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Minireview

The role of phytoplankton photosynthesis in global biogeochemical cycles*

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Abstract

Phytoplankton biomass in the world's oceans amounts to only ~ 1–2% of the total global plant carbon, yet these organisms fix between 30 and 50 billion metric tons of carbon annually, which is about 40% of the total. On geological time scales there is profound evidence of the importance of phytoplankton photosynthesis in biogeochemical cycles. It is generally assumed that present phytoplankton productivity is in a quasi steady-state (on the time scale of decades). However, in a global context, the stability of oceanic photosynthetic processes is dependent on the physical circulation of the upper ocean and is therefore strongly influenced by the atmosphere. The net flux of atmospheric radiation is critical to determining the depth of the upper mixed layer and the vertical fluxes of nutrients. These latter two parameters are keys to determining the intensity, and spatial and temporal distributions of phytoplankton blooms. Atmospheric radiation budgets are not in steady-state. Driven largely by anthropogenic activities in the 20th century, increased levels of IR- absorbing gases such as CO_2, CH_4 and CFC's and NO_x will potentially increase atmospheric temperatures on a global scale. The atmospheric radiation budget can affect phytoplankton photosynthesis directly and indirectly. Increased temperature differences between the continents and oceans have been implicated in higher wind stresses at the ocean margins. Increased wind speeds can lead to higher nutrient fluxes. Throughout most of the central oceans, nitrate concentrations are sub-micromolar and there is strong evidence that the quantum efficiency of Photosystem II is impaired by nutrient stress. Higher nutrient fluxes would lead to both an increase in phytoplankton biomass and higher biomass-specific rates of carbon fixation. However, in the center of the ocean gyres, increased radiative heating could reduce the vertical flux of nutrients to the euphotic zone, and hence lead to a reduction in phytoplankton carbon fixation. Increased desertification in terrestrial ecosystems can lead to increased aeolean loadings of essential micronutrients, such as iron. An increased flux of aeolean micronutrients could fertilize nutrient-replete areas of the open ocean with limiting trace elements, thereby stimulating photosynthetic rates. The factors which limit phytoplankton biomass and photosynthesis are discussed and examined with regard to potential changes in the Earth climate system which can lead the oceans away from steady-state. While it is difficult to confidently deduce changes in either phytoplankton biomass or photosynthetic rates on decadal time scales,

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time-series analysis of ocean transparency data suggest long-term trends have occurred in the North Pacific Ocean in the 20th century. However, calculations of net carbon uptake by the oceans resulting from phytoplankton photosynthesis suggest that without a supply of nutrients external to the ocean, carbon fixation in the open ocean is not presently a significant sink for excess atmospheric CO_2.

Introduction

Terrestrial plants are so much a part of the human experience that the importance of aquatic photosynthetic organisms in global biogeochemical cycles is often overlooked. From a biogeochemical viewpoint, the most important aquatic photosynthetic organisms are, by far, the single-celled oxygenic phytoplankton (planktos, Greek – to drift). Phytoplankton biomass in the oceans only amounts to ~1–2% of the total global plant carbon. Despite this relatively low biomass, these organisms collectively fix between 30 and 50×10^9 metric tons of carbon per annum, which is approximately 40% of the global total (Berger et al. 1989, Falkowski and Woodhead 1992). On geological time scales, the magnitude and importance of phytoplankton carbon fixation in shaping the biogeochemistry of the Earth and its atmosphere, as well as the oceans, is profound (Sarmiento and Bender 1993). The reservoir of atmospheric oxygen, which poisoned most of the Precambrian anaerobic photoautotrophs and simultaneously provided a basis for oxygen-dependent heterotrophic metabolism, was formed about two billion years ago as a result of oxygenic photosynthesis by phytoplankton (Riding 1992). Uplifted sedimentary remains of calcium carbonate-precipitating phytoplankton (i.e., limestone) form the bedrock of mountain ranges in Europe, Asia and the Americas. Fossilized organic remnants of blooms of phytoplankton are found in relict inland seas and shallow continental shelves, and provide a major portion of the organic carbon for the Earth's petroleum reserves. All of these phytoplankton-mediated biogeochemical changes occurred over millions of years, and resulted in, or were the result of, non-steady-state global climatological processes.

As we come to the end of the 20th century, it is increasingly evident that anthropogenic activities are rapidly forcing the atmospheric composition and radiative balance of the Earth away from the quasi-steady state which existed prior to the Industrial Revolution (Houghton et al. 1990). CO_2, CH_4, CFC's, and NO_x all have high IR absorption cross-sections; they absorb outbound longwave radiation and reradiate it back to the Earth. Exponential increases in these greenhouse gases throughout the 20th century have increased the warming potential of the atmosphere on a global scale. Simultaneously, increased atmospheric loading of anthropogenically-produced aerosol sulfate and other particle pollutants has increased the atmospheric shortwave backscatter cross-section and optical depth. The resulting increase in planetary albedo, sometimes called the 'whitehouse effect', counteracts the radiative forcing due to the increase in greenhouse gases, thus reducing the magnitude of the potential warming (Charlson et al. 1992).

Atmospheric chemists, physicists and climate modelers are currently trying to understand the magnitude, effects and feedbacks of the atmospheric radiative forcing functions. However, it is clear that the change in atmospheric radiative balance due to anthropogenic activities will ultimately affect the circulation of the atmosphere and the oceans. The circulation of these two geophysical fluids is coupled and profoundly influences the distribution of phytoplankton and photosynthetic activity. Here I review the basic processes and factors which control or limit the distribution and photosynthetic activity of phytoplankton in the world oceans, and examine how changes in global climate potentially affect this activity and its feedbacks.

Definitions of limitation

Over the past 150 years, two concepts of limiting factors have emerged in ecophysiology. The first, proposed by Liebig (1840), defines limitation in terms of the maximum *yield* that can be supported by the best available substance relative to the requirement for biomass synthesis. The sec-

ond, stemming from the work of Blackman (1905), proposes that the *rate* of growth of a crop is regulated by the availability of a nutrient or resource.

If photosynthesis (carbon fixation) is represented on an areal basis of the Earth's surface, it is the product of the areal distribution of plant biomass and the biomass-specific rate of carbon fixation. Factors which limit the areal distribution of biomass do not necessarily limit the specific rate of carbon fixation. For example, the distribution of phytoplankton biomass can be locally controlled by the availability of fixed nitrogen or herbivory, while the rate of carbon fixation per unit biomass can be controlled by temperature or irradiance. Thus, while intrinsic photosynthetic processes can proceed with a high quantum efficiency, net carbon fixation can be low if the crop is removed or controlled by extrinsic processes. Deriving mathematically meaningful expressions which allow more accurate prediction of the distribution of biomass has proven far more difficult (i.e., less deterministic) than mathematically describing biomass-specific photosynthetic processes (Ascioti et al. 1993). From a biogeochemical viewpoint, however, it is important to consider the factors limiting both the distribution of biomass as well the biomass-specific rates of photosynthesis.

Factors limiting phytoplankton biomass

Metrics of biomass

The most ecologically relevant units of plant biomass are organic carbon and nitrogen. Direct measurements of phytoplankton carbon or nitrogen are, however, inextricably complicated by the presence of varying concentrations of non-phytoplankton particulate matter and the relatively low abundance of particulate material in general (Banse 1977). As a matter of empirical and operational convenience, therefore, biological oceanographers usually infer the distribution of phytoplankton biomass from the distribution of chlorophyll *a*. This pigment is ubiquitous yet specific to photoautotrophs and can be measured with ease, rapidity, and sensitivity (Holm-Hanson et al. 1965), criteria which are important in oceanography.

The ratio of organic carbon to chlorophyll in phytoplankton varies from about 25 to 200 on a weight/weight basis. The variation in carbon/chlorophyll ratios is determined by genetic and environmental factors. For example, dinoflagellates generally have higher carbon/chlorophyll ratios than diatoms or cyanobacteria. Nutrient limitation, especially nitrogen or iron limitation, can lead to marked increases in these ratios. As cells adapt to different irradiance levels or to different temperatures, carbon/chlorophyll ratios change (Geider 1987). These variations, which are easily measured in laboratory monospecific cultures, are extremely difficult to constrain in natural phytoplankton communities. Numerous species of phytoplankton co-exist in the same water mass. Multiple influences, such as light and nutrient limitation, may interact in opposing ways to produce a realized carbon/chlorophyll ratio differing significantly from that which would be produced by a single process alone. Some success has been achieved in constraining carbon/chlorophyll ratios in natural phytoplankton by determining the specific activity of purified chlorophyll *a* following incubation with $H^{14}CO_3^-$ (Redalje and Laws 1981). This method is tedious and subject to error if there is significant biochemical turnover of chlorophyll (Riper et al. 1979). Thus, while it is recognized that chlorophyll *a* is an uncertain proxy for more ecologically relevant measures of phytoplankton biomass, such as organic carbon, unless otherwise stated, the term biomass will refer to phytoplankton chlorophyll *a*.

Redfield ratios

Despite the variability in carbon/chlorophyll ratios, the average bulk elemental composition of particulate matter in the sea is relatively constrained. The commonly taken average proportion of the major elements in phytoplankton is: 106 C : 16 N : 1 P (by atoms). These proportionalities are called the Redfield ratios (Redfield 1934). The low average C:N ratio of 6.6 reveals two characteristics of phytoplankton which are markedly different from those of higher plants, namely (1) phytoplankton are primarily protein synthesizing organisms (Myers 1980), and (2) they have no large sinks for organic carbon. Moreover, vertical profiles of

dissolved inorganic carbon, fixed inorganic nitrogen, and phosphate reveal that these elements, which are relatively abundant in the deep ocean, are also found in Redfield proportions. That both phytoplankton biomass and the elemental composition of nutrients in the deep ocean have the same stoichiometry, reveals the tight coupling between ocean chemistry and phytoplankton physiology. It is impossible to determine if the observed distribution of elements in the ocean is a consequence of the biological activity of phytoplankton or vice versa.

Redfield ratios can be useful in predicting which element will be limiting, and in calculating carbon fixation for a great variety of nutrient scenarios. For example, if prior to the spring bloom, the surface waters of the North Atlantic contain 10 μM NO_3 and 1 μM PO_4, we would expect that if all the nitrogen were consumed, 66.2 μM of phytoplankton carbon (= 10 μmol/l × 106/16) would be formed containing 0.62 μM PO_4. Based on the Redfield ratios, the bloom would be limited by nitrogen, not phosphate, and would yield a chlorophyll concentration of approximately 16 ug l^{-1} (assuming an average carbon/chlorophyll *a* ratio of 50 by weight).

The mixed layer depth

Solar radiation enters the ocean from the surface, while (in the central ocean basins) inorganic nutrients are usually supplied from depth. The spatial and temporal distributions in phytoplankton often reflect a biological compromise to the opposing gradients in energy and nutrients (Cullen 1982).

From a global perspective, the upper ocean is permanently separated from the deep waters of the ocean interior by a thermal gradient called the thermocline. This thermocline is a consequence of the poleward flux of warm, light waters in the upper layer and the return of cold, denser water towards the equator in the ocean interior. Most of the ocean between 30° N and 30° S is permanently stratified because in this region the net flux of heat into the ocean is greater than the net flux out. In temperate and higher latitudes, the upper ocean can be mixed to great depths in the winter (e.g., as much as 800 m in the North Atlantic, typically about 150 m in the North Pacific), when atmospheric temperatures are less than sea surface temperatures. As solar insolation increases in the spring, the rate of heating overcomes turbulent mixing, and a seasonal thermocline can be established. The seasonal thermocline progresses poleward through the spring and summer, after which the upper ocean loses heat to the atmosphere and again destratifies.

The layer of water overlying the thermocline can be mixed by wind friction at the surface, tidal energy or internal waves; this layer is called the upper mixed layer. The depth of the upper mixed layer (Z_{mix}) varies seasonally and with latitude (Fig. 1). The depth of mixing is constrained by the base of the thermocline, which is a layer of water with rapid change in temperature, and therefore density, over depth. The thermocline can be thought of as a soft 'floor' for the mixing of phytoplankton.

The euphotic zone

Net phytoplankton photosynthesis is restricted to an upper portion of the water column called the euphotic zone. The base of the euphotic zone is the compensation depth, and is defined as the depth where gross daily photosynthetic carbon fixation balances phytoplankton respiratory loses integrated over a day; above this depth net, daily photosynthesis is positive, below this depth it is negative. The average nominal compensation depth is frequently taken as the 1% light depth (Parsons et al. 1984); however, this value is somewhat variable. The 1% light depth averages 65 m in the world ocean.

Determining respiration presents the biggest problem in the calculation of the compensation depth. Phytoplankton respiration has traditionally been assumed to be 10% of the maximum photosynthetic rate and relatively independent of irradiance (Ryther 1954). However, direct measurements of oxygen consumption (Falkowski and Owens 1978), as well as measures of stable isotope tracers (Grande et al. 1989a, Weger et al. 1989), have indicated that respiratory losses are highly variable depending upon species, nutrient status and light intensity (Geider 1992). Mitochondrial respiration in the light can be significantly greater than in darkness (Grande et al. 1989a, Weger et al. 1989); this effect is difficult to quantify in situ. Additionally, phytoplankton

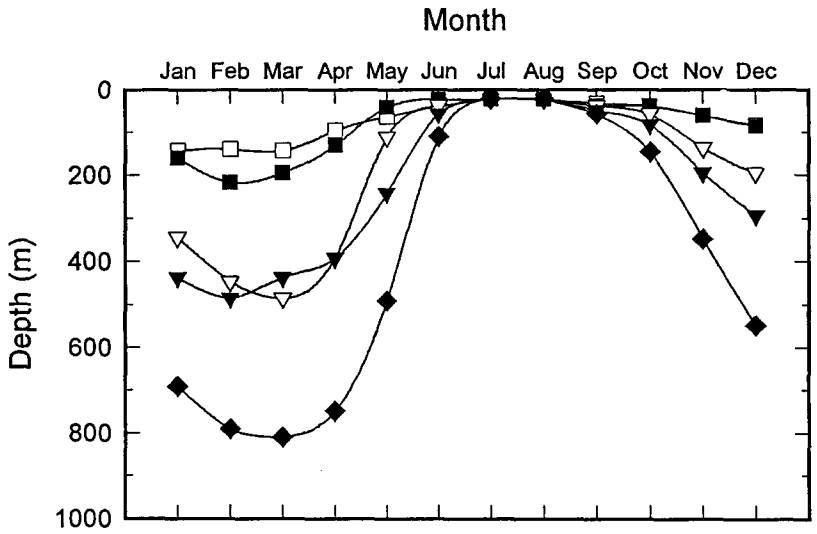

Fig. 1. The spatial and seasonal changes in upper mixed layer depth in the North Atlantic ocean. At low latitudes the upper mixed layer is never deeper than 200 m, and shoals to less than 50 m in the summer. At high latitudes the mixed layer depth can reach 800 m, and shoals to ca. 50 m by July. The mixed layer depth determines the initial concentration of nutrients before the onset of stratification as well as the critical depth.

can adapt to extremely low irradiance levels (Falkowski and Owens 1980, Geider et al. 1986), and respiratory costs are reduced at low growth rates (Geider and Osborne 1989). Because of this, the euphotic zone can extend well beyond the 1% light level frequently accepted to represent the limit of net photosynthesis. Moreover, in principle, the euphotic zone can be influenced by temperature, supraoptimal irradiance levels (which can lead to photoinhibition of photosynthesis near the surface), nutrient limitation (which can reduce photosynthetic quantum efficiency), species composition (photosynthesis: respiration ratios are species specific), the source of nitrogen (as it relates to the photosynthetic quotient), as well as the biochemical composition of the phytoplankton (as it relates to the respiratory quotient). It is impossible to constrain all of these variables, and consequently, the depth of the euphotic zone is difficult to determine directly.

The critical depth

The depth of the upper mixed layer relative to the depth of the euphotic zone is critical to the formation of phytoplankton blooms. If the upper mixed layer is deeper than the euphotic zone, phytoplankton will spend, on average, a lot of time at low irradiances. Under such conditions, integrated water column photosynthesis will be less than the integrated water column respiratory costs, and the phytoplankton *community* cannot sustain net positive growth. At some depth, the photosynthetic rate integrated through the water column over a day equals the daily, water-column integrated respiratory rate; this depth is called the critical depth (Sverdrup 1953). The critical depth is always greater than the compensation depth. It should be noted that the relevant respiratory costs in the derivation of the critical depth include all the heterotrophic consumers, such as bacteria and zooplankton, not merely phytoplankton (Smetacek and Passow 1990).

Phytoplankton blooms can only occur if the mixed layer depth is shallower than the critical depth. Thus, as insolation increases in the spring in temperate regions, the upper mixed layer shoals, and the average irradiance received by the ensemble of cells within the mixed layer increases (Fig. 1). This shoaling of the upper mixed layer allows for a net gain in phytoplankton biomass, and phytoplankton biomass accumulates until the limiting nutrient is depleted or until the crop is removed by grazing. While the critical depth concept is helpful in

understanding the spatial and temporal distribution of phytoplankton blooms, it is easier to define than to measure (Platt et al. 1991).

Vertical fluxes and distributions

With the exception of some species of cyanobacteria which form gas vesicles, the density of the phytoplankton cells is slightly greater than that of seawater, and in the absence of other forces, gravity causes the cells to sink (Smayda 1970, Bienfang 1981). The sinking velocity of cells is approximated by the Stokes equation (Stokes, 1851) and is proportional to the radius, r, to the power 1.5. A cell with a radius of 1 μm sinks about 1 cm d^{-1} while a cell with a radius of 1000 μm sinks > 100 m d^{-1}. Much of the vertical flux of particulate organic carbon which sinks out of the euphotic zone is in the form of large aggregates such as zooplankton fecal pellets or marine snow, not single cells (Goldman 1984, Alldredge and Silver 1988), and hence the actual sinking rate of particulates out of the upper mixed layer can be relatively rapid (Smetacek et al. 1978). To maintain phytoplankton biomass in a steady state from year to year, the downward flux of nutrients contained in sinking phytoplankton particles must be balanced by an input of new nutrients external to the upper mixed layer (Dugdale and Goering 1967, Eppley and Petersen 1979).

In the late 1960s it became increasingly apparent that the major nutrient element limiting phytoplankton biomass throughout most of the world oceans is nitrogen (Dugdale 1967, Ryther 1969). In the central subtropical gyres, the total concentration of fixed inorganic nitrogen, in forms which can be directly assimilated by phytoplankton directly ($NH_4 + NO_2 + NO_3$ + urea), usually is less than 100 nM. Such a low concentration is below the half-saturation constant for uptake by most species of phytoplankton (Eppley et al. 1969).

There are two major sources of nutrients: (1) the local regeneration of simple forms of combined elements (e.g., NH_4^+, PO_4^{2-}, SO_4^{2-}) resulting from the metabolic activity of metazoans and microbial degradation; and (2) the influx of 'new' nutrients, imported from the deep ocean, the atmosphere (i.e., nitrogen fixation, atmospheric pollution), or terrestrial run-off from streams, rivers and estuaries.

Despite the widespread occurrence of extremely low concentrations of fixed nitrogen in the central ocean basins, nitrogen-fixing organisms are rare. While low fixed nitrogen concentrations often result in blooms of heterocystic cyanobacteria in fresh water lakes, there are no heterocystic planktonic cyanobacteria in the ocean. The major oceanic nitrogen fixing cyanobacteria, *Trichodesmium* spp., is a filamentous non-heterocystic genera that fixes nitrogen and carbon simultaneously. *Trichodesmium* spp. can form extensive blooms but bloom formation is sporadic, episodic, and short-lived (Carpenter and Romans 1991). The collapse of *Trichodesmium* blooms can be followed by 'echo blooms' of non-nitrogen fixing phytoplankton (Subramaniam et al. 1992). Hence, nitrogen fixation can provide a conduit for enhancing carbon fixation by non-nitrogen fixing organisms; however, the magnitude of this process is probably less than 10% of the new nitrogen supplied from the deep ocean.

In the open ocean the concept of new and regenerated nutrients (Dugdale and Goering 1967) can be related to the form of inorganic nitrogen assimilated by phytoplankton. Because nitrogen fixation is relatively low in the ocean and nitrification is a relatively sluggish process, nitrogen supplied from local regeneration is assimilated by phytoplankton before it has a chance to become oxidized. Regenerated nitrogen is primarily in the form of ammonium or urea. In contrast, the fixed inorganic nitrogen in the deep ocean has had sufficient time (hundreds of years) to become oxidized, and hence the major source of new nitrogen is in the form of nitrate. Using $^{15}NH_4$ and $^{15}NO_3$ as tracers, it is possible to estimate the fraction of new nitrogen which fuels phytoplankton production. This approach provides an estimation of both the upward flux of nitrate required to sustain the $^{15}NO_3$ supported production, as well as the downward flux of organic carbon which is required to maintain a steady-state balance (Eppley and Petersen 1979, Dugdale and Wilkerson 1992). The estimates of global new production vary widely and are the focus of large, active research programs.

The sinking of organic carbon in the form of phytoplankton cells is an important conduit for the exchange of carbon between the upper ocean and the ocean interior (Berger et al. 1989). This conduit depletes the upper ocean of inorganic carbon and other essential nutrients due to photosynthesis and biosynthesis of organic particles. The fraction of fixed carbon which leaves the surface ocean is called the export production (Eppley and Petersen 1979). Export production is poorly constrained by direct measurement (Broecker 1982, Jenkins and Wallace 1992, Sarmiento and Siegenthaller 1992). In the central ocean basins, export production is probably low, amounting to between 5 and 10% of the total carbon fixed per annum (Dugdale and Wilkerson 1992). At high latitudes and in nutrient-rich areas, however, diatoms and other large, heavy cells can form massive blooms and sink rapidly. In such regions, export production can account for 50% of the total carbon fixation (Sancetta et al. 1991, Berger and Herguera 1992, Bienfang and Ziemann 1992, Campbell and Aarup 1992). The oxidation and subsequent remineralization of the exported production enriches the ocean interior with inorganic carbon by approximately 300 μM in excess of that which would be supported solely by air-sea exchange. This enrichment is called the 'biological pump' (Broecker et al. 1980, Berger et al. 1987, Bender et al. 1992, Sarmiento and Siegenthaler 1992, Sarmiento and Bender 1994). The biological pump is crucial to maintaining the steady-state levels of atmospheric CO_2. Because air-sea exchange of CO_2 is rate limiting, seasonal changes in ocean productivity are not readily perceptible in atmospheric CO_2 concentrations.

Horizontal and temporal distributions of phytoplankton

The introduction of high resolution, satellite-based sensors in the late 1970s allowed oceanographers to measure the global distribution of phytoplankton chlorophyll in the surface ocean with unprecedented spatial resolution. The horizontal distribution of phytoplankton chlorophyll is derived from satellite measurements of ocean color.

To an observer looking down at the surface of the ocean, pure seawater, devoid of all particles, would appear blue as a consequence of absorption and molecular scattering (Morel and Prieur 1977). The Soret absorption bands of chlorophylls and carotenoids can absorb the blue water-leaving photons. Thus, when phytoplankton are abundant in the ocean there is less blue light leaving the ocean. The differences between the blue and green water-leaving radiances are used to quantitatively derive phytoplankton chlorophyll concentrations.

The Coastal Zone Color Scanner (CZCS), which operated aboard Nimbus 7 from October 1978 to May 1986, scanned channels centered at 443, 520, 550, 670, 750 and 11 500 nm and acquired approximately 65 000 two-minute scenes, each covering $2\,200 \times 800$ km with a resolution of 0.825 km at nadir. Water-leaving radiances (L_w) at specific wavelengths were corrected for atmospheric scattering and absorption, and the concentration of chlorophylls, Chl, in $\mu g\,l^{-1}$ (really the total of all blue absorbing pigments) was calculated from blue and green channels from two wavelength ratio algorithms such as:

$$\mathrm{Chl} = 1.15(L_w(443)n/L_w(560)n)^{-1.42} \quad \text{for } \mathrm{Chl} < 1\ \mu g\,l^{-1} \tag{1}$$

and

$$\mathrm{Chl} = 3.64(L_w(500)n/L_w(560)n)^{-2.62} \quad \text{for } 1\ \mu g\,l^{-1} < \mathrm{Chl} > 5\ \mu g\,l^{-1} \tag{2}$$

The coefficient of determination for these equations is >0.95 and the relative error is approximately 20% for Eq. (1) and 30% for Eq. (2) (Lewis 1992).

One important limitation of satellite images of ocean chlorophyll is that they do not provide information about the vertical distribution of phytoplankton. The water-leaving radiances visible to an observer outside of the ocean are approximately confined to the upper 30 to 40 m. The chlorophyll maximum is almost always below 30–40 m (Fig. 2a), and hence is not visible to satellite ocean color sensors. A number of numerical models have been developed to estimate the vertical distribution of chlorophyll based on satellite color data. The models rely on statistical parameterizations and require numer-

ous in situ observations to obtain 'typical' profiles for a given area of the world ocean (Platt and Sathyendranath 1988, Morel 1991, Berthon and Morel 1992). In addition, large quantities of phytoplankton associated with the bottom of ice floes in both the Arctic and Antarctic are not visible to satellite sensors but contribute significantly to the primary production in the polar seas (Smith and Nelson 1990). Despite these deficiencies, the satellite data allow high resolution, large field, synoptic observations of the temporal and spatial changes in phytoplankton chlorophyll in relation to the physical circulation of the atmosphere and ocean on a global scale. It is via changes in physical circulation of the atmosphere and ocean that phytoplankton biomass and photosynthetic rates change.

The global, seasonal distribution of phytoplankton chlorophyll in the upper ocean, derived from a compilation of CZCS images, is shown in Fig. 3. To a first order, the images reveal how the horizontal and temporal distribution of phytoplankton is related to the ratio of the fluxes of new and regenerated nutrients and the critical depth. For example, throughout most of the central ocean basins, between 30° N and 30° S, phytoplankton biomass is extremely low, averaging 0.1 to 0.2 $\mu g\ l^{-1}$ at the sea surface. In these regions the vertical flux of nutrients is, generally, extremely low, limited by diffusion through the thermocline. Most of the chlorophyll biomass is associated with the thermocline. Because there is no seasonal convective overturn in this latitude band, there is no seasonal variation in phytoplankton chlorophyll. A slight elevation in chlorophyll is found at the equator in the Pacific and Atlantic Oceans, and south of the equator in the Indian Ocean. In the equatorial regions the thermocline shoals laterally as a result of long-range wind stress at the surface (Picard and Emery 1990). The wind effectively piles up water along its fetch, thereby inclining the upper mixed layer (Fig. 4). This results in increased nutrient fluxes, shallower mixed layers and higher chlorophyll concentrations on the eastern end of the equatorial band, and decreased nutrient fluxes, deeper mixed layers and lower chlorophyll concentrations on the western end. This effect is most pronounced in the Pacific. The displacement of the band south of the equator in the Indian Ocean is primarily a consequence of basin scale topography.

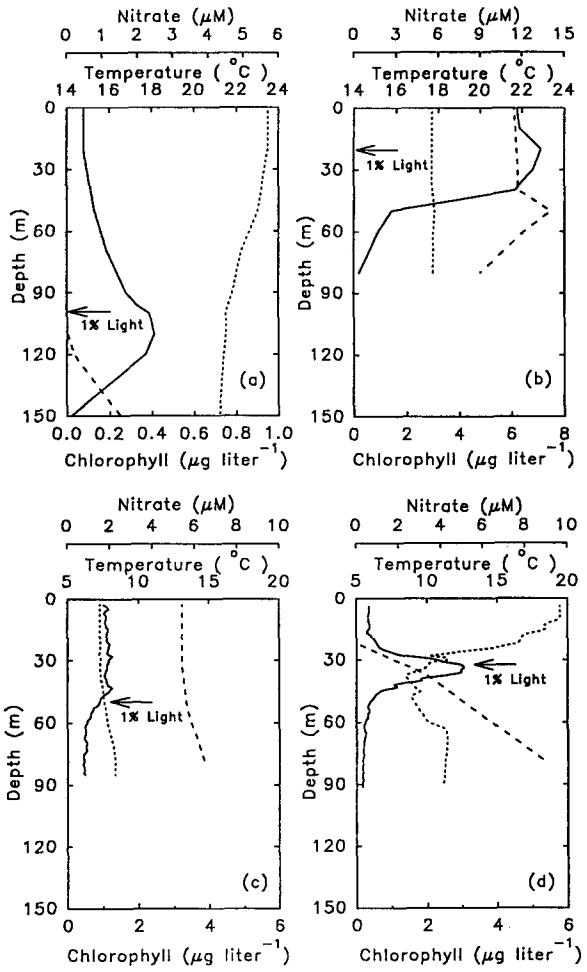

Fig. 2. Representative vertical profiles of chlorophyll *a* (solid line), temperature (dotted line) and nitrate (dashed line) from (a) a typical open ocean condition in the central subtropical Atlantic which is permanently stratified, (b) a nutrient rich upwelling region off the coast of Northwest Africa, (c) a temperate continental margin in winter, and (d) summer from the northeast coast of the United States. Note the scale changes in chlorophyll. One percent light depths (the nominal base of the euphotic zone) are shown by the arrows. Although the 1% light depth is shallower than the mixed layer depth off the coast of Africa, phytoplankton blooms are dramatic because the mixed layer depth is shallower than the critical mixing depth.

There are characteristic 'hot spots' of phytoplankton, where new nutrient fluxes are locally high. For example, a region of very high chlorophyll concentration (for the ocean, this corre-

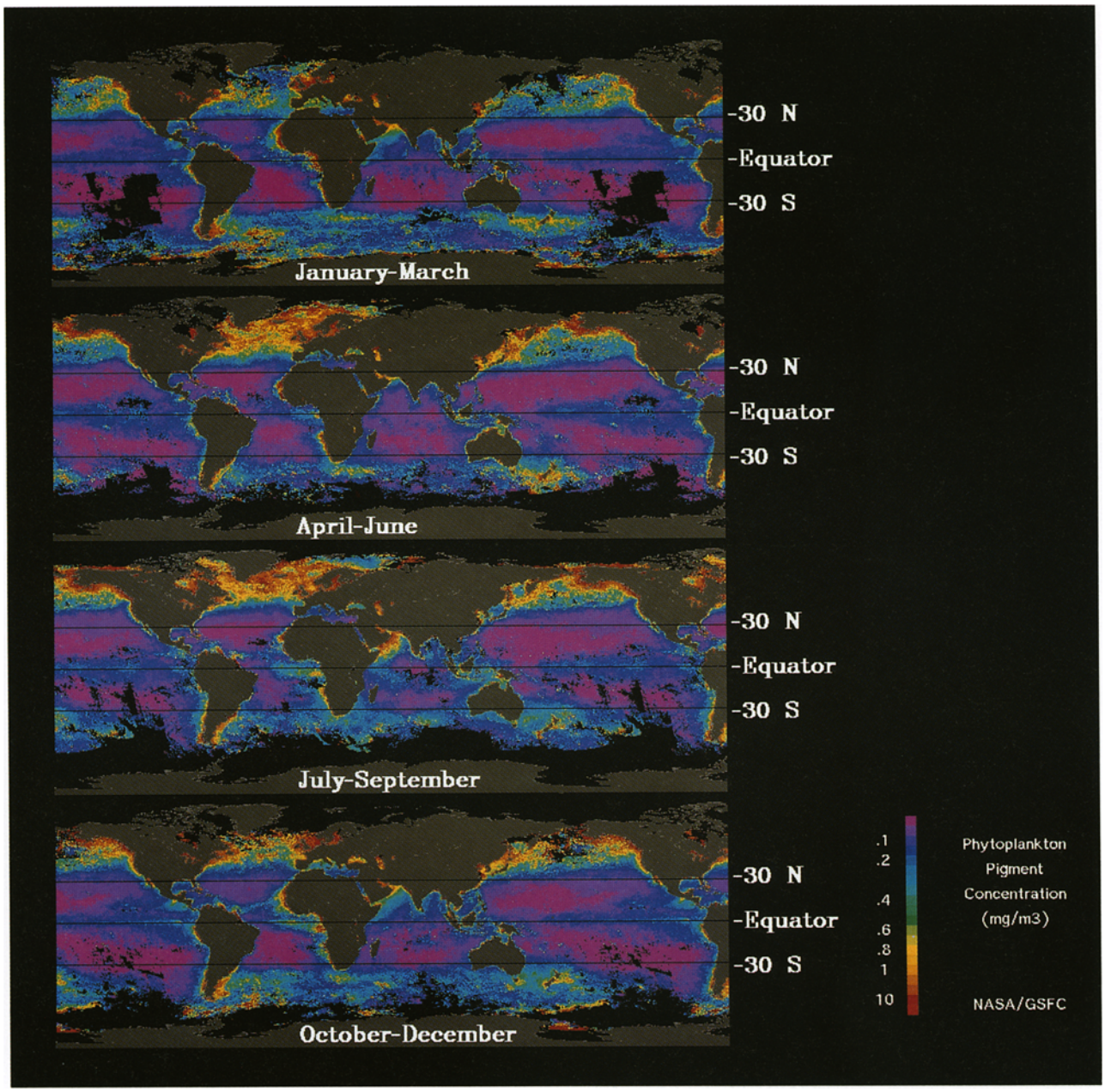

Fig. 3. A false color compilation of Coastal Zone Color Scanner images analyzed for upper ocean chlorophyll concentrations as a function of season. Note the large bloom of phytoplankton in the North Atlantic north of 30° N from April through the summer and compare it with the relative paucity of chlorophyll in the same latitude band in the North Pacific and in the symmetrical latitude band in the southern Hemisphere. Phytoplankton chlorophyll in the central ocean gyres is extremely low, and one can observe evidence of the large scale circulation of the gyres in the distribution of chlorophyll. (Courtesy of Gene Feldman, NASA Goddard Space Flight Center.)

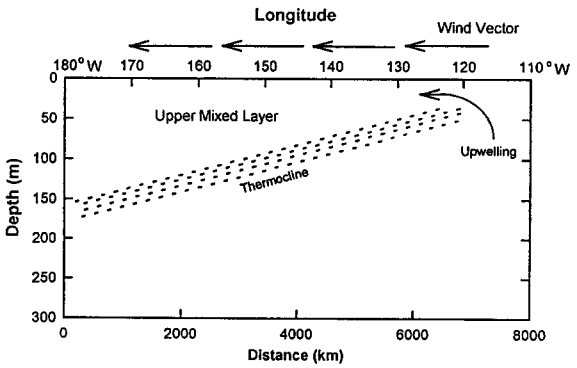

Fig. 4. Schematic cross section in the Equatorial Pacific, showing how the long-range wind stress at the surface leads to an inclination in the thermocline. As a consequence of this inclination, the mixed layer depth is deeper than the critical depth in the western equatorial region, and there is no surface manifestation of a phytoplankton bloom (see Fig. 3). The wind driven upwelling in the eastern region of the equatorial Pacific leads to high nitrate fluxes. Much of this nitrate is not consumed by phytoplankton as a result of iron limitation.

sponds to about 10 μg l^{-1}) appears off the southeast coast of Saudi Arabia in July–September, and is driven by the seasonal monsoons that upwell nutrient-rich, deep waters to the surface (Banse 1987). This is one low latitude region with a seasonal cycle in phytoplankton chlorophyll. Other coastal upwelling areas can be seen off the southwest and northwest coasts of Africa (Fig. 2b), off the east coast of Argentina, and the west coast of the United States. At latitudes above ca. 30°, a seasonal cycle in chlorophyll can occur (Fig. 2c,d). In the northern hemisphere, areas of high chlorophyll are found in open ocean in the North Atlantic in the spring (April–June) and summer (July–September). The southern extent and intensity of the North Atlantic phytoplankton bloom is not found in the North Pacific Ocean. In the Southern Hemisphere, phytoplankton chlorophyll is generally much reduced at latitudes symmetrical with the Northern Hemisphere in corresponding austral seasons. For example, in the austral summer (January–March), phytoplankton chlorophyll is appreciably lower between 30° S and the Antarctic ice sheets, than in the northern hemisphere in July–September (Yoder et al. 1993).

The absolute maximum abundance of phytoplankton biomass is highly correlated with the concentration of inorganic nutrients, especially fixed nitrogen (Ryther 1969). Thus, in tropical and subtropical regions, where the perennial thermocline retards the upward flux of nutrients, phytoplankton biomass is low throughout the year. In temperate regions, the upper ocean becomes recharged with nutrients following deep convective mixing of the surface waters in the winter. At the onset of stratification in the spring, phytoplankton blooms develop, consuming the surface nutrients. The magnitude of the bloom is limited by the initial nutrient concentration set by the depth of mixing in the preceding winter.

There are three major areas of the world ocean where inorganic nitrogen and phosphate are in excess throughout the year, yet the mixed layer depth appears to be shallower than the critical depth; these are: the eastern Equatorial and subarctic Pacific and Southern (i.e., Antarctic) Ocean. In the subarctic Pacific, it has been suggested that there is a tight coupling between phytoplankton production and zooplankton consumption (Miller et al. 1991). This 'grazer limited hypothesis' is offered to explain why the phytoplankton in the North Pacific do not form massive blooms in the spring and summer, like their counterparts in the North Atlantic (Banse 1992). It is recognized, however, that in all three of these regions, iron, which is delivered to the ocean in aeolean dust, blown from continental deserts, is the major element limiting the maximum abundance of phytoplankton and rates of phytoplankton photosynthesis (Martin 1991, Geider and La Roche 1994). An experiment in which iron was artificially added on a relatively large scale (7.5 × 7.5 km) to the waters in the Equatorial Pacific resulted in rapid and dramatic increases in photosynthetic energy conversion efficiency and phytoplankton chlorophyll (Kolber and Falkowski, unpublished). These results suggest that nutrients not only limit biomass, but that photosynthetic energy conversion efficiency is limited as well. This observation underscores an example of the modern manifestation of the apparent difficulty in resolving Liebig's and Blackman's concepts of limitation in phytoplankton ecophysiology. We now examine

the factors limiting photosynthetic energy conversion efficiency.

Limitations on biomass-specific photosynthetic rates

Measurements of photosynthesis

Two basic approaches for deriving photosynthetic rates have emerged in biological oceanography; both require some assumptions about spatial and temporal integration. In the first, carbon fixation or oxygen evolution is determined by incubating subsamples of the water column at specified depths (the in situ method) or on the deck of a ship, using neutral density filters to attenuate solar irradiance and simulate specific depths within the euphotic zone (the simulated in situ method); the incubation period is usually 24 h. The in situ approach accommodates natural variations in both spectral irradiance and temperature. With care, the results provide a measure of daily integrated net photosynthesis in the euphotic zone (Grande et al. 1989b). To calculate areal rates of photosynthesis, in situ or simulated in situ methods do not require knowledge of phytoplankton biomass.

Alternatively photosynthetic rates can be calculated from the functional relationship between photosynthesis (P) and irradiance (E). In this approach P vs. E curves are generated for samples from known light depths in incubators for relatively short time periods (20 min to 2 h); a series of such curves is generated for various times throughout the day (Lewis and Smith 1983). The photosynthetic rates are normalized to chlorophyll and the curves are then described by a mathematical function; the two most commonly used are a hyperbolic tangent and an exponential (Jassby and Platt 1976, Dubinsky et al. 1986). Using measurements and models of the time and depth-dependent changes in irradiance through the water column, the photosynthetic rates are extrapolated to the in situ irradiance field. Such models can be made more complex (and theoretically more realistic) by incorporating spectral responses in the calculation of the optical absorption cross section of the photosynthetic apparatus (Jassby and Platt 1976, Dubinsky et al. 1986, Sathyendranath et al. 1989, Morel 1991).

Phytoplankton photosynthesis typically amounts to between 1 and 10 μg C fixed per liter per hour at light saturation, depending primarily on the chlorophyll concentration. Precise measurements of such low rates of photosynthesis require highly sensitive methods, and biological oceanographers have expended considerable effort in methods development (Geider and Osborne 1992). Two basic approaches are to measure the incorporation of acid-stable radiocarbon into the particulate material or changes in gas concentrations in the bulk fluid. Both gas exchange, as well as the radiocarbon uptake measurements of phytoplankton photosynthesis, require an incubation period. Careful time-course incubations in bottles have indicated that there can be significant changes in the physiology and composition of the plankton assemblage which are difficult to control (Eppley 1980). These so-called 'bottle effects' have provoked considerable debate about the absolute accuracy of many photosynthetic rate measurements. For example, the radiocarbon method was introduced to oceanography by Steemann Nielsen in 1952 and rapidly gained popularity, but many of the radiocarbon measurements of photosynthesis in oligotrophic regions of the ocean made prior to 1980 are suspect because of possible trace metal contamination during sampling and incubation (Carpenter and Lively 1980, Fitzwater et al. 1982). Trace amounts of Zn and Cu can apparently be leached from rubber 'O' rings, which serve as seals on sampling devices, and subnanomolar concentrations of these metals can markedly reduce photosynthetic activity in open ocean phytoplankton (Chavez and Barber 1987, Williams and Robertson 1989).

While radiocarbon incorporation rates remain the most sensitive means of measuring phytoplankton photosynthesis, gas exchange (i.e., O_2) measurements have the advantage of allowing more direct and accurate measurements of respiration (Bender et al. 1987). The earliest biological oceanographers estimated net photosynthesis from measurements of small differences in oxygen concentration in bottles incubated under ambient irradiance compared with samples incubated in darkness. In the open

ocean the changes in oxygen concentration are extremely low; however, they can be detected with reasonable precision by careful titration based on the Winkler method (Williams and Jenkinson 1982). Changes in O_2 concentration are generally too small to be detected with a polarographic electrode, although the introduction of non-stirred, pulsed electrode systems approaches the required sensitivity (Langdon 1984). Alternatively, it is possible to measure changes in inorganic carbon in the water. On average, seawater contains approximately 2.0 mM total dissolved inorganic carbon (TCO_2), of which $>95\%$ is in the form of HCO_3^-. With the introduction of high precision coulometric techniques for measuring total dissolved inorganic carbon, changes of 1 part in 2000 can be detected. This is sensitive enough for open ocean photosynthetic measurements but the method is tedious, and sample throughput is limited (Johnson et al. 1985).

Because of bottle effects and a desire to resolve short-term variations in photosynthesis, alternative methods of deriving photosynthetic rates which do not require an incubation of a sample in a confined container have been developed. Two of these are based on chlorophyll fluorescence, including solar-induced fluorescence (Topliss and Platt 1986, Kiefer et al. 1989) and changes in the quantum yield of fluorescence induced by stimulating flashes (Falkowski et al. 1986b, Falkowski and Kolber 1990, Kolber et al. 1990, Falkowski et al. 1991, Kiefer and Reynolds 1992). A pump-and-probe-based fluorescence method for estimating the rate of electron flow through Photosystem II under ambient irradiance has a precision of about $\pm 10\%$ and appears to be as accurate as the ^{14}C method (Falkowski and Kolber 1993).

Deriving photosynthetic quantum efficiency

One of the most informative means of determining how biomass-specific rates of photosynthesis are affected by environmental limitations is to determine quantum efficiency. The calculation of quantum efficiency of photosynthesis in natural phytoplankton communities is complicated by the determination of absorbed light.

The most important source of photosynthetically active radiation (PAR 400 to 700 nm) is downwelling irradiance (E_d). In pure seawater with a uniform distribution of absorbing and scattering particles, E_d decays exponentially with depth (Z) according to the equation:

$$E_d(z) = E_d(0)\, e^{-K_{d\lambda} Z} \tag{3}$$

where $E_d(z)$ and $E_d(0)$ are the downwelling irradiances at depths Z and just below the surface, respectively, and $K_{d\lambda}$ is the average value of the vertical attenuation coefficient for light at wavelength λ between the surface and depth Z. Because the physical depth corresponding to a constant value of light extinction will vary according to the optical properties of the water column, it is often convenient to define the attenuation of light by optical depth, rather than physical depth; the optical depth corresponding to 1% of the surface value is 4.6.

The ocean behaves like a monochromator, attenuating far-red and red light much more rapidly than blue and green light (Kirk 1983). Thus, near the bottom of the euphotic zone, PAR is confined to spectral bands between 450 and 550 nm, and is mainly absorbed in the Soret region; the red absorption bands of chlorophylls play only a minor role in light absorption in situ and then only in the upper portion of the euphotic zone, where spectral irradiance is relatively broad-band (Morel and Prieur 1977, Morel 1978, Kirk 1983).

Using a mathematical model to describe the functional relationship between photosynthesis and irradiance, three basic parameters, the initial slope, α, the light-saturated rate, P_m, and the light intensity corresponding to the intercept, the so-called E_k value:

$$E_k = P_m/\alpha, \tag{4}$$

can be derived.

If the photosynthetic parameters are normalized to chlorophyll *a*, the initial slope, α, can be related to the maximum quantum yield (ϕ_m) of photosynthesis by:

$$\alpha = a^* \phi_m \tag{5}$$

where α is moles O_2 evolved or CO_2 fixed per mg Chl *a* per mole quanta per m^2 and a^* is the spectrally averaged optical absorption cross sec-

tion normalized to chlorophyll *a* (m^2 mg Chl *a*). The optical absorption cross section, a^*_λ is calculated from the expression:

$$a^*_\lambda = -\ln(E_\lambda / E_{0\lambda}) \ln(10) / \text{mg Chl } a \quad (6)$$

where E_λ and $E_{0\lambda}$ are the spectral irradiances at wavelength λ measured through a suspension of cells with a 1 m pathlength. The average optical absorption cross section, $\bar{a}^*$, is derived by integrating a^*_λ between 400 and 700 nm and accounting for spectral irradiance:

$$\bar{a}^* = \frac{\sum (a^*_\lambda \cdot I_\lambda \cdot \Delta\lambda_n)}{\sum (I_\lambda \cdot \Delta\lambda_n)} \quad (7)$$

Due to variations in cell size and packaging effects, $\bar{a}^*$ varies by about a factor of five in phytoplankton, so that α cannot be taken directly as a measure of quantum efficiency (Berner et al. 1989, Dubinsky 1992). It should be noted that a cell displaced vertically in the water column will have different values of a* depending on the spectral distribution of irradiance at each depth, independent of the absolute photon flux density (Morel 1978).

Alternatively, α can be described in terms of the functional absorption cross section of Photosystem II, $\sigma_{PS\,II}$, and the concentration of photosynthetic units, n (i.e., O_2/ Chl *a*) thus:

$$\alpha = \sigma_{PS\,II} n \quad (8)$$

where $\sigma_{PS\,II}$ is calculated from the single turnover, flash intensity saturation curve of oxygen evolution or variable fluorescence:

$$Y_{(I)} / Y_{max} = 1 - e^{-\sigma PS\,II \cdot I} \quad (9)$$

and $Y_{(I)}$ and Y_{max} are the oxygen (or variable fluorescence) yields induced by a single turnover flash intensity with intensity I and the maximum yield at a saturating intensity, respectively (Ley and Mauzerall 1982, Falkowski et al. 1986a,b). This approach to deriving quantum efficiencies has proven more attractive than those based on measurements of a*, and there are large scale variations in the quantum efficiency of PS II based on pump-and-probe fluorescence methods, for coastal margins (Kolber et al. 1990), the northwest Atlantic (Geider et al. 1993), equatorial Pacific (Falkowski et al. 1991) and upwelling region off the northwest coast of Africa (Falkowski, in preparation).

The light-saturated photosynthetic rate can be related to n via the whole chain electron transport rate, τ, as:

$$P_m = n/\tau , \quad (10)$$

where $1/\tau$ is the maximum rate at which electrons can be transferred from water to the terminal electron acceptor (CO_2) in the steady state (Myers and Graham 1971, Herron and Mauzerall 1972). τ can vary by over an order of magnitude, from ca. $1000\,s^{-1}$ to $70\,s^{-1}$; the variability in τ can be quantitatively related to the ratio of Rubisco to electron transport components (Sukenik et al. 1987). Based on an average photosynthetic unit size of 2000 Chl/O_2 and a value of $1/\tau$ of $1000\,s^{-1}$, the maximum light-saturated rate of photosynthesis is 2.0 μmoles O_2 μg Chl $^{-1}$ h^{-1}, or about 25 μg C μg Chl $^{-1}$ h^{-1} (assuming a photosynthetic quotient of 1.0) (Falkowski 1981). While such high rates of photosynthesis have been measured in natural phytoplankton communities, they are very rare; values less than half of that are much more common.

The light saturation parameter, E_k is useful in relating the irradiance distribution of photosynthetic rates to a depth distribution in the water column (Talling 1957). Recalling the definition of E_k (Eq. (4)) it follows from Eqs. (8) and (10) that $E_k = 1/\tau\sigma_{PS\,II}$ (Falkowski 1992). As both τ and σ can vary as functions of physiological state and species composition, it follows that E_k also varies significantly.

Three environmental factors affect biomass-specific rates of photosynthesis, namely temperature, irradiance and nutrients. We first consider the effect of temperature.

Temperature and constraints on photosynthesis and growth

Temperature in the upper ocean ranges from slightly below 0 °C in poleward areas to about 30 °C in the warmest areas of the eastern Equatorial Pacific. Temperature is an important determinant of species distributions; many polar phytoplankton do not grow above 2 °C, and a

large number of tropical or subtropical species do not grow below 18 °C. The molecular bases of high or low thermal stress are unknown. Because of the high specific heat of water, however, diel changes in temperature are relatively modest and seasonal changes are relatively slow. Short-term changes in temperature markedly affect P_{max}; the initial slope of the photosynthesis-irradiance curve (α) seems less affected, although changes in temperature can alter the carbon/chlorophyll ratio and hence influence a* (Steemann Nielsen and Hansen 1959, Li 1980, Cote and Platt 1984).

By the end of the 21st century, global changes in atmospheric radiative forcing are predicted to raise global atmosphere temperature by as much as 6 °C at high latitudes in the northern hemisphere, and more modestly at lower latitudes (Houghton et al. 1990). This heat will be transferred to and stored by the ocean, and changes in sea surface temperature (SST) have been detected and documented as evidence of increased radiative forcing (Houghton et al. 1990). A compilation of data for cells grown at various temperatures reveals an envelope, the upper bound of which is described by an exponential curve with a slope equal to a Q_{10} of 1.8 (Eppley 1972). Importantly, there is a large scatter beneath this envelope, such that while temperature can empirically be used to predict average maximum specific growth rates, it seldom predicts actual specific growth or photosynthetic rates in situ. Some phytoplankton display a long-term physiological acclimation to temperature; the acclimation process has been primarily related to changes in Rubisco content, which presumably decreases τ (Davison 1991). There is little direct effect of temperature on σ. Thus, it seems likely that a slight elevation in SST at high latitudes would modestly increase P_{max}; there is unlikely to be any direct effect at lower latitudes.

Light as a limiting factor: Photoacclimation and photoinhibition

To a first order, the primary variation in light reaching the ocean surface is created by the path of the sun as it crosses the sky. This path gives the total daily radiation, the length of the day and the maximum intensity at the sea surface. Superimposed on the solar path are local atmospheric conditions, especially clouds, which modify both the intensity of radiation reaching the sea surface as well its angular distribution.

In a rather imaginative paper, Charlson et al. (1987) suggested that phytoplankton may influence their own light regime by affecting cloud albedo. This hypothesis is based on the fact that a number of bloom-forming species of phytoplankton produce dimethylsufide (DMS), a volatile compound that outgasses and oxidizes in the atmosphere to form submicron sulfate particles. These sulfate particles are extremely hygroscopic and serve as cloud condensation nuclei. The biogenic addition of DMS can increase cloud albedo by providing a large number of particles for the same liquid water content. An increase in albedo would effectively reduce the photosynthetically active radiation received by the phytoplankton. Satellite observations of phytoplankton distributions and marine stratus cloud albedo show high correspondence over the Atlantic (Falkowski et al. 1992a); however, a proposed feedback between phytoplankton production and cloud albedo (Charlson et al. 1987) is far from established, let alone widely accepted.

As the incident radiation decreases exponentially in the ocean, the light received by a cell in the turbulent ocean is best predicted from the instantaneous surface irradiance and the depth of the cell. Both day-to-day variations in surface irradiance resulting from atmospheric forcing, and depth variations in cell distributions due to vertical movement of the water, produce stochastic fluctuations in the submarine irradiance experienced by the cells (Lewis et al. 1984). These low frequency fluctuations are physiologically integrated in a process called photoacclimation (Falkowski and LaRoche 1991). Photoacclimation optimizes light harvesting at low fluence rates and reduces light harvesting at high fluence rates. The most striking features of photoacclimation are the relatively large, rapid and reversible changes in the complement of the cellular pool of light harvesting chlorophyll complexes. The changes in pigment content follow first order kinetics and are related to the specific growth rate of the cell; the changes are usually completed within one cell generation (Falkowski 1984, Post et al. 1985, Sukenik et al. 1990).

Vertical profiles of individual cellular chlorophyll contents, measured with a flow cytometer,

reveal an increase in pigments with depth within the euphotic zone of the central ocean (Olson et al. 1991). Profiles of the functional absorption cross section of PS II ($\sigma_{PS\ II}$) obtained with a fast repetition rate fluorometer often reveal an increase in this parameter with depth, especially in nutrient-rich waters (Kolber et al. 1990, Falkowski et al. 1991). Photoacclimation leads to (indeed, was originally inferred from) an alteration in the photosynthesis-irradiance curve. Vertical distributions of photosynthesis-irradiance curves often reveal homogeneous distributions in turbulent mixed layers, and evidence of physiological acclimation in highly stratified water columns (Falkowski 1983, Cullen and Lewis 1988). Cells adapted to higher irradiance levels have higher chlorophyll-specific rates of photosynthesis at light saturation and higher E_k values, while cells adapted to low irradiance levels often have higher light utilization efficiencies per cell (not per unit chlorophyll *a*), and tend to become photoinhibited at lower irradiance levels.

Photoacclimation per se does not affect the quantum efficiency of charge separation in PS II (Kolber et al. 1988), although there may be overall changes in the quantum efficiency of photosynthesis resulting from an increase in both carotenoids and cyclic electron flow around PS II in high light adapted cells (Dubinsky et al. 1986, Falkowski et al. 1986).

Early workers in oceanography recognized that phytoplankton often reveal signs of photoinhibition. While extremely shade adapted cells, such as found at the bottom of ice floes, are easily photoinhibited at relatively low fluence rates, in situ and simulated in situ measurements in the open ocean usually reveal a depression of carbon fixation in the upper few meters of the water column. The question of whether photoinhibition occurs in situ, however, is complicated by the fact that turbulence in the upper ocean may reduce the actual exposure of the phytoplankton to supraoptimal irradiance. While fixed bottle incubation techniques cannot resolve this problem, measurements of the maximum variable fluorescence yields, using either DCMU or saturating pump flashes, reveal a diel rhythm in the photochemical conversion efficiency in PS II, which is taken to infer that significant photoinhibition occurs in nature (Neale 1987, Long et al., in press). Photoinhibition is more pronounced in nutrient poor regions of the open ocean, where cells may not be able to acquire sufficient nutrients to repair photodamaged reaction centers (Herzig and Falkowski 1989). While photoinhibition may be brought about by increases in PAR, UV-B and UV-A radiation can promote the process (Cullen and Neale 1994). The action spectra for UV-B photoinhibition suggest that the primary target is either a quinone, presumably affecting the Q_a–Q_b electron transfer, or a tyrosine, such as Z, on the donor side of PS II. The evidence of localization of the primary damage to the donor or acceptor side of PS II in natural phytoplankton communities seems to favor the latter (Vasilev et al., in prep.).

The integrated effects of physiological acclimation to irradiance and irradiance stress on water column photosynthesis can be assessed by calculating the light utilization efficiency of carbon fixation for the water column. This efficiency, denoted by the term Ψ, is the integrated carbon fixed per square meter of sea surface per gram chlorophyll per mole photons of incident photosynthetically active radiation at the sea surface (Falkowski 1981). Note that Ψ has the same dimensions as α, and is calculated from the slope of biomass specific carbon fixation to incident irradiance. In many nutrient replete areas of the ocean, such as found along the continental margins, Ψ is remarkably constant, averaging about 0.40 g C g^{-1} Chl m^{-2} mole quanta^{-1} (Platt 1986). The constancy of the parameter suggests that in these regions, photosynthesis for a given chlorophyll concentration is linearly related to incident irradiance; i.e., light is the major factor limiting chlorophyll-specific rates of photosynthesis. Throughout most of the nutrient poor regions of the open ocean, however, values of Ψ are highly variable, suggesting that the integrated water column quantum efficiency of photosynthesis is variable and that nutrients not only can limit phytoplankton biomass but also physiologically limit phytoplankton carbon fixation (Balch et al. 1989, Balch et al. 1992).

Nutrients and the limitation of photochemistry

If light were the only factor physiologically limiting phytoplankton photosynthesis in the sea, the quantum efficiency of PS II would be expected to remain relatively constant (Kolber et

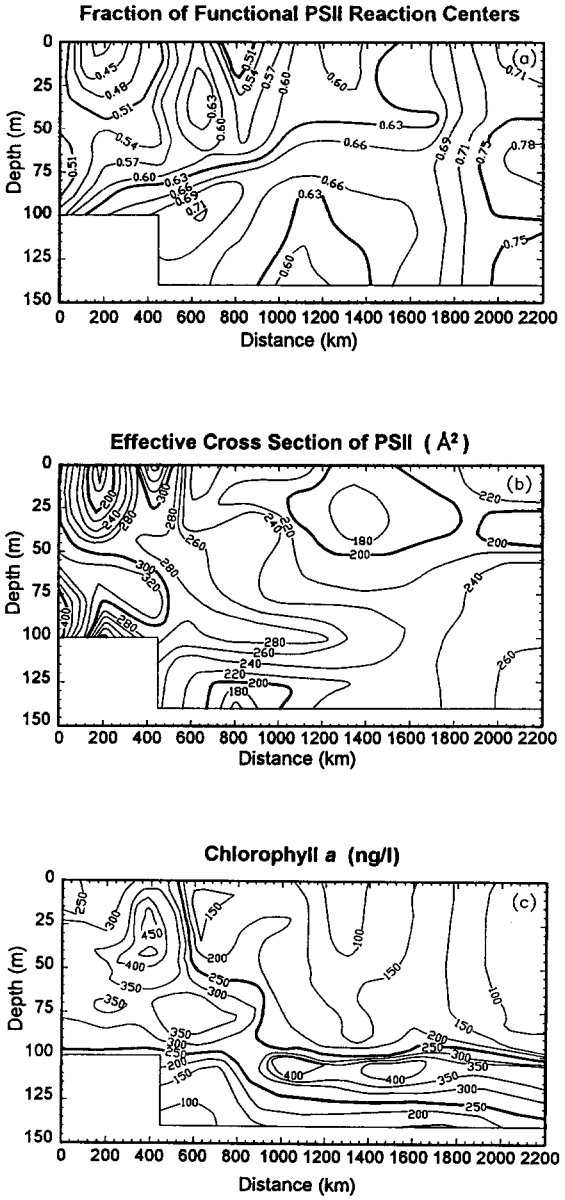

Fig. 5. A section showing (a) the fraction of functional PS II reaction centers, (b) the effective absorption cross section of PS II, and (c) phytoplankton chlorophyll *a* concentrations in the Pacific Ocean from the equator to 18° N at 140° W. These measurements were made with a fast repetition rate fluorometer (Greene et al., in press). Note that in the equatorial region, the fraction of functional PS II reaction centers is extremely low, as a result of iron limitation. Northward, this fraction increases, but is still far from unity, as consequence of nitrogen limitation. The variations in the absorption cross section reflect the concurrent limitations imposed by light and nutrients. The relatively high concentration of phytoplankton chlorophyll, associated with the thermocline, is apparent over 100's of kilometers.

al. 1988, Falkowski and Wilson 1992). Calculations of the maximum quantum efficiency of carbon fixation, based on measurements of the initial slope of the photosynthesis-irradiance curve and measurements of the optical absorption cross section (i.e., Eq. (5)) (Cleveland et al. 1989, Platt et al. 1992), as well as measures of the quantum yield of PS II photochemistry, using pump-and-probe fluorescence techniques (Kolber et al. 1990, Geider et al. 1993), reveal large differences in quantum efficiency as a function of nutrient supply (Fig. 5). For example, in the subtropical Pacific, quantum efficiency increased by over a factor of two for phytoplankton in an eddy, where anticyclonic vorticity upwelled deep, nutrient-rich water into the euphotic zone (Falkowski et al. 1991). Similar variations in quantum efficiency can be found between nutrient-rich upwelling areas off the coast of northwest Africa, and the nutrient-poor

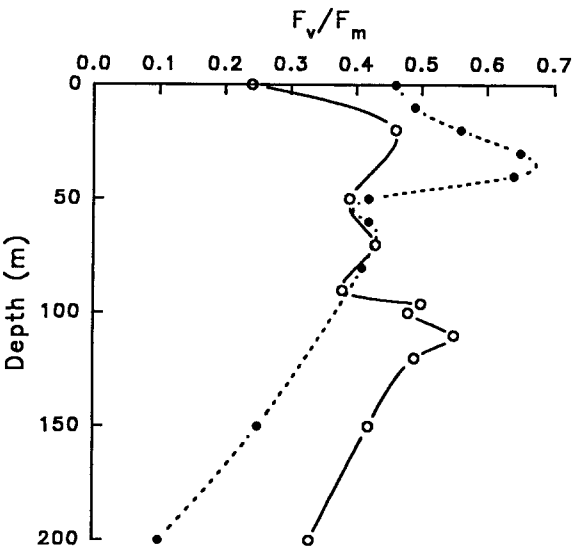

Fig. 6. Comparison of vertical profiles the quantum efficiency of PS II as determined from changes in F_v/F_m with a pump and probe fluorometer (Kolber et al. 1990) in a nutrient replete area off the coast of Northwest Africa (solid circles; refer to Fig. 2b) and a nutrient deficient area in the central subtropical Atlantic (open circles; refer to Fig. 2a). Overall, the quantum efficiency of photochemistry in the nutrient rich area is about 25% higher than in the nutrient depleted area. Addition of 3 μM nitrate to samples of water from the nutrient depleted region resulted in a 20% increase in quantum efficiency within 48 h. Note the depression in quantum efficiency in both profiles at the surface as a result of photoinhibition.

central subtropical Atlantic (Fig. 6). Because of the variations in the quantum efficiency, Ψ is variable; i.e., in the open ocean photosynthetic energy conversion efficiency is influenced by nutrient availability.

The molecular basis of nutrient limitation of the quantum efficiency is complex. With the exceptions of three areas of the world oceans that are thought to be iron-limited, and the eastern Mediterranean basin, which is thought to be phosphorous limited (because it receives so much iron from Saharan dust that phosphate is precipitated from the upper ocean!), phytoplankton productivity is thought to be primarily limited by nitrogen (Dugdale 1967, Eppley and Petersen 1979, Yentsch 1980, Barber 1992). On a molecular level, nitrogen limitation acts as inhibitor of translation by limiting the synthesis of amino acids. As eucaryotic cells become nitrogen limited, chloroplast encoded proteins become more depleted than many cytoplasmic encoded proteins, and key proteins in PS II, such as D1, CP 43 and CP 47, are markedly reduced relative to the light harvesting chlorophyll protein complexes (Kolber et al. 1988, Falkowski 1992). The loss of the reaction center proteins leads to a reduction in the efficiency of transfer of excitation energy from the antennae to the reaction center, and to a loss of functional reaction centers (Geider et al. 1993). The overall effect is a reduction in photochemical efficiency in natural phytoplankton communities which can be alleviated by the addition of micromolar levels of inorganic nitrogen (Falkowski et al. 1992b).

Net carbon fixation from the beginning of the Industrial Revolution

Since the beginning of the Industrial Revolution, atmospheric CO_2 levels have risen exponentially from ca. 275 ppmv to 355 ppmv. Approximately 30% of the CO_2 added to the atmosphere each year as a result of anthropogenic activities is sequestered. Thus, the global carbon cycle is not in steady state. The fate of this 'missing' carbon is unclear; arguments have been made for a high latitude terrestrial sink (Tans et al. 1990) and for diffusive oceanic uptake (Broecker et al. 1980). If either *terrestrial or oceanic* photosynthesis provides a sink, there must be a long term, continuous increase in the rate of photosynthesis *each year*. If, for example, net phytoplankton production changed since the beginning of the Industrial Revolution, it could increase the concentration gradient for CO_2 across the air-sea interface, thereby facilitating the drawdown of atmospheric CO_2. As it seems highly unlikely that phytoplankton photosynthesis is CO_2 limited (Raven 1994), it is doubtful that the additional CO_2 in the atmosphere, or the physical diffusive equilibration of the gas between the atmosphere and the ocean, would have any direct effect on phytoplankton carbon fixation. It remains to be seen, however, whether phytoplankton photosynthesis in the ocean is in steady-state (Bender et al. 1985).

Both the depth and steepness (i.e., the change of temperature per change in depth) of the thermocline are important factors which determine the vertical flux of nutrients (Cullen 1982). Global warming at high latitudes would lead to shallower mixed layer depths in the winter, more intense seasonal stratification and potentially, to shallower upper mixed layers. Model results suggest that these effects would reduce the flux of nutrients to the upper mixed layer, thereby leading to a reduction in phytoplankton biomass and primary production (Woods and Barkmann 1993). The reduction in phytoplankton carbon fixation would lead to a reduction in strength of the biological pump, effectively resulting in a net increase in atmospheric CO_2. This would be a positive feedback on the atmospheric radiation balance.

A second effect of global warming can be envisioned. On the global scale, the upward flux of nutrients to the euphotic zone is driven by the large scale ocean circulation. In the northern hemisphere, the large scale sense of surface ocean currents is clockwise, and anticlockwise in the southern hemisphere. To a first order, the rotation is a consequence of wind stress at the sea surface. Atmospheric warming can produce a higher thermal contrast between the continents and oceans, resulting in higher wind velocities at the ocean margins. A long-term increase in mean wind strength has been observed along the eastern margin of the Pacific (Bakun 1990). An increase in wind strength along the ocean margin

would lead to increased upwelling at the ocean margins and a corresponding increase in phytoplankton production. The effect in the center of the gyre would be negligible. The net effect would be that phytoplankton biomass and carbon fixation will be higher on the ocean margins.

One potential effect of the increased upwelling at the ocean margins is a change in food web structure. One of the most important factors determining food web structure is phytoplankton cell size (Malone 1980, Chisholm 1992). Phytoplankton cell sizes range from 0.6 to 1.0 μm for ubiquitous prochlorophytes and cyanobacteria to more than 1000 μm for some larger diatoms and dinoflagellates. Small cells are generally much more abundant in nutrient-depleted areas of the open ocean (Chisholm 1988), where their high surface/volume ratio is advantageous in the acquisition of low concentrations of nutrients (as a consequence of increased diffusion through a small boundary layer). Small cells are not efficiently transferred to higher trophic levels that are economically beneficial. Larger cells are generally much more abundant in nutrient rich areas, such as coastal margins or upwelling regions (Malone 1980). Larger cells are more efficiently transferred to higher trophic levels; hence, the basis of most commercial fisheries is nutrient-rich areas which support the efficient growth of large phytoplankton cells. Thus, climatologically driven increases in upwelling would potentially alter the trophic structure in marine food chains; the specific effects are extremely hard to predict. Although increased nutrient fluxes would tend to increase phytoplankton photosynthesis and biomass, they do not increase the absorption of CO_2 from the atmosphere.

It must be stressed that when increased upwelling supplies nitrate to the upper ocean from depth (i.e., in upwelling regions), inorganic carbon is simultaneously supplied. The supply of inorganic carbon is a consequence of mass balance. The downward flux of organic matter with an average elemental composition of the Redfield ratio, must be balanced by the upward flux of the nutrients (in an oxidized form) in the Redfield ratio. Thus, unless the Redfield ratio changes, there is little or no *net* flux of inorganic carbon on an annual, global average, between the atmosphere and the ocean from phytoplankton photosynthesis (Sarmiento and Siegenthaler 1992). Significant changes in the Redfield ratio are difficult to imagine; the average elemental composition of phytoplankton has probably remained, on average, extremely constant over hundreds of millions of years. To affect a change in the atmospheric levels of CO_2, phytoplankton photosynthesis must deviate from the steady-state, and the nutrients required to force such a deviation must either be derived externally to the ocean or be supplied in proportions significantly different from those of Redfield (Sarmiento and Siegenthaler 1992). In this context, for example, an increase in biological nitrogen fixation in the ocean would potentially lead to an increased flux of inorganic carbon from the atmosphere to the ocean. Thus, increased upwelling would have little or no effect on atmospheric CO_2 levels or radiative balance.

In 1987, Venrick et al. reported that average chlorophyll *a* concentrations in the central North Pacific gyre had doubled between 1964 and 1984. If such changes occurred throughout the ocean, *and were fueled by nutrients external to the ocean*, the impact on atmospheric CO_2 could be significant. Measurements of ocean transparency can be used to quantitatively derive upper ocean chlorophyll with a precision comparable to that of remote sensing algorithms used to analyze the CZCS data (Lewis et al. 1988). Such measurements have been made since the end of the 19th century, and provide a basis for analyzing changes in open ocean phytoplankton levels from the beginning of the 20th century. Analyses for the north Pacific Ocean suggest that long-term changes in phytoplankton chlorophyll have occurred, especially at the ocean margins and along the equator; overall, however, the changes have been relatively small (Falkowski and Wilson 1992). These changes are consistent with, but do not prove, increased gyre rotation resulting from increased wind stressed forcing. They may also be due to a decreased flux of nutrients from depth as a consequence of increased heating of the surface ocean, which would tend to both deepen the upper mixed layer and reduce vertical eddy diffusivity. Assuming that the average quantum efficiency of photosynthesis, the Redfield ratios, and incident solar irradiance have remained relatively con-

stant, the changes in phytoplankton biomass are much too small to account for significant net uptake of anthropogenic, atmospheric CO_2. Increased fluxes of aerosol iron to nutrient-replete areas of the open ocean may further lead to a draw-down of atmospheric CO_2, and episodic volcanic eruptions can deliver large amounts of aeolean iron. There is little evidence that such a phenomenon has occurred in the nutrient-rich areas of the North Pacific since the beginning of the Industrial Revolution; however, such a phenomenon cannot be dismissed (Sarmiento 1993).

The coastal margins have, in geological times, served as a vast reservoir of stored phytoplankton carbon (Walsh 1988, Berger et al. 1989). Sea level has risen and fallen over 100 m between glacial periods. During interglacial times, continental shelves and shallow seas have experienced large blooms of phytoplankton (Walsh 1983, Berger et al. 1989); the source nutrients fueling the blooms is unknown. Along the coastal margins of the world oceans, anthropogenic eutrophication has led to increased phytoplankton production. This production is fueled by nutrients external to the ocean, such as agricultural run-off and sewage effluent, and potentially could lead to a net draw-down of CO_2. Based on estimates of global anthropogenic nitrogen loading, and assuming carbon fixation will be in the Redfield ratio with nitrogen, approximately 0.3 Gt of carbon could be sequestered annually as a result of enhanced phytoplankton photosynthesis (Walsh 1991). The sequestration would require that the fixed carbon be exported below the main thermocline of the central oceans, or buried in ocean sediments. Large scale particle flux measurements suggest that a significant fraction of the phytoplankton carbon produced on the shelves is exported to the central ocean basin where it is either oxidized in the deep-sea sediments or sequestered (Jahnke and Jackson 1992, Falkowski et al. 1994).

Conclusions

The factors which limit phytoplankton biomass and photosynthesis in the world oceans are complex and interrelated to ocean and atmospheric circulation. Over geological time, proxy indicators of oceanic primary productivity such as organic carbon accumulation rates and the sedimentary distribution of foraminifera imply relatively large natural fluctuations in global rates of oceanic carbon fixation (Berger et al. 1989). The magnitude of these variations is unclear (Bender et al. 1994). Although the causes of these fluctuations can only be speculated, variations in the Earth's orbital cycles, and consequent effects on radiative balance, are often presumed to be the driver over the last several hundred thousand years (Imbrie et al. 1992).

As we approach the end of the 20th century, it is becoming increasingly apparent that anthropogenic activities have rapidly changed the gas composition of the atmosphere, and to some extent the radiative budget of the Earth. However, it is extremely difficult to determine with confidence interdecadal changes in either phytoplankton biomass or photosynthetic efficiency, let alone to attribute any change to a specific limiting factor. It is clear, however, that the steady-state export flux of organic carbon to the deep ocean, facilitated by phytoplankton photosynthesis, is crucial to maintaining a diffusive exchange of both CO_2 and O_2 between the ocean and atmosphere. Changes in global climate almost certainly ensure a deviation of these fluxes from steady-state.

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