CHAPTER 1
THE ROLE OF MARINE BIOTA
IN THE BIOGEOCHEMICAL AND GEOLOGICAL CYCLES OF CARBON

by

Will Berelson
Department of Earth Sciences
University of Southern California
Los Angeles, CA, United States

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www.fbbva.es
AN EXQUISITE BALANCE EXISTS ON THIS PLANET in which inorganic C is consumed, oxygen is produced and the Earth’s temperature and suitability for breathing organisms is thereby regulated. This regulation involves components of biological, physical, chemical and geological systems. A most significant coupling of biological and geological systems is the sedimentation and ultimate burial of photosynthetically produced organic matter \((C_{org})\) resulting in the net oxygenation of the planet. In early Earth history, photosynthesis by cyanobacteria hosted on sedimentary structures known as stromatolites established an oxygen source and a \(C_{org}\) sink in very close proximity. Organic matter that forms on, in or in close proximity to sediments is likely to be buried and escape re-oxidation. Yet soon after the advent of benthic photosynthesizers, the upper ocean’s pelagic realm became populated by cyanobacteria. Here the production of oxygen is readily exchanged with atmospheric gases, but the residual organic carbon must settle through the ocean and become buried by the slow accumulation of pelagic sediments before this \(C_{org}\) production yields net oxygenation.

Photo 1.1: Phytoplankton diatoms
Intimately coupled to the production of oxygen and the oxygenation of the planet is the biogeochemical cycle of CO₂. As the inorganic substrate of organic matter, total CO₂ (or TCO₂) sources and sinks in the ocean are critical in regulating net production. Moreover, the isotopic fractionation of ¹³C and ¹²C between inorganic CO₂ and organic C during carbon fixation provides firm evidence that life on this planet developed the photosynthetic pathway very early on in Earth history. The isotopic record of C through geologic time becomes a strip chart recorder of processes that bury ¹²C and ¹³C.

Although buried bits of C_{org} are the likely remains of phytoplankton from ancient oceans, the process of sediment burial, heating and lithification can obliterate the fidelity of their isotopic values. Fortunately, the history of sedimentation on this planet is also recorded by rocks that are predominantly CaCO₃. Because the carbonate ion-utilizing reaction with calcium samples the oceans TCO₂ pool and results in the mineral calcite, carbonate-rich rocks become a valuable repository of information about the overall C cycle.

Perhaps the most dramatic example of the importance of the carbon cycle in recent Earth history is the record of CO₂ contained within ice that forms and accumulates at very high latitudes. The Vostock ice core (figure 1.1) contains an excellent example of the rhythmic pacing of planetary CO₂ cycles that cor-
respond with planetary temperature fluctuations known to have occurred over hundreds of thousands of years.

In the following sections of this paper I will discuss patterns of $C_{\text{org}}$ and $\text{CaCO}_3$ production in the modern open ocean, and give examples of transformations that occur as particles sink through great ocean depths. This chapter will also include a short discussion of major events in Earth history and the relative response of $C_{\text{org}}$ and $\text{CaCO}_3$ burial through these time periods. I will discuss the advent of the modern pelagic ecosystem (diatoms and coccolithophores) and how the global C cycle responded to this reorganization and finally relate the oceanographic C cycle to the geologic C cycle.

1.1. THE BIOLOGICAL PUMP AND PATTERN OF $C_{\text{org}}$ AND $\text{CaCO}_3$ PRODUCTION

Plant growth in the ocean is partitioned, primarily, between three types of oceanographic regimes, a) the fronts that occur between 40-60° N and S, b) the equatorial upwelling zones and c) within coastal upwelling zones. This distribution (map 1.1) reflects the confluence of environmental parameters (light,
turbulence, temperature) and nutrient availability. In many oceanographic regions the limiting nutrient is iron, as has been demonstrated in numerous iron fertilization experiments (Boyd et al. 2007). Other regions of the surface ocean are limited by the lack of sufficient bio-available phosphorous or nitrate.

The range in primary production of $C_{\text{org}}$ (10’s to > 500 g C m$^{-2}$ yr$^{-1}$) is large and seasonal, and there are also large annual fluctuations in production. Yet the general pattern in primary production is striking in its latitudinal zonation (map 1.2).

If there were a general translation between primary production and the export of $C_{\text{org}}$ from the surface ocean, as may be expected, the latitudinal pattern in phytoplankton growth should be reflected in sedimentary $C_{\text{org}}$ content, however, it is not (map 1.2). Although the common sedimentary measurement of wt. % $C_{\text{org}}$ is not the best metric for $C_{\text{org}}$ flux to the sea floor, the pattern of sediment wt. % $C_{\text{org}}$ in no way reflects the pattern of surface water productivity. This result can be explained in three ways, 1) primary productivity and organic carbon export are very poorly correlated (Michaels and Knap 1996; Buesseler 1998), 2) settling through the water column attenuates

Map 1.2: Distribution of weight % $C_{\text{org}}$ in superficial sediments

C\textsubscript{org} arriving on the sea floor (Francois et al. 2002) and 3) only a very small fraction of the C\textsubscript{org} that arrives on the sea floor makes it into the sediment column (Hedges and Keil 1995).

The loss of C\textsubscript{org} to remineralization as particles leave the upper ocean and sink to the sea floor has been parameterized using a simple power law function first described by Martin et al. (1987). While this function has been used extensively in various models and has been shown to reasonably reflect the C\textsubscript{org} remineralization of sinking particles, it is important to understand this process from a mechanistic perspective. The following equation sets up the mechanics behind the Martin function:

\[
dF/dz = -(1/w) \cdot k \cdot F
\]

Figure 1.2: The pattern of C\textsubscript{org} flux vs. depth in ocean. The equation describes the dependence of various factors on the pattern of flux.

\[
\frac{\partial F}{\partial z} = -(1/w) \cdot k \cdot F
\]

\[k\]
Reactivity dependence
- Temp, C/C\textsubscript{sat}
- Composition, surf. area
- Heterotroph activity
- Protection, inhibitors
- Oxygen concentration

\[w\]
Velocity dependence
- Carbonate vs. Opal (ballast)
- Effective size
- Effective density
- TEP

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\[
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where \(F\) is flux of C\textsubscript{org} with depth (z), \(w\) is the particle sinking velocity, \(k\) is the rate constant for C\textsubscript{org} remineralization (1/time) and \(F\) is the flux of C\textsubscript{org} at any given depth (figure 1.2). Various ecologic and environmental factors can affect both \(w\) and \(k\). Sinking velocity is poorly constrained and is generally thought to occur at rates on the order of 50-200 m/day. Often overlooked are other factors that influence \(w\), mineral ballast is certainly important (Armstrong et al. 2002), as are effective particle size and effective density and these in turn are related to the TEP (transparent extra polymeric substances) content of sinking particles.
Both physical factors, such as the erosion of fine-grained sedimentary materials in continents and their delivery to the ocean and ocean ecosystem structure will play a role in organic carbon export to the deep sea. The more we can learn about the factors that influence $w$ and $k$, the better we will understand the global C cycle.

1.2. TRANSFORMATIONS THAT OCCUR AS PARTICLES SINK

The ocean’s biological pump is important to the export of $C_{org}$ from the upper ocean to the ocean’s interior. Some portion of the produced organic matter will be exported as long as complete remineralization does not occur in the mixed layer of the ocean. Just how effective this pump will be depends on factors that affect both sinking rate ($w$) and remineralization rate ($k$) (figure 1.2). One example of how ocean physics and ecological structure conspire to alter the chemistry of particles that fall through the ocean is the ‘filtering’ effect that takes place within the oxygen minimum zone. As particles containing $C_{org}$ fall through the water column and remineralization takes place, oxygen is consumed. This simple reaction produces $TCO_2$ and depletes the mid-water column of oxygen in a stoichiometry that is roughly 1:1. Hence the production of oxygen near the surface ocean is neutralized by its consumption at depth. Certainly physics plays an important role in the maintenance of the oxygen minimum zone; water masses that have little mixing and that have been isolated from contact with the atmosphere for long periods are waters that have the most depleted oxygen concentrations (map 1.3). Low oxygen zones in today’s oceans are most extensive in the Pacific Ocean, especially along the Eastern boundaries and at low latitudes of this ocean basin. Although most intense to the East, the low oxygen zone in the Pacific extends across the entire basin and is also well expressed in the North Indian Ocean and on the Eastern margins of the Atlantic Ocean basin.

The low oxygen zone (LOZ) acts as a filter to the sedimentation that occurs below it. Particles that pass through the LOZ pass through a water mass with low pH and reduced oxidizing capability. It has been shown that some LOZ’s contain substantial concentrations of ammonia (Cline and Richards 1972; Dalsgaard et al. 2005), methane (Sansone et al. 2004) and even sulfide (Diaz and Rosenberg 2008). Biogenic particles passing through this water mass are altered in ways that bias the sedimentary record with respect to the upper water column ecological community structure. Two examples are offered below.
Through experiments with sediment traps and laboratory remineralization chambers, Devol and Hartnett (2001) and Van Mooy et al. (2002) have shown that the loss of C\textsubscript{org} as particles fall through the low oxygen waters off the Northern Tropical Eastern Pacific is attenuated relative to the loss of C\textsubscript{org} as particles fall through more oxygenated waters. This is reflected in the pattern of flux vs. depth or the Martin ‘b’ value. Less C\textsubscript{org} is remineralized as it falls through low oxygen waters than when it falls through oxygenated waters. This, in part, explains the high C\textsubscript{org} burial efficiencies within sediments underlyng LOZ’s (Henrichs and Reeburgh 1987). The reason this occurs is not well understood, although Van Mooy et al. (2002) ascribe the transformation of organic C from labile to refractory to its passage through the LOZ.

These systems also have an impact on the signature of upper ocean carbonate ecosystems on the rock record. CaCO\textsubscript{3} is supersaturated in the surface ocean and becomes undersaturated within the oxygen minimum zones (Feely et al. 2004, 2008). Sinking carbonate material will dissolve, due to a variety of processes, but more extensive dissolution will occur in highly undersaturated waters. Both aragonite and calcite are susceptible to dissolution, aragonite...
more so than calcite, yet there is evidence that calcitic material dissolves as it falls through the water column (Berelson et al. 2007). The extent of dissolution that occurs as particles sink can be assessed from long-term sediment trap records of flux to different depths. A comparison of long-term trap results from Station P in the NE Pacific where the oxygen minimum zone is extensive, and from the central Equatorial Pacific (Berelson et al. 2007) where the oxygen minimum zone is less extensive, show (figure 1.3) that although a similar quantity of carbonate is falling through 1000 m, there is a loss of carbonate in the 4000 m traps at Sta. P that is not evident in the traps at EqPac. This greater loss of sinking particulate carbonate may be attributed to the more acidic waters through which particles travel in the NE Pacific. This is evidence of the water column ‘filter’ in action.

1.3. MAJOR EVENTS IN EARTH HISTORY AND THE RECORD OF C\text{org} AND CaCO_3 BURIAL

The mass balance of C isotopes (^{12}\text{C} and ^{13}\text{C}) results in one of the most elegant and reliable tools for understanding how ocean ecosystems change through geologic time. As the name ‘mass balance’ implies, the ratio of ^{12}\text{C} and ^{13}\text{C} mol-
molecules that enter the ocean must be conserved by the ratio of these molecules in the various forms by which they are removed from the ocean. The input ratio (reported in isotope geochemistry $\delta$ convention) is set by the gaseous CO$_2$ and CO emitted from volcanoes with a value, $\delta^{13}C = -6$ per mil. If the input ratio has remained constant throughout geologic time, which most assume to be true; this input value sets the net output of $^{12}C$ and $^{13}C$, which takes two primary forms. Most C is removed with sedimenting CaCO$_3$ and the remaining fraction of C is removed as organic C. Because these two forms of solid C tend to show a distinctive offset in their $\delta^{13}C$ values, a very useful mass balance can be constructed (figure 1.4a).

The balance ‘fulcrum’ is the average input value of $\delta^{13}C$ to the global ocean. The removal terms are adjusted in size given the offset between the $\delta^{15}C$ value of $C_{org}$ and CaCO$_3$. This offset (through much of geologic time and at present) is about 27 per mil (figure 1.4b) and is set by the carbon fixation pathway (for example, the Calvin cycle) by which inorganic C is converted to organic C.

A single measurement of either $\delta^{15}C$ of $C_{org}$ or $\delta^{13}C$ of CaCO$_3$ will specify the size of the removal term of one box relative to another. As shown in figure 1.4b, a measured value of $\delta^{13}C$ of CaCO$_3$ will set the $\delta^{13}C$ value of $C_{org}$ and will also define the fraction of $C_{org}$ buried relative to total C-buried.

David Des Marais (2001, 1997) and John Hayes (1999) were among the first scientists who showed how remarkably similar the offset between $\delta^{13}C$ of $C_{org}$ and $\delta^{13}C$ of CaCO$_3$ has remained throughout billions of years of earth history. This implies, to the first order, that the ratio of $C_{org}$ burial to the total C buried has been constant at about 20% for eons. Conversely, this means that the net removal of C as CaCO$_3$ has remained constant at 80% of the total C removed. Throughout millions and millions of years of earth history, and as the oceans evolve and ecosystems change, the net removal of C from the oceans as CaCO$_3$ (primarily as dead plants and biomass) and as CaCO$_3$ (either abiotic or biotic) has held generally constant at a ratio of 0.2 to 0.8.

Both the long term mean and deviations from this mean are fascinating. For example, between 800 and 540 million years ago, just as multi-cellular organisms were developing on Earth, there were at least three major ‘snowball’ events that covered the planet with snow, ice and slush (Kirschvink, 1992). Each of these events was marked by a recovery in which a low fraction of $C_{org}$
Figure 1.4: Isotope mass balance for $^{13}$C

a) Microorganisms

\[ \text{Reduced carbon} \]

\[ \text{Carbonate} \]

\[ \delta^{13}\text{C} \]

\[ \text{Crustal average} \]

b) Mantle carbon input ($-6\%$)

\[ \delta^{13}\text{C}_{\text{org}} \]

\[ \delta^{13}\text{C}_{\text{carb}} \]

\[ \Delta = 27\%\]

\[ \text{Modern ocean} \]

\[ \text{Fraction of } C_{\text{org}} / C_{\text{total}} \text{ buried} \]

was buried relative to CaCO₃ (figure 1.5). Whatever sort of checks and balances normally at work to maintain the ocean C sink and its proportionality between Corg and CaCO₃ fell apart during these snowball recovery periods.

**1.4. MODERN OCEAN ECOLOGY AND THE MODULATION OF THE C ORG AND CaCO₃ FRACTION BURIED**

A final example of how ocean ecology is reflected in long-term records of Earth history is the ‘recent’ invention of coccolithophores and diatoms. These two pelagic photosynthetic micro-organisms stand at the base of today’s oceanic food chain and represent its most significant biogenic particles. Diatoms construct shells or tests made of SiO₂ and represent the single most important component in the oceans’ Si cycle (Ragueneau et al. 2000). They also make up a large fraction of oceanic C fixation, as much as 50% (Treguer et al. 1995). Moreover, export of diatoms via sinking is known to carry Corg to the ocean interior (Buesseler et al. 2007). Coccolithophores are the single most important component of the pelagic ocean carbonate producers and their production of Corg and sinking drives a major part of the oceanic alkalinity and Corg cycles.

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**Figure 1.5: Pattern of the fraction of Corg relative to total C, buried between 500 and 800 million years ago.** Large excursions, known as “snowball events” are marked.

Source: Hayes et al. 1999.
As shown in figure 1.6, the ‘invention’ of these two types of phytoplankton, between 200 and 150 million years ago, had little impact on the global balance with regard to how much C<sub>org</sub> and how much CaCO<sub>3</sub> was buried. In the same way as the global average prior to 200 million years ago, where ~20% of ocean C was buried as C<sub>org</sub> and 80% as CaCO<sub>3</sub>. Yet, upon closer inspection of these plots (figure 1.6), it is apparent that the fluctuations in % C buried as C<sub>org</sub> were greatly attenuated following the evolution of coccolithophores and diatoms. It may be that prior to the production of oceanic phytoplankton that precipitate CaCO<sub>3</sub>, much of the CaCO<sub>3</sub> burial occurred on continental and island margins and shallow platforms. The abundance of the area for this accumulation would be sensitive to the overall distribution of continents through geologic time, i.e. plate tectonic movements. Once the deep sea became a repository for CaCO<sub>3</sub>, following the evolution of coccolithophores, the carbonate burial budget would have become less sensitive to these tectonic factors, giving rise to the attenuated variability in \( f_c \) in figure 1.6 that has occurred in the last 200 million years. Certainly, there are direct linkages and feedbacks between ocean ecology and geologic history.

1.5. THE GEOLOGIC C CYCLE

It is not clear how long this planet has had the tectonic cycle that is active today. One of the greater uncertainties is when large continental plates de-
developed. Yet some form of the geologic C cycle had been active since early earth history because, with the exception of a few global ‘snowball’ events, the earth has had vast oceans for about 3.5 billion years and has buried the same relative fraction of C_{org} and CaCO\textsubscript{3} for this duration. There is no way for this planet to maintain a moderate mean temperature without the feedbacks imposed by the grand geologic C cycle (figure 1.7).

The geologic C cycle involves inputs and removal terms on geologic time scales as well as on the oceanographic time scales mentioned earlier. The key components of the geologic C cycle include weathering, carbonate precipitation within the ocean and tectonic uplift and volcanism. Weathering is the process that ‘scrubs’ the CO\textsubscript{2} out of the atmosphere by combining carbonic acid in rain water with mineral surfaces (rocks) to erode rocks and generate solutes in streams and rivers. The dissolved HCO\textsubscript{3}– load of a stream is a measure of chemical weathering within the watershed. Once bicarbonate is delivered to the ocean, its fate is partly in the control of the biological pump and surface ocean ecosystem. Coccolithophorid primary productivity is responsible for the removal of much of the alkalinity from the

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**Figure 1.7: Geologic C cycle**

Rainfall containing CO\textsubscript{2} weathers rocks on continent, bicarbonate flows down rivers to ocean

CO\textsubscript{2} emitted to atmosphere from volcanoes

Rocks increasingly older

Seafloor spreading

Mid-ocean ridge

Seafloor spreading

Oceanic trench

Lithosphere

Oceanic crust

Rising magma

Subducting oceanic plate

Asthenosphere

Transform fault

Sedimentation of CaCO\textsubscript{3}

Uplift of crustal rocks containing CaCO\textsubscript{3}

Melting and extrusion of magma emitting CO\textsubscript{2} from mantle
ocean today (photo 1.2). The biomineralization process combines carbonate with calcium to yield mineral calcite. This mineral eventually falls through the water column and some fraction is retained in the sediment column. The tectonic forces that move plates apart at spreading centers must also yield convergence and subduction, where one plate re-enters the asthenosphere within the mantle.

Photo 1.2: Specimen of *Gephyrocapsa oceanica* originating from Mie (Japan). Digitally processed from an image obtained from an electronic microscope.
Melting of what the plate has been carrying occurs as does melting of the asthenosphere, and the result is rising magma (molten rock), volcanoes and the emission of CO₂. This greenhouse gas helps to keep this planet warm enough to sustain life. Too much CO₂ and global warming occurs, too little CO₂ and ‘ice house’ conditions ensue. Hence, the importance of precipitation and weathering and the continuance of the cycle. The geologic C cycle, and the important role played by carbonate secreting ocean plants and heterotrophs, is key to planetary homeostasis and survival.

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