioturbated layer. To make things even more complicated, bioturbation rates derived from radionuclides seem to depend on the lifetime of the radionuclide, with faster mixing for the shorter-lived tracer (Fornes *et al.*, 1999; Smith *et al.*, 1993).

Pore-water irrigation. Pore-water irrigation is the exchange of solute chemistry with overlying water resulting from the action of benthic macrofauna, who pump overlying water through their burrows within the sediment. Rates of irrigation can be determined by comparing total oxygen uptake rates, from benthic flux chambers, with diffusive uptake rates, from microelectrodes, which are assumed to be independent of any irrigation influence. In general, pore-water irrigation becomes negligible, or at least unmeasurable, in abyssal sediments (Archer and Devol, 1992; Archer *et al.*, 2001; Reimers and Smith, 1986).

Oxygen. A traditional view of oxygen dependence on organic carbon concentrations of sediments was challenged in the 1980s by laboratory measurements of the degradation of fresh phytoplankton using either O_2 or SO_4^{2-} as an electron acceptor (Henrichs and Reeburgh, 1987). However, degradation rate constants derived from field data appear to diverge as they slow down in the deep (Tromp *et al.*, 1995), to values that differ by five or six orders of magnitude (Figure 5). Calvert and Pederson (1993) compared organic carbon concentrations between oxic and anoxic (Black Sea) settings and concluded that oxygen plays little part in organic carbon preservation. However, Archer *et al.* (2001) summarized data from a wide variety of locations, and found dependence both on oxygen concentration and on organic carbon rain to the seafloor.

Protection by physical adsorption. A third viewpoint comes from the observation that the organic matter concentration of sediment appears

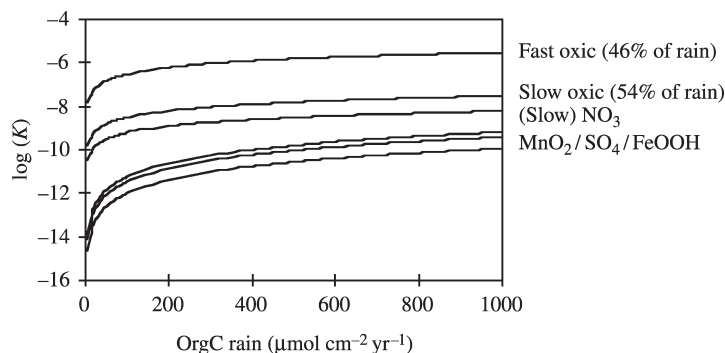


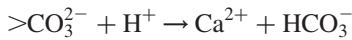
Figure 5 Model-tuned respiration rate constants for various electron acceptors (O_2 , NO_3 , Mn, Fe, and S), and for two fractions of organic matter rain to the seafloor (faster fraction shown for O_2 only). Dependence on organic carbon rain was based on data from Toth and Lehrman (1977), Tromp *et al.* (1995), Westrich and Berner (1984) tuned to reproduce sediment pore-water and solid phase field measurements (Archer *et al.*, 2001).

to correlate inversely with the grain size of the sediment, in such a way as to maintain a constant ratio of organic matter concentration to the surface area of the sediment grains (Hedges and Keil, 1995). Keil *et al.* (1994) were able to chemically extract organic matter from the surfaces of clays, and found that its reactivity was increased significantly by this extraction. We note also the surprising success of the Muds sediment model at predicting organic carbon concentration in sediments, with no consideration of organic adsorption effects at all.

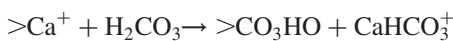
Global sedimentary budget. Finally, on a global scale, we point to an interesting model by Berner and Canfield (1989), which took as a given an organic carbon and reduced sulfur concentration of sediments of different type (nearshore sands, offshore clays, abyssal clays, etc.). In this view, a net source or sink of O₂ to the atmosphere could be driven by rearrangement of the sedimentary rock mass of the Earth, from abyssal clays to nearshore clays, for example.

6.10.3.1.2 CaCO₃

Dissolution kinetics. In contrast to the degradation of organic matter, the dissolution of CaCO₃ in sediments relies on abiotic dissolution which ought, in principle, to be more conservative across regions of the ocean. A complication is that CaCO₃ dissolution into seawater is comprised of multiple chemical reactions such as



and



(Arakaki and Mucci, 1995; Berner and Morse, 1974). The total loss of solid-phase CaCO₃ is determined as the sum of these reactions, and therefore exhibits a complicated dependence on the saturation state of the fluid. This behavior has been parametrized as high-order kinetic rate law of the form

$$R = k(1 - \Omega)^n$$

where *k* is a rate constant, Ω is the saturation state ($= [Ca^{2+}][CO_3^{2-}]/K'_{sp}$), and *n* is a potentially nonunity dissolution rate order (Keir, 1980; Morse, 1979). However, the numerical value of the rate order (the exponent *n* above) is difficult, if not impossible, to extract from field data (Archer *et al.*, 1989a; Hales and Emerson, 1996, 1997a), and sensitive to the imprecision of the saturation state for CaCO₃ in laboratory measurements (Hales and Emerson, 1997b). In general, it has been found that the rate constant (the pre-exponential factor *k* above) varies by orders of magnitude from place to place in the ocean (Hales and Emerson, 1996, 1997a), but less so if linear dissolution kinetics are used. We should also note that laboratory determinations of the rate constant tend to exceed field determinations by two to three orders of magnitude.

Pore-water pH. The dissolution of CaCO₃ in sediments is also complicated by interaction with organic matter diagenesis via the pH equilibrium chemistry of seawater (reaction (1), above). The addition of dissolved CO₂ from organic carbon degradation shifts the equilibrium to the right, decreasing the concentration of CO₃²⁻ in the pore waters. Figure 6 shows a model-generated concentration profile of CO₂, HCO₃⁻, and CO₃²⁻ in sediment pore waters above the saturation horizon for CaCO₃ (i.e., where the [CO₃²⁻] of the overlying water is higher than the equilibrium

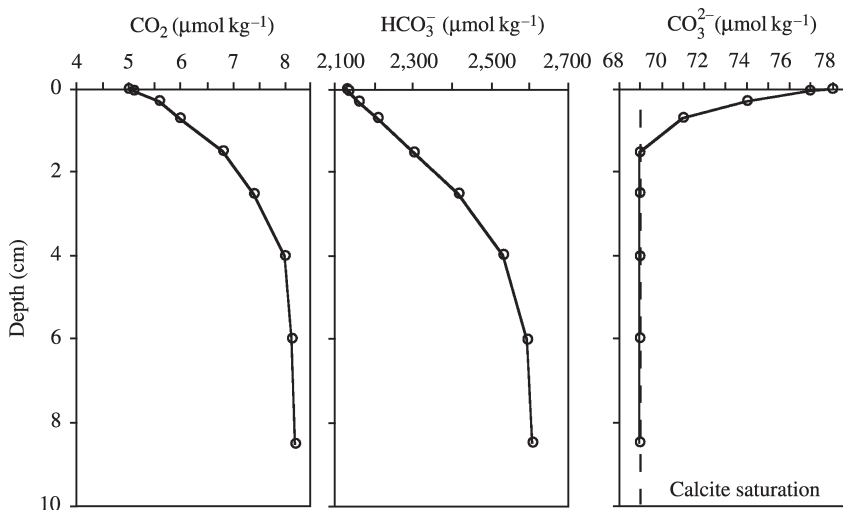


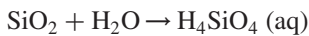
Figure 6 Model profiles of CO₂, HCO₃⁻, and CO₃²⁻ in surface sediments. From the Muds model (Archer *et al.*, 2001).

value with respect to calcite). Sediment chemistry models predict that respiration accounts for a significant dissolution flux from sediments, e.g., 20–40% of the calcite rain to the seafloor may be dissolving, even where the overlying water is saturated with respect to calcite (Archer, 1991; Emerson and Archer, 1990).

The implication of a role for respiration as a driver for CaCO_3 dissolution is that any hypothetical change in the ratio of organic carbon to calcite raining to the seafloor may impact the global burial rate of calcite, and thus (by a mechanism to be explained below) the steady-state pH of the ocean (Archer and Maier-Reimer, 1994).

6.10.3.1.3 SiO_2

On the face of it, the dissolution of SiO_2 from sediments ought to be simpler than that of organic matter, which is driven biologically, or CaCO_3 , with its coupling to pore-water pH and organic carbon respiration. The dissolution reaction for SiO_2 is simply



Although H_4SiO_4 (aq) could be affected by the dissociation reaction



the equilibrium constant for this reaction makes it insignificant in seawater.

However, opal diagenesis in sediments, despite its apparent simplicity, is not without mystery. The asymptotic concentration of silicic acid in pore waters in contact with measurable solid-phase opal ought to reflect the solubility of opal. Instead, what is observed are generally lower concentrations than the laboratory-measured equilibrium values, with a tendency toward correlation with the productivity of the surface ocean. Asymptotic silicon in Southern Ocean sediments reaches 600 μM and up, while in the subtropical oligotrophic ocean asymptotic silicon is only 150–300 μM (Schink *et al.*, 1974). Archer *et al.* (1993) argued that dynamically, with the framework of the diffusive pore-water system, the equilibrium silicon has a greater impact on opal preservation than the rate constant for dissolution. Recent work has found a correlation between the asymptotic (equilibrium) silicon concentration and the concentration of aluminum in the sediment solid phase (Cappellen and Qiu, 1997; Dixit *et al.*, 2001), rationalizing the decreasing solubility as a function of the formation of aluminosilicates on the opal surface. Similar behavior has been documented in the laboratory (Lewin, 1961).

6.10.3.1.4 Indirect atmospheric p_{CO_2} signature of the biological pump

The biological pump also has an indirect mechanism of affecting the p_{CO_2} of the atmosphere, called CaCO_3 compensation. The mechanism is based on the constraint that on long enough timescales, the inputs and outputs of alkalinity to the ocean must balance. The input arises from weathering of carbonate and silicate rocks on land, and removal is by the production and sedimentation of CaCO_3 . The crucial component of this mechanism is that the fraction of CaCO_3 produced that is buried depends on the acidity of the ocean. If input of alkalinity exceeds output, e.g., the buildup of alkalinity in the ocean pulls the pH to higher values, allowing a greater fraction of the CaCO_3 produced to be buried (Broecker and Peng, 1982, 1987). The system approaches equilibrium on a timescale of roughly 5,000 years (Archer *et al.*, 1997). Because the mechanism relies on changing the mean chemistry of the ocean by interaction with the sediments, this mechanism has also been called the “open system” response (and the direct effect described above has correspondingly been called the closed system response (Sigman *et al.*, 1998)). The link to atmospheric p_{CO_2} arises from the dependence of the dissolved CO_2 concentration on seawater pH. As pH rises, less and less of the dissolved carbon is found in the acid form CO_2 .

Weathering. CaCO_3 compensation provides several ways in which the p_{CO_2} of the atmosphere could be affected by the biological pump. Most obviously, if the delivery rate of alkalinity to the ocean from weathering were to increase, then a greater fraction of CaCO_3 production would have to be buried to balance weathering. This would drive ocean pH up, decreasing atmospheric p_{CO_2} (Berger, 1982; Opdyke and Walker, 1992). One mechanism for increasing weathering during glacial time is the exposure of shallow-water reefs and carbonate banks, which therefore transform from significant depocenters of CaCO_3 from the ocean (Kleypas, 1997; Milliman, 1993) to significant weathering sources (Gibbs and Kump, 1994; Munhoven and Francois, 1993). This mechanism must have played some role in glacial p_{CO_2} variations, although the timing of events at the deglaciation precludes a primary sea-level driver of p_{CO_2} (Broecker and Henderson, 1998).

Rain ratio. Somewhat less obviously, a decrease in the production of CaCO_3 would mandate an increase in the burial fraction that must be maintained in order to achieve throughput balance. Third, CaCO_3 dissolution in sediments is promoted by the oxic degradation of organic matter (Emerson and Bender, 1981). Therefore, an increase in organic matter rain to the seafloor could ultimately drive pH toward the basic to

compensate, decreasing atmospheric p_{CO_2} . Both the direct and the indirect effects of organic carbon and CaCO_3 rain depend on the ratio of organic carbon to CaCO_3 produced. This ratio therefore has a name, the “rain ratio.” The effects of organic carbon and CaCO_3 on CaCO_3 compensation are collectively called the rain-ratio hypothesis (Archer and Maier-Reimer, 1994).

6.10.4 SUMMARY

In summary, some advances in the biogeochemical cycles in the ocean have suggested several new sensitivities, ways in which the past or future climate change could impact the p_{CO_2} concentration of the atmosphere. Some of these mechanisms act on the 10^3 -year timescale of ocean/atmosphere p_{CO_2} equilibration, such as the effect of iron on the biological pump. This effect is minimized if (Section 6.10.2.1.2) iron is predominantly recycled within the ocean rather than supplied by deposition of continental dust, and (Section 6.10.2.5.1) if the real ocean behaves as a general circulation model rather than as a box model, in the way that the high-latitude surface ocean interacts with the p_{CO_2} of the atmosphere. Other potential sensitivities include a decrease in calcification with acidity of surface waters (Section 6.10.2.2.2) and an increase in water column redissolution of CaCO_3 (Section 6.10.2.4.2). Alternatively, CaCO_3 production may increase with an increase in the stratification of the water column in a future global warming world (Section 6.10.2.3; Antia *et al.*, 2001), or perturbations in dust deposition due to changes in land use (Sections 6.10.2.1.2 and 6.10.2.3).

On timescales of CaCO_3 compensation (Section 6.10.3.1.4), any changes in calcification rate, or the ratio of calcite to organic carbon reaching the seafloor, have an amplified effect on the p_{CO_2} of the atmosphere. This effect may be minimized if organic matter requires ballasting, predominately from CaCO_3 , to reach the seafloor (Section 6.10.2.4.4). The impact of iron deposition on Si : C ratios of diatoms may affect atmospheric p_{CO_2} (Matsumoto *et al.*, in press), if an increase in silicon availability depresses calcification, an effect which is not clearly seen in sediment trap data (Klaas and Archer, 2002).

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